

## Exploiting the Geometry of Anthanthrone to Harness Optoelectronic Properties

Thèse

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### Résumé

Depuis quelques années, un intérêt marqué pour les pigments de cuve a fait son apparition dans la littérature. Longtemps considérés comme des produits destinés exclusivement à la chimie fine industrielle, les pigments sont de plus en plus utilisés en recherche académique. Ils sont produits à l'échelle de la tonne pour des sommes avantageuses et leurs structures complexes permettent d'accéder à des molécules prisées en peu d'étapes synthétiques. La plupart de ces pigments sont des hydrocarbures aromatiques polycycliques possédant parfois des hétéroatomes, ce qui en fait des molécules de choix pour l'étude de la relation structure-propriété. En conjonction avec le développement des aromatiques polycycliques, l'étude des composés diradicaloïdes ayant des propriétés hors du commun est en plein essor dans la littérature scientifique. Les travaux présentés dans cette thèse rapprochent donc ces deux domaines. Le cœur anthanthrone, un aromatique polycyclique à la réactivité singulière causée par sa géométrie, permet l'exploration de concepts originaux pour la chimie des composés organiques en couche ouverte.

Tout d'abord, un composé à base d'anthanthrone a permis le développement d'une nouvelle méthode pour obtenir des molécules diradicalaires. Il est démontré que la congestion stérique des diphénylméthanes et du cœur anthanthrone se faisant face, facilite une transformation structurelle vers une molécule ayant deux électrons non-appariés. Étonnamment, cette transformation peut avoir lieu à l'état solide en appliquant de faibles pressions. Ainsi, il est possible de briser des liens doubles avec ses propres mains à l'aide d'un pilon et mortier. Ensuite, une molécule similaire utilisant les diphénylamines permet aussi l'obtention de composés en couche ouverte lorsque doublement oxydés. Le produit obtenu est donc isoélectronique à son homologue tout carbone. Encore une fois, la géométrie du cœur anthanthrone produit deux systèmes  $\pi$  perpendiculaires, empêchant la recombinaison des radicaux. Pour poursuivre sur ces composés et augmenter la densité de spin, un polymère « polyradical cation » avec des propriétés optoélectroniques intéressantes a été synthétisé. Finalement, le dernier chapitre de cette thèse exploite toujours la géométrie de l'anthanthrone mais dans un contexte complètement différent. Grâce à la structure unique de l'anthanthrone, il est possible d'obtenir une émission induite par agrégation dans la région du proche infrarouge.

### Abstract

For several years, a keen interest in vat dyes emerged in the literature. Long considered exclusively for the specialty chemical industry, pigments are increasingly used in academia. They are mass-produced at a low cost and their complex structures allow valued molecules to be obtained in few synthetic steps. Most of these pigments are aromatic polycyclic hydrocarbons (PAHs) sometimes including heteroatoms, making them molecules of choice for the study of structure-property relationship. With the development of PAHs, the study of biradicaloids having outstanding properties is thriving in the scientific literature. The work presented in this thesis brings together these two fields of study. The anthanthrone core, a polycyclic aromatic with a singular reactivity caused by its geometry, allows for the exploration of original concepts for the chemistry of organic open-shell compounds.

First of all, anthanthrone-based molecules allowed the development of a new method to obtain open-shell diradicals. It was found that the steric congestion of the diphenylmethane and the anthanthrone core facing each other, facilitate the structural transformation towards a molecule having two unpaired electrons. Surprisingly, this transformation can proceed in the solid state at low pressures. Thus, it is possible to break double bonds with bare hands using a mortar and pestle. Next, similar molecules with diphenylamines also allow the formation of open-shell compounds when doubly oxidized. The obtained products are isoelectronic to their all-carbon counterpart. Again, the geometry of the anthanthrone core produces two perpendicular  $\pi$ -systems, preventing the recombination of the radicals. To follow-up with similar compounds and increase the spin density, a polymer "polyradical cation" possessing intriguing optoelectronic properties was synthesized. Finally, the last chapter of this thesis still exploit the geometry of the anthanthrone dye but in a completely different context. With the unique structure of this core, it is possible to obtain aggregation-induced emission in the near infrared region.

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## List of Abbreviations

Å = Angström AIE = Aggregation-Induced Emission APPI = Atmospheric Pressure Photo-Ionization Aq. = AqueousAtm = Atmospherebr = BroadCalcd = Calculatedd = DoubletDABCO = 1,4-diazabicyclo[2.2.2]octane dba = Dibenzylideneacetone DBTTC = Dibenzotetrathienocoronene DCM = Dichloromethane dd = Doublet of doubletDFT = Density Functional Theory dppf = 1,1'-Bis(diphenylphosphino)ferrocene dt = Doublet of triplet  $E_g = Bandgap$ EPR/RPE = Electron Paramagnetic Resonance/ Résonance Paramagnétique Électronique Et = Ethyl $Fc/Fc^+$  = Ferrocene/ Ferrocenium GPa = Gigapascal h = HourHBC = Hexabenzocoronenes HOMA = Harmonic Oscillator Model of Aromaticity HOMO = Highest Occupied Molecular Orbital HONO = Highest Occupied Natural Orbital HRMS = High Resolution Mass Spectrometry Hz/ MHz= Hertz/ Megahertz LCMS = Liquid Chromatography- Mass Spectrometry LUMO = Lowest Unoccupied Molecular Orbital LUNO = Lowest Unoccupied Natural Orbital m = MultipletMax = Maximum Me = Methylmmol = Millimole Mol = Mole $\mu$ W = Microwaves NICS = Nucleus-Independent Chemical Shift NIR= Near-infrared nm = NanometerNMR/RMN = Nuclear Magnetic Resonance/ Résonance Magnétique Nucléaire  $N_u$  = Number of unpaired electrons o-DCB = Ortho-dichlorobenzene

PAH = Polycyclic Aromatic Hydrocarbon PDI = *Para*-Delocalization Index Pin = Pinacols = SingletSQUID = Superconducting QUantum Interference Device t = Triplet TBAB = Tetrabutylammonium bromide TBPA = Tris(4-bromophenyl)ammoniumyl hexachloroantimonate Tf = TriflateTHF = Tetrahydrofuran TIPSA/TIPS = Triisopropylsilylacetylene/ triisopropylsilyl TOF = Time-of-flight TPE = 1, 1, 2, 2-Tetraphenylethylene TS = Transition State UV-Vis = Ultraviolet-Visible VP = Variable Pressure VT = Variable Temperature

« Pour examiner la vérité il est besoin, une fois dans sa vie, de mettre toutes choses en doute autant qu'il se peut. »

-René Descartes

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### Foreword

The content of chapter 2 and 3 are identical to the published papers but have been reformatted to ensure the coherence of the thesis. X-ray diffraction details and the Cartesians coordinates from DFT calculations have been removed to alleviate the document. They can be retrieved from the website of the respective publishers.

Chapter 2: Desroches, M.; Burrezo, P. M.; Boismenu-Lavoie, J.; Álvarez, M. P.; Gómez-García, C. J.; Matxain, J. M.; Casanova, D.; Morin, J.-F.; Casado, J. *Breaking Bonds and Forming Nanographene Diradicals with Pressure, Angew. Chem. Int. Ed.* **2017**, *56*, 16212-16217.

**Contribution:** I am the first author as I am the principal contributor. I have designed and synthesized the molecules. I also participated in the characterization (NMR, variable-temperature NMR, and crystal growth). I have participated in the elaboration of the hypothesis and discussion. I also have written and edited a major part of the manuscript. P.M.B. performed the variable pressure Raman spectroscopy. J.B.-L. helped to synthesize the compounds, discuss the hypothesis, and characterize the molecule by NMR. M.P.A. helped with the Raman spectroscopy and theoretical calculations. C.J.G.-G. has performed and analyzed the data of the magnetic experiments, SQUID and EPR. J.M.M. and D.C. performed the DFT calculations. J.-F.M. and J.C. have contributed to the manuscript writing and edition.

Chapter 3: Desroches, M.; Morin, J.-F. Wurster-Type Nanographenes as Stable Diradical Dications, Chem. Eur. J. 2018, 24, 2858-2862.

**Contribution:** I am the principal contributor. I have designed, synthesized, and fully characterized the molecules. I have elaborated the hypothesis and I have written and edited the manuscript. J.-F.M. has contributed to the edition of the manuscript.

Chapter 4 is identical to the manuscript accepted in *Macromolecular Rapid Communications* on April 24. DOI: 10.1002/marc.201800214R1, *in press*.

Chapter 4: Desroches, M.; Morin, J.-F. Wurster-type Anthanthrene Polyradicaloid-cations.

**Contribution:** I am the principal contributor. I have designed, synthesized, and fully characterized the molecules. I have elaborated the hypothesis and I have written and edited the manuscript. J.-F.M. has contributed to the edition of the manuscript.

Chapter 5 is identical to the manuscript accepted in *Organic Letters* on April 25, 2018. DOI: 10.1021/acs.orglett.8b00452, *in press*.

**Chapter 5:** Desroches, M.; Morin, J.-F. Anthanthrene as a Super-Extended Tetraphenylethylene for Aggregation-Induced Emission.

**Contribution:** I am the principal contributor. I have designed, synthesized, and fully characterized the molecules. I have elaborated the hypothesis and I have written and edited the manuscript. J.-F.M. has contributed to the elaboration of hypothesis and edition of the manuscript.

### Notes

The data collection and refinement as well as resolution of all the crystal structures were made by Thierry Maris at Université de Montréal.

For the sake of simplification, the molecules in this thesis are numbered independently in every chapter and are true to the numbers given in the published papers. If a compound appears in more than one chapter, it is assigned a new number in each chapter.

### Chapter 1. Introduction

#### **1.1. General Introduction and Objectives**

The objective of this thesis is to explore the structure-property relationship of a very unique dye, anthanthrone. This work presents molecules with remarkable properties and prepared using very few synthetic steps given the already complex structure of Vat Orange 3. The main focus of this thesis is oriented toward a very trendy literature subject that is diradical open-shell compounds. The study of organic magnetic compounds has seen an intense recrudescence for the past 15 years after almost 60 years of radio silence.

The three specific objectives of this thesis are:

- 1. Develop diradical compounds based on the 4,10-dibromoanthanthrone dye.
- 2. Explore the conjugation and geometry of anthanthrone and anthanthrene.
- 3. Extend the study of diradical anthanthrone/anthanthrene to polymers or macromolecules.

#### **1.2. Aromaticity**

Coffee, freshly baked cinnamon buns, and grilled barbecue meat all share the comforting scent of aromatic compounds. Either extracted from plants creating essential oils for medicinal purposes or burnt in a beacon as whale grease to illuminate, aromatic compounds have been useful for many centuries. Since Kekulé proposed the effective structure of benzene in 1865, much research has been directed toward understanding the origin of its unique properties.<sup>1</sup> Indeed, the hexagon-shaped molecule with three unsaturations is outstandingly stable in comparison to the corresponding saturated compounds. While aromaticity cannot be measured directly, several indirect proofs of this property can be collected independently.

The hydrogenation heat of six-membered cycles was initially measured in unsaturated cyclohexane, only to discover an anomaly in benzene. Cyclohexene in Figure 1.1 can be hydrogenated to cyclohexane releasing a  $\Delta H^{\circ} = -120$  kJ/mol. It is expected that in the case

of cyclohexadiene, the hydrogenation heat should be twice as much as cyclohexene. It is in fact very close to the expected value with a  $\Delta H^\circ = -232$  kJ/mol. Then, if the same rule is applied to cyclohexatriene, the hydrogenation heat should be -360 kJ/mol, that is three times the one of cyclohexene. In fact, the hydrogenation heat of benzene is much higher, a  $\Delta H^\circ = -208$  kJ/mol, which is 152 kJ/mol more than the expected result.<sup>1</sup> This anomaly is called resonance energy, which is a measure of the aromatic stability in conjugated systems. The greater the electron delocalization in a compound, the greater the aromatic stability is, and the resonance energy will be affected proportionally.



Figure 1.1. Hydrogenation heat and resonance energy in six-membered cycles.

In 1931, Hückel defined a precise rule to assert the aromaticity of planar closed-shell monocyclic rings. In a  $\pi$  system,  $4n + 2\pi$  electrons are present in aromatic cycles, whereas 4n describes anti-aromatic cycles. This very simple rule is quite efficient, but only describes a very limited number of compounds since it is valid exclusively for monocyclic rings. In 1972, Erich Clar proposed the aromatic  $\pi$ -sextet rule, which is useful to describe the aromatic character of much more complex benzenoid molecules with multiple rings.<sup>2</sup> A sextet is defined as three alternating double bonds in a phenyl ring and these double bonds can only

belong to one ring at a time. The number of sextets and their location portray the reactivity of the molecule. For example, three isomers of  $C_{18}H_{12}$  are presented in Figure 1.2. Triphenylene has three isolated sextets that cannot be delocalized in the structure. As a result, it has a maximum absorption energy in the blue region and a large bandgap (Eg). Chrysene has two sextets that can be delocalized in the adjacent benzene ring. It has a red-shifted maximum absorption of 329 nm and a smaller bandgap than for triphenylene. The remaining compound, tetracene, has one sextet that can be delocalized over the entire four rings. Its maximum absorption is again red-shifted compared to the two other isomers and has the lowest bandgap value. The least reactive compound and the most aromatic goes from triphenylene, chrysene, to tetracene. From three to one aromatic  $\pi$ -sextets, conjugated or not, it has a dramatic impact over the properties of the molecules. The more stable a compound is, the less it is prone to transformations. This rule has enormous implication when designing polyaromatic compounds because of the stability and reactivity duality.



Figure 1.2. Example of Clar's aromatic  $\pi$ -sextet rule with C<sub>18</sub>H<sub>12</sub>.

Experimental evidences can be gathered as indirect measures of the aromatic character. In 1958, the first proof of the structure of benzene by X-ray crystallography allowed to measure its bond length.<sup>3</sup> The average bond length should be 1.41 Å, which is the exact mid-length for a  $sp^2$  C-C double (1.47 Å) and single bond (1.34 Å). In fact, it is closer to an ethylene double bond at 1.39 Å. Indeed, because of the delocalization of  $\pi$  electrons over the six carbon atoms, its bond length tends to be averaged. NMR is also very useful since aromatic compounds show very characteristic signals between 6.0 and 9.5 ppm. Figure 1.3 shows the circulation of  $\pi$  electrons in benzene and its effect on the magnetic environment of protons.

When benzene is placed in a magnetic field, the circulation of electrons with respect to the right-hand rule, induces a local magnetic field ( $B_{induced}$ ) aligned with the applied magnetic field ( $B_0$ ). The overall field will be reinforced and the aromatic protons will be strongly deshielded.<sup>1</sup> As a result, the protons of benzene have a single chemical shift of 7.16 ppm.<sup>4</sup>



Figure 1.3. Induced magnetic field caused by the circulation of  $\pi$  electrons in benzene.<sup>\*</sup>

There are several modern ways to evaluate, quantify and compare aromatic systems. When executed correctly, theoretical calculations are a reliable way to assign an aromatic character. Nucleus-Independent Chemical Shift (NICS) developed by Schleyer *et al.* in 1996 is probably the most widespread calculation method in the literature.<sup>5</sup> It relies on the induced circulation of  $\pi$  electrons when the system is exposed to an external magnetic field. One can retrieve an absolute aromatic character from NICS calculations. The more negative that value, the more aromatic the  $\pi$  system is. On the contrary, positive values characterize anti-aromatic molecules and if that value approaches zero, the system will be identified as non-aromatic. For example, the NICS values of benzene, thiophene and cyclobutadiene are -9.7, -13.6, and 27.6, respectively.<sup>5</sup> Other models, such as the Harmonic Oscillator Model

<sup>\*</sup> Figure reproduced from: https://orgspectroscopyint.blogspot.com/2014/11/magnetic-fields-in-aromatic-rings.html. Consulted on February 15, 2018.

of Aromaticity index (HOMA)<sup>6</sup> and *Para*-Delocalization index (PDI),<sup>7</sup> that rely on bond length and electron delocalization, respectively, have also proven to be useful for the determination of aromatic character.

#### **1.3.** Polycyclic Aromatic Hydrocarbons and Vat Dyes

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting only of carbon and hydrogen atoms and multiple aromatic rings. Naphthalene, anthracene, chrysene, pyrene, coronene are well-known examples. They can be derived from the petroleum industry and are often described as stable or non-reactive.<sup>†</sup> The two resonance structures, presented in Figure 1.4, are aromatic and quinoid. There is an energetic cost associated with the de-aromatization of phenyl rings and thiophene units when going from aromatic to quinoid form. In fact, the quinoid structure is most often higher in energy and less stable.



Figure 1.4. Aromatic versus quinoid structures in PAHs.

Since benzene is planar because of the  $sp^2$  hybridized carbon atoms, PAHs are also planar for similar reasons. However, the arrangement of the phenyl rings, the bulkiness of the adjacent substituents or the incorporation of heteroatoms can induce contortion in the core. The degree of bending is exclusively dependent on the structure. Distortion in a  $\pi$ -system has a serious impact on the aromaticity and delocalization of the electrons. The more distorted

<sup>&</sup>lt;sup>†</sup> According to the definition of PAH, thiophene and its derivatives do not fit in this category. Although, they are often studied like PAHs because they have a similar reactivity. They are also derivatives of the petroleum industry.

the PAHs, the less effective the delocalization is because bending diminishes the overlap between the neighboring p orbitals.



Figure 1.5. Structure modification effects on the contortion in hexabenzocoronene.<sup>‡</sup>

<sup>&</sup>lt;sup>‡</sup> Figure adapted from: Ball, M.; Zhong, Y.; Wu, Y.; Schenck, C.; Ng, F.; Steigerwald, M.; Xiao, S.; Nuckolls, C. *Acc. Chem. Res.* **2015**, *48*, 267–276. Reprinted with permission from ACS.

To illustrate the effect of substituents and heteroatoms on the degree of distortion in PAHs, different hexabenzocoronenes Figure 1.5 shows three (HBC). All-carbon hexabenzocoronene (c-HBC) is highly contorted as shown by the X-ray diffraction structure in Figure 1.5a. If the outer phenyl rings are replaced with thiophenes, dibenzotetrathienocoronene (c-DBTTC) is obtained (Figure 1.5b). This change in the structure diminishes the degree of bending since thiophenes relax the steric interaction at the periphery. Different conformations are possible like butterfly or up-down with interconversion. Then, when fluorine atoms replace protons in the c-HBC molecule, the structure in Figure 1.5c is obtained. Instead of presenting an up-down conformation, the Xray structure shows a bowed central acene, which should theoretically be higher in energy.<sup>8</sup>

With respect to the polycyclic aromatic hydrocarbon definition, vat dyes do not fit the profile. Indeed, most vat dyes have heteroatoms in their structure whereas PAHs only have carbon and hydrogen atoms. Nevertheless, they often possess many aromatic cycles and their heteroatoms bestow a certain versatility in regard of their reactivity. The designation, vat dye, comes from the process in which they are used. For example, indigo, a highly water insoluble molecule, is used to dye jeans. Indigo is reduced to a *leuco* form with sodium dithionite to become a water soluble dianionic salt (Scheme 1.1). Textiles in contact with *leuco*-indigo, a colorless compound, are coated with it. Then they are dried and indigo is oxidized back to its neutral form, a deep blue shade.<sup>9</sup> The jeans can be worn and washed without fading their color.





For academic research, vat dyes are very coveted since they have a complex structure. They are also mass-produced and are usually very cheap. The heteroatoms also allow easy derivatization to make interesting compounds. Because the vat dyeing process requires a

quinoid structure, anthraquinone dyes are the most widely used pigments.<sup>10</sup> 4,10dibromoathanthrone, which is the dye of interest in this thesis, is classified as an anthraquinone dye and will be discussed in detail in section 1.5. Other examples of anthraquinone dyes are shown in Figure 1.6. Indanthrone blue was the first vat dye to be synthesized in a laboratory. It was previously isolated from a plant. Alizarin is a pigment used for textile dyeing since antiquity, but has also been known to stain calcium deposits in medicine.<sup>11</sup> Solvent Violet 13 is used to dye polymethacrylate, polystyrene and polycarbonate because transparency of the plastic can be retained.<sup>10</sup>



Figure 1.6. Examples of anthraquinone dyes.

#### **1.4. PAH-based Diradicals**

#### 1.4.1. Semantics of Unpaired Electron Chemistry

Generally, polycyclic aromatic hydrocarbons are in their closed-shell ground state, that is, all the valence electrons are accommodated in  $\pi$ -bonding orbitals. To the opposite, open-shell molecules are compounds with one or more unpaired electrons. Figure 1.7, left shows phenalene in the closed-shell form where all the electrons are paired. If the compound loses one hydrogen atom through homolytic cleavage, it is transformed to the phenalenyl radical. Analogous to the previous case, trityl radical is obtained from triphenylmethane (Figure 1.7, right).



Figure 1.7. Closed and open-shell configurations of phenalene and triphenylmethane.

There is an important distinction to make between radicals, biradicals and diradicals. To visualize these concepts, Figure 1.8 represents the key words that classify the type of molecules with one or more unpaired electron(s). In Figure 1.7, a chemical reaction involving a homolytic bond cleavage is necessary to obtain a free radical, monoradical or simply called radical: "a molecular entity such as 'CH<sub>3</sub>, 'SnH<sub>3</sub>, Cl' possessing an unpaired electron."<sup>12</sup> The difference between biradicals and diradicals is a bit more finicky. In both cases, there are two radicals (unpaired electrons) in a single molecule. The distinction lies in whether they interact with each other or not through bonding and delocalization. According to the IUPAC Gold Book, a biradical is "an even-electron molecular entity with two (possibly delocalized) radical centers which act nearly independently of each other. Species in which the two radical centers interact significantly are often referred to as 'biradicaloids'. If the two radical centers are located on the same atom, the species are more properly referred to by their generic names: carbenes, nitrenes, etc." A diradical is a "molecular species having two unpaired electrons, in which at least two different electronic states with different multiplicities [electron-paired (singlet state) or electron-unpaired (triplet state)] can be identified."<sup>12</sup> To calculate the multiplicities, the simple equation is 2S+1. The spin of an electron (S) is  $\frac{1}{2}$  and its orientation can be + or - depending on the other electron. In the case of a free radical, the spin is either + or -,  $2(\frac{1}{2})+1 = 2$ . For a free radical, its multiplicity is always doublet and paramagnetic. For diradicals, it depends if the orientation is opposed  $(+\frac{1}{2}, -\frac{1}{2}) 2(0)+1 = 1$ , thus a singlet (diamagnetic), or aligned  $(+\frac{1}{2}, +\frac{1}{2}) 2(1)+1 = 3$ , thus a triplet (paramagnetic). According to Hund's rule, the triplet state with parallel spins is lower in energy than the antiparallel configuration, singlet state. The singlet and triplet classification for diradicals is based on their ground state, but it is possible for a molecule to be excited, thermally for example, to the other configuration.<sup>13</sup> Several examples will be shown in the following section 1.4.3.





The focus of this thesis is mainly on diradical compounds. One key concept to understand these molecules is that they have a diradical character<sup>\*\*</sup> (y) and that they are never fully open-shell. Indeed, there is an equilibrium between the open and closed-shell configurations. As a rule, y = 0 is exclusively closed-shell and y = 1 is exclusively open-shell.<sup>14</sup> No existing diradical has y = 1, typically they have a diradical character somewhere in-between 0 and 1 (0 < y < 1). The more the open-shell form is stabilized, the greater the diradical character is, i.e. close to 1. The diradical character can be calculated by the following equation:

<sup>&</sup>lt;sup>§</sup> Incorrect use of the semantics defined by the IUPAC gold book is common in the literature.

<sup>\*\*</sup> Diradical character and biradical character in the literature and in this thesis are used as interchangeable synonyms.
$$y = 1 - \sqrt{1 - \left(\frac{{}^{1}E_{1u} - {}^{3}E_{1u}}{{}^{1}E_{2g} - {}^{1}E_{1g}}\right)^{2}}$$
 Equation 1.1

The four terms refer to four electronic states:  ${}^{1}E_{1g}$  is a neutral lowest energy singlet state of g symmetry,  ${}^{1}E_{1u}$  is an ionic singlet state with u symmetry,  ${}^{1}E_{2g}$  is an ionic singlet state of g symmetry, and  ${}^{3}E_{1u}$  is a neutral triplet state. The equation can be derived to this second equation:

$$y = 1 - \sqrt{1 - \left(\frac{E_{S_{1u},S_{1g}} - E_{T_{1u},S_{1g}}}{E_{S_{2g},S_{1g}}}\right)^2}$$
 Equation 1.2

Experimentally, the parameters in Equation 1.2 can be measured:  $E_{S_{1u},S_{1g}}$  and  $E_{S_{2g},S_{1g}}$  correspond to the lowest-energy peaks of the one- and two-photon absorption spectra, respectively, and  $E_{T_{1u},S_{1g}}$  can be retrieved from the phosphorescence and EPR spectroscopies.<sup>15</sup> It is also possible to calculate the theoretical diradical character using Density Functional Theory (DFT). Most often in the literature, the diradical character is calculated using DFT, because it is easier to compare the theoretical values to other systems using the same functional and basis set.

To illustrate the equilibrium to open-shell, Figure 1.9 represents a quinoid thiophene that has a diradical character. In the quinoid version, all the electrons are paired in the ground state.<sup>16</sup> To obtain the biradicaloid, double bonds are broken to form single bonds along with two unpaired electrons, resulting in a structural change. In the process, two electrons are promoted to the doubly excited configuration and placed in singly occupied molecular orbitals (SOMOs). In Figure 1.9, they are represented as triplet. The characteristic feature of biradicaloid compounds is that their small bandgap allows for the simultaneous existence of both the doubly excited state and the closed-shell form in the bulk sample under ambient conditions.<sup>17</sup> That is why an equilibrium arrow is drawn between the two forms: the more the doubly excited state is accessible, the more the arrow points toward the right, resulting in a larger diradical character. Again, the low energy cost to carry out this transformation is associated with a small bandgap.



Figure 1.9. Doubly excited configuration in a biradicaloid compound.

## 1.4.2. Three Strategies to Obtain Stable Organic Diradicals

There are three main strategies to obtain stable organic diradicals:

- 1. Pro-aromatic molecules
- 2. Electron withdrawing and blocking groups
- 3. Steric congestion release

First, pro-aromatic molecules are simply quinoid structures that can become aromatic. Quinoid structures are widely used when designing biradicaloids because a double-to-single bond transformation along with the formation two radical centers create an aromatic structure. This thermodynamic stabilization pushes the equilibrium to the diradical form, increasing the diradical character. Quantitatively speaking, whenever a double bond is broken to form a single bond an energetic cost of 270 kJ/mol is necessary. Therefore, an equal or greater stabilization energy is needed to overcome this cost. In section 1.2. the Clar aromatic sextet was discussed to describe the aromatic character of PAHs. The formation of one aromatic sextet stabilizes the molecule by 90 kJ/mol, that is the homodesmic stabilization energy of benzene.<sup>18</sup> According to these numbers, it would take three sextets to stabilize one double bond breaking.<sup>19</sup> Figure 1.10 presents a closed-shell dibenzoheptazethrene with two

aromatic sextets.<sup>20</sup> The center of the molecule is quinoidal, but upon bond breaking, a diradical with two resonance forms is obtained. The aromatic stabilization is only one sextet and this example is one of many to show that the previous deduction is not always useful when designing diradical molecules. Other structure-dependant factors must be considered to fully comprehend the biradicaloid nature of certain compounds.

#### 1,2:9,10-Dibenzoheptazethrene





Second, electron withdrawing and blocking groups have three specific functions when designing diradical compounds. On the practical side, one obvious role is to increase the solubility of PAHs that are often planar and poorly soluble in common organic solvents. This greatly facilitates their processing and study. Specifically, electron withdrawing groups lower the HOMO or SOMO level of the compounds to increase their stability in air. Indeed, these groups increase the oxidation potential of diradical molecules. The last role of sterically hindered groups is to block key positions where the spin density is high. Diradical compounds are often very reactive and tend to dimerize or polymerize with itself or other molecules. Blocking groups can prevent the approach of other molecules to maintain the integrity of the structure. Figure 1.11 illustrates a few examples of electron withdrawing groups, such as nitrile and fluorine, and blocking groups commonly used like triisopropylsilyl and mesityl.<sup>21,22</sup>



Figure 1.11. Examples of electron withdrawing and blocking groups used to stabilize openshell compounds.

Third, steric congestion release can be a powerful tool to make open-shell diradicals. Figure 1.12 shows two examples of this strategy to obtain PAH-based diradicals.<sup>23,24</sup> In the closed-shell form, the double bonds prevent rotation of the peripheral groups aligning every moiety in the same plan, and inducing a strong steric tension. This strain weakens the double bond, that can be easily converted to a single bond with the formation of the open-shell structure. With these newly formed single bonds, the peripheral groups can rotate to be positioned orthogonal to the core. This steric congestion release is a strong driving force to obtain a more stable open-shell form.



Figure 1.12. Steric congestion release as a driving force to form diradical compounds.

## 1.4.3. Types of Benzenoid Open-Shell Hydrocarbons

There are four main categories of PAH-based open-shell molecules, as presented in Figure 1.13. First, zethrenes are z-shaped compounds and were briefly discussed in section 1.4.2. Various numbers of phenyl rings and their positioning can modulate the diradical character. The driving force is always based on the central quinoid phenyl ring that becomes aromatic after one double bond is broken.<sup>25,26</sup> A number of important contributions were made in the development of diradical zethrene using different lengths of  $\pi$ -conjugated phenyl rings and sterically hindered groups.<sup>20,27–29</sup> Second, phenalene has three phenyl rings arranged in a pyramid. It is a quite interesting molecule because three redox species can be obtained: cation, radical, and anion. A deep blue colored phenalenyl radical character and the stability of phenalene,  $\pi$ -bridging units such as s-indacene, shown in Figure 1.13, can be employed to connect two phenalenyl units.<sup>31,32</sup>

For the scope of this thesis, periacenes and Chichibabin-type hydrocarbons are the most interesting and relevant categories of open-shell PAHs and will be discussed in more details. Periacenes and acenes are widely spread in the literature as a scaffold to make open-shell molecules. Basically, acene compounds are linearly fused phenyl rings. In 2004, Bendikov *et al.* predicted by theoretical calculations that heptacenes and longer acenes would have an

open-shell singlet ground state.<sup>33</sup> At the time, pentacene was given a lot of attention as it was a promising semiconductor material,<sup>34–36</sup> but longer acenes were elusive because of the associated synthetic challenges and stability issues. The first synthesis of 7,16-bis(trimethylsilylacetylene)heptacene with spectroscopic characterization was done by Anthony and coworkers in 2005.<sup>37</sup> Despite the theoretical prediction of an open-shell singlet ground state and the low bandgap (1.30 eV), sharp <sup>1</sup>H NMR signals and electron paramagnetic resonance (EPR) spectroscopy confirmed the closed-shell nature of this compound. In 2011, Anthony's group published the synthesis of the nonacene shown in Figure 1.11, left.<sup>21</sup> Proton NMR spectra showed only noise, while UV-visible spectra revealed an unresolved hyperfine coupling consistent with the presence of a radical species.



Figure 1.13. Four main categories of open-shell polycyclic aromatic hydrocarbons.

Next, the term *peri* describes 1,8 substitutions in naphthalene and other acenes. In this context, periacenes are simply *peri*-condensed acenes that ultimately form rectangular PAHs. In these compounds, there is only one Clar sextet per acene, delocalized over the entire row. That is also the explanation for their high reactivity. Consequently, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap is decreased and these compounds have a strong propensity to become open-shell. Kubo,

Champagne *et al.* defined a nomenclature for periacenes, albeit not commonly used in the literature. They conducted a theoretical study to predict the diradical character of these molecules which can be quite enlightening in the context of this thesis (Figure 1.14).<sup>38</sup> Acenes and periacenes are described as (a-b). For example, heptacene would be (7-1) and bisanthene would be (3-3). It is worth noting that some periacenes have a perfect predicted diradical character (or very close), namely (6-3, 7-3, 4-5, 4-7, 5-5, 5-7, 6-5, 6-7, 7-5, 7-7). Although, there are few large periacenes reported in the literature because of the associated synthetic difficulties and stability, they would be very interesting to investigate according to these calculations.

12a							
ŶŶŶŶ	b	a					
		2	3	4	5	6	7
3 armchair edge	1	0.00	0.00	0.01	0.07	0.20	0.40
	3	0.00	0.12	0.60	0.84	0.94	0.98
	5	0.01	0.59	0.91	0.98	0.99	1.00
	7	0.05	0.84	0.98	1.00	1.00	1.00

Figure 1.14. Periacene nomenclature and singlet diradical character (y) of acenes and periacenes.

zigzag edge

Figure 1.13 speaks for itself when understanding the stabilization gain to obtain an open-shell periacene, two additional sextets are formed in a (3-3) periacene. Experimentally, X-ray diffraction structures and aromatic character by theoretical calculations are important indications of the diradical character. First, the bond denoted by z in Figure 1.13 changes from single to double when the periacene adopts the open-shell form. The length of the z bond is a direct evidence of the magnitude of the diradical character, i.e. the closest it is to the length of a regular double bond, the more open-shell the molecule is. Even if a low diradical character of 0.12 was predicted for bisanthene, it was demonstrated experimentally that tetra-*tert*-butylbisanthene is closed-shell.<sup>39</sup> X-ray diffraction showed that the z bond was close to a regular single bond and the proton NMR did not show any signal broadening. The EPR-inactive compound further supports the absence of diradical character.

Champagne, Kubo *et al.* published the synthesis and characterization of teranthene (3-5) in 2010.<sup>19</sup> This compound goes from three to six sextets when passing from the close to open-shell form, thus possessing a theoretical diradical character of 0.42. Line broadening in <sup>1</sup>H NMR along with strong absorption in the NIR are evidences for the doubly excited configuration and the diradical character of teranthene. This molecule is fully consistent with the first strategy to obtain an open-shell compound that is, the aromaticity gain compensates for the loss of double bonds. For this specific system, one double bond is broken along with the formation of three additional Clar sextets, which is quite remarkable. This is also the explanation as to why bisanthene (3-3) is not a diradical because one double bond is broken along with the formation of only two aromatic sextets. Based on the same synthetic strategy, quarteranthene has been synthesized in 2013 by Kubo. It is a (3-7) periacene with an incredibly high diradical character of 0.91.<sup>40</sup>

To continue on periacenes, they can be viewed as zigzag-edge graphene nanoribbons, which fuelled the study of the magnetic properties of graphene.<sup>41</sup> Very recently, Wu and coworkers published an extensive study on the bottom-up synthesis of rylene ribbons with different lengths.<sup>42</sup> Hexarylene and longer periacenes are characterized by a diradical character with a small singlet-triplet gap. This finding further reinforces the idea that the diradical character is accessible through low bandgap molecules.

Chichibabin<sup>††</sup> and Thiele's hydrocarbons consist of the last and most important category of PAH-based open-shell in the context of this thesis. They have been known for more than a century and their structure is presented in Figure 1.15.<sup>43,44</sup> The ground state contribution of both the quinoid and the open-shell aromatic forms has led researchers to suspect a diradical nature even if the technological advances did not allow their study. The high reactivity towards oxygen and their tendency to dimerize and polymerize was also a strong indication of the presence of unpaired electrons. It was much later that the diradical character was assessed using a thorough study of their crystal structures.<sup>45</sup> It was demonstrated that the diphenylmethane in both Chichibabin and Thiele's hydrocarbons are twisted out of the plane

<sup>&</sup>lt;sup>††</sup> Tschitschibabin is the original Russian name translated to Chichibabin in English.

because of steric hindrance caused by the nearby protons. This key element in the design can be exploited to kinetically stabilize the structure in the open-shell diradical form.

Thiele's hydrocarbon, 1904



Chichibabin's hydrocarbon, 1907



Figure 1.15. Thiele's and Chichibabin's hydrocarbons.

In the last 15 years, Chichibabin-like molecules made a come back with a different name: *para*-quinoidimethane. A fancy name to describe essentially the same basic design reported more than 100 years ago. It was in 2001, with the synthesis of a "fairly stable triplet carbene", that the notion of stable open-shell compounds was brought back to the scientific community, although it was not clearly stated in the paper.<sup>46</sup> The carbene is obtained through photolysis of a diazomethane precursor and the radical is delocalized in the anthryl groups. It has a lifetime of about 19 minutes after which, it trimerizes (Figure 1.16). The perpendicular anthryl groups are essential for the stability of the molecule since it can delocalize the radicals, which are also shielded by the four *peri* hydrogens.

In modern versions of Chichibabin's hydrocarbon, the complexity comes from molecular design. Three competitive factors need to be balanced to obtain the highest diradical character. First, the driving force to obtain a diradical is the gain of aromatic sextets by losing a quinoidal form. Another consideration is the steric hindrance which will dramatically influence the geometry and therefore the diradical character. The last factor is the substituents on the germinal carbon that bears the diradical. The nature of these substituents is crucial to the stability of the compound. Basically, the three competitive factors are the same three strategies to obtain stable diradical compounds discussed in section 1.4.2.



Figure 1.16. Triplet carbene that can be delocalized to form a diradical.<sup>‡‡</sup>

A good demonstration of these concepts was made by Wu and coworkers in 2012, presented in Figure 1.17.<sup>47</sup> Two anthracene units were used to induce steric congestion to produce an out of plane twisting (butterfly) as in the Chichibabin and Thiele's hydrocarbons. They are also used to increase the thermodynamic stabilization by introducing more aromatic sextets. It is a rare example reported in the literature where two aromatic sextets are lost in the open-shell form as shown in Figure 1.17 from 1-G/2-E to 1-E/2-G. The open-shell version should not be accessible, but the terminal groups have a dramatic impact on the nature of the ground state. Indeed, molecule 1 has tert-butyl groups for steric protection and increased solubility as for molecule 2, fluorenyl groups are used to improve the radical stability by delocalization. The delocalization in the fluorene unit offers a better thermodynamic stabilization for the radical than in the di-*tert*-butylphenylmethane. Also, the fluorenyl units are much less flexible than the diphenylmethane. The rigid fluorenyl groups induce bending in the structure to decrease the steric congestion. For the diphenylmethane, the phenyl rings can be arranged as to limit contortion. Consequently, molecule 2 has an open-shell ground state with a small singlet-triplet energy gap while molecule 1 has a closed-shell quinoid ground state.

<sup>&</sup>lt;sup>‡‡</sup> Figure adapted from: Tomioka, H.; Iwamoto, E.; Itakura, H.; Hirai, K. *Nature* **2001**, *412*, 626–628. Reprinted with permission from AAAS.



Figure 1.17. Wu and coworkers' work on para-quinoidimethane.<sup>§§</sup>

Although the compounds presented in Figure 1.18 are not diradicals, the findings in this study are quite useful when designing *para*-quinoidimethane compounds. They also present a very intriguing mechanochemically-driven transformation.<sup>48</sup> It was found that the different benzannulations on the fluorenyl unit have a strong impact on the stability of the radical. In order of stability c > b > a, mainly because of steric protection and spin delocalization. Indeed, as shown in the spin density map depicted in the lower portion of Figure 1.18, the spin density is better protected by the benzannulation in c than in b and a. Also, because of the high steric hindrance in a-type molecule, the anthryl moiety is completely perpendicular to the fluorenyl, exposing the radical to side-reactions. It was demonstrated by X-ray diffraction studies that a and c could form a  $\sigma$ -dimers and the dimerization occurs where the spin density is high and accessible. The homolytic bond cleavage of these  $\sigma$ -dimers in the solid state is possible with a mechanochemical stress. Indeed, the crystals a and c-type molecules can be grinded with a mortar and pestle to produce the monomeric radicals, associated with a drastic color change.

<sup>&</sup>lt;sup>§§</sup> Figure adapted from: Sun, Z.; Zeng, Z.; Wu, J. Acc. Chem. Res. 2014, 47, 2582–2591. Reprinted with permission from ACS.



Figure 1.18. Three types of phenyl positioning in extended fluorenyl units and their spin density map (UBLYP/6-31G\*\*).\*\*\*

Moving on to different open-shell species designed to improve the stability of diradicals while keeping a high diradical character. Indeed, pentalene units between benzene rings have been used to rigidify the geometry of biradicaloids (Figure 1.19).<sup>49</sup> The tri*-p*-quinoidimethane is remarkably stable under ambient conditions either in the solid state or in solution. The recovery of three aromatic sextets along with a decrease of the HOMO level with electron-withdrawing nitrile groups near the radical centers allow compound **3** to display a diradical character. A broadened <sup>13</sup>C NMR caused by the contribution of a thermally excited triplet state, <sup>1</sup>H NMR temperature-dependence broadening, EPR spectroscopy, and superconducting quantum interference device (SQUID) measurements confirm an open-shell form with a singlet ground state. This system has a particularly small bandgap (1.02 eV) with absorption in the NIR because of its extended delocalization. Combining these properties with a high solubility imparted by the lateral groups, this compound represents a substantial contribution to the organic diradical field.

<sup>\*\*\*</sup> Figure adapted from: Tian, Y.; Uchida, K.; Kurata, H.; Hirao, Y.; Nishiuchi, T.; Kubo, T. *J. Am. Chem. Soc.* **2014**, *136*, 12784–12793. Reprinted with permission from ACS.



Figure 1.19. Closed- and open-shell forms of tri-*p*-quinoidimethane.

The next system of importance are N-annulated perylenes, a type of diradical that could be inserted in the periacene category, but because their radical centers are mainly localized on the germinal carbons at the periphery rather than in the polycyclic system, they are treated separately. The first report of N-annulated perylene was published by Wu and coworkers in 2013 (Figure 1.20a).<sup>50</sup> After iterative and tedious syntheses, they were able to make polymers containing up to six pervlene monomers with geminal nitrile terminal groups. The smallest unit (n = 1) is a closed-shell quinoid ground state. The longer oligomers (n = 2-6) are proton NMR silent event at low temperature, indicating a significant diradical character. VT-EPR also supports this observation. In the case of n = 2 and n = 4, the signal intensity decreased with decreased temperature, consistent with a singlet diradical ground state in equilibrium with a higher energy triplet. For n = 5 and n = 6, another phenomenon was observed, i.e. the EPR signal intensity increased with lowering the temperature. This observation is in line with two individual radical centers (biradicals) and is explained by the weak coupling induced by the long distance separating the unpaired electrons. The main driving force to produce open-shell species in this system is the newly formed single bonds between the dicyanomethane groups and perylene units, which allow rotation and release of the steric repulsion. Also, no formal aromatic sextets are produced in the open-shell structure, but benzene rings are more aromatic because the two sextets can be delocalized in the underlying benzene.

Further exploiting this framework, the same group reported in 2015 a push-pull asymmetric N-annulated perylene (Figure 1.20b).<sup>23</sup> This is the first report studying an asymmetric diradical system and represents a very original contribution to the understanding of biradicaloids. It was hypothesized that the push-pull effect induced by the 1,2-dithiophenyl and the dicyanomethane groups would produce a stronger diradical character in longer

oligomers along with increased stabilization. Interestingly, the contribution of a zwitterionic and a diradical forms to the ground state increased the aromatic character of the perylene in comparison with the pull-pull type previously described. As demonstrated with molecule **4**, the push-pull molecule **5** with n = 1 is closed-shell, but for n = 2-3 evidences from NMR, ESR, and SQUID support an open-shell singlet ground state. The asymmetric strategy was not efficient in increasing the diradical character as evidenced by SQUID measurements, which allowed to measure slightly smaller contributions of the diradical to the ground state compared to the pull-pull type molecules. It was explained that in the zwitterionic form, different energies where required to break a double bond.

In a parallel study, Wu *et al.* attempted to fuse the N-annulated perylene to eliminate the steric repulsion between the neighboring units producing highly planar molecules (Figure 1.20c).<sup>51</sup> The extended version of perylene was intended to increase the conjugation, resulting in a smaller bandgap. As expected, n = 0 is a closed-shell ground state and a longer oligomer is necessary to obtain a biradicaloid (n = 1). SQUID measurements confirmed that the singlet-triplet gap was much larger (4.21 kcal/mol) for the fused system than for the parent molecules **4** (0.107 kcal/mol), indicating a small diradical character. The overall finding of this study was that steric repulsion between neighboring units (non-fused **4**) is a stronger driving force for the molecule to adopt an open-shell structure than increased delocalization in a planar structure (fused **5**).

Additionally, slight modifications on structure **5** were made in 2014, which "turned on" the diradical character of a single perylene unit (Figure 1.21).<sup>52</sup> Both molecules **7** and **8** possess a singlet diradical ground state in thermal equilibrium with a triplet state. In contrast with parent **4** (n = 1), **5** (n = 1), and **6** (n = 0), compound **7** has an open-shell diradical character that is ascribed to the increased aromaticity provided by the thiophene unit together with the steric repulsion of the perylene and thiophenes. This is a great example how slight structural changes can have a dramatic impact on the properties.



Figure 1.20. Examples of *para*-quinoidimethane with their open-shell form a) N-annulated perylene, b) push-pull N-annulated perylene, and c) fused N-annulated perylene.

The last systems of interest are indenofluorenes and could stand as the fifth category of open-shell benzenoid PAHs, but because they are quinoid structures like the previous *para*-quinoidimethane, they belong to the same category. There are numerous studies on the indenofluorene structures but not all of them show a significant diradical character.<sup>53,54</sup> Also, open-shell indenofluorenes were difficult to study because of their high reactivity. In 2011, the first investigation on biradicaloid indenofluorene was reported by Tobe and Shimizu (Figure 1.22a).<sup>55</sup> In this compound, only one double bond is broken in the transition to

open-shell whereas three aromatic sextets are formed. The aromatic gain compensates for the loss of double bonds. Indeno[2,1-a]fluorene did not show temperature-dependence in <sup>1</sup>H NMR, but theoretical calculation predicted a small diradical character.



Figure 1.21. Fused N-annulated perylene with 4-dicyanomethanethiophene terminal groups with their corresponding open-shell form.

Next indeno[2,1-b]fluorene, which was synthesized by the same group in 2013 (Figure 1.22b), is much more reactive and its calculated diradical character is much higher (0.68 versus 0.33) than the previous compound.<sup>56</sup> The *meta*-quinoidimethane isomer was expected to have an increased diradical character compared to its *ortho* analogue. Indeed, proton NMR peaks are very broad, nearly silent and sharpen at lower temperature. Strong absorption in the NIR to almost 2000 nm, even if it has a very short delocalization pathway, is another indication of its singlet ground state with a low-lying triplet state.

Moving on to the *para*-substituted indeno[2,1-c]fluorene synthesized by Haley and coworkers in 2013 (Figure 1.22c).<sup>57</sup> In the original article, the calculated diradical character was not significant and it was concluded that it is a quinoid closed-shell ground state. In each structure presented in Figure 1.22, one double bond is broken, and they have a) 3 additional

sextets, b) 2 additional sextets, and c) 1 additional sextet. From this observation a should have the largest diradical character, but only b has a significant y factor. The explanation resides in the *meta* substitution of the central benzene ring, because the radicals cannot interact or recombine as opposed to the *ortho* or *para* substitution.

Out of the five possible indenofluorene regioisomers, the last to be synthesized and characterized was indeno[1,2-a]fluorene (Figure 1.22d) in 2017.<sup>58</sup> This molecule has a triplet ground state confirmed by very broad peaks in <sup>1</sup>H NMR that sharpened with increased temperature as well as a signal intensity increase with decreased temperature in EPR spectroscopy. The high diradical character (y = 0.80) stands in contrast with its indeno[1,2-a]fluorene analogue, that shows very modest diradical character (y = 0.26).<sup>58,59</sup>

One very significant contribution to the field of biradicaloid indenofluorenes was made by Haley and co-workers in 2016 (Figure 1.22e).<sup>60</sup> This molecule is very stable with a high diradical character of 0.62, enabling a more in-depth study of its properties. This compound is characterized by a singlet ground state in equilibrium with a low-lying excited triplet state. It shows broad absorption in the NIR as well as peak broadening until complete disappearance at 150 °C in the proton NMR.

A last example worth noting here was reported by Itami in 2016 (Figure 1.22f).<sup>61</sup> This extended indenofluorene possess an anti-aromatic pentalene in its center. A hybrid closed-shell/open-shell structure contributes to the ground state with a diradical character of y = 0.55. Because of the long distance between the radical centers, the solid state EPR did not show spin-spin coupling, so in the solid state it could be qualified as a biradical. Finally, mesityl groups seem to be the most efficient and synthetically convenient substituents to add steric protection on indenofluorene. They are most often placed in the five-membered ring because the spin density is always the highest in this position.



Figure 1.22. Selected examples of open-shell diradical indenofluorenes with their diradical character.  $^{\dagger\dagger\dagger}$ 

 $<sup>^{\</sup>dagger\dagger\dagger}$  The diradical character has been calculated using DFT.

#### **1.4.4.** Bis(triarylamines) Diradical Dications

A parallel subject to PAHs-based open-shell systems are bis(triarylamine) diradical dications. These molecules are closely related to the *para*-quinoidimethane diradicals, the main difference resting on the amine as a replacement for the germinal carbon with a radical center. Studies of the dicationic amines led to the discovery of very stable open-shell systems with interesting optoelectronic properties. These studies mainly arise from the interest of high-spin organic molecules and molecular magnets in vogue in the 90s and early 2000s. Keeping the viewpoint of open-shell compounds, oxidized nitrogen is isoelectronic to carbon and that is what propelled researchers to make nitrogen analogs of the all-carbon open-shell structures. Because nitrogen is more electronegative than carbon, the radicals tend to be much more stable than in their parent carbon analogs, making the amine derivatives convenient to study.<sup>62</sup> In this section, the work in the field of bis(triarylamine) diradical dications has mostly been directed towards new bridging units to make stable open-shell molecules with a large diradical character.

Tanaka *et al.* made the first significant contribution in 2003 (Figure 1.23).<sup>63</sup> From the schematic drawing of the frontier molecular orbitals, it was deduced that the spin in each pyridine-based anthracene could only interact with each other when the orbitals are antisymmetric (AA = antisymmetric, AS = symmetric) in both planes. Theoretical calculations showed that the HOMO for **9** is doubly degenerate, and for its doubly oxidized homologue (**9**<sup>2+</sup>), is two degenerate, singly occupied molecular orbitals (SOMOs). The radicals are separated in two orthogonal  $\pi$ -systems, but these systems are separated by a single silicon atom, making them close enough to interact with each other. Therefore, the EPR spectroscopy showed that the doubly oxidized compound **9** has a triplet ground state.



Figure 1.23. Spiro-fused **9** with a schematic drawing of the frontier molecular orbitals.<sup>‡‡‡</sup> Bis(triarylamine) diradical dications that rely on the quinoid to aromatic transformation were first reported by Marder and co-workers in 2006 with complete characterization (Figure

<sup>&</sup>lt;sup>‡‡‡</sup> Figure adapted from: Ito, A.; Urabe, M.; Tanaka, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 921–924. Reprinted with permission from John Wiley and Sons 4296620850009, license date Feb 26, 2018.

1.24).<sup>64</sup> It was expected that upon double oxidation of compound **10**, the dication would adopt a closed-shell quinoid structure **11**. A closer analysis of the bond length in the X-ray diffraction structure suggested that the double and single bonds were not "fully quinoidal". The reality was rather a hybrid structure between **11** and **12**, possessing and open-shell singlet ground state confirmed by NMR and EPR spectroscopies. Adoption of the quinoidal structure **11** would require the de-aromatization of two phenyl groups which has a non-negligible energetic cost.



Figure 1.24. Bis(triarylamine) dications with nonquinoidal geometry.

Wang and colleagues have published the next series of reports presented here, spanning from 2013 to 2016 (Figure 1.25). First, The synthesis of compound **13** was not intentional.<sup>65</sup> Oxidation of the mono six-ring amine (half-molecule **13**) with two equivalent of  $B(C_6F_5)_3$  led to a dimerization, producing bipolarons **13**. The <sup>1</sup>H NMR spectrum showed broad peaks that sharpen at low temperature, indicating a ground state singlet also supported by SQUID measurements. The X-ray diffraction structure showed twisting of 12.6° between the two planes confirming a single bond character of 1.467 Å, slightly shorter than typical biphenyl single bonds of 1.48 Å, and much longer than a regular double bond of 1.34 Å.

Second, molecule **14** (Figure 1.25) with a diradical character of 0.79 was reported in 2014 and showed how crucial substituents in *para* of the amine were for the existence of an open-

shell structure.<sup>66</sup> Indeed, the presence of protons or methyl groups in *para* with the same structure provided closed-shell molecules, standing in sharp contrast with molecule **14** bearing methoxy groups. These methoxy groups have two roles: decreasing the oxidation potential of the amines and delocalizing the spin density for an increased overall stability.

Third, compound **15** (Figure 1.25) exhibited a magnetic bistability that was never reported in discrete organic radicals. This compound has the shortest phenyl bridging unit amongst bis(triarylamine) dications in which the radicals cannot recombine because of the perpendicular  $\pi$ -systems caused by the steric crowding of the peripheral methyl substituents, yet the radicals still can interact with each other. Simply put, this compound has two distinct singlet diradical dications.

Fourth, the last molecule of interest in the series of contributions from Wang's group is molecule **16** containing a terphenyl bridging unit (Figure 1.25).<sup>67</sup> They were able to confirm by EPR and SQUID that **16** has a singlet diradical ground state in thermal equilibrium with a triplet state. Interestingly, that singlet-triplet gap can be modulated with the angle between the terphenyl bridge. Indeed, the diradical character is proportional to the angle between rings a and b in Figure 1.25, bottom. For a twisting angle of  $3.78^{\circ}$ , y = 0.79, for  $26.76^{\circ}$ , y = 0.89 and for  $32.17^{\circ}$ , y = 0.93. The degree of twisting in the terphenyl bridge is correlated to the temperature, so the diradical character can be thermally controlled, an unprecedented finding.

Compound **17** presented in Figure 1.26 was reported by Ito in 2016.<sup>68</sup> It is similar in design to Wang's work, but the anthracene added a much interesting structural parameter to the study. It was demonstrated that the N-substituents are also very important in determining the ground state of the dicationic amines. It was found that 1-anisyl,1'-methylamino anthracene undergoes structural changes to a butterfly structure when oxidized to maintain two aromatic sextets and a closed-shell structure. On the contrary, with compound **17**, adopting the quinoid form is highly disfavored because of the high steric hindrance. For that reason, **17** has an accessible open-shell structure.



Figure 1.25. Wang et al. contributions to bis(triarylamine) dications.

Finally, the last relevant system was published very recently by Casado and co-workers. Compound **18** contains highly planar  $\pi$ -bridging units (Figure 1.26).<sup>69</sup> Casado *et al.* synthesized a series of bis(aminorayl)oligo(phenylenevinylene), with up to four oligo(phenylenevinylene)s. It was found that for n = 1-2, the compounds were closed-shell quinoidal molecules while longer oligomers (n = 3-4) were open-shell. The diradical nature was confirmed by X-ray diffraction structures in which longer oligomers exhibited bond lengths somewhere between quinoid and bis(radical cation)s. UV-visible spectra for the longer dicationic oligomers (n = 3-4) showed broad absorption in the NIR as far as 2500 nm.



Figure 1.26. 9,10-diaminoanthracene dication and bis(aminoaryl)oligo(phenylenevinylene).

The four classes of benzenoid open-shell PAHs and bis(triarylamine) diradical dications presented in these sections do not cover all the different molecules synthesized in the literature and there are as many different categories as there are different authors. Still, this selection represents a good overview of the research relevant to the contributions described this thesis.

## **1.5.** Anthanthrone Dye

In 2012, Jean-Benoît Giguère, a former PhD student in the Morin group introduced a new dye in the chemical cabinet, 4,10-dibromoanthanthrone. It was supplied by Heubach, a German company specialized in pigment production. It bears several different names such as Vat Orange 3, Pigment red 168 or anthanthrone red. Doctor Giguère has been a pioneer for the development of the chemistry of Vat Orange 3 and its derivatives. Albeit fairly new to the field of physical organic and materials chemistry, anthanthrone has been known for more than 100 years. Anthanthrone synthesis was achieved for the first time in 1914 by Ludwig Kalb.<sup>70</sup> It is now produced industrially from naphtostyril, according to Scheme 1.2.<sup>10</sup> 8-amino-1-naphthoic acid is formed by hydrolysis of naphtostyril, then 8-amino-1-naphthoic acid is formed by hydrolysis of naphtostyril, then 8-amino-1-naphthoic acid is diazotized with NaNO<sub>2</sub> and dimerized along with release of nitrogen gas, forming 1,1'-binaphthalene-8,8'-dicarboxylic acid. Anthanthrone is formed by a condensation

reaction in sulfuric acid and directly subjected to a bromination in presence of iodine to obtain the final dye.



Scheme 1.2. Industrial synthesis of 4,10-dibromoanthanthrone.

4,10-dibromoanthanthrone provided by Heubach is quite pure compared to the usual technical grade of vat dyes, normally used for bulk applications. The presence of position isomerism in the pigment is inevitable but does not represent an obstacle since the isomers can be removed by subsequent derivatization.

## 1.5.1. Semantics: Anthanthrone versus Anthanthrene

In this thesis, the word anthanthrone refers the anthanthrone core in the quinoidal form regardless of the presence of oxygen atoms in the 6 and 12 positions (*vide infra*). The word anthanthrene describes the anthanthrene core in the aromatic form Figure 1.27.



Figure 1.27. Structure of anthanthrone and anthanthrene.

#### 1.5.2. Reactivity

This thesis is mainly focused on recent developments based on the functionalization in the 4,10 and 6,12 positions (Figure 1.28). As demonstrated by Dr. Giguère, anthanthrone is a very stable molecule, which can sometimes be an obstacle to the synthesis of new derivatives.



Figure 1.28. Anthanthrone position numbering.

There are three key synthetic steps directly performed on the anthanthrone core to make the derivatives of interest in this thesis (Figure 1.29). The first reaction is a Sonogashira coupling using triisopropylsilylacetylene on the bromine atoms of anthanthrone to provide the soluble compound **19**. It is also the first successful synthesis reported by Dr. Giguère<sup>71</sup> Although the reaction was reported using THF as the solvent, *o*-dichlorobenzene, a quite marginal solvent for palladium cross-coupling reactions, has proven to be more efficient in solubilizing the starting material. Yields as high as 89% could be obtained after three days of reaction in comparison with 70% in THF.

The second key synthetic step is the Ramirez olefination on the ketone in 6 and 12 positions, producing the tetrachloro derivative **20**. Because the ketones of anthanthrone have a quite remarkable stability, substantive efforts have been devoted to the development of conditions for the installation of a geminal carbon in the 6 and 12 positions by my predecessor.<sup>71</sup> The successful conditions to obtain compound **20** are performed in tetrachloromethane at 150 °C for 20 minutes. The final compound is highly sensitive to light in ambient conditions and tends to oxidize back to the ketone starting material and other unknown decomposition products. Therefore, a simple protection from light with aluminum foil is necessary for storage. It is also possible to perform this reaction with different substituents in the 4 and 10 positions such as diphenylamines or alkylthiophenes.<sup>§§§</sup> One interesting thing about compound **20** is that the chloroalkenes are highly reactive compared to the usually low reactivity of chloro-compounds in Suzuki cross-coupling reactions. Subsequent installation of phenyl substituents on compound **20** can be performed at temperatures as low as 50 °C

<sup>&</sup>lt;sup>§§§</sup> Unpublished work, Maude Desroches

with the most standard  $PdCl_2(PPh_3)_2$ /triphenylphosphine catalyst/ligand couple. Indeed, increasing temperature to 100 °C leads to decomposition products, which was the starting point for the study of diradical compounds discussed in Chapter 2.

Sonogashira Cross-Coupling



Figure 1.29. Key synthetic steps for the anthanthrone functionalization.

The third key reaction for this thesis is the imine condensation and subsequent reduction to amine.<sup>72</sup> Again, the development of specific reaction conditions is a testament to the low reactivity of the ketone functionality of the anthanthrone dye. The use of TiCl<sub>4</sub> as a Lewis acid and dehydrating agent in combination with a high boiling point solvent, o-dichlorobenzene, employed at high temperature is necessary for the reaction to proceed.

Compound **21** is obtained in two-steps without purification through an imine condensation and further reduction with hydriodic acid. This provides secondary amines in the 6 and 12 positions which can be further cross-coupled in a catalytic Buchwald-Hartwig amination coupling to obtain an anthanthrene-based tertiary amine. It is important to note that 4,10-dibromoanthanthrone is not very soluble in common organic solvents and each reaction performed on the pristine material should be left to react for at least 24 h, and preferably 72 h.

### 1.5.3. Geometry

Both 4,10-dibromoanthanthrone and anthanthrene are highly planar polycyclic aromatic cores, as evidenced by the crystal structures in Figure 1.30.<sup>73,74</sup> As previously discussed in section 1.4.3. the anthanthrone core is not a proper periacene because it does not have the *peri* fused anthracene. The two anthracenes are directly fused to one another, resulting in absolutely unique properties.



Figure 1.30. 4,10-dibromoanthanthrone, left and 6,12-triisopropylsilylethynylanthanthrene, right, X-ray crystal structures.

Substituents in the 6,12 positions have proven to induce contortion in the core as reported by my predecessor Dr. Giguère (Figure 1.31).<sup>71</sup> Theoretical calculations also showed the same contorted aromatic core with different substituents, such as 1,2-benzenedithiol, to make a

*super*extended tetrathiafulvalene.<sup>75</sup> The curvature of the anthanthrone core is used to bind fullerenes such as  $C_{60}$  and  $C_{70}$ . The contorted anthanthrone core has led to the development of a new reactivity and has been a starting point for the development of diradical chemistry discussed in detail in Chapter 2.



Figure 1.31. X-ray diffraction structure of 4,10-Bis[(triisopropylsilyl)ethynyl]-6,12-bis(dicyanovinylene)anthanthrene.

## 1.5.4. Aromaticity and Conjugation Channels

According to NICS calculations for the different cycles in anthanthrene, the most aromatic ring is C with -12.70, then comes B with -10.06, and A is non-aromatic with -1.90 (Figure 1.32).<sup>76</sup> Because ring A is not aromatic, its double bond can be seen as an isolated alkene. Therefore, it should be easier to form an addition product on ring A rather than a substitution product. However, experience from previous laboratory members and numerous attempts to functionalize other positions of anthanthrene have led us to believe that anthanthrone is a very stable compound. Indeed, the double bond in ring A does not react under standard alkene functionalization conditions.<sup>\*\*\*\*</sup>

<sup>\*\*\*\*</sup> Unpublished results: Joël Boismenu-Lavoie, Isabelle Levesque, Bianka Turgeon, Maude Desroches, Antoine Lafleur-Lambert, and Jean-Benoît Giguère.



Figure 1.32. Clar valence structures of anthanthrene.

Anthanthrone possesses two major conjugation pathways, either 4,10 or 6,12 axes. The second channel is more effective than the first as J.-B.G. reported in 2014.<sup>77</sup> In this work, acetylenic linkers were used with different substituents in each conjugation channel. Varying these acetylenic moieties provided insights into the conjugation channel by the evaluation of the optoelectronic properties. Since the 4,10 axis did not strongly influence the properties of anthanthrene, it can be used to fine tune the solubility and packing of the compounds depending on specific application needs. It is worth noting that addition of substituents in the 6 and 12 positions on the anthanthrone core induces contortion with various bending degrees depending on the bulkiness of these substituents. Consequently, the aromatic character in the anthanthrone core can be diminished since orbitals are not perfectly overlapped. As a result,  $\pi$  electrons cannot circulate freely. Overall, to induce the most significant alterations of the optoelectronic properties, the 6,12 axis should be the center of attention when designing new molecules.



Figure 1.33. Mesomeric structures of anthanthrene and anthanthrone.

Interestingly, transformations from the quinoidal anthanthrone to fully aromatic anthanthrene should not be accompanied with aromatic stabilization. That is because both anthanthrone and anthanthrene possess two Clar aromatic  $\pi$ -sextets (Figure 1.27). There are four mesomeres of anthanthrone and anthanthrene illustrated in Figure 1.33. Because ring C is the most aromatic followed by ring B (same ring numbering as in Figure 1.32), the most stable

mesomer of anthanthrene should be **M1**. There is certainly an energetic cost associated with the de-aromatization of rings B and C in **M2**, making conjugation channel 4,10 much less effective. In the case of anthanthrone, both **M3** and **M4** possess an aromatic C ring, therefore they should be more stable than **M2**. For **M4**, both axes are quinoidal with aromatic C rings, making both 4,10 and 6,12 effective conjugation channels. In **M3**, only the 6,12 axis is conjugated,<sup>72</sup> making the 6,12 channel open in the two mesomers of anthanthrone. From these simple observations, the 6,12 conjugation channel is more effective in both anthanthrone and anthanthrene, in line with the experimental findings published by my predecessor.<sup>77</sup>

#### **1.5.5.** Other Anthanthrone Contributions

Since the first report of the synthesis of anthanthrone in 1914, there has been other publications on the study of anthanthrone and its derivatives, mostly related to the field of organic electronics. A thorough literature review on the subject has been published recently,<sup>78</sup> and some selected articles are described here to underline the versatility of this vat dye. The first molecule of interest in this section is compound **22** in Figure 1.34 reported by Neckers and Shi in 2006.<sup>79</sup> **22** is a blue emitter with a solid-state quantum yield of 47%. It has been used in an organic light-emitting diodes (OLEDs) with an initial luminescence of about 600 cd/m<sup>2</sup> and a very long half-life of more than 3500 h.

The second example is compound **23**, a nanohoop composed of four anthanthrene molecules reported by Isobe and coworkers in 2015.<sup>80</sup> They were able to demonstrate that the arylene and the anthanthrene rotated synchronously in solution.

The third and fourth molecules of interest are compounds **24** and **25**.<sup>81</sup> Asymmetric anthanthrenes are quite hard to prepare since their syntheses involve statistical reactions, which inherently lead to low yields. In the case of compound **24**, a mono Suzuki coupling on the 4,10-bis[4-(2-ethylhexyl)phenyl]-6,12-dibromoanthanthrene in the 6 or 12 positions using one equivalent of triphenylamine boronic ester afforded the asymmetrical anthanthrene in an impressive 53% yield. For compound **25**, the same strategy is employed, only that the Suzuki coupling is performed on the 4,10-dibromo-6,12-bis(octyloxy)anthanthrene in the 4 or 10 positions, affording the asymmetrical compound in 49% yield.





Figure 1.34. Selected examples of anthanthrone and anthanthrene molecules reported in the literature.<sup> $\dagger\dagger\dagger\dagger$ </sup>

The last example shown in Figure 1.34, bottom, is a polymer-based anthanthrone synthesized by my colleague Antoine Lafleur-Lambert in 2015.<sup>82</sup> Anthanthrone, with its ketones is a good prospect to be a n-type material. In this study, a photoinduced electron transfer from the

<sup>&</sup>lt;sup>††††</sup> Figure adapted from: Lafleur-Lambert, A.; Giguère, J.-B.; Morin, J.-F. *Macromolecules* **2015**, *48*, 8376–8381. Reprinted with permission from ACS.

fluoride anion to the 4,10-bis(thienophen-2-yl)anthanthrone polymer is characterized by a color change from purple (**26**) to blue-green (**27**).

Finally, 4,10-dibromoanthanthrone has also been used as a p-type material in OFET by Sariciftci in 2010.<sup>83</sup> Hole mobility of  $\mu$ = 1.9 x 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> has been measured with a bottom-gate, top-contact device setup.

Because anthanthrone has a very unique reactivity and geometry, but also because it is not much explored in the literature, we were curious to explore the open-shell possibilities offered by this singular polycyclic aromatic core.

# Chapter 2. BreakingBondsandFormingNanographene Diradicals with Pressure

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## 2.1. Résumé

Un nouveau composé aromatique polycyclique à base d'anthanthrone possédant des groupes quinodiméthanes encombrés en périphérie a été préparé. À son état fondamental, en couche fermé, le composé adopte une structure papillon où une inversion fluxionnelle courbée à plan passe par un état de transition biradicaloïde ayant une faible barrière d'énergie. La force motrice principale de cette inversion est la diminution de l'encombrement stérique aux positions *péri* du cœur anthanthrone. L'état diradicalaire de faible énergie est accessible par l'aplanissement du cœur aromatique, qui peut être obtenu en solution à des températures modérées. L'aspect le plus important de cette transformation est que l'application de faibles pressions à l'état solide permet aussi l'aplanissement du cœur aromatique, la spectroscopie RMN <sup>1</sup>H, la spectroscopie Raman et des expériences magnétiques sont en accord avec la formation d'une structure de type nanographène possédant des radicaux localisés sur les carbones *exo* de l'anthanthrone.

# 2.2. Abstract

New anthanthrone-based polycyclic scaffolds possessing peripheral crowded quinodimethanes have been prepared. While the compounds adopt a closed-shell butterfly-shaped structure in the ground state, a curved-to-planar fluxional inversion is accessible with a low energy barrier through a biradicaloid transition state. Inversion is primarily driven by the release of strain associated with steric hindrance at the *peri* position of the anthanthrone core; a low-lying diradical state is accessible through planarization of the core, which is attained in solution at moderate temperatures. The most significant aspect of this transformation is that planarization is also achieved by application of mild pressure in the solid state, wherein the diradical remains kinetically trapped. Complementary information from quantum chemistry, <sup>1</sup>H NMR, and Raman spectroscopies, together with magnetic experiments, is consistent with the formation of a nanographene-like structure that possesses radical centers localized at the exo-anthanthrone carbons bearing phenyl substituents.

# **2.3. Introduction**

The study of nanographene diradicals has been the subject of intense research because of the outstanding spin and electronic properties of graphene (of which nanographenes are a molecular version),<sup>84–87</sup> the intrinsic beauty of stable high-spin molecules, and the opportunity to investigate fundamental aspects of chemical bonding.<sup>14,88–90</sup> Several strategies for attaining such biradicaloid molecules with varying degrees of diradical character<sup>17,19,28,56</sup> have been developed and some are presented Scheme 2.1. Such strategies include: 1) accumulation of proaromatic (that is, quinodimethanes or quinoidal) rings in oligomeric structures, which leads to the formation of a singlet diradical by the recovery of Hückel aromaticity;<sup>29,50,51,91,92</sup> 2) construction of antiaromatic molecules;<sup>56,93</sup> and 3) design of nanographenes with appropriate zig–zag edge states (that is, metallic or half-metallic) such as acenes and fused acenes.<sup>33,41,94–96</sup>



Scheme 2.1. a) Tetracyanoquinoidal arylenes (n > 1) form a diradical upon gaining aromaticity.<sup>51</sup> b) Formation of diradical states on the zig–zag edges of acenes  $(n > 0)^{33}$  or nanographenes.<sup>41,94–96</sup>

Singlet diradical molecules are characterized by unique optoelectronic properties<sup>89,92,97</sup> relevant to the field of nonlinear optics,<sup>98,99</sup> spintronics,<sup>100</sup> and organic photovoltaics,<sup>101–103</sup> among others. However, to enable the exploration of the unique properties of diradicals in a practical setting it is necessary to consider their chemical stability. In cases 1) and 2) above, smaller oligomers are highly stable molecules owing to a full bonding electronic configuration, whereas diradical character is observed in longer oligomers.<sup>29,50,51,91,92</sup> Yet the preparation of such elongated  $\pi$  systems often requires tedious synthesis and the oligomers suffer from poor stability. Following the pioneering work of Hirai and coworkers on the
observation of a fairly stable triplet carbene,<sup>46</sup> the anthracene substructure has been utilized in the design of biradicaloid molecules.<sup>47,48,60,104</sup>

In pursuit of a robust polycyclic framework to accommodate stable diradicals, we report the preparation and characterization of a new "nanographene" based on the low-cost commercially available 4,10-dibromoanthanthrone building block.<sup>71</sup> While the anthanthrone core can be viewed as a fusion of two anthracene moieties with lateral functionalization, its chemical and physical properties stand in sharp contrast with the parent anthracene subunit;<sup>72,77</sup> anthanthrone exhibits remarkable stability because of extended delocalization. Taking advantage of the readily available molecular complexity provided by this polycyclic aromatic hydrocarbon, we aimed to exploit the intrinsic steric congestion and contortion of a disubstituted quinoidal anthanthrone motif to promote diradical formation. We hypothesized that the general target structure shown in Scheme 2.2 would possess an accessible diradical state upon core planarization, as this would result in the release of steric strain along with the formation of two perpendicular  $\pi$  systems.<sup>44</sup> Interestingly, this system would provide a rare example of a closed-shell to diradical transition fueled by strain release.



Scheme 2.2. The studied compounds 1 (R' = tBu) and 2 (R' = CN) in a) closed-shell quinoidal and b) diradical canonical forms.

# 2.4. Results and Discussion

## 2.4.1. Synthesis

The syntheses of **1**, **2**, and **3** are depicted in Scheme 2.3. 4,10-Bis(triisopropylsilylethynyl)-6,12-bis(*gem*-dichlorovinylene)dihydroanthanthrenes were prepared in two straightforward steps from 4,10-dibromoanthanthrone using a previously reported method (Supporting Information).<sup>71</sup> For **1** and **2**, a four-fold Suzuki-Miyaura coupling using the corresponding *para*-substituted phenylboronic acid or ester was performed using  $PdCl_2(PPh_3)_2$  as the catalyst, to provide the desired compounds in 89 and 74 % yield, respectively. For **3**, a strategy was attempted based on a double fluorene ring-closing reaction by Suzuki-Miyaura coupling using 2,2'-bis(pinacolborane)biphenyl. Despite numerous efforts, **3** could not be isolated. Instead, the protonated derivative was obtained, suggesting that, once formed, **3** rapidly transformed into a reactive species that trapped a proton from the solvent. To verify this hypothesis, we performed the reaction using  $D_2O$  and deuterated **3** was formed in 17 % yield.



Scheme 2.3. Synthesis of **1**, **2**, and **3** and the lateral view of the crystal structure of **2** (isopropyl groups and H atoms are omitted for clarity; obtained at 150 K). Key: triisopropylsilyl (TIPS), bis(pinacolato)diboron (BPin), tetra-*n*-butylammonium bromide (TBAB).

## 2.4.2. Crystal Structure of Compound 2

Crystals of **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of pentane from a chloroform solution of **2** at -30 °C. **2** crystallizes in a *Pbcn* orthorhombic

space group and adopts a bent, butterfly structure, in which the angle of the terminal methylene groups are twisted by 27° (significantly deviated from Thiele's hydrocarbon (13.9°);<sup>45</sup> Supporting Information, Figure 2.14) and the anthanthrone core is highly contorted along the transversal aromatic axis. Furthermore, the length of the C-C double bond between the core and the germinal carbon that bears the 4-cyanophenyl groups is 1.358 Å, which is 0.018 Å longer than the average double bond in olefins (1.33 to 1.34 Å) and still shorter than Thiele's hydrocarbon analogous C-C bond (1.381 Å).<sup>45</sup> This butterfly conformation is imposed by the steric congestion between the protons at the *peri* position of the anthanthrone core and the protons from the peripheral phenyl groups. This steric effect will become a key consideration in the proceeding discussion.

## 2.4.3. Variable-Temperature NMR

While these data suggest a closed-shell ground state singlet in the crystalline form, variabletemperature (VT) <sup>1</sup>H NMR experiments in solution were performed to determine if a diradical state could be accessed by thermal excitation (Figure 2.1). Notably, peaks at 7.45 and 7.60 ppm, present at 0 °C and attributed to non-equivalent protons b and c (Scheme 2.3), coalesced into one broad peak at 35 °C, corresponding to a transition from a conformation with locked phenyl groups to another with freely rotating groups (for 2D <sup>1</sup>H NMR spectra and assignments of 1 and 2 see the Supporting Information, Figure 2.15). Additionally, quantum chemical simulations of the <sup>1</sup>H NMR spectra of the closed-shell and diradical species were carried out (described in the Supporting Information, 2.7.7. Quantum Chemical Calculations of the <sup>1</sup>H NMR Spectra.). Besides this thermally accessible transition, an overall loss of signal intensity and slight band broadening was observed when the sample was heated above 70 °C. The decrease of the peak intensity and eventual disappearance is attributed to the formation of an NMR-silent diradical species. This NMR behavior is in accordance with several other reports of hydrocarbon molecules exhibiting a diradical character.<sup>24,47,49,92,105</sup> Interestingly, the original spectrum at 0 °C can be recovered reversibly after cooling, without significant sign of decomposition. The formation of a diradical species in solution is also supported by the formation of the protonated (and deuterated) product 3 (Scheme 2.3), most likely by proton abstraction of the solvents used in the reaction. In the case of 1, the same line broadening and intensity decrease was observed, although a significant amount of

product degradation occurred after heating. This suggests that the electron-withdrawing nature of the nitrile groups better-stabilizes 2 compared to 1.



Figure 2.1. VT <sup>1</sup>H NMR spectra of the aromatic region of **2** in  $[D_2]$ tetrachloroethane. The spectra were taken from 0 °C to 110 °C (10 °C increment). Letters refer to the peak assignment displayed in Scheme 2.3.

## 2.4.4. Quantum Chemical Calculations

Quantum chemical calculations for **2** have been carried out to understand the origin of the spectral changes (for details see the Supporting Information, 2.7.10. Theoretical Procedures). In the most stable (ground state) structure, the anthanthrone core of **2** adopts a butterfly quinoidal shape (Figure 2.2), which emulates the structural parameters resolved from the X-ray diffraction study (that is, the triplet excited state at this butterfly conformation is + 58.9 kcalmol<sup>-1</sup> at the RAS-SF/6-31G(d) level). A relatively small energy barrier of + 8.3 kcalmol<sup>-1</sup> is found for the quinoidal to diradical conversion. This can be overcome at room temperature through fluxional inversion, giving rise to a local metastable, fully planar structure with a net singlet diradical character and a small singlet-triplet gap of only + 0.3 kcalmol<sup>-1</sup> (Figure 2.2).

In the diradical structure, spin density is primarily located at the *exo*-acene carbon atoms. As no new Clar's sextet was formed during this transformation (two sextets in both the closedshell and open-shell forms), the driving force for this transformation is likely to be the release of strain induced by the steric hindrance at the *peri* position of the anthanthrone. To test this hypothesis, phenyl-free 4,10-bis[(triisopropylsilyl)ethynyl]-6,12a new bis(dicyanovinylene)dihydroanthanthrene<sup>71</sup> derivative in which no steric hindrance is present at the peri position was studied by VT-NMR (Figure 2.16). As expected, compared with the equivalent signals of 2, no distinct changes in the shape of the <sup>1</sup>H resonances were observed between 0 and 110 °C, suggesting that the phenyl groups are dynamic in solution; this effect may be related to free rotation of the phenyl groups at high temperatures when the thermal energy is enough to surpass the steric impediment. Aside from this, some band broadening (that is, a similar extent of broadening for 2 compared to the cyano analogue) is observed at high temperatures. Nonetheless, the situation is rather complex in solution, where NMR signals associated with a variety of conformational effects overlap with those of formed diradical species. In fact, Eyring plots intended to derive activation parameters for diradical formation were inconclusive because it was not possible to separate the effects.



Figure 2.2. a) Structures of **2** along the diradical/planar reaction path with relative Gibbs free energies at 298.15 K (UB3LYP) and vertical singlet-triplet gaps (RAS-SF computational level) for the planar structure. b) Highest occupied natural orbital (HONO) and lowest unoccupied natural orbital (LUNO) expressed in terms of their electron occupancies and the number of unpaired electrons (N<sub>U</sub>), for the butterfly, TS, and planar structures (obtained at the RAS-SF computational level).

## 2.4.5. Variable Pressure Raman Spectroscopy

As DFT calculations showed that only a small energy input associated with the planarization of the core could induce  $\pi$  bond breaking, we attempted to access the diradical species by applying mild pressure. Upon grinding of an orange powder of 2 with a mortar and pestle, the orange samples color changed to dark brown and reversed back to orange by solvent vapor annealing with dichloromethane (Supporting Information, Figure 2.17). Variable-pressure (VP) Raman spectroscopy can provide information at the molecular level for this unusual solid mechanochromic transformation (for experimental details see the Supporting Information, 2.7.9. Raman Spectroscopic Measurements).<sup>106</sup> Compound 2 changes color from orange to black when compressed in a KBr pellet (ca. 10 Toncm<sup>-2</sup>). The Raman spectrum of 2 at ambient pressure (Figure 2.3a) shows two main bands at 1613 and 1577 cm<sup>-1</sup> arising from v(C=C) stretching modes of the central naphtoquinoid moiety and the peripheral benzenoid groups, respectively. The Raman spectrum of the 10 Toncm<sup>-2</sup> pressed KBr black sample of 2 is characterized by a new and more intense band at 1598  $\text{cm}^{-1}$ , while the two bands of the non-pressed sample are present but with weak intensity. The VP Raman experiment in a diamond anvil cell shows that, between 0.05 and 0.3 GPa (ca. 3 Ton  $\text{cm}^{-2}$ ), the peaks attributed to the orange sample at 1613/1577 cm<sup>-1</sup> completely vanish to make way for a new band at 1598 cm<sup>-1</sup> associated with the black powder (Figure 2.3b). Upon release of pressure, a partial recovery of the initial spectrum is observed. As for compound 1, no significant changes in the vibrational Raman spectra were observed after application of pressure.



Figure 2.3. a) Raman spectra of **2** recorded with a 785 nm excitation laser: i) of the orange solid at 80 K and at 1 atm; ii) in a KBr pellet at 80 K after the application of about 10 Toncm<sup>-2</sup> of pressure; iii) in a KBr pellet at room temperature after the application of about 10 Toncm<sup>-2</sup> of pressure. b) VP spectra upon steps of 0.05 GPa up to 0.3 GPa, where light-blue deconvolutions correspond to ambient pressure bands and dark-blue deconvolutions are the bands emerging with pressure. c) iv) 785 nm experimental Raman spectrum of KBr black solid (upon application of pressure) at 80 K; v) 785 nm experimental Raman spectrum of orange solid at 80 K; vi) UB3LYP/6-31G\*\* theoretical Raman spectrum of the planar diradical state; vii) B3LYP/6-31G\*\* theoretical Raman spectrum of the butterfly quinoidal singlet ground electronic state.

At the (U)B3LYP/6–311 ++ G(2df,2p) level we have calculated the molar volumes for the butterfly and diradical structures, 864.418 and 821.380 cm<sup>3</sup>mol<sup>-1</sup>, respectively, suggesting that pressure can in fact produce the diradical species. The theoretical Raman spectrum for the butterfly structure (Figure 2.3c) displays two main bands at 1670 and 1590 cm<sup>-1</sup> that can be correlated with the experimental bands measured at 1613 and 1577 cm<sup>-1</sup>, respectively, for the non-pressed sample. For the planar diradical state, the Raman spectrum has also been calculated (Figure 2.3c), which exhibits a main band at 1615 cm<sup>-1</sup> that nicely correlates with the spectrum of 2 under pressure (1597  $\text{cm}^{-1}$ ; for a full-range wavenumber comparison of the experimental and theoretical spectra see the Supporting Information, Figure 2.18). The theoretical band at 1670 cm<sup>-1</sup> is present in the spectra of the closed-shell and planar diradical species, indicating that a molecular fragment from the central quinodimethane unit remains unaltered by planarization. Therefore, it is reasonable to assume that under pressure, the anthanthrone core becomes increasingly planar and the molecule progressively transforms to a diradical, consistent with the observed changes in the Raman spectra. The fact that pressure release does not produce full recovery of the initial spectrum can also be addressed by the fact that the diradical species is a local minimum on the potential energy surface. Indeed, for

the conversion from planar to butterfly structure to occur, a barrier of 7 kcalmol<sup>-1</sup> needs to be overcome (Figure 2.2). The UV/Vis absorption and emission spectra of orange solids **1** and **2** as a function of the temperature are also fully consistent with this description (Supporting Information, Figure 2.19 and Figure 2.20 and associated discussion).

### 2.4.6. Magnetic Experiments

For compound **2**, other indications of the formation of a triplet excited state are provided by electron paramagnetic resonance (EPR) and magnetic measurements with a SQUID magnetometer (Figure 2.4). For the non-pressed pristine material, no SQUID response was observed in the range of temperature analyzed. For **2**, after application of a pressure of 10 Toncm<sup>-2</sup> a clear increase of the  $\chi_m T$  value was observed with increased temperature up to 400 K.



Figure 2.4. a) Representation of the molar magnetic susceptibility  $(\chi_m)$  multiplied by the temperature (T) versus temperature for the non-pressed orange solid of 2 (inset: orange solid; —) and for the pressed sample (inset: black solid; —). J is obtained from the Bleaney-Bowers fit. b) The EPR spectra at 300 K of the non-pressed orange solid of 2 (—) and the pressed sample of 2 (—). c) The EPR spectra of the pressed sample of 2 at 300 K and after cooling to 200 K.

This behavior is typical of singlet diradicals in thermal equilibrium with a triplet biradical. The  $\chi_m T$  behavior can be adjusted to the Bleaney-Bowers model (Figure 2.4), from which a singlet-triplet energy gap of -0.8 kcalmol<sup>-1</sup> is estimated.<sup>107</sup> This is confirmed by EPR spectroscopy, which shows a signal at 300 K whose absorbance decreases upon cooling at 200 K, in line with the SQUID measurements (Figure 2.4c). These data are also in agreement with quantum chemical calculations, which predict an excited triplet state at + 0.3 kcalmol<sup>-1</sup> for the planar diradical geometry (note, the first triplet excited state from the transition state

is at + 26.6 kcalmol<sup>-1</sup> at the RAS-SF/6-31G(d) level). For compound **1** the same SQUID and EPR pressure dependent experiments were carried out (Supporting Information, Figure 2.21) without any sign of magnetically active species after application of pressure.

# **2.5.** Conclusion

In summary, a chemically robust, highly contorted anthanthrone-based quinodimethane was prepared. Upon application of mild mechanical stress (0.3 GPA), the molecule undergoes planarization in the solid state, forming a kinetically trapped diradical, which has been characterized by Raman and EPR spectroscopies in combination with quantum chemical calculations. The main driving force for the stabilization of the diradical in the quinodimethane units is the release of strain induced by the peripheral benzene rings on the anthanthrone core, providing a rare example of a quinoidal to diradical transition that is not driven by the formation of additional Clar's sextets. This rare example of  $\pi$  bond breaking by mechanochemistry opens the way to the generation of diradicaloid species with accessible high spin states from robust quinoidal structures. Current work is focused on stabilizing the diradical state through the design of novel functionalized anthanthrone-based polycyclic aromatics.

# 2.6. Acknowledgements

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# 2.7. Supporting Information

#### 2.7.1. Materials and Methods

Chemical reagents were purchased from Sigma-Aldrich Co. Canada and were used as received. Toluene used for organic synthesis was purified using a Solvent Purifier System (Vacuum Atmosphere Co., Hawthorne, USA). NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz and Agilent DD2 500 MHz. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm ( $\delta$ ) relative to residual solvent peak. High-resolution mass spectra (HRMS) were recorded using an Agilent 6210 time-of-flight (TOF) LCMS apparatus equipped with an APPI ion source (Agilent Technologies, Toronto, Canada).

#### 2.7.2. Synthesis

## Compound 1

4,10-Bis (triisopropylsilylethynyl)-6,12-bis(gem-dichlorovinylene)-dihydroanthanthrene (0.300 g, 0.375 mmol), 4-tert-butylphenylboronic acid (0.534 g, 3.00 mmol), potassium phosphate tribasic (1.27 g, 5.98 mmol), tetrabutylammonium bromide (0.060 g, 0.186 mmol), dichlorobis(triphenylphosphine)palladium (0.053 g, 0.075 mmol) and triphenylphosphine (0.020 g, 0.076 mmol) were dissolved in degassed toluene (36 mL) and water (6 mL). The mixture was heated at 60 °C for 16 h. The solution was cooled, diluted in CH<sub>2</sub>Cl<sub>2</sub>, extracted three times with water and dried over magnesium sulfate. The solvent was removed in vacuo. The crude product was triturated with CH<sub>3</sub>OH and purified by silica gel column chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 19:1) to afford compound 1 (0.400 g, 89%) as a yelloworange powder. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 50 °C)  $\delta$  8.01 (d, J = 8.2 Hz, 2H), 7.56 (s, 2H), 7.32 (s, 16H), 7.23 (d, J = 7.6 Hz, 2H), 7.03 (t, J = 7.9 Hz, 2H), 1.32 (s, 36H), 1.13 (d, J = 1.4 Hz, 42H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.73, 144.13, 140.68, 133.97, 133.26, 132.21, 131.43, 131.41, 129.32, 128.19, 128.12, 127.45, 125.70, 125.54, 124.87, 119.47, 105.49, 95.17, 34.65, 31.52, 18.95, 11.50. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>86</sub>H<sub>78</sub>Si<sub>2</sub>: 1166.5642; found: 1166.5651 [M\*]+.

## Compound 2

4,10-Bis (triisopropylsilylethynyl)-6,12-bis(gem-dichlorovinylene)-dihydroanthanthrene (0.100 g, 0.125 mmol), 4-cyanophenylboronic acid pinacol ester (0.229 g, 0.999 mmol), potassium phosphate tribasic (0.424 g, 1.998 mmol), tetrabutylammonium bromide (0.020 g, 0.062 mmol), dichlorobis(triphenylphosphine)palladium (0.018 g, 0,025 mmol) and triphenylphosphine (0.007 g, 0.025 mmol) were dissolved in degassed toluene (12 mL) and water (1 mL). The mixture was heated at 50 °C for 16 h. The solution was cooled, diluted in CHCl<sub>3</sub>, extracted three times with water and dried over sodium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (CHCl<sub>3</sub> to CHCl<sub>3</sub>/acetone 9:1) to afford compound **2** (0.098 g, 74%) as an orange powder. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.12 (dd, J = 8.2, 1.1 Hz, 2H), 7.64 (d, J = 7.7 Hz, 8H), 7.50 (br d, 8H), 7.40 (s, 2H), 7.26 (dd, *J* = 7.4, 1.3 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 1.15 (s, 42H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.06, 139.88, 134.89, 133.01, 132.89, 131.83, 131.72, 130.69, 130.07, 129.90, 127.44, 126.86, 126.77, 126.39, 120.75, 118.44, 111.52, 104.12, 98.06, 18.88, 11.39. HRMS (APPI<sup>+</sup>): *m/z* calcd for C<sub>74</sub>H<sub>66</sub>N<sub>4</sub>Si<sub>2</sub>: 1066.4826; found: 1066.4840 [M\*]<sup>+</sup>.

### Compound **3** (proton)

4,10-Bis (triisopropylsilylethynyl)-6,12-bis(*gem*-dichlorovinylene)-dihydroanthanthrene (0.50 g, 0.062 mmol), 2,2'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl (0.089 g, 0.219 mmol), potassium carbonate (0.138 g, 0.999 mmol), tetrabutylammonium bromide (0.010 g, 0.031 mmol), dichlorobis(triphenylphosphine)palladium (0.009 g, 0.012 mmol) and triphenylphosphine (0.003 g, 0.012 mmol) were dissolved in degassed toluene (5 mL) and water (0.5 mL). The mixture was heated at 60 °C for 3 days. The solution was cooled, diluted in CHCl<sub>3</sub>, extracted three times with water and dried over magnesium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes/CHCl<sub>3</sub> 9:1 to 4:1) to afford protonated compound **3** (0.010 g, 17%) as a light green powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.24 (d, *J* = 8.6 Hz, 2H), 8.69 (d, *J* = 7.4 Hz, 2H), 8.28 (dd, *J* = 8.5, 7.4 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 4H), 7.31 (s, 2H), 7.19 (td, *J* = 7.4, 1.1 Hz, 4H), 7.11 (dd, *J* = 7.5, 0.9 Hz, 4H), 6.83 (s, 2H), 1.17 (s, 42H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.42, 140.46, 132.41, 131.83,

131.29, 130.47, 127.76, 127.50, 127.33, 126.87, 124.63, 123.96, 123.45, 122.85, 122.33, 120.90, 120.87, 105.37, 95.32, 77.48, 77.16, 76.84, 19.03, 11.52. HRMS (APPI<sup>+</sup>): *m/z* calcd for C<sub>70</sub>H<sub>68</sub>Si<sub>2</sub>: 964.4859; found: 964.4868 [M\*]<sup>+</sup>.

## Compound **3** (deuterium)

4.10-Bis (triisopropylsilylethynyl)-6,12-bis(gem-dichlorovinylene)-dihydroanthanthrene (0.50 g, 0.062 mmol), 2,2'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl (0.089 g, 0.219 mmol), potassium carbonate (0.138 g, 0.999 mmol), tetrabutylammonium bromide (0.010 g, 0.031 mmol), dichlorobis(triphenylphosphine)palladium (0.009 g, 0,012 mmol) and triphenylphosphine (0.003 g, 0,012 mmol) were dissolved in degassed toluene (5 mL) and water (0.5 mL). The mixture was heated at 60 °C for 3 days. The solution was cooled, diluted in CHCl<sub>3</sub>, extracted three times with water and dried over magnesium sulfate. The solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (hexanes/CHCl<sub>3</sub> 9:1 to 4:1) to afford deuterated compound 3 (0.010 g, 17%) as a light green powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.23 (d, J = 8.3 Hz, 2H), 8.69 (d, J = 7.3 Hz, 2H), 8.28 (dd, J = 8.5, 7.4 Hz, 2H), 8.04 (d, J = 7.7 Hz, 4H), 7.47 (td, J = 7.5, 1.1 Hz, 4H), 7.31 (s, 2H), 7.22 – 7.16 (m, 4H), 7.11 (d, J = 7.5 Hz, 4H), 1.17 (s, 42H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.42, 140.46, 132.41, 131.83, 131.29, 130.47, 127.76, 127.50, 127.33, 126.87, 124.63, 123.96, 123.45, 122.85, 122.33, 120.90, 120.87, 105.37, 95.32, 19.03, 11.52. <sup>2</sup>H NMR (77 MHz, CHCl<sub>3</sub>) δ 6.85. HRMS (APPI<sup>+</sup>): *m/z* calcd for C<sub>70</sub>H<sub>67</sub>D<sub>2</sub>Si<sub>2</sub>: 967.5057; found: 967.5057 [M+H]<sup>+</sup>.

# 2.7.3. NMR Spectra



Figure 2.5. <sup>1</sup>H NMR spectrum of compound **1**.



Figure 2.6. <sup>13</sup>C NMR spectra of compound **1**.



Figure 2.7. <sup>1</sup>H NMR spectrum of compound **2**.



Figure 2.8. <sup>13</sup>C NMR spectra of compound **2**.



Figure 2.9. <sup>1</sup>H NMR spectrum of compound **3** (proton).



Figure 2.10. <sup>13</sup>C NMR spectra of compound **3** (proton).



Figure 2.11. <sup>1</sup>H NMR spectrum of compound **3** (deuterium).



Figure 2.12. <sup>13</sup>C NMR spectra of compound **3** (deuterium).



Figure 2.13. <sup>2</sup>H NMR spectra of compound **3** (deuterium).

## 2.7.4. X-Ray Diffraction

Data collection was carried out on a Bruker Venture Metaljet diffractometer using GaK $\alpha$  radiation ( $\lambda = 1.34139$  Å). During all the experiments the sample was kept at 150 K using an Oxford CryoStream liquid N<sub>2</sub> cooler device. The cell lattice parameters values were determined using reflections taken from three sets of 104 frames measured and harvested within the *APEX3*<sup>108</sup> suite of programs. Frames integration was performed using *SAINT* and a semi-empirical absorption correction was applied with *SADABS*<sup>109</sup>. The structure was solved by direct methods using *SHELXT*<sup>110</sup> and the refinement was carried out using *SHELXL-2016/6*.<sup>111</sup> All the calculations have been performed within the *OLEX2* GUI software.<sup>112</sup> The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F<sup>2</sup>. The H atoms were included in calculated positions and treated as riding atoms using *SHELXL* default parameters. The crystal did not diffract well at high angle, despite the use of high-intensity source, so the data collection had to be truncated at low resolution (theta max = 47.6). The structure includes chloroform solvent molecules that were found disordered to different extent. Some of them could be modelled by splitting the atoms in the disordered

part, but others have to be accounted using the *SQUEEZE* option implemented in *PLATON*.<sup>113</sup> *PLATON* calculated a solvent accessible volume of 730 Å<sup>3</sup> occupied by c.a. 248 electrons, an electron count approximately corresponding to 4 chloroform molecules. Crystallographic information for all obtained phases is summarized in Table S1. Atomic coordinates and additional structural information are provided in the .cif files of the Supporting Information. Crystallographic data have been deposited with CCDC (CCDC 1542456). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.



Figure 2.14. ORTEP of compound **2** with thermal ellipsoids set at the 50% probability level. H atoms are shown as spheres with arbitrary radii.

Table 2.1. Crystal data and structure refinement for 2.

Identification code	COURT3_sq
Empirical formula	$C_{78}H_{70}Cl_{12}N_4Si_2$
Formula weight	1544.96
Temperature/K	150

Crystal system	orthorhombic	
Space group	Pbcn	
a/Å	21.1635(10)	
b/Å	23.7027(10)	
c/Å	16.3658(7)	
$\alpha'^{\circ}$	90	
β/°	90	
$\gamma^{/\circ}$	90	
Volume/Å <sup>3</sup>	8209.6(6)	
Z	4	
$\rho_{calc}g/cm^3$	1.250	
$\mu/\text{mm}^{-1}$	2.867	
F(000)	3192.0	
Crystal size/mm <sup>3</sup>	$0.45 \times 0.07 \times 0.07$	
Radiation	GaKa ( $\lambda = 1.34139$ )	
$2\Theta$ range for data collection/°	4.87 to 95.328	
Index ranges	$\begin{array}{l} -23 \leq h \leq 23,  -26 \leq k \leq 26,  -18 \leq \\ l \leq 17 \end{array}$	
Reflections collected	49499	
Independent reflections	5464 [ $R_{int} = 0.0735$ , $R_{sigma} = 0.0381$ ]	
Data/restraints/parameters	5464/332/535	
Goodness-of-fit on F <sup>2</sup>	1.783	
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.1329, wR_2 = 0.3917$	
Final R indexes [all data]	$R_1 = 0.1537, wR_2 = 0.4106$	
Largest diff. peak/hole / e Å <sup>-3</sup>	0.93/-0.77	

# 2.7.5. 2D-NMR Spectra





Figure 2.15. 2D <sup>1</sup>H NMR spectra of compounds 1 (a and b) and 2 (c and d) in tetrachloroethane- $d_2$ .

## 2.7.6. VT-NMR



Figure 2.16. Variable-temperature <sup>1</sup>H NMR spectra of the aromatic region of 4,10bis[(triisopropylsilyl)ethynyl]-6,12-bis(dicyanovinylene)dihydroanthanthrene in tetrachloroethane- $d_2$ . The spectra were taken from 0 °C to 110 °C (10 °C increment).

# 2.7.7. Quantum Chemical Calculations of the <sup>1</sup>H NMR Spectra.

We have calculated the <sup>1</sup>H NMR spectra of the closed-shell (butterfly) and diradical (planar) forms at the (U)B3LYP/6-311++G(2df,2p) level of theory. Unfortunately, even with this level of theory, the theoretical spectrum does not satisfactorily reproduce the main bands of the experimental one. This is not surprising, and these types of discrepancies are well known, particularly in complex polycyclic aromatic compounds.

# 2.7.8. Qualitative Pressure Experiment



Figure 2.17 Compound **2** (left), grinding (middle), solvent vapor annealing (dichloromethane, right).



Figure 2.18. Full range comparison of (a) B3LYP/6-31G\*\* theoretical Raman spectrum of the butterfly quinoidal singlet ground electronic state, (b) UB3LYP/6-31G\*\* theoretical Raman spectrum of the planar diradical state; (c) 785 nm experimental Raman spectrum of orange solid at 80 K, and (d) 785 nm experimental Raman spectrum of KBr black solid (upon application of pressure) at 80 K.



Figure 2.19. Absorption/excitation (black line) and emission spectra (grey lines) of: a) **1** at room temperature in THF, b) **2** at room temperature in THF, and c) **2** at 80 K in THF.



Figure 2.20. Excited state scheme describing the photophysics of 2.

**DISCUSSION**: The excitation and emission spectra of **1** and **2** are shown in Figure 2.19 with the main band centered around 490 nm. The emission spectrum of **2** at 80 K displays a small stokes shift from the excitation spectrum also at 80 K. Surprisingly this stokes shift completely disappears at room temperature for **2**, which is the opposite behavior of what is commonly found in the photophysics of polycyclic molecules. Such behavior can be rationalized as the emission from a planar singlet excited state to the diradical state both with very similar planar geometry such as described in Figure 2.2.



Figure 2.21. Left) representation of the molar magnetic susceptibility times the temperature versus temperature for the non-pressed orange solid of **1** (red line) and for the pressed sample (blue line). Middle: EPR spectra of non-pressed **1** as a function of the temperature; right) EPR spectrum of pressed **1** at 300 K.

## 2.7.9. Raman Spectroscopic Measurements

Raman measurements were carried out with a Bruker Senterra dispersive Raman spectrometer with 785 nm as excitation wavelength and spectral resolution of 3 cm<sup>-1</sup> under an inert atmosphere. Pressure studies were conducted in a sapphire anvil cell (SAC) with anvils with a diameter culet of 400 µm with which pressures up to 12 GPa. Non pressure transmitting medium was used and diamond chips were used as pressure calibrants.<sup>114</sup> The high pressure cell was loaded in a glove box under nitrogen atmosphere. Second derivative analysis of the spectra combined with Lorentzian curve fittings were used to obtain the Raman shifts.<sup>115</sup>

## 2.7.10. Theoretical Procedures

In order to characterize the geometries of the butterfly and diradicaloid structures, along with the transition state connecting both, geometry optimizations and harmonic vibrational frequency calculations were carried out in gas phase for **0**, **1** and **2** (R = H, *t*Bu and CN, respectively). The Cartesian coordinates for all these 9 structures are given below. Such calculations were performed within the Density Functional Theory framework,<sup>114,115</sup> using the hybrid B3LYP functional<sup>116–118</sup> combined with the double-zeta quality 6-31G(d) basis set, hereafter denoted as DZ. Harmonic vibrational frequencies were obtained by analytical differentiation of the gradients to determine whether the structures were minima or transition states and to evaluate the Gibbs free energy corrections ( $G_{corr}^{DZ}$ ) in the harmonic oscillator

approximation. Electronic energies were further refined by single-point calculations at the optimized geometries by using the triple-zeta quality 6-311++G(2df,2p) basis set, hereafter denoted as TZ, both in gas phase and in solution. Concretely, the integral equation formalism of the polarized continuum model (IEFPCM) of Tomasi and coworkers<sup>119,120</sup> was used to estimate the effects of bulk solvent, employing a dielectric constant of  $\varepsilon = 7.6$ . All these calculations have been carried out using the Gaussian09 package.<sup>121</sup> In this vein, the Total Gibbs Free Energies, in gas phase and solution, of a given species are calculated as

$$G^{TZ,gas} = E_{elec}^{TZ,gas} + G_{corr}^{DZ,gas}$$
  
 $G^{TZ,solv} = E_{elec}^{TZ,solv} + G_{corr}^{DZ,gas}$ 

and are further used to calculate the corresponding  $\Delta G^{TZ,gas}$  and  $\Delta G^{TZ,solv}$ , in order to calculate the energy barrier needed to be gained to change from the butterfly conformation to the diradicaloid one, and the energy differences between both conformations. The obtained values are collected in Table 2.2.

	Transition State		Diradicaloid	
	$\Delta G^{TZ,gas}$	$\Delta G^{TZ,solv}$	$\Delta G^{TZ,gas}$	$\Delta G^{TZ,solv}$
<b>0</b> (R: H)	7.44	8.15	2.98	3.55
<b>1</b> (R: <i>t</i> But)	9.23	11.74	1.73	2.22
<b>2</b> (R: CN)	7.76	8.29	0.81	1.29

Table 2.2. Calculated energy barriers to allow conformational change, and energy differences between conformations, in kcal/mol.

According to the data, it may be seen that the implicit solvation effects are small in general. However, for **1** they are larger, specially for the Transition State. In general, the energy differences between both conformers are very small, and the energy barriers as well. Consequently, at room temperature it would be possible to have both conformers, as observed experimentally.

To characterize the diradical character of **2** we conducted electronic structure calculations at the restricted active space spin-flip (RAS-SF)<sup>122</sup> level of theory with 4 electrons in 4 orbitals in the active space and with the 6-31G(d) basis set. The same methodology was employed to

estimate the vertical singlet-triplet gaps. The diradical character degree of all states was estimated by the number of unpaired electrons  $(N_U)$  according to equation 1, where  $\{n_i\}$  are the natural occupation numbers from the one-particle density matrix. All these results are shown in Figure 2.2 of the main manuscript.

$$N_U = \sum_{i} (1 - abs(1 - n_i))$$
(1)

These calculations were done with the Q-Chem program.<sup>123</sup>

# 2.8. Note

This following section is not part of the published paper.

While trying to crystallize compound 4, the X-ray diffraction showed a much different 7 and structure. Indeed. functionalization on the 13 positions on the anthanthrone/anthanthrene is unprecedented in the literature and amongst unpublished work of the Morin group. This very intriguing structure can only be formed upon decomposition of diradical compound 5 through Scheme 2.4. Although this specific molecule was not studied in this chapter, it has a known history of decomposition in ambient conditions and under heat. Because of its low stability compared to its substituted homologues 1 and 2, it was not used for this publication.



Figure 2.22. X-ray diffraction structure of the decomposition product of compound **4**. H atoms have been omitted for clarity. Thermal ellipsoids are at 50% probability.

First, it is assumed that in the bulk of compound 4 (Scheme 2.4) a non-negligible amount of diradical molecules is present (compound 5). Anthanthrene 5 can react with triplet oxygen present in air to form the oxygenated species 6. Then, it can abstract a proton in the 7 and 13 positions on the anthanthrene core to produce peroxide 7. Then, the radicals on the anthanthrene core react with the oxygen to form the 5-membered ring and an homolytic bond cleavage form two hydroxy radical per molecule (8). Each of these hydroxy radical attacks one of the phenyl ring to induce a cascade rearrangement in the anthanthrene core to ultimately form anthanthrone 9 with two fused-furan moieties. Again, this decomposition pathway is another indirect evidence of the diradical nature of these tetraphenyl-anthanthrone derivatives. Also, this decomposition product was not observed in other para-substituted tetraphenylanthanthrone derivatives but could be present. Compound 1 decomposes in solution, but we were never able to identify the decomposition products as it gives a complex mixture of different species. It can also be hypothesized that the steric bulk provided by the *tert*-butyl groups prevents the approach of an oxygen molecule. In the case on compound 2, the nitrile electron-withdrawing groups provide even more delocalization of the radical in the phenyl moieties than the *tert*-butyl or unsubstituted derivatives. The nitrile groups also lower the oxidation potential of compound 2. Consequently, compound 2 is much more stable than its homologues, therefore no decomposition product is observed. The proposed mechanism in Scheme 2.4 was not proven experimentally.

Crystallographic data have been deposited with CCDC (CCDC 1825304). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.



Scheme 2.4. Suggested decomposition pathway of compound 4 to cyclized 9.

# Chapter 3. Wurster-Type Nanographenes as Stable Diradical Dications

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# 3.1. Résumé

Trois nouveaux diradicaux dications stables basés sur le 4,10-dibromoanthanthrone ont été synthétisés et caractérisés. Dans leur état dicationique, les amines démontrent un caractère biradicalaire à l'état fondamental. Leurs propriétés magnétiques ont été étudiés par RMN et RPE (résonance paramagnétique électronique). Les sels dicationiques montrent un important signal d'absorption optique dans la région du proche infrarouge. La principale force motrice pour obtenir un état fondamental diradicalaire est l'importante congestion stérique empêchant l'aplanissement des diphénylamines avec le cœur aromatique anthanthrone. Les radicaux cations sont donc isolés dans deux systèmes  $\pi$  perpendiculaires tels que démontré par les structures de diffraction des rayons X. Cette étude fournit une nouvelle unité liante en quête de sels de bis(triarylamines) diradicalaires.

# **3.2.** Abstract

Three new and stable diradical dications based on the 4,10-dibromoanthanthrone have been synthesized and characterized. In their dicationic state, the amines show a biradical character in the ground state. Their magnetic properties have been investigated by NMR and EPR spectroscopies. The dicationic salts show strong and broad optical absorption in the near-infrared region. The main driving force to obtain a ground state biradical is the high steric hindrance that prevent planarization of the diphenylamines with the anthanthrone aromatic core. The radical cations are isolated in two perpendicular  $\pi$ -systems as demonstrated by X-ray diffraction structures. This work provides a new bridging unit in the search for biradical bis(triarylamines) salts.

# **3.3. Introduction**

Open-shell biradical hydrocarbons have attracted a lot of interest in recent years. Their interesting properties have fueled their development for potential applications in optoelectronics,<sup>89,92</sup> nonlinear optics,<sup>98,99</sup> spintronics<sup>100</sup> and organic photovoltaics.<sup>101–103</sup> Their low stability in ambient conditions, that is, dimerization, oxidation and decomposition is a major limitation to their thorough study. One interesting approach adopted by Wang, Ito, and Tanaka, among others, is to study bis(trisubstituted)amines with different  $\pi$ -bridging units since they present intriguing properties in the radical cation state and even biradical character when oxidized to dications.<sup>63–69,124</sup> Aminium ions are isoelectronic to carbon and the higher electronegativity of the nitrogen atom contributes to their high stability in the biradical form.<sup>62</sup> The doubly oxidized molecules can be viewed as bipolarons or Wurstertype reagents.<sup>64,68</sup> Their low oxidation potential, easy synthesis and open-shell diradical character has driven the efforts towards their synthesis. Earlier this year, it was reported by Wang and Tan that the  $\pi$ -bridging unit between the bis(triarylamines) dication had a crucial role in determining the electronic structure and singlet-triplet gap.<sup>62</sup>

Our group has been focusing on 4,10-dibromoanthanthrone (vat orange 3), a robust and cheap building block, over the past five years.<sup>71</sup> While searching for new biradical molecules, we used the anthanthrone core as a starting point. The highly planar core of anthanthrone can be viewed as two-fused anthracenes, however its properties differ tremendously from these of anthracene.<sup>77</sup> It has been previously demonstrated that anthanthrone can form a stable biradical in an excited state by mechanochemistry on the solid sample (Figure 3.1, top).<sup>125</sup> The major driving force is attributed to the steric bulk between the core and adjacent phenyl substituents (**A**) that induce a double-to-single bond transformation along with the formation of a biradical (**B**). Following the same idea, we hypothesized that changing the geminal carbon for a nitrogen atom (**C**) would produce the same steric hindrance and drive the formation of a single bond upon oxidation to the isoelectronic dicationic species (**D**) to form a diradical dication in the ground state. Herein, we report the synthesis and characterization of three new and stable bis(triarylamines) diradical dications based on the anthanthrone core. We show that upon double oxidation, two isolated radical cations are formed and the

recombination of the radicals in the anthanthrone core is prevented since the diphenylamines are oriented perpendicularly to the polycyclic aromatic. The diradical dications were studied by cyclic voltammetry, NMR and VT-NMR spectroscopy, X-ray diffraction, solution EPR spectroscopy and spectroelectrochemistry.



Figure 3.1. Mechanochemical formation of a biradical planar anthanthrone (top) and twoelectrons oxidation of anthanthramine to form a diradical dication (bottom).

# **3.4.** Synthesis

The synthesis of the anthanthramine derivatives starts with 4,10-dibromoanthanthrone and is achieved in three easy and high-yielding steps (Scheme 3.1). The introduction of amine moieties at the 6- and 12-positions of the anthanthrone core started with an imine

condensation with 4-octyloxyaniline using TiCl<sub>4</sub> in *o*-dichlorobenzene. The imine was reduced with hydriodic acid in chloroform and water to afford compound **1** in 78% yield. Compound **2** was synthesized according to a previously reported method.<sup>72</sup> Then, a Castro-Stephens-Sonogashira coupling using triisopropylsilylacetylene (TIPSA) with compound **1** or compound **2** in toluene afforded compounds **3** and **4** respectively, both in 99% yield. A second aryl substituent on the nitrogen was introduced by a Buchwald-Hartwig amination coupling with 4-bromooctyloxybenzene and compound **3** to afford compound **5** in 78% yield. The same method was employed to synthesize compound **6** in 88% yield, this time with 4-bromooctylbenzene as the coupling partner. Compound **7** was synthesized according to a previously reported method.<sup>71</sup> An imine condensation using 4-octyloxyaniline followed by reduction with sodium borohydride in THF afforded compound **8** in 64% yield. A Buchwald-Hartwig amination coupling was used to add the second aryl on the nitrogen to afford compound **9** in 96% yield.



Scheme 3.1. Synthesis of compounds 5, 6, and 9 from 4,10-dibromoanthanthrone.
# 3.5. X-Ray Diffraction of the Neutral Amine and Redox Properties

Crystals suitable for X-ray diffraction of compound **5** were obtained from slow evaporation of THF/EtOH at room temperature. Compound **5** crystallizes in a P-1 triclinic space group (Figure 3.2a). As expected, the nitrogen adopts a trigonal planar geometry with the phenyl groups and the highly planar anthanthrone core arranged in a propeller shape.

The redox properties of compounds **5**, **6** and **9** were investigated by cyclic voltammetry in  $nBu_4NPF_6$  saturated DCM using platinum electrodes with an Ag/AgCl reference electrode. The potentials are reported at the onset against Fc/Fc<sup>+</sup>. All three compounds **5**, **6** and **9** show two reversible one-electron oxidation processes as shown in Figure 3.2b and summarized in Table 3.1.



Figure 3.2. a) X-ray crystal structure of compound **5** (thermal ellipsoids are at 50% probability and H and C<sub>7</sub>H<sub>14</sub> have been omitted for clarity), b) cyclic voltammetry of **5** (red), **6** (blue), and **9** (green) in DCM with 0.1 M  $nBu_4PF_6$  as the supporting electrolyte at a scan rate of 50 mVs<sup>-1</sup>.

The oxidation stages are associated with successive oxidation of the amine at the 6- and 12-positions, from neutral to dication passing through the radical cation. This is in contrast with the parent anthracene analog, 9,10-bis(N,N-dimethylamino)anthracene (Figure 3.3, **E**) which only shows one reversible two-electron oxidation process. It has been previously demonstrated by Evans *et al.*<sup>126</sup> and discussed by Ito and co-workers<sup>68</sup> that an important

structural change occurs from planar to a bent and distorted anthracene in the oxidized stages. Thus, the structural change associated with a high energy barrier results in a high oxidation potential for the first electron. Consequently, the oxidation peak of the second electron overlaps with the first, resulting in a single quasi-reversible two-electron oxidation peak.



Figure 3.3. Substituent dependence on the structural change from neutral to dication.

In the case of anthanthrone compounds 5, 6, and 9, the two electron processes are distinct, indicating that no structural change occurs from the neutral to dicationic species. This observation is in line with the molecular structure (see Figure 3.4) that shows retention of planarity in the anthanthrone core upon oxidation (vide infra). The cyclic voltammetry of all three anthanthramines stand in sharp contrast with the N-anisyl-substituted 9,10-diaminoanthracene shown in Figure 3.3 (F). They all show two well-resolved oxidation and reduction peaks, while in the case of the anthracene-based compound, differential pulse voltammetry is necessary to distinguish the two oxidation processes.68 For the 6,12-anthanthramine, the oxidation of diarylamines to the dicationic stage could result in the formation of a double bond between the amine and the anthanthrone core. However, this is expected to be disfavored due to the high steric demand associated with the contortion of the anthanthrone core, a highly planar structure (Figure 3.2a). Indeed, the effect of the high steric strain of diphenylmethane moieties on the 6- and 12-positions of the anthanthrone core has been discussed in detail in a previous study of the isoelectronic carbon analog, showing that the driving force to break a  $\pi$ -bond and form a biradical is in part attributed to the highly bent aromatic core. Consequently, the oxidation of the anthanthramine to a bipolaron produces

two perpendicular  $\pi$ -systems, isolating the two electrons from each other. This phenomenon is analogous to the case of the spiro-fused triarylamine radical cation described by Tanaka.<sup>63</sup>

	$V_{ox}(V)^{[a]}$				E <sub>HOMO</sub> (eV)		
5	0.80	0.98	1.55	-	-5.82		
6	0.92	1.11	-	-	-5.93		
9	0.72	0.90	1.27	1.44	-5.75		

Table 3.1. Electrochemical properties of compound 5, 6 and 9.

[a] V is the potential reported at the onset versus  $Fc/Fc^+$ , scan rate of 50 mVs<sup>-1</sup>.

Then, for compound **5**, an additional reversible oxidation process takes place at 1.55 mV, which can be attributed to the oxidation of the alkoxy phenyl group. As for compound **9**, two reversible oxidation processes at 1.27 and 1.44 mV are associated with the diphenylamine in the 4- and 10-positions. Compound **9** has a lower oxidation potential than that of compounds **5** and **6** due to its high electron density owing to the presence of two diphenylamine units at the 4- and 10-positions. Compound **6** has the highest oxidation potential because of the absence of electron-donating alkoxy groups that are present in both **5** and **9**.

## **3.6.** Variable-Temperature NMR

Compound **5** was studied by variable-temperature NMR (VT-NMR) (Supporting Information, Figure 3.33). Compound **5** was oxidized using an excess amount of AgOTf in CDCl<sub>3</sub>. Compound **5**<sup>2+</sup> is NMR silent at room temperature, but a new broad peak appears at -50 °C. Upon warming, the peak intensity diminishes to vanish completely at -10 °C. This is consistent with a dicationic compound with a populated triplet state at room temperature. At low temperature, the decreased population of the triplet state allows the observation of a broad proton resonance. These observations are also in agreement with the solution electron paramagnetic resonance (EPR) spectroscopy (see Supporting Information Figure 3.34), in wich compound **5**<sup>2+</sup> shows a single resonance peak with its intensity decreasing upon cooling the sample.

# 3.7. Electron Transfer Quantification by NMR

In order to confirm the effective twofold oxidation of the anthanthramine, an NMR experiment using tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TBPA) as a oneelectron oxidant was designed. Upon oxidation of the anthanthramine 5 by TBPA, the neutral tris(4-bromophenyl)amine is generated. This NMR active compound can be quantified using hexamethylbenzene as an internal standard (Supporting Information Figure 3.27). As expected, one equivalent of TBPA reveals two doublets that integrate for 12 protons, while all signals associated with the anthanthramine disappear except the end of alkyl chains. The absence of anthanthramine NMR signals is consistent with its oxidation to the radical cation. Also, the ends of alkoxy chains reveal NMR signals because of the long distance separating them from the radical. Upon addition of a second equivalent of TBPA, the same two doublets integrate for 24 protons and no new signal appears (Supporting Information Figure 3.28). The oxidation of the radical cation anthanthramine to dication generates an NMR inactive product, consistent with the presence of unpaired electrons. The same scenario is observed for compound 9 (Supporting Information Figure 3.31 and Figure 3.32) and for the first equivalent of TBPA with compound 6 (Supporting Information Figure 3.29), while the second equivalent of oxidant shows large and undefined peaks (Supporting Information Figure 3.30). This can be rationalized by the higher oxidation potential for the second electron to be removed, leading to an incomplete oxidation.

# **3.8. X-Ray Diffraction of the Salt**

Crystals of compound  $5^{2+}$  suitable for X-ray diffraction were obtained from slow evaporation of a DCM/hexanes solution at -15 °C (Figure 3.4).  $5^{2+}$  crystallizes in a *I2/a* monoclinic space group. The presence of two counter-ions (SbCl<sub>6</sub><sup>-</sup>) confirms the dicationic nature of the oxidized amine. Again, the anthanthrone core is planar and the diphenylamines form two perpendicular  $\pi$ -systems. It is hypothesized that only a single C-N bond, that allows rotation, is accessible due to the steric bulk. Therefore, the dicationic anthanthramine is expected to stay in the same configuration as the neutral molecule.



Figure 3.4. Front view, left and side view, right of crystal structure of  $5^{2+}$  (thermal ellipsoids are at 50% probability and H atoms and C<sub>7</sub>H<sub>14</sub> have been omitted for clarity).

Because of the low resolution of the X-ray data attributed to the presence of volatile DCM in the crystals, an optimized structure of the neutral and dicationic structure of **5** was modeled using DFT calculations. In the neutral form, the C-N bond length between the anthanthone core and the diphenylamine is 1.39 Å, associated with a single aromatic bond (Supporting Information Figure 3.24). While in the dicationic open-shell form, the bond is elongated to 1.44 Å, exhibiting more of a single bond character (Supporting Information Figure 3.25).

# **3.9. Optical Properties**

The optical properties of compound **5**, **6** and **9** (Figure 3.5, Supporting Information Figure 3.37, and Figure 3.38, respectively) and their oxidized derivatives were investigated by UV/visible spectroscopy in DCM (Supporting Information Table 3.4). The oxidation from neutral to radical cation is accompanied for **5**, **6** and **9** by a significant redshift of 0.86, 0.86, and 0.93 eV, respectively. The removal of the second electron is also accompanied with a significant redshift, 0.29 for **5**, 0.43 for **6**, and 0.21 eV for **9**. These redshifts stand in sharp contrast with the usually blue shifted lower energy absorption band associated with the

formation of a closed-shell bipolaron. In the case of anthanthramine, they can likely be associated to SOMO-LUMO and HOMO-SOMO transitions because of the presence of two unpaired electrons isolated by the formation of two distinct diphenylamines  $\pi$ -systems.<sup>66,68,127,128</sup> Comparing with *N*-anisyl-substituted 9,10-diaminoanthracene (Figure 3.3, **F**), the oxidation of **5** to radical cation in Figure 3.5 shows a maximum absorption at 936 nm and the lowest energy transition for compound **5**<sup>2+</sup> in the near-infrared (NIR) region at 1201 nm is even more red-shifted than for the parent dicationic anthracene (982 nm) showing the extended delocalization in the anthanthrone core.<sup>124</sup>



Figure 3.5. Optical properties of 5,  $5^{+}$ , and  $5^{2+}$ .

# 3.10. Spectroelectrochemistry and Chemical Titration

Spectroelectrochemical experiments were conducted to compare with the chemical oxidative titration with TBPA for compound **5**, **6** and **9** (Figure 3.6, Supporting Information Figure 3.39, and Figure 3.40, respectively). A two-steps process occurs where the radical cation and dication are clearly distinguished. The curves in the electrochemical and chemical titration display the same behavior from neutral to dicationic. The presence of clear isosbestic points

along with the absence of traceable impurities strongly suggest that the oxidized species are stable under the experimental conditions, that is, non-degassed solvent and aerobic conditions. The only marked difference in the spectroelectrochemical and chemical titration data is for the transformation of compound  $6^{+}$  to  $6^{2+}$  (Supporting Information Figure 3.39). In the chemical oxidation of  $6^{+}$  with TBPA, the spectrum (Supporting Information Figure 3.39d) retains features of the radical cation at 813 and 912 nm. These peaks are much less intense not to say absent with the electrochemical oxidation, which is in perfect agreement with the incomplete oxidation observed in the NMR characterization.



Figure 3.6. Spectroelectrochemical and chemical titration with TBPA of a, c) 5 to  $5^{+}$  and b, d)  $5^{+}$  to  $5^{2+}$ , respectively.

# **3.11.** Conclusion

To summarize, we have synthesized three anthanthrone-based diphenylamines. They can be stepwise and cleanly oxidized to stable radical cation and dication using cheap and commercially available oxidants. The dicationic salts display broad bands in the NIR that are red-shifted compared to their parent radical cation and neutral states. The dicationic salts of these amines have two unpaired electrons as demonstrated by NMR and EPR spectroscopy experiments. The major driving force is the high steric congestion between the anthanthrone core and the phenyl-substituted amines in the *ipso* region that forces two perpendicular  $\pi$ -systems, preventing the electrons to recombine in the aromatic core. Evidences by X-ray diffraction structures, NMR of the oxidized species and spectroelectrochemistry strongly supports the presence of a biradical anthanthramine salt. Future work is currently directed towards new  $\pi$ -bridging units between the diphenylamines.

## **3.12.** Acknowledgements

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## **3.13. Supporting Information**

# 3.13.1. General

Chemical reagents were purchased from Sigma–Aldrich Co. Canada, Alfa Aesar Co. or TCI America Co. and were used as received. 4,10-Dibromoanthanthrone was a courtesy from Heubach GmbH as Monolite Red 316801 product. Solvents used for organic synthesis were purified using a Solvent Purifier System (Vacuum Atmosphere Co., Hawthorne, USA). NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz or an Agilent DD2 500 MHz. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets) and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm ( $\delta$ ) relative to residual solvent peak. High-resolution mass spectra (HRMS) were recorded using an Agilent 6210

time-of-flight (TOF) LCMS apparatus equipped with an APPI ion source (Agilent Technologies, Toronto, Canada). UV-visible absorption spectra were recorded using a Varian diode-array spectrophotometer (Cary 5000 model).

### 3.13.2. Synthesis

### Compound 1

A dry flask under argon was charged with 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.16 g, 10.3 mmol), 4-octyloxyaniline (763 mg, 3.45 mmol), and anhydrous o-dichlorobenzene (30 mL). The solution was stirred vigorously and heated at 80 °C. A solution of TiCl<sub>4</sub> in dichloromethane (3.45 mL, 3.45 mmol, 1 M) was added dropwise over 5 min and the mixture was stirred for an additional 5 min before 4,10-dibromoanthanthrone (800 mg, 1.72 mmol) was added and the temperature was raised to 115 °C. The resulting solution was stirred vigorously at that temperature for 3 h. Once cooled to room temperature, the reaction mixture was poured into methanol (100 mL) and the precipitate was filtered off and rinsed with methanol. The crude residue was suspended in chloroform (50 mL) and HI (55% w/w in H<sub>2</sub>O, 0.6 mL, 550 mg, 4.30 mmol) diluted in H<sub>2</sub>O (5 mL) was added after which the solution was stirred overnight. Methanol (30 mL) was added, and the precipitate was recovered via vacuum filtration and air-dried. The residue was dissolved in hot chloroform (200 mL), filtered on a silica gel pad and washed with hot chloroform. Evaporation of the filtrate afforded compound **1** as a red solid (1.13 g, 78 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.63 – 8.59 (m, 6H), 8.11 (dd, J = 8.4, 7.5 Hz, 2H), 6.74 (d, J = 9.0 Hz, 4H), 6.61 (d, J = 9.0 Hz, 4H), 5.97 (s, 2H), 3.87 (t, J = 6.6 Hz, 4H), 1.74 (dt, J = 14.2, 6.7 Hz, 6H), 1.46 – 1.39 (m, 6H), 1.36 - 1.25 (m, 12H), 0.91 - 0.86 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.97, 141.79, 131.76, 130.33, 128.52, 127.40, 126.84, 126.77, 125.48, 124.51, 124.44, 123.87, 120.39, 115.88, 115.83, 68.75, 31.97, 29.59, 29.53, 29.39, 26.23, 22.80, 14.24. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>50</sub>H<sub>53</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: 873.2454 found: 873.2456 [M + H]<sup>+</sup>.

Compound 2 was synthesized according to previously to a previously reported method.<sup>72</sup>

### Compound 3

A flask under argon was charged with compound **1** (968 mg, 1.11 mmol), dichlorobis(triphenylphosphine)palladium (0.039 g, 0.055 mmol), copper iodide (0.010 g,

0.052 mmol), triethylamine (2 mL), toluene (22 mL) and triisopropylsilylacetylene (0.75 mL, 3.32 mmol). The solution was heated at 80 °C and stirred vigorously overnight. Once cooled to room temperature, the mixture was extracted three times with dichloromethane and saturated aqueous ammonium chloride and dried with magnesium sulfate. The crude product was purified by silica gel column chromatography (hexanes/dichloromethane 3:2) to afford compound **3** as a red solid (1.19 g, 99 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.67 (dd, *J* = 7.4, 0.9 Hz, 2H), 8.43 (dd, *J* = 8.3, 1.0 Hz, 2H), 8.19 (s, 2H), 8.03 (dd, *J* = 8.3, 7.4 Hz, 2H), 6.69 (d, *J* = 9.0 Hz, 4H), 6.54 (d, *J* = 9.0 Hz, 4H), 5.77 (s, 2H), 3.84 (t, *J* = 6.6 Hz, 4H), 1.78 – 1.68 (m, 4H), 1.46 – 1.25 (m, 54H), 1.11 (d, *J* = 3.0 Hz, 8H), 0.91 – 0.85 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.67, 142.06, 132.15, 130.57, 128.89, 128.04, 126.19, 125.11, 123.67, 123.59, 123.34, 120.98, 119.94, 115.99, 115.65, 105.71, 96.59, 31.97, 29.60, 29.53, 29.40, 26.24, 22.80, 19.12, 19.07, 18.72, 18.62, 14.24, 11.77, 11.19. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>72</sub>H<sub>95</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>: 1075.6927 found: 1075.6939[M + H]<sup>+</sup>.

#### Compound 4

A flask under argon was charged with compound 2 (1.03 g, 1.22 mmol), dichlorobis(triphenylphosphine)palladium (0.043 g, 0.061 mmol), copper iodide (0.011 g, 0.058 mmol), triethylamine (2.3 mL), toluene (23 mL) and triisopropylsilylacetylene (0.82 mL, 3.67 mmol). The solution was heated at 80 °C and stirred vigorously overnight. Once cooled to room temperature, the mixture was extracted three times with dichloromethane and saturated aqueous ammonium chloride and dried with magnesium sulfate. The crude product was purified by silica gel column chromatography (hexanes/chloroform 3:2) to afford compound 4 as a red solid (1.26 g, 99 %). <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.68 \text{ (d, } J = 7.3 \text{ Hz}, 2\text{H}), 8.42 \text{ (d, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.04 \text{ (t, } J = 8.3 \text{ Hz}, 2\text{H}), 8.15 \text{ (s, } 2\text{H}), 8.15 \text{$ J = 7.8 Hz, 2H), 6.91 (d, J = 8.2 Hz, 4H), 6.52 – 6.46 (m, 4H), 5.76 (s, 2H), 2.48 (t, J = 7.8Hz, 4H), 1.55 (t, J = 7.0 Hz, 4H), 1.46 - 1.21 (m, 54H), 1.11 (d, J = 3.2 Hz, 8H), 0.93 - 0.84(m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.95, 133.34, 131.63, 131.61, 130.45, 129.18, 128.85, 128.08, 126.22, 125.49, 123.61, 123.51, 123.46, 120.98, 119.93, 114.50, 105.63, 96.72, 35.28, 32.06, 31.92, 29.66, 29.58, 29.43, 22.83, 19.13, 18.72, 18.61, 14.27, 11.76, 11.47, 11.16. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>72</sub>H<sub>95</sub>N<sub>2</sub>Si<sub>2</sub>: 1043.7028 found: 1043.7046 [M  $+ H]^+$ .

#### Compound 5

A dry flask under argon was charged with compound **3** (200 mg, 0.186 mmol), 4-bromooctyloxybenzene (0.159 g, 0.558 mmol), tris(dibenzylideneacetone) dipalladium (0.009 g, 0.009 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.005 g, 0.019 mmol), sodium *tert*-butoxide (0.089 g, 0.930 mmol) and toluene (10 mL). The solution was heated at 100 °C and stirred overnight. Once cooled to room temperature, the mixture was extracted three times with dichloromethane and water and dried with magnesium sulfate. The crude product was purified by silical gel column chromatography (hexanes/dichloromethane 8:2) to afford compound **5** as a dark purple solid (0.217 g, 78 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.72 (dd, *J* = 7.5, 1.0 Hz, 2H), 8.70 – 8.66 (m, 4H), 8.09 (dd, *J* = 8.4, 7.5 Hz, 2H), 7.12 (d, *J* = 9.1 Hz, 8H), 6.76 (d, *J* = 9.1 Hz, 8H), 3.89 (t, *J* = 6.6 Hz, 8H), 1.79 – 1.70 (m, 8H), 1.49 –1.39 (m, 8H), 1.37 – 1.26 (m, 32H), 1.26 – 1.20 (m, 42H), 0.93 – 0.85 (m, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.89, 142.43, 137.26, 130.88, 130.23, 130.09, 128.54, 127.13, 124.91, 124.34, 124.20, 122.49, 122.47, 121.81, 115.48, 105.52, 96.60, 68.44, 31.96, 29.53, 29.52, 29.40, 26.23, 22.81, 18.98, 14.25, 11.57. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>100</sub>H<sub>135</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>: 1484.9985 found: 1484.9968 [M + H]<sup>+</sup>.

#### Compound **6**

A dry flask under argon was charged with compound **4** (200 mg, 0.192 mmol), 4-bromooctylbenzene (0.155 g, 0.575 mmol), tris(dibenzylideneacetone) dipalladium (0.010 g, 0.010 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.006 g, 0.019 mmol), sodium *tert*-butoxide (0.092 g, 0.958 mmol) and toluene (10 mL). The solution was heated to 100 °C and stirred overnight. Once cooled to room temperature, the mixture was extracted three times with dichloromethane and water and dried with magnesium sulfate. The crude product was purified by silica gel column chromatography (hexanes) to afford compound **6** as a red solid (0.241 g, 88 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.75 (dd, *J* = 7.5, 1.0 Hz, 2H), 8.72 – 8.68 (m, 4H), 8.11 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 8H), 7.04 (d, *J* = 8.6 Hz, 8H), 2.58 – 2.52 (m, 8H), 1.60 (d, *J* = 7.4 Hz, 8H), 1.33 (s, 40H), 1.25 (d, *J* = 3.9 Hz, 42H), 0.96 – 0.86 (m, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.26, 137.14, 136.03, 130.88, 130.22, 130.05, 129.31, 128.63, 127.20, 124.85, 124.39, 124.28, 122.60, 122.55, 120.66,

105.48, 96.60, 35.45, 32.07, 31.74, 29.66, 29.60, 29.43, 22.84, 19.00, 18.98, 14.28, 11.57. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>100</sub>H<sub>135</sub>N<sub>2</sub>Si<sub>2</sub>: 1421.0189 found: 1421.0236 [M +H]<sup>+</sup>.

Compound 7 was synthesized according to previously to a previously reported method.<sup>71</sup>

### Compound 8

A dry flask under argon was charged with 1,4-diazabicyclo[2.2.2]octane (DABCO) (525 mg, 4.68 mmol), 4-octyloxyaniline (345 mg, 1.56 mmol) and anhydrous o-dichlorobenzene (14 mL). The solution was stirred vigorously and heated at 80 °C. A solution of TiCl<sub>4</sub> in dichloromethane (3.45 mL, 3.45 mmol, 1 M) was added dropwise over 5 min and the mixture was stirred for an additional 5 min before compound 7 (500 mg, 0.78 mmol) was added and the temperature was raised at 115 °C. The resulting solution was stirred vigorously at that temperature for 3 h. Once cooled to room temperature, the crude product was purified by silica gel column chromatography (hexanes/dichloromethane 1:1 to dichloromethane) to afford imine (purple solid) and compound 8 (red solid). The imine (495 mg, 0.473 mmol) and sodium borohydride (286 mg, 3.78 mmol) were charged in flask with THF (10 mL) and three drops of methanol. The solution was stirred at room temperature for three hours. The mixture was extracted three times with dichloromethane and water and dried with magnesium The crude product purified by silica gel column chromatography sulfate. (hexanes/dichloromethane 3:7 to dichloromethane) and was combined with the other fraction to afford compound 8 as a deep red solid (527 mg, 64 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 8.65 - 8.58 (m, 2H), 8.33 (dd, J = 7.7, 0.8 Hz, 2H), 8.27 (s, 2H), 7.93 (dd, J = 8.3, 7.6 Hz, 2H), 7.17 (d, J = 4.3 Hz, 16H), 6.94 (d, J = 4.3 Hz, 4H), 6.69 – 6.59 (m, 8H), 6.14 (s, 2H), 3.85 (t, J = 6.6 Hz, 4H), 1.74 (dt, J = 14.3, 6.6 Hz, 4H), 1.43 (d, J = 7.7 Hz, 4H), 1.29 (d, J = 7.7 Hz, 4 12.5 Hz, 16H), 0.92 – 0.84 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.75, 148.25, 143.82, 141.87, 132.08, 130.35, 129.25, 128.99, 126.54, 126.46, 125.72, 125.06, 122.38, 122.22, 122.09, 121.99, 120.39, 116.11, 115.60, 68.61, 31.97, 29.60, 29.55, 29.41, 26.26, 22.81, 14.26. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>74</sub>H<sub>73</sub>N<sub>4</sub>O<sub>2</sub>: 1049.5728 found: 1049.5762 [M + H]<sup>+</sup>.

#### Compound **9**

A dry flask under argon was charged with compound **8** (200 mg, 0.191 mmol), 4-bromooctyloxybenzene (0.163 g, 0.572 mmol), tris(dibenzylideneacetone) dipalladium

(0.010 g, 0.010 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.006 g, 0.019 mmol), sodium *tert*-butoxide (0.092 g, 0.953 mmol) and toluene (10 mL). The solution was heated to 100 °C and stirred overnight. Once cooled to room temperature, the mixture was extracted three times with dichloromethane and water and dried with magnesium sulfate. The crude product was purified by silica gel column chromatography (hexanes/dichloromethane 1:1) to afford compound **9** as a dark red solid (0.268 g, 96 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.60 (dd, *J* = 8.3, 0.9 Hz, 2H), 8.29 (dd, *J* = 7.6, 1.0 Hz, 2H), 8.26 (s, 2H), 7.86 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.20 – 7.13 (m, 8H), 7.12 – 7.06 (m, 8H), 6.99 – 6.93 (m, 12H), 6.64 (d, *J* = 9.1 Hz, 8H), 3.88 (td, *J* = 6.6, 3.9 Hz, 8H), 1.83 – 1.73 (m, 8H), 1.52 – 1.42 (m, 8H), 1.42 – 1.27 (m, 32H), 0.95 – 0.86 (m, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  153.61, 148.46, 145.07, 142.41, 136.75, 130.55, 129.95, 129.56, 129.19, 126.79, 126.05, 124.76, 123.73, 122.55, 122.32, 122.16, 121.83, 121.67, 115.33, 68.30, 31.97, 29.57, 29.54, 29.41, 26.27, 22.81, 14.26. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>102</sub>H<sub>112</sub>N<sub>4</sub>O<sub>4</sub>: 1457.8711 found: 1457.8730 [M\*]<sup>+</sup>.



#### 3.13.3. NMR Spectra

Figure 3.7. <sup>1</sup>H NMR spectrum of compound **1**.



Figure 3.8. <sup>13</sup>C NMR spectra of compound **1**.



Figure 3.9. <sup>1</sup>H NMR spectrum of compound **3**.



Figure 3.10. <sup>13</sup>C NMR spectra of compound **3**.



Figure 3.11. <sup>1</sup>H NMR spectrum of compound **4**.



Figure 3.12. <sup>13</sup>C NMR spectra of compound **4**.



Figure 3.13. <sup>1</sup>H NMR spectrum of compound **5**. 98



Figure 3.14. <sup>13</sup>C NMR spectra of compound **5**.



Figure 3.15. <sup>1</sup>H NMR spectrum of compound **6**. 99



Figure 3.16. <sup>13</sup>C NMR spectra of compound **6**.



Figure 3.17. <sup>1</sup>H NMR spectrum of compound **8**. 100



Figure 3.18. <sup>13</sup>C NMR spectra of compound **8**.







Figure 3.20. <sup>13</sup>C NMR spectra of compound **9**.

### 3.13.4. X-Ray Diffraction of Compound 5

Data collection was carried out on a Bruker Venture Metaljet diffractometer using GaKa radiation ( $\lambda = 1.34139$  Å). During all the experiments, the sample was kept at 150 K using an Oxford CryoStream liquid N<sub>2</sub> cooler device. The cell lattice parameters values were determined using reflections taken from three sets of 104 frames measured and harvested within the *APEX3*<sup>108</sup> suite of programs. Frames integration was performed using *SAINT* and a semi-empirical absorption correction was applied with *SADABS*.<sup>109</sup> The structure was solved by direct methods using *SHELXT*<sup>5</sup> and the refinement was carried out using *SHELXL-2016/6*.<sup>110</sup> All the calculations have been performed within the *OLEX2* GUI software.<sup>112</sup> The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F<sup>2</sup>. The H atoms were included in calculated positions and treated as riding atoms using *SHELXL* default parameters. The crystal did not diffract well at high angles, despite the use of high intensity source, so the data collection had to be truncated to theta max = 48.5°. Atomic coordinates and additional structural information are provided in the .cif files of the Supporting Information. Crystallographic data have been deposited with CCDC

(CCDC 1578947). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.



Figure 3.21. ORTEP of compound **5** with thermal ellipsoids set at the 50% probability level. H atoms are shown as spheres with arbitrary radii.

Table 3.2. Crystal data and structure refinement for compound **5**.

Identification code	COURT42			
Empirical formula	$C_{100}H_{134}N_2O_4Si_2$			
Formula weight	1484.26			
Temperature/K	150			
Crystal system	triclinic			
Space group	P-1			
a/Å	15.564(3)			
b/Å	18.462(4)			

c/Å	19.260(4)
α/°	118.364(9)
β/°	104.121(10)
$\gamma/^{\circ}$	97.379(10)
Volume/Å <sup>3</sup>	4524.9(15)
Z	2
$\rho_{calc}g/cm^3$	1.089
$\mu/mm^{-1}$	0.473
F(000)	1616.0
Crystal size/mm <sup>3</sup>	$0.28 \times 0.14 \times 0.05$
Radiation	GaKa ( $\lambda = 1.34139$ )
$2\Theta$ range for data collection/°	4.76 to 103.218
Index ranges	$-18 \le h \le 18,  -21 \le k \le 21,  -22 \le l \le 22$
Reflections collected	84112
Independent reflections	14505 [ $R_{int} = 0.0798$ , $R_{sigma} = 0.0508$ ]
Data/restraints/parameters	14505/133/1005
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0754, wR_2 = 0.1876$
Final R indexes [all data]	$R_1 = 0.1007, wR_2 = 0.2066$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.51/-0.43

# **3.13.5.** Cyclic Voltammetry

All cyclic voltammograms were acquired using a three-electrode BASI Epsilon potentiostat (purchased from Bioanalytical Systems). The potential was referenced to a Ag/AgCl saturated KCl electrode (purchased from Bioanalytical Systems) and Pt wire working and counter electrodes. Supporting electrolyte of dichloromethane saturated with  $(nBu)_4NPF_6$  (0.1M) was purged with nitrogen prior to electrochemical measurements. For determination of vacuum levels, the potentials were calibrated against ferrocene/ferrocenium external standard measured at 0.309 mV versus Ag/AgCl and the saturated calomel electrode.



Figure 3.22. Cyclic voltammogram of TBPA oxidizing agent.

# 3.13.6. X-Ray Diffraction of Compound 5<sup>2+</sup>



Figure 3.23. ORTEP of compound  $5^{2+}$  with thermal ellipsoids set at the 50% probability level. H atoms are shown as spheres with arbitrary radii.

court7
$C_{200}H_{268}Cl_{24}N_4O_8Sb_4Si_4$
4306.33
150
monoclinic
I2/a
17.174(8)
35.467(17)
18.624(8)
90
92.704(10)
90
11331(9)
2
1.262
4.682
4456.0
$0.19 \times 0.13 \times 0.07$
$GaK\alpha \ (\lambda = 1.34139)$
11.6 to 79.168
$-16 \le h \le 16, -33 \le k \le 33, -17 \le l \le 10$
10453
4945 [ $R_{int} = 0.1362$ , $R_{sigma} = 0.1673$ ]
4945/570/553
1.426
$R_1 = 0.1664, wR_2 = 0.4200$
$R_1 = 0.2397, wR_2 = 0.4643$
1.63/-0.89

Table 3.3. Crystal data and structure refinement for compound  $\mathbf{5}^{2+}$ .

Note: good quality crystals of compound  $5^{2+}$  has proven difficult to obtain since the structure incorporated dichloromethane molecules and decomposed quickly under the acquisition conditions.

### **3.13.7.** Computational Details

For computation time considerations, the decyl alkyl chains were replaced by a simple methyl group and the side-chain functionalities were omitted. Calculations were performed with the GAUSSIAN 09 programs.<sup>123</sup> Geometries were optimized using the B3LYP functional<sup>119,120,129,130</sup> in combination with the 6-31+G\* basis set for all atoms, including hydrogen. The stationary points were characterized as minima on the potential energy surface by full vibration frequencies calculations (no imaginary frequency). All geometry optimizations were carried out without any symmetry constraints. All structures with their associated free enthalpy and Gibbs free energies as well as their cartesian coordinates are fully detailed in the online version of the supporting information available on Chemistry – A European Journal website.



Figure 3.24. Optimized structure of compound 5 with methoxy groupsSum of electronic and thermal Enthalpies=-2489.453763Sum of electronic and thermal Free Energies=-2489.591730



Figure 3.25. Optimized structure of compound  $5^{2+}$  singlet with methoxy groups. Sum of electronic and thermal Enthalpies= -2489,59593

Sum of electronic and thermal Energies= -2489,733055



Figure 3.26. Optimized structure of compound  $5^{2+}$  triplet with methoxy groups Sum of electronic and thermal Enthalpies= -2489,599628

Sum of electronic and thermal Energies= -2489,738002

# 3.13.8. NMR Oxidation Experiments with TBPA



Scheme 3.2. General reaction for the oxidation of anthanthramine to radical cation. Anthanthramine (10 mg, 0.007 mmol), hexamethylbenzene (1 mg, 0.007 mmol), and tris(4bromophenyl)ammoniumyl hexachloroanthimonate (6 mg, 0.007 mmol) were charged in an NMR tube and dissolved in CDCl<sub>3</sub> (0.80 mL). An NMR spectrum was recorded.



Scheme 3.3. General reaction for the oxidation of radical cation to dication.

A second equivalent of tris(4-bromophenyl)ammoniumyl hexachloroanthimonate (6 mg, 0,007 mmol) was added to the mixture and a second NMR spectra was recorded.



Figure 3.27. <sup>1</sup>H NMR spectra of compound **5** with 1 equivalent of TBPA.



Figure 3.28. <sup>1</sup>H NMR spectra of compound **5** with 2 equivalents of TBPA.



Figure 3.29. <sup>1</sup>H NMR spectra of compound **6** with 1 equivalent of TBPA.



Figure 3.30. <sup>1</sup>H NMR spectra of compound **6** with 2 equivalents of TBPA.



Figure 3.31. <sup>1</sup>H NMR spectra of compound **9** with 1 equivalent of TBPA.



Figure 3.32. <sup>1</sup>H NMR spectra of compound 9 with 2 equivalents of TBPA.

# 3.13.9. Variable Temperature NMR

Attempts to lower the temperature resulted in precipitation of compound **5**. It should be noted that the other peaks present in all spectra are associated with 4,10-di(triisopropylsilyl)anthanthrone, which is a decomposition product resulting from the hydrolysis of compound **5** in the presence of adventitious moisture.



Figure 3.33. VT-NMR of compound 5<sup>2+</sup> in CDCl<sub>3</sub>.

# 3.13.10. Solution EPR



Figure 3.34. EPR spectra of  $5^{2+}$  in dichloromethane at different temperature.



Figure 3.35. EPR spectra of  $6^{2+}$  in dichloromethane at different temperature.



Figure 3.36. EPR spectra of  $9^{2+}$  in dichloromethane at different temperature.

3.13.11. Optical Properties



Figure 3.37. UV-visible spectra of 6 (red),  $6^{+}$  (blue), and  $6^{2+}$  (green).



Figure 3.38. UV-visible spectra of 9 (red),  $9^{+}$  (blue), and  $9^{2+}$  (green).

Table 3.4. Maximum absorption a	d molar absorptivity of	compounds 5, 6 and 9.
---------------------------------	-------------------------	-----------------------

Optical properties									
	5	5 <sup>++</sup>	5 <sup>2+</sup>	6	6.+	62+	9	<b>9</b> <sup>.</sup> +	<b>9</b> <sup>2+</sup>
$\lambda_{max}$ (nm)	568	936	1201	558	908	1321	542	910	1072
$\epsilon_{\lambda max}$ (M <sup>-1</sup> cm <sup>-1</sup> )	15084	11402	28213	14251	12812	20630	21611	24191	15320

### 3.13.12. Spectroelectrochemistry and UV-Visible Titration with TBPA

Spectroelectrochemical measurements performed with Honeycomb were a spectroelectrochemical cell kit from Pine Research. Gold electrodes were used with an All Ag/AgNO<sub>3</sub> reference electrode. measurements performed in were dichloromethane 0.1 M (n-Bu)<sub>4</sub>NPF<sub>6</sub>. For the chemical titration with TBPA, nine solutions were prepared with a constant concentration of the substrate. Aliquot of a standard solution of TBPA were added to the substrate. The higher molar absorptivity around 300 nm for all chemical titrations can be attributed to TBPA, as these absorption bands are not present in the electrochemical titration.



Figure 3.39. Spectroelectrochemical and chemical titration with TBPA of a), c) **6** to  $6^{+}$  and b), d)  $6^{+}$  to  $6^{2+}$ , respectively.



Figure 3.40. Spectroelectrochemical and chemical titration with TBPA of a), c) 9 to  $9^{+}$  and b), d)  $9^{+}$  to  $9^{2+}$ , respectively.
# Chapter 4. Wurster-Type Anthanthrene Polyradicaloid-Cations

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#### 4.1. Résumé

Le 4,10-dibromoanthanthrone, un précurseur très robuste, a été utilisé pour synthétiser un polymère de bis(triarylamine). Le polymère peut être oxydé deux fois pour former une macromolécule polycationique qui montre des propriétés magnétiques en spectroscopie RPE. Dans son état diocationique, la présence de radicaux isolés est possible grâce à l'interruption de conjugaison entre les diphénylamines et le cœur anthanthrone. L'encombrement stérique empêche l'aplanissement des substituants adjacents, résultant en un polymère polyradical cationique. Le polymère oxydé montre un important signal d'absorption optique dans la région du proche infrarouge ainsi que des processus d'oxydoréduction réversibles.

## 4.2. Abstract

4,10-dibromoanthanthrone, a highly robust building block, has been used to synthesize a bis(triarylamine) polymer. The polymer can be oxidized twice to form a polycationic macromolecule showing magnetic properties by EPR spectroscopy. In its dicationic state, the presence of isolated radicals is possible because of the interrupted conjugation between the diphenylamine with the anthanthrone core. The high steric hindrance prevents the planarity of the adjacent groups resulting in a polyradical cationic polymer. The oxidized polymer has a strong absorption in the near infrared region along with reversible redox stages.

## **4.3. Introduction**

Owing to their very intriguing physical and chemical properties, open-shell polycyclic hydrocarbons have been the subject of intense research during the past decade. The study of *p*-quinodimethane,<sup>23,47,49,50</sup> extended zethrene, 20, 25-29 different structures like indenofluorene,<sup>55,56,60,61</sup> and periacene<sup>19,40,42</sup> have led us to better understand the kinetic and thermodynamic roles in stabilizing these unique molecules. Their optoelectronic properties combined with their magnetic behavior makes them good candidates for the development of potential applications in optoelectronics,<sup>89,92</sup> nonlinear optics,<sup>98,99</sup> spintronics<sup>100</sup> and organic photovoltaics.<sup>101–103</sup> While these compounds are sometimes difficult to study due to their short lived lifetime and low solubility, a different approach is to study much more robust isoelectronic homologues that are doubly oxidized bis(triarylamines).<sup>64,65,67,69</sup> The more electronegative nitrogen atom has proven to improve the stability of the radicals and the  $\pi$ -bridging unit between the amines can modulate the optoelectronic properties and singlet-triplet gap of the diradical-dicationic species.<sup>62</sup> Combined with these findings, new macromolecular and polyradical compounds such as 3-dimensional diradical cages,<sup>131</sup> macrocycles,<sup>132</sup> multiradicaloids<sup>133,134</sup> and polymer-based diradicals<sup>135</sup> have emerged in search for a better understanding of the open-shell compounds.



Scheme 4.1. Steric congestion release in a butterfly anthanthrone molecule (**A**) to form a planar diradical structure (**B**). Diradical dication (**D**) formed upon double oxidation of anthanthrone-based bis(triarylamine) (**C**). Poly-bis(triarylamines) (**P1**) oxidation to Polyradicaloid cations (**P1**<sup>2+</sup>).

In a recent study, we have reported an anthanthrone-based nanographene where the steric congestion of the facing protons in the diphenylmethane and anthanthrone core moieties causes the structure to adopt a butterfly structure (Scheme 4.1,  $\mathbf{A}$ ).<sup>125</sup> The *exo* double bonds are weakened by the steric tension, driving the transformation to single bonds, thus producing

a planar anthanthrene core and two radical centers (**B**). It was found that this structural change can occur by heating in solution or by applying pressure in the solid state. Pursuing isoelectronic structures, we have reported the synthesis and characterization of three new anthanthrene-based bis(triarylamines) (Scheme 4.1, **C**).<sup>136</sup> It was demonstrated that because of the same high steric hindrance that is present in the all-carbon system, the doubly oxidized anthanthrene has two isolated radical cations (**D**). These bipolarons cannot recombine to form closed-shell dications because of the  $\pi$ -conjugation interruption caused by the perpendicular arrangement. In these systems, only two radicals are present per molecule. It is hypothesized that an accumulation of radicals in a polymer could produce intriguing properties such as absorption in the near infrared region, a very desirable, yet difficult to obtain optoelectronic property. The aminium cations are much more persistent than the all-carbon homologue, hypothetically because of the higher electronegativity of the nitrogen atom which further stabilizes the diradical state.<sup>62</sup>

Herein, we report an anthanthramine-based polymer (**P1**) that can be oxidized to form multi-cationic radical species (**P1**<sup>2+</sup>) (Scheme 4.2). The polymer was characterized by size-exclusion chromatography, cyclic voltammetry, UV-visible spectroscopy, solution, and thin-film spectroelectrochemistry, <sup>1</sup>H NMR and EPR spectroscopies. All of these structures are based on 4,10-dibromoanthanthrone vat dye, a robust and cheap building block that our group has been focussed on for the past several years.<sup>71,72,82</sup> Anthanthrone is a highly planar aromatic polycyclic with very unique reactivity and properties.<sup>77,78</sup>

#### 4.4. Synthesis of P1

The synthesis of **P1** is presented in Scheme 4.2. Compound **1** was synthesized in three steps in 60% overall yield according to a previously reported method.<sup>136</sup> Starting from 4,1-dibromoanthanthrone, imine condensation on the 6 and 12 positions using 4-octyloxyaniline and titanium tetrachloride. Reduction of the imine to an amine is achieved with hydriodic acid. The triisopropylsiliacetylene solubilizing groups in the 4,10 positions are introduced with a Castro-Stephens-Sonogashira coupling. To obtain the tertiary amine, a Buchwald-Hartwig amination coupling using 4-bromooctyloxybenzene is performed, generating the desired compound **1** in good yield. Then, triisopropylsilyl groups were removed by tetra-*n*-butylammonium fluoride solution in THF to obtain compound 2 in quantitative yield. 1,4-diiodo-2,5-dioctylbenzene was synthesized according to a previously reported method.<sup>137</sup> Compound 2 was polymerized by a Castro-Stephens-Sonogashira coupling polymerization with 1,4-diiodo-2,5-dioctylbenzene using standard conditions at 50 °C to obtain **P1** as a brown solid in 86% yield, after Soxhlet extraction. **P1** is highly soluble in chloroform, dichloromethane, and toluene. High temperature size-exclusion chromatography (SEC) was conducted on **P1** using polystyrene standards and 1,3,4-trichlorobenzene as eluent (Figure 4.7). Chromatogram of **P1** exhibit a unimodal molecular weight distribution of  $\overline{M_n}$  of 16200 g/mol, corresponding to a degree of polymerization (Đ) of 11 and a polydispersity index (I<sub>p</sub>) of 2.5.



Scheme 4.2. Synthesis of P1 from 4,10-dibromoanthanthrone.

# 4.5. Cyclic Voltammetry

In order to verify the possibility of oxidizing each monomer to a dication, ultimately forming a polyradical polymer, the redox properties of **P1** were investigated in solution by cyclic

voltammetry in  $nBu_4NPF_6$  saturated DCM using platinum electrodes with an Ag/AgCl reference electrode (Figure 4.1a). The potentials are reported at the onset against Fc/Fc<sup>+</sup>. For cyclic voltammetry in the solid state, **P1** was drop casted on an ITO/glass electrode or dip coated on a Pt wire working electrode with a Pt counter electrode, with an Ag/AgNO<sub>3</sub> reference electrode (Figure 4.8). A supporting electrolyte solution of MeCN saturated with  $nBu_4NPF_6$  was employed for these measurements. The **P1** film on ITO/glass electrode shows two irreversible oxidations and the dip coated Pt wire in **P1** shows two partly reversible oxidation processes.



Figure 4.1. a) Cyclic voltammetry of **P1** in DCM with 0.1M  $nBu_4PF_6$  as the supporting electrolyte at a scan rate of 50 mVs<sup>-1</sup>, b) optical properties of **P1** and its radical cation and dication counterparts.

The cyclic voltammogram of **P1** in solution shows two reversible one-electron oxidation processes. Compared to single molecule **1** in solution, the oxidation potential for **P1** was found to be much higher (0.80/0.98, and 1.16/1.32, respectively), which is the opposite of what is expected for a polymer with an extended conjugation. Indeed, as shown in our previous study, the diradical dications are not conjugated with the anthanthrene core,<sup>136</sup> making them isolated from the linear conjugation in the polymer. Yet, in such a case, the oxidation potentials should not show such a large discrepancy with the monomeric unit. One explanation for this behavior could reside in the difficulty for the large counter ion, in this case  $PF_{6}^{-}$ , to shield the cation-cation and electronic repulsive effects because of the high steric hindrance caused by the neighboring diarylamines.<sup>138,139</sup> For the polymer, the amines are constrained closer to each other than for the small molecule in solution. In addition, the

concentration of charge on a polymer is much higher than for a single molecule and could explain the higher oxidation potential.

## **4.6. Optical Properties**

The optical properties of **P1** and its oxidized derivatives were investigated by UV-visible spectroscopy in dichloromethane (Figure 4.1b, Table 4.1). A significant redshift marks the oxidation of **P1** to radical cation of 0.86 eV, identical to its molecular analogue **1**. The oxidation of **P1**<sup>++</sup> to **P1**<sup>2+</sup> is again accompanied with a redshift of 0.33 eV, that is 0.04 eV larger than molecule **1**. Indeed, **P1** possesses very similar curve shapes as compound **1** with the same bands and clear isosbestic points present in both two oxidation stages. This behaviour can be ascribed to the fact that the planar trigonal amine moieties are not conjugated with the anthanthrone core due to their perpendicular arrangement. In the case of the polymer, each monomer acts as individual bis(triarylamine). The only difference is the lower energy band for the second oxidation process in **P1**, where a 52 nm redshift is observed. This phenomenon can hypothetically be ascribed to the proximity of the cations in the polymer chain, promoting a through-space charge transfer between the bis(arylamine) units.<sup>140</sup>

Table 4.1. Maximum absorption, and molar absorptivity in DCM solution of 1, 1<sup>+</sup>, 1<sup>2+</sup>, P1, P1<sup>+</sup>, and P1<sup>2+</sup>, and maximum absorption in thin film of P1, P1<sup>+</sup>, and P1<sup>2+</sup>.

		1	1.+	12+	<b>P1</b> <sup>[a]</sup>	P1 <sup>.+</sup>	P1 <sup>2+</sup>
Solution	$\lambda_{max}$ (nm)	568	936	1201	568	937	1253
	$\epsilon\lambda_{max} (M^{-1}cm^{-1})$	15084	11402	28213	10722	9283	24447
Thin Film	λmax (nm)	-	-	-	-576	941	1163

[a] The molecular weight of **P1** is assumed based on Mn and the oxidations took place quantitatively.

## 4.7. Spectroelectrochemistry and Chemical Titration

**P1** was subjected to a chemical titration with tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TBPA), also referred to as "Magic Blue". This titration is compared with the electrochemical titration by spectroelectrochemistry in solution (Figure 4.2). Both sequential oxidation shows the same peaks without formation of traceable impurities,

attesting the robust nature of the oxidized amines. There is only one irregularity in the chemical titration with TPBA at 1.75 equivalents (gray line). Surprisingly, the curve is a perfect fit with the one at 1 equivalent (black line), which means that  $P1^{+}$  on its way to  $P1^{2+}$  is reduced back to  $P1^{+}$  precisely at 1.75 equivalents of TPBA. This is probably the result of an incomplete oxidation or a fast reduction/oxidation between the polymer and TPBA. In the electrochemical titration, this effect is not observed at any point during the oxidation of P1 because of the absence of oxidizing agent or its associated large counterions. For thin film spectroelectrochemistry, P1 was drop casted on an ITO/glass electrode (Figure 4.9 and Figure 4.10). The curves are quite similar with the same evolution upon oxidation to the electrochemical titration in solution.



Figure 4.2. Spectroelectrochemical and chemical titration with TPBA of a), c) **P1** to **P1**<sup>+</sup> and b), d) **P1**<sup>+</sup> to **P1**<sup>2+</sup>, respectively.

In order to confirm the two-fold oxidation of the anthanthramine with TPBA, **P1** was charged in an NMR tube with hexamethylbenzene as an internal standard with the addition of one equivalent of TBPA, followed by a second equivalent (Figure 4.11, and Figure 4.12, respectively). As expected, the <sup>1</sup>H NMR spectra of **P1**<sup>++</sup> and **P1**<sup>2+</sup> did not show any peaks, confirming the presence of unpaired electrons in either of the oxidation stages. But, the peaks associated with the now neutral TBPA, i.e. tris(4-bromophenyl)amine, were not discernable in the spectra. This is in sharp contrast to what is observed with molecule **1**<sup>++</sup> and **1**<sup>2+</sup> since it was possible to quantify the number or transferred electrons from the oxidant with the peak integrations associated with the neutral tris(4-bromophenylamine).<sup>136</sup> It is probable that a rapid reduction/oxidation process with TPBA is faster than the NMR time-scale, producing very large peaks of low intensity, which are lost in the baseline. The more pronounced redox processes between the Magic Blue oxidant and the polymer are consistent with the higher oxidation potential of the polymer (*vide supra*).

## **4.8. Magnetic Properties**

The magnetic properties of the polyradical polycationic polymer was investigated by solution electron paramagnetic resonance (EPR) (Figure 4.3). The polymer was oxidized using an excess of silver triflate in DCM. The spectra were acquired in frozen DCM at 128, 140, and 158K. As shown in Figure 4.3, the signal intensity increases with a decreased temperature, consistent with two individual radical centers (biradical). The perpendicular  $\pi$  systems interrupt the conjugation, preventing the radical to couple. A similar phenomenon is observed when the weakly coupling radicals are separated by a long distance.<sup>50</sup>



Figure 4.3 EPR spectra of **P1** oxidized with AgOTf to  $P1^{2+}$  in DCM at 128, 140 and 158 K. 128

#### **4.9.** Conclusion

To conclude, we have successfully synthesized a poly-bis(triarylamines) based on the vat dye 4,10-dibromoanthanthrone. The polymer can be doubly oxidized easily with a commercial oxidant to produce a very stable diradical dication. The oxidized polymer has a broad absorption in the near infrared region and each diarylamine units act as independent radical cation with through space charge delocalization because of the proximity of the neighboring amines. Future work is currently directed in making pressure-driven diradical polymers with the all-carbon homologues **A**, **B** showed in Scheme 4.1.

## 4.10. Acknowledgements

M.D. thanks the NSERC for a Ph.D. scholarship.

#### **4.11. Supporting Information**

#### 4.11.1. General

Chemical reagents were purchased from Sigma–Aldrich Co. Canada and were used as received. 4,10-Dibromoanthanthrone was a courtesy from Heubach GmbH as Monolite Red 316801 product. Solvents used for organic synthesis were purified using a Solvent Purifier System (Vacuum Atmosphere Co., Hawthorne, USA). NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak. High-resolution mass spectra (HRMS) were recorded using a Agilent 6210 time-of-flight (TOF) LCMS apparatus equipped with an APPI ion source (Agilent Technologies, Toronto, Canada). UV-visible absorption spectra were recorded using a Varian diode-array spectrophotometer (Cary 5000 model). Number-average (Mn) and weight-average (Mw) molecular weights were obtained by size exclusion chromatography (SEC) using a high temperature Varian Polymer Laboratories GPC220 equipped with an RI detector. The column set consists of 2 PL gel Mixed C (300 x 7.5 mm) columns and a PL gel Mixed C guard column. The flow rate was mixed at 1 mL min-1 using 1,2,4- trichlorobenzene (TCB)

(with 0.0125% BHT w/v) as the eluent. The temperature of the system was set to 110 °C. The sample was prepared at a nominal concentration of 3.0 mg/mL in TCB. Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vials were held at 110 °C with shaking for 1 h for complete dissolution. The solutions were filtered through a 2 mm porous stainless-steel filter used with a 0.40 mm glass filter into a 2 mL chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards Easi-Vials PS-M from Varian Polymer Laboratories which were dissolved in TCB. EPR was performed on a Bruker Elexsys 580 FT/CW console.

#### 4.11.2. Synthesis

Compound 1 was synthesized according to a previously reported method.<sup>136</sup>

#### Compound 2

To a solution of compound **1** (0.120 g, 0.081 mmol) in degassed THF (4 mL) was added tetrabutylammonium fluoride solution (1.0 M in THF) (0.65 mL, 0.65 mmol). The reaction was stirred at room temperature for about 15 minutes. The reaction mixture was diluted in DCM, extracted three times with water, and dried over magnesium sulfate. The solvents were removed in vacuo. The crude product was purified by silica gel column chromatograpy (hexanes/ DCM, 3:2) to afford compound **2** as a purple solid (0.095 g, Qt). <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>)  $\delta$  8.76 – 8.68 (m, 6H), 8.10 (t, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 8H), 6.77 (d, *J* = 9.1 Hz, 8H), 3.87 (t, *J* = 6.5 Hz, 8H), 3.53 (s, 2H), 1.80 – 1.68 (m, 8H), 1.47 – 1.38 (m, 10H), 1.34 – 1.25 (m, 30H), 0.93 – 0.84 (m, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.85, 142.10, 137.47, 130.79, 130.47, 130.19, 128.73, 127.24, 124.98, 124.52, 124.27, 122.60, 121.58, 121.47, 115.48, 82.54, 82.52, 82.21, 68.42, 31.94, 29.51, 29.37, 26.20, 22.79, 14.25. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>82</sub>H<sub>94</sub>N<sub>2</sub>O<sub>4</sub>: 1170.7214 found: 1170.7174 [M + H]<sup>+</sup>.

#### 4.11.3. Polymerization

To a solution of compound **2** (0.095 g, 0.081 mmol) and 1,4-diiodo-2,5-dioctylbenzene<sup>137</sup> (0.048 g, 0.081) in degassed THF (3 mL) and Et<sub>3</sub>N (0.8 mL) were added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.006 g, 0.008 mmol) and CuI (0.001 g, 0.004 mmol). The reaction was heated to 50 °C and stirred

for 18 hours. The solution was cooled and precipitated in 35 mL of ice cooled MeOH. The precipitate was filtered under reduced pressure and rinsed with MeOH. The polymer was subjected to a Soxhlet in acetone to remove oligomers and catalyst residues, followed by a Soxhlet in CHCl<sub>3</sub> to recover the polymer. The solid was dried under reduced pressure at 50 °C to afford **P1** as a brown solid (0.106 g, 86 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.05, 8.81, 8.71, 8.68, 8.12, 7.24, 7.19, 7.17, 7.14, 6.78, 6.76, 4.21, 4.07, 4.05, 3.87, 2.06, 1.73, 1.59, 1.41, 1.28, 1.25, 1.20, 1.19, 0.86, 0.84, 0.76.





Figure 4.4. <sup>1</sup>H NMR spectra of compound **2**.



Figure 4.5. <sup>13</sup>C NMR spectra of compound **2**.



Figure 4.6. <sup>1</sup>H NMR spectra of **P1**.



Figure 4.7. Size-exclusion chromatogram of P1.

 $\overline{M_n} = 16\ 266\ Da$  $\overline{M_w} = 41\ 189\ Da$  $I_p = 2.53$  $D = 11\ units$ 

#### 4.11.6. Cyclic Voltammetry

All cyclic voltammograms were acquired using a three-electrode BASI Epsilon potentiostat (purchased from Bioanalytical Systems). The potential was referenced to a Ag/AgCl saturated KCl electrode (purchased from Bioanalytical Systems) and Pt wire working and counter electrodes. Supporting electrolyte of DCM saturated with *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.1M) was purged with nitrogen prior to electrochemical measurements. For determination of vacuum levels, the potentials were calibrated against ferrocene/ferrocenium external standard measured at 0.441 mV versus Ag/AgCl and the saturated calomel electrode. For the cyclic voltammetry in the solid state, **P1** was drop casted on an ITO/glass electrode or dip coated on a Pt wire working electrolyte of MeCN saturated with *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.1M) was purged with nitrogen prior to electrochemical measurements.



Figure 4.8. Solid state cyclic voltammetry of **P1** a) drop casted on ITO, b) dip coated on a Pt wire.

#### 4.11.7. Optical Properties

#### Spectroelectrochemistry and UV-Visible titration with TBPA in solution:

Spectroelectrochemical measurements were performed with a Honeycomb spectroelectrochemical cell kit from Pine Research. Gold electrodes were used with an Ag/AgNO<sub>3</sub> reference electrode. All measurements were performed in dichloromethane 0.1M  $nBu_4NPF_6$ . For the chemical titration with TBPA, nine solutions were prepared with a constant concentration of the substrate. Aliquot of a standard solution of TBPA were added to the substrate. The higher molar absorptivity around 300 nm for all chemical titrations can be attributed to TBPA, as these absorption bands are not present in the electrochemical titration.

#### Thin film spectroelectrochemistry:

**P1** was drop-casted on an ITO/glass electrode with a Pt counter electrode with a Ag/AgNO<sub>3</sub> reference electrode. Supporting electrolyte of MeCN saturated with  $nBu_4NPF_6$  (0.1M).



Figure 4.9. Thin film optical properties of **P1** and its radical cation and dication counterparts.



Figure 4.10. Spectroelectrochemical titration of a) **P1** to **P1**<sup>+</sup> and b) **P1**<sup>+</sup> to **P1**<sup>2+</sup> drop casted on an ITO/glass electrode.

#### 4.11.8. Oxidation Experiment with TBPA

**P1** (14.0 mg, 0.009 mmol), hexamethylbenzene (1 mg, 0.009 mmol), and tris(4-bromophenyl)ammoniumyl hexachloroanthimonate (7 mg, 0.009 mmol) were charged in an NMR tube and dissolved in  $CDCl_3$  (0.70 mL).



Figure 4.11. NMR spectra of **P1** with 1 equivalent of TBPA.



Figure 4.12. NMR spectra of **P1** with 2 equivalents of TBPA.

# Chapter 5. Anthanthrene as a Super-Extended Tetraphenylethylene for Aggregation-Induced Emission

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#### 5.1. Foreword

This chapter is out of the initial scope of this thesis but still uses the very unique geometry of anthanthrone to harness new optoelectronic properties. In the course of my PhD studies, I synthesized numerous molecules that had the same general motif as the tetraphenylethylene (TPE), a compound known for its aggregation-induced emission properties (AIE). AIE has not a well-defined structure-property relationship because this phenomenon happens in the bulk rather than at the molecular level. Therefore, it is hard to predict the AIE of certain compounds before testing them experimentally. Some design elements like multiple rotors attached to a stator (*vide infra*) were present in several anthanthrone derivatives in hand, enough to produce a complete AIE study. To our delight, the anthanthrone has a very interesting role in making red-shifted fluorescence emission, that is not very common in the literature.

#### 5.2. Résumé

Sept nouveaux dérivés  $\pi$ -étendus du TPE ont été étudiés pour leurs propriétés d'émission induite par agrégation. Les propriétés d'émission de ces luminogènes à base d'anthanthrone ont été modulées par de simples modifications chimiques sur les quatre différentes positions du cœur anthanthrone. Les propriétés optiques, ainsi que les structures de diffraction des rayon X et les structures optimisées par DFT, ont été étudiées. Ce travail constitue une nouvelle unité liante pour l'architecture TPE avec une émission décalée vers le rouge.

### **5.3.** Abstract

Seven new  $\pi$ -Extended derivatives of the known tetraphenylethylene (TPE) have been studied for their aggregation-induced emission (AIE) properties. Modulation of the emission properties of these anthanthrone-based luminogens has been accomplished through simple chemical modifications on four different positions of the anthanthrone core. The optical properties, along with X-ray diffraction and DFT-optimized structures, were studied. This work provides a new, easily accessible bridging unit for the TPE framework with a red-shifted emission.

## **5.4. Introduction**

Aggregation-induced emission has been extensively studied for the past 16 years.<sup>141,142</sup> It has shed light on a solid-state phenomenon that consists of increased photoluminescence intensity with aggregation, while in most organic molecules the exact opposite effect is observed. In fact, fluorescence is usually inhibited by  $\pi$ - $\pi$  interactions and stacking, a phenomenon called aggregation-caused quenching.<sup>143–145</sup> This quenching has hampered the uses of these molecules in light-emitting devices (OLEDs), as emission in the thin-film state is required.<sup>146</sup> Thus, molecules exhibiting enhanced fluorescence in the solid, thin-film or aggregated state is certainly a desirable feature. One of the best strategies to obtain AIE properties is to design molecules that contain a fixed, rigid part (stator) bearing several moving parts (rotors) whose intramolecular motions can be inhibited upon aggregation, enabling an accessible radiative deactivation pathway.<sup>147</sup> The most common example of such systems is tetraphenylethylene (TPE) (Figure 5.1), an almost non-emissive chromophore in solution that can be highly emissive in the solid state due to its twisted structure that prevents  $\pi$ - $\pi$  stacking.<sup>148,149</sup> Other classes of molecules such as 1,1,2,3,4,5-hexaphenylsilole (HPS),<sup>150</sup> bis(4-(N-(1-naphthyl)-phenylamino)phenyl)fumaronitrile (NPAFN)<sup>151</sup> and malononitrilesubstituted-pyran<sup>152</sup> exhibit AIE properties as a result of restricted molecular motion in the solid state. Several applications can take advantage of the increased photoluminescence intensity in the solid state such as chemical sensors for the detection of trinitrotoluene,<sup>153</sup> chirality,<sup>154</sup> and metal ions,<sup>155</sup> among others.<sup>156</sup> Also, fine-tuning of the substituents on the TPE framework has been used to develop OLEDs from blue to red.<sup>146</sup>

Our group has been interested in the 4,10-dibromoanthanthrone dye for different applications.<sup>71,82,125</sup> The conjugated anthanthrone core is a quinoidal polycyclic hydrocarbon made of two fused anthracenes. When the 6 and 12 positions are substituted with bis(diphenylmethylene) moieties, the resulting molecule can be seen as an extended version of the tetraphenylethene unit known for its aggregation-induced emission properties (Figure 5.1).



Figure 5.1 Structure of TPE and its extended version with the anthanthrone dye.

Because of the high steric bulk between the anthanthrone core and its adjacent phenyl groups, this molecule can replicate the propeller shape of TPE that allows restricted intramolecular motion. While similar to the TPE in general structure, the anthanthrone core benefits from a wide range of properties upon very small changes either in the 4,10 or 6,12 conjugation channels.<sup>72,77</sup> It was demonstrated that the steric bulk between these adjacent moieties is so high that it is the driving force for a double-to-single bond transformation along with the creation of a stable diradical species.<sup>125</sup> Most recently, an isoelectronic nitrogen-based dicationic analogue was shown to be open-shell, where the radicals recombination is prevented by steric bulk.<sup>136</sup> Several anthracene-based motifs have demonstrated some aggregation-induced emission in the green and yellow region of the visible spectrum.<sup>157,158</sup> With its extended conjugation pathway, it was hypothesized that the anthanthrone core as the stator could produce AIE-active fluorophores in the red to near-infrared (NIR) region, which is of great interest for bioimaging.<sup>159</sup> Herein we report the synthesis and characterization of seven anthanthrone-based derivatives with different substituents in the 4,10 and 6,12positions (Figure 5.2). The influence of the bis(diphenylmethylene) versus diphenylamines at the 6 and 12 positions, and the planarity of the polycyclic aromatic core on the photoluminescence intensity is discussed. These molecules have been studied by UV-visible absorption and emission spectroscopy, and X-ray crystallography. DFT calculations were also performed to obtain the optimized structures.



Figure 5.2. Seven anthanthrone- and anthanthrene-based derivatives studied for AIE.

# 5.5. Synthesis

Compounds  $1,^{71} 2^{125}$ , **4** and  $5^{136}$ , and **6** and  $7^{71}$  were synthesized according to a previously reported method. Compound **3** was synthesized from compound **7** by a Ramirez olefination with PPh<sub>3</sub> and CCl<sub>4</sub> in the microwave at 150 °C to afford compound **8** in 99% yield. Compound **8** was subjected to a 4-fold Suzuki-Miyaura coupling with 4-cyanophenylboronic acid pinacol ester at 50 °C to afford compound **3** in 54% yield (Scheme 5.1).



Scheme 5.1. Synthetic scheme of compound **3**.

## **5.6. Optical Properties**

The optical properties of all compounds are reported in Table 5.1. As expected, the nature of the functional groups positioned at the 4, 6, 10 and 12 positions has a significant influence the optical properties of the anthanthrene and anthanthrone core. In the on bis(diphenylmethylene) series (compounds 1-3), the addition of diphenylamine unit at the 4 and 10 positions (compound 3) induces a bathochromic shift of 25 nm of the absorption spectrum relative to the TIPS-acetylene derivative 2. The same transformation on anthanthrone (compound 6 to 7) produces an even larger bathochromic shift (114 nm) due to the creation of a stronger donor-acceptor complex. In case of compounds 4 and 5, the replacement of TIPS-acetylene by diphenylamine resulted in a small hypsochromic shift, which can be attributed to the loss of conjugation and the absence of a donor-acceptor substitution impacted complex. These small changes also significantly the photoluminescence spectra of the anthanthrone and anthanthrene derivatives. In fact, emission in solution from green (515 nm, compound 1) to red (749 nm, compound 7) can be obtained. Solution quantum yields were measured for 1, 2, 4, and 5 (0.3, 2.6, 1.4, 4.5%, respectively) and emit very weakly.

	$\lambda_{max}$	ελmax	$\lambda_{onset}$	$\lambda_{exc}$	$\lambda_{Em.}$	Eg	<i>φ</i> solution	$\Phi_{ m solid}$
	(nm)	$(M^{-1} cm^{-1})$	(nm)	(nm)	(nm)	(eV)	(%)	(%)
1	485	43937	521	470	515	2.38	0.3	$1.3\pm0.4$
2	488	45717	526	488	559	2.36	2.6	$1.3\pm0.4$
3	513	23937	578	612	711	2.15	-	-
4	576	17147	635	565	674	1.95	1.4	$6.4\pm1$
5	562	20123	615	550	651	2.02	4.5	$18.5\pm2$
6	513	30794	543	612	644	2.28	-	-
7	627	15481	712	630	749	1.74	-	-

Table 5.1. Summary of the optical properties of compound 1-7 in THF.

Calculated at the onset of the absorption spectrum,  $E_g$  was determined at  $\lambda_{onset}$ , standard used for solution QY, fluorescein 0.1 M NaOH (91%) for 1 and 2, and cresyl violet in ethanol (57.8%) for 4 and 5.

## 5.7. Aggregation-Induced Emission Properties

The AIE properties of compounds 1-7 have been studied by addition of distilled water fractions in THF solution of the chromophore. Because of their similar structure, both compounds 1 and 2 showed analogous behaviour with increased water fraction ( $f_w$ ) (Figure 5.3, Figure 5.11, and Figure 5.12, respectively). The photoluminescence was low until  $f_w = 30\%$  with a dramatic increase to a maximum of 40 % water in THF. The solid-state quantum yields were measured and both compounds 1 and 2 have a low value of 1.3%. From solution to solid-state, there is an increase of 1% for 1 and 1.3% for 2. This increased intensity trend is also observed in the aggregated state with 2 having a more drastic increase than 1 from  $f_w = 30$  to 40 Figure 5.11 and Figure 5.12c, respectively).



Figure 5.3. a) absorption and emission spectra, b) emission spectra in function of the water fraction of compound **1** in THF.

In the case of compound **3**, no significant photoluminescence was observed upon addition of water (Figure 5.13), meaning that the presence of diphenylamine units at the 4 and 10 positions is detrimental for the restriction of intramolecular motions. From the X-ray diffraction data of compound **2**,<sup>125</sup> the structure of **3** was optimized (Figure 5.4 and Figure 5.25). It was demonstrated that because of the steric congestion between the diphenylmethylene and the anthanthrone core, compound **2** adopts a butterfly structure, which is also replicated in the optimized structure of **3**. One major difference dwells in the trigonal planar geometry of the diphenylamine units at the 4 and 10 positions of **3**, increasing the steric bulk on the butterfly structure. One can assume that the high steric congestion prevents the free rotation of the phenyl both in solution and in the solid state. It is also possible that intramolecular  $\pi$ -interactions occur between the neighboring phenyl rings, reducing the rotational movements both in solution and in the solid state. From these observations, it is interesting to note that the presence of a propeller-shaped triphenylamine unit does not guarantee enhanced photoluminescence in the aggregated state.



Figure 5.4. Front view and side view of the optimized structure of compound **3**. H atoms have been removed for clarity.

For the 6,12-bis(diphenylamine) series, compounds **4** and **5** (Figure 5.14 and Figure 5.5, respectively) both showed AIE upon addition of water to reach a maximum at  $f_w = 90$  %. The photoluminescence is more intense in the case of compound **5**, compared to **4**, with the only structural difference residing in the substituents at the 4 and 10 positions. Indeed, the presence of diphenylamine units increased the maximum photoluminescence intensity compared to the triisopropylsilyl groups. The presence of four additional rotors in **5** could explain the enhanced AIE effects. The solid-state quantum yield of **4** and **5** were measured and **5** has the highest value of 18.6% followed by **4** with 6.4%. Compound **5** has the most dramatic increase in its quantum yield value from solution to solid state, while not being the most emissive of the series. This trend is also reproduced in the aggregated state, with **5** having the highest increase in the emission intensity from  $f_w = 0$  to 90% (Figure 5.14c and Figure 5.15).



Figure 5.5. a) absorption and emission spectra, b) emission spectra in function of the water fraction of compound **5** in THF.

The aggregation induced emission behavior of compound **5** stands in sharp contrast with the previously drawn conclusions for the diphenylmethylene series in compound **3**. Again, the explanation could reside in the X-ray diffraction structure of compound  $4^{136}$  The diphenylamine units at the 6 and 12 positions are arranged in a trigonal planar geometry, meaning that no significant steric bulk between the anthanthrone core and the adjacent phenyl rings is present, resulting in a perfectly planar aromatic core. This geometry, also replicated in the DFT-optimized structure of **5** (Figure 5.27), should provide plenty of space for the free-rotation of the diphenylamines at the 4 and 10 positions in solution, which is not the case in compound **3**.

Interestingly, compound 1 and 4 show very different behaviors in the aggregated state. The maximum photoluminescence intensity was reached for compound 1 at a much lower  $f_w$  value than for 4 (40 and 90%, respectively), which could be attributed to the poorer solubility of compound 1. Figure 5.6a shows solutions of compounds 1, 2, 4 and 5 at different  $f_w$  values, corresponding to the maximum photoluminescence intensity. Compounds 4 and 5 both show emission in the red, and their CIE coordinates are (0.55, 0.28) and (0.62, 0.37), respectively (Figure 5.6b). These coordinates are very close to the pure red (0.67, 0.33) especially for compound 5, which could be interesting for the development of OLEDs and for bioimaging applications. SEM images of the dried sample 1, 2, 4, and 5 from THF were compared to the aggregated samples with water at their maximum fluorescence intensity (Figure 5.6c,d, and

Figure 5.18 to Figure 5.21). It is clear that all the samples in presence of a nonsolvent contain large domains of aggregates.

The ketones series (compounds **6** and **7**, Figure 5.16 and Figure 5.17, respectively), do not show strong photoluminescence, most probably due to the absence of phenyl rotors in **6**. As for **7**, the photoluminescence intensity is very low but still shows AIE at a  $f_w$  of 70%, which could be attributed to the diphenylamine units at the 4 and 10 positions (see the Supporting Information, X-ray diffraction details). In both compounds **6** and **7**, the presence of fluorescence quenching ketones could also result in very low emissive properties, therefore not showing strong AIE behavior.



Figure 5.6. a) Photoluminescence at maximum water fraction of 1, 2, 4, and 5, left to right, b) CIE coordinates of 4 (X) and 5 (+), c) SEM image of aggregated 2, scale 10  $\mu$ m, d) SEM image of aggregated 4, scale 100  $\mu$ m.

#### **5.8.** Conclusion

In conclusion, we have studied seven new AIE luminogens bearing an extended polycyclic aromatic core, anthanthrone, to replicate the propeller shape of the AIE-active TPE. Slight changes in the substituents at the 4,10 and 6,12 positions have a dramatic effect on the optical and AIE properties. The extended conjugation of the anthanthrone stator allows emission in the NIR with compound **5** having the closest CIE coordinates to pure red.

## 5.9. Acknowledgements

M. Desroches thank the NSERC for a PhD scholarship. We also thank Thierry Maris at Université de Montréal for the DRX analysis, Thaksen Vasant Jadhav and Dmitrii Perepichka from McGill University for solid-state quantum yield measurements, and André Ferland at Université Laval for the SEM analysis.

#### 5.10. Supporting Information

#### 5.10.1. General

Chemical reagents were purchased from Sigma–Aldrich Co. Canada or Oakwood Products, Inc. and were used as received. 4,10-Dibromoanthanthrone was a courtesy from Heubach GmbH as Monolite Red 316801 product. Solvents used for organic synthesis were purified using a Solvent Purifier System (Vacuum Atmosphere Co., Hawthorne, USA). NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz or an Agilent DD2 500 MHz. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm ( $\delta$ ) relative to residual solvent peak. Highresolution mass spectra (HRMS) were recorded using an Agilent 6210 time-of-flight (TOF) LCMS apparatus equipped with an APPI ion source (Agilent Technologies, Toronto, Canada). UV-visible absorption spectra were recorded using a Varian diode-array spectrophotometer (Cary 5000 model). Fluorescence spectroscopy was performed using a fluorescence spectrophotometer (Cary Eclipse model). Scanning Electron Microscopy (SEM) images were taken using a JEOL JSM-840a with a 15 kV tension.

#### 5.10.2. Synthesis

Compounds 1, 6 and 7,  $^{71}$  2,  $^{125}$  4 and 5 $^{136}$  were synthesized according to a previously reported method.

#### Compound 8

A dry microwave flask under argon was charged with compound **7** (0.25 g, 0.39 mmol), PPh<sub>3</sub> (0.816 g, 3.11 mmol), and CCl<sub>4</sub> (6.18 g, 3.88 mL, 40.2 mmol). The mixture was degassed with a flow of argon for 10 min and heated in a microwave apparatus to 150 °C for 10 min, followed by 10 min at that same temperature. Once cooled, CH<sub>2</sub>Cl<sub>2</sub> was added and the crude reaction mixture was filtered on a silica pad and rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was evaporated, and the residue was purified by silica gel column chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 4:1 v/v) to afford compound **8** as red solid (0.299 g, 99%; the product should be kept in the dark as it darkens under prolonged exposure to ambient light). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, *J* = 7.5 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.90 (s, 2H), 7.43 (dd, *J* = 8.4, 7.5 Hz, 2H), 7.25 – 7.20 (m, 8H), 7.09 (d, *J* = 8.0 Hz, 8H), 6.98 (t, *J* = 7.2 Hz, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  148.48, 143.13, 132.23, 131.04, 129.86, 129.63, 129.38, 128.67, 128.08, 127.72, 126.08, 125.22, 124.74, 122.61, 122.42, 120.77. HRMS (APPI<sup>+</sup>): m/z calcd for C<sub>48</sub>H<sub>28</sub>Cl<sub>4</sub>N<sub>2</sub>: 772.1007; found: 772.0992 [M\*]<sup>+</sup>.

#### Compound 3

Compound **8** (0.197 g, 0.254 mmol), 4-cyanophenylboronic acid pinacol ester (0.350 g, 1.52 mmol), potassium phosphate tribasic (0.864 g, 4.07 mmol), tetrabutylammonium bromide (0.041 g, 0.127 mmol), dichlorobis(triphenylphosphine)palladium (0.036 g, 0.051 mmol) and triphenylphosphine (0.013 g, 0.051 mmol) were dissolved in degassed toluene (25 mL) and water (2 mL). The mixture was heated at 30 °C for 20 h. The solution was cooled, diluted in CH<sub>2</sub>Cl<sub>2</sub>, extracted three times with water and dried over sodium sulfate. The solvent was removed in vacuo without heating. The crude product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to afford compound **3** (0.142 g, 54%) as red powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 46.5 Hz, 16H), 7.21 – 7.12 (m, 12H), 7.04 – 6.93 (m, 6H), 6.80 – 6.74 (m, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.04, 147.92, 147.25, 142.96, 139.40, 135.26, 134.29, 132.88, 131.08, 130.60, 130.32,

130.00, 129.32, 129.20, 128.46, 126.10, 125.89, 124.92, 122.59, 122.01, 118.62, 116.43, 111.25. HRMS (APPI<sup>+</sup>): *m/z* calcd for C<sub>76</sub>H<sub>44</sub>N<sub>6</sub>: 1040.3628; found: 1040.3578 [M\*]<sup>+</sup>.



# 5.10.3. NMR Spectra

Figure 5.7 <sup>1</sup>H NMR spectra of compound **8**.





Figure 5.9. <sup>1</sup>H NMR spectra of compound **3**.



Figure 5.10. <sup>13</sup>C NMR spectra of compound **3**.

**5.10.4.** Optical Properties



Figure 5.11. Normalized integrated area of the emission spectra function of the water fraction of compound 1 in THF,  $\lambda_{exc}$ = 470 nm.



Figure 5.12. a) absorption and emission spectra, b) emission spectra in function of the water fraction, c) normalized integrated area of the emission spectra function of the water fraction of compound 2 in THF,  $\lambda_{exc}$ = 488 nm.



Figure 5.13. a) absorption and emission spectra, b) emission spectra in function of the water fraction of compound **3** in THF,  $\lambda_{exc}$ = 612 nm.



Figure 5.14. a) absorption and emission spectra, b) emission spectra in function of the water fraction, c) normalized integrated area of the emission spectra function of the water fraction of compound **4** in THF,  $\lambda_{exc}$ = 565 nm.



Figure 5.15. Normalized integrated area of the emission spectra function of the water fraction of compound 5 in THF,  $\lambda_{exc}$ = 550 nm.



Figure 5.16. a) absorption and emission spectra, b) emission spectra in function of the water fraction of compound **6** in THF,  $\lambda_{exc}$ = 612 nm.



Figure 5.17. a) absorption and emission spectra, b) emission spectra in function of the water fraction of compound 7 in THF,  $\lambda_{exc}$ = 630 nm.
#### 5.10.5. Quantum Yield Measurements in Solution

For compounds **1** and **2**, fluorescein in 0.1M NaOH solution was used as the standard with a 470 nm excitation wavelength. 91% was used as the quantum yield reference.<sup>160</sup> For compounds **4** and **5**, cresyl violet in ethanol was used as the standard with a 575 nm excitation wavelength for **4** and 560 nm for **5**. 57.8% was used as the quantum yield reference.<sup>161</sup>

## 5.10.6. SEM Images



Figure 5.18. SEM images of compound 1 a) dropcasted solution in THF, scale 10  $\mu$ m, b) aggregated scale 10  $\mu$ m, c), and d) aggregated scale 1  $\mu$ m.



Figure 5.19. SEM images of compound **2** a) dropcasted solution in THF, scale 100  $\mu$ m, b) dropcasted solution in THF, scale 10  $\mu$ m, c) dropcasted solution in THF, scale 1  $\mu$ m, and d) aggregated scale 1  $\mu$ m.



Figure 5.20. SEM images of compound 4 a) dropcasted solution in THF, scale 100  $\mu$ m, b) aggregated scale 10  $\mu$ m.



Figure 5.21. SEM images of compound 5 a) dropcasted solution in THF, scale 10  $\mu$ m, b) dropcasted solution in THF, scale 1  $\mu$ m, c) aggregated scale 100  $\mu$ m, and d) aggregated scale 10  $\mu$ m.

Note for compound **4** and **5** in dropcasted solution (Figure 5.20a and Figure 5.21a,b): the solution of these compounds made a very thin film on the sample holder. The cracks present in these images are the sample holder itself.

## 5.10.7. X-Ray Diffraction Details

#### Compound 7

Crystallographic data have been deposited with CCDC (CCDC 1581831). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.



Figure 5.22. X-ray diffraction structure of **7**.

Table 5.2. Crystal data and structure refinement for compound 7.	
Identification code	COURT8
Empirical formula	C <sub>29</sub> H <sub>19.68</sub> Cl <sub>0.32</sub> NO
Formula weight	409.31
Temperature/K	150
Crystal system	triclinic
Space group	P-1
a/Å	8.6756(2)
b/Å	9.8735(2)
c/Å	13.4539(3)
$\alpha^{\prime \circ}$	110.956(1)
β/°	103.842(1)
$\gamma/^{\circ}$	91.855(1)
Volume/Å <sup>3</sup>	1036.08(4)
Z	2
$\rho_{calc}g/cm^3$	1.312
$\mu/\text{mm}^{-1}$	0.638
F(000)	428.0
Crystal size/mm <sup>3</sup>	$0.2\times0.13\times0.08$
Radiation	$GaK\alpha \ (\lambda = 1.34139)$
$2\Theta$ range for data collection/°	6.354 to 121.444
Index ranges	$\text{-}11 \leq h \leq 11,  \text{-}12 \leq k \leq 12,  \text{-}17 \leq l \leq 17$
Reflections collected	25358
Independent reflections	4762 [ $R_{int} = 0.0242, R_{sigma} = 0.0175$ ]

Tabl 5 2 C. ratal date 1 f: nt fo 4 **7** 

Data/restraints/parameters	4762/0/285
Goodness-of-fit on F <sup>2</sup>	1.046
Final R indexes [I>=2 $\sigma$ (I)]	$R_1 = 0.0587,  wR_2 = 0.1482$
Final R indexes [all data]	$R_1 = 0.0613,  wR_2 = 0.1516$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.95/-0.40

#### **5.10.8.** Computational Details

For computation time considerations, the decyl alkyl chains of compounds **5** and **6** were replaced by a simple methyl group. Calculations were performed with the GAUSSIAN 09 programs.<sup>123</sup> Geometries were optimized using the B3LYP functional<sup>130</sup> in combination with the 6-31+G\* basis set for all atoms, including hydrogen for compounds **1**, **3**, **6**, and **7**. As for compounds **2**, **4**, and **5** geometries were optimized using the B3LYP functional in combination with the 6-31+G basis set for all atoms, including hydrogen. The stationary points were characterized as minima on the potential energy surface by full vibration frequencies calculations (no imaginary frequency). All geometry optimizations were carried out without any symmetry constraints. All structures with their associated free enthalpy and Gibbs free energies as well as their cartesian coordinates are fully detailed in the following section.

#### Compound 1



Figure 5.23. Front view, left and side view of the optimized structure of compound 1.

Thermal correction to Gibbs Free Energy= 1.079256 Sum of electronic and thermal Free Energies= -3287.529876 Compound 2



Figure 5.24. Front view, left and side view of the optimized structure of compound 2.

Thermal correction to Gibbs Free Energy= 1.072442 Sum of electronic and thermal Free Energies= -3655.699165

Compound 3



Figure 5.25. Front view, left and side view of the optimized structure of compound **3**.

Thermal correction to Gibbs Free Energy= 0.863194 Sum of electronic and thermal Free Energies= -3250.202628

# Compound 4



Figure 5.26. Front view, left and side view of the optimized structure of compound **4**.

Thermal correction to Gibbs Free Energy= 1.178362 Sum of electronic and thermal Free Energies= -3738.688689

Compound 5



Figure 5.27. Front view, left and side view of the optimized structure of compound 5.

Thermal correction to Gibbs Free Energy= 1.005750 Sum of electronic and thermal Free Energies= -3371.662748

#### Compound 6



Figure 5.28. Optimized structure of compound **6**.

Thermal correction to Gibbs Free Energy= 0.734952 Sum of electronic and thermal Free Energies= -2435.556329

Compound 7



Figure 5.29. Optimized structure of compound 7.

Thermal correction to Gibbs Free Energy= 0.536672 Sum of electronic and thermal Free Energies= -2029.242994

#### 5.10.9. Cyclic Voltammetry

Cyclic voltammetry of compounds **4** and **5**,<sup>136</sup> **6** and **7**<sup>71</sup> have been reported in other publications. All cyclic voltammograms were acquired using a three-electrode BASI Epsilon potentiostat (purchased from Bioanalytical Systems). The potential was referenced to an Ag/AgCl saturated KCl electrode (purchased from Bioanalytical Systems) and Pt wire working and counter electrodes. Supporting electrolyte of dichloromethane saturated with (*n*Bu)4NPF<sub>6</sub> (0.1M) was purged with nitrogen prior to electrochemical measurements. For determination of vacuum levels, the potentials were calibrated against ferrocene/ferrocenium external standard measured at 0.503 mV for compound 1, 0.531 mV for compound **2** versus Ag/AgCl and the saturated calomel electrode.



Figure 5.30. voltammetry of compound 1 in DCM, scan rate 100 mV/s.



Figure 5.31. Cyclic voltammetry of compound **1** in DCM, scan rate 100 mV/s.



Figure 5.32. Cyclic voltammetry of compound **3** in DCM, scan rate 50 mV/s.

# Chapter 6. Conclusion, Perspectives, and Other Contributions

To conclude, this thesis has provided examples illustrating that a single aromatic core can be used to develop many different areas of research. Chapter 2 featured an unprecedented strategy to obtain a diradical. It was demonstrated that  $\pi$ -bonds can be broken with bare hands using a mortar and pestle due to the double bonds being weakened by steric hindrance. A kinetically trapped organic diradical can thus be produced in the solid state, a new concept in the field of diradicals. Chapter 3 presented a new bridging unit, anthanthrene, for the formation of a diradical dicationic amine. Based on Wurster's reagent, the bis(triarylamine) dicationic salts of anthanthrone exhibit a ground state biradical. This class of compounds is very stable and show strong absorption in the NIR. The X-ray diffraction structure of the neutral amine compared to the dicationic salt were employed to confirm that recombination of the radicals was not possible due to the interruption of the  $\pi$ -systems. Chapter 4 is an extension of the project described in Chapter 3. A polymer made of anthanthramine can be oxidized to a very stable diradical dication. It was shown that a through-space delocalization of the neighboring amines produced a strong absorption in NIR akin to the phenomena observed in the molecular version. Chapter 5 demonstrated that the geometry of the anthanthrone and anthanthrene could reproduce the propeller shape of the TPE unit for aggregation-induced emission. The same anthanthrene-based amines synthesized in Chapter 3 presented strong emission in the NIR, which is quite uncommon in the aggregation-induced emission literature.

On another note, this thesis rests upon a sole compound, but my PhD work has not been focused only on a single aromatic core. I have explored different structures for diradical chemistry that have not been published but their investigation could potentially be very interesting. One in particular is based on Coppinger's radical, bisgalvinoxyl,<sup>162</sup> and the general structure of the TPE subunit often employed for AIE (Figure 6.1). The closed-shell structure of  $1^{2+}$  already has been investigated for its luminescent and charge transport properties.<sup>140,163</sup> Only two of the four amines would be easily oxidized, since the potential

increases dramatically after the first oxidation, then only a diradical dication would be obtained. One could also imagine a polymer  $P^{2+}$ , again in the mindset of increasing the radical density over an organic molecule, could also be an interesting to study. Since TPE-like molecules are synthesized by a McMurry condensation reaction, it is not an easy task to make them asymmetric. But it would be possible to make polymers through functionalization of the *cis* phenyls.



Figure 6.1. Bisgalvainoxyl and proposed diradical cation TPE-amine and its polymer version. I would also like to look back at my pre-doctoral examination that contained many different diradical structures based on other vat dyes than anthanthrone. The three main objectives back then were to make diradicals based on vat dyes, functionalize them to modify their properties, and make open-shell polymers with those dyes. I can confidently say that I was able to achieve these goals, albeit I did not have to look further than anthanthrone. Figure 6.2 contains a sample of the molecules proposed in my pre-doctoral examination. This project was very interesting because it would enable the study of a wide variety of compounds with simple modifications on already complex PAHs. The major problem with vat dyes is that they are synthesized industrially for bulk applications such as paint or pigmentation. Therefore, no particular interest is given to their purity since the cost of the final product would be impacted greatly. In these bulk chemicals, there are numerous position isomers that are very difficult to isolate since they have almost the same polarity and solubility properties. In the specific case of 4,10-dibromoanthanthrone, Heubach has provided a compound pure enough to make fine chemicals and it was assumed, rather naively, that other vat dyes would be of the same purity. As it was not the case, I tried to purify them using Soxhlet extractors and recrystallisation without success. Indeed, the project could never be investigated further because of the limited purity of the starting material. Although, if a reliable source of dye could be found, it would definitively be a high-impact research worth investigating.



Figure 6.2. Vat dyes and their diradical structures proposed in my pre-doctoral examination. As the scientific literature on diradicals continues to evolve, a lot of visionary avenues are developing such as 2D and 3D structures, multiradical, polymers, and dynamic structures. Very recently, Wu and coworkers studied a molecular cage where triphenylmethane units at

the apex of the cage would produce an all-conjugated diradical 3D scaffold (Figure 6.3a).<sup>131</sup> The same group also published studies on fluorenyl-based polymers and macrocycles showing multiradical character (Figure 6.3b).<sup>132,135</sup> The use of very bulky substituents, such as 9-anthryl-3,5-di-*tert*-butylphenyl in position 9 of the fluorene to kinetically block the spin and increase delocalization, enables the study of otherwise unstable compounds. Again, this very productive group showed in 2017 that long rylene ribbons displayed diradical character and very low bandgaps (Figure 6.3c). This innovative work provided new insight into the properties of graphene nanoribbons.<sup>42</sup>



Figure 6.3. a) 3D diradical cage, b) fluorenyl-based polymer and macrocycles, and c) rylene ribbons with a diradical character.<sup>‡‡‡‡</sup>

Herges and coworkers in 2011 developed a molecular switch incorporating a pro-radical molecule that changes its structure upon exposure to light. The principle of this system rests on the *cis/trans* isomerisation of azopyridine. Upon exposure to UV light (365 nm) the azopyridine is in *cis* configuration and cannot coordinate to the nickel center because of steric hindrance. But, if the solution is irradiated with a violet-blue light (455 nm) azopyridine is

<sup>&</sup>lt;sup>‡‡‡‡</sup> Figure adapted from:Wu, J.; Gu, X.; Gopalakrishna, T. Y.; Phan, H.; Ni, Y.; Herng, T. S.; Ding, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 1583–15387. Reprinted with permission from John Wiley and Sons, 4294330337100, license date: Feb 22, 2018.

b) Figure adapted from: Lu, X.; Lee, S.; Hong, Y.; Phan, H.; Gopalakrishna, T. Y.; Herng, T. S.; Tanaka, T.; Sandoval-Salinas, M. E.; Zeng, W.; Ding, J.; Casanova, D.; Osuka, A.; Kim, D.; Wu, J. *J. Am. Chem. Soc.* **2017**, *139*, 13173–13183. Reprinted with permission from ACS.

c) Figure adapted from: Zeng, W.; Phan, H.; Zeng, W.; Phan, H.; Herng, T. S.; Gopalakrishna, T. Y.; Aratani, N.; Zeng, Z.; Yamada, H.; Ding, J.; Wu, J. *Chem* **2017**, *2*, 81–92. Reprinted with permission from Elsevier 4294330667051, license date: Feb 22, 2018.

*trans* and acts as a ligand for the Ni-porphyrin, changing its coordination sphere to obtain a paramagnetic species. As a result, the percentage of paramagnetic nickel porphyrin can be switched with different light sources.



Figure 6.4. Paramagnetic and diamagnetic switch of a nickel porphyrin in response to different wavelength.<sup>§§§§</sup>

<sup>&</sup>lt;sup>§§§§</sup> Figure adapted from: Lu, X.; Lee, S.; Hong, Y.; Phan, H.; Gopalakrishna, T. Y.; Herng, T. S.; Tanaka, T.; Sandoval-Salinas, M. E.; Zeng, W.; Ding, J.; Casanova, D.; Osuka, A.; Kim, D.; Wu, J. *J. Am. Chem. Soc.* **2017**, *139*, 13173–13183. Reprinted with permission from ACS.

Some other avenues with the molecules presented in Chapter 2 and Chapter 3 could be interesting to study. Because of their bowl-shaped structure, molecules **1**, **2**, and **4** in Chapter 2 could be used as hosts for fullerene binding (Figure 6.5). It was shown by Dr. Giguère that indeed, anthanthrone can associate with fullerenes while mimicking the tetrathiafulvalene structure.<sup>75</sup> Preliminary results with  $C_{60}$  and curved anthanthrone suggest that there is some weak binding, but due to the lack of time, this work was not pursued further. It is hypothesized that changing the substituent on the germinal *exo* carbon of anthanthrone could lead to a strong binding with fullerenes.



Figure 6.5. Schematic representation of two possible ways to bind  $C_{60}$  with a contorted anthanthrone.

Keeping the same molecules in mind, there were strong color changes associated with the grinding of molecule 2 in Chapter 2 (see Figure 2.17). Thus, it would be interesting to make a pressure-induced color-based sensor. Pressure sensors could find applications in the sport industry as many athletes suffer from the effect of repeated blows to the head and concussions. One could think of applying these compounds to a helmet for example and measuring the force of impact to the person wearing it by a colorimetric change. But of course, this is still very hypothetical.

After seeing the X-ray diffraction structure of compound **5** in Chapter 3, we thought that like a receptacle that would potentially disperse carbon nanotubes. The polymer version (**P1**) in Chapter 4 could be a good candidate to wrap and solubilize the carbon nanotubes. What is more, amines are electron-rich and can be oxidized, so it is reasonable to assume that this polyamine might dope the nanotubes. A single dispersion experiment was not successful, probably because of the high steric hindrance of the phenyl-substituted nitrogen, making the anthanthrone inaccessible for  $\pi$  interactions with the nanotubes. Ideally, the phenyl moieties should be replaced with alkyl chains for such application.

As it was discussed in Chapter 1, several past members of the Morin group repeatedly attempted to extend the conjugation of anthanthrone without success. The exception was uncovered by my colleague Antoine Lafleur-Lambert in 2016.<sup>\*\*\*\*\*</sup> Anthanthrene bearing nitrophenyl groups in the 4 and 10 positions can be transformed to a carbazole-anthanthrene by the Cadogan reaction (Scheme 6.1), in analogy to the previously reported preparation of carbazoles by Morin and Leclerc in 2001.<sup>164</sup> The simple use of neat triethylphosphite at 140 °C produced the target compound **4** in 59% yield. The reaction proceeds through a short-lived nitrene intermediate and is shown in Scheme 6.1, bottom. Interestingly, the solution spectroelectrochemistry of alkylated compound **4** reveals bands in the NIR, indicating the presence of unpaired electrons. This study is currently ongoing with our collaborator in Spain, Juan Casado.

<sup>\*\*\*\*\*</sup> Unpublished results



Scheme 6.1. Carbazole-anthanthrene formation by the Cadogan reaction.

In the course of my graduate studies, I also pursued the synthesis of extended anthanthrone and anthanthrene molecules. Building on A.L.L.'s work, it is safe to assume that a carbene will behave the same way the nitrene did to form an all-carbon scaffold due to the simultaneous presence of both empty and filled orbitals at the carbon center. Therefore, a synthetic route to make an all-carbon anthanthrene is shown in Scheme 6.2. Starting from a benzylic phenyl attached to the anthanthrene core, a non-nucleophilic base such as lithium bis(trimethylsilyl)amide in an aprotic solvent, such as benzene, would suffice to produce a carbene. One can predict that the carbene will likely attack at the same position as in the Cadogan reaction shown in Scheme 6.1. Then, the resulting extended anthanthrene core could be oxidized with DDQ in benzene to produce a fluorenyl-anthanthrene diradical.<sup>48</sup> It is worth noting that the anthanthrene core possess two Clar aromatic sextets both in the starting material 6 and final compound 7. Therefore, the formation of a diradical would not be stabilized by the gain of aromaticity but by other factors such as planarization of the core as discussed in Chapter 2. Also, if diradical compound 7 cannot be obtained or is unstable, compound 6 would likely exhibit interesting optoelectronic properties and could be studied independently.



Scheme 6.2. Synthesis of the extended all-carbon anthanthrone, compound 7.

I would also like to do a small parenthesis on my master's work on phenylacetylene macrocycles that also deserves to be included this thesis. Between 2013 and 2015, I synthesized three phenylacetylene macrocycles shown in Figure 6.6. The initial goal was to synthesize graphdiyne nanoribbons using an alkyne-rich phenyl and polymerize it through Glaser-Hay homocoupling. Unfortunately, we were never successful in the design and synthesis of a monomer that would produce a soluble polymer. Instead, we designed alkyne-rich macrocycles to explore new connections and various types of "yne" materials with this type of macromolecule. Mesh **1** and **2** were synthesized in 15 and 9 steps, respectively.<sup>165</sup> This work provided examples of the conjugation disruption caused by the *meta* substitution at the phenyl apexes. From the precursors of the meshes, tetrayne (Figure 6.6 right) was synthesized.<sup>166</sup> It was the first example for a macrocycle containing an alkyne, a diyne and a tetrayne. Despite its originally anticipated bent structure as drawn in the figure, X-ray crystallography confirmed that this compound is not strained and is, in fact, very stable.



Figure 6.6. Phenylacetylene macrocycles synthesized during my Master's degree.

For six months in 2016, I was a visiting student in Timothy M. Swager's group at the Massachusetts Institute of Technology (MIT) to develop an oxygen sensor. This work is out of the scope of this thesis but still deserves to be briefly outlined. The goal was to develop a sensor to detect air ingress in a package for the food packaging industry. I worked with two postdoctoral associates: Bora Yoon and Rong Zhu. Together, we were successful with a three-component system: iron complex, carbon nanotubes, and poly-4-vinylpyridine (Figure 6.7).<sup>167,168</sup> The first component responsible for the detection of oxygen is Fe(II), that is oxidized to Fe(III). The complex used here is  $Fe(MeCN)_6 \cdot 2BF_4$ , synthesized easily from cheap iron metal in acetonitrile. The second component are carbon nanotubes, inducing a difference in the device conductivity. The third constituent, poly-4-vinylpyridine, has two roles: disperse carbon nanotubes and act as a ligand for the iron complex. The sensor uses Radio-Frequency Identification Tags (RFID) shown in Figure 6.7a which can be read by every smartphone. The chemiresistor consisting of a solution of the three-component system is drop-casted on the CARD (Chemically Actuated Resonant Device). Exposure to oxygen oxidizes the iron complex in close contact with the carbon nanotubes. Since carbon nanotubes are very sensitive to their environment, this change in the oxidation state of iron will p-dope the tubes, decreasing their resistivity. The signal intensity is proportional to the concentration of oxygen exposed to the tag, where it can be read by a smartphone. The system is also a dosimeter, which means that once Fe(II) is oxidized to Fe(III), there is no coming back. This feature is quite important for the food packaging industry, since food that is exposed to air is prompt to accelerate the growth of bacteria, which will among other things, breathe. Consequently, they will decrease the amount of oxygen and increase the carbon dioxide content of the package. Therefore, it is critical to detect the primary air ingress to adequately account for compromised packaging. This system was the first to detect oxygen where conductivity is the trigger to activate a response. Other systems are based on optical methods where luminescence or colorimetric-based indicators would require a trained operator to read a response.



Figure 6.7. a) Conversion of a commercially available NFC tag into a wireless sensor (*p*-CARD) via deposition of chemiresistive material ( $R_s$ ) at the indicated locations. The circuit diagram of *p*-CARD is shown. C, tuning capacitor; L, inductor (antenna); RIC, resistance of integrated circuit (IC);  $C_{IC}$ , capacitance of IC;  $R_s$ , chemiresistor. b) Poly(4-vinylpyridine) disperses single-walled carbon nanotubes and coordinates to Fe(II) ions. This hybrid system is a sensitive chemiresistor that displays irreversible (dosimetric) response to oxygen exposure to enable an O<sub>2</sub>-*p*-CARD.<sup>†††††</sup>

<sup>&</sup>lt;sup>†††††</sup> Figure adapted from: Zhu, R.; Desroches, M.; Yoon, B.; Swager, T. M. *ACS Sensors* **2017**, *2*, 1044–1050. Reprinted with permission from ACS.

As a final thought, future members of the Morin group can find comfort in this statement: anthanthrone has yet to reveal all its secrets and will continue to unfold different avenues of research. There is much to do in the field of vat dyes and polycyclic aromatic hydrocarbons as this thesis consists only of a very modest contribution. Their stability along with their low cost makes them a hot topic in the literature. This thesis has shown that anthanthrone is very versatile as it is also the case for other PAHs. Slight changes in their structures either in the core or their substituents have dramatic impact on the resulting properties. This behaviour is the fuel to pursue the study of structure-property relationship and will most certainly eventually lead to innovative technologies.

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