

**Synthesis and Properties of Electron-Deficient  
Polycyclic Aromatic Compounds**

**Chaolumen**

**2017**

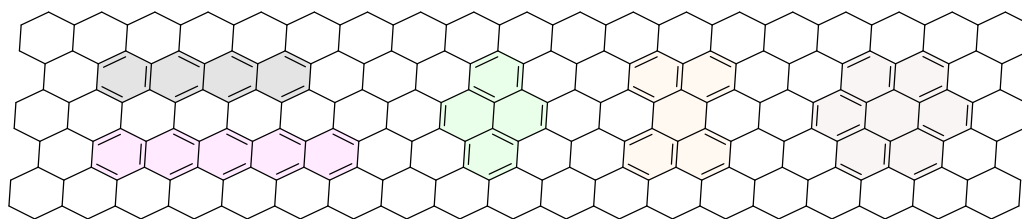
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# General Introduction

## Introduction

Polycyclic aromatic hydrocarbons (PAHs), the well-defined segments of graphene (Figure 1),<sup>1</sup> represent one of the most intensively investigated classes of carbon-rich compounds.<sup>2</sup> Their synthesis, characterization, and electronic properties have been widely studied for nearly one century.<sup>3</sup> At the turn of the 21st century, the research on PAHs gained new impetus with the prospect of its application in molecular electronics.<sup>4</sup> For example, by changing size or shape, and doping of heteroatoms, numerous number of two and three dimensionally  $\pi$ -extended PAHs and their heteroatom analogues (hetero-PAHs) have been synthesized and become attractive objects as NIR dyes,<sup>5</sup> two-photon absorbers,<sup>6</sup> stable  $\pi$ -aromatic cations,<sup>7</sup> and high-spin organic molecules.<sup>8</sup>



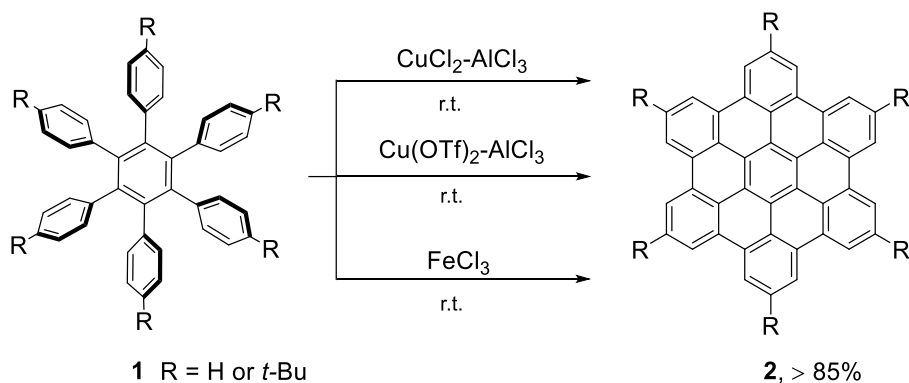
**Figure 1.** Graphene and its representative segments such as tetracene, pentacene, pyrene, perylene, and coronene.

As to the synthetic approaches for PAHs and hetero-PAHs, diverse methods have been developed such as cycloadditions of arynes and alkynes,<sup>9</sup> transition metal-catalyzed cross-coupling reactions,<sup>10</sup> and photo-induced cyclo-dehydrogenations.<sup>11</sup> In addition, the Scholl-type oxidative C-H coupling has been developed over two decades, as one of the most powerful methods to access PAHs and their derivatives.<sup>12</sup> The Scholl reaction is typically based on intramolecular oxidative dehydrogenation of rationally designed oligophenylene precursors.<sup>13</sup>

## The Scholl Reaction

Since the pioneering work by Scholl<sup>14</sup> and Clar,<sup>15</sup> the Scholl reaction had been further developed throughout the 20th century.<sup>12</sup> Particularly, Müllen and co-workers achieved highly efficient synthesis of hexa-*peri*-hexabenzocoronene **2** through the Scholl reaction of

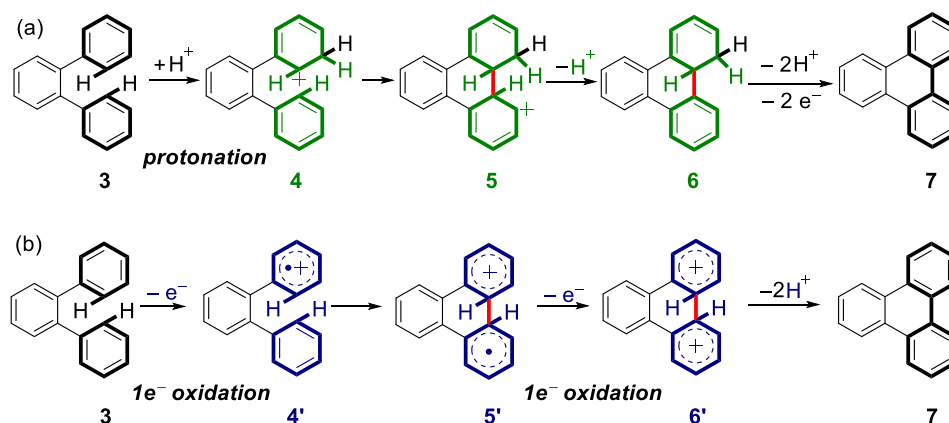
hexaarylbenzene **1** using  $\text{CuCl}_2\text{-AlCl}_3$ ,  $\text{Cu}(\text{OTf})_2\text{-AlCl}_3$ , or  $\text{FeCl}_3$  over 85% yield under the mild reaction conditions (Scheme 1).<sup>16</sup>



**Scheme 1.** Synthesis of hexa-*peri*-hexabenzocoronene **2**

This significant progress of the Scholl reaction has allowed the efficient synthesis of numerous PAHs with large and complex conjugated systems.<sup>17</sup> Among reported examples, a large PAH molecule consisting of up to 222 carbons was reported as the largest example of PAHs to date.<sup>17b</sup> However, many researchers noticed that the factors controlling this reaction are still under discussion.<sup>18</sup>

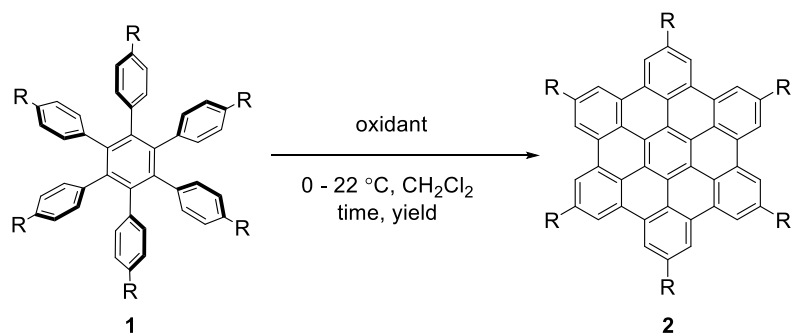
The Scholl reaction has been considered to proceed *via* either arenium ion or radical cation pathway. The arenium ion pathway was initially proposed by Baddeley<sup>19</sup> and his hypothesis was further supported by Nenitzescu and Balaban.<sup>20</sup> In the case of cyclization of terphenyl derivative **3**, the arenium ion pathway (Scheme 2a) is explained by following steps: protonation of **3** to generate arenium ion **4**, C-C bond formation to give **5**, and subsequent deprotonation, followed by rearomatization of **6** to afford **7**. The radical cation pathway (Scheme 2b) was advocated by Kenner,<sup>21</sup> Rooney,<sup>22</sup> and Clover.<sup>23</sup> The first step is generation of the radical cation **4'** from **3** by one electron transfer, and then the C-C bond is newly formed to give **5'**, followed by one electron oxidation and deprotonation to form **7**.



**Scheme 2.** (a) Arenium ion pathway, and (b) radical cation pathway proposed for the Scholl reaction

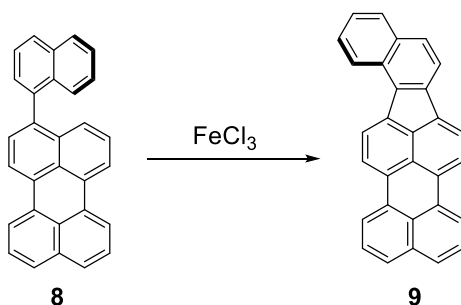
In recent years, intense discussion has been evolved by research groups of the King and Rathore, independently. King and co-workers published a series of reports, which support the arenium ion pathway by theoretical calculations.<sup>24</sup>

Rathore and co-workers studied the oxidative cyclization of aromatic compounds such as hexaarylbenzenes **1** (Table 1) and presented some important evidences for radical cation pathway.<sup>25</sup> Compound **1** ( $R = t\text{-Bu}$ ) with  $E_{\text{ox}} < 1.7$  V (vs SCE) readily underwent oxidative C-C bond formation by DDQ/MeSO<sub>3</sub>H as an oxidant (Scheme 3, entry 1), whereas no reaction of those with  $E_{\text{ox}} > 1.7$  V occurred (entries 2 and 3). In contrast, **1** ( $R = \text{H}$ ) with  $E_{\text{ox}} > 1.8$  V underwent oxidative cyclo-dehydrogenation in the presence of FeCl<sub>3</sub> (entry 4). However, noteworthy that electron-deficient **1** ( $R = \text{Br}$ ) ( $E_{\text{ox}} > 2.1$  V) failed to undergo oxidative cyclo-dehydrogenation even upon prolonged exposure to a large excess amount of FeCl<sub>3</sub> for a week (entry 5). They also emphasized that the strong oxidants were required for the success of this reaction. This result is inconsistent with the arenium ion pathway, since oxidation of intermediates such as **6** (Scheme 2a) can be easily accomplished even with molecular oxygen.

**Table 1 Effects of redox potentials on the oxidative C-H coupling of hexaarylbenzenes 1**

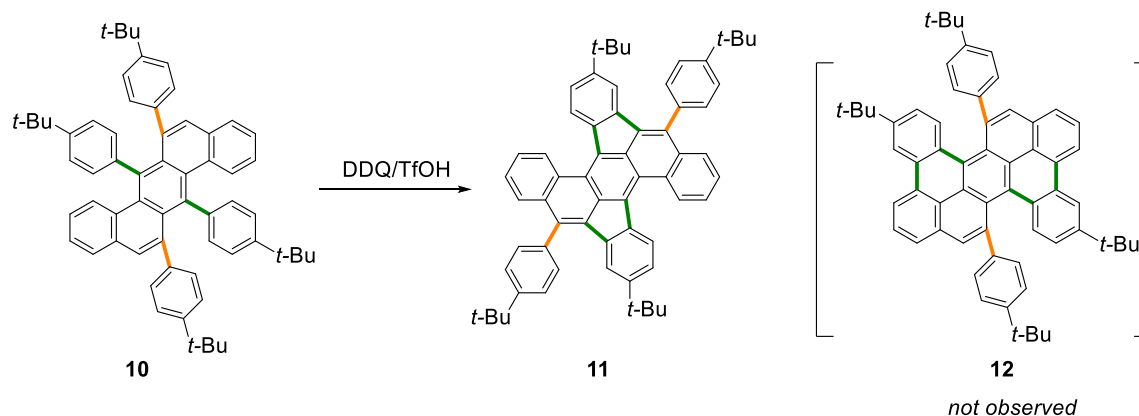
| entry | R            | $E_{\text{ox}}$ (vs SCE) | oxidant                 | time   | yield (%) |
|-------|--------------|--------------------------|-------------------------|--------|-----------|
| 1     | <i>t</i> -Bu | 1.6 V                    | DDQ/MeSO <sub>3</sub> H | 2 h    | 99        |
| 2     | H            | 1.8 V                    | DDQ/MeSO <sub>3</sub> H | 72 h   | 0         |
| 3     | Br           | 2.1 V                    | DDQ/MeSO <sub>3</sub> H | 72 h   | 0         |
| 4     | H            | 1.8 V                    | FeCl <sub>3</sub>       | ----   | 95        |
| 5     | Br           | 2.1 V                    | FeCl <sub>3</sub>       | 1 week | 0         |

Based on these results, the radical cation pathway is experimentally more supported than arenium ion pathway. However, in a few cases,<sup>26</sup> the radical cation pathway still cannot explain the regioselectivity of the Scholl cyclization. Müllen and co-workers reported that the cyclization of a naphthylperylene derivative **8** by FeCl<sub>3</sub> selectively gave **9** with a pentagonal ring (Scheme 3), while the Scholl reaction involves hexagonal ring formation in most cases. The pentagonal ring formation of **9** cannot be explained by radical cation and arenium ion pathways of the Scholl reaction.<sup>27</sup>

**Scheme 3.** Oxidative cyclization of a naphthylperylene derivative **8**

Quite recently, Müllen and co-workers reported an oxidative dehydrogenation of tetraarylbenzotetraphene **10**. The reaction proceeds *via* a twofold cyclization accompanied by aryl migrations to furnish product **11** with two pentagonal rings, instead of **12** with two

hexagonal rings (Scheme 4). The pathways based on both radical cations and arenium ions were proposed for this unique cyclization, supported by density functional theory (DFT) calculations.<sup>28</sup>

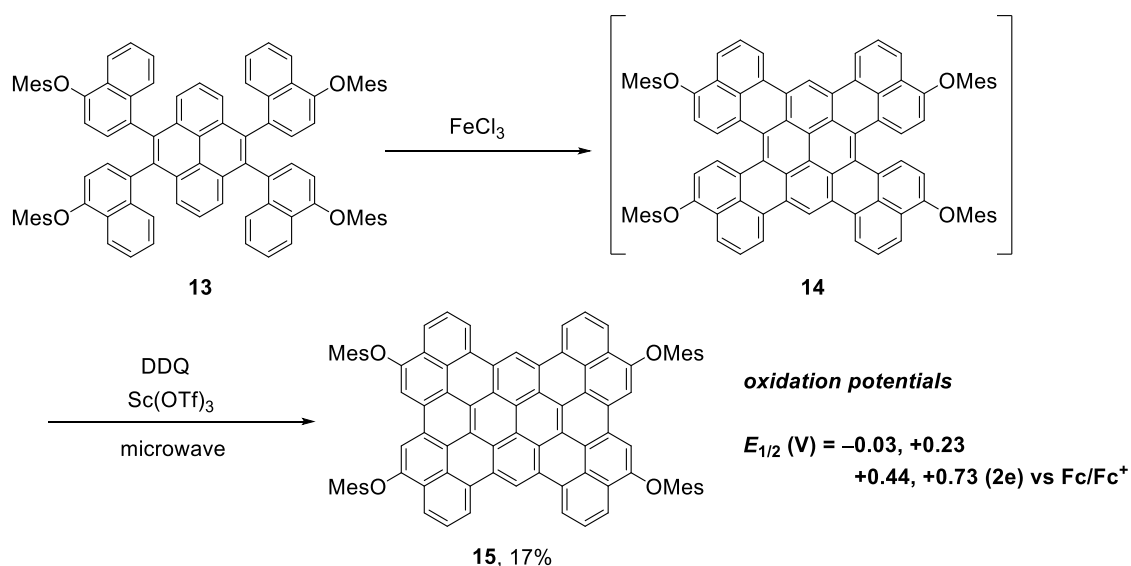


**Scheme 4.** Oxidative cyclization of tetraarylbenzotetraphene **10**

According to these reported examples, the mechanism of the Scholl reaction is still under discussion and the resulting products of the Scholl cyclization cannot be completely predicted.

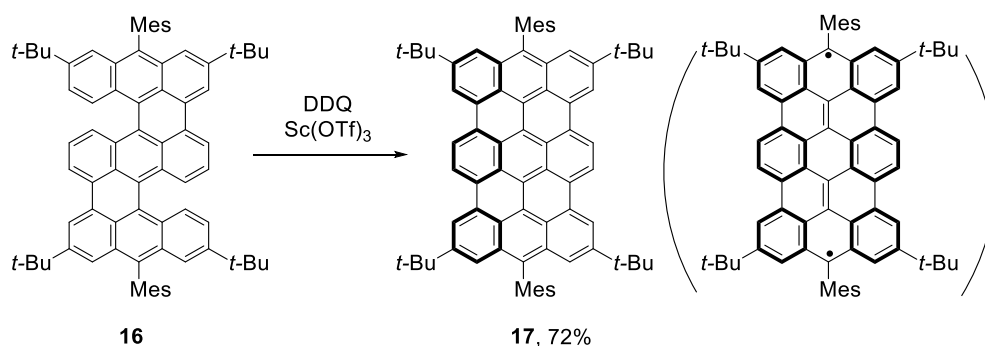
### Synthesis of PAHs with Novel Structures and Properties.

Although the mechanism is under discussion, the Scholl reaction is one of the most powerful method to synthesize various PAHs. As recent representative examples, in 2015, Yamada and co-workers reported an oxidative dehydrogenation of tetranaphthylpyrene **13** (Scheme 5). The Scholl cyclizations with  $\text{FeCl}_3$  only gave partially cyclized product **14**. This compound was subjected to DDQ/ $\text{Sc}(\text{OTf})_3$  system to afforded fully cyclized tetrabenzo-*peri*-pentacene **15**. Interestingly, **15** possesses strong electron-donating ability and cyclic voltammograms exhibit reversible five-electron oxidation waves.<sup>29</sup>



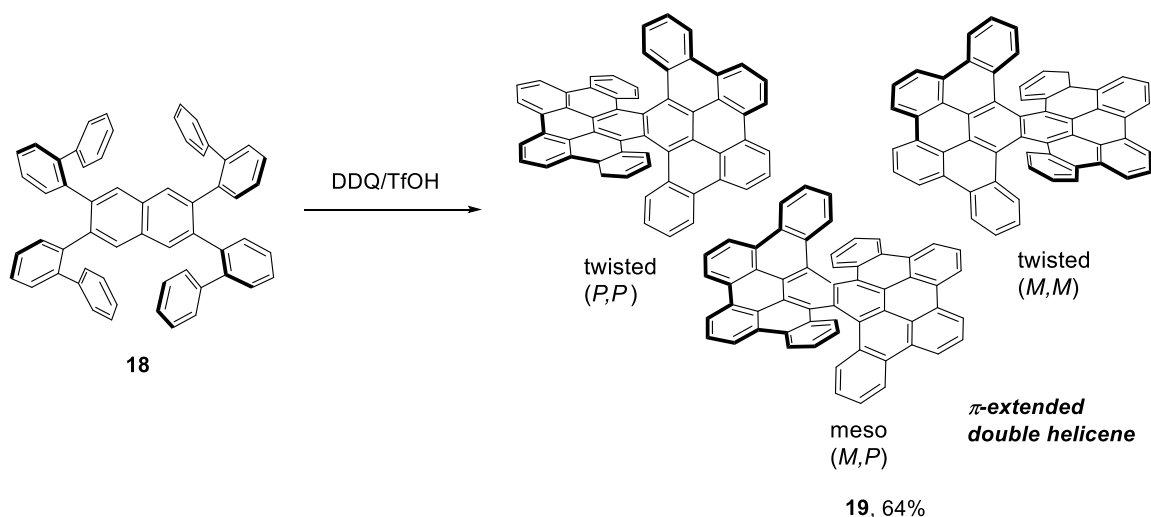
**Scheme 5.** Synthesis of tetrabenzoperi-pentacene derivative **15**

In 2010, Kubo and co-workers reported the synthesis of teranthene **17** from partially cyclized precursor **16** using DDQ/Sc(OTf)<sub>3</sub> system as an oxidant (Scheme 6). Both experimental and theoretical studies clearly showed the contribution of resonance structure with two unpaired electrons localized at the zigzag edges, significantly. Consequently, **17** exhibits singlet biradical character at the ground state.<sup>30</sup>



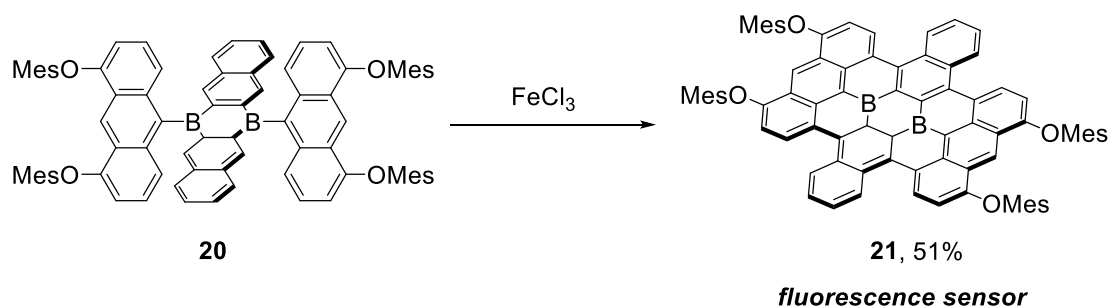
**Scheme 6.** Synthesis of teranthene derivative **17**

In 2015, Itami and co-workers synthesized  $\pi$ -extended double helicene **19** (Scheme 7) from **18** using DDQ/TfOH system as an oxidant (Scheme 7). Due to the two helical substructures, **19** was obtained as three conformational mixtures including enantiomers in a twisted form [(*P,P*) and (*M,M*)] and one diastereoisomer (*M, P*) in a meso form.<sup>31</sup> After successfully separated by chiral HPLC, the enantiomers were characterized by circular dichroism spectroscopy.



**Scheme 7.** Synthesis of  $\pi$ -extended double helicene **19**

In 2012, Yamaguchi and co-workers synthesized stable boron-containing PAH **21** from precursor **20** using  $\text{FeCl}_3$  as an oxidant (Scheme 8).<sup>32</sup> In **21**, two boron atoms were embedded in a planarized framework.<sup>33</sup> Interestingly, the boron atoms in **21** still maintain Lewis acidity and this compound can be used as a fluorescence sensor for  $\text{NH}_3$  gas.<sup>34</sup>



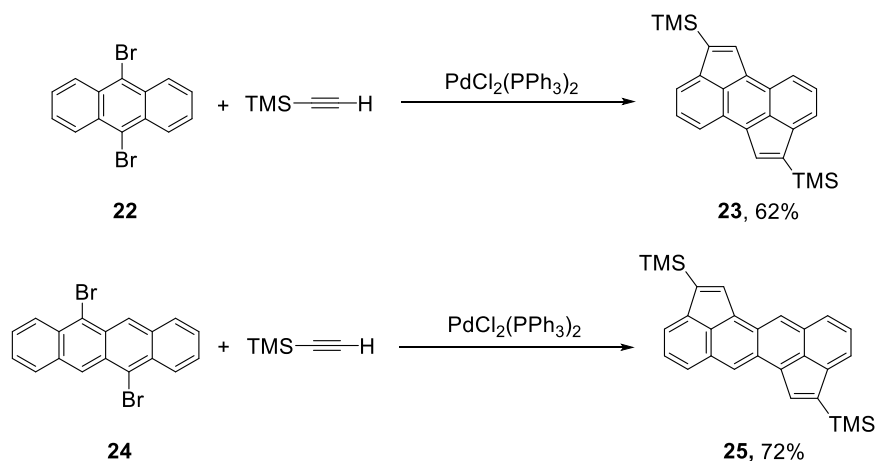
**Scheme 8.** Synthesis of boron-containing PAH **21**

In these recent reports, the Scholl reaction is effective to create various PAHs, which fully consist of hexagonal rings.

## Synthesis of PAHs with Pentagonal Rings.

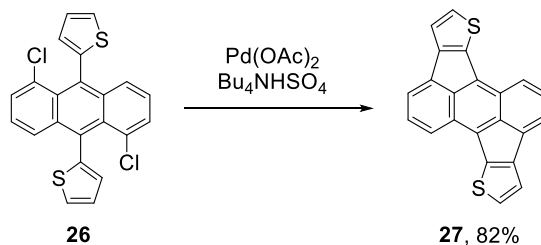
PAHs containing non-hexagonal rings such as pentagonal rings have been known to show unique properties. These class of compounds, the so-called cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs), have been received considerable attention due to their high electron affinities, which resulted in their potential applications including various electronic devices such as organic photovoltaic devices (OPVs) and organic field-effect transistors (OFETs).<sup>35</sup> although synthesis of CP-PAHs has been extensively studied in many years,<sup>36</sup> very few CP-PAHs have been utilized as active components in electronic devices.<sup>37</sup> One reason for this lack of development can be attributed to the limitations toward efficient methods for the pentagonal ring formations in sufficient quantities. The traditional synthetic route is too laborious or too harsh (e.g., flash vacuum pyrolysis<sup>38</sup>). Nowadays, although new synthetic procedures have been developed for certain CP-PAHs such as corannulene<sup>39</sup> in large quantities, concise and efficient strategies to synthesize diverse CP-PAHs are still extremely limited.

In 2013, Plunkett and co-workers reported palladium-catalyzed cross-coupling reaction to synthesize CP-PAHs **23** and **25** (Scheme 9). In addition, these new CP-PAHs contain TMS groups that would allow further chemical functionalization.<sup>40</sup>



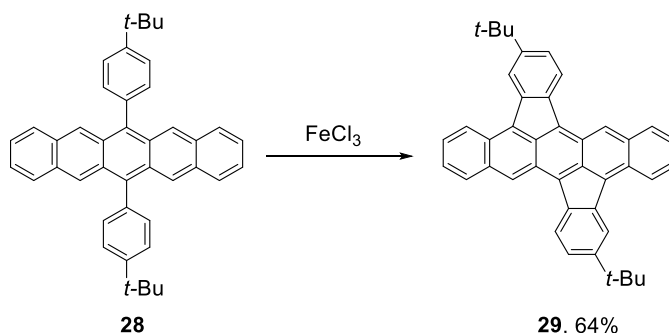
**Scheme 9.** Synthesis of CP-PAHs **23** and **25**

In 2011, Wudl and co-workers reported an efficient method of palladium-catalyzed C-H arylation) for synthesis of dithiarubicene **27** (Scheme 10), which is also expected further functionalization due to the reactive position of fused thiophene.<sup>41</sup>



**Scheme 10.** Synthesis of dithiarubicene **27**

In contrast to PAHs with only hexagonal rings, which can be effectively synthesized from their well-designed precursors by the Scholl reaction, the synthesis of CP-PAHs with electron-deficient properties are quite limited and currently depends on palladium-catalyzed reactions. In order to overcome this problem, the author focused his attention on the synthesis of CP-PAHs by the Scholl reaction and investigated their properties. It should be noted that, in 2015, Chi group reported a twofold Scholl cyclization of diphenylpentacene to give bisindeno-annulated pentacene **29** using  $\text{FeCl}_3$ -mediated Scholl reaction (Scheme 11).<sup>42</sup>

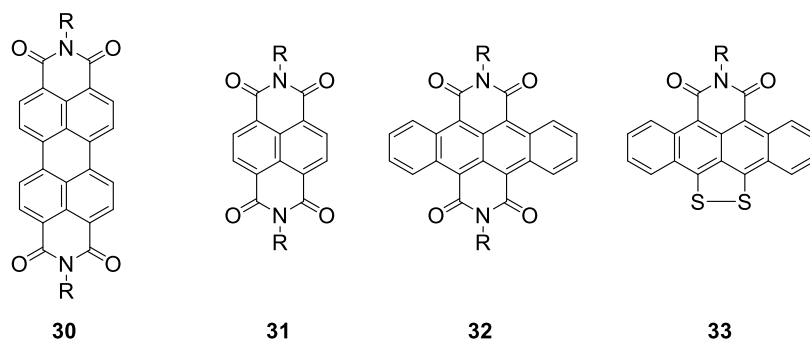


**Scheme 11.** Synthesis of bisindeno-annulated pentacene **29**

## Electron-Deficient Polycyclic Aromatic Compounds Based on Perylene Bisimides

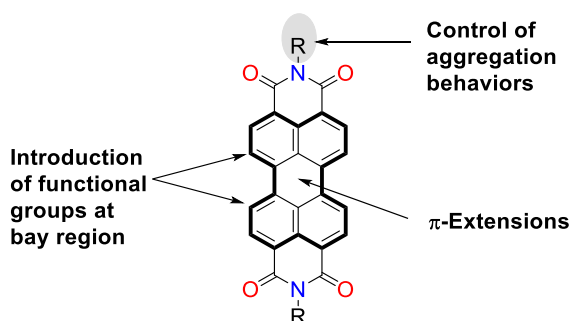
Besides CP-PAHs, introduction of strong electron-withdrawing subunits such as tetracarboxylic bisimides into PAHs is effective way to obtain electron-deficient compounds.<sup>4a</sup> For example, perylene tetracarboxylic bisimides (PBIs) **30**,<sup>4a</sup> naphthalene tetracarboxylic bisimides (NBIs) **31**,<sup>43</sup> tetracene tetracarboxylic bisimides (TBIs) **32**,<sup>44</sup> and tetracene

dicarboxylic imide disulfide (TIDS) **33**<sup>45</sup> have been reported as electron-deficient materials (Figure 2). Among them, due to the photo- and electrochemical stability, PBIs **30** have been extensively studied as promising building blocks for electron-deficient materials with NIR absorption.<sup>4a</sup>



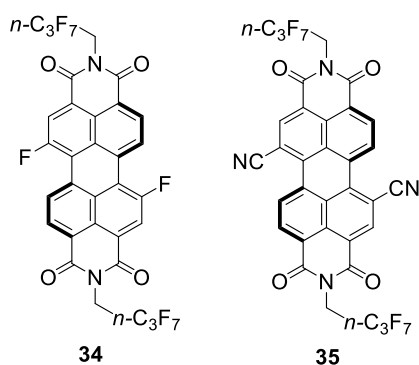
**Figure 2.** Representative examples of rylene derivatives as electron-deficient materials.

Several strategies have been developed to diversify PBI derivatives. Introduction of different N-substituents on **30** is effective to control their aggregation properties in solution and solid states. It was also reported that introducing electron-withdrawing groups at the bay region or  $\pi$ -extension of perylene core has significant impacts on its electronic structures (Figure 3).<sup>4c</sup>



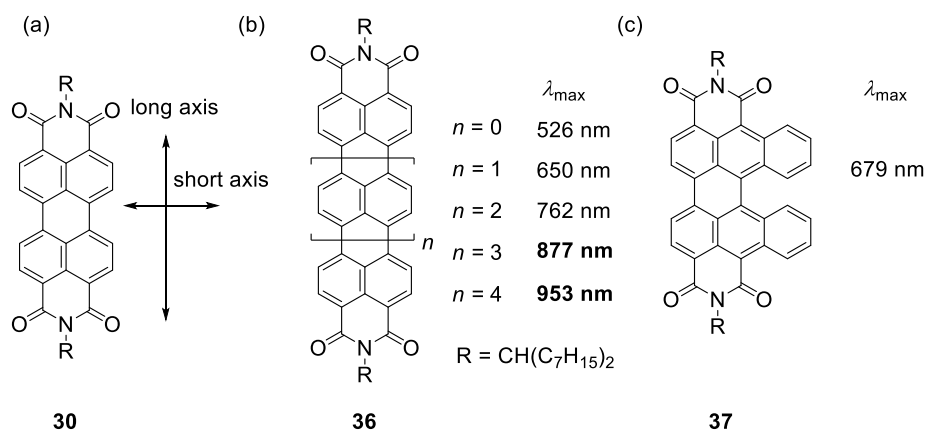
**Figure 3.** Strategies for structural modification for PBIs **30**.

Due to introduction of electron-withdrawing groups such as F and CN at the bay position (Figure 4), PBI derivatives **34** and **35** (Figure 4) exhibited excellent air-stability and solubility in organic solvents.<sup>45</sup> In addition, the twisted structures of  $\pi$ -framework can drastically affect their electron mobility.

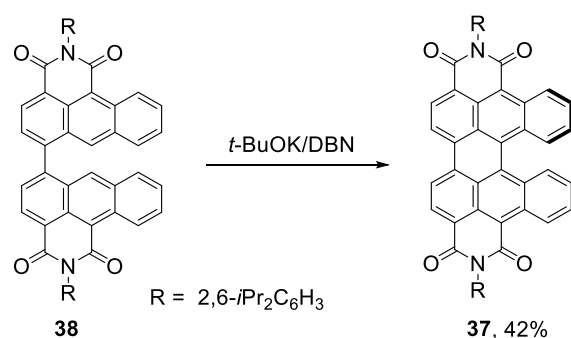


**Figure 4.** PBI derivatives with electron-withdrawing groups at the bay position.

The most drastic structural modification of PBI is  $\pi$ -extension of the perylene core, which enables PBI derivatives to be electron-accepting materials with NIR absorption.<sup>4a</sup> There are two different ways to extend the  $\pi$ -conjugation of PBIs:  $\pi$ -extension along the long axis or short axis (Figure 5a). In order to obtain NIR dyes, rylenees **36** ( $n > 2$ ) are NIR dyes (Figure 5b).<sup>46</sup> In contrast,  $\pi$ -extension along the short axis to construct oligoacene cores larger than a naphthalene core has high impacts on the electronic properties of PBIs.<sup>47</sup> For example, Wu and co-workers synthesized **37** by base-promoted cyclization of **38** (Scheme 12) and demonstrated that introduction of two benzene rings at each side of both naphthalene moieties in PBIs can cause the effective bathochromic shift of the absorption profile, probably due to the effective  $\pi$ -conjugation of two anthracene moieties (Figure 5c).<sup>47c</sup> However, examples of  $\pi$ -extension along the short axis of PBI **30** are still limited to only a few examples.<sup>47</sup>



**Figure 5.** Representative examples of PBI derivatives  $\pi$ -extended along long and short axes.

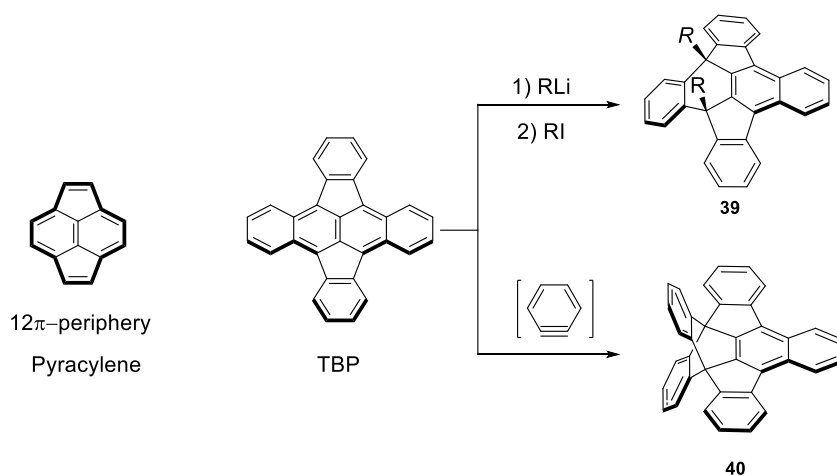


**Scheme 12.** Base-promoted cyclization to **37**

## Survey of This Thesis

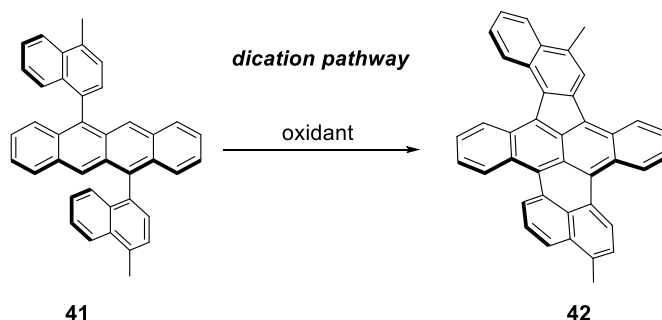
As described above, concise and effective synthesis of CP-PAHs and  $\pi$ -extended PBIs derivatives have a significant impact to their applications as electron-deficient materials. In this thesis, the author developed a series of electron-deficient  $\pi$ -systems using the Scholl reaction and base-promoted cyclization.

In this thesis, Chapter 1 describes efficient synthesis, structure and properties of tetrabenzofused pyracylene, TBP. It is known that pyracylene exhibits a considerable antiaromatic contribution to its electronic structure, as well as a high electron affinity based on its  $12\pi$ -electron framework.<sup>48</sup> TBP was shown to possess high electron affinity and found to undergo unprecedented addition reactions of *n*-butyl lithium or benzyne (Scheme 13). These unique reactions allowed to create 1,4-addition and triptycene-type compounds (**39** and **40**) with a distinct emission behavior in solid state.



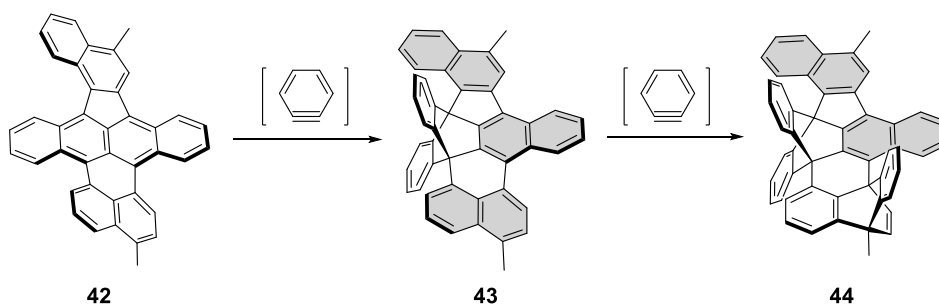
**Scheme 13.** Efficient synthesis and unique reactivity of tetrabenzofused pyracylene (TBP)

Chapter 2 describes the intramolecular Scholl cyclization of 5,11-dinaphthyltetracene derivative **41**. A twofold Scholl cyclization proceeded effectively to give naphthalene-fused tetracene **42** with one unsaturated pentagonal ring and one hexagonal ring (Scheme 14). A combination of experimental and theoretical studies showed that such unsymmetric Scholl cyclizations can be rationalized in terms of a mechanism that involves *dication* intermediates, which is totally different from previously reported pathways based on radical cations and arenium ions.



**Scheme 14.** Twofold Scholl cyclization of 5,11-dinaphthyltetracene **41** to **42** via *dication* pathway

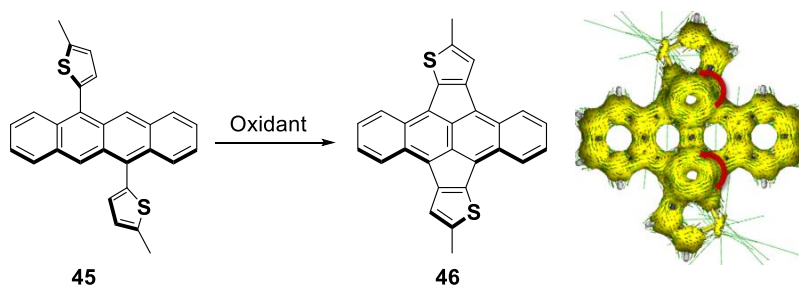
Chapter 3 describes cycloadditions of benzyne with the twisted  $\pi$ -surface of naphthalene-fused tetracene **42** synthesized in Chapter 2. The reaction kinetically furnished mono- and bis-adduct (**43** and **44**) via the concerted [4+2] cycloaddition (Scheme 15). The structural characterizations of the benzyne adducts and their photophysical properties, as well as theoretical studies on the selectivity of the cycloaddition to mono-adduct are discussed.



**Scheme 15.** Cycloadditions of benzyne with the naphthalene-fused tetracene **42** and subsequently with **43**

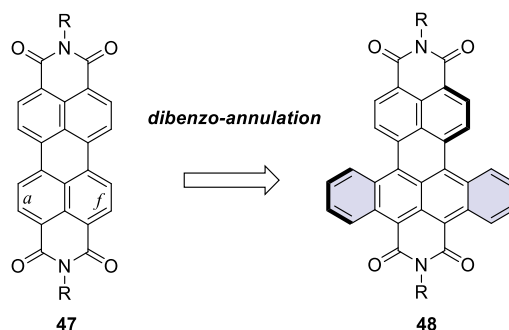
Chapter 4 describes synthesis and properties of dithieno-fused CP-PAHs with a pyracylene segment. A combination of experimental and theoretical studies revealed that two pentagonal rings have a strong contribution of antiaromatic character to the electronic structure

of dithieno-fused CP-PAH **46**. Anisotropy of current-induced density clearly indicates a strong paramagnetic ring current on the two pentagonal rings (Scheme 16). In addition, the enhanced electron affinity and a consequently decreased HOMO-LUMO gap were observed.



**Scheme 16.** Synthesis of dithieno-fused tetracene **46** from **45** with distinct antiaromatic character

Chapter 5 describes the effects of introducing dibenzo-fused structure in the perylene moiety of PBI (Figure 6). The benzo-fusion at both sides of a naphthalene core, which construct a tetracene core, effectively raise the HOMO level with reference to one ring fusion at each naphthalene core, which construct two anthracene cores (**37** in Figure 5). As a result, the dibenzo[*a,f*]-fused PBI derivative showed a red-shifted absorption band at 735 nm with a shoulder band tailing to 900 nm.



**Figure 6.** Synthesis of the dibenzo[*a,f*]-fused PBI derivative **48** with NIR absorption.

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# Electron-Deficient Tetrabenzo-Fused Pyracylene and Conversions into Curved and Planar $\pi$ -Systems with Distinct Emission Behaviors

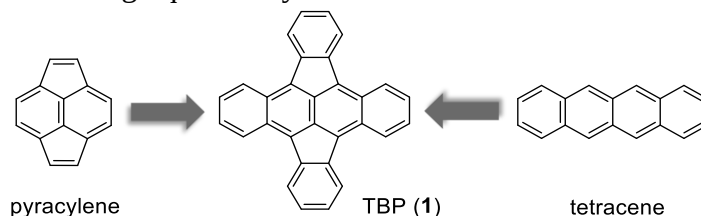
### Abstract

Polycyclic aromatic compounds containing fully unsaturated pentagonal ring(s) (CP-PAHs) have been intensively studied because of their unique properties such as high electron affinity and reactivity. The author demonstrated here an efficient route for the synthesis of tetrabenzo-fused pyracylene (TBP), which includes both pyracylene and tetracene moieties as key segments, using intramolecular oxidative C-H coupling. TBP was shown to possess high electron affinity and was found to undergo addition reactions of *n*-butyllithium or benzyne. These unique reactions allowed to create 1,4-addition compound or triptycene-type adduct with a curved or planar  $\pi$ -system, respectively. Although these compounds exhibited similar sky-blue emissions in a dilute solution, the emission band of the 1,4-addition compound was significantly red-shifted in crystals to exhibit intense yellow emission attributable to excimer, while the triptycene-type adduct retained intense blue color emission in crystals.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) containing fully unsaturated pentagonal rings, the so-called cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs), have received attention for their unusual properties such as high electron affinity<sup>1</sup> and chemical reactivity<sup>2</sup> as well as for their potential use in organic electronic devices.<sup>3</sup> CP-PAH molecules such as rubicenes,<sup>4</sup> dithiarubicene (so-called emeraldicenes),<sup>5</sup> and cyclopenta[*hi*]aceanthrylenes<sup>6</sup> have been reported as electron-accepting (n-type) and ambipolar materials for organic photovoltaics (OPVs) or organic field-effect transistors (OFETs).

Among CP-PAHs, pyracylene has been known to possess antiaromatic character and high electron affinity, thus resulting from the contribution of  $12\pi$ -electron periphery with a strongly localized interior double bond (1.35 Å).<sup>7</sup> In contrast, tetracene and its derivatives thereof have attracted particular interest as excellent charge transporting materials.<sup>8</sup> In this chapter, the author focused on tetrabenzo-fused pyracylene **1** (abbreviated as TBP), which includes both pyracylene and tetracene moieties, to elucidate the electronic properties and chemical reactivity (Scheme 1). Although the synthesis of TBP **1** was reported in 1956 by Theiling et al.,<sup>9</sup> this method was recently reported to be low yielding.<sup>10</sup> Here, we report an efficient route for the synthesis of TBPs by intramolecular oxidative C-H coupling and its unique reactivity, thus leading to the formation of intriguing  $\pi$ -systems with distinct emission properties in crystals with high quantum yields.



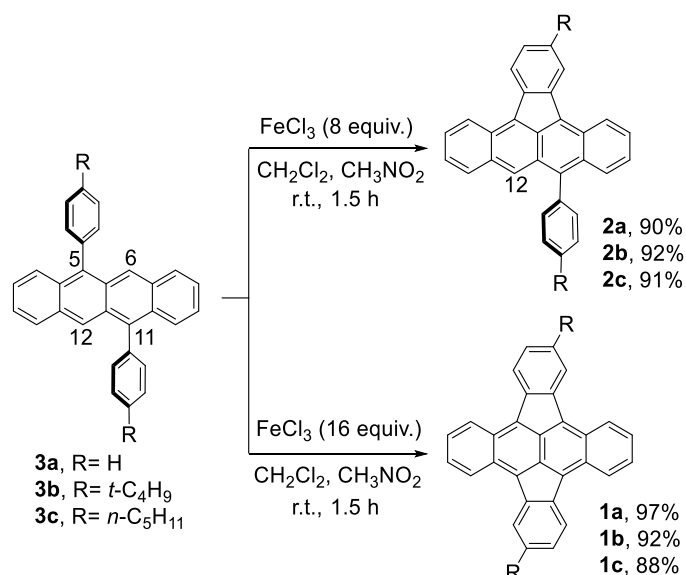
**Scheme 1.** Structures of TBP (**1**) and its key segments, pyracylene and tetracene

## Results and Discussion

### Synthesis

The synthesis of TBPs **1a-c** was conducted by the Scholl reaction of 5,11-diaryltetracene derivatives **3a-c** using  $\text{FeCl}_3$  as an oxidant (Scheme 2). Mono-cyclization and double-cyclization proceeded regioselectively at ambient conditions in a controlled manner depending on the amounts of  $\text{FeCl}_3$  to afford **2a-c** and **1a-c** as deep purple and deep blue solids, respectively. Whereas a similar reaction was recently reported for pentacene derivatives by Chi

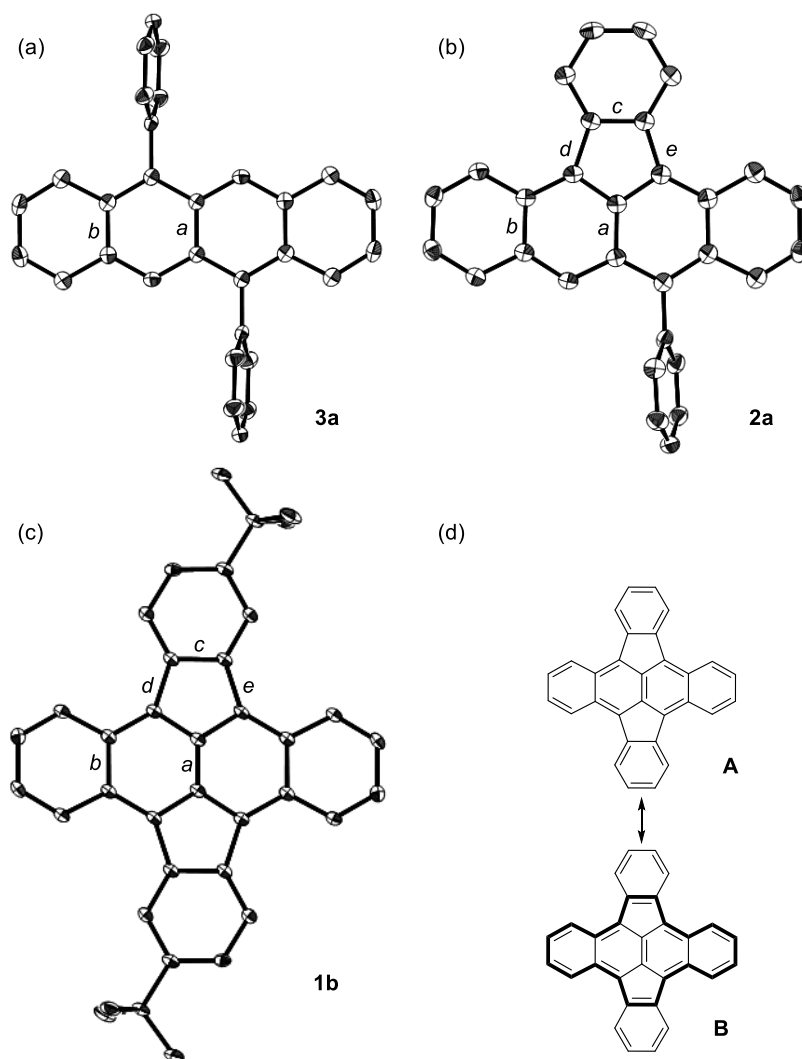
et al.,<sup>11</sup> the construction of a pyracylene moiety by a twofold Scholl cyclization is unprecedented. The Scholl reactions have been considered to proceed *via* radical cation or arenium ion intermediates,<sup>12</sup> and I will discuss a new pathway for the mechanism of the Scholl reaction in chapter 2.



**Scheme 2.** Intramolecular oxidative cyclizations of 5,11-diaryltetracene derivatives **3a-c**

### X-Ray Crystal Structures

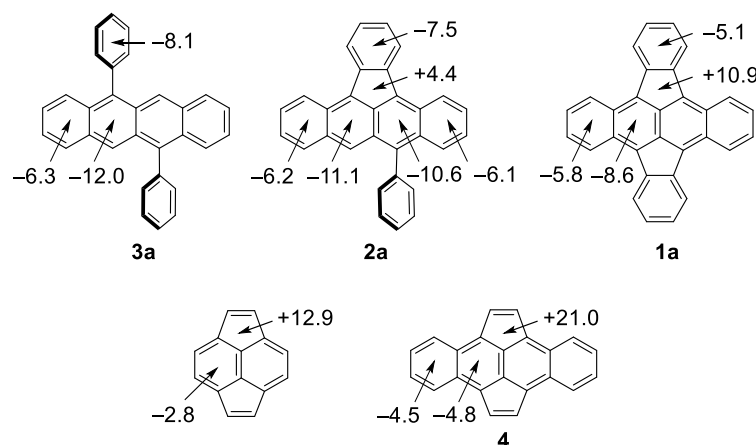
The X-ray diffraction analyses were performed for **3a**, **2a**, and **1b** (Figure 1a-c). The results demonstrated that the cyclizations of the two phenyl rings to form pentagonal rings cause significant changes in the bond lengths. In particular, the bonds denoted as *a* became shortened [1.451(3) Å for **3a**, 1.417(2) Å for **2a**, 1.381(3) Å for **1b**], while the bonds *b* became elongated [1.442(2) Å for **3a**, 1.450(2) Å for **2a**, 1.474(2) Å for **1b**]. The enhanced double bond character of bond *a* in **1b** appeared to be similar to the characteristics of pyracylene [the corresponding bond length is 1.35 Å].<sup>[13]</sup> On the other hand, when we compare the structures of indeno-moieties, bond *c* is elongated in **1b** [1.438(2) Å] after the second cyclization with reference to bond *c* in **2a** [1.421(2) Å]. In addition, the slight elongation of bonds *d* and *e* in **1b** [1.485(2) Å and 1.486(2) Å, respectively] was observed compared to those bond lengths in **2a** [1.474(2) Å and 1.478(2) Å, respectively]. It is notable that the bond *c* of **1b** is clearly longer than the corresponding bond in parent pyracylene [1.366 Å],<sup>13</sup> likely due to the effect to avoid contribution of antiaromatic character. These data indicate that the major contribution of resonance structure is form **A**, among the possible resonance structures including form **B**, in which 20π-antiaromatic periphery can be drawn as shown with a bold line in Figure 1d.



**Figure 1.** The ORTEP drawings (50 % probability for thermal ellipsoids) of (a) **3a**, (b) **2a**, (c) **1b**, and (d) selected resonance structures of **1a**. Selected bond lengths [Å] for **3a**: bond *a* 1.451(3); *b* 1.442(2). Selected bond lengths [Å] for **2a**: bond *a* 1.417(2); *b* 1.450(2); *c* 1.421(2); *d* 1.474(2); *e* 1.478(2). Selected bond lengths [Å] for **1b**: bond *a* 1.381(3); *b* 1.474(2); *c* 1.438(2); *d* 1.485(2); *e* 1.486(2).

## DFT Calculations

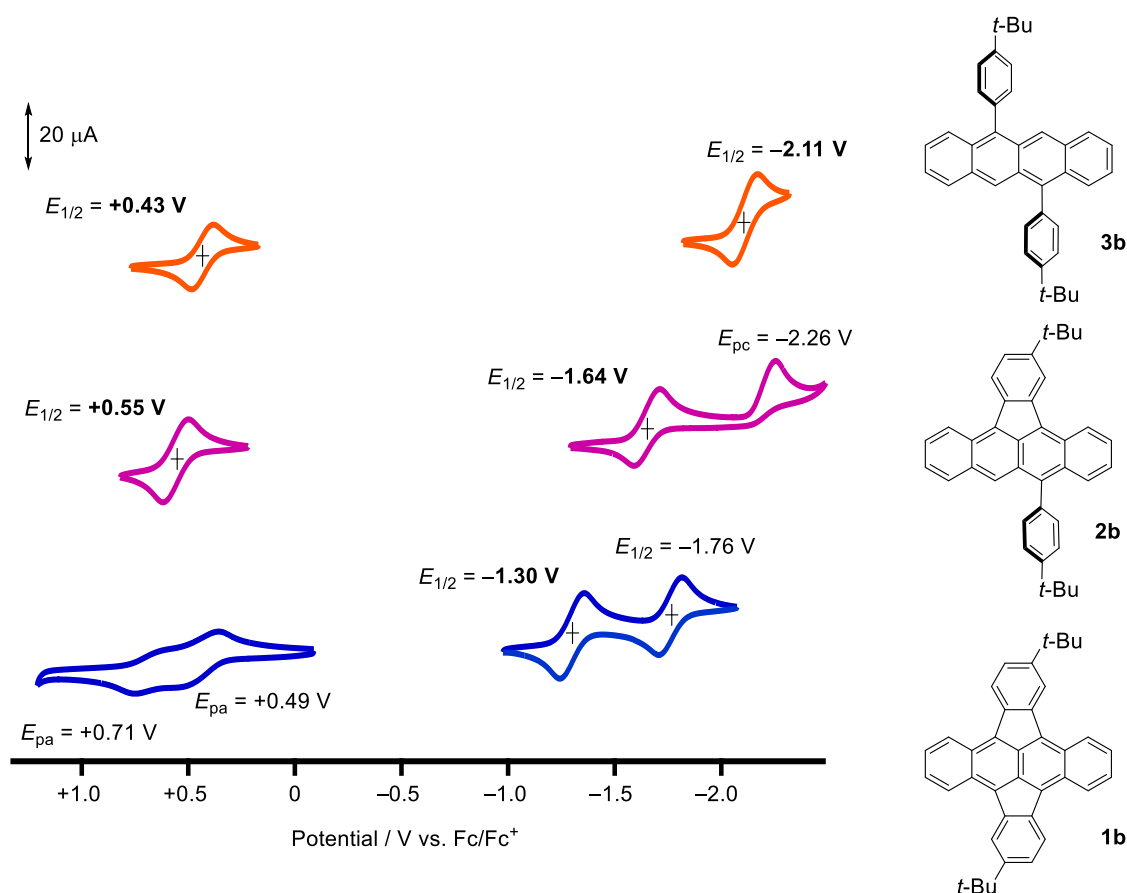
This consideration is supported by the results of DFT calculations.<sup>14</sup> The structural optimization for **1a-3a** calculated at the B3LYP/6-31G\* level of theory well reproduced the crystal structural analysis. The NICS(0) (nucleus independent chemical shifts)<sup>15</sup> values for the optimized structures are summarized in Figure 2. Although the changes in the NICS(0) values after mono-cyclization are small, both of the negative values for hexagonal rings and the positive value for the pentagonal rings become more positive in **1a** with reference to **2a** after the second cyclization. The NICS(0) calculations for model compound **4** indicated that introduction of two fused rings on the naphthalene moiety in pyracylene significantly increases the positive values for pentagonal rings compared to those for pyracylene (from +12.9 for pyracylene to +21.0 for **4**), indicating the contribution of 20 $\pi$ -antiaromatic periphery. The introduction of two fused rings on the two pentagonal rings of **4** has a strong impact to weaken the antiaromatic contribution, while it enhances the aromatic characters in the tetracene moiety. Therefore, we considered that TBP should possess the electronic properties analogous to both pyracylene and tetracene.



**Figure 2.** NICS(0) values for **1a-3a**, pyracylene, and dibenzo-fused pyracylene **4** calculated at the HF/6-311+G\*\*//B3LYP/6-31G\* level.

## Electrochemical Properties

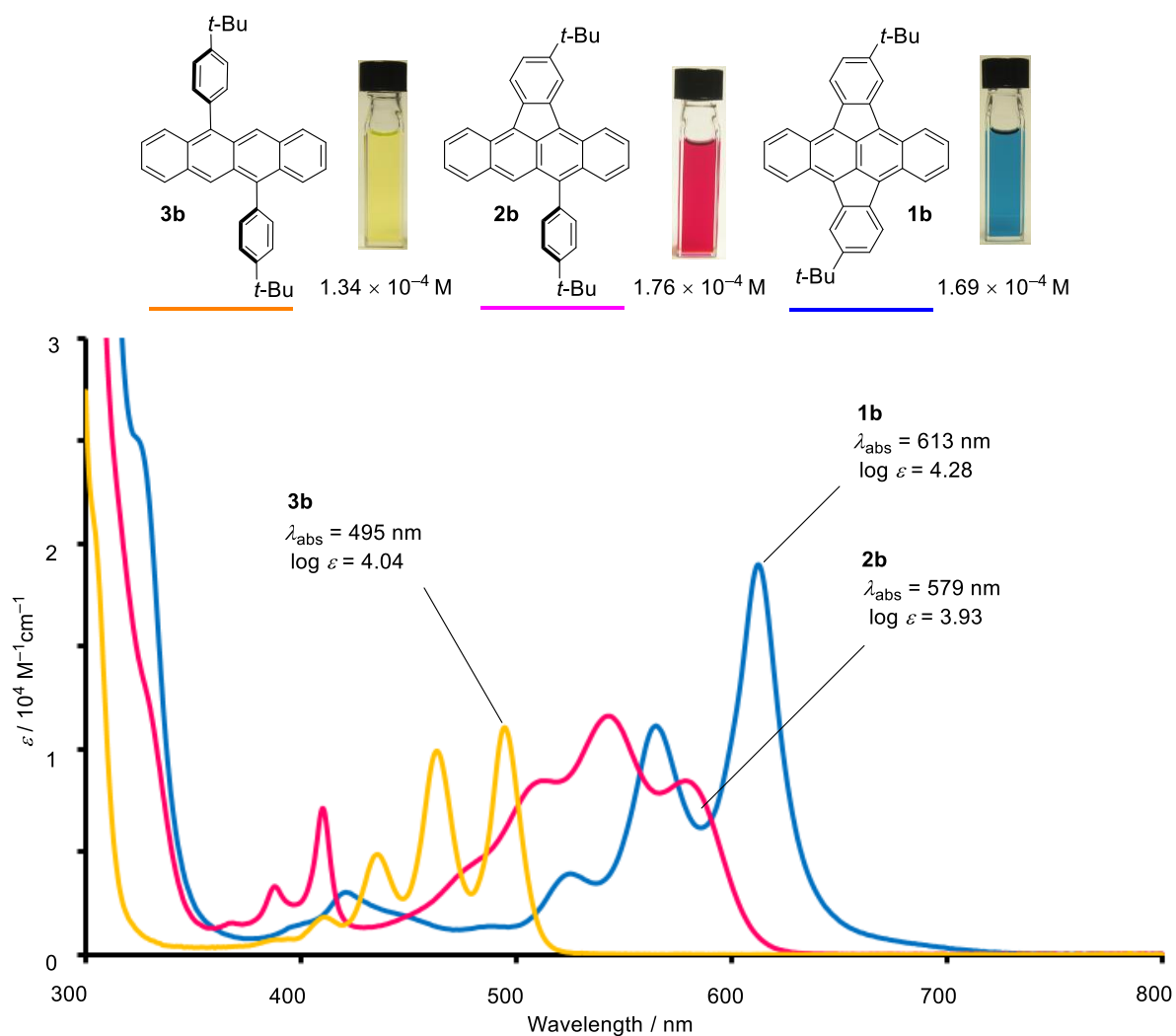
To clarify the electronic properties, we conducted cyclic voltammetry (CV) for **1b-3b** (Figure 3). In the reduction region, **3b** and **2b** exhibited one reversible reduction wave ( $E_{1/2} = -2.11$  V vs.  $\text{Fc}/\text{Fc}^+$  for **3b** and  $-1.64$  V for **2b**). The formation of one-indeno moiety causes a positive shift of the potential of **2b** with reference to **3b** by  $\Delta E_{1/2} = 0.47$  V. Compound **1b** exhibited two reversible waves ( $E_{1/2} = -1.30$  V and  $-1.76$  V) with the first reduction potential shifted to more positive by  $\Delta E_{1/2} = 0.34$  V than that of **2b**, indicative of high electron affinity of the TBP skeleton. In the oxidation region, **3b** and **2b** exhibited one reversible oxidation wave ( $E_{1/2} = +0.43$  V for **3b** and  $+0.55$  V for **2b**), but the difference ( $\Delta E_{1/2} = 0.12$  V) is apparently smaller than those observed in the reduction process. The shape of the oxidation wave of **1b** ( $E_{\text{pa}} = +0.49$  V) was broad but reproducible for several cycles in a range of  $+1.0$  to  $-2.0$  V, indicating the effect of aggregation.



**Figure 3.** Cyclic voltammograms of **1b-3b** in  $\text{CH}_2\text{Cl}_2$  (1 mM); supporting electrolyte: 0.1 M  $[(n\text{-Bu})_4\text{N}][\text{PF}_6]$ ; scan rate:  $100 \text{ mV s}^{-1}$ ; internal standard:  $\text{Fc}/\text{Fc}^+$ .

## Photophysical Properties

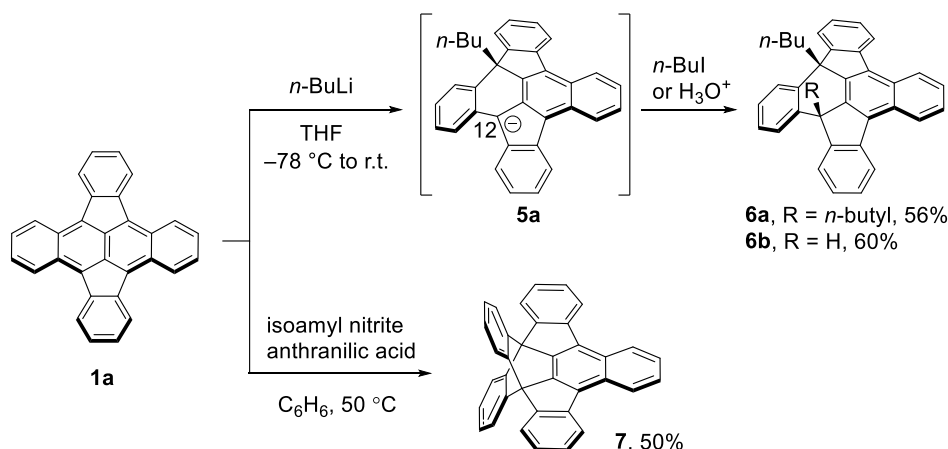
The absorption spectra were also measured in toluene (Figure 4). Reflecting the low-lying LUMO, **1b** showed an intense absorption band ( $\lambda_{\text{max}} = 613 \text{ nm}$ ,  $\log \varepsilon = 4.28$ ), which is notably red-shifted by 118 nm compared to that of **3b** ( $\lambda_{\text{max}} = 495 \text{ nm}$ ,  $\log \varepsilon = 4.04$ ) and by 34 nm compared to that of **2b** ( $\lambda_{\text{max}} = 579 \text{ nm}$ ,  $\log \varepsilon = 3.93$ ). Considering the electron affinity and the absorption profile, TBP can be used as a potential building block for n-type materials in OPVs.<sup>1c,4d</sup>



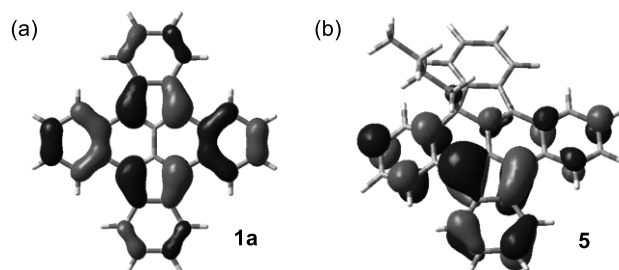
**Figure 4.** UV-vis absorption spectra of **1b-3b** in toluene.

## Reactivity

Unique addition reactions<sup>17</sup> or substitution reaction<sup>5a</sup> of CP-PAHs with alkyllithium reagents have been reported. The author then studied reactivity of TBP. When *n*-butyllithium was added to a suspension of **1a** in THF at  $-78\text{ }^{\circ}\text{C}$ , the dark blue powder of **1a** smoothly dissolved to afford a deep purple solution. Quenching this solution with *n*-butyl iodide or acidic water provided 1,4-addition products **6a** and **6b**, respectively (Scheme 3). Compounds **6a,b** have a curved  $\pi$ -surface as confirmed by the single crystal X-ray diffraction analyses (*vide infra*). The LUMO of **1a** delocalizes over the entire molecular surface except for the interior double bond (Figure 5a). The HOMO of anion **5a** is relatively localized on the pentagonal ring with the highest coefficient at C12 (Figure 5b). Thus, the quenching reactions selectively proceeded at C12 to give 1,4-addition products **6a** and **b** under the kinetic control. In addition, benzyne was found to undergo addition to **1a** to afford **7** with an intriguing triptycene type structure (Scheme 3), indicating that TBP retains the reactivity characteristics of tetracene.<sup>18</sup>



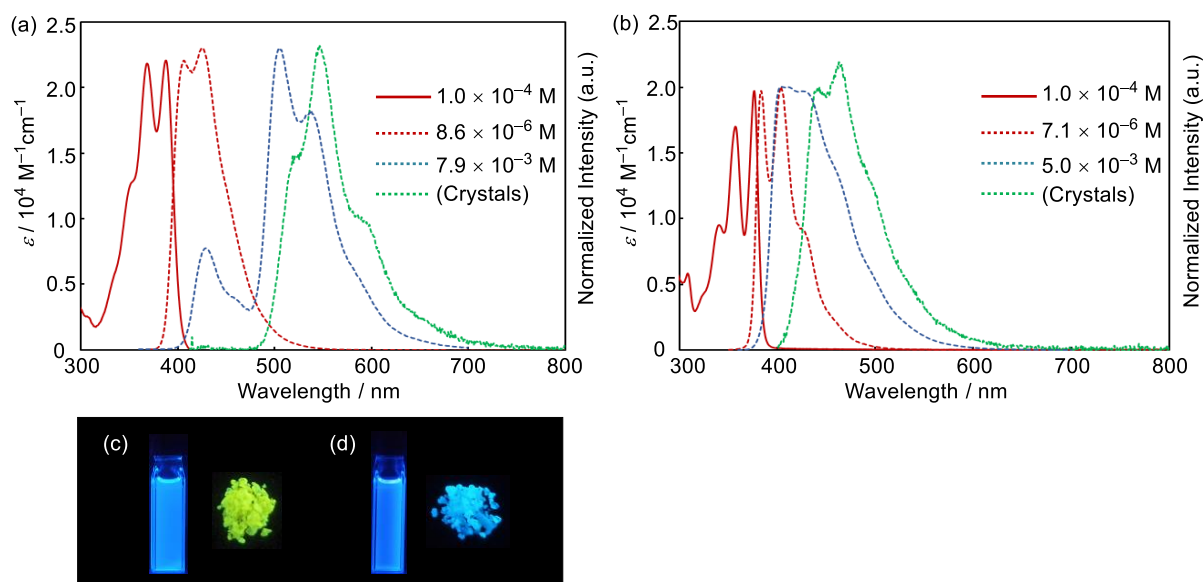
**Scheme 3.** Regioselective addition reactions of **1a**



**Figure 5.** Plot of (a) the LUMO of **1a** (B3LYP/6-31G\*) and (b) the HOMO of anion intermediate **5a** (B3LYP/6-31+G\*).

## Photophysical Properties

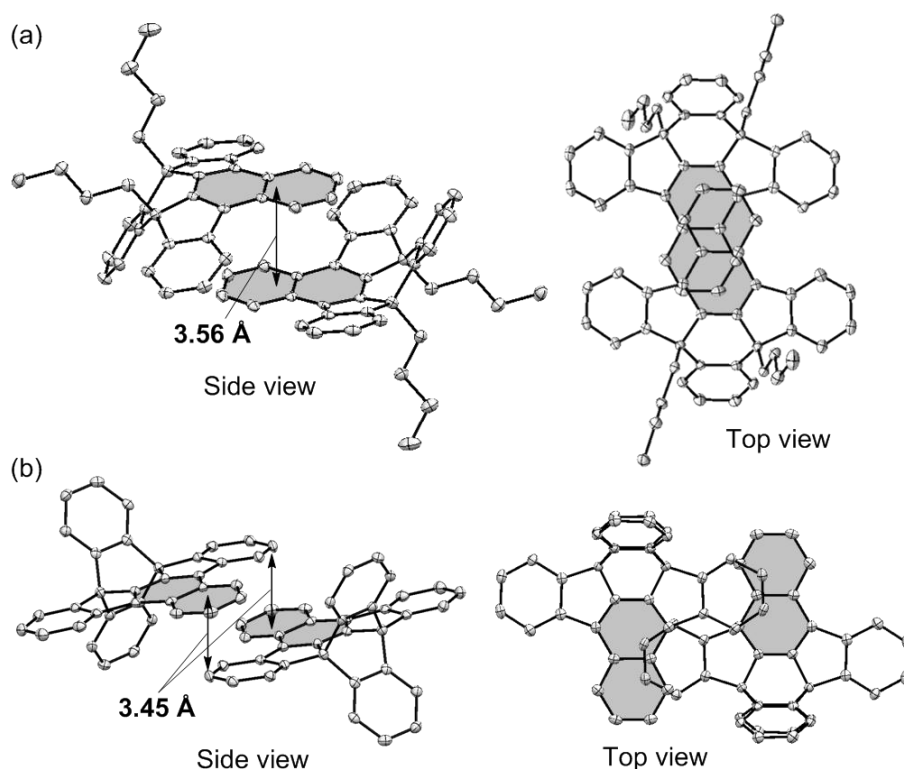
In a toluene solution, compounds **6a** and **7** showed an absorption band in a similar region with the maximum wavelengths ( $\lambda_{\text{abs}}$ ) at 388 and 376 nm, respectively, which were hypsochromically shifted with reference to that of **1a** ( $\lambda_{\text{abs}} = 611$  nm), reflecting the partial scission of the  $\pi$ -system of **1a** (Figure 6). Compounds **6a** and **7** ( $8.6 \times 10^{-6}$  and  $7.1 \times 10^{-6}$  M in toluene, respectively) exhibited intense sky-blue fluorescence with the maximum wavelengths ( $\lambda_{\text{em}}$ ) of 407 nm ( $\Phi_{\text{F}} = 0.99$ ,  $\tau = 3.2$  ns) and 388 nm ( $\Phi_{\text{F}} = 0.98$ ,  $\tau = 2.3$  ns), respectively. The rigidly fixed conformations of **6a** and **7** likely contribute to the small Stokes shifts (19 nm and 7 nm, respectively) as well as the high quantum yields. However, **6a** and **7** showed distinct emission behaviors in a concentrated solution and solid state, while the absorption profiles were almost unchanged. Compound **6a** exhibited a new red-shifted emission band ( $\lambda_{\text{em}} = 509$  nm,  $\Phi_{\text{F}} = 0.51$ ,  $\tau = 7.1$  ns) in a higher concentration ( $7.9 \times 10^{-3}$  M in toluene) (Figure 6a).<sup>[19]</sup> The longer fluorescence lifetime for **6a** in the high concentration indicates that the red-shifted emission is attributable to the excimer.<sup>[20]</sup> Interestingly, the crystals of **6a** showed intense yellow emission at  $\lambda_{\text{em}} = 547$  nm with keeping the high quantum yield ( $\Phi_{\text{F}} = 0.88$ ). In contrast, the red-shift of the emission band for compound **7** was not remarkable and showed intense sky-blue emission in the concentrated solution ( $\lambda_{\text{em}} = 404$  nm,  $\Phi_{\text{F}} = 0.50$ ,  $\tau = 2.8$  ns) as well as in crystals ( $\lambda_{\text{em}} = 441$  nm,  $\Phi_{\text{F}} = 0.73$ ) (Figure 6b).



**Figure 6.** UV-vis absorption spectra (solid line) and normalized fluorescence spectra (dashed line) of (a) **6a** and (b) **7** in toluene and crystals. The pictures of the toluene solution and crystals of (c) **6a** and (d) **7** with irradiation at 365 nm (the concentrations of the solutions:  $8.6 \times 10^{-6}$  M and  $7.1 \times 10^{-6}$  M for **6a** and **7**, respectively).

## Solid State Packing

The packing structures of **6a** and **7** in crystal gave a deeper understanding of the difference in the emission behaviors. Compound **6a** has the curved  $\pi$ -system and forms a dimeric structure in a face-to-face fashion between the concave surfaces (Figure 7a). The distance between the mean planes of the overlapping naphthalene moieties ( $3.56\text{ \AA}$ ) is within a range of typical  $\pi$ -stacked structure ( $3.4\text{--}3.7\text{ \AA}$ ). On the other hand, nearly-planar  $\pi$ -surface of compound **7** are arranged in a significantly slipped fashion. Although the  $\pi$ -stacked distance of **7** measured between the mean plane of the naphthalene moiety and the closest carbon atom in the benzene moiety ( $3.45\text{ \AA}$ ) is shorter than that of **6a**, contacts between the  $\pi$ -systems in the dimer of **7** is small due to the slipped-stacking arrangement (Figure 7b). From these data, the author considered that the curved  $\pi$ -skeleton of **6a** has an effect to restrict the geometry for the  $\pi$ - $\pi$  interactions in such a way that the central naphthalene moieties can overlap effectively. This effect leads to the stabilization of the excimer of **6a** to show markedly red-shifted emission in crystals as compared to those of **7**.



**Figure 7.** The face-to-face dimeric structures in crystal of (a) **6a** and (b) **7**.

## Conclusion

In summary, the author demonstrated an efficient route for the synthesis of electron-deficient tetrabenzofused pyracylene (TBP) and its derivatives by using intramolecular oxidative C-H coupling. The X-ray diffraction analysis showed that TBP possesses the structural feature similar to both tetracene and pyracylene. The author also disclosed that TBP undergoes unique addition reactions with *n*-butyllithium or benzyne to give the 1,4-addition product or the triptycene-type adduct with a curved or planar  $\pi$ -surface, respectively. These compounds showed distinct emission in the concentrated solution and in crystal with high quantum yields. X-ray diffraction analyses demonstrated that the 1,4-addition compound forms dimers with effective  $\pi$ -overlap, which can cause the significant red-shift in fluorescence by the stabilization of excimer.

## Experimental Section

### General

Melting points (mp) were measured on a Yanaco MP-S3 instrument. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were carried out with a Varian Mercury 300 instrument, a JEOL ECA 500 instrument, or a Bruker Avance III 600US instrument. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of  $\text{CDCl}_3$  ( $\delta$  7.26 ppm in  $^1\text{H}$  NMR,  $\delta$  77.0 ppm in  $^{13}\text{C}$  NMR) and  $\text{CD}_2\text{Cl}_2$  ( $\delta$  5.32 ppm in  $^1\text{H}$  NMR,  $\delta$  53.5 ppm in  $^{13}\text{C}$  NMR). UV-vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer. Fluorescence measurements were performed with a HORIBA FluoroMax 4P-NIR. Quantum yields were determined with a Hamamatsu Photonics Quantaaurus QY C11347 with calibrated integrating sphere system. Fluorescence lifetime measurements were performed using a Hamamatsu Photonics Quantaaurus-Tau C11367-02. APCI mass spectra were measured on a Bruker micrOTOF-Q II spectrometer. EI mass spectra were measured on a JEOL MStation JMS-MS 700V. Cyclic voltammetry (CV) was performed on a BAS ALS620A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an  $\text{Ag}/\text{AgNO}_3$  reference electrode. The measurements were carried out under an argon atmosphere using a  $\text{CH}_2\text{Cl}_2$  or THF solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{N}^+\text{PF}_6^-$ ) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Preparative GPC was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H columns.

## Synthesis

### 5,11-dibromotetracene

5,11-Dibromotetracene was prepared according to the literature.<sup>21</sup>

### 5,11-Diphenyltetracene Derivatives (3a-c)

**General procedure for preparation of 3a-c:** To a mixture of 5,11-dibromotetracene (386 mg, 1.00 mmol), phenylboronic acid derivative (3.00 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (31 mg, 30 μmol), Sphos (49 mg, 0.12 mmol) and K<sub>2</sub>CO<sub>3</sub> (415 mg, 3.00 mmol) were added toluene (50 mL) and distilled water (5 mL) in a 200 mL two-necked flask and the solution was stirred at 95 °C for 7 h. After cooling to room temperature, to the resulting mixture was added distilled water (25 mL). The aqueous layer was extracted with toluene (40 mL) and the combined organic layer was washed with brine (40 mL). After drying with MgSO<sub>4</sub>, the solvent was evaporated. Then, the crude product was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as an eluent. The solvent was evaporated and the product was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/methanol to give **3** as a yellow solid.

**3a:** Yield: 296 mg (78%); mp 211–212 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.37 (s, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.69–7.66 (m, 4H), 7.64–7.59 (m, 4H), 7.55–7.53 (m, 4H), 7.33–7.30 (m, 2H), 7.27–7.24 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 139.11, 136.82, 131.49, 130.99, 129.34, 129.02, 128.96, 128.50, 127.57, 126.58, 125.93, 125.27, 124.48; HRMS (+EI): [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>20</sub> 380.1565, found 380.1561.

**3b:** Yield: 399 mg (81%); mp 220–221 °C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.40 (s, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.71–7.67 (m, 4H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.48–7.44 (m, 4H), 7.34–7.23 (m, 4H), 1.52 (s, 18H); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 150.93, 137.43, 136.20, 131.43, 129.82, 129.56, 129.19, 127.02, 126.10, 125.79, 125.48, 125.04, 35.07, 31.66, (one sp<sup>2</sup> signal was overlapped with other signal); HRMS (–APCI): [M]<sup>–</sup> calcd for C<sub>38</sub>H<sub>36</sub> 492.2817, found 492.2804.

**3c:** Yield: 432 mg (83%); mp 213–214 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.38 (s, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 4H), 7.43 (d, *J* = 7.5 Hz, 4H), 7.33–7.30 (m, 2H), 7.27–7.24 (m, 2H), 2.84 (t, *J* = 8.0 Hz, 4H), 1.85–1.82 (m, 4H), 1.49–1.45 (m, 8H), 1.00 (t, *J* = 6.5 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 142.20, 136.99, 136.19, 131.33, 130.94, 129.41, 129.19, 128.97, 128.45, 126.73, 125.86, 125.07, 124.55, 35.94, 31.79, 31.26, 22.66, 14.15; HRMS (+EI): [M]<sup>+</sup> calcd for C<sub>40</sub>H<sub>40</sub> 520.3130, found 520.3126.

## Indenotetracene Derivatives (2a-c)

**General procedure for preparation of 2a-c:** 5,11-diphenyltetracene derivative **3** (0.20 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) in a 100 mL two-necked flask. After stirring for 20 min under argon, a solution of anhydrous iron(III) chloride (260 mg, 1.60 mmol) in dry nitromethane (4 mL) was injected through a syringe. The solution was stirred at room temperature in the dark for 1.5 h under argon. Dry methanol (250 mL) was added to the solution. The resulting precipitate was filtered, rinsed with methanol, and dried. Then, the crude product was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as an eluent. The solvent was evaporated and the product was recrystallized from toluene to give **2** as a reddish violet solid.

**2a:** Yield: 68 mg (90%); mp 259–260 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.92 (d, *J* = 8.5 Hz, 1H), 8.84 (d, *J* = 9.5 Hz, 1H), 8.58–8.53 (m, 2H), 8.33 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.68–7.60 (m, 7H), 7.54–7.50 (m, 2H), 7.42–7.36 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 140.01, 139.92, 139.61, 138.06, 134.04, 131.79, 131.04, 130.78, 130.57, 129.39, 129.02, 128.92, 128.48, 128.12, 128.03, 128.00, 127.79, 127.47, 126.75, 126.69, 125.66, 124.63, 124.54, 124.36, 123.23, 124.10 (two sp<sup>2</sup> signals were overlapped with other signals); HRMS (+EI): [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>18</sub> 378.1409, found 378.1409.

**2b:** Yield: 90 mg (92%); mp 289–290 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.91 (d, *J* = 9.0 Hz, 1H), 8.81 (d, *J* = 9.0 Hz, 1H), 8.59 (d, *J* = 1.5 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 8.34 (s, 1H), 8.20–7.96 (m, 2H), 7.69–7.61 (m, 4H), 7.59–7.51 (m, 3H), 7.41–7.35 (m, 2H), 1.57 (s, 9H), 1.52 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 150.59, 149.87, 140.22, 139.72, 137.48, 134.95, 133.97, 131.91, 131.50, 131.01, 130.95, 130.74, 129.34, 129.19, 128.90, 128.65, 127.65, 127.60, 127.36, 125.83, 124.97, 124.35, 124.28, 124.20, 123.76, 123.67, 121.38, 35.13, 34.81, 31.69, 31.56 (one signal was overlapped with other signal); HRMS (–APCI): [M]<sup>–</sup> calcd for C<sub>38</sub>H<sub>34</sub> 490.2666, found 490.2652.

**2c:** Yield: 114 mg (91%); mp 138–139 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.91 (d, *J* = 9.5 Hz, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.35 (s, 1H), 8.32 (s, 1H), 7.98–7.95 (m, 2H), 7.67–7.63 (m, 1H), 7.61–7.58 (m, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.40–7.35 (m, 2H), 7.32–7.31 (m, 1H), 2.92–2.79 (m, 4H), 1.87–1.80 (m, 4H), 1.53–1.43 (m, 8H), 1.00 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 142.48, 141.76, 140.31, 139.71, 137.68, 135.17, 133.97, 131.83, 131.68, 131.02, 130.97, 130.54, 129.34, 129.06, 128.71, 128.58, 128.07, 127.63, 127.50, 127.26, 126.76, 125.80, 124.59, 124.38, 124.19, 123.90, 36.59, 35.92, 31.77, 31.70, 31.64, 31.25, 22.68, 22.66, 14.14

(two  $sp^2$  signals and one  $sp^3$  were overlapped with other signals); HRMS (+EI):  $[M]^+$  calcd for  $C_{40}H_{38}$  518.2974, found 518.2977.

### Tetrabenzo-Fused Pyracylene Derivatives (TBPs 1a-c)

**General procedure for preparation of 1a-c:** 5,11-diphenyltetracene derivative **3** (0.20 mmol) was dissolved in dry dichloromethane (30 mL) in 100 mL two-necked flask. After stirring for 20 min under argon, a solution of anhydrous iron(III) chloride (518 mg, 3.20 mmol) in dry nitromethane (8 mL) was injected through a syringe. The solution was stirred at room temperature in the dark for 1.5 h under argon. Dry methanol (200 mL) was added to the solution. The resulting precipitate was filtered, rinsed with methanol, and dried. Then, the crude product was purified by silica gel column chromatography using  $CH_2Cl_2$  as an eluent. The solvent was removed and the product was further purified by recrystallization from toluene to give **1** as a dark blue solid.

**1a:** Yield: 73 mg (97%); mp  $>300\text{ }^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $CS_2$ - $CD_2Cl_2$  (5:1)):  $\delta$  8.46–8.43 (m, 4H), 7.95–7.92 (m, 4H), 7.55–7.52 (m, 4H), 7.20–7.17 (m, 4H); HRMS (+EI):  $[M]^+$  calcd. for  $C_{30}H_{16}$  376.1252, found 376.1250. ( $^{13}\text{C}$  NMR signals of **1a** could not be observed likely due to severe broadening caused by the aggregation.)

**1b:** Yield: 90 mg (92%); mp  $>300\text{ }^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $CS_2$ - $CD_2Cl_2$  (5:1)):  $\delta$  8.46–8.39 (m, 4H), 7.94 (d,  $J = 1.5\text{ Hz}$ , 2H), 7.81 (d,  $J = 7.8\text{ Hz}$ , 2H), 7.54–7.47 (m, 4H), 7.18 (dd,  $J = 1.8, 8.1\text{ Hz}$ , 2H), 1.52 (s, 18H);  $^{13}\text{C}$  NMR (75 MHz,  $CS_2$ - $CD_2Cl_2$  (5:1))  $\delta$  150.42, 143.23, 140.18, 133.96, 133.62, 131.39, 131.14, 128.99, 126.46, 126.34, 126.24, 126.12, 124.46, 124.34, 122.31, 34.40, 31.12; HRMS (–APCI):  $[M]^-$  calcd. for  $C_{38}H_{34}$  488.2509, found 488.2511.

**1c:** Yield: 91 mg (88%); mp 232–233  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $CS_2$ - $CD_2Cl_2$  (5:1)):  $\delta$  8.43–8.36 (m, 4H), 7.78 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.71 (s, 2H), 7.52–7.47 (m, 4H), 6.97 (d,  $J = 7.5\text{ Hz}$ , 2H), 2.71 (t,  $J = 7.5\text{ Hz}$ , 4H), 1.81–1.77 (m, 4H), 1.50–1.46 (m, 8H), 1.02 (t,  $J = 6.8\text{ Hz}$ , 6H); HRMS (+EI):  $[M]^+$  calcd. for  $C_{40}H_{36}$  516.2817, found 516.2819. ( $^{13}\text{C}$  NMR signals of **1c** could not be observed likely due to severe broadening caused by the aggregation.)

### Addition of *n*-Butyllithium to TBP

**General procedure for preparation of 6a,b:** To a suspension of TBP **1a** (37 mg, 0.10 mmol) in anhydrous THF (20 mL) at  $-78\text{ }^\circ\text{C}$  was added *n*-butyllithium (0.30 mmol) dropwisely. The mixture was stirred at  $-78\text{ }^\circ\text{C}$  for 2 h. The reaction was added by excess amount of *n*-butyl

iodide (7.45 mmol, 1 mL) or acidic water (saturated  $\text{NH}_4\text{Cl}$  aq.) at room temperature for 1 h and extracted with  $\text{CH}_2\text{Cl}_2$  (30 mL). The organic layers were combined, washed by brine (20 mL), and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ $\text{CH}_2\text{Cl}_2$  (5:1) as eluent and GPC (toluene) to give compound **6**.

**6a**: Yield: 27 mg (56%); pale yellow solid; mp 273–274 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.78–8.75 (m, 2H), 8.28 (d,  $J$  = 7.5 Hz, 2H), 8.06 (d,  $J$  = 7.5 Hz, 2H), 8.02–7.99 (m, 2H), 7.71–7.68 (m, 2H), 7.52–7.44 (m, 4H), 7.20–7.17 (m, 2H), 2.61–2.55 (m, 2H), 2.53–2.46 (m, 2H), 1.19–1.03 (m, 6H), 0.92–0.83 (m, 2H), 0.73 (t,  $J$  = 7.5 Hz, 6H),  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  151.32, 145.94, 143.39, 143.05, 134.68, 130.47, 127.72, 126.45, 126.20, 126.02, 125.99, 125.24, 122.65, 56.72, 43.65, 27.43, 23.24, 14.02 (one  $\text{sp}^2$  signal was overlapped with other signal); HRMS (–APCI):  $[\text{M}]^-$  calcd. for  $\text{C}_{38}\text{H}_{34}$  488.2509, found 488.2511.

**6b**: Yield: 26 mg (60%); pale brown solid; mp 252–253 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.79–8.77 (m, 2H), 8.38 (d,  $J$  = 7.5 Hz, 1H), 8.33 (d,  $J$  = 7.5 Hz, 1H), 8.14 (d,  $J$  = 7.5 Hz, 1H), 8.04 (d,  $J$  = 6.5 Hz, 1H), 7.89–7.85 (m, 2H), 7.70–7.66 (m, 2H), 7.58–7.47 (m, 4H), 7.17–7.15 (m, 2H), 5.32 (s, 1H), 2.42–2.36 (m, 2H), 1.14–1.08 (m, 2H), 1.02–0.87 (m, 2H), 0.67 (t,  $J$  = 7.5 Hz, 3H),  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  149.95, 146.15, 146.08, 144.10, 143.83, 142.63, 138.10, 133.98, 133.77, 130.58, 127.97, 127.93, 127.67, 126.44, 126.37, 126.18, 126.04, 125.98, 125.93, 125.87, 125.69, 125.39, 125.33, 123.40, 123.30, 56.82, 47.45, 39.73, 27.76, 23.33, 14.07 (three  $\text{sp}^2$  signals were overlapped with other signals); HRMS (+APCI):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{34}\text{H}_{27}$  435.2107, found 435.2096.

### Addition of Benzyne to TBP

To a solution of **1a** (37 mg, 0.10 mmol) and isoamyl nitrite (235 mg, 1.98 mmol) in dry benzene (20 mL) was added anthranilic acid (272 mg, 1.99 mmol), and the mixture was stirred at 50 °C under argon atmosphere. After 24 h, solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ , 5:1) and GPC (toluene) to give compound **7** (23 mg, 0.50 mmol) as colorless solids in 50% yield.

**7**: mp >300 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.51–8.48 (m, 2H), 8.34 (d,  $J$  = 7.0 Hz, 2H), 8.30 (d,  $J$  = 7.5 Hz, 2H), 7.72–7.64 (m, 4H), 7.61–7.58 (m, 2H), 7.51–7.47 (m, 4H), 7.00–6.96 (m, 4H),  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.77, 147.36, 145.38, 143.01, 130.66, 129.21, 129.02, 128.13, 126.13, 125.98, 125.41, 125.17, 124.61, 121.45, 60.54; HRMS (+APCI):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{36}\text{H}_{21}$  453.1638, found 453.1649.

## Computational Method

DFT calculations for optimizations were conducted using the Gaussian 09 program.<sup>14</sup>

## X-Ray Crystal Structure Analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1061675 (**3a**), CCDC-1061674 (**2a**), CCDC-1061673 (**1b**), CCDC-1061676 (**6a**), CCDC-1061677 (**6b**), and CCDC-1061678 (**7**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Compound 3a:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX) with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 5154 reflections were measured at the maximum  $2\theta$  angle of  $51.0^\circ$ , of which 3614 were independent reflections ( $R_{\text{int}} = 0.018$ ). The structure was solved by direct methods (SHELXS-97<sup>22</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>22</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>30</sub>H<sub>20</sub>; FW = 380.46, crystal size  $0.30 \times 0.25 \times 0.10$  mm<sup>3</sup>, Triclinic,  $P-1$ ,  $a = 9.2769(9)$  Å,  $b = 10.8876(11)$  Å,  $c = 10.9105(11)$  Å,  $\alpha = 66.823(2)^\circ$ ,  $\beta = 89.653(2)^\circ$ ,  $\gamma = 80.044(2)^\circ$ ,  $V = 995.46(17)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.269$  g cm<sup>-3</sup>. The refinement converged to  $R_1 = 0.047$ ,  $wR_2 = 0.109$  ( $I > 2\sigma(I)$ ), GOF = 1.03.

**Compound 2a:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX) with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 7912 reflections were measured at the maximum  $2\theta$  angle of  $51.0^\circ$ , of which 3342 were independent reflections ( $R_{\text{int}} = 0.021$ ). The structure was solved by direct methods (SHELXS-97<sup>22</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>22</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>30</sub>H<sub>18</sub>; FW = 378.44, crystal size  $0.30 \times 0.10 \times 0.10$  mm<sup>3</sup>, monoclinic,  $P2_1/n$ ,  $a = 8.0531(6)$  Å,  $b = 12.3414(10)$  Å,  $c = 18.4991(15)$  Å,  $\beta = 95.4150(10)^\circ$ ,  $V = 1830.4(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.373$  g cm<sup>-3</sup>. The refinement converged to  $R_1 = 0.041$ ,  $wR_2 = 0.104$  ( $I > 2\sigma(I)$ ), GOF = 1.02.

**Compound 1b:** Intensity data were collected on a BL38B1 beamline in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute with a diffractometer ( $\lambda = 0.75$  Å) equipped with an ADSC Quantum 315 CCD detector at 100 K. The collected diffraction

data were processed with the HKL2000 software program.<sup>23</sup> A total of 16270 reflections were measured at the maximum  $2\theta$  angle of  $51.2^\circ$ , of which 3852 were independent reflections ( $R_{\text{int}} = 0.025$ ). The structure was solved by direct methods (SHELXS-97<sup>22</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>22</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $\text{C}_{38}\text{H}_{32}$ ; FW = 488.64, crystal size  $0.03 \times 0.01 \times 0.01 \text{ mm}^3$ , Triclinic,  $P-1$ ,  $a = 7.0756(1) \text{ \AA}$ ,  $b = 12.9306(2) \text{ \AA}$ ,  $c = 14.3203(2) \text{ \AA}$ ,  $\alpha = 78.5052(9)^\circ$ ,  $\beta = 82.5538(10)^\circ$ ,  $\gamma = 81.4224(10)^\circ$ ,  $V = 1262.79(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.285 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.041$ ,  $wR_2 = 0.103$  ( $I > 2\sigma(I)$ ), GOF = 1.12.

**Compound 6a:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and graphite monochromator. A total of 12586 reflections were measured at the maximum  $2\theta$  angle of  $50.2^\circ$ , of which 4637 were independent reflections ( $R_{\text{int}} = 0.035$ ). The structure was solved by direct methods (SHELXS-97<sup>22</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>22</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $\text{C}_{38}\text{H}_{34}$ ; FW = 490.65, crystal size  $0.07 \times 0.07 \times 0.05 \text{ mm}^3$ , monoclinic,  $P2_1/c$ ,  $a = 10.3410(11) \text{ \AA}$ ,  $b = 15.4282(16) \text{ \AA}$ ,  $c = 16.5483(17) \text{ \AA}$ ,  $\beta = 97.6351(15)^\circ$ ,  $V = 2616.8(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.245 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.043$ ,  $wR_2 = 0.094$  ( $I > 2\sigma(I)$ ), GOF = 1.04.

**Compound 6b:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX) with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and graphite monochromator. A total of 10671 reflections were measured at the maximum  $2\theta$  angle of  $50.0^\circ$ , of which 3877 were independent reflections ( $R_{\text{int}} = 0.044$ ). The structure was solved by direct methods (SHELXS-97<sup>22</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>22</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $\text{C}_{34}\text{H}_{26}$ ; FW = 434.55, crystal size  $0.20 \times 0.10 \times 0.07 \text{ mm}^3$ , monoclinic,  $P2_1/n$ ,  $a = 12.5978(18) \text{ \AA}$ ,  $b = 11.8394(18) \text{ \AA}$ ,  $c = 15.850(2) \text{ \AA}$ ,  $\beta = 109.981(3)^\circ$ ,  $V = 2221.7(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.299 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.051$ ,  $wR_2 = 0.105$  ( $I > 2\sigma(I)$ ), GOF = 1.05.

**Compound 7:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and graphite monochromator. A total of 10682 reflections were measured at the maximum  $2\theta$  angle of  $50.2^\circ$ ,

of which 3974 were independent reflections ( $R_{\text{int}} = 0.044$ ). The structure was solved by direct methods (SHELXS-97<sup>22</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>22</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $\text{C}_{36}\text{H}_{20}$ ; FW = 452.52, crystal size  $0.10 \times 0.10 \times 0.07 \text{ mm}^3$ , monoclinic,  $P2_1/n$ ,  $a = 11.952(2) \text{ \AA}$ ,  $b = 11.161(2) \text{ \AA}$ ,  $c = 16.994(3) \text{ \AA}$ ,  $\beta = 98.683(3)^\circ$ ,  $V = 2240.9(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.341 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.041$ ,  $wR_2 = 0.102$  ( $I > 2\sigma(I)$ ), GOF = 1.03.

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### Unsymmetrical Twofold Scholl Cyclizations of 5,11-Dinaphthyltetracene: Selective Formation of Pentagonal and Hexagonal Rings via a Dication Pathway

#### Abstract

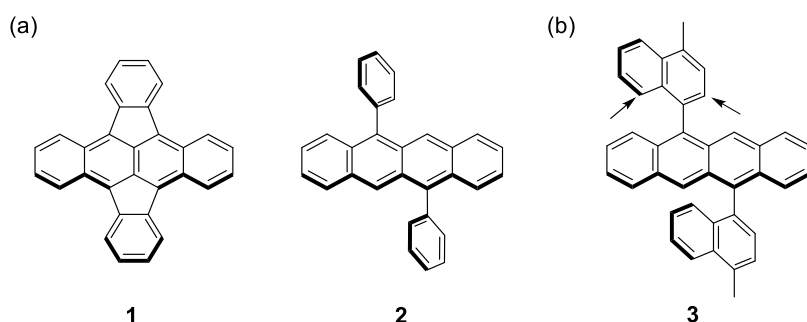
Even though the Scholl reaction is one the most powerful methods for the synthesis of polycyclic aromatic hydrocarbons (PAHs), its mechanism still remains a subject of discussion. Herein, the author report a unique twofold Scholl cyclization of a 5,11-dinaphthyltetracene. A single-crystal X-ray diffraction analysis of the cyclization product revealed that unsymmetric cyclizations of the two naphthyl groups resulted in the formation of fully unsaturated pentagonal and hexagonal rings. Thus, the obtained product exhibits a twisted  $\pi$ -surface and an absorption band that reaches up to 950 nm. A combination of experimental and theoretical studies showed that such unsymmetric Scholl cyclizations can be rationalized in terms of a mechanism that involves *dication* intermediates, which stands in contrast to the previously reported pathways based on radical cations and arenium ions.

## Introduction

The Scholl reaction describes oxidative C-H coupling reactions mediated by a variety of oxidants such as  $\text{FeCl}_3$  or  $\text{DDQ}/\text{H}^+$ . It is one of the most effective and versatile C-C bond forming reactions to generate polycyclic aromatic hydrocarbons (PAHs).<sup>1</sup> Müllen and co-workers have made numerous invaluable contributions to the synthesis of PAHs such as hexa-*peri*-hexabenzocoronene (HBC), and their efforts have made a variety of PAHs accessible in high yield under mild reaction conditions.<sup>2</sup> Today, the Scholl reaction is widely used for the synthesis of two- or three-dimensionally expanded PAHs, as well as for the synthesis of heteroatom-containing PAHs.<sup>3</sup> In most cases, the Scholl reaction involves the formation of hexagonal rings, while in a few cases, the unexpected formation of products that contain pentagonal rings, such as benzoindenoperylenes,<sup>4</sup> benzofluoranthenes,<sup>5</sup> or dibenzocorannulene-fused porphyrin dyads<sup>6</sup> has been reported. Although the Scholl reaction is considered to proceed *via* pathways that include either radical cations<sup>7</sup> or arenium ions,<sup>8</sup> these do not always explain or allow a prediction of the regioselectivity. Recently, Müllen and co-workers reported an oxidative C-H coupling of tetraarylbenzotetraphene, which included a twofold cyclization accompanied by aryl migrations to furnish a product with two pentagonal rings. Based on density functional theory (DFT) calculations, pathways based on both radical cations and arenium ions were suggested to be involved in this unique cyclization.<sup>9</sup>

PAHs with fully unsaturated pentagonal ring(s), the so-called cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs), have received considerable attention due to their unusual properties, which include high electron affinity<sup>10</sup> and chemical reactivity,<sup>11</sup> as well as for their potential use in organic electronic devices.<sup>12</sup> In chapter 1, the author has described that electron-deficient tetrabenzo-fused pyracylene (TBP) **1** with two pentagonal rings can be efficiently synthesized *via* a twofold Scholl cyclization of 5,11-diphenyltetracene **2** (Figure 1a).<sup>13</sup> During our study on synthetic routes to CP-PAHs with a larger  $\pi$ -system than that of **1**, the author conducted the Scholl cyclization of 5,11-dinaphthyltetracene **3** (Figure 1b). Theoretically, the formation of three structural isomers should be expected for **3** (*vide infra*), due to two possible reaction sites at each naphthyl group (indicated with arrows in Figure 1b). However, the Scholl reaction of **3** afforded an unsymmetrically cyclized product with both pentagonal and hexagonal rings in a high yield. Herein, the author reports the structure and electronic properties of the resulting CP-PAH, which exhibits a twisted  $\pi$ -surface, as well as experimental and theoretical studies on the mechanism for the twofold cyclization. The data indicate that the unsymmetric cyclizations of **3** should most likely be explained by a mechanism

that involves *dication* intermediates, which stands in contrast to the previously reported pathways based on radical cations<sup>7</sup> or arenium ions.<sup>8</sup>



**Figure 1.** Chemical structures of (a) previously reported TBP **1** obtained from a twofold Scholl cyclization of precursor **2**, and (b) 5,11-dinaphthyltetracene **3** examined in this chapter.

## Results and Discussion

### Synthesis

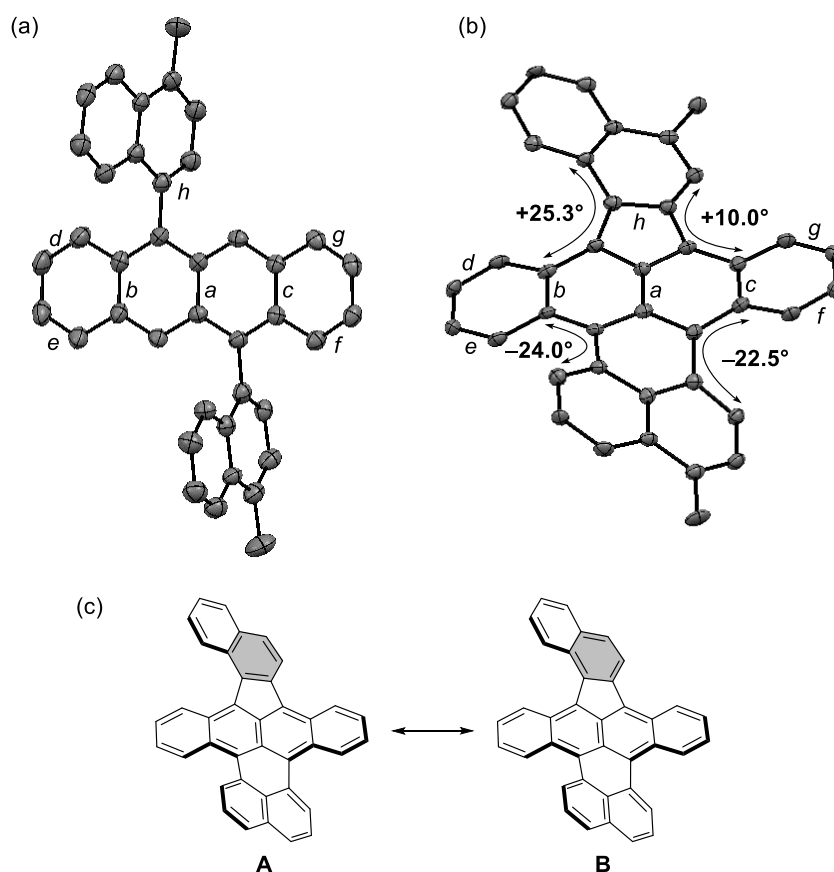
In this chapter, the author used 5,11-dinaphthyltetracene **3** as a precursor, because the introduction of a methyl group in each naphthyl group effectively avoided the formation of chlorinated products. According to the discussion in chapter 1 for the synthesis of TBP **1**,<sup>13</sup> **3** was treated with FeCl<sub>3</sub> at room temperature (entry 1, Table 1). The color of the solution immediately changed from yellow to dark green. After quenching the reaction mixture with hydrazine,<sup>14</sup> unsymmetrically cyclized **4** was obtained in 77% yield as a dark green powder, even though the symmetrically cyclized **6** with two hexagonal rings should be more stable than **4** based on DFT calculations on the M06-2X/6-31G\*\* level of theory ( $\Delta E = -8.3$  kcal/mol).<sup>15</sup> When the dichlorodicyano-*p*-benzoquinone (DDQ)/TfOH system was used, **4** was also obtained in 67% yield (entry 2), and mono-cyclized products were not observed, even upon decreasing the amount of DDQ. This observation stands in contrast to the Scholl cyclizations of **2**, which afforded the mono-cyclized product effectively ( $\leq 92\%$ ) upon reducing the amount of oxidant,<sup>13</sup> indicating that the second cyclization of the naphthyl group occurs instantaneously after the first cyclization of **3** to afford **4**. The used of the DDQ/MeSO<sub>3</sub>H system failed to afford any cyclized product (entry 3).

**Table1 Twofold Scholl Cyclization of 5,11-Dinaphthyltetracene 3**

| Entry | Oxidant (equiv.)              | Solvent                                                          | 4 (%) |
|-------|-------------------------------|------------------------------------------------------------------|-------|
| 1     | FeCl <sub>3</sub> (16)        | CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> NO <sub>2</sub> | 77    |
| 2     | DDQ (2.4)/TfOH                | CH <sub>2</sub> Cl <sub>2</sub>                                  | 67    |
| 3     | DDQ (2.4)/MeSO <sub>3</sub> H | CH <sub>2</sub> Cl <sub>2</sub>                                  | 0     |

### X-Ray Crystal Structures

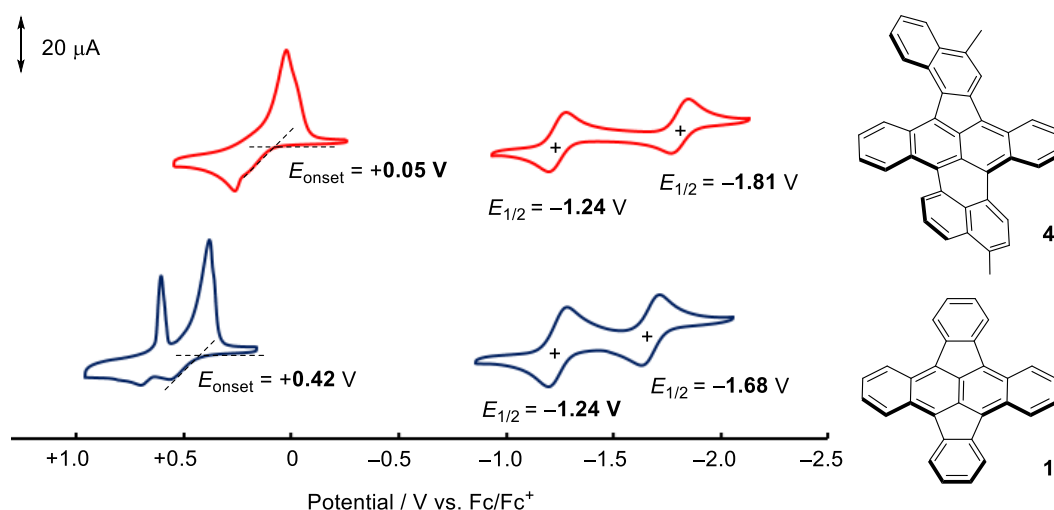
The structure of **4** was unambiguously determined by a single-crystal X-ray diffraction analysis (Figure 2), which revealed a substantially twisted structure, including four kinds of helicene-type substructures with dihedral angles of 10.0–25.3° on account of the steric repulsion between the *peri*-hydrogen atoms (Figure 2b). The data also show that the twofold cyclization caused significant changes in the bond lengths. In particular, the bond *a* in **4** [1.405(3) Å] is shortened relative to that in **3** [1.444(4) Å], while bonds *b* [1.452(3) Å] and *c* [1.456(4) Å] in **4** are elongated compared to those in **3** [*b*: 1.436(4) Å, *c*: 1.440(4) Å]. It should also be noted that bond *h* in the naphthyl moiety of **4** [1.398(3) Å] is elongated relative to that in **3** [1.368(4) Å]. The bond lengths for *d*, *e*, *f*, and *g* [1.342(4)–1.375(4) Å] fall within the realm of typical C=C double bonds. These results indicate major contributions from resonance structures **A** and **B** (Figure 2c) to the molecular structure. The packing structure of **4** within the crystal is characterized by one-dimensional on-top  $\pi$ -stacks with intermolecular distances of 3.37–3.61 Å, which is within the range of typical  $\pi$ -stacked structures (3.4–3.7 Å). DFT calculations suggested low inversion barriers for the flipping of the four helicene-type moieties in **4** ( $\Delta E^\ddagger < 11.1$  kcal/mol at the B3LYP/6-31G\* level), which consequently indicate that flipping should proceed easily in solution. In fact, evidence for a conformational mixture was not observed in the <sup>1</sup>H NMR spectrum of **4** in CDCl<sub>3</sub> at room temperature.



**Figure 2.** X-ray crystal structures of (a) **3** and (b) **4** with dihedral angles. (c) Selected resonance structures **A** and **B** for the  $\pi$ -skeleton of **4**. Selected bond lengths [Å] for **3**: *a* 1.444(4); *b* 1.436(4); *c* 1.440(4); *d* 1.375(4); *e* 1.355(4); *f* 1.357(4); *g* 1.342(4); *h* 1.368(4). Selected bond lengths [Å] for **4**: *a* 1.405(3); *b* 1.452(3); *c* 1.456(4); *d* 1.346(3); *e* 1.352(3); *f* 1.356(4); *g* 1.358(4); *h* 1.398(3).

## Electrochemical Properties

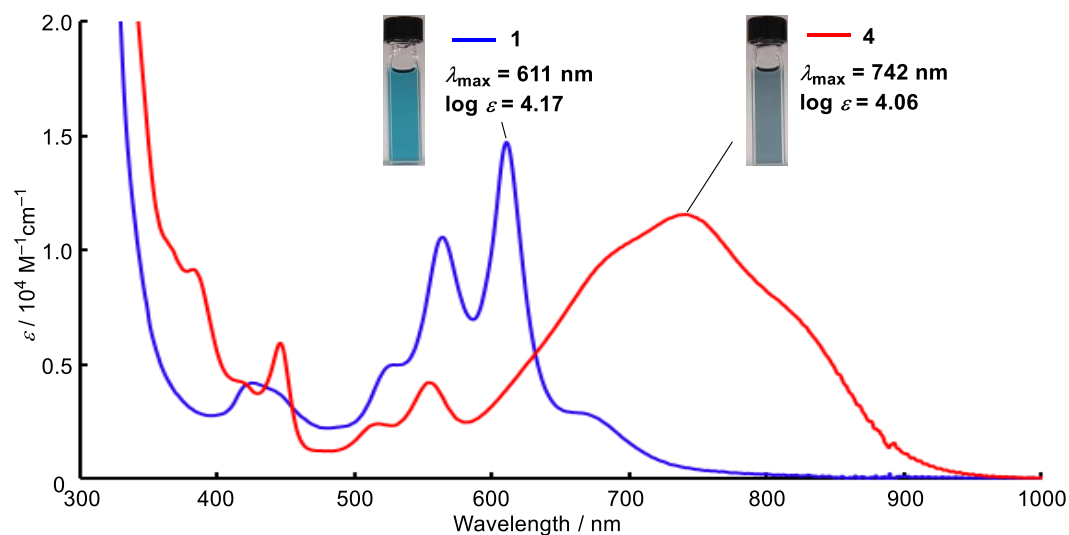
To examine its electronic properties, cyclic voltammograms and absorption spectra were measured for **4**, together with those for TBP **1** for comparison (Figure 3). In the reduction region, **4** exhibited two reversible waves ( $E_{1/2} = -1.24$  and  $-1.81$  V vs.  $\text{Fc}/\text{Fc}^+$ ), whereby the first reduction potential is consistent with that of TBP **1** ( $E_{1/2} = -1.24$  V),<sup>13</sup> indicating a high electron affinity of **4**. In the oxidation region, **4** exhibited an irreversible wave ( $E_{\text{onset}} = +0.05$  V), which is negatively shifted ( $\Delta E_{\text{onset}} = 0.37$  V) with respect to that of TBP **1** ( $E_{\text{onset}} = +0.42$  V).<sup>13</sup> The shape of the oxidation wave of **4** was broad but reproducible for several cycles in the range of  $+0.6$  to  $-1.5$  V, which is similar to the behavior of **1**,<sup>13</sup> and thus indicative of aggregation.



**Figure 3.** Cyclic voltammograms of **1** and **4** in  $\text{CH}_2\text{Cl}_2$  (1 mM); supporting electrolyte: 0.1 M  $[(n\text{-Bu})_4\text{N}][\text{PF}_6]$ ; scan rate: 100  $\text{mV s}^{-1}$ ; internal standard:  $\text{Fc}/\text{Fc}^+$ .

### Photophysical Properties

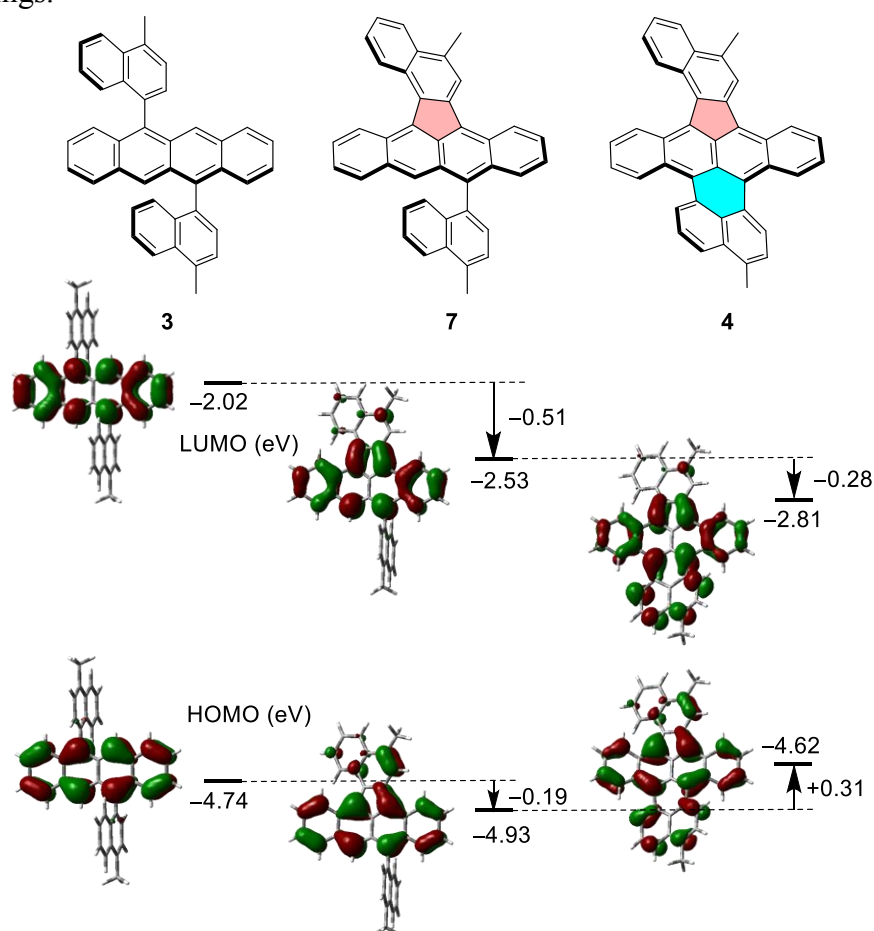
In the absorption spectrum (Figure 4), **4** showed a longest-wavelength absorption at  $\lambda_{\text{max}} = 742 \text{ nm}$  ( $\log \varepsilon = 4.06$ ), which tailed up to 950 nm, reflecting a low-lying LUMO and a high-lying HOMO. This band is markedly red-shifted ( $\Delta\lambda = 131 \text{ nm}$ ) compared to that of **1** ( $\lambda_{\text{max}} = 611 \text{ nm}$ ,  $\log \varepsilon = 4.17$ ).<sup>13</sup> The broadening in the absorption band in **4** should probably be ascribed to the conformational flexibility of **4**.



**Figure 4.** UV-vis-NIR absorption spectra of **4** (red) and TBP **1** (blue) in toluene with their pictures.

## DFT Calculations

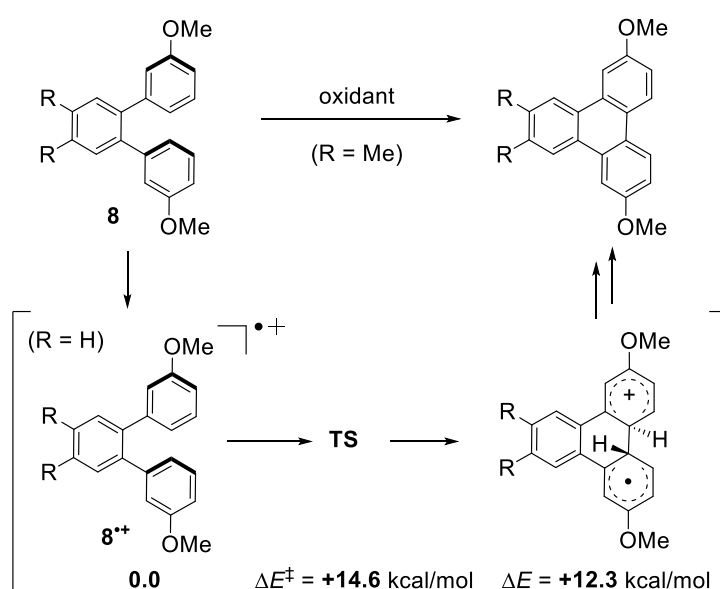
In order to better understand the formation of one pentagonal and one hexagonal rings, we conducted DFT calculations on **3** and **4**, as well as on mono-cyclized **7**, which contains a pentagonal ring (Figure 5). The results indicated that the  $\pi$ -extension of the tetracene core in **3** by a naphthyl moiety *via* the pentagonal ring lowers the LUMO ( $-0.51$  eV) more than the HOMO ( $-0.19$  eV). Further  $\pi$ -extension of **7** *via* a hexagonal ring further lowers the LUMO level ( $-0.28$  eV), but raises the HOMO level ( $+0.31$  eV). The latter trend is thus opposed to that for the formation of a pentagonal ring. As a result of the formation of pentagonal or hexagonal rings, the HOMO-LUMO gap in **4** is narrower than that in TBP **1** with two pentagonal rings.



**Figure 5.** HOMO and LUMO plots for **3** and **4**, together with mono-cyclized **7**, which contains a pentagonal ring (B3LYP/6-31G\*).

## Mechanistic discussion of the Scholl Reaction for the Formation of **4**

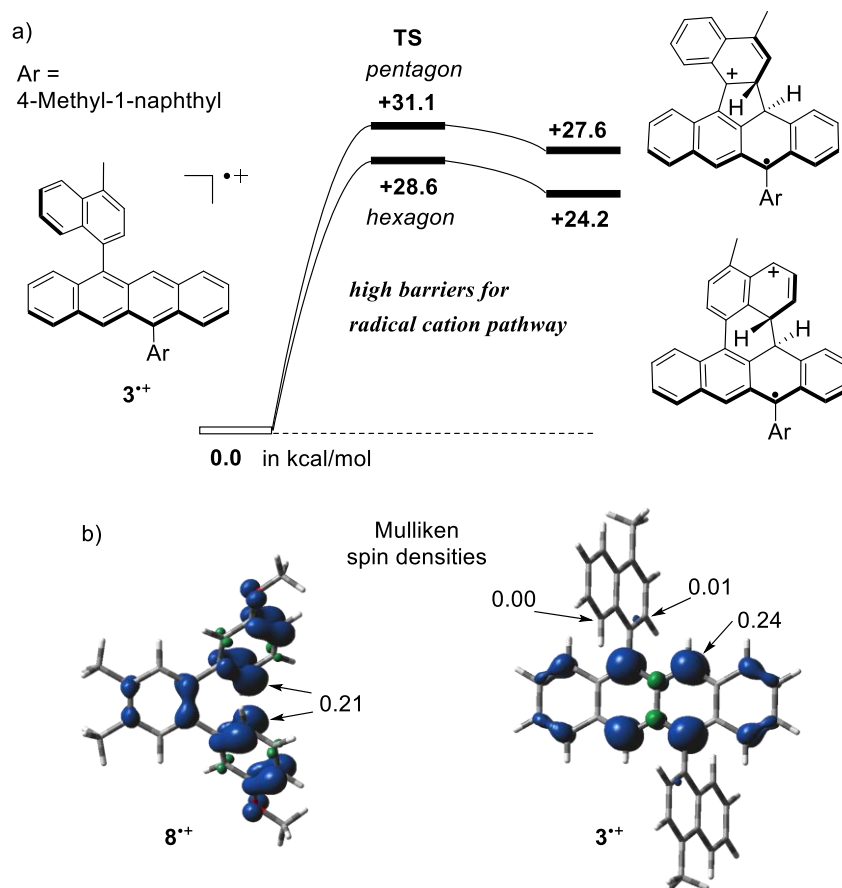
The Scholl reaction is considered to proceed *via* pathways that include radical cations<sup>7</sup> or arenium ions<sup>8</sup> (*vide supra*). Rathore and co-workers have demonstrated that *o*-terphenyl derivatives such as **8** undergo efficient Scholl cyclizations mediated by DDQ/MeSO<sub>3</sub>H *via* the generation of radical cations such as **8**<sup>•+</sup> (Figure 6).<sup>7f</sup> Consistent with the reported results for **8**,<sup>7f</sup> cyclization or aryl migration<sup>16</sup> was not observed for **3** in even acidic media using MeSO<sub>3</sub>H, implying that the cyclization of **3** is unable to proceed *via* the arenium ion pathway. Based on their oxidation potentials [ $E_{\text{onset}} = +0.42$  V (**3**) and  $+0.90$  V (**8**)], **3** should be more susceptible to oxidation than **8** (*vide infra*), and therefore it seems reasonable to assume that the Scholl reaction of **3** proceeds *via* the radical cation pathway.



**Figure 6.** Results of the DFT calculations for the Scholl cyclization of **8** (R = H)<sup>7f</sup> *via* the radical cation pathway.

In order to afford a better insight into the mechanism that underpins this cyclization, we conducted DFT calculations on **3** and **8**. All structures were optimized at the spin-unrestricted UM06-2X/6-31G\*\* level of theory, while single point calculations were carried out based on the polarizable continuum model (PCM) using dichloromethane at the same level of theory. The author first performed calculations for the Scholl cyclization of **8**, considering that the previous reports demonstrated the cyclization to proceed *via* a radical cation pathway.<sup>7f</sup> The results of our calculations suggest that the barrier for the cyclization of **8**<sup>•+</sup> (R = H) is very low ( $\Delta E^\ddagger = +14.6$  kcal/mol), i.e. it should proceed at room temperature (Figure 6). Conversely, the

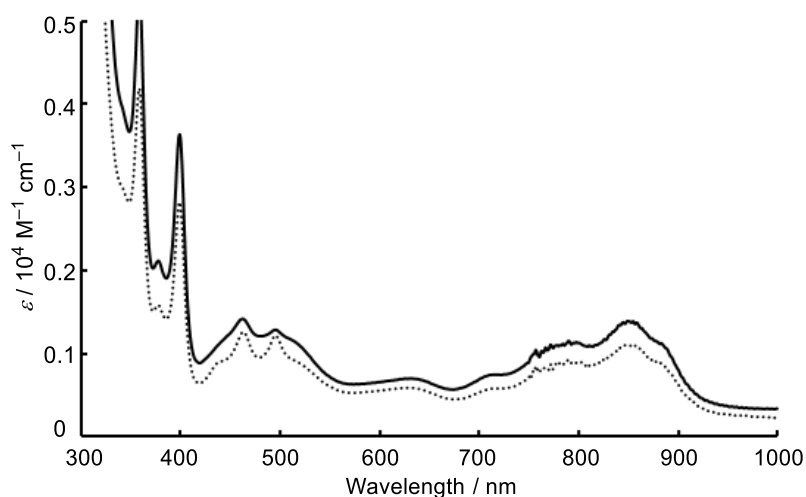
barriers for the cyclization of the radical cation of **3** are substantially higher, i.e.,  $\Delta E^\ddagger = +31.1$  or  $+28.6$  kcal/mol for the formation of pentagonal or hexagonal rings, respectively (Figure 7a). The Mulliken spin density for the radical cation of **3** resides almost completely on the tetracene core, and no spin density is delocalized over the naphthyl groups (Figure 7b). In **8**<sup>•+</sup> (R = H), in contrast, substantial spin density resides on the two carbon atoms where the Scholl cyclization occurs, which suggests that high spin density on both reaction centers is important for the reaction to proceed.



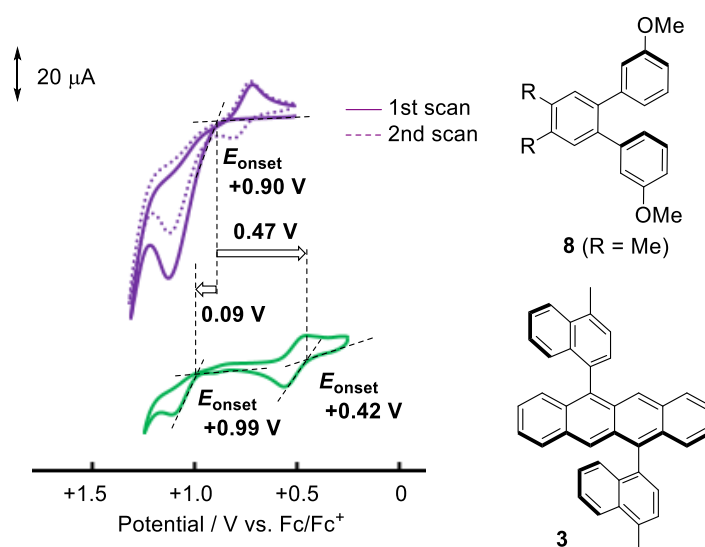
**Figure 7.** (a) Calculated barriers for the Scholl cyclization of **3** via a radical cation pathway, and (b) Mulliken spin density contour maps for the radical cations of **8** (R = H) and **3**, including values for selected carbon atoms. Blue and green represent positive and negative spin densities, respectively.

In this context it should be noted that, upon addition of DDQ/MeSO<sub>3</sub>H (entry 3, Table 1), the color of the solution of **3** immediately changed from yellow to green, even though the author could not obtain any cyclized product. The UV-vis-NIR absorption spectrum of this green solution exhibited broad absorption bands between 700-900 nm, which is similar to the reported data for radical cations of tetracene.<sup>17</sup> Furthermore, almost the same absorption

spectrum was obtained by oxidation of a solution of **3** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature with the one-electron oxidant tris(4-bromophenyl)aminium hexachloroantimonate (magic blue, 1.0 equiv)<sup>18</sup> (Figure 8). These results indicate that although the generation of radical cation **3**<sup>•+</sup> was most likely mediated by DDQ/MeSO<sub>3</sub>H, it did not lead to the formation of **4**.



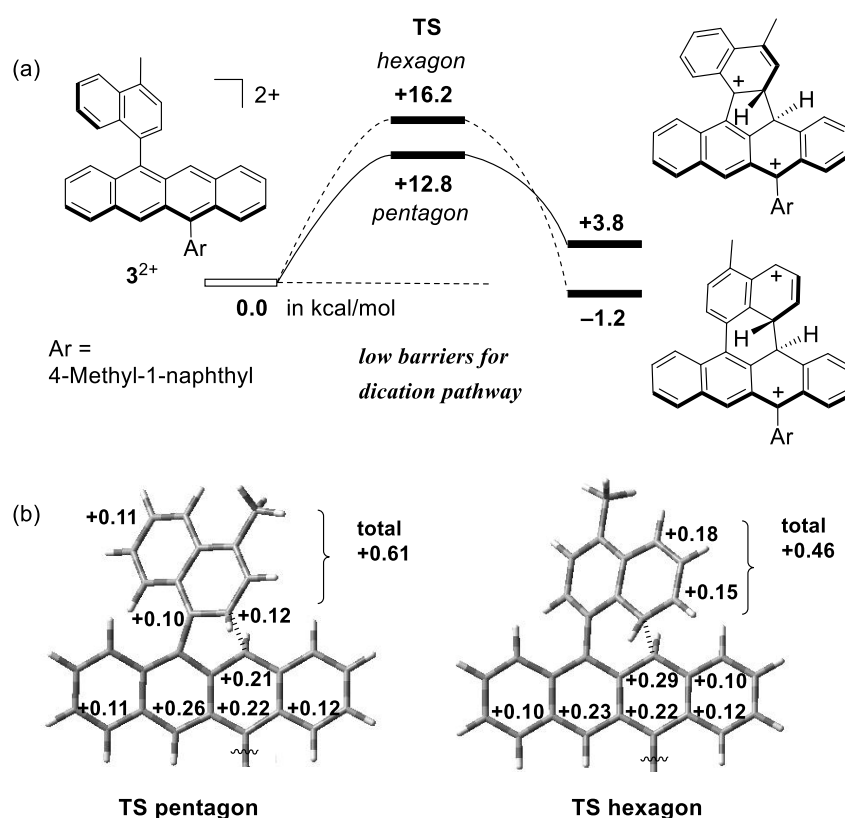
**Figure 8.** UV-vis NIR absorption spectra for **3**<sup>•+</sup> generated by DDQ/MeSO<sub>3</sub>H (dashed line) or magic blue (solid line) in CH<sub>2</sub>Cl<sub>2</sub>.



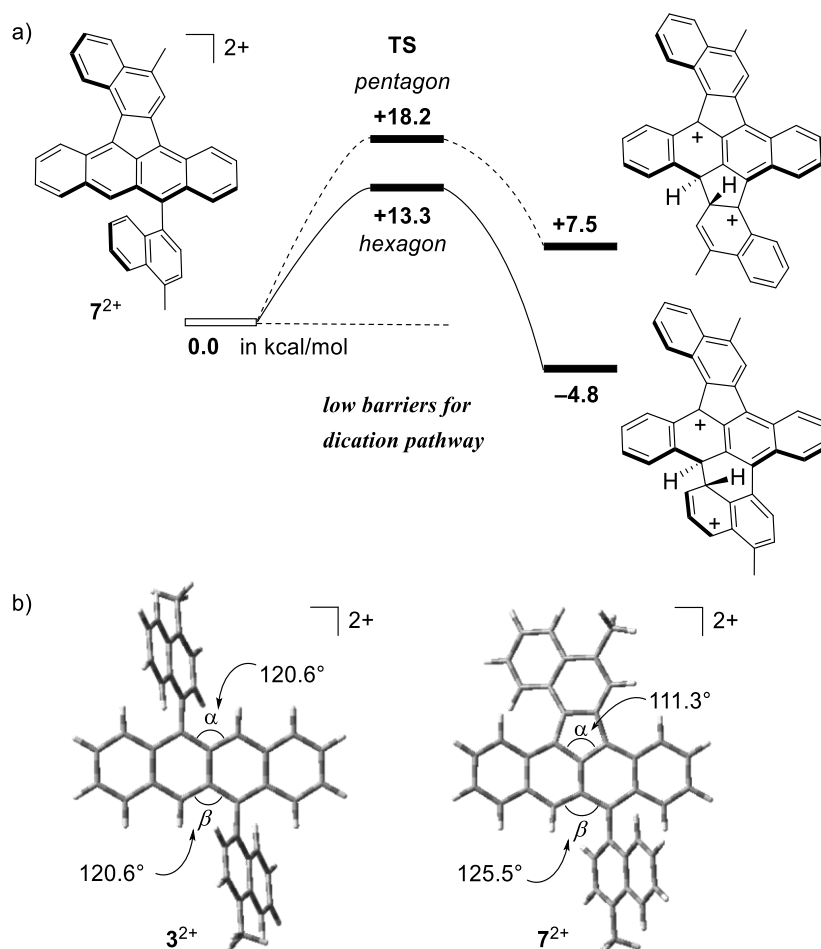
**Figure 9.** Cyclic voltammograms of **8** and **3**: the oxidation processes were measured in CH<sub>2</sub>Cl<sub>2</sub> (1 mM); supporting electrolyte: 0.1 M [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>]; scan rate: 100 mV s<sup>-1</sup>; internal standard: Fc/Fc<sup>+</sup>.

Notably, the cyclic voltammogram of **3** exhibited a second irreversible oxidation wave at  $E_{\text{onset}} = +0.99$  V, which is similar to the first oxidation wave of **7** ( $E_{\text{onset}} = +0.90$  V) (Figure 9). This result indicates that it should be possible to generate *dication* **3**<sup>2+</sup> by the use of oxidants

such as DDQ/TfOH or FeCl<sub>3</sub>, which are stronger than the DDQ/MeSO<sub>3</sub>H system. In order to get insight into the cyclization pathway *via* the unprecedented *dication* pathway, the DFT calculations were carried out using the same method applied for the radical cation pathway (Figure 10a). *Dication* **3**<sup>2+</sup> should have a singlet ground state, which is more stable by  $\Delta E = -8.7$  kcal/mol than the corresponding triplet state. Compared to the values for the radical cation pathway, the activation energies for the cyclization decreased reasonably for the formation of pentagonal ( $\Delta E^\ddagger = +12.8$  kcal/mol) and hexagonal rings ( $\Delta E^\ddagger = +16.2$  kcal/mol) (Figure 10a), on account of the reduced Coulomb repulsion between two charges in the transition states. The formation of a pentagonal ring is kinetically favored ( $\Delta\Delta E^\ddagger = -3.4$  kcal/mol) relative to the formation of a hexagonal ring, probably due to more delocalized positive charges over the cyclizing naphthyl moiety in the transition state (Figure 10b). Note that a rate-determining step in the *dication* pathway should be the initial  $\sigma$ -bond formation, because deprotonations from the  $\sigma$ -bonded intermediate are shown to proceed faster.



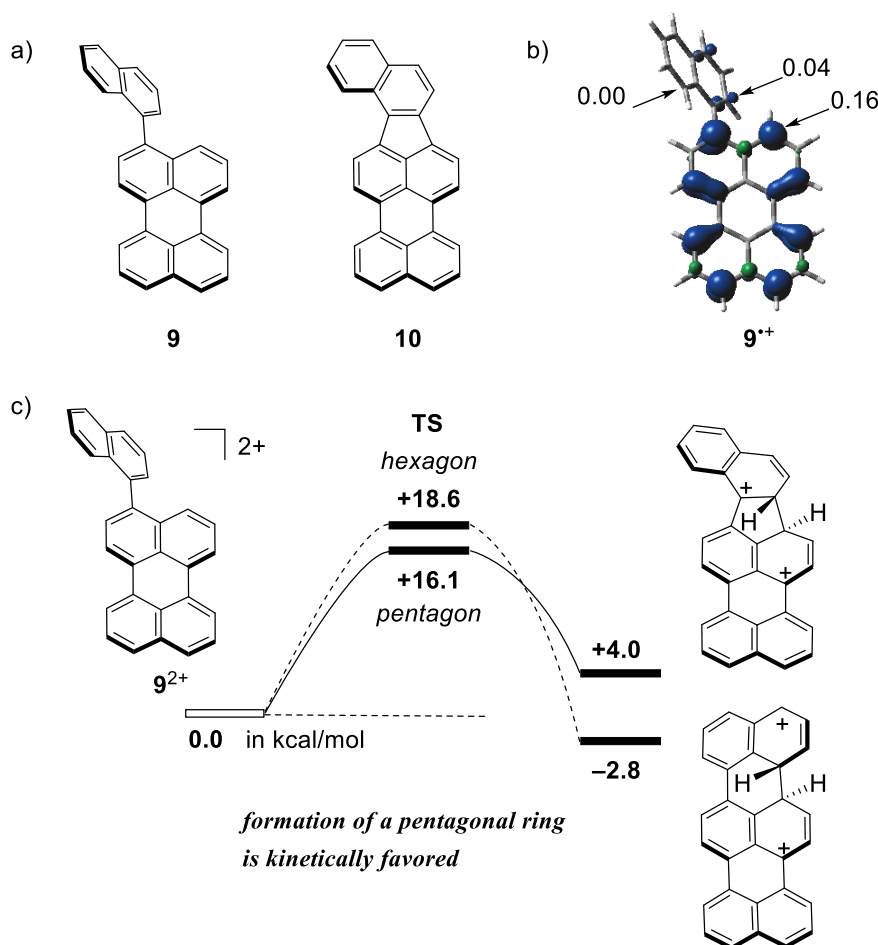
**Figure 10.** (a) Calculated barriers for the Scholl cyclization for model compound **3** *via* the *dication* pathway, and (b) NPA atomic charges for the selected carbon atoms in TS pentagon and TS hexagon.



**Figure 11.** (a) Calculated barriers for the second Scholl cyclization of model compound **7** via a *dication* pathway, and (b) optimized structures for the *dications* of **3** and **7** with selected bond angles.

Subsequently, we performed DFT calculations on the second cyclization of the naphthyl group in **7** (Figure 11a). In a similar manner to the first cyclization (Figure 10a), the activation energies for the second cyclization decreased reasonably for the formation of pentagonal ( $\Delta E^\ddagger = +18.2$  kcal/mol) and hexagonal rings ( $\Delta E^\ddagger = +13.3$  kcal/mol) when compared to the values for the radical cation pathways. Importantly, in contrast to the first cyclization, the formation of a hexagonal ring is kinetically favored ( $\Delta\Delta E^\ddagger = -4.9$  kcal/mol) relative to the formation of the pentagonal ring, which promotes unsymmetric Scholl cyclizations. In addition, the barrier for the second cyclization to form a hexagonal ring ( $\Delta E^\ddagger = +13.3$  kcal/mol) is comparable to that of the first cyclization to form a pentagonal ring ( $\Delta E^\ddagger = +12.8$  kcal/mol), which corroborates the experimental results, i.e., mono-cyclized products were not observed even upon decreasing the amount of oxidant. As a possible explanation for the unsymmetric cyclization, we considered that the initial formation of a pentagonal ring reduces the bond angle  $\alpha$  in *dication* **3**<sup>2+</sup> (120.6°) to that in *dication* **7**<sup>2+</sup> (111.3°) (Figure 11b). This structural constraint

causes an expansion of the bond angle  $\beta$  in  $\mathbf{3}^{2+}$  ( $120.6^\circ$ ) to that of  $\mathbf{7}^{2+}$  ( $125.5^\circ$ ) (Figure 11b), which should increase the activation energy for the formation of a second pentagonal ring.



**Figure 12.** (a) Molecular structures of **9** and **10**.<sup>[4b]</sup> (b) Mulliken spin density contour maps for radical cation  $\mathbf{9}^{+}$ , including values for selected carbon atoms. (c) Calculated barriers for the Scholl cyclization of **9** via the dication pathway.

Finally, in order to get insight into the applicability of the *dication* pathway, we performed DFT calculations for a Scholl cyclization of naphthylperylene **9**,<sup>[4b]</sup> which was reported by Müllen and co-workers to furnish **10** containing a pentagonal ring by using  $\text{FeCl}_3$  as an oxidant at  $25^\circ\text{C}$  (Figure 12a). The Mulliken spin density for  $\mathbf{9}^{+}$  mostly resides on the perylene core, in a similar manner to  $\mathbf{3}^{+}$ , on account of the electron-rich character of the perylene moiety (Figure 12b). Thus the barriers for the Scholl cyclization of  $\mathbf{9}^{+}$  via the radical cation pathway is substantially high, i.e.,  $\Delta E^\ddagger = +35.8$  or  $+29.7$  kcal/mol for the formation of pentagonal or hexagonal rings, respectively (Figures 12c). As can be expected from the above discussion, the activation energies for the cyclization via the *dication* pathway reasonably

decreased and the formation of a pentagonal ring is kinetically more favored ( $\Delta\Delta E^\ddagger = -2.5$  kcal/mol) than the formation of a hexagonal ring (Figure 12c), which corroborates the experimental results.<sup>[4b]</sup> Even though further studies are necessary, the *dication* pathway should be applicable to Scholl cyclizations for various precursors containing an electron-rich  $\pi$ -system.

## Conclusion

The author have demonstrated that the Scholl reaction of a 5,11-dinaphthyltetracene **3** undergoes an unsymmetric twofold cyclization to form fully unsaturated pentagonal and hexagonal rings. A single-crystal X-ray diffraction analysis revealed a twisted  $\pi$ -surface for the resulting product **4**, as well as one-dimensional on-top  $\pi$ -stacking in the solid state. The HOMO-LUMO gap of **4** is very narrow on account of the  $\pi$ -extension by the naphthalene units *via* the pentagonal and hexagonal rings, which is reflected in a broad NIR absorption reaching up to 950 nm. Based on the experimental and theoretical studies, the high selectivity of this unsymmetric twofold Scholl cyclization was rationalized in terms of a mechanism that proceeds *via* a *dication* pathway, which is different from the previously reported pathways that include radical cations or arenium ions. The mechanistic insight reported in this Chapter should hopefully contribute to a more rational design and synthesis of PAHs by using the Scholl reaction.

## Experimental Section

### General

Melting points (mp) were measured on a Yanaco MP-S3 instrument. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were carried out with a JEOL ECA 500 instrument or a Bruker Avance III 600US instrument. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of  $\text{CDCl}_3$  ( $\delta$  7.26 ppm in  $^1\text{H}$  NMR,  $\delta$  77.0 ppm in  $^{13}\text{C}$  NMR) and  $\text{CD}_2\text{Cl}_2$  ( $\delta$  5.32 ppm in  $^1\text{H}$  NMR,  $\delta$  53.5 ppm in  $^{13}\text{C}$  NMR). UV-vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer. APCI mass spectra were measured on a Bruker micrOTOF-Q II spectrometer. Cyclic voltammetry (CV) was performed on a BAS ALS620A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The measurements were carried out under an argon atmosphere using a  $\text{CH}_2\text{Cl}_2$  solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate ( $(n\text{-Bu})_4\text{N}^+\text{PF}_6^-$ ) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard.

## Synthesis

### 5,11-Dibromotetracene

5,11-Dibromotetracene was prepared according to the literature.<sup>19</sup>

### 5,11-Dinaphthyltetracene Derivative 3

To a mixture of 5,11-dibromotetracene (1.50 g, 3.89 mmol), 4-methyl-1-naphthaleneboronic acid (1.74g, 9.32 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (120 mg, 0.12 mmol), Sphos (190 mg, 0.47 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.61 g, 11.66 mmol) were added degassed toluene (18 mL) and distilled water (1.8 mL) in a Schlenk tube and the solution was stirred at 110 °C for 10 h. After cooling to room temperature, to the resulting mixture was added distilled water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layer was washed with brine. After drying with Na<sub>2</sub>SO<sub>4</sub>, the solution was filtered and the solvent was evaporated. Then, the crude product was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as an eluent. The solvent was evaporated to give **3** (1.26 g, 2.48 mmol) as a yellow solid in 64% yield.

**3**: mp >300 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.25 (d, *J* = 8.5 Hz, 2H), 8.22 (s, 2H), 7.70 (d, *J* = 8.5, Hz, 2H), 7.65 (d, *J* = 7.5, Hz, 2H), 7.58–7.54 (m, 4H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.25–7.21 (m, 4H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.13–7.10 (m, 2H), 2.95 (s, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 139.64, 135.93, 135.45, 135.32, 134.32, 133.61, 131.73, 130.96, 130.49, 129.65, 129.35, 127.73, 127.15, 127.07, 126.71, 126.38, 125.90, 125.35, 125.11, 20.04; HRMS (+APCI): [M+H]<sup>+</sup> calcd. for C<sub>40</sub>H<sub>29</sub> 509.2264, found 509.2275.

### Naphthalene-Fused Tetracene 4

**Method 1**: 5,11-Dinaphthyltetracene derivative **3** (59 mg 0.10 mmol) was dissolved in dry dichloromethane (10 mL) in a 50 mL two-necked flask. After stirring for 5 min under argon, a solution of anhydrous iron (III) chloride (260 mg, 1.60 mmol) in dry nitromethane (2 mL) was injected through a syringe. The solution was stirred at room temperature for 1 h under argon. Excessive hydrazine was added to the solution. The resulting solution was directly evaporated. Then, the crude product was purified by silica gel column chromatography using CS<sub>2</sub> as an eluent. The solvent was removed and product **4** (39 mg, 0.077 mmol) was obtained in 77% as a dark green solid.

**Method 2**: 5,11-Dinaphthyltetracene derivative **3** (17 mg 0.033 mmol) was dissolved in dry dichloromethane (10 mL) in a 50 mL 2-necked flask. After stirring for 5 min under argon, DDQ (18 mg, 0.080 mmol) was added to the solution. Then TfOH (0.1 mL) was injected through a syringe. The solution was stirred for 1 h and quenched by excessive hydrazine. The resulting

solution was directly evaporated. Then, the crude product was purified by silica gel column chromatography using CS<sub>2</sub> as an eluent. The solvent was removed and product **4** (11 mg, 0.022 mmol) was obtained in 67% as a dark green solid.

**4**: mp >300 °C; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>-CDCl<sub>3</sub> (5:1)): δ 8.94–8.91 (m, 2H), 8.83 (d, *J* = 9.5 Hz, 1H), 8.78 (d, *J* = 8.0 Hz, 2H), 8.57 (d, *J* = 7.5 Hz, 1H), 8.47 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.84 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.67 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.63–7.58 (m, 4H), 7.55–7.48 (m, 4H), 2.974 (s, 3H), 2.966 (s, 3H); <sup>13</sup>C NMR (126 MHz, CS<sub>2</sub>-CDCl<sub>3</sub> (5:1)) δ 138.51, 135.92, 133.01, 132.55, 132.18, 131.40, 130.94, 130.00, 129.91, 129.84, 129.80, 129.50, 129.33, 129.04, 128.37, 128.33, 127.64, 127.32, 127.10, 126.90, 126.84, 126.74, 126.27, 126.24, 125.78, 125.21, 125.04, 124.83, 124.75, 124.71, 124.41, 123.89, 121.75, 118.17, 114.59, 108.07, 107.83, 106.05, 20.84, 19.89; HRMS (–APCI): [M]<sup>–</sup> calcd. for C<sub>40</sub>H<sub>24</sub> 504.1883, found 504.1864.

## Computational Method

DFT calculations for optimizations and mechanistic discussion were conducted using the Gaussian 09 program.<sup>15</sup>

## X-Ray Crystal Structure Analysis

**Compound 3**: Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation ( $\lambda$  = 0.71073 Å) and graphite monochromator. A total of 12549 reflections were measured at the maximum  $2\theta$  angle of 50.0°, of which 4748 were independent reflections ( $R_{\text{int}}$  = 0.0555). The structure was solved by direct methods (SHELXS-97<sup>20</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>20</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>40</sub>H<sub>28</sub>; FW = 508.62, crystal size 0.30 × 0.25 × 0.10 mm<sup>3</sup>, Monoclinic, *C*2/*c*, *a* = 22.926(5) Å, *b* = 8.7002(18) Å, *c* = 27.244(6) Å,  $\beta$  = 98.318(3)°, *V* = 5376.9(19) Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.257 g cm<sup>–3</sup>. The refinement converged to  $R_1$  = 0.0580,  $wR_2$  = 0.1313 ( $I > 2\sigma(I)$ ), GOF = 1.020.

**Compound 4**: Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation ( $\lambda$  = 0.71073 Å) and graphite monochromator. A total of 20041 reflections were measured at the maximum  $2\theta$  angle of 50.0°, of which 4067 were independent reflections ( $R_{\text{int}}$  = 0.0983). The structure was solved by direct

methods (SHELXS-97<sup>20</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>20</sup>). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>40</sub>H<sub>24</sub>; FW = 504.59, crystal size 0.05 × 0.05 × 0.04 mm<sup>3</sup>, monoclinic,  $P2_1/c$ ,  $a = 24.166(8)$  Å,  $b = 3.8334(13)$  Å,  $c = 26.768(9)$  Å,  $\beta = 110.841(4)^\circ$ ,  $V = 2317.5(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.446$  g cm<sup>-3</sup>. The refinement converged to  $R_1 = 0.0589$ ,  $wR_2 = 0.1138$  ( $I > 2\sigma(I)$ ), GOF = 1.026.

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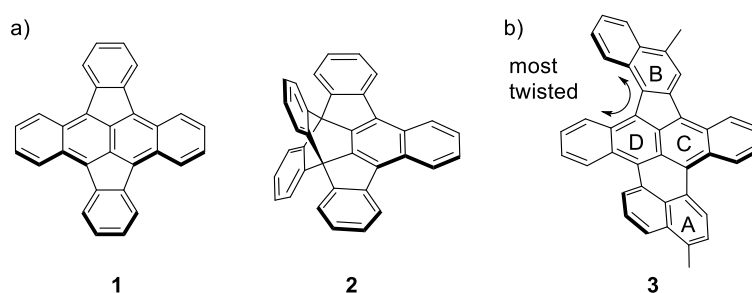
### Cycloaddition of Benzyne to Naphthalene-Fused Tetracene with a Twisted $\pi$ -Surface

#### Abstract

The functionalization of polycyclic aromatic hydrocarbons (PAHs) with arynes has received substantial attention as it offers a way to create  $\pi$ -extended PAHs as well as compounds containing rigid three dimensional structures. In this chapter, the author presents cycloaddition of benzyne to a  $\pi$ -extended tetracene with a twisted framework. Under kinetic control, this reaction furnished mono- and bis-adducts *via* concerted [4+2] cycloadditions, which was supported by theoretical studies. The bis-adduct exhibits blue emission in the solid state on account of the steric protection arising from the two [2.2.2] bicyclic moieties.

## Introduction

Cycloadditions of highly reactive dienophiles such as arynes to polycyclic aromatic hydrocarbons (PAHs) have attracted substantial interest as they can create a variety of extended  $\pi$ -systems *via* [4+2] cycloadditions on the perimeter of smaller  $\pi$ -systems.<sup>1</sup> Moreover, arynes can add to the surface of  $\pi$ -systems to create compounds with a unique three-dimensional (3D) structure. Swager and co-workers have developed highly emissive materials with triptycene-type structures that result from [4+2] cycloadditions to anthracene frameworks.<sup>2</sup> However, studies on the surface-functionalization of PAHs using arynes have mostly been limited to  $\pi$ -systems, which include acenes,<sup>3</sup> fullerenes<sup>4</sup> and subunits thereof,<sup>5</sup> as well as carbon nanotubes<sup>6</sup> and graphene.<sup>7</sup>



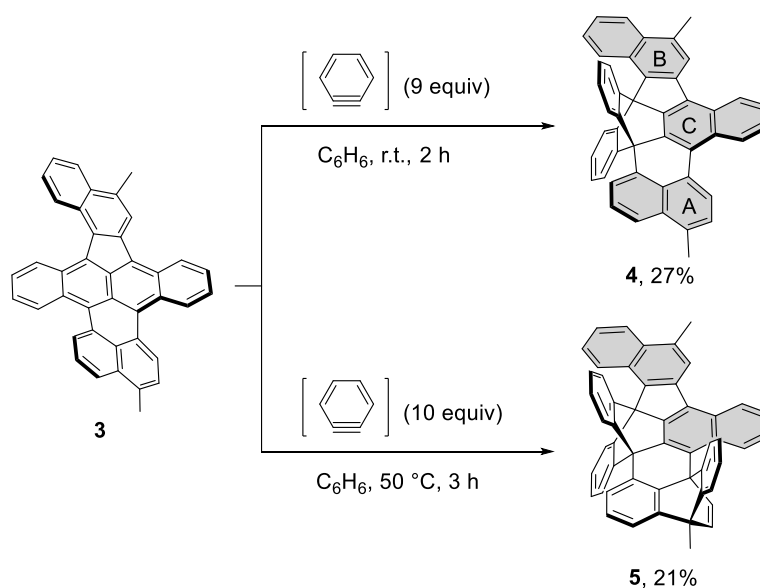
**Figure 1.** Structures of (a)  $\pi$ -extended tetracene **1** and benzyne monoadduct **2**, as well as (b)  $\pi$ -extended tetracene **3**, which is examined in this chapter.

The author have already discussed in chapter 1 that  $\pi$ -extended tetracene **1** undergoes a selective [4+2] cycloaddition with benzyne to furnish mono-adduct **2**, which exhibits intense blue emission in the solid state (Figure 1a).<sup>8</sup> During the study on the reactivity of  $\pi$ -extended tetracenes, the author succeeded in the synthesis of **3** in chapter 2,<sup>9</sup> in which two naphthalene units are fused to the tetracene core *via* a pentagonal ring and a hexagonal ring (Figure 1b). In this chapter, the author examined the reaction of **3** with benzyne, which furnished the mono- and bis-adducts. This result stands in contrast to the reactivity of **1**, for which the formation of the bis-adduct was not observed.<sup>8</sup> Herein, the author describes the cycloaddition of benzyne with **3**, the structural characterization of the benzyne adducts and their photophysical properties, as well as a theoretical study on the selectivity of the cycloaddition.

## Results and Discussion

### Synthesis

Compound **3** adopts a substantially twisted structure that includes a fourfold helicene-type structure due to the steric repulsion between the *peri*-hydrogen atoms.<sup>9</sup> Following our previous report on the synthesis of **2** in chapter 1,<sup>8</sup> a reaction between **3** and benzyne was carried out by adding isoamyl nitrite to a benzene solution containing **3** and anthranilic acid (Scheme 1). This reaction proceeded at room temperature and furnished benzyne mono-adduct **4** in 27% yield. The cycloaddition with hexagonal ring **D** (indicated in Figure 1) of the tetracene framework of **3** is favored over that with **C** due to substantial relief of strain in the most twisted moiety of **3**. Furthermore, in this reaction, the gradual formation of benzyne bis-adduct **5** with two [2.2.2] bicyclic moieties was observed, under concomitant consumption of mono-adduct **4**, via a selective cycloaddition with hexagonal ring **A** in **4**. After optimizing the reaction conditions ( $T = 50\text{ }^{\circ}\text{C}$ ), bis-adduct **5** was obtained in 21% yield from **3** (Scheme 1).

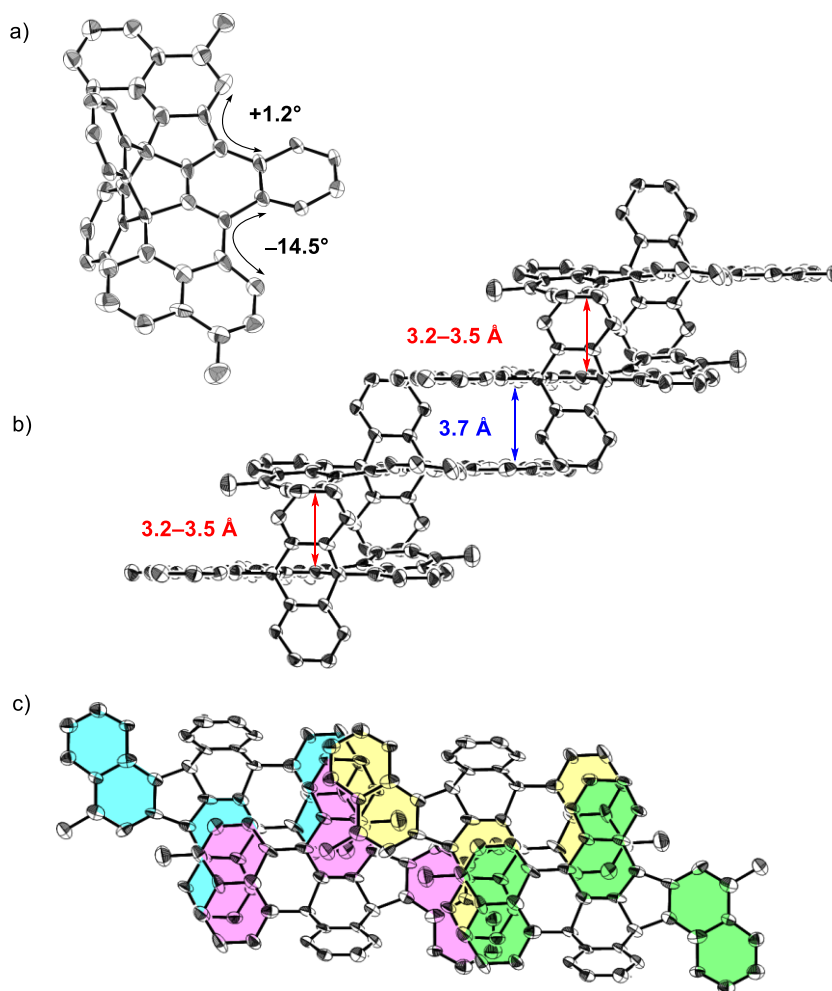


**Scheme 1.** [4+2] Cycloadditions between **3** and benzyne

### X-Ray Crystal Structure

The structure of mono-adduct **4** was unambiguously determined by single-crystal X-ray diffraction analysis, which revealed a slightly twisted structure, including two helicene-type structures with dihedral angles of  $1.2^{\circ}$  and  $14.4^{\circ}$  (Figure 2a). The data also showed that the packing structure of **4** within the crystal is characterized by one-dimensional  $\pi$ -stacks with

intermolecular distances of 3.2–3.7 Å, which is within the range of typical  $\pi$ -stacked structures (3.4–3.7 Å)<sup>10</sup> (Figure 2b and c). This result stands in sharp contrast to the packing structure of mono-adduct **2**, which forms a dimeric structure in a slipped fashion with a substantial offset.<sup>8</sup> This difference should be attributed to the extension of the  $\pi$ -system in **4** by the two naphthalene moieties, which may overrule the steric repulsion between the [2.2.2] bicyclic moieties and thus allow effective intermolecular  $\pi$ - $\pi$  interactions.

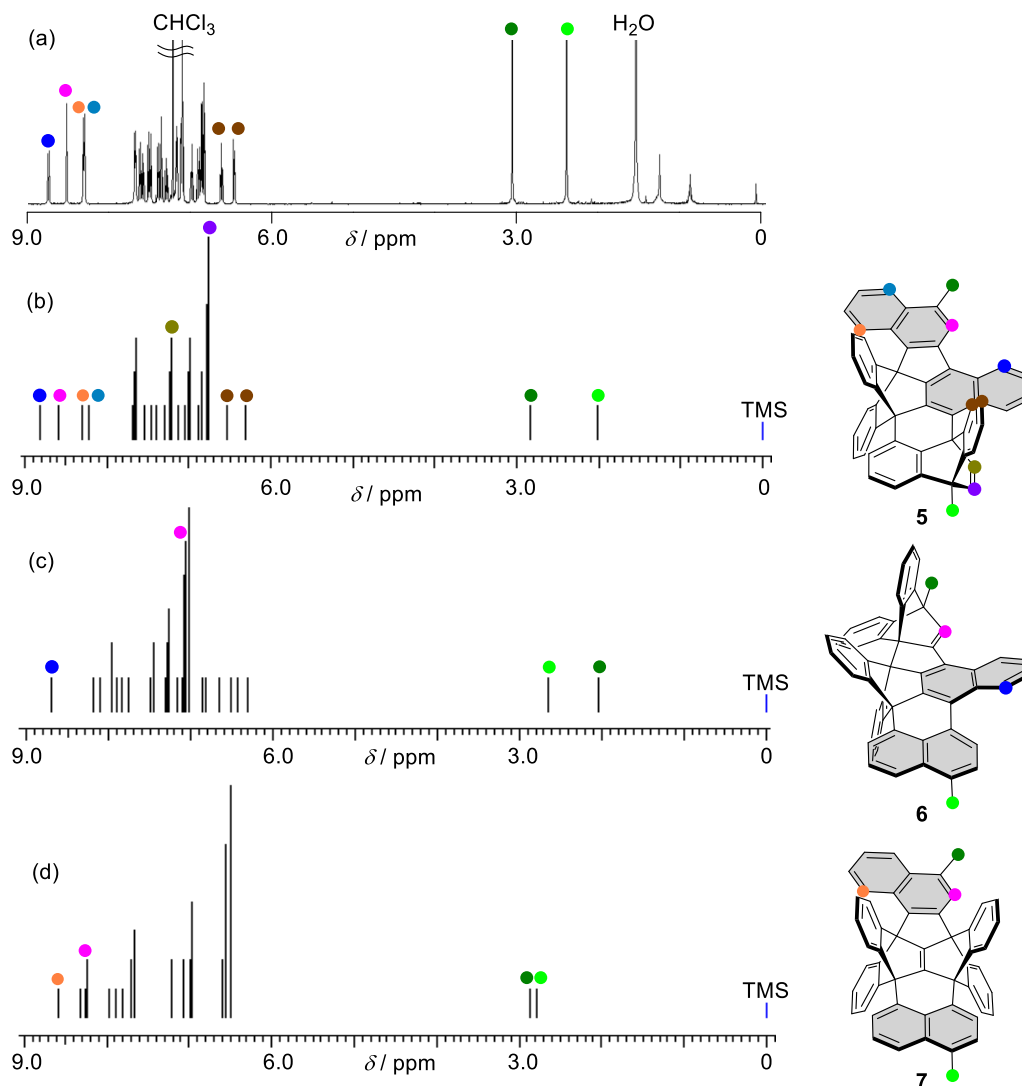


**Figure 2.** (a) X-ray crystal structure of mono-adduct **4** with dihedral angles. (b) Side view and (c) top view of the packing structure of **4** with intermolecular distances. Solvent molecules ( $\text{CHCl}_3$ ) were omitted for clarity.

## NMR Analysis

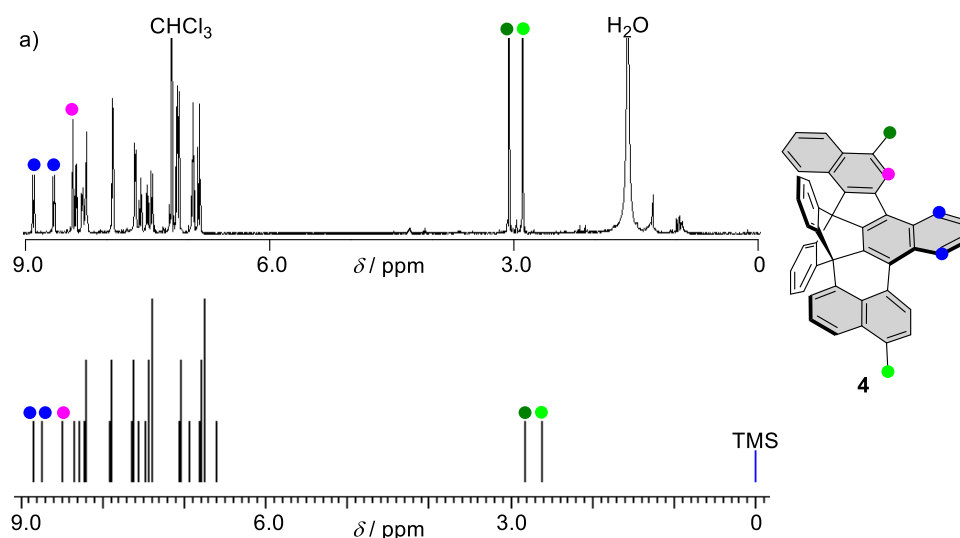
Bis-adduct **5** was characterized by a combined experimental and theoretical approaches.<sup>11</sup> Even though the  $^1\text{H}$  NMR spectrum of **5** does not exhibit any signal assignable to a methine proton in the aliphatic region, the data cannot be used to exclude the possible

formation of **6** and **7** (Figure 3c and 3d), which may be formed *via* the cycloaddition of benzyne to the hexagonal rings **B** or **C** in **4**, respectively.

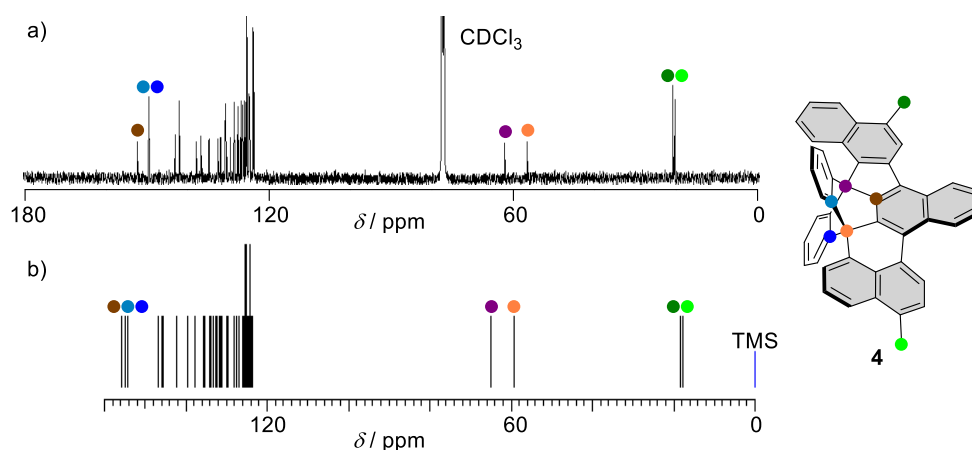


**Figure 3.** The experimentally obtained and calculated  $^1\text{H}$  NMR spectra for bis-adducts **5**, **6**, and **7**. The GIAO calculations were carried out at the B3LYP/6-311G\*\*//B3LYP/6-31G\* level of theory: (a) experimentally observed for **5**, and calculated for (b) **5**, (c) **6**, and (d) **7**.

A comparison of the experimental and calculated  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra may offer further information in this case, and we were able to confirm the validity of such a comparison by using the spectrum of **4** (Figure 4 and 5), for which the crystal structure was also determined by XRD analysis.



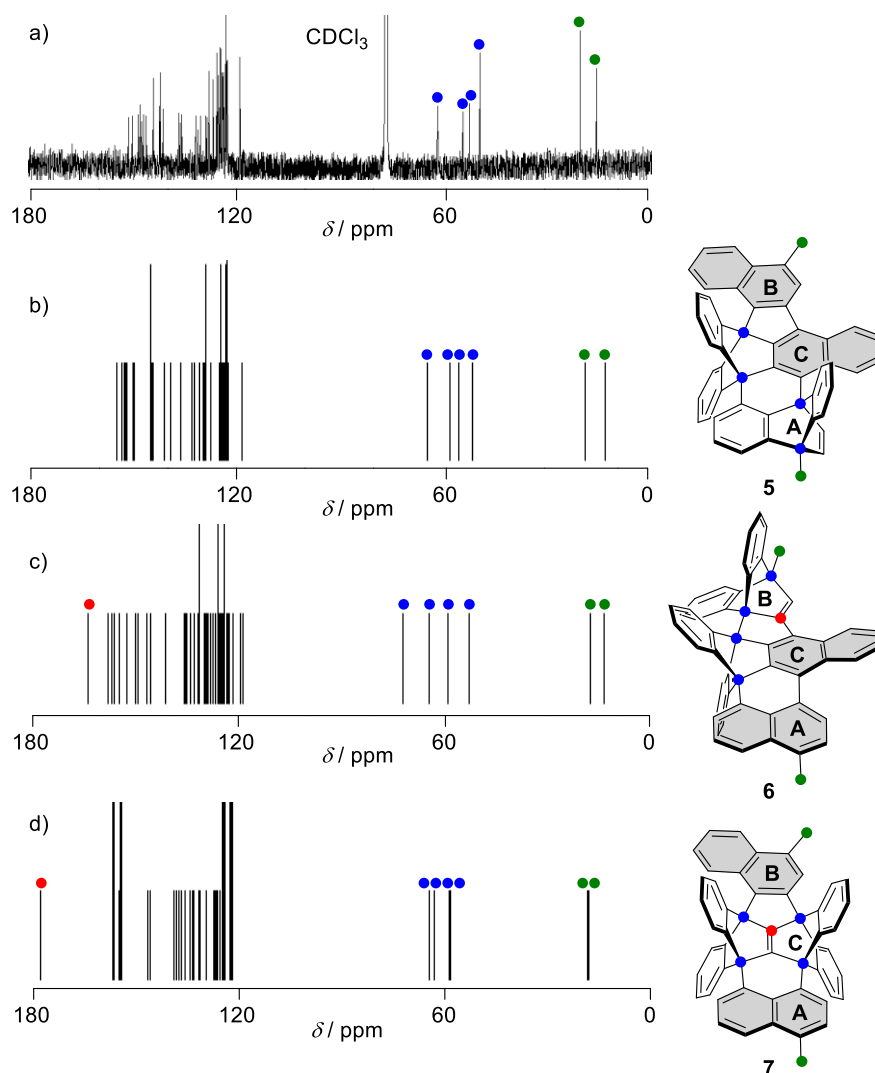
**Figure 4.** (a) Experimentally obtained and (b) calculated  $^1\text{H}$  NMR spectra for **4**. The GIAO calculations were carried out at the B3LYP/6-311G\*\*//B3LYP/6-31G\* level of theory.



**Figure 5.** (a) Experimentally obtained and (b) calculated  $^{13}\text{C}$  NMR spectra for **4**. The GIAO calculations were carried out at the B3LYP/6-311G\*\*//B3LYP/6-31G\* level of theory.

Subsequently GIAO calculations were carried out for **5**, **6**, and **7** at the B3LYP/6-311G\*\*//B3LYP/6-31G\* level of theory. As shown in Figure 6a, the experimental  $^{13}\text{C}$  NMR spectrum of **5** is characterized by two signals for the methyl groups (green dots), four signals for the quaternary  $\text{sp}^3$ -carbon atoms (blue dots), and the signals for the  $\text{sp}^2$ -carbon atoms ( $\delta = 152.22\text{--}119.47$  ppm). The corresponding calculated  $^{13}\text{C}$  NMR spectra are shown in Figure 6b-d. The best agreement between the experimental and the calculated spectra was observed for **5**,

as **6** and **7** should exhibit a characteristic signal for the  $sp^2$ -carbon atoms (red dots), which should be downfield shifted relative to the other signals of the  $sp^2$ -carbon atoms.

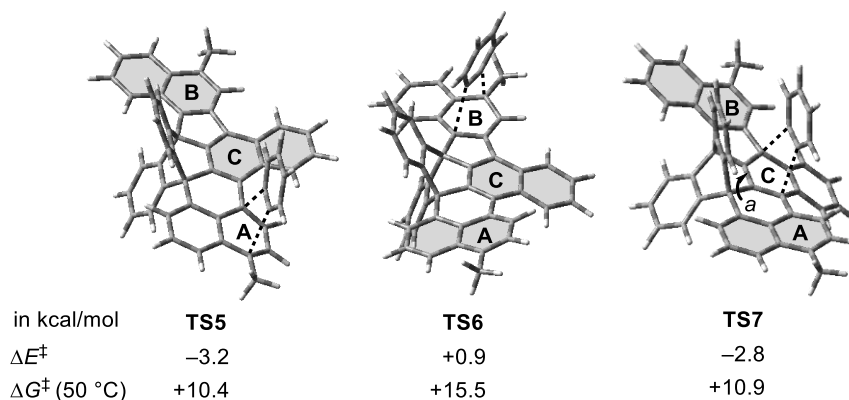


**Figure 6.** Experimentally obtained and calculated  $^{13}\text{C}$  NMR spectra for bis-adducts **5**, **6**, and **7**. GIAO calculations were carried out at the B3LYP/6-311G\*\*//B3LYP/6-31G\* level of theory: (a) experimentally observed for **5**, and calculated for (b) **5**, (c) **6**, and (d) **7**.

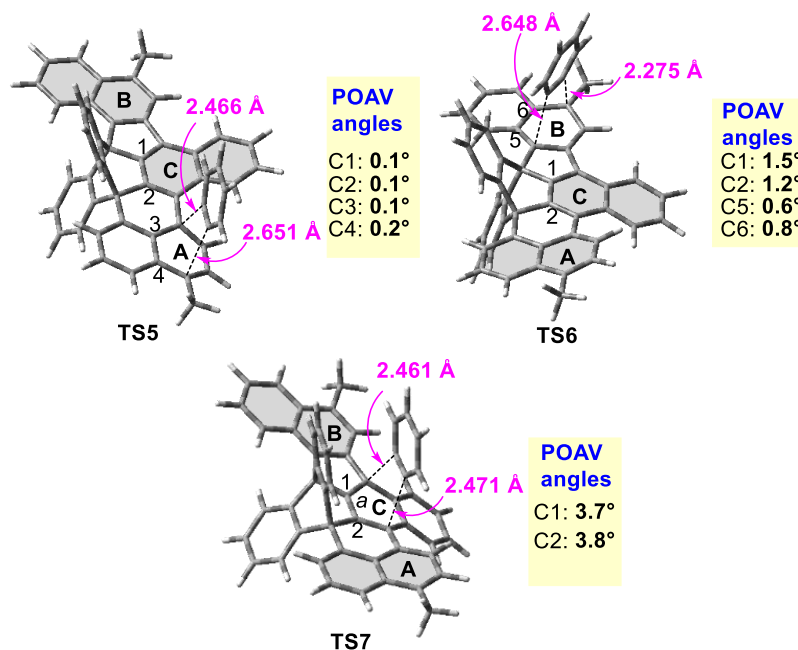
### Transition-State Calculations

In order to afford better insight into the formation of bis-adduct **5**, DFT calculations were performed at the M06-2X/6-31G\* level of theory for three pathways, *i.e.*, cycloadditions to the hexagonal rings **A**, **B**, or **C** in **4** (Figure 7). The results suggest that at  $T = 50^\circ\text{C}$ , the barrier for the formation of **5** *via* transition state **TS5** ( $\Delta G^\ddagger = +10.4$  kcal/mol) should be lower than that for the pathways leading to **6** *via* **TS6** ( $\Delta G^\ddagger = +15.5$  kcal/mol) and to **7** *via* **TS7** ( $\Delta G^\ddagger = +10.9$  kcal/mol).

kcal/mol). The pathway leading to **6** includes the highest activation barrier on account of the steric repulsion between benzyne and the triptycene moieties in **TS6** as judging from the substantial degree of asynchronicity (Figure 8). The pathway to **7** includes a slightly higher barrier than that to **5**. The difference should be attributed to the pyramidalization strain induced in bond *a* in **TS7** (Figure 8), while such a strain should not exist in **TS5**. The data consequently suggest that **5** should be formed under kinetic control, which is corroborated by the characterization of **5** (*vide supra*).



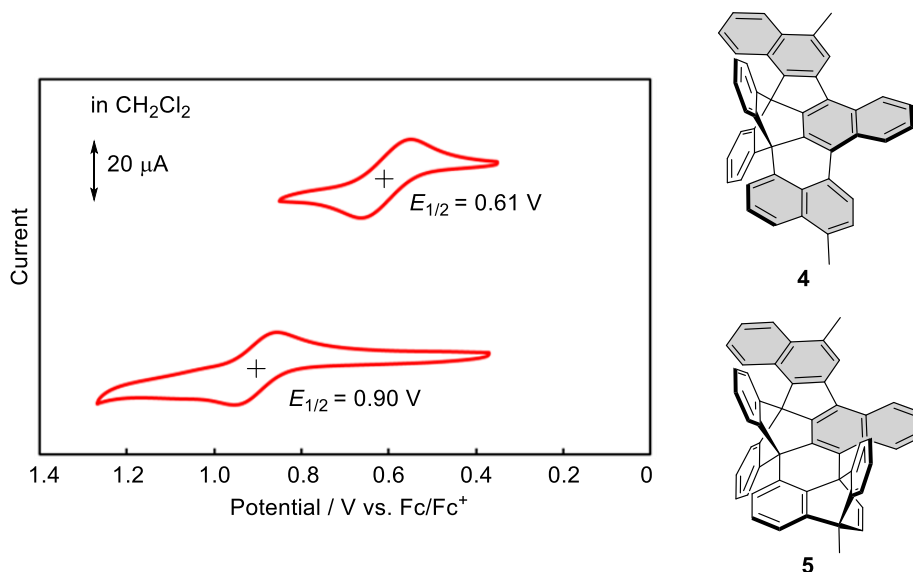
**Figure 7.** Structures of the transition-states **TS5-TS7** for the concerted [4+2] cycloaddition of benzyne with **4** as well as activation energies ( $\Delta E^\ddagger$  and  $\Delta G^\ddagger$  at 50 °C) relative to the sum of the corresponding energies for **4** and benzyne (M06-2X/6-31G\*).



**Figure 8.** Structures of transition-states **TS5-TS7** with selected distances and p-orbital axis vector (POAV) angles (M06-2X/6-31G\*).

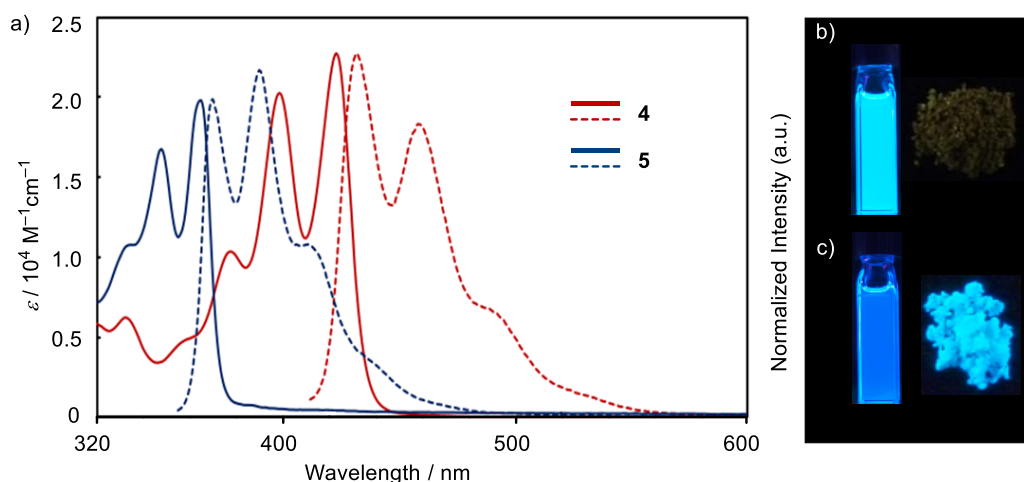
## Electrochemical and Photophysical Properties

In order to elucidate the electronic properties, cyclic voltammograms as well as absorption and emission spectra were measured for **4** and **5**. In the oxidation region of the cyclic voltammograms, which were measured in CH<sub>2</sub>Cl<sub>2</sub> (Figure 9), **4** and **5** exhibited one reversible wave at  $E_{1/2} = +0.61$  V and  $+0.90$  V (vs. Fc/Fc<sup>+</sup>), respectively. In contrast, reduction waves were not observed for both compounds. The oxidation potential of **5** is positively shifted ( $\Delta E_{1/2} = +0.29$  V) with respect to that of **4** on account of the partial scission of the  $\pi$ -system.



**Figure 9.** Cyclic voltammograms of **4** and **5** in CH<sub>2</sub>Cl<sub>2</sub> (1 mM); supporting electrolyte: 0.1 M [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>]; scan rate: 100 mV s<sup>-1</sup>; internal standard: Fc/Fc<sup>+</sup>.

In toluene, **4** and **5** showed a longest-wavelength absorption band at  $\lambda_{\text{abs}} = 423$  nm and 366 nm, respectively (Figure 10a). The  $\lambda_{\text{abs}}$  value for **5** is hypsochromically shifted ( $\Delta\lambda_{\text{max}} = 57$  nm) with respect to that of **4**, indicating an increased HOMO-LUMO gap in **5**. Compounds **4** and **5** exhibited intense blue fluorescence with a maximum at  $\lambda_{\text{em}} = 432$  nm ( $\Phi_{\text{F}} = 0.69$ ,  $\tau = 2.1$  ns) and 370 nm ( $\Phi_{\text{F}} = 0.91$ ,  $\tau = 3.9$  ns), respectively. The rigidly fixed conformations of **4** and **5** most likely contribute to the very small Stokes shifts for **4** ( $\Delta\lambda = 9$  nm,  $493$  cm<sup>-1</sup>) and for **5** ( $\Delta\lambda = 4$  nm,  $295$  cm<sup>-1</sup>) as well as to their high quantum yields. As expected from the one-dimensional  $\pi$ -stacks of **4** (Figure 2b and c) in the crystalline state, crystals of **4** did not show any appreciable emission (Figure 10b), which may be attributed to aggregation-caused quenching (ACQ).<sup>12</sup> In contrast, crystalline or amorphous solids of **5** exhibited blue emission ( $\lambda_{\text{em}} = 464$  nm,  $\Phi_{\text{F}} = 0.08$ ) (Figure 10c) on account of the steric protection in **5** arising from the two [2.2.2] bicyclic moieties, which should reduce the ACQ.



**Figure 10.** UV-vis absorption spectra (solid lines) and normalized fluorescence spectra (dashed lines) for (a) **4** (red line) and **5** (blue line) in toluene. Images of toluene solutions and crystals of (b) **4** and (c) **5** upon irradiation at 365 nm ([**4**]:  $8.6 \times 10^{-6}$  M, [**5**]:  $2.5 \times 10^{-6}$  M).

## Conclusion

The author have demonstrated that a  $\pi$ -extended tetracene **3**, which contains two fused naphthalene moieties, undergoes [4+2] cycloadditions on the surface of its  $\pi$ -system to form the corresponding mono- (**4**) and bis-adducts (**5**) with one or two [2.2.2] bicyclic moieties, respectively. The structure of **5** was characterized by a combined experimental and theoretical approaches. While crystals of **4** did not show appreciable emission due to formation of one-dimensional  $\pi$ -stacks therein, **5** exhibited blue emission in the solid state on account of the steric protections arising from two [2.2.2] bicyclic moieties. The insight into the reactivity of  $\pi$ -extended tetracenes reported herein should contribute to the understanding of the chemical surface functionalization of PAHs or nanocarbon compounds based on cycloaddition reactions.

## Experimental Section

### General

Melting points (mp) were measured on a Yanaco MP-S3 instrument. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were carried out with a JEOL ECA 500 instrument or a Bruker Avance III 600US instrument. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of  $\text{CDCl}_3$  ( $\delta$  7.26 ppm in  $^1\text{H}$  NMR,  $\delta$  77.16 ppm in  $^{13}\text{C}$  NMR) and  $\text{CD}_2\text{Cl}_2$  ( $\delta$  5.32 ppm in  $^1\text{H}$  NMR,  $\delta$  53.5 ppm in  $^{13}\text{C}$  NMR). UV-vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer. Fluorescence measurements were performed with a

HORIBA FluoroMax 4P-NIR. Quantum yields were determined with a Hamamatsu Photonics Quantaaurus QY C11347 with calibrated integrating sphere system. Fluorescence lifetime measurements were performed using a Hamamatsu Photonics Quantaaurus-Tau C11367-02. APCI mass spectra were measured on a Bruker micrOTOF-Q II spectrometer. Preparative GPC was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H columns. Cyclic voltammetry (CV) was performed on a BAS ALS620A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The measurements were carried out under an argon atmosphere using a CH<sub>2</sub>Cl<sub>2</sub> solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate ((*n*-Bu)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup>) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard.

## Synthesis

### Compound 4

To a solution of **3** (16 mg, 0.032 mmol) and anthranilic acid (39 mg, 0.28 mmol) in dry benzene (10 mL) was added isoamyl nitrite (37 mg, 0.32 mmol) through a syringe, and the mixture was stirred at room temperature under argon atmosphere. After 2 hours, solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 5:1) and then GPC (CHCl<sub>3</sub>) to give compound **4** (5 mg, 8.6 μmol) as yellowish solids in 27% yield.

**4**: mp >300 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.98 (d, *J* = 7.0 Hz, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 8.49 (s, 1H), 8.45 (d, *J* = 7.5 Hz, 1H), 8.38–8.36 (m, 1H), 8.34–8.31 (m, 2H), 7.99 (d, *J* = 5.0 Hz, 2H), 7.72–7.70 (m, 2H), 7.66–7.63 (m, 1H), 7.57–7.54 (m, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.20–7.16 (m, 4H), 7.01–6.98 (m, 2H), 6.93–6.90 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 152.37, 149.50, 143.09, 141.98, 137.82, 136.64, 134.72, 134.62, 132.58, 131.93, 131.84, 130.78, 130.66, 130.35, 129.53, 128.51, 127.79, 127.59, 126.84, 126.47, 126.02, 125.80, 125.62, 125.49, 125.41, 125.35, 125.22, 124.96, 124.84, 124.79, 123.93, 123.85, 123.69, 62.08, 56.48, 20.72, 20.25 (three sp<sup>2</sup> signals were overlapped with other signal); HRMS (+APCI): [M+H]<sup>+</sup> calcd. for C<sub>46</sub>H<sub>29</sub> 581.2264, found 581.2248.

## Compound 5

To a solution of **3** (50 mg, 0.10 mmol) and anthranilic acid (137 mg, 1.00 mmol) in dry benzene (25 mL) was added isoamyl nitrite (115 mg, 0.98 mmol) through a syringe, and the mixture was stirred at 50 °C under argon atmosphere. After 3 hours, solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 5:1) and then GPC (CHCl<sub>3</sub>) to give compounds **5** (14 mg, 0.021 mmol) and **4** (4 mg, 7.1 μmol) as colorless and yellowish solids in 21% and 7% yield, respectively.

**5**: mp > 300 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.57 (s, 1H), 8.36–8.35 (m, 2H), 7.74–7.70 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.64–7.61 (m, 1H), 7.57–7.53 (m, 2H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.42–7.39 (m, 1H), 7.35–7.32 (m, 1H), 7.22–7.20 (m, 2H), 7.16–7.13 (m, 3H), 7.04–7.01 (m, 1H), 6.97–6.87 (m, 5H), 6.67–6.64 (m, 1H), 6.50 (d, *J* = 7.0 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 152.22, 150.96, 149.23, 148.64, 148.36, 147.85, 146.91, 144.97, 143.20, 142.91, 142.15, 142.05, 137.45, 137.14, 136.63, 132.53, 131.28, 129.68, 129.32, 128.80, 128.68, 127.52, 126.43, 126.09, 125.58, 125.39, 125.31, 125.22, 124.84, 124.74, 124.46, 124.04, 123.87, 123.66, 123.54, 123.46, 122.36, 119.84, 119.74, 62.33, 54.93, 52.89, 49.95, 20.77, 16.05 (seven sp<sup>2</sup> signals were overlapped with other signal); HRMS (+APCI): [M+H]<sup>+</sup> calcd. for C<sub>52</sub>H<sub>33</sub> 657.2577, found 657.2571.

## Computational Method

DFT calculations for optimizations and transition state were conducted using the Gaussian 09 program.<sup>11</sup>

## X-Ray Crystal Structure Analysis

**Compound 4**: Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 7719 reflections were measured at the maximum 2θ angle of 50.0°, of which 5568 were independent reflections (*R*<sub>int</sub> = 0.0386). The structure was solved by direct methods (SHELXS-97<sup>13</sup>) and refined by the full-matrix least-squares on *F*<sup>2</sup> (SHELXL-97<sup>13</sup>). Chloroform molecule C47-H47-Cl1-Cl2-Cl3 was disordered, which was solved using appropriate models. Thus, two sets of chloroform molecules, i.e., (C47A-H47A-Cl1A-Cl2A-Cl3A) and (C47B-H47B-Cl1B-Cl2B-Cl3B) were placed and their occupancies were refined to

be 0.71 and 0.29, respectively. All non-hydrogen atoms, except for chloroform molecule (C47B-H47B-Cl1B-Cl2B-Cl3B), were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>47</sub>H<sub>29</sub>Cl<sub>3</sub>; FW = 700.05, crystal size 0.04 × 0.02 × 0.02 mm<sup>3</sup>, Triclinic, *P*-1, *a* = 12.179(6) Å, *b* = 12.893(6) Å, *c* = 12.970(6) Å,  $\alpha$  = 62.588(6)°,  $\beta$  = 64.686(7)°,  $\gamma$  = 73.463(6)°, *V* = 1624.5(13) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.431 g cm<sup>-3</sup>. The refinement converged to *R*<sub>1</sub> = 0.0927, *wR*<sub>2</sub> = 0.2438 (*I* > 2σ(*I*)), GOF = 1.018.

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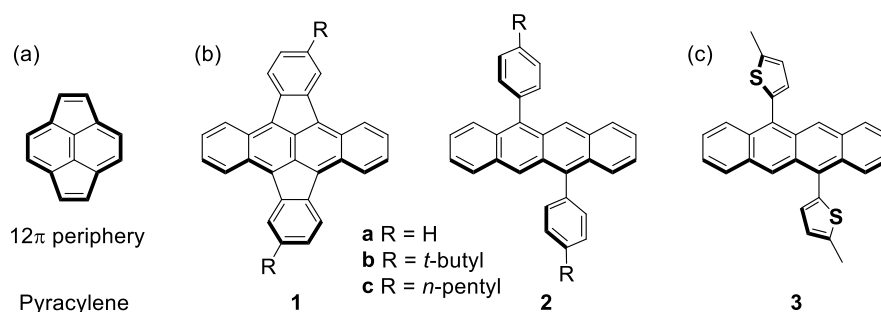
### **Dithieno-Fused Polycyclic Aromatic Hydrocarbon with a Pyracylene Moiety: Strong Antiaromatic Contribution to the Electronic Structure**

#### **Abstract**

Even though polycyclic aromatic hydrocarbons containing fully unsaturated pentagonal ring(s) (CP-PAHs) have attracted substantial interest due to their perturbed electronic properties, their aromatic characters have received less attention than that of PAHs. In this chapter, the author presents a synthetic route to dithieno-fused CP-PAHs with a pyracylene segment based on a twofold Scholl cyclization. A combination of experimental and theoretical studies revealed a strong contribution of antiaromatic character to the electronic structure of this dithieno-fused CP-PAH. Anisotropy of current-induced density (ACID) calculations indicated a significantly increased paramagnetic ring current on the two pentagonal rings, which is more prominent than that of the dibenzo-fused analogue. Furthermore, enhanced electron-affinity and a consequently decreased HOMO-LUMO gap were observed for this dithieno-fused CP-PAH.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) with fully unsaturated pentagonal ring(s), the so-called cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs), have attracted substantial interest on account of their unusual properties, which include high electron affinity<sup>1</sup> and reactivity,<sup>2</sup> as well as due to their applications in materials science.<sup>3</sup> Particularly, cyclopentadiene- or indene-fused structures have been generated on the periphery of a variety of  $\pi$ -skeletons, which include not only PAHs such as acenes,<sup>4</sup> pyrene,<sup>5</sup> and corannulene,<sup>6</sup> but also porphyrins.<sup>7</sup> Such modifications induce significant perturbations of the electronic structure of the  $\pi$ -system and consequently the aromatic character. However, the change of the aromatic character of CP-PAHs has not been examined<sup>8</sup> as thoroughly as that of PAHs. Recently, Matsuo and co-workers have reported that the introduction of one thieno-fused moiety *via* a pentagonal ring on the periphery of a porphyrin derivative enhances the antiaromatic contribution to the electronic structure of the resulting  $\pi$ -extended porphyrin.<sup>7a</sup>



**Figure 1.** Chemical structures of (a) pyracylene, (b) previously reported CP-PAHs **1**,<sup>10</sup> which were obtained from a twofold Scholl cyclization of precursor **2**, and (c) 5,11-dithienyltetracene **3**.

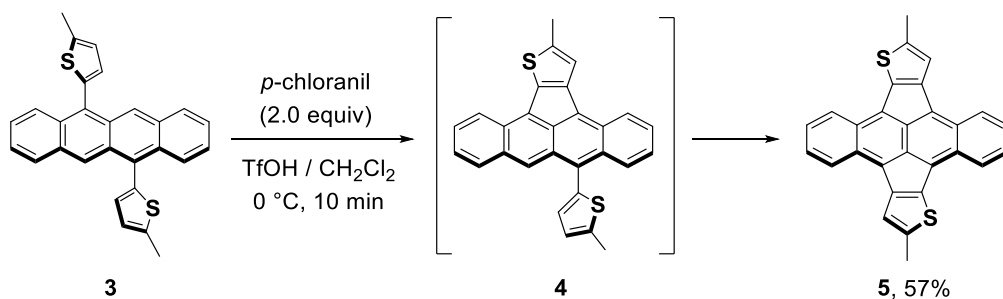
Among the reported CP-PAHs, pyracylene exhibits a considerable antiaromatic contribution to its electronic structure, as well as a high electron affinity based on its 12 $\pi$ -electron framework (Figure 1a).<sup>9</sup> The author has discussed in chapter 1 that tetrabenzo-fused pyracylene (TBP) **1** can be obtained from an efficient twofold Scholl cyclization of 5,11-diphenyltetracene **2** (Figure 1b).<sup>10</sup> TBP **1** exhibited an electron-deficient character, which can be attributed to the contribution from the pyracylene segment. During the study on the electronic properties and aromaticity of CP-PAHs, the author conducted a twofold Scholl cyclization of 5,11-dithienyltetracene **3** (Figure 1c). Although there are, to the best of our knowledge, no reports on a Scholl cyclization that realizes a thieno-fusion *via* a fully unsaturated pentagonal ring, the symmetric Scholl cyclizations of **3** proceeded to afford dithieno-fused CP-PAH (*i.e.*, **5**), which contains a pyracylene segment. Herein, the author

present the synthesis and structural characterization of **5**, as well as experimental and theoretical studies on its aromaticity. The obtained data indicate a distinct antiaromatic contribution to its electronic structure and an electron affinity that is higher than that of **1**.

## Results and Discussion

### Synthesis

In this chapter, 5,11-dithienyltetracene **3** was used as a precursor, because the introduction of a methyl group in each thienyl group effectively suppressed polymerization. Following our previous report for the synthesis of **1**,<sup>10</sup> initially FeCl<sub>3</sub> was attempted for the Scholl reaction of **3** as an oxidant, but this reactions only afforded insoluble black solids. When the dichlorodicyano-*p*-benzoquinone (DDQ)/TfOH system was used, symmetrically cyclized **5** could be isolated in 22% yield. Using *p*-chloranil/TfOH system, i.e. milder oxidation conditions, furnished **5** in improved yield (57%) (Scheme 1). Upon reducing the amount of oxidant, mono-cyclized **4** was obtained in 53% yield. It is noteworthy here that fusion of a thiophene ring *via* a fully unsaturated pentagonal ring by the Scholl reaction is unprecedented.<sup>11</sup> For that purpose, Pd-catalyzed cyclizations have been used so far.<sup>2c,7a</sup>

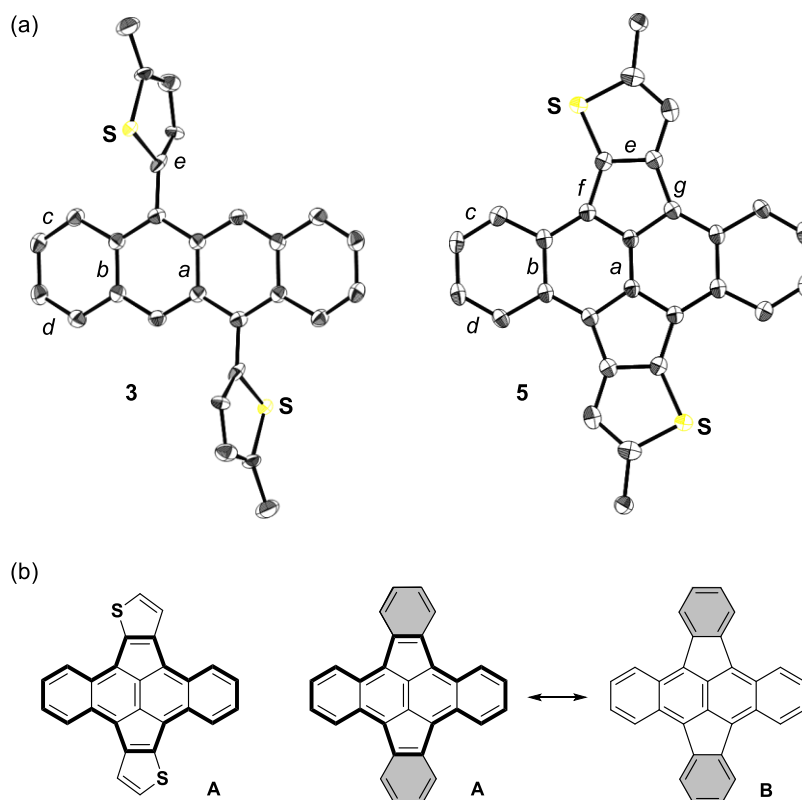


**Scheme 1.** Twofold Scholl Cyclization of 5,11-Dithienyltetracene **3**

### X-Ray Crystal Structures

The molecular structures of **3** and **5** were unambiguously determined by single-crystal X-ray diffraction analyses (Figure 2a). The obtained data show that the twofold cyclization induces significant bond length alterations. Particularly, the interior bond *a* in **5** [1.362(5) Å] is substantially shorter than those of **3** [1.445(2) Å] and **1b** [1.381(3) Å],<sup>10</sup> and comparable to that of pyracylene [1.360(3) Å],<sup>12</sup> which indicates a localized double bond character for bond *a* in **5**. Moreover, bond *b* in **5** [1.477(4) Å] is elongated with respect to that in **3** [1.4399(18) Å], and comparable to that in **1b** [1.474(2) Å].<sup>10</sup> It should be noted that bond *e* in **5** [1.398(3) Å] is considerably shorter than that in **1b**

[1.438(2) Å],<sup>10</sup> which reflects the 2,3-thieno-fused structure. These data indicate that in **5**, contributions from resonance structure **A** with a  $20\pi$ -antiaromatic periphery should predominate (Figure 2b). This stands in sharp contrast to the structural features of **1**, in which contributions from **B** predominate.<sup>10</sup> Consequently, **5** should contain a higher degree of antiaromatic contributions relative to **1**.

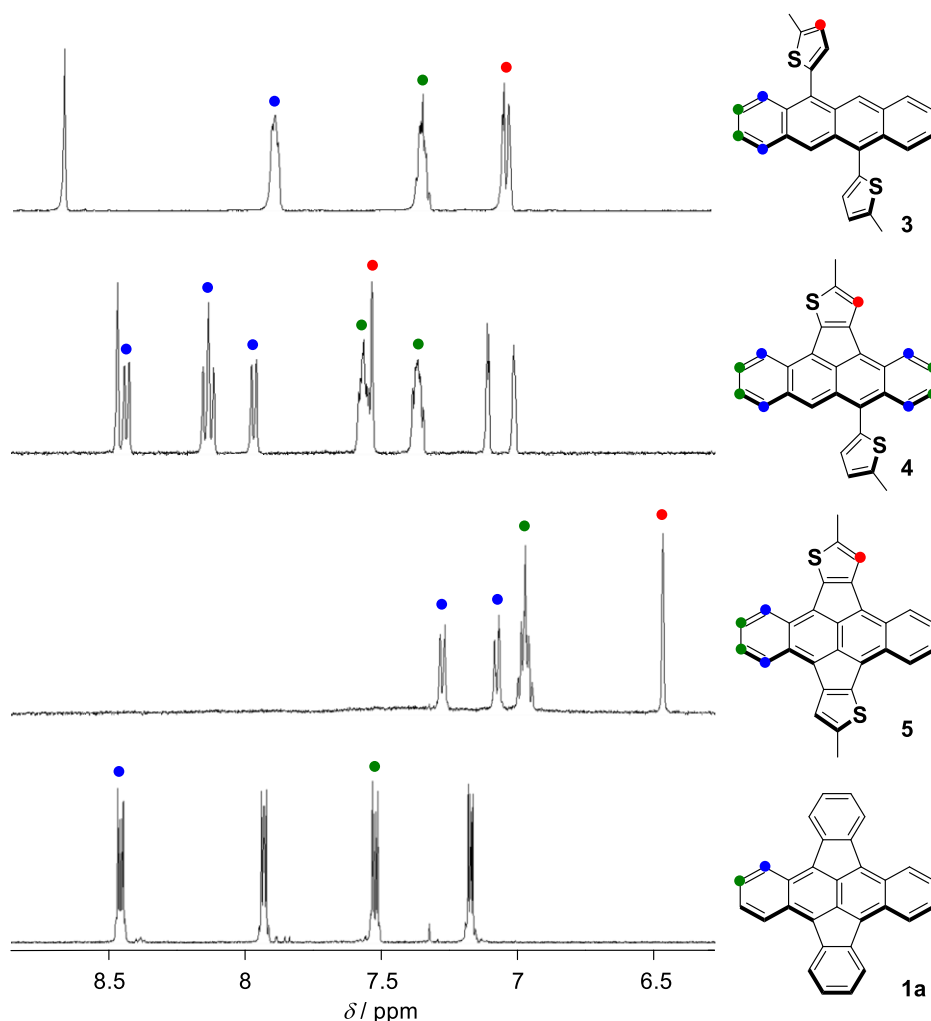


**Figure 2.** X-ray crystal structures of (a) **3** and **5**. (b) Selected resonance structures for the  $\pi$ -framework of **5** and **1**. Selected bond lengths [Å] for **3**: *a* 1.445(2); *b* 1.4399(18); *c* 1.3592(19); *d* 1.3549(19); *e* 1.410(7). Selected bond lengths [Å] for **5**: *a* 1.362(5); *b* 1.477(4); *c* 1.363(4); *d* 1.360(3); *e* 1.398(3); *f* 1.473(3); *g* 1.482(4).

### <sup>1</sup>H NMR Properties

This notion is also consistent with the <sup>1</sup>H NMR spectra of **3**, **4**, **5**, and **1a**,<sup>10</sup> measured in CD<sub>2</sub>Cl<sub>2</sub> (Figure 3). The observed signals were assigned based on DFT calculations<sup>13</sup> at the GIAO-B3LYP/6-311G\*\*//B3LYP/6-31G\* level of theory. A comparison of the data for **3–5** revealed that signals associated with the aromatic protons shift upfield after the second cyclization, while such a trend was not observed after the first cyclization. For example, the singlet signal for the fused thiophene rings in **5**, marked with a red dot in Figure 3, is upfield shifted ( $\Delta\delta = 1.1$  ppm) compared to that in **4**. The aromatic signals of **5** are shifted upfield even compared to those of **1a**, which

reflects the substantially decreased aromaticity of **5**. In particular, protons of **5** that are located in the close vicinity of the pentagonal rings (marked with blue dots) exhibit more pronounced upfield shifts ( $\Delta\delta = 1.4$  and 1.2 ppm) than those marked with green dots in **5** ( $\Delta\delta = 0.5$  ppm) with respect to those in **1a**. This result implies that, compared to **1a**, the dithieno-fused structure in **5** induces a strong paramagnetic ring current in the two pentagonal rings.

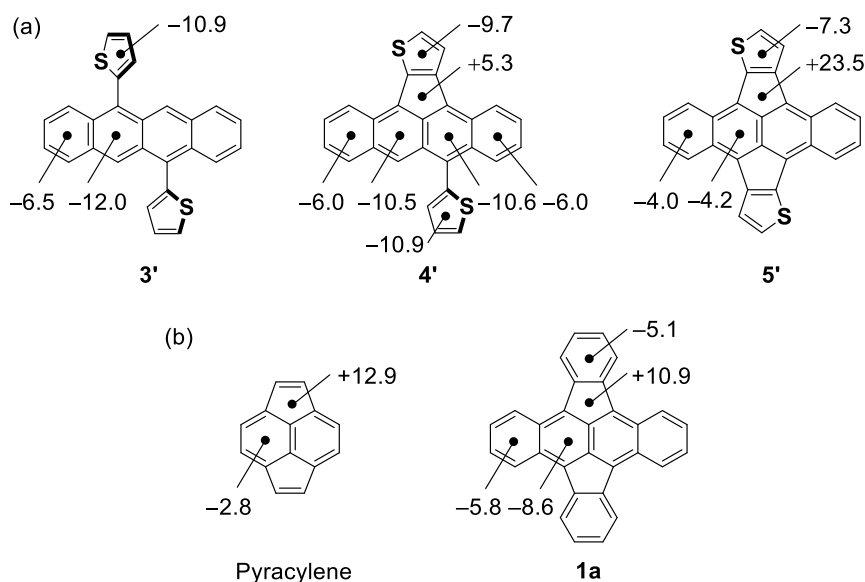


**Figure 3.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **3**, **4**, **5**, and **1a**.<sup>10</sup> Red, blue, and green dots indicate the assignment of the corresponding proton signals.

### DFT Calculations

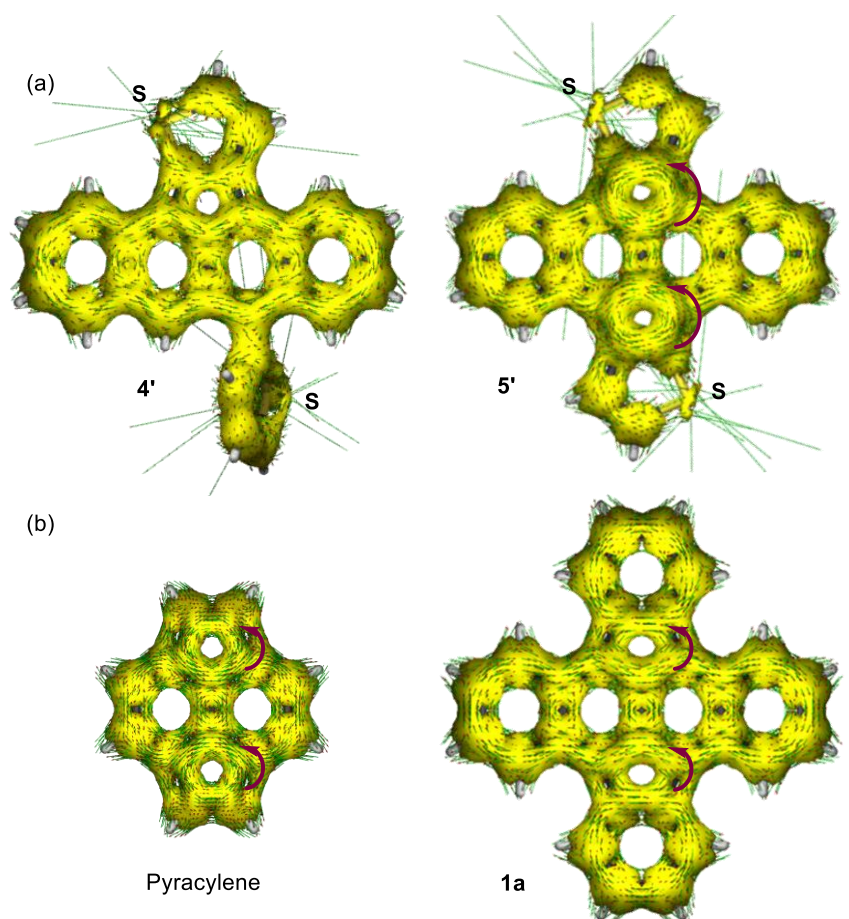
In order to obtain a better insight into their aromatic character, nucleus-independent chemical shifts (NICS)<sup>14</sup> were calculated for model structures **3'**–**5'**, in which the methyl groups were replaced with hydrogen atoms (Figure 4a). Even though the changes in the NICS(0) values after the first cyclization are small, both the negative values for the hexagonal rings and the positive value for the two pentagonal rings

become more positive in **5'**, with respect to those in **4'** after the second cyclization. The increase of the positive value at the two pentagonal rings in **5'** (+23.8) is particularly interesting, as it is indicative of a strong antiaromatic contribution to the electronic structure. It should also be noted that the value for the pentagonal rings in **5'** is much higher than the corresponding value in **1a** (+10.9)<sup>10</sup> and pyracylene (+12.9)<sup>10</sup> (Figure 4b).



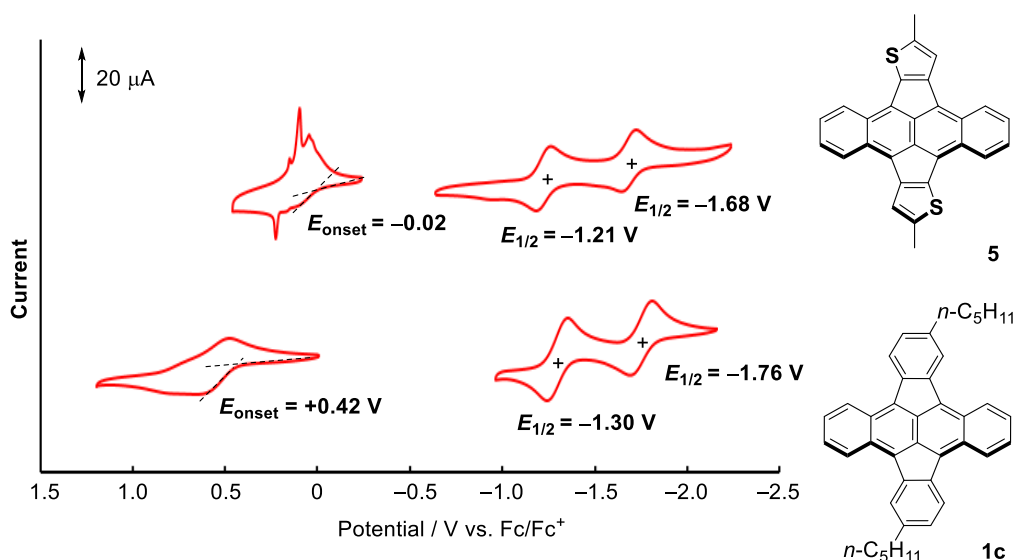
**Figure 4.** NICS (0) values for (a) model compounds **3'**–**5'**, and (b) pyracylene as well as **1a** (values calculated at the HF/6-311+G\*\*//B3LYP/6-31G\* level of theory).

Subsequently, calculated the anisotropy of current-induced density (ACID)<sup>15</sup> was calculated (Figure 5). ACID plots illustrate diamagnetic and paramagnetic ring currents as clockwise and counter-clockwise ring currents, respectively. When the ACID plots for **4'** and **5'** with one and two pentagonal rings, respectively, are compared, counter-clockwise paramagnetic ring currents are evident on the two pentagonal rings in **5'**, while such a current is virtually absent in the pentagonal ring in **4'** (Figure 5a). Similar counter-clockwise ring currents were obtained for the two pentagonal rings in pyracylene and **1a** (Figure 5b), although they are not as pronounced as those in **5'**. The results for **5'** suggest a strong antiaromatic contribution to the electronic structure, and thus corroborate the experimental and theoretical results, i.e. the upfield shifts of the <sup>1</sup>H NMR signals and positively increased NICS(0) values in the two pentagonal rings for **5** relative to those of **1a**.<sup>10</sup>



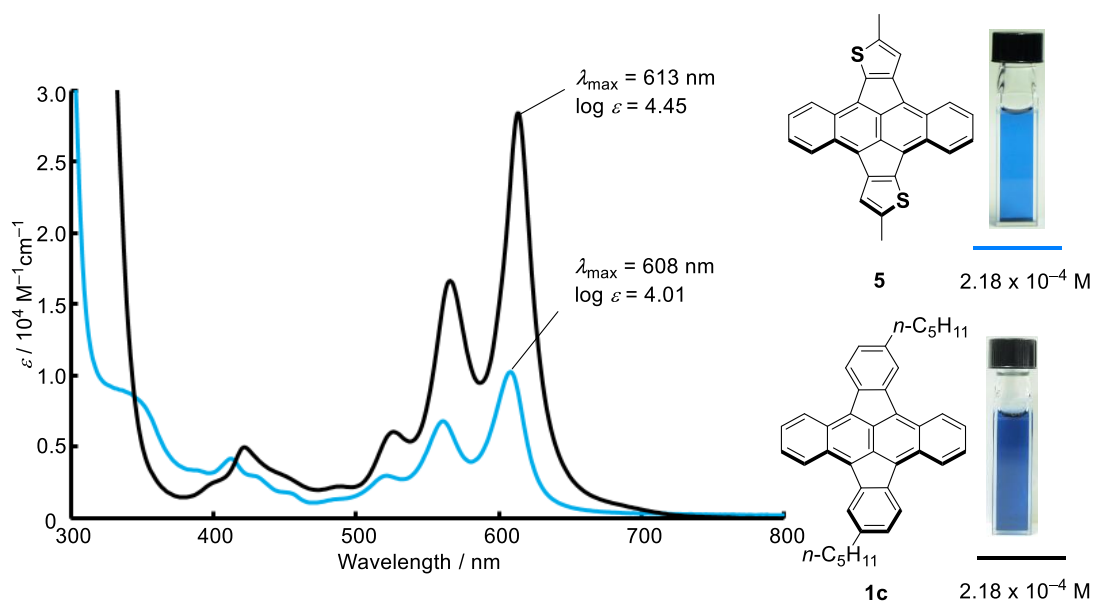
**Figure 5.** ACID plots for (a) **4'** and **5'**, and (b) pyracylene and **1a** (HF/6-311+G\*\*//B3LYP/6-31G\*).

In order to elucidate the electronic properties, cyclic voltammograms were measured for **5**, together with those for **1c** for comparison (Figure 6). In the oxidation region, **5** exhibited an irreversible wave ( $E_{\text{onset}} = -0.02$  V vs. Fc/Fc<sup>+</sup>), which is negatively shifted ( $\Delta E_{\text{onset}} = 0.44$  V) with respect to that of **1c** ( $E_{\text{onset}} = +0.42$  V).<sup>10</sup> This difference was largely ascribed to the dithieno-fused structure. The shape of the oxidation wave of **5** was broad, but reproducible for several cycles in the range of +0.5 to -1.5 V, which is similar to the behavior of **1**,<sup>10</sup> and thus indicative of aggregation. In the reduction region, **5** exhibited two reversible reduction waves ( $E_{1/2} = -1.21$  and  $-1.68$  V). The first reduction potential of **5** is shifted to more positive values ( $\Delta E_{1/2} = 0.09$  V) compared to that of **1c** ( $E_{1/2} = -1.30$  V), indicating that the electron affinity of **5** is higher than that of **1c**. The strong antiaromatic contribution in **5** can be attributed to the change in electron affinity, which overrules the effect of two electron-rich thiophene rings.



**Figure 6.** Cyclic voltammograms of **5** and **1c** in  $\text{CH}_2\text{Cl}_2$  (1 mM); supporting electrolyte: 0.1 M  $[(n\text{-Bu})_4\text{N}][\text{PF}_6]$ ; scan rate:  $100 \text{ mV s}^{-1}$ ; internal standard:  $\text{Fc}/\text{Fc}^+$ .

The absorption spectrum of **5** showed the longest-wavelength absorption at  $\lambda_{\text{max}} = 608 \text{ nm}$  ( $\log \varepsilon = 4.01$ ), which is similar to that of **1c** ( $\lambda_{\text{max}} = 613 \text{ nm}$ ,  $\log \varepsilon = 4.45$ ) (Figure 7), even though **5** should possess a narrower HOMO-LUMO gap than **1c**. TD-DFT calculations on **1c** and **5** at the CAM-B3LYP/6-31G\*\*/B3LYP/6-31G\* level of theory suggested that the transition with a predominant contribution from the HOMO $\rightarrow$ LUMO is forbidden in **5**, while it is allowed in **1c**. Thus, the observed absorption band for **5** should be assigned to a  $\pi\text{-}\pi^*$  transition with a major contribution from the HOMO-1 $\rightarrow$ LUMO, which is consistent with the similar  $\lambda_{\text{max}}$  values observed for **1c** and **5**.



**Figure 7.** UV-vis-NIR absorption spectra of **5** (red) and **1c** (blue) in toluene with their pictures.

## Conclusion

The author have synthesized a dithieno-fused CP-PAH (**5**) that contains a pyracylene moiety *via* the symmetric twofold Scholl cyclization of 5,11-dithienyltetracene (**3**). A single-crystal X-ray diffraction analysis of **5** revealed distinct structural similarity to pyracylene on account of the introduction of two thieno-fused structures. Based on the experimental and theoretical results, **5** exhibits a strong contribution of antiaromatic character to its electronic structure. ACID calculations for **5** indicate substantially increased paramagnetic ring currents on the two pentagonal rings, which are more prominent than those in tetrabenzofused pyracylene (**1**). Thiophene-fused **5** exhibited an enhanced electron affinity and thus a decreased HOMO-LUMO gap compared to **1**.

## Experimental Section

### General

Melting points (mp) were measured on a Yanaco MP-S3 instrument. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were carried out with a JEOL ECA 500 instrument or a Bruker Avance III 600US instrument. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of  $\text{CDCl}_3$  ( $\delta$  7.26 ppm in  $^1\text{H}$  NMR,  $\delta$  77.16 ppm in  $^{13}\text{C}$  NMR) and  $\text{CD}_2\text{Cl}_2$  ( $\delta$  5.32 ppm in  $^1\text{H}$  NMR,  $\delta$  53.5 ppm in  $^{13}\text{C}$  NMR). UV-vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer. APCI mass spectra were measured on a Bruker micrOTOF-Q II spectrometer. Cyclic voltammetry (CV) was performed on a BAS ALS620A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an  $\text{Ag}/\text{AgNO}_3$  reference electrode. The measurements were carried out under an argon atmosphere using a  $\text{CH}_2\text{Cl}_2$  solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate ( $(n\text{-Bu})_4\text{N}^+\text{PF}_6^-$ ) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. All reactions were carried out under an argon atmosphere.

## Synthesis

### 5,11-dibromotetracene

5,11-Dibromotetracene was prepared according to the literature.<sup>21</sup>

### 5,11-Dithienyltetracene 3

**3:** To a mixture of 5,11-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetracene (47 mg, 0.10 mmol), 2-bromo-5-methylthiophene (53 mg, 0.29 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (4 mg, 4 μmol), Sphos (5 mg, 12 μmol) and K<sub>3</sub>PO<sub>4</sub> (152 mg, 0.59 mmol) were added degassed toluene (1.0 mL) and distilled water (0.10 mL) in a Schlenk tube and the solution was stirred at 110 °C for 5 h. After cooling to room temperature, to the resulting mixture was added distilled water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layer was washed with brine. After drying with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. Then, the crude product was purified by silica gel column chromatography using *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> (5:1) as an eluent. The solvent was evaporated to give **3** (20 mg, 0.048 mmol) in 48% yield as a yellow solid.

**3:** mp > 300 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.67 (s, 2H), 7.92–7.90 (m, 4H), 7.36–7.32 (m, 4H), 7.05 (d, *J* = 3.5 Hz, 2H), 7.02–7.01 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 141.48, 136.82, 131.41, 131.25, 130.37, 129.79, 129.24, 129.14, 127.12, 126.67, 125.96, 125.54, 125.06, 15.70; HRMS (+APCI): [M+H]<sup>+</sup> calcd. for C<sub>28</sub>H<sub>21</sub>S<sub>2</sub> 421.1079, found 421.1062.

### Compound 4

**4:** A mixture of 5,11-dithienyltetracene derivative **3** (42 mg, 0.10 mmol) and *p*-chloranil (25 mg, 0.10 mmol) was dissolved in dry dichloromethane (10 mL) in a 50 mL two-necked flask. TfOH (0.10 mL) was injected through a syringe. The solution was stirred at 0 °C for 10 min under argon and quenched by excessive hydrazine. The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layer was washed with brine. After drying with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated. Then, the crude product was purified by silica gel column chromatography using *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> (5:1) as an eluent. The solvent was evaporated to give **4** (22 mg, 0.053 mmol) in 53% yield as a deep purple solid.

**4:** mp 231–232 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.49 (s, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.18–8.14 (m, 2H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.61–7.57 (m, 2H), 7.56 (s, 1H), 7.41–7.37 (m, 2H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.04–7.03 (m, 1H), 2.75 (s, 3H), 2.69 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 143.80, 143.72, 141.96, 137.50, 135.67, 134.27, 133.30, 131.40, 130.88,

130.70, 130.45, 129.79, 128.68, 128.35, 128.15, 127.43, 127.39, 127.16, 126.93, 126.55, 125.41, 125.12, 124.98, 124.94, 120.28, 16.63, 15.63 (one  $sp^2$  signal was overlapped with other signal); HRMS (+APCI):  $[M+H]^+$  calcd. for  $C_{28}H_{19}S_2$  419.0923, found 419.0914.

## Compound 5

**5:** A mixture of 5,11-dithienyltetracene derivative **3** (42 mg, 0.10 mmol) and *p*-chloranil (49 mg, 0.20 mmol) was dissolved in dry dichloromethane (10 mL) in a 50 mL 2-necked flask. TfOH (0.10 mL) was injected through a syringe. The solution was stirred at 0 °C for 10 min under argon and quenched by excessive hydrazine. The solvent was evaporated and the product was further washed by water, methanol and acetone. Then the product was dried under vacuum to give **5** (24 mg, 0.057 mmol) in 57% yield as a dark blue solid.

**5:** mp > 300 °C;  $^1H$  NMR (500 MHz,  $CS_2$ - $CD_2Cl_2$  (5:1)):  $\delta$  7.31–7.29 (m, 2H), 7.11–7.09 (m, 2H), 7.02–6.97 (m, 4H), 6.50 (s, 2H), 2.40 (s, 6H); HRMS (+APCI):  $[M+H]^+$  calcd. for  $C_{28}H_{17}S_2$  417.0766, found 417.0778. We could not observe  $^{13}C$  NMR signals of **5** likely due to severe broadening caused by the aggregation.

## Computational Method

DFT calculations for optimizations, NICS, ACID, and TD-DFT were conducted using the Gaussian 09 program.<sup>13</sup>

## X-Ray Crystal Structure Analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1523048 (**3**) and CCDC-1523049 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Compound 3:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 4977 reflections were measured at the maximum  $2\theta$  angle of 50.0°, of which 1896 were independent reflections ( $R_{int} = 0.0266$ ). The structure was solved by direct methods (SHELXS-97<sup>17</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>17</sup>).

5-Methylthienyl group C10-C11-C12-C13-S1-C14 was disordered, which was solved using appropriate models. Thus, two sets of 5-Methylthienyl groups, i.e. (C10A-C11A-C12A-C13A-S1A-C14A) and (C10B-C11B-C12B-C13B-S1B-C14B) were placed and their occupancies were refined to be 0.61 and 0.39, respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>28</sub>H<sub>20</sub>S<sub>2</sub>; FW = 420.56, crystal size 0.25 × 0.20 × 0.20 mm<sup>3</sup>, Monoclinic, C2/c, *a* = 20.153(3) Å, *b* = 7.6811(12) Å, *c* = 14.612(2) Å, β = 107.931(2)°, *V* = 2152.1(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.298 g cm<sup>-3</sup>. The refinement converged to *R*<sub>1</sub> = 0.0332, *wR*<sub>2</sub> = 0.0838 (*I* > 2σ(*I*)), GOF = 1.051.

**Compound 5:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 4121 reflections were measured at the maximum 2θ angle of 50.1°, of which 1645 were independent reflections (*R*<sub>int</sub> = 0.0325). The structure was solved by direct methods (SHELXS-97<sup>17</sup>) and refined by the full-matrix least-squares on *F*<sup>2</sup> (SHELXL-97<sup>17</sup>). The fused thiophene moiety C10-C11-C12-C13-S1-C14 was disordered, which was solved using appropriate models. Thus, two sets of the fused thiophene moieties, i.e. (C10-C11-C12A-C13-S1A-C14A) and (C10-C11-C12B-C13-S1B-C14B) were placed and their occupancies were refined to be 0.81 and 0.19, respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>28</sub>H<sub>16</sub>S<sub>2</sub>; FW = 416.53, crystal size 0.07 × 0.07 × 0.02 mm<sup>3</sup>, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 9.6951(15) Å, *b* = 5.6063(9) Å, *c* = 17.751(3) Å, β = 104.5642(19)°, *V* = 933.8(3) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.481 g cm<sup>-3</sup>. The refinement converged to *R*<sub>1</sub> = 0.0470, *wR*<sub>2</sub> = 0.0951 (*I* > 2σ(*I*)), GOF = 1.101.

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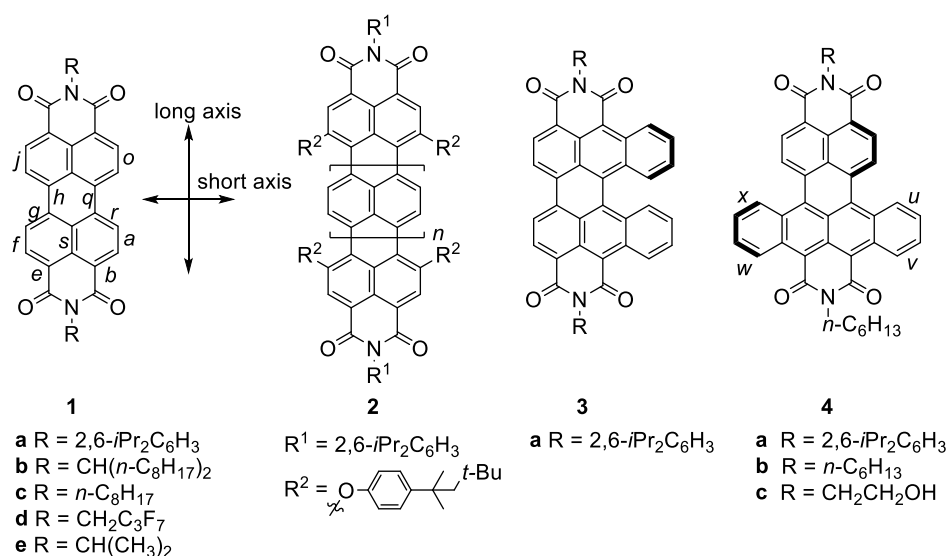
### Dibenzo[*a,f*]perylene Bisimide: Effects of Introducing Two Fused Rings

#### Abstract

Perylene bisimides (PBIs) are fascinating dyes with various potential applications. In order to study the effects of introducing dibenzo-fused structure in the perylene moiety, the author synthesized  $\pi$ -extended PBI derivatives with a dibenzo-fused structure at both of the *a* and *f* bonds. The twisted structure was characterized by X-ray crystal structure analysis. In cyclic voltammograms, the dibenzo[*a,f*]-fused PBI showed a reversible oxidation wave at much less positive potential, relative to a dibenzo[*a,o*]-fused PBI derivative. These data indicated that two ring fusions at both sides of a naphthalene core, which construct a tetracene core, effectively raise the HOMO level with reference to one ring fusion at each naphthalene core, which construct two anthracene cores. The dibenzo[*a,f*]-fused PBI derivative showed an absorption band at 735 nm with a shoulder band reaching to 900 nm.

## Introduction

Molecular systems based on perylene bisimides (PBIs) **1** (Figure 1) have been extensively investigated in the past several decades, due to their versatile optical properties, photochemical and thermal stabilities.<sup>1</sup> Recently,  $\pi$ -extended PBIs based on polycyclic aromatic hydrocarbons (PAHs) are discovered to serve as good dyes with near-infrared (NIR) absorption which show potential applications in a variety of fields such as organic field effect transistors,<sup>2</sup> artificial photosynthetic systems,<sup>3</sup> photovoltaics,<sup>4</sup> and columnar liquid crystals.<sup>5</sup>



**Figure 1.** Structures of perylene bisimides **1**, rylene bisimides **2**, dibenzo[*a,o*]-fused derivative **3**, and dibenzo[*a,f*]-fused derivatives **4**.

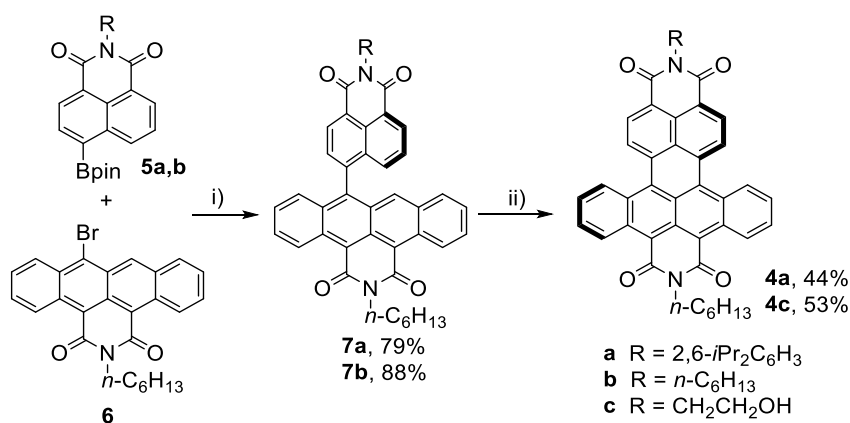
The most straightforward way to alter their photophysical properties is structural modifications of  $\pi$ -conjugated skeleton of the PBI core.<sup>6</sup> Extension of the  $\pi$ -conjugation of the PBI core along a long axis is widely studied to produce NIR dyes. The rylene bisimides derivatives with ladder-type  $\pi$ -systems **2**, such as quaterylene ( $n = 2$ ), pentarylene ( $n = 3$ ), and hexarylene ( $n = 4$ ) have been reported by Müllen and co-workers (Figure 1).<sup>7</sup> However, in this approach,  $\pi$ -conjugated system larger than that of quaterylene ( $n = 2$ ) is necessary to achieve the NIR absorption due to the relatively ineffective conjugation between the naphthalene cores. In contrast,  $\pi$ -extension along the short axis to introduce oligoacene cores larger than naphthalene should have high impacts on the electronic properties of PBIs.<sup>8</sup> For example, Wu and co-workers demonstrated that introduction of fused rings at the *a* and *o* bonds of the PBI core, which constructs two anthracene cores, can cause effective bathochromic shift of the absorption profile (compound **3**, Figure 1).<sup>9</sup> However, until today, the derivatives with a  $\pi$ -extended structure along the short axis have been limited to only a few examples.<sup>6a-c,9,10</sup> In this

chapter, in order to understand the effects of the position of introducing fused rings, the author synthesized [*a,f*]-fused derivatives **4a-c**, which have fused rings at both sides of the naphthalene core of the PBI, and discussed their structure-properties relationships.

## Results and Discussion

### Synthesis

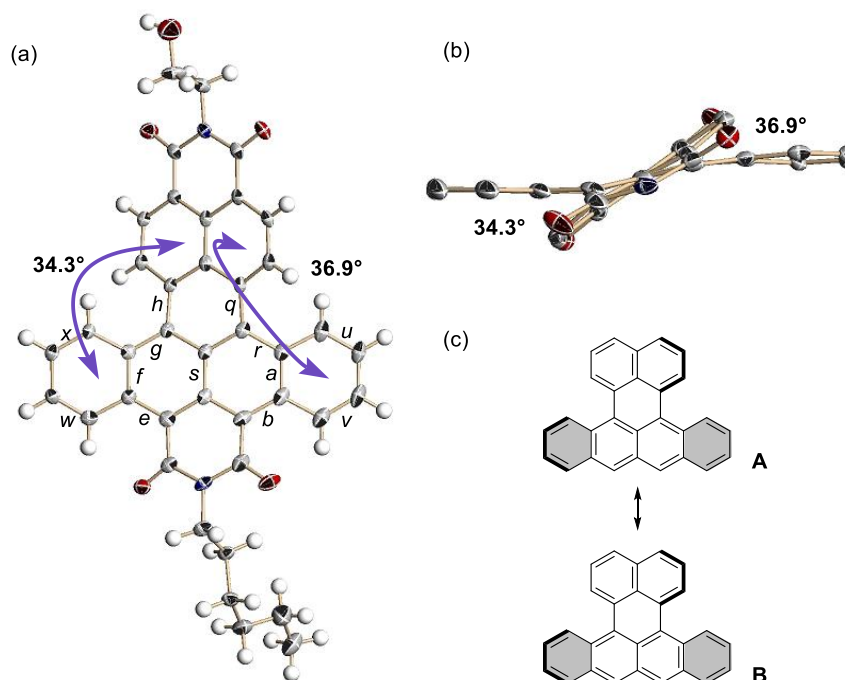
The synthesis of dibenzo[*a,f*]-fused PBI **4a** and **4c** is shown in Scheme 1. Boronic ester derivatives **5a** and **5b** were synthesized according to a reported procedure.<sup>11</sup> Bromotetracene imide **6** was synthesized according to the procedure reported for tetracene imide.<sup>12</sup> Compounds **5a** and **6** were subjected to Suzuki coupling reaction to give **7a**. Pd(PPh<sub>3</sub>)<sub>4</sub> was firstly employed as a catalyst,<sup>11c</sup> but the yield of **7a** was only moderate (42%) probably due to the steric congestion of **7a**. After several trials, Pd-PEPPSI-IPr<sup>13</sup> was found to be the best catalyst, and precursors **7a** and **7b** were obtained in 79% and 88% yields, respectively. Then, the base-promoted cyclization<sup>11a,c,14</sup> of precursors **7a** and **7b** was conducted using K<sub>2</sub>CO<sub>3</sub> in ethanolamine. When **7a** with a bulky aryl group (R = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was employed, desired product **4a** was obtained in 44% yield. However, cyclization of **7b** with a linear alkyl group (R = *n*-hexyl) under the same conditions afforded the compound **4c** (53%), in which the *n*-hexyl group on the naphthalene imide moiety was replaced by a 2-hydroxyethyl group. The replacement of the substituent was not observed on the tetracene imide unit probably due to the less electrophilicity of the carbonyl carbons caused by the electron-donating character of the tetracene core. In order to seek conditions with a high functional group tolerance, the reaction was carried out in other solvents such as DMF, pyridine, and THF. All the reaction conditions failed to give **4b**, except for the conditions using ethylene glycol; **4b** was isolated in 35% yield. In addition, it is noted that the *n*-hexyl groups in cyclized compound **4b** were not replaced by 2-hydroxyethyl group under the reaction conditions in ethanolamine. This indicates that the replacement of the *n*-hexyl group of **7b** proceeded prior to the cyclization. Compounds **4a** and **4b** exhibited good solubility in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and toluene with reference to PBI **1c** with *n*-octyl groups, though **4c** showed substantially decreased solubility.



**Scheme 1.** Synthetic routes to compounds **4a** and **4c**: i) Pd-PEPPSI-IPr, K<sub>2</sub>CO<sub>3</sub>, toluene/H<sub>2</sub>O/EtOH (10:2:1), 90 °C, 12 h; ii) K<sub>2</sub>CO<sub>3</sub>, ethanolamine, 120 °C, 2 h, then 0.5% H<sub>2</sub>O<sub>2</sub>

### X-Ray Crystal Structure

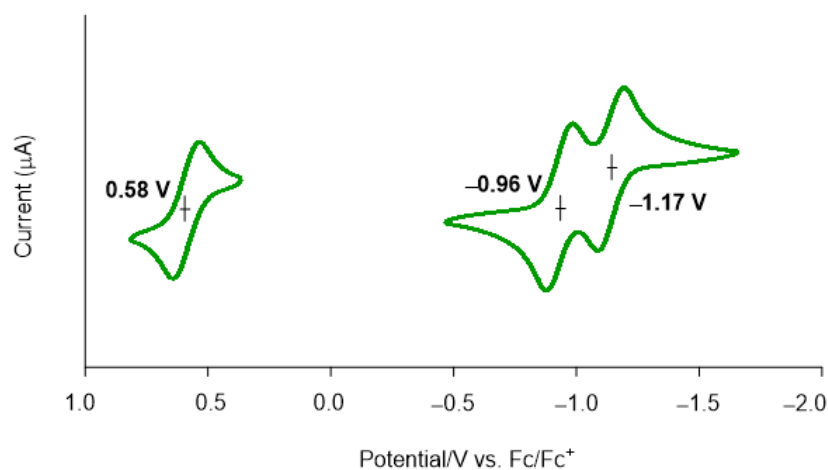
The structure of **4c** was unambiguously determined by the single crystal X-ray analysis. As shown in Figure 2a and b, **4c** has a substantially twisted structure; twist angles between the benzene planes in the naphthalene and the tetracene moieties are 34.3° and 36.9°, respectively, due to the steric repulsion of the *peri*-hydrogen atoms.<sup>15</sup> Bond distances of *a* [1.431(6) Å], *f* [1.449(6) Å], and *s* [1.434(6) Å] in **4c** are clearly elongated as compared to those of PBI **1d** [1.393(3) Å for *a* and *f* bonds, 1.419(3) Å for *s* bond, respectively].<sup>16</sup> In addition, bond distances of *u*, *v*, *w*, and *x* bonds fall within 1.351(6)–1.363(7) Å, indicating the strong C=C double bond character. Because these structural feature can be explained by the contribution of possible resonance structures of **A** and **B** (Figure 2c), dibenzo[*a,f*]-annulation to the PBI core can induce a tetracene-like structural feature.<sup>17</sup>



**Figure 2.** (a) Top view and (b) Side view of X-ray structure of **4c**. (c) Resonance structures of the main  $\pi$ -skeleton of **4c**. The purple arrows in (a) illustrate the twist angles between two benzene rings. Solvent molecules are omitted for clarity in (a), and alkyl groups are also omitted for clarity in (b).

## Electrochemical Properties

To evaluate the effects of the position of the ring-fusion on the electronic properties, cyclic voltammetry (CV) of dibenzo[*a,f*]-fused PBI **4a** was conducted in  $\text{CH}_2\text{Cl}_2$  (Figure 3) and the results, together with those reported for PBI **1b**<sup>18</sup> and dibenzo[*a,o*]-fused PBI **3a**,<sup>9</sup> are summarized in Table 1. In the reduction region, the first reduction potential of **4a** is less negative by 0.14 V compared to that of **1b**,<sup>18</sup> while it is more negative by 0.22 V compared to that of **3a**.<sup>9</sup> In the oxidation process, **4a** showed one reversible wave at  $E_{\text{ox}}^1 = 0.58$  V, which is less positive by 0.36 V and 0.65 V compared to that of **3a**<sup>9</sup> and **1b**<sup>18</sup>, respectively. The data indicated that the dibenzo[*a,f*]-fusion effectively raises the HOMO level with reference to the dibenzo[*a,o*]-fusion. As a result, the HOMO-LUMO gap ( $E_g$ ) of **4a** estimated from the half-wave potentials is 1.54 eV, which is narrower by 0.14 eV than that of **3a** ( $E_g = 1.68$  eV).



**Figure 3.** Cyclic voltammogram of **4a** in CH<sub>2</sub>Cl<sub>2</sub> (1 mM); measured with [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>] (0.1 M) as a supporting electrolyte at a scan rate of 100 mV s<sup>-1</sup>.

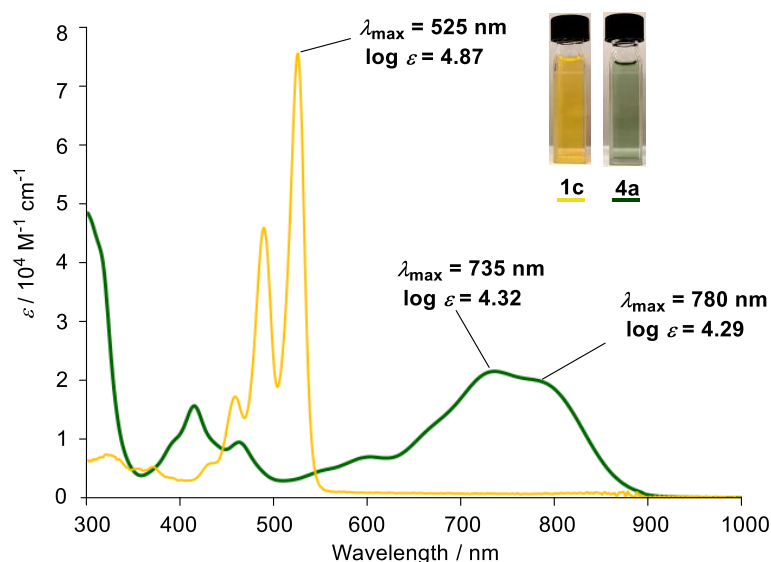
**Table 1. Redox Potentials<sup>a</sup> of Dibenzo-fused Compounds **4a**, **3a** and PBI **1b** (in V vs. Fc/Fc<sup>+</sup>)**

| Compd                  | $E_{\text{ox}}^1$ (V) <sup>a</sup> | $E_{\text{red}}^1$ (V) <sup>a</sup> | $E_{\text{red}}^2$ (V) <sup>a</sup> | $E_g$ [eV]        |
|------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------|
| <b>4a</b>              | 0.58                               | -0.96                               | -1.17                               | 1.54              |
| <b>3a</b> <sup>b</sup> | 0.94 <sup>b</sup>                  | -0.74 <sup>b</sup>                  | -0.95 <sup>b</sup>                  | 1.68 <sup>b</sup> |
| <b>1b</b> <sup>c</sup> | 1.23 <sup>c</sup>                  | -1.10 <sup>c</sup>                  | -1.30 <sup>c</sup>                  | 2.33 <sup>c</sup> |

<sup>a</sup> Half wave potentials. <sup>b</sup> The data are taken from ref. 9. <sup>c</sup> The data are taken from ref. 18.

## Photophysical Properties

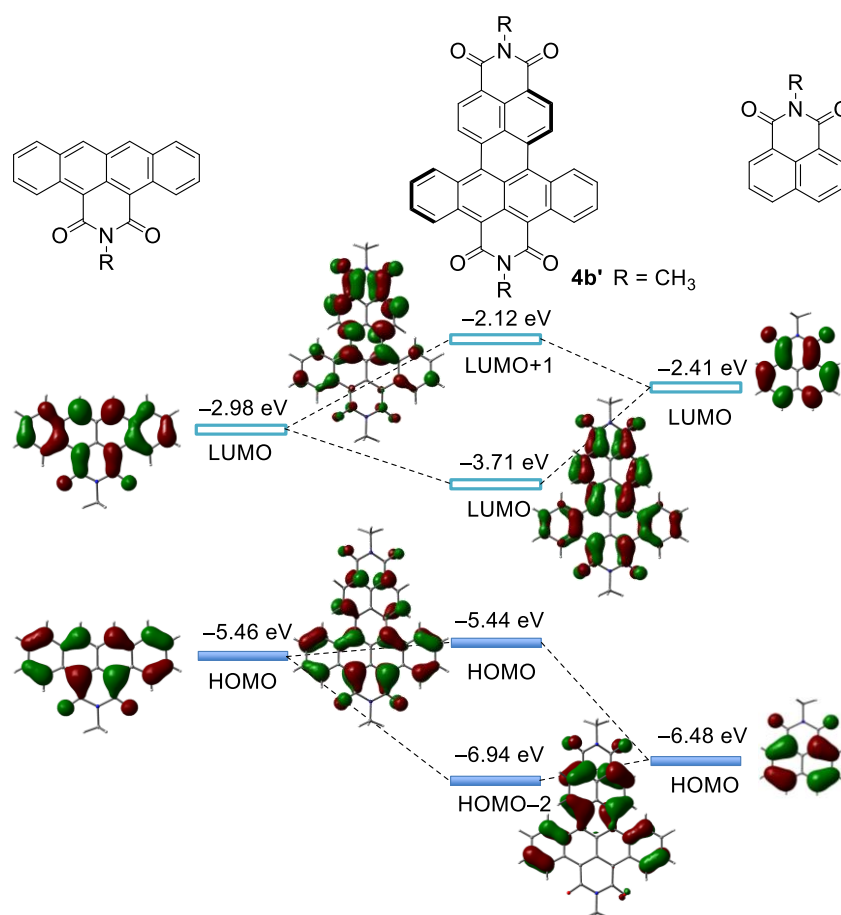
The absorption spectrum of **4a**, together with that of PBI **1c** for comparison, were measured in CH<sub>2</sub>Cl<sub>2</sub> (Figure 4). As is well-known, PBI **1c** showed an intense and sharp absorption with a maximum at  $\lambda_{\max} = 525$  nm ( $\log \varepsilon = 4.87$ ).<sup>7a</sup> Dibenzo[*a,f*]-fused **4a** showed absorption band at  $\lambda_{\max} = 735$  nm ( $\log \varepsilon = 4.32$ ) with a shoulder band ( $\lambda_{\text{abs}} = 780$  nm,  $\log \varepsilon = 4.29$ ) tailing to 900 nm. This band is markedly red-shifted by 255 nm compared to that of **1c** and by 83 nm even compared to that of [a,*o*]-fused **3a** ( $\lambda_{\max} = 697$  nm,  $\log \varepsilon = 4.67$ ).<sup>9</sup> As for the reason for the broadening band in **4a**, the contributions of 1) intramolecular charge transfer (CT) character and 2) the conformational flexibility of **4a**<sup>15</sup> are conceivable. As to the former point, we observed small solvent polarity effects on the absorption profile:  $\lambda_{\max} = 730$  nm in toluene, 735 nm in CH<sub>2</sub>Cl<sub>2</sub>, 745 nm in PhCN, 752 nm in DMF, indicating the small contribution of the CT character.



**Figure 4.** UV-vis-NIR absorption spectra of **1c** and **4a** in CH<sub>2</sub>Cl<sub>2</sub>. The pictures of their CH<sub>2</sub>Cl<sub>2</sub> solutions are included.

## DFT Calculations

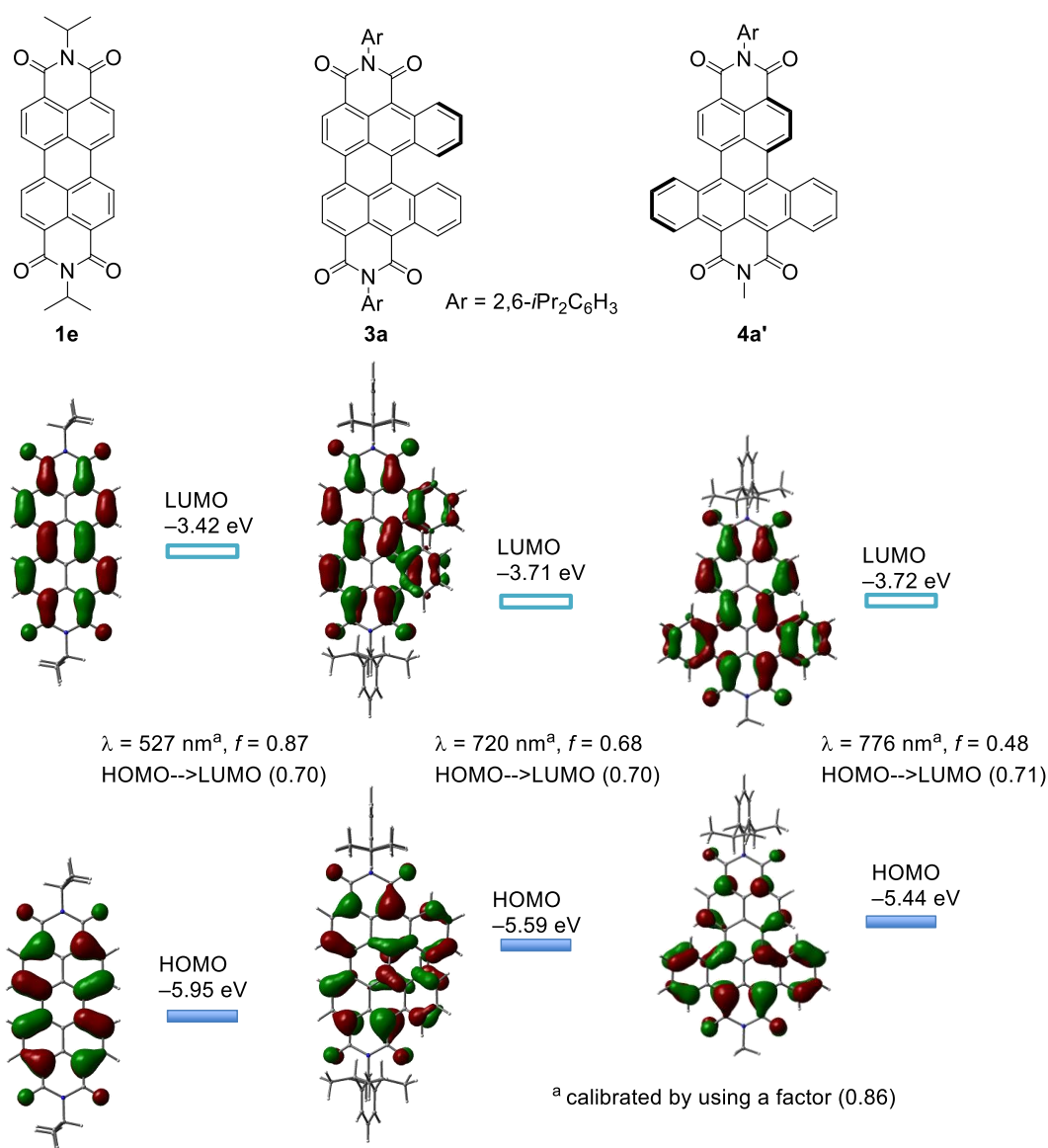
In order to get deep understanding of the electronic properties, the structure of dibenzo[*a,f*]-fused **4b'** (the two *n*-hexyl groups are replaced with methyl groups) are partitioned into tetracene imide and naphthalene imide fragments, and the orbital-interaction diagram<sup>19</sup> is shown in Figure 5. The  $\pi^*$  orbitals of the two fragments effectively interact to give the well-delocalized LUMO of **4b'**, whereas less interaction between the  $\pi$  orbitals of the two fragments are indicated presumably due to the substantially higher HOMO level of the tetracene fragment than that of the naphthalene fragment. Hence, the HOMO of **4b'** has a major contribution of the tetracene imide character.



**Figure 5.** Orbital interaction diagram for dibenzo[*a,f*]-fused PBI **4b'** (the two *n*-hexyl groups being replaced with methyl groups) partitioned into tetracene imide and naphthalene imide fragments (B3LYP/6-31G\*).

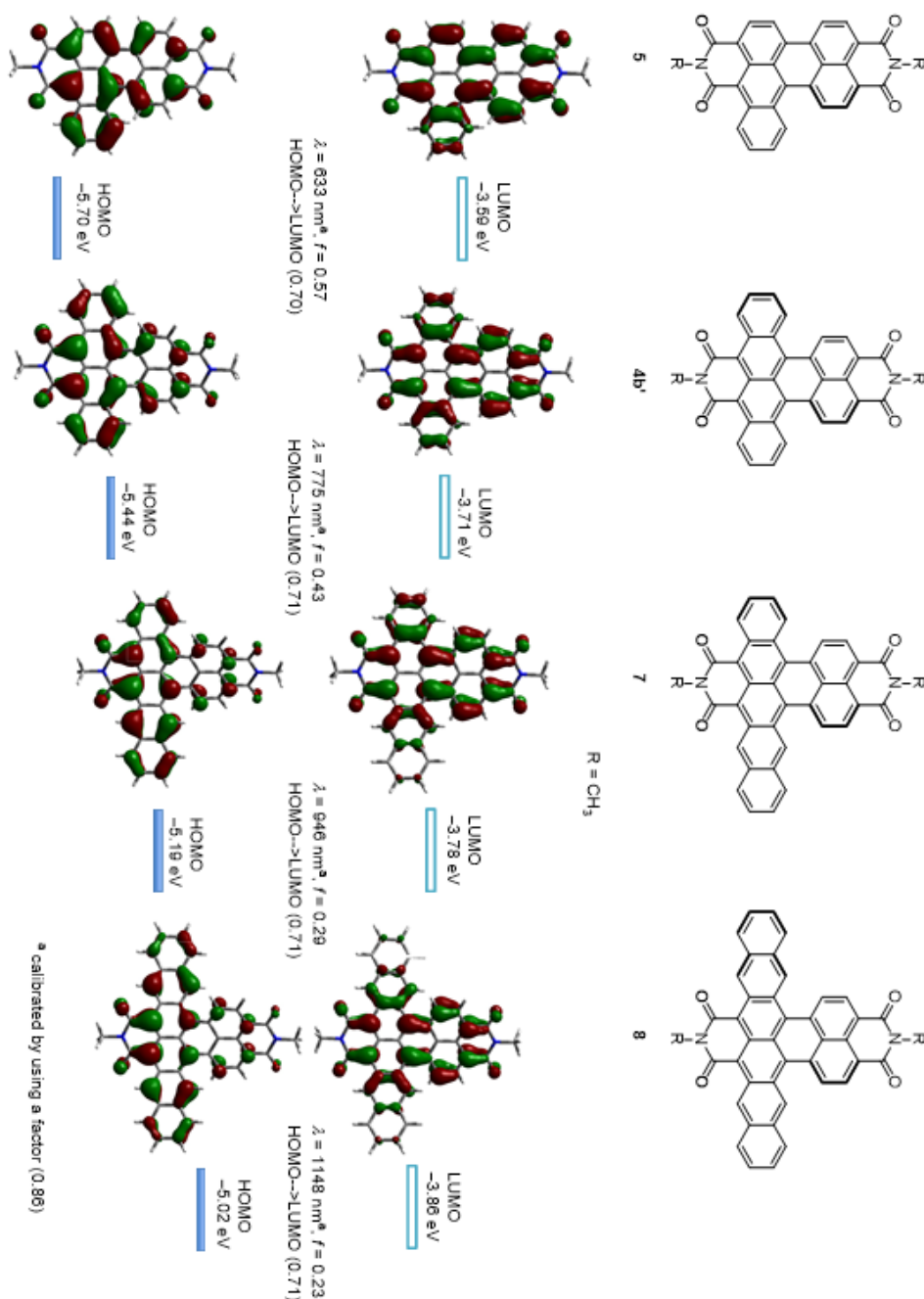
According to TD-DFT calculations (TD-CAM-B3LYP/6-31G\*\*/B3LYP/6-31G\*) (Figure 6), the intense absorption band of [*a,f*]-fused structure **4a'** (the hexyl group is replaced with a methyl group) is assignable to the transition containing a major contribution from the

HOMO to the LUMO (oscillator strength,  $f = 0.48$ ), as is the case for that of **1e** ( $f = 0.87$ ) and **3a** ( $f = 0.68$ ). The decreased oscillator strength of **4a'** can be explained by the less effective overlap between the relatively localized HOMO and well delocalized LUMO, leading to a contribution of the CT character, though the transition still maintains the significant  $\pi$ - $\pi^*$  character.



**Figure 6.** Pictorial presentation of the frontier orbitals, a plot of the HOMO and LUMO energy levels (B3LYP/6-31G\*), and optical transitions with oscillator strength (TD-CAM-B3LYP/6-31G\*\*/B3LYP/6-31G\*) for **1e**, **3a**, and **4a'** (the hexyl group being replaced with a methyl group).

Indeed, the TD-DFT calculations for model compounds **5**, **6**, and **7** in which the tetracene core of **4b'** is replaced by more electron rich pentacene or hexacene, indicated further localizations of HOMO on the longer acene moiety with a concomitant decrease in the oscillator strengths ( $f = 0.29$  for pentacene derivative,  $f = 0.23$  for hexacene derivative) (Figure 7).



**Figure 7.** Pictorial presentation of the frontier orbitals, a plot of the HOMO and LUMO energy levels (B3LYP/6-31G\*), and optical transitions with oscillator strength (TD-CAM-B3LYP/6-31G\*//B3LYP/6-31G\*) for model compounds **4b'**, **5**, **6**, and **7**.

## Conclusion

The author synthesized dibenzo[*a,f*]-fused PBI derivatives **4a-c** and clarified the twisted structure of **4c** by the X-ray crystal analysis. The benzannulations at *a* and *f* bonds of the PBI core, which create a tetracene core, effectively elevate the HOMO level compared to the ring fusions at *a* and *o* bonds to create two anthracene cores. The smaller HOMO-LUMO gap of the [a,*f*]-fused PBI structure was demonstrated by CV, UV-vis-NIR, as well as DFT calculations. In particular, [a,*f*]-fused PBI structure exhibited broad absorption with a tail up to 900 nm, which is red-shifted with reference to [a,*o*]-fused PBI derivative. These results would provide useful insights for further structural modifications of the PBI scaffolds.

## Experimental Section

### General

Melting points (m.p.) were measured on a Yanaco MP-S3 instrument. The <sup>1</sup>H and <sup>13</sup>C NMR measurements were carried out with a JEOL ECA 500 instrument. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of CDCl<sub>3</sub> ( $\delta$  7.26 ppm in <sup>1</sup>H NMR, and  $\delta$  77.16 ppm in <sup>13</sup>C NMR) and DMSO-*d*<sub>6</sub> ( $\delta$  2.50 ppm in <sup>1</sup>H NMR, and  $\delta$  39.52 ppm in <sup>13</sup>C NMR). UV-vis-NIR absorption spectra were measured with a Shimadzu UV-3150 spectrometer. APCI mass spectra were measured on Bruker micrOTOF-Q II spectrometer. Cyclic voltammetry (CV) was performed on a BAS ALS620A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The measurements were carried out under an argon atmosphere using a CH<sub>2</sub>Cl<sub>2</sub> solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup>) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Preparative GPC was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H columns. All reactions were carried out under an argon atmosphere.

## Synthesis

### Precursor 7a

Compound **6** (105 mg, 0.229 mmol), **5a** (155 mg, 0.321 mmol, 1.5 eq.) and K<sub>2</sub>CO<sub>3</sub> (645 mg, 4.68 mmol, 20 equiv) were dissolved in toluene (2.3 mL), water (0.5 mL) and EtOH (0.2 mL), and the mixture was flushed with argon three times. The Pd-PEPPSI-IPr catalyst (7.4 mg, 0.012

mmol, 5 mol%) was added and the reaction mixture was stirred for 12 h at 90 °C. After cooling to room temperature, the reaction mixture was quenched with water, extracted with toluene, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:5) to give compound **7a** (134 mg, 0.182 mmol) in 79% yield as purple powder.

m.p. 214–215 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 10.26 (d, *J* = 9.0 Hz, 1H, ArH), 10.09 (d, *J* = 10.0 Hz, 1H, ArH), 8.96 (d, *J* = 7.0 Hz, 1H, ArH), 8.71 (dd, *J* = 7.0, 1.0 Hz, 1H, ArH), 8.48 (s, 1H, ArH), 7.98 (d, *J* = 7.0 Hz, 1H, ArH), 7.85–7.80 (m, 3H, ArH), 7.56–7.47 (m, 4H, ArH), 7.43–7.40 (m, 4H, ArH), 4.45 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 2.92 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.96–1.90 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.61–1.55 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.48–1.35 (m, 4H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.31–1.23 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.94 (t, *J* = 7.0 Hz, 3H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 164.9, 164.9, 164.1, 145.8, 145.8, 143.0, 142.6, 135.9, 135.3, 135.0, 132.8, 132.53, 132.45, 132.1, 131.7, 131.2, 131.1, 130.7, 130.4, 130.1, 129.9, 129.1, 128.1, 127.8, 127.7, 127.6, 127.2, 127.0, 126.6, 126.5, 124.34, 124.31, 123.6, 123.36, 116.6, 115.6, 41.4, 31.9, 29.8, 29.4, 28.4, 27.2, 24.3, 24.3, 24.3, 22.8, 14.3 (three signals were overlapped with other signals); HRMS (+APCI): [MH]<sup>+</sup> calcd for C<sub>50</sub>H<sub>45</sub>N<sub>2</sub>O<sub>4</sub> 737.3374, found 737.3365.

### Precursor **7b**

Compound **6** (105 mg, 0.229 mmol), **5b** (146 mg, 0.355 mmol, 1.5 equiv) and K<sub>2</sub>CO<sub>3</sub> (646 mg, 4.68 mmol, 20 equiv) were dissolved in a mixture of toluene (2.3 mL), water (0.5 mL) and EtOH (0.2 mL) and the mixture was flushed with argon three times. The Pd-PEPPSI-IPr catalyst (7 mg, 0.01 mmol, 5 mol%) was added and the reaction mixture was stirred for 12 h at 90 °C. After cooling to room temperature, the reaction mixture was diluted with water, extracted with toluene, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The crude product was subjected to column chromatography on silica gel (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:5) to give compound **7b** (134 mg, 0.182 mmol) in 88% yield as purple powder. **7b**:

m.p. 228–229 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 10.24 (d, *J* = 9.5 Hz, 1H, ArH), 10.08 (d, *J* = 9.0 Hz, 1H, ArH), 8.90 (d, *J* = 7.5 Hz, 1H, ArH), 8.65 (d, *J* = 6.0 Hz, 1H, ArH), 8.37 (s, 1H, ArH), 7.91 (d, *J* = 7.0 Hz, 1H, ArH), 7.83–7.78 (m, 2H, ArH), 7.72 (d, *J* = 8.5 Hz, 1H, ArH), 7.50–7.44 (m, 2H, ArH), 7.41–7.35 (m, 2H, ArH), 7.32 (d, *J* = 9.0 Hz, 1H, ArH), 4.45 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 4.29 (t, *J* = 7.5 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.95–1.89 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.87–1.81 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.60–1.49 (m, 4H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>),

1.47–1.37 (m, 8H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 0.95–0.92 (m, 6H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 165.0, 164.9, 164.13, 164.06, 143.2, 142.2, 135.9, 135.3, 135.0, 132.5, 132.4, 132.0, 131.92, 131.87, 131.7, 131.1, 130.6, 130.2, 130.0, 128.6, 128.0, 127.74, 127.69, 127.5, 127.2, 126.9, 126.6, 126.5, 123.8, 123.4, 116.5, 115.6, 41.4, 40.9, 31.9, 31.8, 28.4, 28.3, 27.3, 27.0, 22.85, 22.78, 14.3 (one signal was overlapped with other sp<sup>3</sup>-carbon signals); HRMS (–APCI): [M<sup>–</sup>] calcd for C<sub>44</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub> 660.2994, found 660.3002.

### Dibenzo[a,f]perylene Bisimide 4a

Compound **7a** (91 mg, 0.12 mmol) and K<sub>2</sub>CO<sub>3</sub> (856 mg, 6.20 mmol, 50 equiv) were suspended in ethanolamine (4.0 mL) and the mixture was stirred for 2 h at 120 °C. After cooling to room temperature, the red reaction mixture was quenched with 0.5 % H<sub>2</sub>O<sub>2</sub> solution under air. The color of the solution turned from red to green within 15 min. Then the solution was diluted with water, extracted with toluene, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:3) to give compound **4a** (24 mg, 0.033 mmol) in 42% yield as green powder.

m.p. 362–363 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 9.87 (d, *J* = 9.0 Hz, 2H, Ar*H*), 8.87 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.68–8.66 (m, 4H, Ar*H*), 7.84 (dd, *J* = 9.0, 6.3 Hz, 2H, Ar*H*), 7.73–7.70 (m, 2H, Ar*H*), 7.54 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.40 (d, *J* = 8.0 Hz, 2H, Ar*H*), 4.40 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 2.88 (septet, *J* = 7.0 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.93–1.87 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.58–1.53 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.47–1.35 (m, 4H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.24 (d, *J* = 7.0 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.93 (t, *J* = 7.3 Hz, 3H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 164.7, 163.8, 145.9, 134.9, 134.2, 132.6, 131.9, 130.9, 130.7, 130.6, 129.9, 129.0, 128.9, 128.0, 127.5, 125.7, 124.3, 122.7, 122.5, 117.1, 41.5, 31.8, 29.9, 29.4, 28.6, 27.2, 24.2, 22.8, 14.3 (two signals were overlapped with other signals); HRMS (–APCI): [M]<sup>–</sup> calcd for C<sub>50</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub> 734.3150, found 734.3173.

### Compound 4b

Precursor **7b** (84 mg, 0.13 mmol) and K<sub>2</sub>CO<sub>3</sub> (89 mg, 6.4 mmol, 50 equiv) were suspended in 5.0 mL ethylene glycol and stirred for 18 h at 140 °C. After cooling to room temperature, the red reaction mixture was quenched with 0.5% H<sub>2</sub>O<sub>2</sub> solution under air. The color of the solution turned from red to green within 15 min. Then the solution was diluted with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced

pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:3) to give compound **4b** (29 mg, 0.045 mmol) in 35% yield as green powder.

m.p. 261–263 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 9.86 (d, *J* = 9.0 Hz, 2H, Ar*H*), 8.73 (d, *J* = 7.5 Hz, 2H, Ar*H*), 8.53–8.51 (m, 4H, Ar*H*), 7.83–7.80 (m, 2H, Ar*H*), 7.68–7.65 (m, 2H, Ar*H*), 4.39 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 4.29 (t, *J* = 7.7 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.93–1.87 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.85–1.79 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.58–1.48 (m, 6H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.47–1.37 (m, 6H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 0.93 (t, *J* = 7.3 Hz, 6H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 164.7, 163.6, 134.8, 133.8, 132.6, 131.8, 130.7, 123.0, 128.8, 128.2, 127.9, 127.6, 127.5, 125.6, 122.8, 122.4, 116.9, 41.5, 40.9, 31.82, 31.76, 28.6, 28.4, 27.2, 27.0, 22.84, 22.77, 14.3 (four signal was overlapped with other signals); HRMS (–APCI): [M]<sup>–</sup> calcd for C<sub>40</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub> 658.2837, found 658.2866.

### Compound 4c

Precursor **7b** (70 mg, 0.11 mmol) and K<sub>2</sub>CO<sub>3</sub> (737 mg, 5.352 mmol, 50 equiv) were suspended in 3.5 mL ethanolamine and stirred for 2 h at 120 °C. After cooling to room temperature, the red reaction mixture was quenched with 0.5% H<sub>2</sub>O<sub>2</sub> solution under air. The color of the solution turned from red to green within 15 min. Then the solution was diluted with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The crude product was purified by recycling HPLC (CH<sub>3</sub>Cl, 3.4 mL/min, retention time: 48 min.) to give compound **4c** (36 mg, 0.058 mmol) in 53% yield as green powder.

m.p. 286–288 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 9.78 (d, *J* = 9.0 Hz, 2H, Ar*H*), 8.61 (d, *J* = 7.5 Hz, 2H, Ar*H*), 8.36–8.34 (m, 4H, Ar*H*), 7.77 (dd, *J* = 9.0, 6.5 Hz, 2H, Ar*H*), 7.58 (m, 2H, Ar*H*), 4.59 (t, *J* = 5.3 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>OH), 4.37 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 4.12 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>OH), 2.60 (s, 1H, CH<sub>2</sub>CH<sub>2</sub>OH), 1.92–1.86 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.59–1.53 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.48–1.36 (m, 4H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 0.94 (t, *J* = 7.0 Hz, 3H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 164.42, 164.36, 134.6, 133.7, 132.2, 131.5, 130.7, 130.4, 130.1, 128.9, 128.1, 127.6, 127.4, 127.3, 125.4, 122.3, 122.1, 116.8, 61.9, 43.3, 41.6, 31.8, 28.5, 27.2, 22.8, 14.3; HRMS (–APCI): [M]<sup>–</sup> calcd for C<sub>40</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub> 618.2186, found 618.2184.

### Computational Method

DFT calculations for optimizations and TD-DFT were conducted using the Gaussian 09 program.<sup>19</sup>

## X-Ray Crystal Structure Analysis.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1002950 (**4c**). This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**4c:** Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 14284 reflections were measured at the maximum  $2\theta$  angle of  $50.1^\circ$ , of which 10201 were independent reflections ( $R_{\text{int}} = 0.0414$ ). The structure was solved by direct methods (SHELXS-97<sup>20</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>20</sup>). 2-Hydroxyethyl group C73-C74-O11 was disordered, which was solved using appropriate models. Thus, two sets of 2-hydroxyethyl groups, *i.e.*, (C73-C74A–O11A) and (C73-C74B–O11B), were placed and their occupancies were refined to be 0.78 and 0.22, respectively. All non-hydrogen atoms, except for C74B in the 2-hydroxyethyl group, were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>81</sub>H<sub>64</sub>N<sub>4</sub>O<sub>11</sub>; FW = 1269.36, crystal size  $0.10 \times 0.05 \times 0.03$  mm<sup>3</sup>, Triclinic, *P*-1,  $a = 11.122(2)$  Å,  $b = 15.010(3)$  Å,  $c = 18.735(4)$  Å,  $\alpha = 97.463(3)^\circ$ ,  $\beta = 99.494(3)^\circ$ ,  $\gamma = 105.346(3)^\circ$ ,  $V = 2924.9(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.441$  g cm<sup>-3</sup>. The refinement converged to  $R_1 = 0.0693$ ,  $wR_2 = 0.1518$  ( $I > 2\sigma(I)$ ), GOF = 1.020.

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## List of Publications

### Publications included in this thesis

#### Chapter 1

Chaolumen, Michihisa Murata,\* Yasunori Sugano, Atsushi Wakamiya, Yasujiro Murata\*  
“Electron Deficient Tetrabenzo-Fused Pyracylene and Conversions into Curved and Planar  $\pi$ -Systems with Distinct Emission Behaviors”  
*Angew. Chem., Int. Ed.* **2015**, 54, 9308–9312. (DOI: 10.1002/anie.201503783)

#### Chapter 2

Chaolumen, Michihisa Murata,\* Atsushi Wakamiya, Yasujiro Murata\*  
“Unsymmetric Twofold Scholl Cyclization of 5,11-Dinaphthyltetracene: Selective Formation of Pentagonal and Hexagonal Rings via a Dication Pathway”  
*Angew. Chem., Int. Ed.* **2017**, DOI: 10.1002/anie.201701054.

#### Chapter 3

Chaolumen, Michihisa Murata,\* Atsushi Wakamiya, Yasujiro Murata\*  
“Cycloaddition of Benzyne to Naphthalene-Fused Tetracene with a Twisted  $\pi$ -Surface”  
*Chem. Lett.* **2017**, DOI: 10.1246/cl.161170.

#### Chapter 4

Chaolumen, Michihisa Murata,\* Atsushi Wakamiya, Yasujiro Murata\*  
“Dithieno-Fused Polycyclic Aromatic Hydrocarbon with a Pyracylene Moiety: Strong Antiaromatic Contribution to the Electronic Structure”  
*Org. Lett.* **2017**, 19, 826–829. (DOI: 10.1021/acs.orglett.6b03819)

#### Chapter 5

Chaolumen, Hiroki Enno, Michihisa Murata,\* Atsushi Wakamiya, Yasujiro Murata\*  
“Dibenzo[*a,f*]perylene Bisimide: Effects of Introducing Two Fused Rings”  
*Chem. Asian J.* **2014**, 9, 3136–3140. (DOI: 10.1002/asia.201402688)

### **Publications not included in this thesis**

(1) Cholmen Xarnod (Chaolumen), Wei Huang, Rong-Guo Ren, Ru-Cheng Liu, Bang-Guo Wei\*

“A Flexible Approach to Construct Three Contiguous Chiral Centers of Sphingolipids, and Asymmetric Synthesis of D-ribo-phytosphingosine and Its Derivatives”

*Tetrahedron* **2012**, 68, 6688–6695. (DOI: 10.1016/j.tet.2012.05.120)

(2) Wen-Feng Huang, Qian-Ru Li, Lu-Men Chao (Chaolumen), Xin-Sheng Lei, Bang-Guo Wei\*

“Asymmetric Synthesis of Ceramide Sphingolipid Based on (2S,3S,4S)-3,4-dihydroxy-5-(hydroxymethyl) Pyrrolidine Lactam”

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