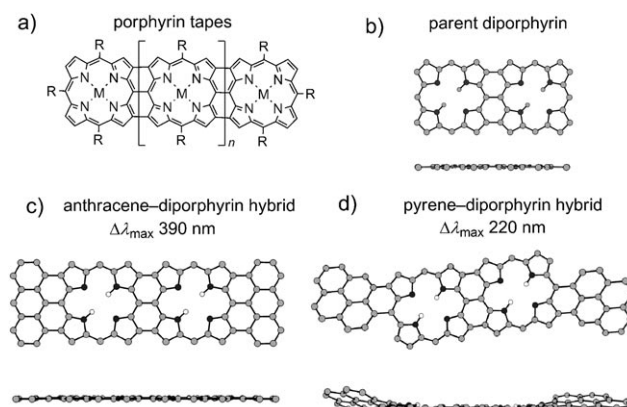


# Fused Pyrene–Diporphyrins: Shifting Near-Infrared Absorption to 1.5 $\mu\text{m}$ and Beyond\*\*

Vyacheslav V. Diev, Kenneth Hanson, Jeramy D. Zimmerman, Stephen R. Forrest, and Mark E. Thompson\*

Porphyrins have been explored for a number of potential optoelectronic applications that require strong absorption in the near-infrared (NIR) spectral region; these applications include organic electronics,<sup>[1,2]</sup> nonlinear optics,<sup>[3]</sup> and telecommunication technologies.<sup>[4]</sup> Porphyrins have also been investigated as active materials in photovoltaic cells<sup>[1]</sup> because of their high efficiency of charge separation and transport,<sup>[5]</sup> strong absorbance in the visible region, high chemical stability, and the ease with which their optoelectronic properties can be tuned with chemical modification.<sup>[6]</sup> The absorption bands of porphyrins are not readily shifted into the deep-red and NIR spectral regions, and also tend to be narrow, thus minimizing their overlap with the solar spectrum. Triply bridged, ( $\beta$ , meso,  $\beta$ ), porphyrin tapes (Figure 1a,  $n = 0$ –22) show marked red-shifts in the porphyrin absorption bands, which extend deep into the NIR region.<sup>[7,8a]</sup> Triply fused porphyrins with  $n = 1, 2$  give absorbance in the mid-NIR region (i.e., conventional wavelengths for telecommunications, ca. 1.5  $\mu\text{m}$ ), however, these porphyrins are difficult to synthesize, have low solubility, and are isolated only in small quantities.<sup>[8]</sup> Triply connected porphyrin dimers (Figure 1a,  $n = 0$ ) have a strong absorbance at  $\lambda = 1050$  nm, are photo- and chemically stable, have a high solubility, and can be easily prepared from monoporphyrins.<sup>[7]</sup> Development of new organic dyes based on these accessible porphyrin dimers with absorption at the wavelengths for telecommunications ( $\lambda = 1.5$   $\mu\text{m}$ ) still remains a challenge.

Extending the size of  $\pi$  conjugation in porphyrin systems results in most cases in a bathochromic (red) shift of the absorption.<sup>[7,8b,c]</sup> The conjugation of porphyrin dimers can be



**Figure 1.** a) General structure of triply fused porphyrins. b)–d) Structures of diporphyrin hybrids calculated at B3LYP/6-31G with calculated red-shifts of the lowest-energy transitions compared to the parent diporphyrin.

extended through several modes of substitution involving the meso, ( $\beta$ ,  $\beta$ ), ( $\beta$ , meso) and ( $\beta$ , meso,  $\beta$ ) positions. For diporphyrins substituted with two alkyne groups at the terminal meso positions, the Q band is red-shifted by 130 nm ( $\lambda = 1181$  nm) relative to the parent dimer.<sup>[9]</sup> In contrast, extending the conjugation in porphyrin dimers by benzannulating  $\beta$ ,  $\beta$ -pyrrolic positions red-shifts the Q band by only 18 nm, and the resulting compounds have poor solubility.<sup>[8b]</sup> Recently, it has been shown that anthracene rings can be fused to porphyrin dimers through the ( $\beta$ , meso,  $\beta$ ) mode, which leads to a red-shift of the Q band to 1495 nm.<sup>[8c]</sup> However, the anthracene-fused diporphyrin exhibits the same undesirable difficulties found with higher porphyrin tapes, for example, synthetic difficulty, low yields and low solubility.<sup>[8c]</sup> Moreover, fusion of anthracene rings is limited only to alkoxy-substituted derivatives.

The effects of aromatic ring fusion to porphyrin tapes in a (meso,  $\beta$ ) mode have not been explored. We have analyzed the structures of the diporphyrin core (Figure 1b), a ( $\beta$ , meso,  $\beta$ ) triply fused aromatic system (Figure 1c), and a ( $\beta$ , meso) doubly fused molecule (Figure 1d) using standard DFT methods. Significant bathochromic shifts of the lowest-energy transition are expected in all cases. Unlike the case of anthracene-fused porphyrins and porphyrin tapes, in which the planarity causes aggregation and low solubility, the pyrene-( $\beta$ , meso)-fused diporphyrin displays out-of-plane distortion that is known to improve solubility and processibility in conjugated aromatics.<sup>[10]</sup> By taking into account the predicted bathochromic shift, distortion from planarity, and ease of synthesis, the ( $\beta$ , meso)-fused pyrene diporphyrin from

[\*] Dr. V. V. Diev, Dr. K. Hanson, Prof. M. E. Thompson  
 Department of Chemistry, University of Southern California  
 Los Angeles, CA 90089 (USA)  
 Fax: (+1) 213-740-8594  
 E-mail: met@usc.edu  
 Homepage: <http://met.usc.edu>

Dr. J. D. Zimmerman, Prof. S. R. Forrest  
 Department of Electrical Engineering and Computer Science  
 and Department of Physics  
 University of Michigan, Ann Arbor, MI 48109(USA)

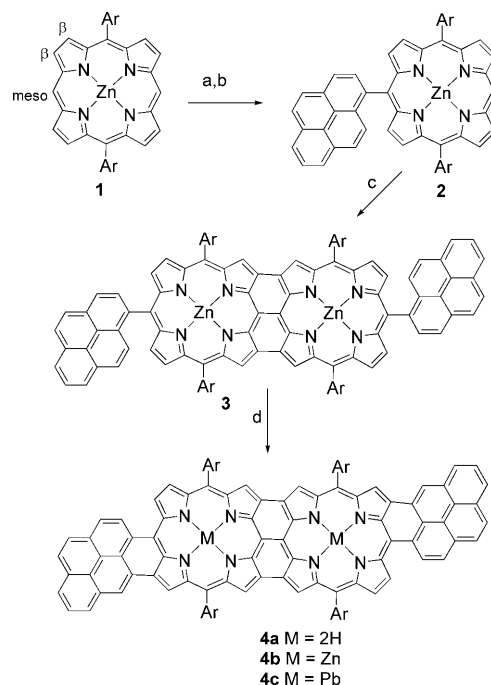
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this molecular class has an optimal design for numerous applications. We report herein the synthesis and properties of a new class of diporphyrin–pyrene hybrid compounds (Figure 1d) with relatively simple synthesis and very good solubility.

The key step in the synthesis of pyrene-fused diporphyrins is the oxidative ring closure of the pyrene with the porphyrin core. Although there are several reports of the direct fusion of polycyclic aromatic rings with monoporphyrins, these procedures employ electron-rich aromatic rings (e.g., rings that are activated by several alkoxy groups,<sup>[8c,11a,c]</sup> or appropriately arranged azulene rings<sup>[11d]</sup>), and/or nickel(II) porphyrins to direct fusion.<sup>[11a,b,d]</sup> Attempts to fuse unsubstituted pyrene rings with porphyrins were unsuccessful.<sup>[11a]</sup>

The pyrene-substituted porphyrin dimer **3** was prepared in two steps (Suzuki coupling and Osuka's oxidative fusion of porphyrin rings) starting from the disubstituted porphyrin building block **1** (Scheme 1; detailed synthetic procedures and characterization of **1–4** are given in the Supporting Informa-



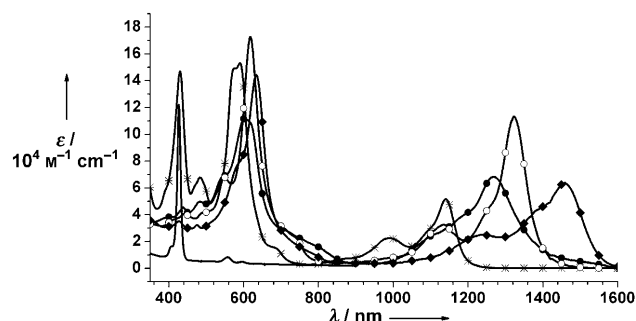
**Scheme 1.** Synthesis of fully fused pyrene diporphyrin hybrids (**4a–c**, Ar = 3,5-di-*tert*-butylphenyl). a) NBS, CH<sub>2</sub>Cl<sub>2</sub>, pyridine, –10 °C; b) 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane, [Pd(PPh<sub>3</sub>)<sub>4</sub>], Cs<sub>2</sub>CO<sub>3</sub>, toluene, 110 °C; c) Sc(OTf)<sub>3</sub>, DDQ, toluene, 110 °C; d) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, then aq HCl (M = 2H); Zn(OAc)<sub>2</sub>, MeOH, CH<sub>2</sub>Cl<sub>2</sub> (M = Zn); Pb(OAc)<sub>2</sub>, pyridine, CH<sub>2</sub>Cl<sub>2</sub> (M = Pb). DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, NBS = *N*-bromosuccinimide, Tf = trifluoromethanesulfonyl.

tion).<sup>[7]</sup> After examining several different reaction conditions, we found that the double fusion of two pyrene rings with the diporphyrin moiety in **3** can be achieved by using anhydrous FeCl<sub>3</sub> in dichloromethane to give **4a**. The crude product of this reaction can be readily metalated with Zn(OAc)<sub>2</sub> to give the fully fused porphyrin hybrid **4b** (68–77% yields based on

**3**). To the best of our knowledge, this reaction represents the first example of direct fusion of aromatic rings to porphyrins without the need to activate porphyrin rings with nickel, or the aromatic rings with alkoxy groups. The formation of only one isomer of doubly fused diporphyrins was observed (confirmed by <sup>1</sup>H NMR spectroscopy and TLC). Based on previously reported data on the selectivity of oxidative coupling of porphyrins,<sup>[11d,12]</sup> the formation of anti-regioisomeric porphyrins is proposed.

Among other possible metalloporphyrins, the Q bands of the Pb<sup>II</sup> derivatives exhibit strong red-shifts.<sup>[13]</sup> We found that the free-base derivative of the pyrene–diporphyrin hybrid **4a** can be metalated with Pb(OAc)<sub>2</sub> to give **4c**. Taking into account the size of their extended  $\pi$ -conjugation systems, the fully fused products **4a**, **4b**, and especially **4c** display surprisingly good solubility in organic solvents.

The absorption spectra of the pyrene dimer **3** and metalated fused pyrene diporphyrins **4b** and **4c** in dichloromethane containing 1% pyridine are shown in Figure 2. The



**Figure 2.** UV/Vis–NIR absorption spectra of **2** (—), **3** (\*), **4a** (●), **4b** (○), and **4c** (◆) in dichloromethane/1% pyridine. The  $\epsilon$  value for **2** has been multiplied by 0.2 in order to present all the spectra in the same plot.

starting porphyrin dimer **3** have a strong Soret band absorption near  $\lambda = 420$  nm, which is similar to that in unperturbed monoporphyrin **2**, and a strongly red-shifted Soret band near  $\lambda = 580$  nm.<sup>[7b]</sup> Upon pyrene ring fusion, both Soret bands are red-shifted and appear as one broad band at  $\lambda \approx 600$  nm. The most significant differences in absorption spectra are observed for the Q bands. The increase in conjugation of the porphyrin dimer by adding two fused pyrene rings results in a large bathochromic shift of the Q band from  $\lambda = 1141$  nm in the pyrene dimer **3** to  $\lambda = 1323$  nm in the fused pyrene dimer **4b**. Upon metalation with Pb<sup>II</sup>, the Q band is shifted to  $\lambda = 1459$  nm. Thus, the overall effect of ring fusion and metal substitution (**4c**) is a red-shift of 318 nm compared to **3**. In the case of the Pb<sup>II</sup> derivative **4c** the Q band is quite broad, and covers the NIR region from approximately  $\lambda = 1150$  to 1530 nm. Substitution with two singly connected pyrene rings in compound **3** does not change the energy of the Q band, but causes significant enhancement of its intensity (2.7 times) compared to the parent (*t*Bu)<sub>2</sub>Ph-substituted porphyrin dimer.<sup>[14]</sup> This effect is even more pronounced for the fused products **4a–4c** with the Q band almost five times as intense than for the reference di-

*tert*-butyl porphyrin dimer,<sup>[14]</sup> and is comparable to the intensity of the Q bands in porphyrin trimers.<sup>[15]</sup>

The electrochemical properties of zinc porphyrins **2**, **3**, and **4b,c** have been studied by cyclic voltammetry (versus ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), Table 1). Consistent with

**Table 1:** Redox potentials of pyrene-functionalized porphyrins.<sup>[a]</sup>

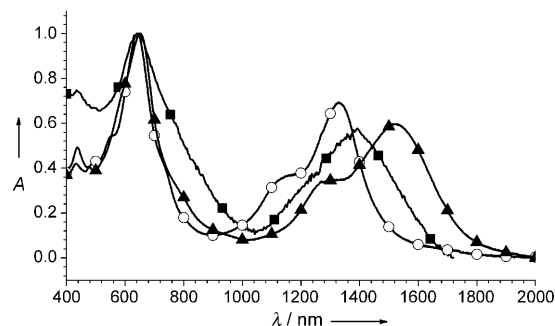
Compound	$E_{1/2}^{\text{ox},3}$	$E_{1/2}^{\text{ox},2}$	$E_{1/2}^{\text{ox},1}$	$E_{1/2}^{\text{red},1}$	$E_{1/2}^{\text{red},2}$	$\Delta E^{\text{ox-red}}$
<b>2</b>	1.26	0.81	0.52	-1.78	-2.18	2.3
<b>3</b>	0.89	0.35	-0.01	-1.10	-1.27	1.09
<b>4b</b>	–	0.18	-0.13	-0.97	-1.14	0.84
<b>4c</b>	–	0.15	-0.18	-0.95	-1.18	0.77

[a] Values recorded in dichloromethane and reported in V versus Fc/Fc<sup>+</sup>.

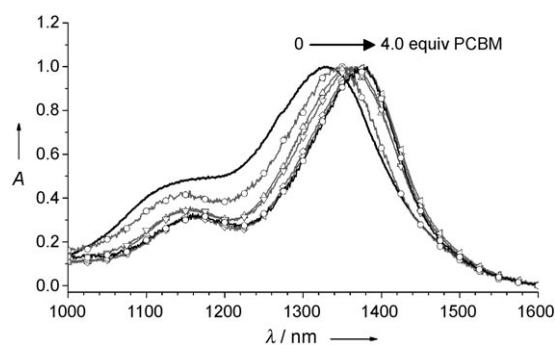
previously reported data,<sup>[7,14,15]</sup> the triply connected porphyrin dimers show a significant decrease in the separation between  $E_{1/2}^{\text{ox},1}$  and  $E_{1/2}^{\text{red},1}$  potentials ( $\Delta E^{\text{ox-red}}$ ) relative to the monoporphyrin values, for example,  $\Delta E^{\text{ox-red}}(\mathbf{2}) = 2.3$  V, and  $\Delta E^{\text{ox-red}}(\mathbf{3}) = 1.09$  V.  $\Delta E^{\text{ox-red}}$  decreases further to 0.84 V for the fused pyrene diporphyrin **4b**; this value is close to that of triply connected porphyrin trimers (Figure 1a,  $n = 1$ ).<sup>[15]</sup> Theoretical calculations (B3LYP/6-31G) performed on the model free-base diporphyrins also predict a smaller energy gap for the fused pyrene-diporphyrin compared to porphyrin dimer with significant contribution from the fused pyrene rings to both the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively, see the Supporting Information).

The <sup>1</sup>H NMR spectra of **4a–4c** exhibited only broad signals at temperatures ranging from -40 °C to 70 °C in a variety of solvents. Such behavior is common for larger porphyrin tapes<sup>[7,8]</sup> and is usually attributed to aggregation of oligoporphyrin molecules by strong  $\pi$ - $\pi$  interactions in solution. A well-resolved <sup>1</sup>H NMR spectrum of **4b** could be obtained in benzene at 70 °C if a small amount of pyridine was added. The pyridine apparently prevents aggregation by coordinating to Zn<sup>II</sup> (see the Supporting Information). Aggregation in the solid state is expected to be even more pronounced than in solution. The fused pyrene moieties of **4a–c** are not shielded and are therefore suited for intermolecular attractive pyrene-pyrene interactions.<sup>[16]</sup> The thin-film absorption spectra of fused porphyrins **4a–c** exhibit a considerable red-shift of the Q band, for example, for **4c** to 1527 nm at peak maximum (ca. 70 nm shift) compared to  $\lambda = 1459$  nm in solution. Thin films of the Pb<sup>II</sup> diporphyrin **4c** have a measurable absorption that extends to  $\lambda = 1.9 \mu\text{m}$  (Figure 3).

Selective noncovalent interactions between porphyrins and  $\pi$ -conjugated acceptors, such as fullerenes, have previously been exploited to prepare extended assemblies with applications in surface engineering and organic electronics.<sup>[17]</sup> To investigate this type of interaction, the spectral changes for thin films comprised of fused porphyrins **4a–c** with different ratios of porphyrin to PCBM were examined (PCBM = [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester; Figure 4). An increase in the concentration of PCBM results in a shift of the peak position of the Q band further into the NIR region (Figure 4).



**Figure 3.** UV/Vis-NIR absorption spectra of thin films of **4a** (■), **4b** (○), and **4c** (▲) on glass. Samples were spin-cast from toluene/5% pyridine solutions.



**Figure 4.** Spectral changes of the NIR absorption of thin films of **4b**/[C<sub>60</sub>]-PCBM mixtures. Equivalents of PCBM added: 0 (—), 0.5 (○, gray line), 1.0 (△), 2.0 (▽), 2.5 (◇), 3.0 (◁), 4.0 (○, black line).

The red-shift (45 nm) is saturated at approximately  $\lambda = 1375$  nm for the film containing fused porphyrin **4b** and PCBM (1:3 ratio). Fused porphyrins **4a** and **4b** exhibit similar behavior in the thin films with the maximum absorption of the Pb dimer **4c** at  $\lambda = 1566$  nm (40 nm shift). These shifts in absorption are attributed to electronic interactions between the porphyrins and the fullerene.

Pyrene-fused dimers **4a–4c** have been used as active materials in NIR photodetectors, and give external quantum efficiencies (EQEs) of up to 6.5% at  $\lambda = 1350$  nm for **4b**.<sup>[18]</sup> To the best of our knowledge, this efficiency is among the highest EQE values reported for NIR organic dyes.

In summary, fusion of the two pyrene units with diporphyrin tape in the (meso,β) fashion can be accomplished with high efficiency by using a FeCl<sub>3</sub>-mediated oxidative ring-closure reaction. This is the first example of direct fusion of aromatic rings with porphyrins which does not require activation of porphyrins or aromatic rings. The fused pyrene-diporphyrin hybrid structures **4a–c** resemble porphyrin trimers in their absorption and electrochemical properties. However, pyrene-fused dimers have the advantages of a simple preparation, high solubility, and film processibility. This method represents a straightforward route to obtain NIR dyes with high absorption. The two pyrene rings of the products are suited for both intermolecular interactions and supramolecular contacts with fullerene acceptors.

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