**Fused-Ring Systems**

**Fused Pyrene–Diporphyrins: Shifting Near-Infrared Absorption to 1.5 μm and Beyond**

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

Porphyrrins 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,[1,2] nonlinear optics,[3] and telecommunication technologies.[4] Porphyrrins have been investigated as active materials in photovoltaic cells[5] because of their high efficiency of charge separation and transport,[5] strong absorbance in the visible region, high chemical stability, and the ease with which their optoelectronic properties can be tuned with chemical modification.[6] The absorption bands of porphyrrins 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, (β, meso, β) porphyrrin tapes (Figure 1a, n = 0–22) show marked red-shifts in the porphyrrin absorption bands, which extend deep into the NIR region.[7, 8a] Triply fused porphyrrins with n = 1.2 give absorbance in the mid-NIR region (i.e., conventional wavelengths for telecommunication technologies). Triply connected porphyrrin dimers (Figure 1a, n = 0) have a strong absorbance at λ = 1050 nm, are photo- and chemically stable, have a high solubility, and can be easily prepared from monoporphyrins.[7] Development of new organic dyes based on these accessible porphyrrin dimers with absorption at the wavelengths for telecommunication (λ = 1.5 μm) still remains a challenge.

Extending the size of π conjugation in porphyrrin systems results in most cases in a bathochromic (red) shift of the absorption.[7,8a] The conjugation of porphyrrin dimers can be extended through several modes of substitution involving the meso, (β, β), (β, meso) and (β, meso, β) positions. For diporphyrins substituted with two alkyne groups at the terminal meso positions, the Q band is red-shifted by 130 nm (λ = 1181 nm) relative to the parent dimer.[9] In contrast, extending the conjugation in porphyrrin dimers by benzannulating β,pyrrolic positions red-shifts the Q band by only 18 nm, and the resulting compounds have poor solubility.[8b] Recently, it has been shown that anthracene rings can be fused to porphyrrin dimers through the (β, meso, β) mode, which leads to a red-shift of the Q band to 1495 nm.[8d] However, the anthracene-fused diporphyrin exhibits the same undesirable difficulties found with higher porphyrrin tapes, for example, synthetic difficulty, low yields and low solubility.[8c] Moreover, fusion of anthracene rings is limited only to alkoxy-substituted derivatives.

The effects of aromatic ring fusion to porphyrrin tapes in a (meso, β) mode have not been explored. We have analyzed the structures of the diporphyrin core (Figure 1b), a (β, meso, β) triply fused aromatic system (Figure 1c), and a (β, 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 porphyrrins and porphyrrin tapes, in which the planarity causes aggregation and low solubility, the pyrene–(β, meso)-fused diporphyrin displays out-of-plane distortion that is known to improve solubility and processibility in conjugated aromatics.[10] By taking into account the predicted bathochromic shift, distortion from planarity, and ease of synthesis, the (β, meso)-fused pyrene diporphyrin from

---

**Figure 1.** a) General structure of triply fused porphyrrins. 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.
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, or appropriately arranged azulene rings), and/or nickel(II) porphyrins to direct fusion. Attempts to fuse unsubstituted pyrene rings with porphyrins were unsuccessful.

The pyrene-substituted porphyrin dimer 3 was prepared in two steps (Suzuki coupling and Osaka’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 Information). 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 FeCl₃ in dichloromethane to give 4a. The crude product of this reaction can be readily metalated with Zn(OAc)₂ to give the fully fused porphyrin hybrid 4b (68–77% yields based on the starting porphyrin dimer 3) have a strong Soret band absorption near λ = 420 nm, which is similar to that in unperturbed monoporphyrin 2, and a strongly red-shifted Soret band near λ = 580 nm. Upon pyrene ring fusion, both Soret bands are red-shifted and appear as one broad band at λ ≈ 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 bands. 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 }

![Scheme 1](image)

**Scheme 1.** Synthesis of fully fused pyrene diporphyrin hybrids (4a–c, Ar = 3,5-di-tert-butylphenyl). a) NBS, CH₂Cl₂, pyridine, –10°C; b) 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane, [Pd(PPh₃)₄], Cs₂CO₃, toluene, 110°C; c) Sc(OTf)₃, DDQ, toluene, 110°C; d) FeCl₃, CH₂Cl₂, 20°C, then aq HCl (M = 2H); Zn(OAc)₂, MeOH, CH₂Cl₂ (M = Zn); Pb(OAc)₂, pyridine, CH₂Cl₂ (M = Pb). DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzquionine, NBS = N-bromosuccinimide, TFS = trifluoromethanesulfonyl.

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 1H NMR spectroscopy and TLC). Based on previously reported data on the selectivity of oxidative coupling of porphyrins, the formation of anti-regiosomeric porphyrins is proposed.

Among other possible metalloporphyrins, the Q bands of the Pb²⁺ derivatives exhibit strong red-shifts. We found that the free-base derivative of the pyrene–diporphyrin hybrid 4a can be metalated with Pb(OAc)₂ to give 4c. Taking into account the size of their extended π-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](image)

**Figure 2.** UV/Vis–NIR absorption spectra of 2 (——), 3 (●), 4a (●), 4b (●), and 4c (●) in dichloromethane/1% pyridine. The ε value for 2 has been multiplied by 0.2 in order to present all the spectra in the same plot.
tert-butyl porphyrin dimer,\textsuperscript{14} and is comparable to the intensity of the Q bands in porphyrin trimers.\textsuperscript{15}

The electrochemical properties of zinc porphyrins 2, 3, and 4b,c have been studied by cyclic voltammetry (versus ferrocene/ferrocenium (Fc/Fc’). Table 1). Consistent with previously reported data,\textsuperscript{7,14,15} the triply connected porphyrin dimers show a significant decrease in the separation between \( E_{\text{ox}}^{1/2} \) and \( E_{\text{red}}^{1/2} \) potentials (\( \Delta E^{\text{ox-red}} \)) relative to the monomp-orphyrin values, for example, \( \Delta E^{\text{ox-red}}(2) = 2.3 \) V, and \( \Delta E^{\text{ox-red}}(3) = 1.09 \) 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, \( n = 1 \)).\textsuperscript{15} 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 \( ^1\text{H} \) NMR spectra of 4a–4c exhibited only broad signals at temperatures ranging from \(-40^\circ\text{C}\) to \(70^\circ\text{C}\) in a variety of solvents. Such behavior is common for larger porphyrin tapes\textsuperscript{7,8} and is usually attributed to aggregation of oligoporphyrin molecules by strong \( \pi-\pi \) interactions in solution. A well-resolved \( ^1\text{H} \) NMR spectrum of \( n \)-triply connected porphyrin trimers (Figure 1a, \( n = 1 \), \( 4 \)).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_{\text{ox}}^{1/2} ) (V)</th>
<th>( E_{\text{ox,1}}^{1/2} ) (V)</th>
<th>( E_{\text{ox,2}}^{1/2} ) (V)</th>
<th>( E_{\text{red}}^{1/2} ) (V)</th>
<th>( E_{\text{red,1}}^{1/2} ) (V)</th>
<th>( E_{\text{red,2}}^{1/2} ) (V)</th>
<th>( \Delta E^{\text{ox-red}} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.26</td>
<td>0.81</td>
<td>0.52</td>
<td>-1.78</td>
<td>-2.18</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.89</td>
<td>0.35</td>
<td>-0.01</td>
<td>-1.10</td>
<td>-1.27</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>-</td>
<td>0.18</td>
<td>-0.13</td>
<td>-0.97</td>
<td>-1.14</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>-</td>
<td>0.15</td>
<td>-0.18</td>
<td>-0.95</td>
<td>-1.18</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

[a] Values recorded in dichloromethane and reported in V versus Fc/Fc’.

![Figure 3. UV/Vis–NIR absorption spectra of thin films of 4a (m), 4b (c), and 4c (a) on glass. Samples were spin-cast from toluene/5% pyridine solutions.](image)

![Figure 4. Spectral changes of the NIR absorption of thin films of 4b(Pc61)-PCBM mixtures. Equivalents of PCBM added: 0 (——), 0.5 (○), 1.0 (△), 2.0 (○○), 2.5 (○○○), 3.0 (○○○○), 4.0 (○○○○○, black line).](image)

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.\textsuperscript{16} 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,\( \beta \)) fashion can be accomplished with high efficiency by using a FeCl\textsubscript{3}-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–4c 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.
Keywords: fused-ring systems · dyes/pigments ·
organic electronics · porphyrinoids · noncovalent interactions


