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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-11-2015-009128.R1
Article Type:	Communication
Date Submitted by the Author:	11-Dec-2015
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A Quinoidal *Bis*-Phenalenyl-Fused Porphyrin with Supramolecular Organization and Broad Near-Infrared Absorption

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A *bis*-phenalenyl-fused porphyrin has been synthesized by thermal dehydro-aromatization reaction regioselectively as a single syn-isomer. X-ray crystal structure revealed that both phenalenyl units of this porphyrin have close π - π contacts forming continuous network of interacting porphyrin rings. A broad and intense NIR absorption can be attributed to quinoidal character of *bis*-phenalenyl-fused porphyrin.

Large π -extended porphyrins obtained by *meso*, β annulations of a porphyrin core with polycyclic aromatic hydrocarbons (PAHs) have attracted significant attention recently due to strong near infrared (NIR) absorption¹⁻³ and fluorescence in the biological window.^{1,g,k,3} Such *meso*, β -fused porphyrin hybrids have been used in NIR photodetectors,⁴ NIR active organic solar cells^{1d,i,3} and in non-linear optical applications.^{1c} Further development of the chemistry of these PAH-porphyrin hybrids is advantageous to help understand the structure–property relationships of fused porphyrins and assist in molecular engineering the electronic properties of these compounds.

To date, all of the PAHs fused to a porphyrin ring in a *meso*, β manner belong to benzenoid Kekulé-type hydrocarbons.¹ⁿ However, the electronic properties of PAHs can be varied over a large range, depending on the topology of hydrocarbon rings, arrangement of double bonds, *etc.*⁵ Here we report an example of a non-Kekulé PAH, phenalene, coupled to a porphyrin using *meso*, β fusion. Porphyrins fused with phenalene are of interest for investigation of their molecular structure and solid-state organization. For example, an unstable biradicaloid porphyrin has been reported recently that shares common carbon–carbon bonds with two phenalenyl rings (which can also be viewed as a porphyrin ring fused in a β ,*meso*, β -fashion with two meta-xylylene

biradicals).¹¹ In principle, two phenalenyls bis-annulated to a metallo-porphyrin in a *meso*, β manner can be represented either in a quinoidal form or as a structure with significant biradical character (Figure 1). Quinoidal porphyrins have unique electronic and optical properties with absorption transitions that extend to the NIR region.⁶ It has also been shown that *bis*-phenalenyl-fused hydrocarbons can form one-dimensional (1D) chains in crystals with short π - π contacts at the overlapping phenalene rings.⁷ Similarly, formation of face-to-face dimers has been experimentally demonstrated for crystals of fused PAH-porphyrins.^{1c,h} Thus, porphyrins that possess solid state organization typical for *bis*-phenalenyl fused hydrocarbons may have high carrier mobility and long exciton diffusion lengths, of significant importance in organic electronics.⁸ Herein, we demonstrate that a stable quinoidal porphyrin ring fused with two phenalenyl radicals in *meso*, β -fashion can be obtained by a thermal cyclodehydrogenation route.

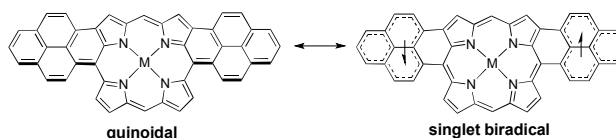


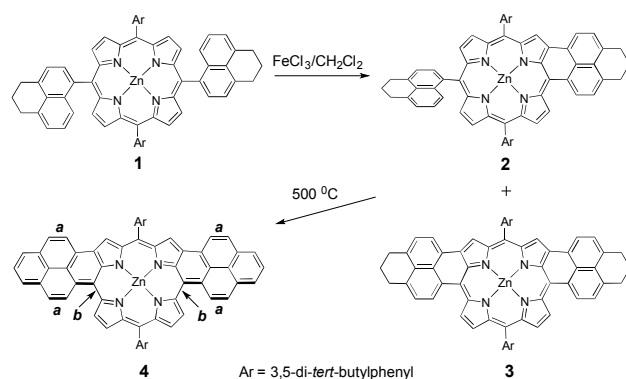
Figure 1. Quinoidal and singlet biradical representations of a *bis*-phenalenyl fused metallo-porphyrin.

Synthesis of *meso*, β -fused porphyrins is typically accomplished by intramolecular oxidative coupling of the PAH rings and porphyrin core of singly (*meso*) connected PAH-porphyrins.¹⁻³ Unfortunately, the phenalene ring itself is an air-sensitive hydrocarbon with properties of a neutral radical, thus handling and manipulations of it in synthesis is problematic.⁹ Therefore, to extend the *meso*, β fusion approach to the synthesis of a *bis*-phenalenyl-fused porphyrin, we use a stable, partially-saturated aromatic precursor, 2,3-dihydro-1*H*-phenalene. Singly connected 5,15-*bis*(2,3-dihydro-1*H*-phenalenyl) porphyrin **1** (Scheme 1) was synthesized from 5,15-dibromoporphyrin and pinacol boronate ester of 2,3-dihydro-1*H*-phenalene under Suzuki coupling conditions (Pd(PPh₃)₄/Cs₂CO₃, reflux in toluene) in

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† Electronic Supplementary Information (ESI) available: Details of experimental procedures, spectroscopic and calculation data. Copies of ¹H, ¹³C NMR and mass spectra for compounds **1-4**, cyclic voltammetry traces for **1-4**, photodegradation study and a CIF file for **4**. CCDC 1434349. See DOI: 10.1039/c000000x/

85% yield. Fusion of 2,3-dihydro-1*H*-phenalene rings to a porphyrin core of **1** proceeds under standard Scholl reaction conditions ($\text{FeCl}_3/\text{CH}_2\text{Cl}_2$, room temperature) with the formation of mono-fused **2** (40%) and the doubly-fused **3** (30%), with the latter obtained exclusively as the *syn* regioisomer. Apparently, the alkyl groups are strong enough donors to activate alkyl bridged naphthalene rings for oxidative coupling with the porphyrin, and simultaneously appear to promote regioselective fusion across the porphyrin ring. Thermal reactions are known as effective methods for the synthesis of PAHs.¹⁰ We found that both porphyrins **2** and **3** undergo one-step thermal cyclodehydrogenation/dehydroaromatization at high temperatures (500°C) to afford the fully unsaturated, doubly-fused porphyrin **4** (20–30% yields, Scheme 1). We also attempted a direct, one-step synthesis of **4** by thermolysis of **1**. The reaction did show the appearance of **4** when monitored by UV-visible spectroscopy; however, significant loss of *tert*-butyl groups occurred using this approach, likely due to the high melting point of **1** (> 500°C).



Scheme 1.

Porphyrins **1–4** were characterized using elemental analysis, mass and NMR spectroscopy (see Supporting Information). Porphyrin **3** was structurally assigned, as described previously,³ to the *syn*-regioisomer due to the presence of two equivalent di-*tert*-butylphenyl groups in the ¹H NMR spectrum. The ¹H-NMR spectrum of **4** is temperature independent and displays sharp signals with no significant line broadening at elevated temperatures (80°C). The β -protons are far up-field ($\delta = 7.3\text{--}8.1$ ppm) when compared to either non-fused **1** ($\delta = 9.2\text{--}9.5$ ppm) or doubly-fused **3** ($\delta = 9.2\text{--}9.6$ ppm). The up-field shift in **4** indicates a reduced diatropic character in the porphyrin that is consistent with quinoidal electron configuration disrupting the aromatic ring currents (Figure 1).⁶

X-ray analysis on crystals of **4** (as a pyridine adduct obtained from 1% pyridine in benzene) confirmed the structure and shows the conjugated π -system is significantly distorted from planarity, with a dihedral angle between the phenalenyl moiety and non-fused pyrrole ring of 21°. The twisting distortion is due to unfavorable steric interactions between the β -pyrrolic protons and α -protons of phenalenyl rings (mean distance = 2.08 Å). Bond lengths of phenalenyl

and pyrrolic rings vary in a range between 1.34–1.46 Å for C–C and 1.35–1.40 Å for the C–N bonds. Noteworthy are distances for bonds labeled “*a*” (average = 1.354(8) Å) and “*b*” (average = 1.455(8) Å) in Scheme 1. The short values for the *a*-bonds are consistent with aromatization of the outermost six-membered rings whereas the long *b*-bonds indicate disruption in the aromatic character of the porphyrin ring. The variation in bond lengths provides further evidence for quinoidal alteration of the porphyrin ring brought about by the phenalenyl moieties.

The solid-state packing in **4** displays supramolecular organization as continuous 1D slip-stack chains are arranged *via* multiple types of π - π interaction (Figure 2). One side of each **4** has short phenalene-phenalene contacts with an adjacent molecule (the shortest distance is 3.44 Å), whereas the other phenalene is involved in a porphyrin-phenalene contact with another adjacent molecule (the shortest distance is 3.47 Å). The phenalene-phenalene contacts in **4** likely originate from conventional dispersion forces since these distances are longer than values often observed for biradicaloid phenalenyl compounds, but typical for π - π interactions in a number of polycyclic aromatic hydrocarbons. The biradicaloid species have characteristically short (3.0–3.1 Å) intermolecular contacts in the solid state due to bonding interactions between unpaired phenalenyl electrons.⁷ Each chain of molecules in **4** contacts with two neighboring chains *via* pairs of pyridine ligands (the shortest contact between pyridines is 3.44 Å) coordinated to Zn atoms of adjacent chains (Figure 2, bottom).

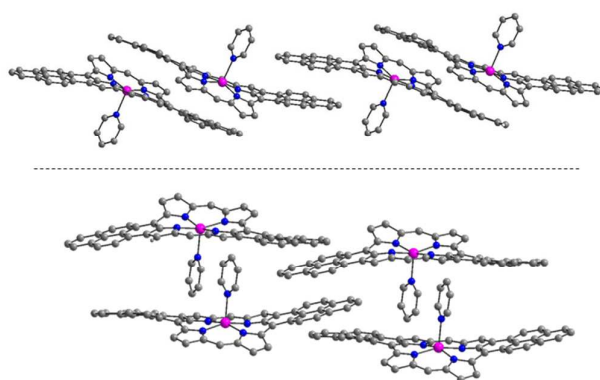


Figure 2. Two views from the x-ray structure of **4** that shows close phenalene-phenalene and porphyrin-phenalene contacts within a chain (top) and pyridyl-pyridyl contacts between chains (bottom). *Tert*-butylphenyl groups, hydrogen atoms and solvent molecules are omitted for clarity.

Theoretical calculations (B3LYP/LACVP**) of **4'** (*tert*-butyl groups replaced with H) show an asymmetric distribution in the valence orbitals leading to a HOMO–LUMO transition that has substantial charge transfer character. Calculations using spin-unrestricted broken-symmetry (UB3LYP(BS)/6-31G*/LANL2DZ) on model **4''** (*meso*-3,5-di-*tert*-butylphenyl groups replaced with H) predict < 3%, and thus insignificant,¹¹ biradical character (see ESI for

Mulliken atomic spin densities) in agreement with the ^1H NMR and x-ray data.

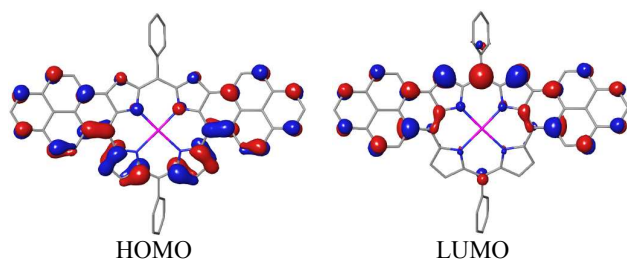


Figure 3. Frontier molecular orbitals of **4'** (isovalue = -0.032).

The electrochemical properties of porphyrins **1–4** were analyzed using cyclic voltammetry (see ESI). All of the compounds display reversible oxidation and reduction waves in dichloromethane with the separation in potentials of porphyrin **1** ($\Delta E^{\text{ox-red}} = 2.23$ V) decreasing upon ring fusion in **2** ($\Delta E^{\text{ox-red}} = 1.83$ V) and **3** ($\Delta E^{\text{ox-red}} = 1.58$ V), and aromatization in **4** ($\Delta E^{\text{ox-red}} = 1.36$ V). The redox potentials in **4** ($E_{1/2}^{\text{ox}} = 0.04$ V, $E_{1/2}^{\text{red}} = -1.32$ V vs Fc^+/Fc) are also anodically shifted relative to values in **3** ($E_{1/2}^{\text{ox}} = -0.08$ V, $E_{1/2}^{\text{red}} = -1.66$ V).

Absorption spectroscopy shows Soret and Q-bands that are, compared to porphyrin **1** ($\lambda_{\text{max}} = 425$ and 550 nm), bathochromically shifted in **2** ($\lambda_{\text{max}} = 484$ and 670 nm) and **3** ($\lambda_{\text{max}} = 497$ and 753 nm) (Figure 4). In contrast, the Soret band in **4** has a hypsochromic shift ($\lambda_{\text{max}} = 477$ nm), whereas the Q-band is bathochromically shifted into the NIR ($\lambda_{\text{max}} = 796$ nm). In addition, the Soret band of **4** has greatly diminished intensity whereas the Q-band is broadened (full width at half-maximum (fwhm) = 2140 cm^{-1}) and has twice the integrated area as the Q-band of **3** (fwhm = 770 cm^{-1}). A further broadening and redshift in the Q-band of **4** occurs in the solid state ($\lambda_{\text{max}} = 870$ nm, see ESI) with absorption tailing out to 1100 nm.

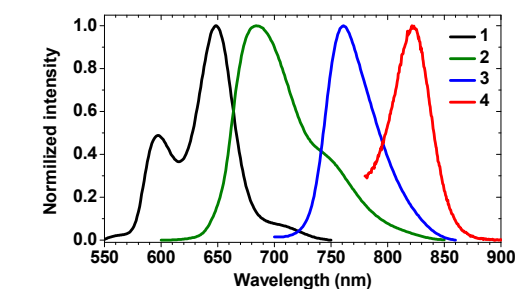
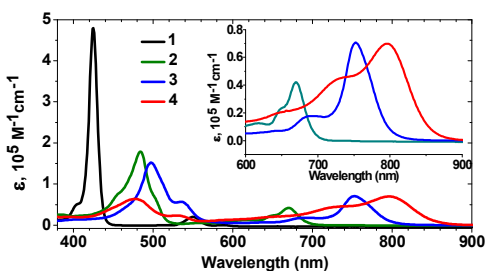


Figure 4. Optical absorption (top) and emission (bottom) spectra of **1–4** in CH_2Cl_2 solution.

Porphyrins **1–4** display emission at room temperature that shifts with extending conjugation from **1** ($\lambda_{\text{max}} = 598$ nm) to $\lambda_{\text{max}} = 700$, 765 , and 835 nm for **2**, **3** and **4**, respectively (Figure 4). The excited state lifetime of **1** ($\tau = 2.1$ ns) is shorter in **2** and **3** ($\tau = 1.6$ ns for both). The photoluminescent quantum yield of **3** ($\Phi_{\text{PL}} = 11\%$ in CH_2Cl_2) is relatively high for porphyrinoids and in line with our previous observation of high fluorescence quantum efficiencies in fused porphyrins. The quantum efficiency of **4** is low ($\Phi_{\text{PL}} = 0.3\%$) and decays with a double exponential lifetime ($\tau_1 = 160$ ps, 72% , $\tau_2 = 890$ ps, 28%).

Chemical oxidation of **3** causes a marked decrease in the intensity of the Soret and Q-bands with the appearance distinct isobestic points and very broad peaks for the cation centered at 550 and 900 nm (Figure 5). Likewise, oxidation of **4** causes significant changes in the electronic spectrum; a red-shift in the Soret band, disappearance of the broad Q-band and appearance of very strong and narrow band (fwhm = 480 cm^{-1}) at ca. 1000 nm. The intense absorption band for the cation radical of **4** may reflect increased aromatic character of oxidized form. The optical features are similar to absorption features found in oxidized mono-cations of other quinoidal porphyrins.¹²

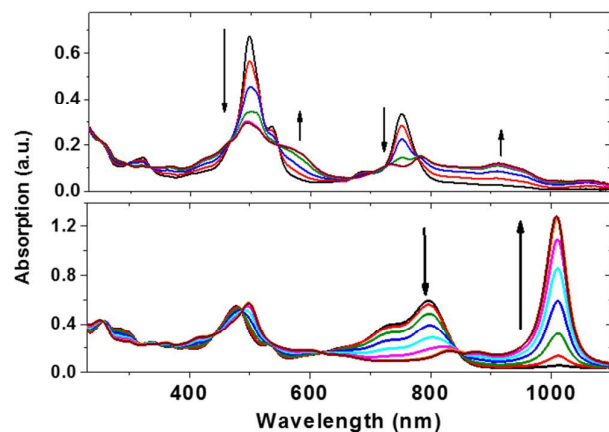
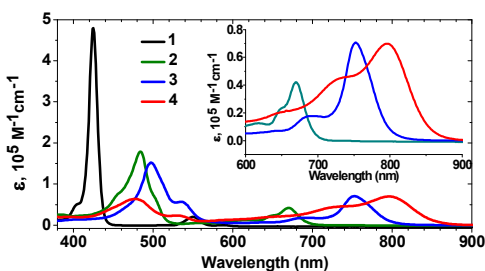


Figure 5. Absorption spectra of **3** (top) and **4** (bottom) upon chemical oxidation with AgPF_6 in CH_2Cl_2 solution.

In summary, we have efficiently synthesized a quinoidal *bis*-phenalenyl-fused porphyrin using a masked phenalene precursor. The porphyrin has a highly perturbed electronic

structure, enhanced NIR absorption, excellent photostability (see ESI) and hierarchical supramolecular organization in the crystal. *Bis*-phenalenyl-fused porphyrin forms 1D chains in the crystal through two types of alternating π - π interactions, porphyrin-to-phenalene and phenalene-to-phenalene. The quinoidal hybrid displays unusually broad and intense Q-band reaching 800–900 nm. Analysis of frontier molecular orbitals suggests that such broadening of the Q-band is due to contribution from a charge transfer from one of the dipyrromethene moieties into another one inside a porphyrin ring.

The authors would like to thank funding from the Universal Display Corporation.

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