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Bis-Anthracene Fused Porphyrins: Synthesis, Crystal Structure, and Near-IR Absorption

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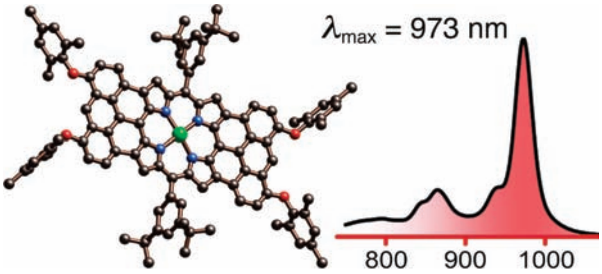
ABSTRACT



Synthesis of fused bis-anthracene porphyrin monomers and dimers has been achieved by oxidative ring closure using $FeCl_3$ and $Sc(OTf)_3$/DDQ, respectively. The fused compounds display red-shifted absorption spectra with maxima in the near-IR at 973 and 1495 nm, respectively, and small electrochemical HOMO−LUMO gaps. The crystal structure of the fully fused bis-anthracene porphyrin shows that it has a regular planar π-system.

The fusion of aromatic rings to porphyrin cores has received much attention recently.[1−12] The unusual optical and electronic properties of these expanded π-systems make them interesting for a variety of applications including photodynamic therapy,[13] two-photon absorption,[14] nonlinear optics,[8,15−17] organic semiconductors[18] and photovoltaics.[6,19,20]

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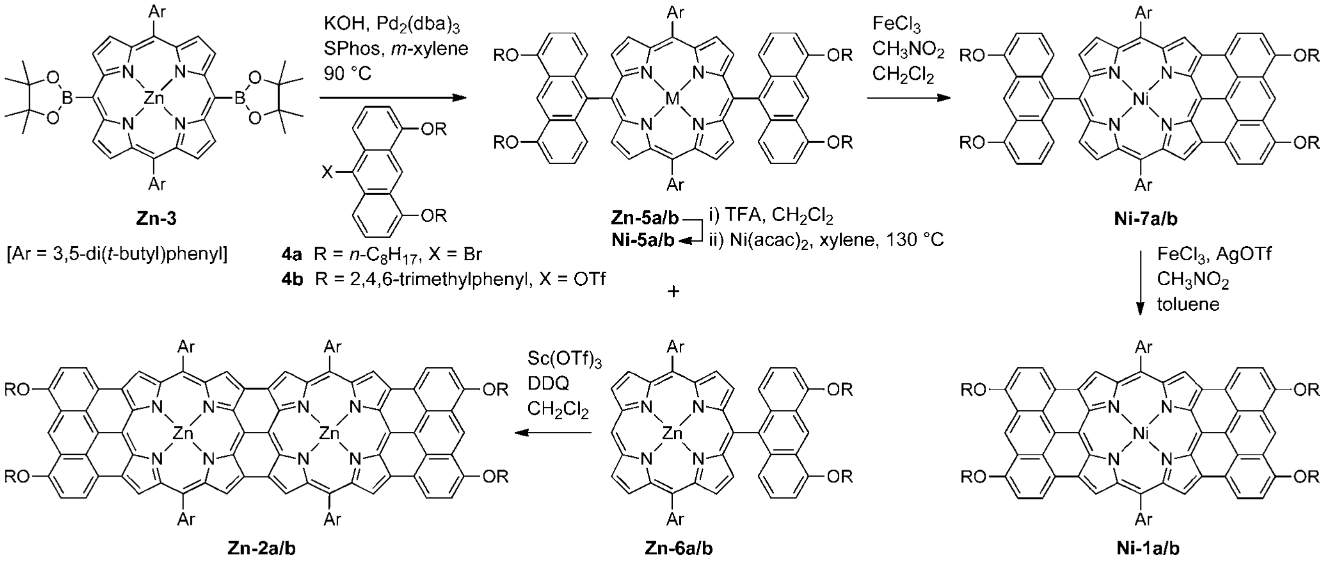
Scheme 1. Synthesis of Anthracene-Fused Porphyrins[a]



[a] **a** denotes R = n-C_8H_{17}, **b** denotes R = 2,4,6-trimethylphenyl.

Anthracene matches well to the geometry of the porphyrin ring periphery, indicating that fusion may occur without loss of planarity to generate highly delocalized π-systems with strong near-IR absorption. Previously, we reported the synthesis of a pair of fused monoanthracene porphyrins and demonstrated that electron-donating alkoxy substituents are required on the anthracene in order to achieve oxidative fusion to the porphyrin.[4] Here we report the synthesis of a fused bis-anthracene porphyrin monomer and dimer, together with an investigation of their optical and electrochemical properties. We demonstrate that bulky aryl ether substituents can be used to limit the aggregation of these large flat π-systems.

Anthracene porphyrins **Ni-1b** and **Zn-2b** were synthesized as shown in Scheme 1. Initially, synthesis was carried out with n-octyl ether substituents to promote solubility. 10-Bromo-1,8-bis(octyloxy)anthracene **4a** was subjected to Suzuki coupling with diboronic ester **Zn-3** to afford bis- and monoanthracene porphyrins **Zn-5a** and **Zn-6a**. A variety of conditions were explored for fusion of the anthracene units to the ring periphery. When **Zn-5a** was treated with $Sc(OTf)_3$/DDQ the only product isolated was the partially fused porphyrin **Zn-7a**; treatment of **Zn-7a** with further $Sc(OTf)_3$/DDQ resulted in no reaction.

Iron(III) chloride has been widely used for oxidative ring closures.[3,19,21] In order to apply this methodology, the coordinated zinc metal was replaced with nickel(II) to prevent demetalation. When **Ni-5a** was treated with 10 equiv of $FeCl_3$ in dichloromethane, the product was found to be partially fused porphyrin **Ni-7a**. Subjection of **Ni-7a** to a further 10 equiv of $FeCl_3$ led to formation of fully fused bis-anthracene porphyrin **Ni-1a**.

Purification and characterization of **Ni-1a** proved to be challenging due to strong aggregation. A clean MALDI-TOF mass spectrum was obtained; however, the ^1H NMR spectrum was broad, even at 140 °C in $C_2D_2Cl_4$.

Osuka and Tsuda have reported the synthesis of porphyrin tapes consisting of porphyrin units fused across the *meso*, β and β' positions with $Sc(OTf)_3$/DDQ.[22] Reaction of **Zn-6a** under these conditions yielded the fully fused porphyrin dimer **Zn-2a** in a one-pot procedure, as confirmed by the MALDI-TOF spectrum. The product displayed absorption in the near-IR, consistent with a highly conjugated porphyrin system; however, purification of **Zn-2a** by chromatography proved impossible due to its low solubility. Strong aggregation led to a featureless ^1H NMR spectrum.

In order to circumvent recurring problems of insolubility and aggregation, the anthracene moiety was redesigned to bear bulky 2,4,6-trimethylaryl ether substituents. The use of bulky aryl ether substituents to limit aggregation has been successfully employed in phthalocyanines, which are notorious for their insolubility and aggregation.[23]

Synthesis of anthracene triflate **4b** was achieved as shown in Scheme 2. Nucleophilic aromatic substitution of 1,8-dichloroanthraquinone by 2,4,6-trimethylphenol gave anthraquinone **8**.[24] Reduction with $NaBH_4$ followed by acid work up gave anthracenone **9**, which was converted into anthracene triflate **4b** by treatment with lithium hexamethyldisilazane and triflic anhydride at −78 °C.[25,26]

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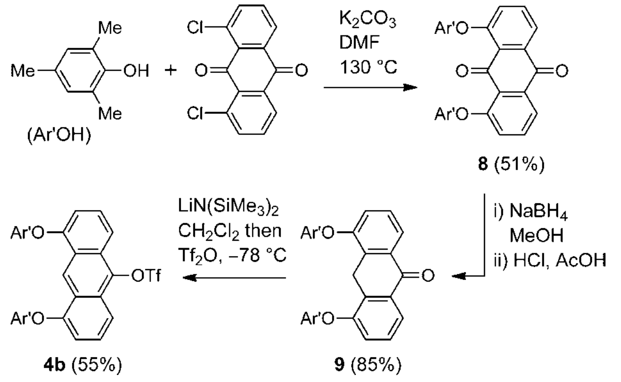
Scheme 2. Synthesis of Anthracene Triflate **4b**



Suzuki coupling between **4b** and **Zn-3** led to the formation of **Zn-5b** and **Zn-6b** in 15 and 44% yields, respectively. Demetalation of **Zn-5b** with TFA and treatment with $Ni(acac)_2$ gave porphyrin **Ni-5b**, which underwent intramolecular oxidative ring closure with $FeCl_3$ to give **Ni-7b** in 72% yield. Further reaction with $FeCl_3$ gave the fully fused porphyrin **Ni-1b**. However, this compound was contaminated with chlorinated byproduct, which was difficult to remove, so efforts were directed toward suppressing chlorination. AgOTf was added to the reaction mixture to scavenge chloride ions, and this strategy reduced the degree of chlorination. Small amounts of monochlorinated fused porphyrin were still observed by MALDI-TOF and ^{1}H NMR of the crude reaction mixture, but these byproducts were removed by silica chromatography to give **Ni-1b** in 15% yield.

Crystals of **Ni-1b** were grown by addition of methanol to a solution in chloroform. Although the crystals were small and highly solvated, with 52% of the unit cell being occupied by disordered solvent, we were able to obtain a low-resolution crystal structure (Figure 1).[27] This structure confirms the regular planar geometry of the π-system and shows that the aryl ether substituents lie perpendicular to the anthracene−porphyrin core, thereby inhibiting π-stacking. The effectiveness of these substituents in preventing aggregation is demonstrated by the ^{1}H NMR spectrum of **Ni-1b**, which shows sharp signals, in contrast to the very broad spectrum of **Ni-1a**.

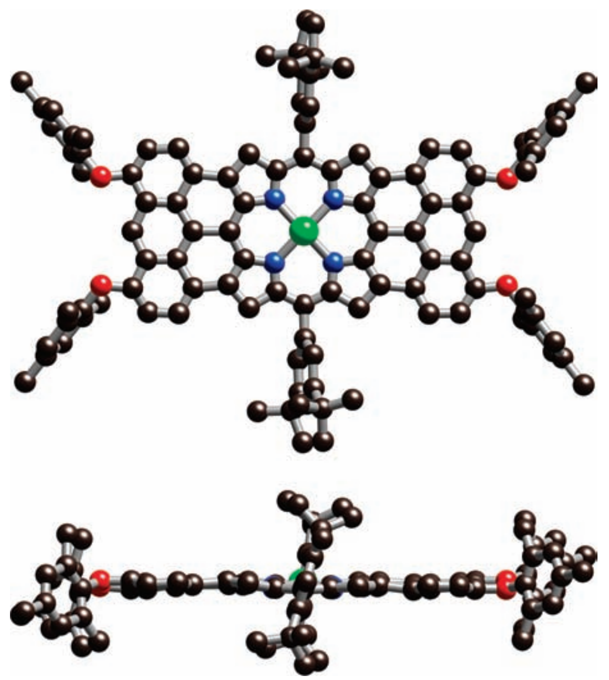


Figure 1. Two orthogonal views of the molecular structure of **Ni-1b** in the crystal (hydrogens omitted for clarity).[27]

The bis-anthracene-fused dimer **Zn-2b** was synthesized in a one-pot procedure from **Zn-6b** using $Sc(OTf)_3$/DDQ in a 13% yield. It is soluble in many organic solvents and gives a sharp ^{1}H NMR spectrum in d_5-pyridine.

Unfused porphyrins **Ni-5b** and **Zn-6b** display absorption spectra typical of simple porphyrin monomers, with intense Soret bands at 427 and 429 nm, respectively (Figure 2).[3,6] However expansion of the π-system by fusion to an anthracene unit greatly perturbs the electronic structure. As a result, the absorption spectrum of **Ni-7b** is red-shifted, displaying a λ_{max} at 828 nm and a highly distorted spectral shape, with lower peak intensities than **Ni-5b**. Such perturbations have been reported previously in low-symmetry porphyrins.[3,19] Fusion of the second anthracene unit to the porphyrin core in **Ni-1b** restores the D_{2h} symmetry to give a simpler spectrum and a larger red-shift (λ_{max} 973 nm). The sharpness and intensity of this absorption band is unusual ($\varepsilon = 1.4 \times 10^5$ M^{-1} cm^{-1}; fwhm = 300 cm^{-1}); porphyrins fused to naphthalene or azulene rings display broad peaks with lower intensity.[3,9,19] The spectrum of **Zn-2b** extends well into the near-IR with a λ_{max} at 1495 nm. Furthermore, it displays a similar spectral shape to **Ni-1b** indicating that the chromophore also possesses D_{2h}-symmetry.

Cyclic and square wave voltammetry were carried out on **Ni-1b**, **Ni-5b**, **Ni-7b**, **Zn-2b**, and **Zn-6b** to determine their redox potentials (Table 1). Porphyrins **Ni-5b** and **Zn-6b** display $E_1^{ox}-E_1^{red}$ values typical of unfused porphyrin monomers.[28,29] The separation of E_1^{ox} and E_1^{red} decreases as the π-system is expanded by fusion to anthracene units.

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[27] X-ray diffraction data for crystals of **Ni-1b** were collected at 150 K (Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105–107) with synchrotron radiation using I19 (EH1) at the Diamond Light Source. Data were collected and reduced using CrystalClear (Rigaku Inc., 2009). The structure was solved using SIR92 (Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined using the CRYSTALS software suite. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487. The structure contains large solvent accessible voids comprising weak, diffuse electron density. The discrete Fourier transforms of the void regions were treated as contributions to the A and B parts of the calculated structure factors using PLATON/SQUEEZE (Spek, A. *J. Appl. Crystallogr.* **2003**, *36*, 7−13; van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201) integrated with the CRYSTALS software. The sample consisted of very thin plates which were highly prone to solvent loss, leading to very weak data with high agreement factors and the requirement for copious restraints. Full refinement details are given in the SI and the CIF file. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 771217), and copies of these data can be obtained free of charge via www. ccdc.cam.ac.uk/data_request/cif.

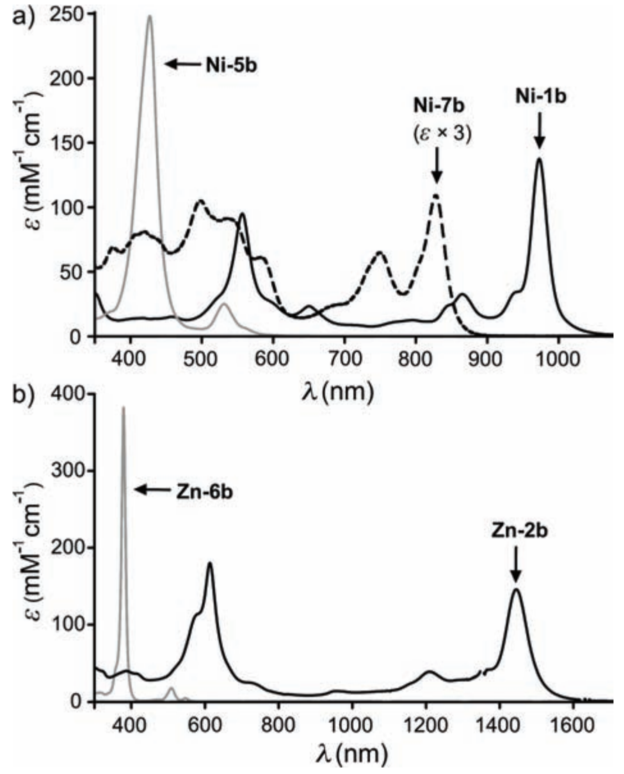

Figure 2. UV−vis−NIR absorption spectra in $CHCl_3$/1% pyridine for (a) **Ni-5b** (gray), **Ni-7b**, $\varepsilon \times 3$ (black dash), **Ni-1b** (black), (b) **Zn-6b** (gray) and **Zn-2b** (black).

Table 1. Redox Potentials of Compounds **Ni-1b**, **Ni-7b**, **Ni-5b**, **Zn-2b**, and **Zn-6b**[a]

compd	E_1^{ox} (V)	E_1^{red} (V)	$E_1^{ox} - E_1^{red}$
Ni-1b	0.07	−1.20	1.27
Ni-7b	0.08	−1.33	1.41
Ni-5b	0.63	−1.47	2.10
Zn-2b	−0.24	−1.01	0.77
Zn-6b	0.44	−1.56	2.00

[a] In THF with 0.1 M Bu_4NPF_6 vs internal ferrocene/ferrocinium.

These electrochemical gaps match well with the optical gaps of 1.50, 1.28, and 0.83 eV measured for the fused porphyrins **Ni-7b**, **Ni-1b**, and **Zn-2b**, respectively, at their near-IR maxima (in $CHCl_3$ with 1% pyridine). Furthermore, dimer **Zn-2b** displays optical and electrochemical properties similar those reported for triply fused porphyrin dimers and trimers.[28,30]

In conclusion, fully fused bis-anthracene porphyrin monomers and dimers have been synthesized for the first time. Oxidation with $Sc(OTf)_3$/DDQ was used to form the anthracene end-capped fused dimer, while it was necessary to employ $FeCl_3$ to synthesize the fully fused bis-anthracene porphyrin monomer. Use of bulky aryl ether groups on the anthracenes is an effective strategy for preventing aggregation. The crystal structure of the fully fused porphyrin **Ni-1b** demonstrates the planarity of the central π-system and shows that the aryl ethers are perpendicular to this core. Anthracene-fused porphyrins display extensive absorption in the near-IR and small HOMO−LUMO gaps indicating potential application in the fields of nonlinear optics[8,15−17] and solar cells.[6,19,20] The optimal HOMO−LUMO gap for a dye-sensitized solar cell is about 1.3 eV, which matches the 1.28 eV gap of **Ni-1b**.[31]

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Supporting Information Available: Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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