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A Porphyrin Fused to Four Anthracenes

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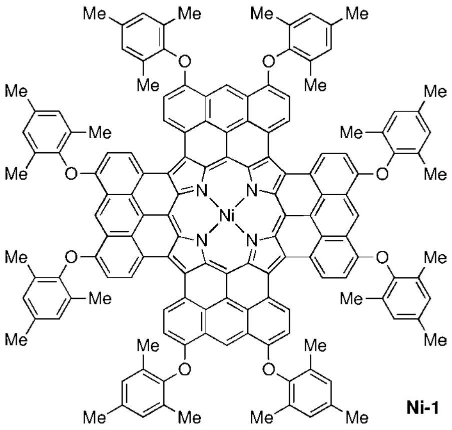
Abstract: We have synthesized a fused tetraanthracenylporphyrin by oxidation of a *meso*-anthracenyl nickel(II) porphyrin with $FeCl_3$. This compound exhibits an intense red-shifted absorption spectrum ($\lambda_{max} = 1417$ nm; $\varepsilon = 1.2 \times 10^5$ M^{-1} cm^{-1}) and a small electrochemical HOMO−LUMO gap (0.61 eV). The crystal structure shows that it forms π-stacked dimers with a short Ni···Ni distance (3.32 Å).

The synthesis of large, flat π systems, or "molecular graphenes", is a growing field of research aimed at creating materials for use as organic semiconductors and nonlinear optical dyes.[1] Recently, work in this area has focused on π-expanded porphyrins, in which aromatic units are fused to the porphyrin ring.[2−10]

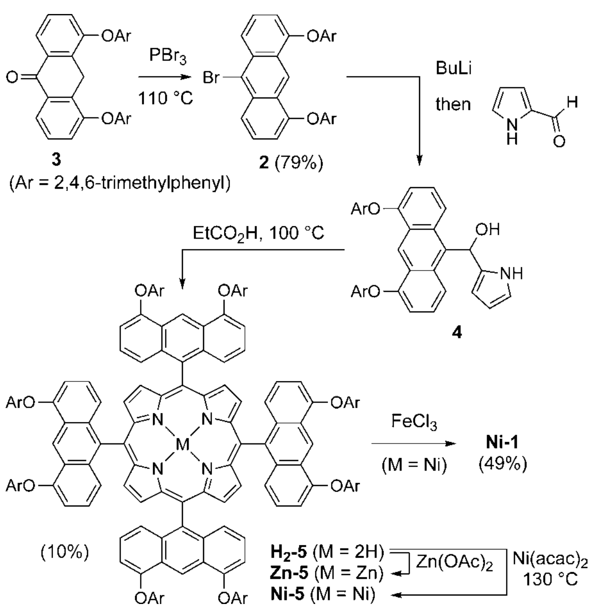
For over 35 years, chemists have been intrigued by the possibility of synthesizing fused tetraanthracenylporphyrins.[11] The high symmetry and large π system of such a molecule suggest that it should have unusual optoelectronic properties. Here we report the synthesis of a fully fused tetraanthracenylporphyrin, **Ni-1**. The near-IR (NIR) absorption of this porphyrin is remarkably red-shifted and intense ($\lambda_{max} = 1417$ nm; $\varepsilon = 1.2 \times 10^5$ M^{-1} cm^{-1}). The crystal structure of **Ni-1** shows that it forms tight π-stacked dimers and suggests that similar molecules with less bulky side chains may form discotic columnar liquid crystals with useful charge-transport behavior.[12]



Ni-1

We previously found that expanded porphyrins can be difficult to purify or characterize because of aggregation and that this problem can be alleviated by attaching bulky aryl ether substituents.[7b] Hence, we adopted the same strategy here. Bromoanthracene **2** was synthesized in 79% yield by reacting anthrone **3** with phosphorus tribromide (Scheme 1). Lithium−halogen exchange followed by addition of pyrrole-2-carboxaldehyde gave alcohol **4** (not isolated), which was tetramerized with propionic acid to give **H_2-5** in 10% yield.[13]

Scheme 1. Synthesis of Fused Tetraanthracenylporphyrin **Ni-1**



Initial experiments (using MALDI mass spectrometry and NMR analysis) indicated that the fully fused zinc derivative **Zn-1** was formed when **Zn-5** was treated with scandium(III) triflate and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). However, we were not able to isolate **Zn-1** from the complex mixture of products, so we explored other oxidants. Iron(III) chloride has been widely used to fuse aromatic moieties to the porphyrin periphery.[1,3,5b,6,7b] This reagent demetalates zinc porphyrins, so we tested its reaction with the nickel(II) complex **Ni-5**. We were delighted to find that treatment of **Ni-5** with excess $FeCl_3$ in dichloromethane results in eightfold oxidative ring closure to give the fully fused product, **Ni-1**, in 49% yield.

Crystals of **Ni-1** were grown by diffusing ethanol vapor into a solution of the porphyrin in benzene and then analyzed by X-ray diffraction.[14] Molecules of **Ni-1** form π-stacked dimers in the crystal (Figure 1), with two crystallographically independent porphyrin molecules. The planes of the two molecules are almost parallel (angle between the mean planes of the 24-atom porphyrin cores: 1.4°), and the two porphyrins in the dimer are twisted by ∼20° with respect to each other. The mean distance of the core of one porphyrin to the plane of the other is 3.41 Å, with a Ni···Ni distance of 3.316(2) Å. Both porphyrins adopt ruffled conformations; the mean deviation from planarity for the 24 atoms of each porphyrin core (0.20 Å) is similar to that in a typical meso-tetrasubstituted nickel(II) porphyrin and less than in Osuka's quadruply azulene-fused porphyrin (0.40 and 0.46 Å).[5b] The ^1H NMR spectrum of **Ni-1** in C_6D_6 exhibits just six resonances at normal chemical shifts (see the Supporting Information), showing that the dimer aggregate dissociates in solution.

Conversion of **Ni-5** to **Ni-1** results in a dramatic change in the UV−vis−NIR absorption spectrum (Figure 2). The absorption

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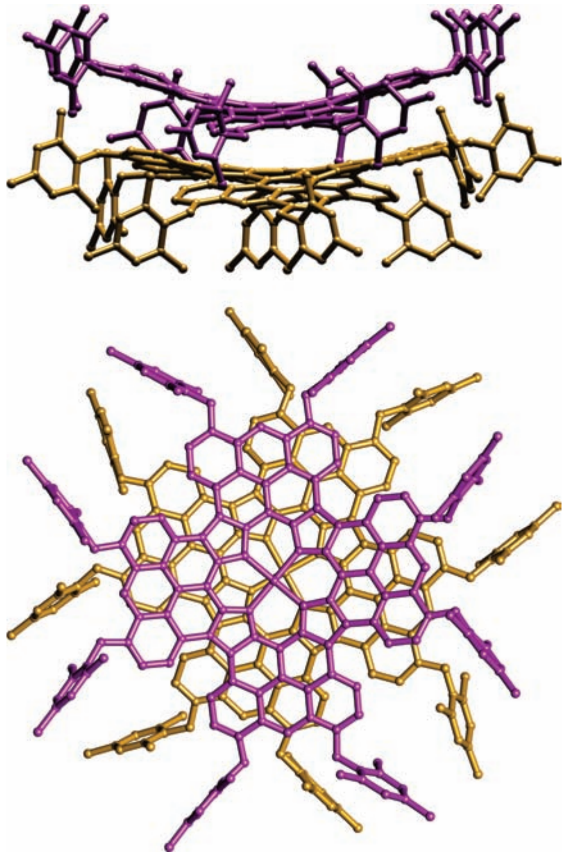

Figure 1. Two orthogonal views of the dimeric arrangement of **Ni-1** in the crystal (hydrogens have been omitted for clarity).

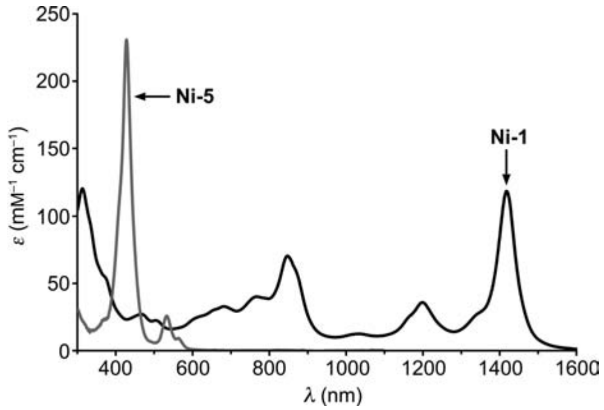

Figure 2. UV−vis−NIR spectra of unfused tetraanthracenylporphyrin **Ni-5** (gray) and fused tetraanthracenylporphyrin **Ni-1** (black) in toluene.

spectrum of **Ni-1** shows a maximum at 1417 nm (optical HOMO−LUMO gap: 0.87 eV). This peak is extremely sharp ($\varepsilon = 1.2 \times 10^5$ M^{-1} cm^{-1}; fwhm = 284 cm^{-1}), reflecting the high symmetry and rigid geometry of the chromophore. The Q band of **Ni-1** occurs at a longer wavelength than those reported for all other porphyrin monomers,[5b] and it is more red-shifted than those of most conjugated porphyrin oligomers. As expected, **Ni-1** has a small electrochemical HOMO−LUMO gap and is easily oxidized. Square-wave and cyclic voltammetry were carried out on **Ni-5** and **Ni-1** in THF with 0.1 M NBu_4PF_6. **Ni-1** shows a first oxidation wave at −0.44 V and a first reduction at −1.05 V ($E^1_{\rm ox} - E^1_{\rm red} = 0.61$ eV; all potentials relative to internal ferrocene, Fc/Fc$^+$), whereas **Ni-5** has the typical electrochemistry of a porphyrin monomer ($E^1_{\rm ox} = 0.61$ V; $E^1_{\rm red} = -1.81$ eV; $E^1_{\rm ox} - E^1_{\rm red} = 2.42$ eV).

In conclusion, we have synthesized a fused tetraanthracenylporphyrin, **Ni-1**, by the oxidation of a *meso*-anthracenyl porphyrin, **Ni-5**, through a reaction first proposed by Yen in 1975.[11] The key to this successful synthesis was the use of bulky aryloxy substituents to facilitate oxidative ring closure and to hinder formation of extended aggregates, although these substituents do not prevent the formation of dimeric aggregates in the solid state. This porphyrin has an exceptionally small HOMO−LUMO gap ($\lambda_{\rm max} = 1417$ nm; $E^1_{\rm ox} - E^1_{\rm red} = 0.61$ eV). These results suggest that fused tetraanthracenylporphyrins may by useful materials for light harvesting and charge transport in photovoltaic devices.

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Supporting Information Available: Procedures for the synthesis of **Ni-1**, spectroscopic data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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