Synthesis of Tetraphenyltetraacenaphthoporphyrin: A New Highly Conjugated Porphyrin System with Remarkably Red-Shifted Electronic Absorption Spectra

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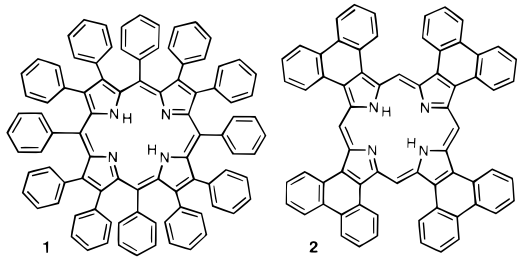
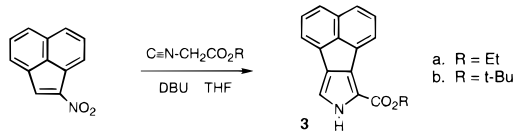
Red-shifted porphyrinoid chromophores have been the subject of extensive studies over the last few years. This is due in part to their potential utility as photosensitizers in photodynamic therapy (PDT).[1] However, these pigments have many additional applications including uses as fluorescent probes and near-infrared dyes, and as components of photosynthetic antenna arrays.[2] A number of approaches for the construction of porphyrinoid systems with high-wavelength absorptions have been reported, including the synthesis of expanded porphyrins,[3] porphyrin linkage isomers,[4] and heterocyclic analogs.[5] The intriguing observation that sterically crowded (and hence distorted) porphyrin structures, such as dodecaphenylporphyrin **1**, have significantly red-shifted major absorption bands provides an alternative avenue to systems of this type.[6] We have previously investigated the influence of fused aromatic subunits on the porphyrin chromophore.[7−10] Regretfully, the influence of one or more fused naphthalene,[7] phenanthrene,[8] or 1,10-phenanthroline[9] rings gave surprisingly small red shifts in the UV−vis absorption spectra, and even the highly symmetrical tetraphenanthroporphyrin **2** showed smaller bathochromic shifts

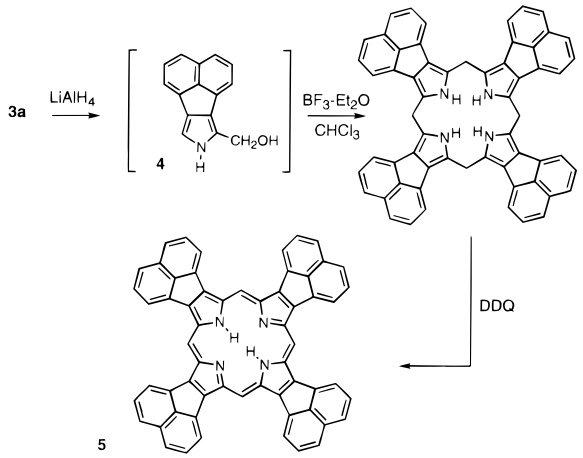


than might have been expected.[10,11] Indeed, these fused aromatic ring systems behave more like auxochromes than part of truly extended chromophores.[9] We have now extended our investigations to encompass the synthesis of tetraacenaphthoporphyrins and report, in striking contrast to the previous studies, on the extraordinarily red-shifted UV−vis absorption spectra exhibited by these tetraannelated porphyrins.

Scheme 1



Scheme 2



Nitroarenes that have a significant amount of nitroalkene character have been shown to condense with esters of isocyanoacetic acid in the presence of a non-nucleophilic base to give polycyclic *c*-annelated pyrroles.[12,13] For instance, 9-nitrophenanthrene afforded phenanthropyrroles in excellent yields,[11] and these tetracycles were utilized in our syntheses of phenanthroporphyrins (e.g., **2**).[8,10] Similarly, 1-nitroacenaphthylene, obtained by nitrating acenaphthylene with nitryl chloride in carbon tetrachloride at 0 °C,[14] condensed with ethyl or *tert*-butyl isocyanoacetate in the presence of DBU to give acenaphthopyrroles **3** in good yields (Scheme 1). Reduction of **3a** with lithium aluminum hydride afforded the related carbinol **4** (Scheme 2). Following the same procedure used in the preparation of tetraphenanthroporphyrin **2**,[10] **4** was treated with boron trifluoride etherate in chloroform, stirred at room temperature for 2 h, and oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Following workup, the highly insoluble porphyrin **5** was obtained in impure form and low yield (approximately 5%). The new porphyrin system was somewhat soluble in TFA−chloroform, producing green solutions of the corresponding dication $\mathbf{5}H_2^{2+}$. The UV−vis spectrum for the dication showed absorptions that were shifted to unusually high wavelengths; the Soret band appeared at 525 nm, and two smaller bands were evident at 628 and 701 nm.

Although the low yields and purity obtained for **5** were disappointing at best, the remarkable bathochromic shifts exhibited for the corresponding dication $\mathbf{5}H_2^{2+}$ suggested that the acenaphthylene ring system is particularly effective at inducing desirable long-wavelength absorptions. In order to further investigate this phenomenon, the related *meso*-tetraphenylporphyrin **6** was targeted for synthesis (Scheme 3). It was anticipated that there would be sufficient room for phenyl groups to be sandwiched between the acenaphthylene rings. As the

(1) Brown, S. B.; Truscott, T. G. *Chem. Br.* **1993**, *29*, 955. Dolphin, D. *Can. J. Chem.* **1994**, *72*, 1005. Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19.
(2) E.g., see: Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *115*, 7519.
(3) Sessler, J. L.; Burrell, A. K. *Top. Curr. Chem.* **1991**, *161*, 177−273. Franck, B.; Nonn, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1795.
(4) E.g., see: Vogel, E.; Kocher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257. Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779. Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767.
(5) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc. C* **1971**, 3681. Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406. Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533.
(6) (a) Shelnutt, J. A.; Medforth, C. J.; Berber, M. D.; Barkigia, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077. (b) Medforth, C. J.; Senge, M. O.; Smith, K. M.; Sparks, L. D.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 9859.
(7) (a) Lash, T. D. *Energy Fuels* **1993**, *7*, 166. (b) Lash, T. D.; Roper, T. J. *Tetrahedron Lett.* **1994**, *35*, 7715. c. Lash, T. D.; Denny, C. P. *Tetrahedron* **1995**, *51*, 59.
(8) Lash, T. D.; Novak, B. H. *Tetrahedron Lett.* **1995**, *36*, 4381.
(9) Lin, Y.; Lash, T. D. *Tetrahedron Lett.* **1995**, 36, 9441.
(10) Lash, T. D.; Novak, B. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 683.
(11) Lash, T. D.; Novak, B. H.; Lin, Y. *Tetrahedron Lett.* **1994**, *35*, 2493.
(12) Ono, N.; Hironaga, H.; Simizu, K.; Ono, K.; Kuwano, K.; Ogawa, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1019.
(13) See also: Barton, D. H. R.; Kervagoret, J.; Zard, S. Z. *Tetrahedron* **1990**, *46*, 7587. Lash, T. D.; Bellettini, J. R.; Bastian, J. A.; Couch, K. B. *Synthesis* **1994**, 170.
(14) Iida, H.; Kajiyama, I.; Yamada, K. *Nippon Kagaku Kaishi* **1972**, 137; *Chem. Abstr.* **1972**, *76*, 99395m.

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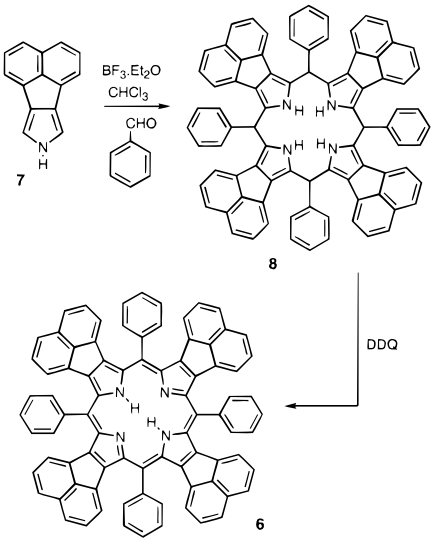
Scheme 3



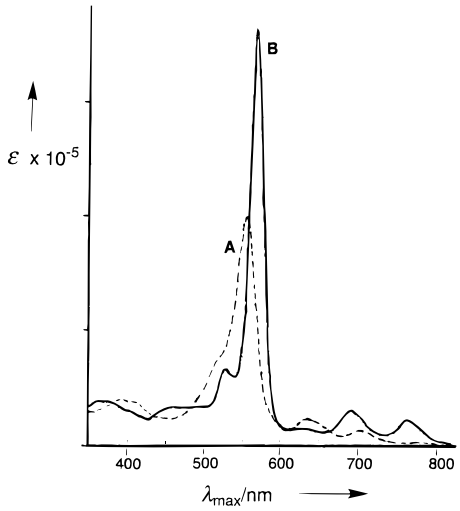


Figure 1. (A) UV−vis spectrum of tetraphenyltetraacenaphthoporphyrin **6** in chloroform. (B) UV−vis spectrum of **6** in 0.5% TFA−chloroform (dication).

phenyl groups will be unable to lie in the same plane as the porphyrin macrocycle, they should disrupt intermolecular $\pi-\pi$ stacking and hence might have the added advantage of imbuing the compound with significantly increased solubility.

Treatment of **3a** with potassium hydroxide in refluxing ethylene glycol afforded the unsubstituted acenaphthopyrrole **7** in 70−83% yield. Reaction with 1 equiv of benzaldehyde in de-ethanolated chloroform, using boron trifluoride as a catalyst,[10,15] gave the porphyrinogen **8**. Dehydrogenation with DDQ, followed by chromatography on silica eluting with 1% triethylamine−chloroform and recrystallization from chloroform−methanol, gave the desired tetraphenyltetraacenaphthoporphyrin **6** in 24−43% yield. The presence of trace ethanol slightly decreased the yield of **6**, in contrast to observations noted previously for the tetraphenanthroporphyrin **2**.[10] The product gave violet solutions in organic solvents and crystallized as a dark green flaky solid.

The structure of **6** was demonstrated by mass spectrometry, proton NMR, carbon-13 NMR, IR, and UV−vis spectroscopy. The proton NMR spectrum for the dication $\mathbf{6}H_2^{2+}$ in TFA−deuteriochloroform showed an upfield doublet for eight acenaphthylene protons at 6.1 ppm; this abnormal degree of shielding is consistent with these protons lying over the top of the *meso*-phenyl substituents. The *ortho* protons of the phenyl substituents are directed toward the porphyrin macrocycle and are consequently deshielded by the macrocyclic ring current, giving a doublet for 8H at close to 9 ppm. The remaining protons fell into a typical aromatic range, with chemical shifts lying between 7.2 and 8.2 ppm. Carbon-13 NMR spectroscopy in TFA−$CDCl_3$ showed the presence of 13 aromatic carbon resonances, confirming the high level of symmetry in this 84-carbon system. The structure was further supported by FAB MS, which gave the expected $[M + H]^+$ peak at *m/z* 1111.

The 300 MHz proton NMR spectrum for the sparingly soluble free base in deuteriochloroform also confirmed the structure of **6**, although the internal NH protons were somewhat less shielded than is typical for porphyrins, appearing as a broad resonance near −0.5 ppm. The *ortho* protons of the phenyl substituents appeared as a relatively deshielded doublet at 8.83 ppm, while an 8H acenaphthylene resonance was again abnormally shielded and appeared as a broadened doublet at 5.71 ppm. Computer simulations suggest that **6** favors a distorted saddle-shaped conformation which can undergo a macrocyclic inversion process (this has been previously demonstrated[6] for dodecaphenylporphyrin **1**). For the NMR data to be consistent with this conformer, saddle to saddle inversion and NH tautomerization at room temperature must be rapid on the NMR time scale. In variable-temperature NMR studies, the resonances for the *o*-phenyl and acenaphthylene H_a protons broadened at 0 °C, and split into two pairs of doublets at −60 °C; these data were consistent with a coincidental slowing of both macrocyclic ring inversion and NH tautomerization.

The UV−vis spectrum of **6** in chloroform showed a Soret band at 556 nm, together with several smaller absorptions (Q bands) that extended into the near-infrared region (Figure 1). The Soret band is shifted by over 140 nm compared to *meso*-tetraphenylporphyrin, and this represents the largest bathochromic shift ever observed for a nonexpanded porphyrin system. While the macrocyclic distortion in **6** no doubt contributes to these remarkable shifts, the Soret band for the highly crowded porphyrin system **1** was only red shifted to 468 nm.[6b] This implies that the effect is primarily due to conjugation between the porphyrin core and the four fused acenaphthylene subunits. In 0.5% TFA−chloroform, the dication $\mathbf{6}H_2^{2+}$ showed a Soret band at 565 nm (compared to 490 nm for $\mathbf{1}H_2^{2+}$), and several additional absorptions were present at longer wavelengths (Figure 1).

This study demonstrates that the presence of fused acenaphthylene rings produces a profound disturbance to the core porphyrin electronic spectrum which results in record-breaking bathochromic shifts for the tetraacenaphthoporphyrins. There is every expectation that these novel tetrapyrroles will stimulate considerable interest, and syntheses of related structures are currently under investigation.

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Supporting Information Available: Experimental procedures and spectroscopic characterization of **3a**, **6**, and **7** and molecular mechanics computer simulation of porphyrin **6** (5 pages). See any current masthead page for ordering and Internet access instructions.

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(15) (a) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A.M. *J. Org. Chem.* **1987**, *52*, 827. (b) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.