ORGANIC LETTERS

2008
Vol. 10, No. 18
3945−3947

Expanding the Porphyrin π-System by Fusion with Anthracene

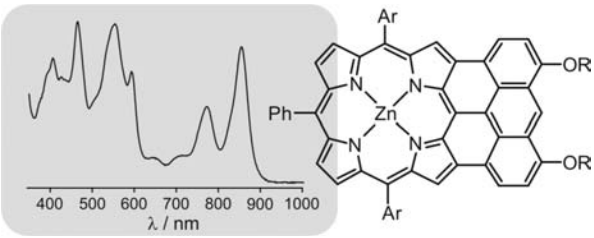
Nicola K. S. Davis, Miłosz Pawlicki, and Harry L. Anderson*

Department of Chemistry, Chemistry Research Laboratory, University of Oxford,
12 Mansfield Road, Oxford OX1 3TA, U.K.

harry.anderson@chem.ox.ac.uk

Received July 2, 2008

ABSTRACT



Synthesis of β,*meso*,β-anthracene triply fused and β,*meso*-anthracene doubly fused porphyrins has been achieved via oxidative intramolecular ring closure of *meso*-(9-anthryl)porphyrins and *meso*-(1-anthryl)porphyrins, respectively. Fusion was only possible when the anthracene carried electron-donating alkoxy substituents. The fused porphyrins exhibit strongly red-shifted UV−vis absorption spectra and reduced electrochemical HOMO−LUMO gaps (relative to the unfused tetraaryl porphyrin precursor).

The synthesis of very large flat π-conjugated chromophores and "molecular-graphenes" is an important recent development in materials science, stimulated by the remarkable electronic properties emanating from the small HOMO−LUMO gaps of these molecules. Examples include the hexabenzocoronenes developed by Müllen and co-workers[1] and the edge-fused porphyrin tapes from Osuka's group, which have electronic absorption bands stretching far into the infrared.[2] A variety of π-extended porphyrins have been synthesized by fusing benzene,[3] naphthalene,[4] pyrene,[5] and azulene[6] across the *meso*- and β-positions of porphyrins. Anthracene-fused porphyrins represent a notable absence from this family of compounds, which is surprising in the light of the good geometrical match between the β,*meso*,β-edge of a porphyrin and the 1,9,8-edge of an anthracene.[7] Here, we report the first synthesis of triply fused (β,*meso*,β) and doubly fused (β,*meso*) anthracene−porphyrin conjugates **1c** and **2**, respectively. Fusion to an anthracene unit strongly perturbs the electronic structure of the porphyrin, shifting the absorption into the near-infrared and reducing the electrochemical HOMO−LUMO gap by making the macrocycles easier to oxidize.

Anthracene-fused porphyrins **1c** and **2** were synthesized as shown in Scheme 1. Initially, we attempted to prepare the triply fused compound with an unsubstituted anthracene **1a**. Suzuki coupling of porphyrin boronic ester **3**[5,8] with 9-bromoanthracene **4a** in the presence of Buchwald's SPhos

---

(1) (a) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718–747. (b) Müllen, K.; Rabe, J. P. *Acc. Chem. Res.* **2008**, *41*, 511–520.

(2) (a) Tsuda, A.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2549–2552. (b) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79–82.

(3) (a) Barloy, L.; Dolphin, D.; Dupré, D.; Wijesekera, T. P. *J. Org. Chem.* **1994**, *59*, 7976–7985. (b) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168–6179. (c) Fox, S.; Boyle, R. W. *Chem. Commun.* **2004**, 1322–1323. (d) Shen, D.-M.; Liu, C.; Chen, Q.-Y. *Chem. Commun.* **2005**, 4982–4984. (e) Hao, E.; Fronczek, F. R.; Vincente, M. G. H. *J. Org. Chem.* **2006**, *71*, 1233–1236. (f) Shen, D.-M.; Liu, C.; Chen, Q.-Y. *J. Org. Chem.* **2006**, *71*, 6508–6511. (g) Fox, S.; Boyle, R. W. *Tetrahedron* **2006**, *62*, 10039–10054.

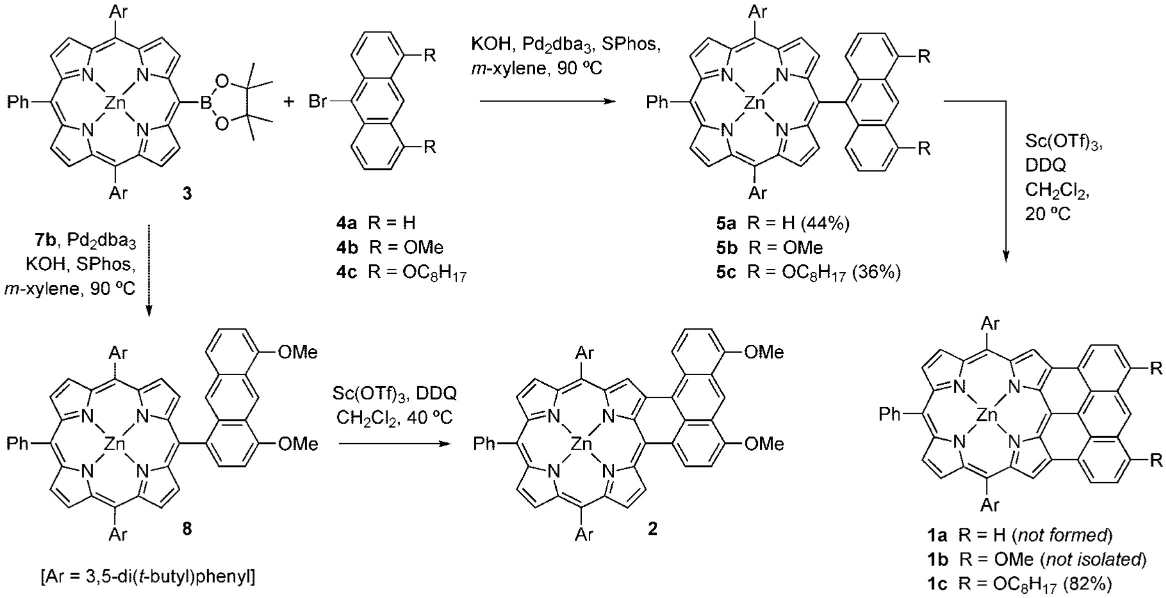
(4) (a) Gill, H. S.; Marmjanz, M.; Santamaría, J.; Finger, I.; Scott, M. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 485–490. (b) Cammidge, A. N.; Scaife, P. J.; Berber, G.; Hughes, D. L. *Org. Lett.* **2005**, *7*, 3413–3416. (c) Tanaka, M.; Hayashi, S.; Eu, S.; Umeyama, T.; Matano, Y.; Imahori, H. *Chem. Commun.* **2007**, 2069–2071.

(5) Yamane, O.; Sugiura, K.; Miyasaka, H.; Nakamura, K.; Fujimoto, T.; Nakamura, K.; Kaneda, T.; Sakata, Y.; Yamashita, M. *Chem. Lett.* **2004**, *33*, 40–41.

(6) Kurotobi, K.; Kim, K. S.; Noh, S. B.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 3944–3947.

10.1021/ol801500b CCC: $40.75

Scheme 1. Synthesis of Anthracene-Fused Porphyrins

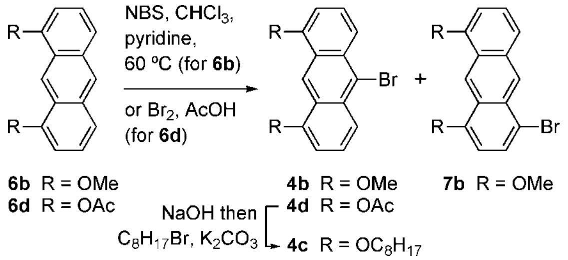


ligand (2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl)[9] and potassium hydroxide gave the *meso*-(9-anthryl)porphyrin **5a** in 44% yield (whereas under standard Suzuki coupling conditions protodeboronation predominates). Oxidative fusion of **5a** to **1a** was attempted both using DDQ/$Sc(OTf)_3$[2b] and using tris(4-bromophenyl)aminium hexachloroantimonate (BAHA),[2a] but in both cases ring-fused products were not detected and unreacted **5a** was reisolated. Attempts at the oxidative fusion of other *meso*-(9-anthryl)porphyrins[10] also failed, so we decided to test whether electron-rich alkoxyanthracenes would be more amenable to this reaction, as found with pyrene.[5]

Synthesis of 10-bromo-1,8-dimethoxyanthracene **4b** was first attempted by bromination of 1,8-dimethoxyanthracene **6b** with NBS; however, this gave an inseparable 1:2 mixture of **4b** and **7b** (Scheme 2, see the Supporting Information). Suzuki coupling of this mixture of bromoanthracenes with **3** yielded a 1:4 mixture of porphyrins **5b** and **8**, which also proved to be inseparable. Oxidative fusion of this mixture of isomers with DDQ/$Sc(OTf)_3$ gave the doubly fused anthracene−porphyrin **2** as the only isolable product.[11]

Regioselective synthesis of a 10-bromo-1,8-dialkoxyanthracene was achieved as shown in Scheme 2. The presence of acetoxy substituents results in exclusive bromination at the 10-position of 1,8-diacetoxyanthracene **6d** to give **4d** (45% yield). The acetoxy groups were then hydrolyzed. Octyl chains were introduced at this stage, to give **4c**, in order to increase the solubility of the final fused porphyrin. The Suzuki coupling of **4c** with **3** gave **5c** with 36% yield. Oxidative fusion of **5c** was carried out using $Sc(OTf)_3$/DDQ in dichloromethane.[2a] After workup, no starting material was detected, and the triply fused porphyrin **1c** was isolated in 82% yield.

Scheme 2. Synthesis of Anthracene Derivatives



The expansion of the π-system in porphyrins **1c** and **2** results in dramatic changes to their UV−vis absorption spectra (Figure 1). Porphyrin **2** displays a similar spectrum to naphthalene-fused porphyrins.[4] Striking differences are be observed between the spectra of the unfused and fused porphyrins **5c** and **1c**. The fused anthracene-porphyrins **1c** and **2** display significant bathochromic shifts with longest wavelength absorption maxima at 855 and 725 nm respectively.

Cyclic and square wave voltammetry were carried out on **5c**, **2**, and **1c** so as to determine their redox potentials (in THF with 0.1 M Bu_4NPF_6, relative to internal ferrocene/ferrocinium). The three compounds are reduced at about the same potential (−1.21, −1.23, and −1.19 V vs Fc/Fc^+, respectively), whereas their first oxidation potentials (0.39, 0.02, and 0.00 V vs Fc/Fc^+, respectively) show that fusion to the anthracene π-system reduces the HOMO−LUMO gap and makes the porphyrin easier to oxidize.

In conclusion, doubly and triply fused anthracene−porphyrins have been synthesized. Under the reaction conditions used in this work, ring fusion between the anthracene and the porphyrin does not occur unless the anthracene has alkoxy substituents. The red-shifted absorption spectra of anthracene-fused porphyrins point to possible applications

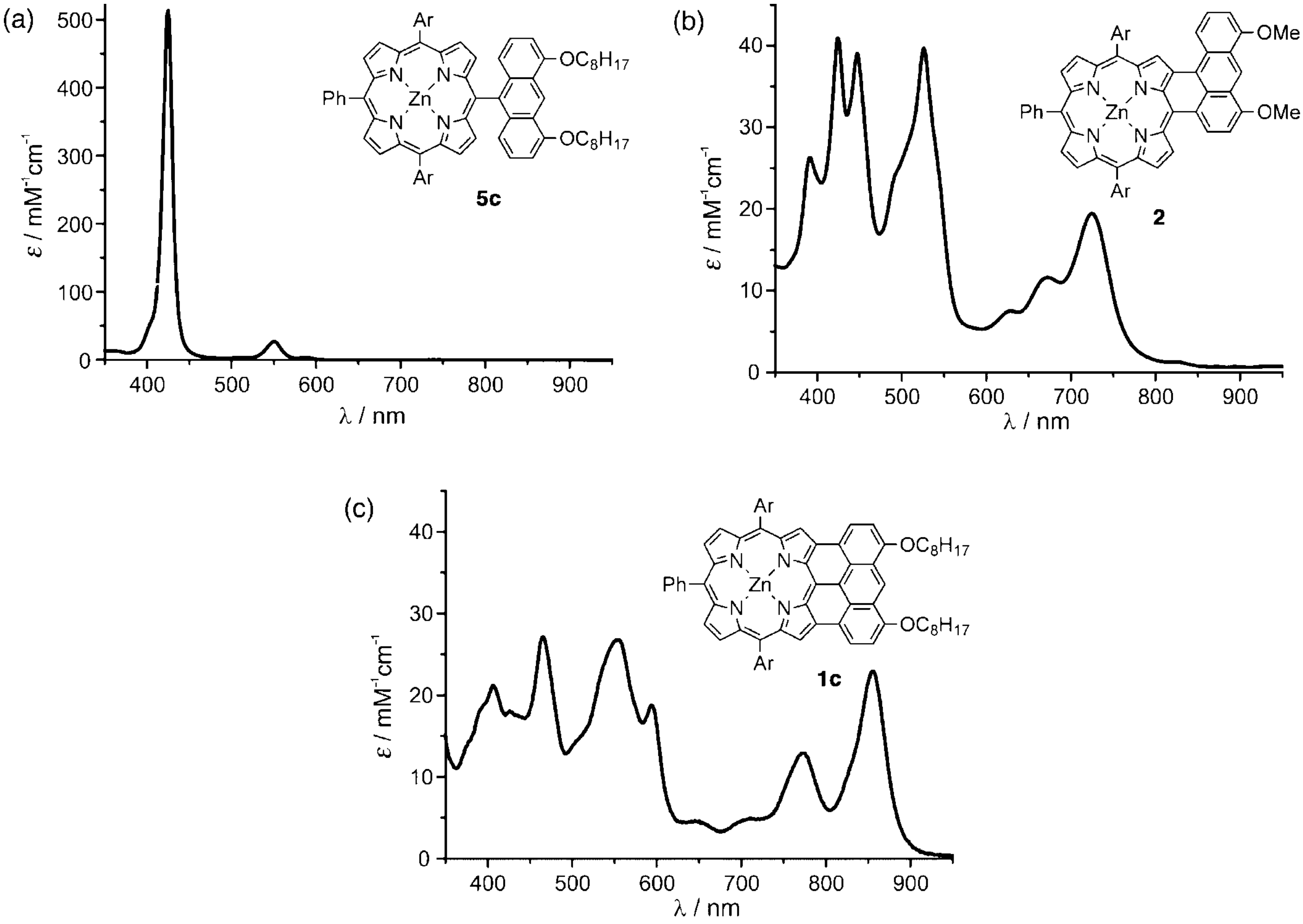


Figure 1. Absorption spectra in chloroform. *meso*-(9-anthryl)porphyrin **5c** (a) has a typical porphyrin spectrum, whereas the spectra of the *β,meso* doubly fused porphyrin **2** (b) and the *β,meso,β* triply fused porphyrin **1c** (c) are distorted and red-shifted.

in areas such as photovoltaics,[12] photodynamic therapy,[13] and nonlinear optics.[14]

Acknowledgment. We thank the EPSRC and the European Comission (Intra-European Fellowship to M.P. MEIF-CT-2006-041629) for support and the EPSRC Mass Spectrometry Service (Swansea) for mass spectra.

Supporting Information Available: Experimental details, characterization data, ^{1}H, ^{13}C NMR and mass spectra, and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL801500B

---

[7] The idea of synthesizing anthracene-fused porphyrins was suggested by: Yen T. F. In *The Role of Trace Metals in Petroleum*; Yen, T. F., Ed.; Ann Arbor Scientific: Ann Arbor, 1975; pp 1−30. We thank a reviewer for drawing this article to our attention.

[8] Hyslop, A. G.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676–12677.

[9] Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696.

[10] Krivokapic, A.; Anderson, H. L. *Org. Biomol. Chem.* **2003**, *1*, 3639–3641.

[11] The triply-fused porphyrin **1b** is probably formed during the DDQ/Sc(OTf)$_3$ oxidation of the 1:4 mixture of **5b** and **8** and no unreacted **5b** is detected in the product mixture, but if **1b** is formed in this reaction it appears to be so insoluble that it is lost during chromatography; **1b** was not isolated.

[12] Rio, Y.; Rodrı́guez-Morgade, M.; Torres, T. *Org. Biomol. Chem.* **2008**, *6*, 1877–1894.

[13] MacDonald, I. J.; Dougherty, T. J. *J. Porphyrins Phthalocyanines* **2001**, *5*, 105–129.

[14] Senge, M. O.; Fazekas, M.; Notaras, E. G. A.; Blau, W. J.; Zawadzka, M.; Locos, O. B.; Mhuircheartaigh, E. M. N. *Adv. Mater.* **2007**, *19*, 2737–2774.