Crown-Linked Porphyrin Systems

Sandhya A. Duggan,[1] Gary Fallon,[1]
Steven J. Langford,*[,1] Vei-Lin Lau,[1]
Jacqueline F. Satchell,[1] and Michael N. Paddon-Row[2]

School of Chemistry, Monash University, Clayton, Victoria, Australia 3800, and School of Chemistry, University of New South Wales, Kensington, New South Wales, Australia 2052

s.langford@sci.monash.edu.au

Received December 4, 2000

(Revised Manuscript Received March 21, 2001)

Introduction

The success of the photosynthetic reaction center[3] as a transducer of light into chemical potential depends primarily on the assembly being able to exert strict control over a number of design features, such as the separation and orientation of the various redox centers and the nature of the medium separating them. Therefore, an important aspect of designing artificial photosynthetic devices based particularly on the multiporphyrin arrays found in light harvesters and in the initial processes of such reaction centers, is the selection of an appropriate organizing principle that will control these same features.[4] Multiporphyrin systems in which the porphyrin subunits are interlinked using covalent bonds have produced an array of elegant structures, some of which display reaction-center-like processes.[4,5] However, a disadvantage of using these arrays as potential energy transduction devices[6] usually lies in their synthesis, which is not trivial and can be extremely difficult and expensive to realize on a large scale. These difficulties may be overcome by employing molecular recognition events to facilitate the association and orientation of the porphyrinic chromophores.[7]

Our approach to a series of multiporphyrin arrays is through crown ether systems[8] of the type 3*n*-crown-*n*

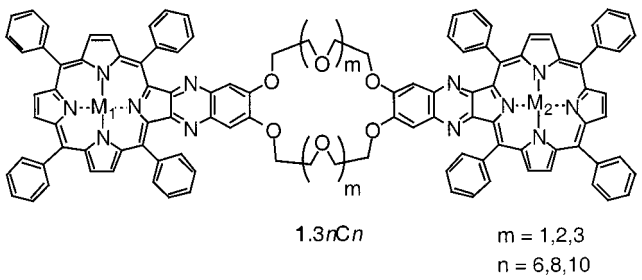


Figure 1. The general structure of our crown-ether-based multiporphyrin systems.

which contain porphyrin subunits antipodally displaced on the macrocycle. System **1** (Figure 1) is representative of the types that we wish to synthesize. By varying the size of the crown ether, we can modulate the center-to-center distances between the porphyrin rings. Molecular modeling has been used to determine the approximate center-to-center distances in the extended forms of **1** (Figure 1) for $m = 0-3$ to be 15−26 Å. Both the 12C4 and 18C6 analogues of **1** have porphyrin-to-porphyrin distances that are comparable to that found between the special pair (SP) and bacteriopheophytin (BPh) in the photosynthetic reaction center for the purple bacteria *Rhodopseudomonas viridis*.[9] Larger derivatives of **1** incorporating 24C8 and 30C10 crown ether systems will allow the addition of structural[10,11] and chromophoric[12] auxiliaries to be complexed within the cavity. Here, we report the first synthesis of free-base analogues of **1** involving 18-crown-6, 24-crown-8, and 30-crown-10 bridges, monofunctionalized dibenzocrown ethers and some open chain polyether analogues. X-ray crystallography has been used to characterize the tetranitro analogue of DB30C10—a precursor to **1**.30C10. Complexation of **1**.24C8 with $(C_6H_5CH_2)_2NH_2PF_6$ illustrates the potential use of organic cations as structural auxiliaries.

Results and Discussion

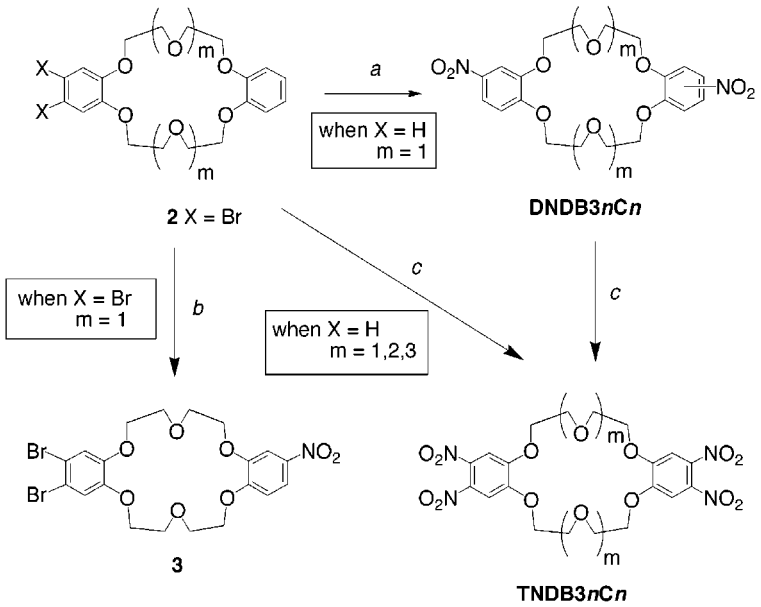
Our strategy has centered about an efficient means of attaching potent chromophores, such as the porphyrins,

* To whom correspondence should be sent. Phone: + 03 9905 4569. Fax: + 03 9905 4597.
(1) Monash University.
(2) University of New South Wales.

(3) Deisenhofer, J.; Epp, O.; Miki, K.; Huber R.; Michel, H. *Nature* **1985**, *318*, 618.
(4) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198.
(5) (a) Sessler, J. L.; Hugdahl, J.; Johnson, M. R. *J. Org. Chem*. **1986**, *51*, 2838. (b) Atkinson, E. J.; Oliver, A. M.; Paddon-Row, M. N. *Tetrahedron Lett*. **1993**, *34*, 6147. (c) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759. (d) Wennerstrom, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett*. **1989**, *30*, 1129. (e) Osuka, A.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Mataga, N. *Tetrahedron Lett*. **1995**, *36*, 5781.
(6) (a) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (b) Paddon-Row, M. N. *Acc. Chem. Res*. **1994**, *27*, 18.
(7) (a) Hayashi, T.; Ogoshi, H. *Chem. Soc. Rev*. **1997**, *26*, 355. (b) Amabilino, D. B.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun*. **1996**, 2441. (c) Hunter, C. A.; Shannon, R. J. *J. Chem. Soc., Chem. Commun*. **1996**, 1361. (d) Imahori, H.; Yoshizawa, E.; Yamada, K.; Hagiwara, K.; Okada, T.; Sakata, Y. *J. Chem. Soc., Chem. Commun*. **1995**, 1133. (e) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5679. (f) Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem*. Commun. **1994**, 2313. (g) Crossley, M. J.; Burn, P. L. *J. Chem. Soc. Chem*. Commun. **1991**, 1569. (h) Chichak, K.; Branda, N. R. *J. Chem. Soc. Chem*. Commun. **2000**, 1211. (i) Haycock, R. A., Yartsev, A.; Michelsen, U.; Sundström, V.; Hunter, C. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3616.
(8) Other multichromophoric crown ether systems have been prepared in the past with success: (a) Thanabal, V.; Krishnan, V. *J. Am. Chem. Soc.* **1982**, *104*, 3643. (b) Iyoda, T.; Morimoto, M.; Kawasaki, N.; Shimidzu T. *J. Chem. Soc., Chem. Commun*. **1991**, 1480. (c) Yoon, D. I.; Berg-Brennan, C. A.; Lu, H.; Hupp, J. T. *Inorg. Chem*. **1992**, *31*, 3192. (d) Gunter, M. J.; Johnston, M. R. *Tetrahedron Lett*. **1992**, *33*, 1771. (e) Martensson, J.; Sandros, K.; Wennerstrom, O. *Tetrahedron Lett*. **1993**, *34*, 541. (f) Vacus, J.; Memetzidis, G.; Doppelt, P.; Simon, J. *J. Chem. Soc., Chem*. Commun. **1994**, 697. (g) Berg-Brennan, C. A.; Yoon, D. I.; Slone, R. V.; Kazala, A. P.; Hupp, J. T. *Inorg. Chem*. **1996**, *35*, 2032. (h) Lange, S. J.; Sibert, J. W.; Barrett, A. G. M.; Hoffman, B. M. *Tetrahedron* **2000**, *56*, 7371. (i) Shinmori, H.; Osuka, A. *Tetrahedron Lett.* **2000**, *41*, 8527.
(9) Benniston, A. C.; Mackie, P. R. In *Handbook of Nanostructured materials and Nanotechnology*; Nalwa, H. S., Ed.; Academic Press: London, 2000; Vol. 5, p 227.
(10) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495, 7017. (b) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021.
(11) (a) Cram, D. J.; Cram, J. M. *Acc. Chem. Res*. **1978**, *11*, 8. (b) Kolchinski, A. G.; Busch, D. H.; Alcock, N. W. *J. Chem. Soc., Chem. Commun*. **1995**, 1289. (c) Glink, P. T.; Schiavo, C.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun*. **1996**, 1483. (d) Bryant, W. S.; Guzei, I. A.; Rheingold, A. L.; Gibson, H. W. *Org. Lett*. **1999**, *1*, 47. (e) Rowan, S. J.; Cantrill, S. J.; Stoddart, J. F. *Org. Lett*. **1999**, *1*, 129.
(12) Ishow, E.; Credi, A.; Balzani, V.; Spadola, F.; Mandolini, L. *Chem. Eur. J*. **1999**, *5*, 984.

10.1021/jo001700p CCC: $20.00 © 2001 American Chemical Society
Published on Web 05/23/2001

Scheme 1



[a] HNO_3, CH_2Cl_2, r.t., 88%. [b] HNO_3, CH_2Cl_2, 0 °C, 81%. [c] HNO_3, H_2SO_4, CH_2Cl_2, r.t. 63−96%.

to a crown ether system. We decided to take advantage of tetraarylporphyrin-2,3-diones such as **4**,[13] which have served us well in the past as a means of making highly rigid multichromophoric systems which undergo efficient ET[14] and EnT[15] processes. Condensation of the porphyrin-2,3-dione **4** with an *ortho*-diamine functionalized crown would lead to the desired crown ether appended porphyrin systems. Commercially available DB18C6, DB24C8, and DB30C10[16] were nitrated[17] (HNO_3, H_2SO_4, CH_2Cl_2) using a biphasic system (Scheme 1) to yield the corresponding TNDB18C6,[18] TNDB24C8, and TNDB30C10 as bright yellow solids in excellent yield. This nitration is stepwise, forming the two intermediate isomeric dinitrocrown-ethers[19] in which one nitro group has been added to each of the catechol rings. At room temperature this reaction is fast in the presence of an excess of HNO_3. The 1,2,4-substitution pattern of each catechol ring in DN3*n*C*n* is borne out by the splitting patterns seen in the ^{1}H NMR spectrum of such samples. The DN3*n*C*n* is the major isolable product (>80% yield) when (a) only nitric acid is added to a CH_2Cl_2 solution of crown ether or (b) a dilute CH_2Cl_2 solution (HNO_3, H_2SO_4, CH_2Cl_2) is used. The rate for the second nitration is much slower and can be easily monitored by ^{1}H NMR spectroscopy in particular, the eventual presence of a four proton singlet at ca. δ 7.5. The aromatic substitution pattern of the desired tetranitro-crown ethers was supported by X-ray crystallography. Yellow crystals suitable for X-ray analysis were grown by slow evaporation of a solution of TNDB30C10 in MeCN.[21] Clearly indicated is the 1,2,4,5-arrangement of the *nitro* and *alkoxy* groups on both benzene units of the crown—consistent with the ^{1}H NMR spectra of this series of molecules. There was no appreciable sign of intramolecular $\pi-\pi$ stacking interactions between the aromatic moieties[22] nor was there any solvent (MeCN) included within the crystal lattice. Interestingly enough, all attempts to nitrate the 2,3-dibromocrown ether **2**[20] under the same conditions failed to give any of the corresponding 12,13-dinitrocrown ether. Controlled nitration of **2** was possible (Scheme 1), yielding the 12-nitro-2,3-dibromocrown ether **3** in 81% yield after recrystallization. Compound **3** became central to our strategy of appending a single porphyrin unit to the crown ethers.

Reduction of the crown ethers TNDB18C6, TNDB24C8, and TNDB30C10 ($NH_2NH_2 \cdot H_2O$, Pd/C, EtOH) under anaerobic conditions gave the colorless and highly air-sensitive TADB18C6, TADB24C8, and TADB30C10, respectively (Scheme 2). Two approaches to the condensation of these amines with **4** to form the target photoactive crowns were made. Initially, the putative tetraaminocrown ethers were condensed (after filtration of the catalyst) with a deoxygenated solution of the porphyrin-2,3-dione **4** in CH_2Cl_2 (Scheme 2). However, a shortcoming of this reaction sequence was the presence of excess hydrazine hydrate, which is able to condense with **4**, forming undesirable side-products. We have recently found it more efficient to precipitate the tetra-amines from the ethanol solution as the highly stable and

(13) (a) Crossley, M. J.; King, L. G. *J. Chem. Soc., Chem. Commun.* **1984**, 921. (b) Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921.

(14) (a) Antolovich, M.; Oliver, A. M.; Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 2* **1989**, 783. (b) Ranasinghe, M. G.; Oliver, A. M.; Rothenfluh, D. F.; Salek, A.; Paddon-Row, M. N. *Tetrahedron Lett.* **1996**, *37*, 4797. (c) Jolliffe, K. A.; Bell, T. D. M.; Ghiggino, K. P.; Langford S. J.; Paddon-Row, M. N. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 915. (d) Jolliffe, K. A.; Langford, S. J.; Oliver, A. M.; Shephard, M. J.; Paddon-Row, M. N. *Eur. J. Chem.* **1999**, *5*, 2518.

(15) Jolliffe, K. A.; Langford, S. J.; Ranasinghe, M. G.; Shephard, M. J.; Paddon-Row, M. N. *J. Org. Chem.* **1999**, *64*, 1238.

(16) We have decided to use acronyms to describe our poly-nitro and poly-amino systems. For example, TNDB18C6 relates to the *T*etra*N*itro derivative of *Di**B**enzo-**18**-C*rown-*6*.

(17) (a) Ungaro, R.; El Haj, B.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98*, 5198. (b) Rogers, R. D.; Henry, R. F.; Rollins, A. N. *J. Inclusion Phenom.* **1992**, *13*, 219. (c) Forget, S.; Verber M.; Strzelecka, H. *Mol. Cryst. Liq. Cryst.* **1995**, *258*, 263.

(18) Chang, S. H.; Cho, S. A. *J. Korean Chem. Soc.* **1988**, *32*, 71.

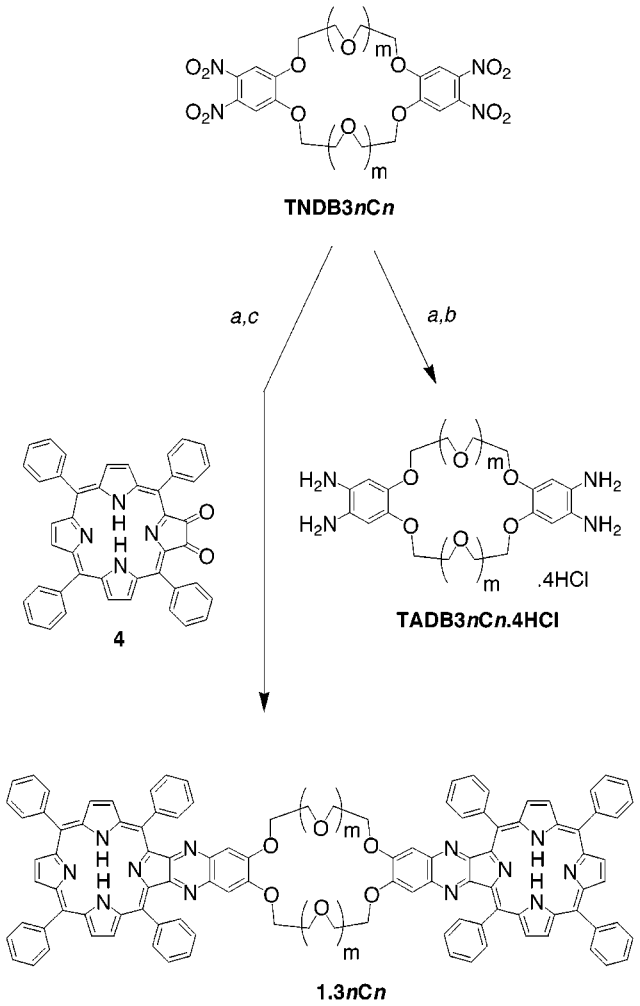
(19) Feigenbaum, W. M.; Michel, R. H. *J. Polym. Sci. A* **1971**, *9*, 817.

(20) van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957.

(21) Crystal data for $C_{28}H_{36}N_4O_{18}$: MW = 716.61, monoclinic, $P2_1/c$, a = 13.9862(6) Å, b = 7.5273(4) Å, c = 15.4139(7) Å, β = 104.874(3)°, V = 1568.4(1) Å^3, Z = 2, T = 123 ± 1 K, μ(Mo Kα) = 1.28 cm^{-1}, D_{calcd} = 1.517 gcm^{-3}, R = 6.3% for 2545 observed independent reflections. Hydrogen atoms were treated as idealized contributions.

(22) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

Scheme 2



[a] Hydrazine hydrate, Pd/C, EtOH, reflux, Ar. [b] Concentrated HCl, EtOH. [c] **4**, CH_2Cl_2, reflux. [d] **4**, pyridine, reflux, 36−63% for 2 steps.

crystalline tetrahydrochloride salts.[23] In each case, the resulting condensation products were purified by column chromatography (silica) to yield the free-base porphyrin-appended crown ethers **1** as bright purple solids in good yield. The 400 MHz ^{1}H NMR spectrum of **1**.18C8 is shown in Figure 2. The spectrum is well resolved and clearly indicates the symmetrical nature of the molecule. UV−vis spectra of **1**.3*n*C*n* (n = 6,8,10) were identical (λ_{max} ($CDCl_3$): 430, 524, 596, 649 nm), indicating little electronic coupling between the porphyrin units in the ground state.

One of our long-term goals is to assemble nanometer-sized multiporphyrin arrays using a structural auxiliary and **1** as a scaffold. Molecular modeling suggests that such arrays will closely mimic, in terms of porphyrin-to-porphyrin distance, the arrangement between the special pair, BChl and BPhe, within the reaction center of the purple bacteria. To determine this study's viability, we investigated the complexation of **1**.24C8 with $[Bn_2NH_2]^+$-PF_6^- in $CDCl_3$ at 300 K. Equimolar mixes of the two components display the 1:1 complex formed between these two species, and both uncomplexed **1**.24C8 and $[Bn_2NH_2]^+PF_6$ within the ^{1}H NMR spectrum. The signals attributed to the uncomplexed species resonate at the same δ values as they do in the ^{1}H NMR spectra of the individual components and the stoichiometry of the complex is readily determined as 1:1 by integration of relevant probe protons on both the host and guest species. This situation is clearly one of slow kinetics between complexation and decomplexation at 300 MHz and 300 K. The observation of both signals attributable to complexed and uncomplexed species allows for the determination of the association constants (K_a) by single point analysis.[11c] The high value obtained ($K_a = 10^5$ M^{-1}) is consistent with the results obtained by both Stoddart's and Gibson's groups for $[Bn_2NH_2]^+PF_6$ with DB24C8.[11] The addition of CD_3SOCD_3 (20%) to the NMR sample leads to complete decomplexation.

Our approach to the formation of crown ethers and their derivatives bearing a single porphyrin group, e.g. **9** and **15**, began by investigating the cyclization of the polyether derivatives **5**.[24] Compounds **9** and **15** are pivotal to any derivatization by allowing the introduction of electrophiles[25] or other electron acceptors to the crown ether periphery. Diacetates **5** were chosen as our starting point for three reasons. First, the acidic conditions of the nitration of the unprotected diol would surely lead to a range of byproducts, the diacetate is easily formed,[24] and the acetate group is easily removed under the subsequent reduction conditions. The diacetates **5a** and **5b** were nitrated cleanly (Scheme 4) in high yield after purification by column chromatography to give bright yellow oils that solidified on standing. Deprotection of **6** (K_2CO_3, MeOH) followed by tosylation (TsCl, NEt_3, CH_2Cl_2) of the diol **7**, gave the bistosylate **8** in high yield. All attempts to cyclize **8** with catechol under differing conditions of base, solvent, and temperature failed to give any of the corresponding dinitro-DB18C6. This observation was consistent with literature reports on the effect of nucleophilic ring cleavage of nitro crown ethers by alcoholic bases.[18] Using a similar synthetic strategy to that outlined for **1**, compounds **6a** and **6b** were subjected to reduction ($NH_2NH_2 \cdot H_2O$, Pd/C, EtOH) followed by condensation with **4** to yield **9a** and **9b**, respectively (Scheme 4), in excellent yield. In this case, the highly nucleophilic nature of the hydrazine allows the hydroxy groups to be regenerated during this reaction sequence.

Alternatively, we proposed that the desired regioselectivity in **15** could be introduced into a dibenzocrown ether by way of appropriate blocking groups (Scheme 5). Nitration of **2** (Scheme 1) proceeded smoothly and in high yield. Hydrazine reduction of **3** yielded the amine **11**,[26] in which removal of the bromo groups were also observed. This was surprising in light of our earlier results on rigid-norbornylogous bridged systems where debromination did not occur under similar conditions.[14a] The debromination posed a potential problem in itself. The highly activated nature of the two aromatic units within the crown ether meant that the subsequent functionalization might not occur *ortho* to the amino group. Interestingly, there have been no reports in the literature of regioselectivity in electrophilic aromatic substitution between activated dibenzo-crown ether units. Protection of the amine (Ac_2O, CH_2Cl_2) allows for the regiospecific nitration of **12** *ortho* to the acetamide group in high yield.

(23) Aqueous solutions of the tetrahydrochloride salt have a limited shelf life, darkening considerably over a two day period.

(24) Hiratani, K.; Aiba, S. *Bull. Chem. Soc. Jpn*. **1984**, *57*, 2657.
(25) Diederich, F.; Jonas, U.; Gramlich, V.; Herrmann, A.; Ringsdorf, H.; Thilgen, C. *Helv. Chim. Acta* **1993**, *76*, 2445.
(26) Jeong, K.-S.; Cho, Y. L. *Bull. Korean Chem. Soc.* **1994**, *15*, 705.

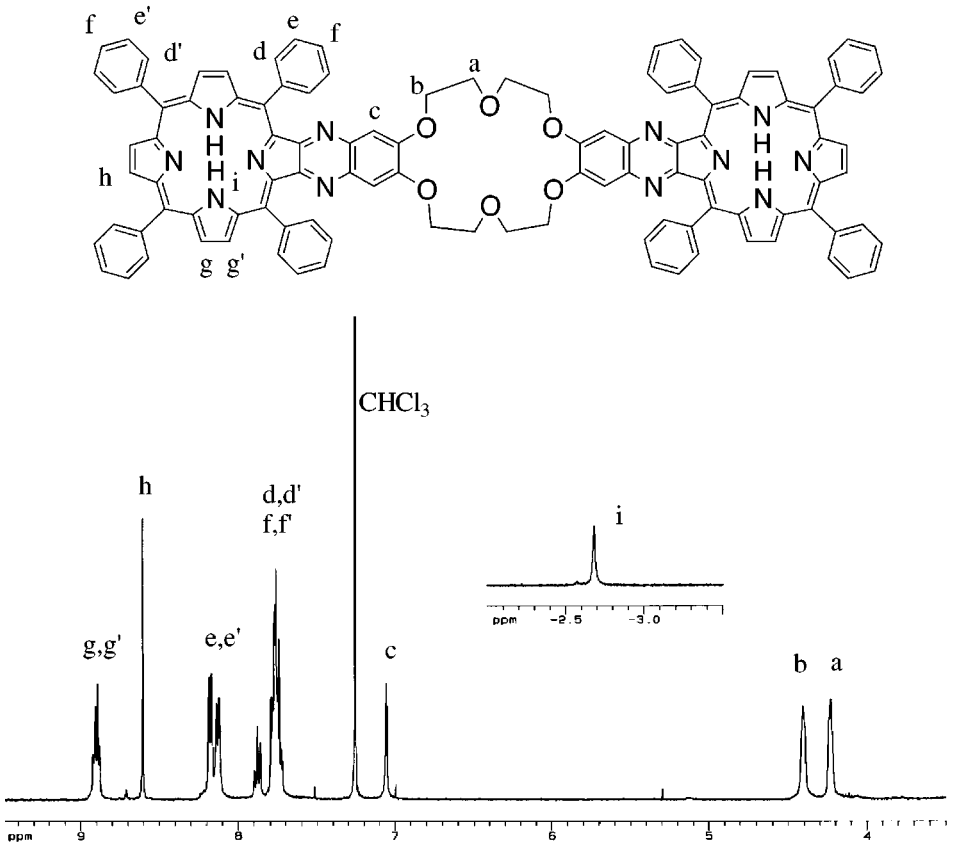
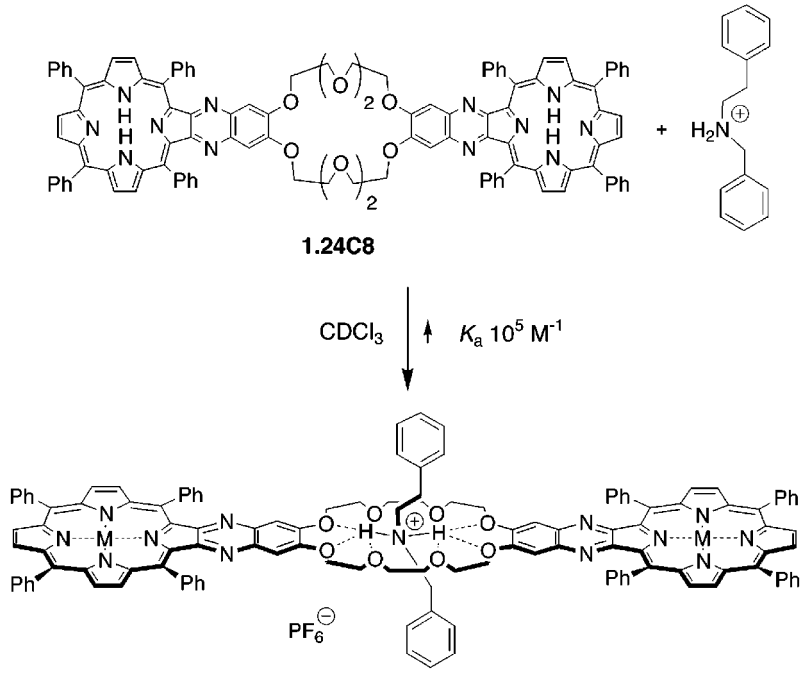


Figure 2. 400 MHz ^{1}H NMR spectrum of **1**.18C6 in $CDCl_3$ at 300 K.

Scheme 3. Preliminary Complexation Study between 1.24C8 and $[Bn_2NH_2]^+PF_6^-$ in $CDCl_3$



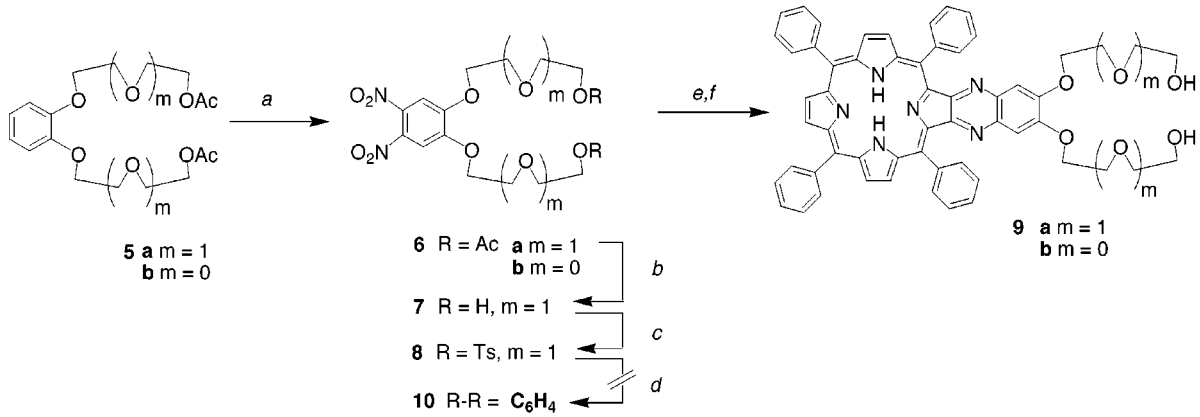
None of the alternate isomers, where nitration occurs in the other ring, were observed. This regiospecificity was somewhat surprising taking into account steric effects known for the acetamide group, the competition between the equally strong directing groups, and the size of the incoming electrophile.[27] Deprotection of **13** (1M HCl, 60 °C, 3 days) occurred cleanly to give the nitroamine **14** as an orange solid in excellent yield. Reduction of **14** (NH_2-NH_2·H_2O, Pd/C, EtOH) and condensation with **4** gave **15** in 76% yield as a bright purple solid (Scheme 5).

(27) *Advanced Organic Chemistry*, 4th Ed.; March, J., Ed.; Wiley: New York, 1992; p. 513.

Conclusion

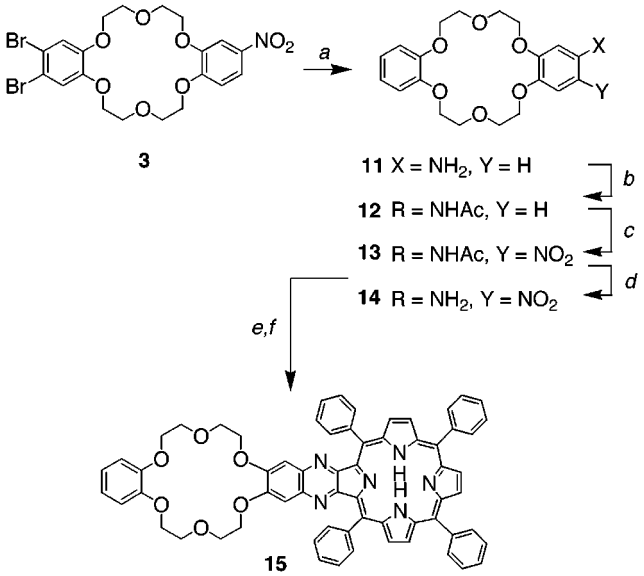
Our work describes an efficient method for the synthesis of a series of porphyrin-appended crown ether

Scheme 4



[a] HNO_3, H_2SO_4, CH_2Cl_2, r.t. 92−95%. [b] MeOH, K_2CO_3, 15 min. [c] TsCl, NEt_3, CH_2Cl_2, 0 °C, 72%. [d] Catechol, base, solvent. [e] Hydrazine hydrate, Pd/C, EtOH, reflux, Ar. [f] **4**, CH_2Cl_2, reflux, 84−86% for 2 steps.

Scheme 5



[a] Hydrazine hydrate, Pd/C, EtOH, reflux, Ar, 96%. [b] Ac_2O, r.t., 86%. [c] HNO_3, CH_2Cl_2, 0 °C, 80%. [d] 1 M HCl, 60 °C, 3 days, 72%. [e] Hydrazine hydrate, Pd/C, EtOH, reflux, Ar. [f] **4**, CH_2Cl_2, reflux, 76% for 2 steps.

systems in which the catechol unit of the crown ethers are fused to two β-pyrrolic positions of the porphyrin periphery. Critical to this strategy was the preparation of crown ethers bearing *ortho*-amine groups. In the case of the doubly appended systems **1**, tetranitration, the subsequent reduction and condensation were achieved in high yield in 3 steps from commercially available starting materials. We have also demonstrated for the first time the regiospecific nitration of a dibenzocrown ether bearing *five* activating groups. This regiospecificity leads to the efficient preparation of the singularly appended crown ether **15.** We are at present investigating ways of incorporating other electron accepting groups into **1** using **9** and **15** as precursors, making metalated variants of **1** to investigate ET and EnT processes,[28] and investigating the ability of systems **1**, **9**, and **15** to act as fluorescent sensors for a range of organic and metal cations.

Experimental Section

General Methods. Chemicals were purchased from Aldrich and used as received. Solvents were dried and reagents were purified where necessary using literature methods.[29] Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with Merck 5735 Kieselgel 60F. Column chromatography was carried out using Kieselgel 60 (0.040−0.063 mm mesh, Merck 9385). Melting points are uncorrected. Microanalyses were carried out within the Chemistry Department, University of Otago, New Zealand. Low resolution mass spectra were recorded on a micromass platform spectrometer (QMS, quadrupole mass electrospray) and high-resolution mass spectra were recorded on a Bruker BioApex 47e Fourier transform mass spectrometer equipped with an Analytica ESI source. In both cases, samples were prepared as either aqueous methanol or dichloromethane solutions. Nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz for proton frequency and 75 MHz for carbon frequency using the DEPT pulse sequence. Reflection data were measured with an Enraf-Nonius KappaCCD diffractometer at 123 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Reflections with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct methods.

Synthesis of TNDB-3*n*-crown-*n*. General Procedure. To a stirred solution of DB-3*n*-crown-*n* (0.4−1.2 mmol) in dichloromethane were added dropwise concentrated nitric acid (1 mL) and, after 5−10 min, concentrated sulfuric acid (0.5 mL). The reaction mixture was stirred at room temperature for 2−4 days.

2,3,12,13-Tetranitro-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxadibenzo[*b*,*k*]cyclooctadecene (TNDB18C6) was synthesized from DB18C6 (0.55 g, 1.20 mmol), by nitration over 2 days. The product precipitated out of solution, pure, as a fine yellow powder (0.73 g, 96%), which was obtained by filtering the reaction mixture, washing with water, and drying in the oven. Mp 228−229 °C. ESI HRMS (+ve): Found *m*/*z* 563.0866 $[M + Na]^+$ (Calculated for molecular formula $C_{20}H_{20}N_4O_{14}Na$, 563.0874). ^1H NMR (300 MHz, CD_3CN): δ 3.90−3.92 (8H, m, OCH_2), 4.27−4.31 (8H, m, OCH_2), 7.53 (4H, s, ArH). ^{13}C NMR (75 MHz, d_6-DMSO): δ 69.3, 70.3, 109.3, 136.9, 151.8.

2,3,16,17-Tetranitro-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenz[*b*,*n*]-1,4,7,10,13,16,19,22-octaoxacyclotetracosin (TNDB24C8) was synthesized from DB24C8 (0.41 g, 0.90 mmol) by nitration over 4 days, after which dichloromethane was added (30 mL) and the organic layer collected, washed with water (2 × 30 mL), and dried over anhydrous sodium sulfate. The mixture was filtered and the solvent removed under reduced pressure to afford a yellow grainy solid (0.55 g, 96%). Mp 197−198 °C. ESI HRMS (+ve): Found *m*/*z* 651.1416 $[M + Na]^+$ (Calculated for molecular

(28) (a) Rege P. J. F.; Williams, S. A.; Therien, M. J. *Science* **1995**, *269*, 1409. (b) Harriman, A.; Sauvage, J.-P. *Chem. Soc. Rev.* **1996**, 41.

(29) *Purification of Laboratory Chemicals*, 3rd ed.; Perrin, D. D., Armarego, W. L., Eds.; Pergamon Press: New York, 1988.

formula $C_{24}H_2N_4O_{16}Na$, 651.1398). ^{1}H NMR (300 MHz, CD_3CN): δ 3.70 (8H, s, OCH_2), 3.83−3.87 (8H, m, OCH_2), 4.26−4.29 (8H, m, OCH_2), 7.52 (s, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.7, 70.7, 71.9, 109.0, 136.9, 151.7.

2,3,19,20-Tetranitro-6,7,9,10,12,13,15,16,23,24,26,27,29,-30,32,33-hexadecahydrodibenzo[*b*,*q*]-1,4,7,10,13,16,19,22,-25,28-decaoxacyclotriacontin (TNDB30C10) was synthesized from DB30C10 (217 mg, 0.40 mmol), by nitration over 2 days, after which dichloromethane was added (30 mL) and the organic layer collected, washed with water (2 × 30 mL), and dried over anhydrous sodium sulfate. The mixture was filtered, the solvent removed under reduced pressure, and the resulting solid dried in the oven for 0.5 h to afford a yellow grainy solid, which was recrystallized from an acetonitrile solution (133.9 mg, 46%). Mp 165−166 °C. ESI HRMS (+ve): Found *m*/*z* 739.1912 $[M + Na]^+$ (Calculated for molecular formula $C_{28}H_{36}N_4O_{18}Na$, 739.1922). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.58−3.68 (16H, m, OCH_2), 3.83−3.86 (8H, m, OCH_2), 4.25−4.28 (8H, m, OCH_2), 7.40 (4H, s, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.8, 70.3, 71.1, 71.5, 109.2, 136.8, 151.8.

Synthesis of 1. General Procedure. To a tetranitrodibenzo-3*n*-crown-*n* (0.19−0.68 mmol) was added degassed ethanol (10 mL), Pd/C (100 mg), and degassed hydrazine hydrate (20 drops). The mixture was stirred and heated to reflux in an overnight reaction under an argon atmosphere, in darkness. Upon completion, the reaction mixture was filtered, under argon, though a plug of Celite into a round-bottom flask containing degassed dichloromethane (40 mL) and 2,3-dioxo-5,10,15,20-tetraphenylchlorin **4**. The Celite plug was washed with a further amount of dichloromethane (10 mL). This mixture was then heated to reflux under an argon atmosphere and allowed to react overnight. TLC was used to monitor the reaction's progress. Once complete, the solvent was removed from the completed reaction mixture under reduced pressure to give a red/purple solid that was purified by column chromatography.

1.18C6 was synthesized from TNDB18C6 (102.9 mg, 0.19 mmol) and **4** (156.8 mg, 0.24 mmol). Chromatography: chloroform, then increasing to 7%, *N*,*N*-dimethylformamide in chloroform. The first band to elute was unreacted **4** (88.1 mg), the second band was the targeted bis-porphyrin, which was isolated as a red-purple solid. The product was then recrystallized from a methanol and dichloromethane mixture and filtered to yield **1**.18C6 as fine red-purple crystals (52.9 mg, 51% based on recovered **4**). Mp > 350 °C. ESI HRMS (+ve): Found *m*/*z* 819.3061 $[M + 2H]^{2+}$ (Calculated for molecular formula $C_{108}H_{78}N_{12}O_6$: 1638.6167, $C_{54}H_{38}N_6O_3$: 819.3038); λ_{max} ($CHCl_3$): 384 sh (log ϵ, 5.13), 430 (5.58), 524 (4.70), 559 (4.19), 596 (4.36), 649 nm (3.55). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.69 (4H, br s, inner NH), 4.21−4.25 (8H, m, OCH_2), 4.38−4.42 (8H, m, OCH_2), 7.05 (4H, s, ArH), 7.70−7.92 (24H, m, *meso*-ArH), 8.12−8.22 (16H, m, *meso*-ArH), 8.63 (4H, s, β-pyrrolic H), 8.80−8.94 (8H, ABq, J = 4.8 Hz, β-pyrrolic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.5, 69.8, 104.6, 108.5, 114.3, 116.9, 121.4, 126.8, 127.4, 127.8, 127.9, 133.8, 134.0, 134.5, 139.6, 140.8, 146.1, 150.3, 151.2, 152.1, 154.6.

1.24C8 was synthesized from TNDB24C8 (74.1 mg, 0.12 mmol) and **4** (88.1 mg, 0.14 mmol). Chromatography: 3:2 dichloromethane/hexane to elute any unreacted **4** (36.7 mg) and subsequently 2:98 methanol/dichloromethane mixture. **1**.24C8 was obtained as a red-purple solid (24.5 mg, 36% based on recovered **4**). Mp > 350 °C. ESI HRMS (+ve): Found *m*/*z* 1725.6564 $[M + H]^+$ (Calculated for molecular formula $C_{112}H_{85}N_{12}O_6$, 1725.6613). Found *m*/*z* 1747.6351 $[M + Na]^+$ (Calculated for molecular formula $C_{112}H_{84}N_{12}O_6Na$, 1747.6433); λ_{max} ($CHCl_3$): 384 sh (log ϵ, 5.13), 430 (5.58), 524 (4.70), 559 (4.19), 596 (4.36), 649 nm (3.55). ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.65 (4H, br s, inner NH), 3.95−4.00 (8H, m, OCH_2), 4.07−4.14 (8H, m, OCH_2), 4.32−4.40 (8H, m, OCH_2), 7.03 (4H, s, ArH), 7.60−7.88 (24H, m, *meso*-ArH), 8.00−8.22 (16H, m, *meso*-ArH), 8.66 (4H, s, β-pyrrolic H), 8.87−8.96 (8H, m, β-pyrrolic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.0, 68.8, 69.3, 121.7, 126.9, 127.0, 127.1, 127.6, 128.1, 128.1, 128.2, 134.3, 134.7, 138.0, 138.1, 139.8, 141.3, 142.2, 142.3, 146.2, 151.5, 151.9, 154.6.

1.30C10 was synthesized from TNDB30C10 (57.7 mg, 0.08 mmol) and **4** (105.1 mg, 0.16 mmol). Chromatography: 3:2 dichloromethane/hexane to elute any unreacted **4** (56.6 mg) and subsequently 2:98 and 4:96 methanol/dichloromethane mixtures. **1**.30C10 was obtained as a red-purple solid (86.0 mg, 63% based on recovered **4**). Mp > 350 °C. ESI HRMS (+ve): Found *m*/*z* 1813.7138 $[M + H]^+$ (Calculated for molecular formula $C_{116}H_{93}N_{12}O_{10}$, 1813.7138). Found *m*/*z* 1835.6930 $[M + Na]^+$ (Calculated for molecular formula $C_{116}H_{92}N_{12}O_{10}Na$, 1835.6957); λ_{max} ($CHCl_3$): 384 sh (log ϵ, 5.13), 430 (5.58), 524 (4.70), 559 (4.19), 596 (4.36), 649 nm (3.55). ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.68 (4H, br s, inner NH), 3.76−3.82 (8H, m, OCH_2), 3.87−3.93 (8H, m, OCH_2), 4.02−4.10 (8H, m, OCH_2), 4.32−4.37 (8H, m, OCH_2), 7.02 (4H, s, ArH), 7.74−7.88 (24H, m, *meso*-ArH), 8.07−8.20 (16H, m, *meso*-ArH), 8.64 (s, 4H, β-pyrrolic H), 8.89−8.90 (8H, m, β-pyrrolic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.3, 69.8, 71.1, 71.5, 108.9, 109.0, 117.1, 121.6, 127.0, 127.6, 128.0, 128.1, 133.8, 134.0, 134.2, 134.7, 138.0, 138.2, 139.8, 142.1, 142.3, 146.3, 151.4, 152.4, 154.8.

4,5-Dinitro-1,2-bis(2-(2-(2-acetoxy(ethoxyethoxy))))benzene 6a. To **5a**[22] (4.12 g, 10.8 mmol) were added concentrated nitric acid (8 mL, 177.8 mmol), dichloromethane (50 mL), and concentrated sulfuric acid (4 mL, 73.5 mmol). The mixture was stirred for 2 days and then quenched by addition of ice water (100 mL). The organic layer was collected, washed with a sodium carbonate solution (5%, 70 mL) and water (2 × 70 mL), then dried over anhydrous sodium sulfate and filtered, and the solvent removed under reduced pressure to give **6a** as a yellow oil which solidified on standing (4.71 g, 95%). The product was chromatographed on silica (ethyl acetate/hexane; 2:1). Mp 48−49 °C. ESI HRMS (+ve): Found *m*/*z* 483.1231 $[M + Na]^+$ (Calculated for molecular formula $C_{18}H_{24}N_2O_{12}Na$, 483.1227). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (6H, s, $COCH_3$), 3.75 (4H, t, J = 4.5 Hz, OCH_2), 3.90 (4H, t, J = 4.5 Hz, OCH_2), 4.22 (4H, t, J = 4.5 Hz, OCH_2), 4.30 (4H, t, J = 4.5 Hz, OCH_2), 7.43 (2H, s, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 63.2, 69.1, 69.3, 69.7, 108.9, 136.4, 151.3, 170.6. Anal. Calcd for $C_{18}H_{24}N_2O_{12}$: C, 45.2; H, 4.3; N, 7.5. Found C, 45.3; H, 4.2; N, 7.6.

4,5-Dinitro-1,2-bis(2-(2-(2-acetoxy(ethoxyethoxy))))benzene 6b. The compound was formed from **5b**[22] (1.30 g, 4.6 mmol) in a manner similar to that described above for **6a** (1.39 g, 92%). Mp 108−110 °C. ESI MS (+ve): Found *m*/*z* 395.0 $[M + Na]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09 (6H, s, $COCH_3$), 4.34 (4H, m, OCH_2), 4.45 (4H, m, OCH_2), 7.39 (2H, s, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 62.3, 68.4, 109.4, 137.0, 151.4, 170.8.

4,5-Dinitro-1,2-bis(2-(2-(2-tosyloxy(ethoxyethoxy))))benzene 8. To a solution of **6a** (1.02 g, 2.20 mmol) in MeOH (50 mL) was added K_2CO_3 (0.56 g, 4.05 mmol) and the mixture stirred at room temperature for 15 min. Once complete, the mixture was filtered to remove any excess K_2CO_3 and then the filtrate was extracted into dichloromethane (100 mL), washed with water (3 × 30 mL), and dried (Na_2SO_4) and the solvent removed under vacuum at ambient temperature. The diol **7** was isolated as a yellow solid (0.74 g, 89%) and used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.67, 4H, m, OCH_2), 3.73, 4H, m, OCH_2), 3.96, 4H, m, OCH_2), 4.27, 4H, m, OCH_2), 7.38, 2H, s, ArH. ESI MS (+ve): Found *m*/*z* 399.2 $[M + Na]^+$. To an ice cold solution of **7** (0.74 g, 1.96 mmol) and triethylamine (0.59 g, 5.87 mmol) in dry dichloromethane (50 mL) was added TsCl (0.83 g, 4.31 mmol) and the reaction allowed to proceed overnight at 4 °C. Once complete, the organic solution was washed with 1 M HCl (2 × 20 mL) and then water (1 × 20 mL), dried (Na_2SO_4), and the solvent removed under vacuum. The residue was chromatographed on silica (EtOAc/hexane; 2:1) to yield **8** (0.75 g, 72%) as a yellow oil. ESI MS (+ve): Found *m*/*z* 707.2 $[M + Na]^+$; ESI HRMS (+ve): Found *m*/*z* 707.1196 $[M + Na]^+$ (Calculated for molecular formula $C_{28}H_{32}N_2O_{14}S_2Na$, 707.1187). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (6H, s, CH_3), 3.77 (4H, t, J = 4.6 Hz, OCH_2), 3.87 (4H, t, J = 4.1 Hz, OCH_2), 4.16 (4H, t, J = 4.6 Hz, OCH_2), 4.23 (4H, t, J = 4.1 Hz, OCH_2), 7.32 (4H, d, J = 8.2 Hz, ArH), 7.37 (2H, s, ArH), 7.77 (4H, d, J = 8.2 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 63.2, 69.1, 69.3, 69.7, 108.9, 136.4, 151.3, 170.6.

9a. To **6a** (260 mg, 56.37 mmol) were added degassed ethanol (15 mL), Pd/C (78.3 mg), and hydrazine hydrate (0.5 mL, 16.05 mmol). The mixture was degassed to remove traces of oxygen, then stirred and heated to reflux overnight under argon, in

darkness. Upon completion, the reaction mixture was filtered though a plug of Celite into a solution of **4** (250 mg, 38.44 mmol) in dichloromethane (50 mL). The Celite plug was washed with a further amount of dichloromethane (20−30 mL). This mixture was then heated to reflux under an argon atmosphere, and allowed to react overnight. TLC was used to monitor the reaction progress. Once complete, the solvent was removed under reduced pressure to yield a dark red-purple solid. This was purified using column chromatography (dichloromethane and consequently Me_2CO/CH_2Cl_2; 1:3), to yield **9a** as a dark red-purple solid (300 mg, 86%). Mp 294−295 °C. ESI HRMS (+ve): *m/z* 925.3727 $[M + H]^+$ (Calculated for molecular formula $C_{58}H_{49}N_6O_6H$, 925.3714); 947.3536 $[M + Na]^+$ (Calculated for molecular formula $C_{58}H_{48}N_6O_6Na$, 947.3533). ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.63 (2H, br s, inner NH), 3.76−3.80 (8H, m, OCH_2), 4.05 (4H, m, OCH_2), 4.35 (4H, m, OCH_2), 7.05 (2H, s, ArH), 7.72−7.87 (12H, m, *meso*-ArH), 8.14−8.22 (8H, m, *meso*-ArH), 8.69 (2H, s, β-pyrrolic H), 8.91 (4H, ABq, J = 5.1 Hz, β-pyrrolic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 20.9, 21.1, 25.7, 108.8, 117.0, 121.6, 126.9, 127.5, 123.0, 128.1, 134.1, 134.6, 137.9, 137.9, 139.6, 142.0, 142.1, 146.0, 150.0, 151.3, 151.7, 168.0, 171.0, 173.8.

9b was formed from **6b** (250 mg, 0.66 mmol) and **4** (370 mg, 0.57) in a similar procedure to yield **6b** (384 mg, 80%). Mp >300 °C. ESI HRMS (+ve): Found *m/z* 837.3154 $[M + H]^+$ (Calculated for molecular formula $C_{54}H_{41}N_6O_4$, 837.3189). ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.59 (2H, br s, inner NH), 4.10−4.13 (4H, m, OCH_2), 4.30−4.33 (4H, m, OCH_2), 7.13 (2H, s, ArH), 7.72−7.89 (12H, m, *meso*-ArH), 8.13−8.23 (8H, m, *meso*-ArH), 8.70 92H, s, β-pyrrolic H), 8.92 (4H, AB q, J = 5.1 Hz, β-pyrrolic H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.1, 71.2, 110.1, 117.1, 121.6, 126.8, 126.9, 127.6, 128.0, 128.1, 128.2, 134.1, 134.6, 137.9, 138.2, 139.7, 142.1, 142.2, 149.2, 151.6, 152.2, 154.9, 173.4.

2,3-Dibromo-13-nitro-6,7,9,10,17,18,20,21-octahydro-5,8,-11,16,19,22-hexaoxadibenzo[*a,j*]cyclooctadecene 3. Concentrated nitric acid (57 μL, 0.9 mmol, 2 equiv) was added to a stirring solution of dibromo-dibenzo-18-crown-6 **11**[18] (229 mg, 0.4 mmol) in dichloromethane (5 mL) and allowed to stir overnight. The reaction mixture was then washed with a saturated solution of sodium carbonate (2 × 30 mL) and water (2 × 30 mL) and dried with sodium sulfate. The dichloromethane was removed under vacuum to yield the mono-nitrated product, which was recrystallized in chloroform to give rise to **12** (202 mg, 81%) as a pale yellow solid. Mp 216−218 °C. ESI MS (+ve): *m/z* 586.0 $[M + Na]^+$. ^{1}H NMR (CD_3CN): δ 3.85 (t, 8H, J 6.2 Hz, OCH_2), 4.08 (m, 4H, OCH_2), 4.21 (m, 4H, OCH_2), 7.03 (d, 1H, J = 9.0 Hz, ArH), 7.17 (s, 2H, ArH), 7.73 (d, 1H, J = 2.7 Hz, ArH), 7.88 (dd, 1H, J = 9.0 Hz, J = 2.6 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 68.8, 68.9, 69.0, 69.3, 69.4, 100.2, 107.4, 114.5, 117.1, 117.2, 118.4, 141.3, 148.3, 148.8. Anal. Calcd for $C_{20}H_{21}NO_8Br_2$: C, 42.6; H, 3.8; N, 2.4. Found C, 42.5; H, 3.8; N, 2.2.

6,7,9,10,17,18,20,21-Octahydro-5,8,11,16,19,22-hexaoxadibenzo[*a,j*]cyclooctadecen-2-yl Amine 11. Nitro-dibenzo-18-crown-6, **12** (201.5 mg, 0.36 mmol), and 10% palladium on carbon (112 mg) were combined in absolute ethanol (20 mL) and stirred, under argon. This mixture was allowed to reflux and hydrazine hydrate (20 drops) was added dropwise. The reaction was monitored by TLC and, on completion, was hot filtered through Celite and the solvent removed under reduced pressure. Dichloromethane (100 mL) and water (50 mL) were added to the residue, and the aqueous layer was extracted with dichloromethane (50 mL). The organic layer was washed with water (2 × 30 mL) and dried (Na_2SO_4) and the solvent removed under reduced pressure. The product **11** (129 mg, 96%) was isolated as a white solid. Mp 156−158 °C, lit.[26] 159−163 °C. ESI MS (+ve): *m/z* 398.2 $[M + Na]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.02 (m, 8H, OCH_2), 4.10 (m, 4H, OCH_2), 4.16 (m, 4H, OCH_2), 6.21 (dd, 1H, J = 8.4 Hz, J = 2.60 Hz, ArH), 6.29 (d, 1H, J = 2.6 Hz, ArH), 6.88 (m, 4H, ArH), 6.70 (d, 1H, J = 8.4 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.8, 69.1, 70.1, 70.2, 70.5, 102.7, 107.5, 113.6, 113.8, 121.5, 121.6, 148.8.

6,7,9,10,17,18,20,21-Octahydro-5,8,11,16,19,22-hexaoxadibenzo[*a,j*]cyclooctadecen-2-yl Acetamide 12. To a solution of the amine **11** (107 mg, 0.29 mmol) in anhydrous dichloromethane (10 mL) was added acetic anhydride (58 mg, 2 equiv). The resulting mixture was stirred at room temperature under argon for 2 h. More dichloromethane (20 mL) was added to the reaction mixture, and it was then was washed with a saturated sodium carbonate solution (2 × 30 mL) and water (2 × 30 mL) and dried (Na_2SO_4). The dichloromethane was removed under vacuum to yield the desired product **12** (99 mg, 86%) as a bright yellow solid. An analytically pure sample was recrystallized from dichloromethane. Mp 185−186 °C. ESI MS (−ve): *m/z* 553.2 $[M + Cl]^-$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H, CH_3), 4.01 (m, 8H, OCH_2), 4.18 (m, 6H, OCH_2), 4.28 (m, 2H, OCH_2), 6.74 (d, 1H, J = 8.5 Hz, ArH), 6.86 (m, 4H, ArH), 7.28 (s, 1H, NH), 7.26 (d, 1H, J = 1.6 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.9, 68.5, 68.7, 69.8, 105.4, 111.6, 113.1, 121.5, 133.7, 144.5, 148.3, 148.7, 168.5. Anal. Calcd for $C_{22}H_{27}NO_7.CH_2Cl_2$: C, 54.9; H, 5.8; N, 2.8. Found C, 54.8; H, 6.0; N, 2.9.

3-Nitro-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxadibenzo[*a,j*]cyclooctadecen-2-yl Acetamide 13. Concentrated nitric acid (2 equiv, 25 μL) was added to a stirring solution of acetamide **12** (78 mg, 0.19 mmol) in an ice bath. This was left to stir overnight, and reaction progress was monitored by TLC (by disappearance of starting materials). Once complete, the reaction mixture was washed with a saturated sodium carbonate solution (2 × 30 mL) and water (2 × 30 mL), dried (Na_2SO_4), and the solvent removed in vacuo. The nitro-acetamide **13** (69 mg, 80%) was recrystallized from chloroform. Mp 226−227 °C. ESI MS (+ve): *m/z* 485.3 $[M + Na]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H, $COCH_3$), 4.01 (s, 8H, OCH_2), 4.15 (m, 6H, OCH_2), 4.28 (t, 2H, J = 3.4 Hz, OCH_2), 6.87 (m, 4H, ArH), 7.65 (s, 1H, ArH), 8.46 (s, 1H, ArH), 10.75 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 68.1, 68.2, 68.9, 69.1, 69.3, 69.4, 70.0, 70.1, 103.6, 108.0, 112.5, 121.2, 128.3, 132.4, 143.8, 148.5, 155.5, 169.5. Anal. Calcd for $C_{22}H_{26}N_2O_9.0.5CHCl_3$: C, 51.7; H, 5.2; N, 5.3. Found C, 51.6; H, 5.3; N, 5.2.

3-Nitro-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxadibenzo[*a,j*]cyclooctadecen-2-yl Amine 14. Nitro-acetamide **13** (31 mg, 0.06 mmol) was dissolved in absolute ethanol (3 mL), and hydrochloric acid was added (10 drops, 1 M). The reaction mixture was allowed to stir under argon. Reaction progress was monitored by ^{1}H NMR. On completion, dichloromethane (10 mL) was added to the reaction mixture and it was washed with sodium carbonate (2 × 20 mL) and water (2 × 20 mL) and dried with sodium sulfate. The solvent was removed under vacuum to yield **14** as a bright yellow solid (23 mg, 72%) which was recrystallized from dichloromethane. Mp 75−76 °C. ESI MS (+ve): *m/z* 443.3 $[M + Na]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.01 (s, 8H, OCH_2), 4.01 (m, 8H, OCH_2), 4.13 (m, 8H, OCH_2), 4.15 (m, 6H, OCH_2), 6.13 (s, 1H, ArH), 6.21 (s, broad, 2H, NH), 6.87 (m, 4H, ArH), 7.47 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.3, 68.5, 68.9, 69.3, 69.6, 70.0, 70.1, 70.2, 99.8, 107.7, 112.9, 113.1, 121.2, 121.4, 121.5, 140.8, 142.9, 148.5, 148.7, 156.5. Anal. Calcd for $C_{20}H_{24}N_2O_8.CH_2Cl_2$: C, 5.0; H, 5.1; N, 5.5. Found C, 50.0; H, 5.1; N, 5.4.

Porphyrin-Crown 15. Degassed ethanol (5 mL) was added to **14** (45 mg, 0.107 mmol), Pd/C (50 mg), and hydrazine hydrate (5 drops). The mixture was stirred and heated to reflux in an overnight reaction under an argon atmosphere, in darkness. Upon completion, the reaction mixture was filtered under argon, through a plug of Celite, into a round-bottom flask containing degassed dichloromethane (10 mL) and 2,3-dioxo-5,10,15,20-tetraphenylchlorin **4** (30 mg, 0.0466 mmol). The Celite plug was washed with a further amount of dichloromethane (2 mL). This mixture was then heated to reflux under an argon atmosphere, and allowed to react overnight. TLC was used to monitor the reaction's progress. Once complete, the solvent was removed in vacuo and the sample was purified by column chromatography to give **15** as a red/purple solid (35 mg, 76% yield). Mp > 350 °C. ESI MS (+ve): *m/z* 999.3 $[M + H]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.61 (s, 2H, inner NH), 4.09 (m, 4H, OCH_2), 4.15 (m, 4H, OCH_2), 4.19 (m, 4H, OCH_2), 4.35 (m, 4H, OCH_2), 6.87 (m, 4H, ArH), 7.02 (s, 2H, ArH), 8.17 (m, 4H, *meso*-ArH), 8.24 (m, 4H, *meso*-ArH), 8.71 (d, 2H, J = 8.8 Hz, β-pyrrolic), 8.93 (d, 4H, J = 8.8 Hz, β-pyrrolic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.7, 69.1, 69.8, 70.5, 108.5, 113.4, 117.2, 121.5, 121.7, 127.0, 127.1, 127.6, 128.0, 128.1, 128.2, 134.2, 134.3, 134.7, 138.0, 138.3, 139.8, 142.2, 142.3, 146.4, 148.8, 151.4, 152.3, 154.9.

Acknowledgment. This research was funded by the Special Monash University Research Fund (SMURF)

and by the Australian Research Council's Small Grant Scheme. An ARC Senior Research Fellowship (to M.N.P.-R.) is also gratefully acknowledged.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters for TNDB30C10, and copies of ^{1}H and ^{13}C NMR spectra for TNDB18C6, TNDB24C8, TNDB30C10, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001700P