JOC The Journal of Organic Chemistry

Note

Expanded porphyrin-like structures based on twinned triphenylenes

Hemant Gopee, Xiangfei Kong, Zhiqun He, Isabelle Chambrier, David L. Hughes, Graham J. Tizzard, Simon J. Coles, and Andrew N. Cammidge

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo401551c • Publication Date (Web): 29 Aug 2013

The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Expanded porphyrin-like structures based on twinned triphenylenes

Hemant Gopee,[†] Xiangfei Kong,[†,§] Zhiqun He,[§] Isabelle Chambrier,[†] David L. Hughes,[†] Graham J. Tizzard,[¶] Simon J. Coles[¶] and Andrew N. Cammidge[†]*

[†]School of Chemistry, University of East Anglia, Norwich NR4 7TJ, UK. [§] Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, PR China. [¶] UK National Crystallography Service, School of Chemistry, University of Southampton SO17 1BJ, UK.

a.cammidge@uea.ac.uk

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

Abstract

Triphenylene twins are intriguing structures and those bridged through their 3,6-positions by dipyrromethene units give a new class of macrocycle that can be viewed as rigid, expanded porphyrin derivatives in which co-planarity is enforced in a formally antiaromatic π-system. Somewhat surprisingly however, macrocyclization leads to significant overall stabilization of the dipyrromethene chromophores.

Macrocyclic, aromatic chromophores are extremely important chemical entities, exemplified by porphyrin and phthalocyanine.[1] The former are widespread in Nature and their function has inspired imaginative purpose-designed analogues. Their function and applications are too numerous and diverse to list, spanning the full scientific spectrum from biochemistry through to electronic engineering, with corresponding applications from medicine through to ubiquitous consumer devices.[1] Synthetic breakthroughs have advanced the scope of materials available, and an area of particular recent interest has been the investigation of core-modified structures to enhance and expand materials properties. Structures include expanded and contracted systems, confused and mixed-heteroatom systems, and hybrid structures.[2-8] The chemistry of expanded porphyrins in particular has received accelerated attention and progressed rapidly over recent years.[9] Advances include substantial synthetic effort and investigation of "higher" porphyrinoids, most extensively the hexaphrins (**2**) but including octaphrins and others.[10] Separately more complex and diverse expanded structures likened to porphyrins have been successfully targeted[9] and representative extreme structures include expanded system **3**[11] and rosarin derivative **4** (Figure 1).[12]

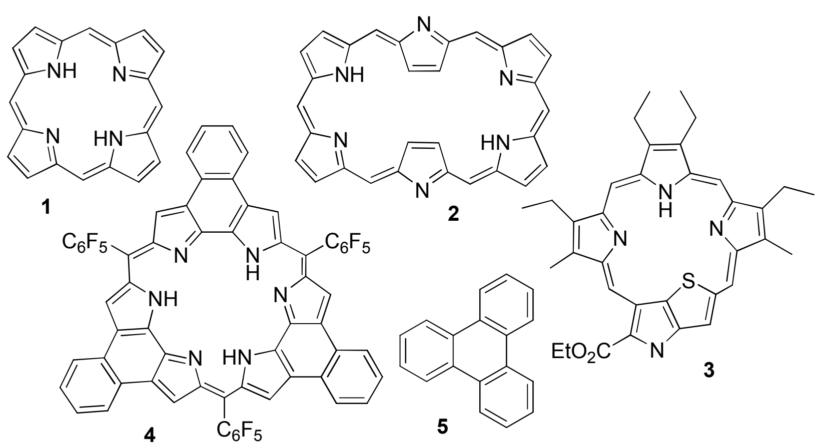


Figure 1. Parent structure of porphyrin **1** and triphenylene **5**, plus examples of more exotic porphyrinoids **2-4**.

Triphenylenes are an important class of discotic benzenoid aromatic compounds. They are the most widely studied discotic liquid crystals.[13] Synthetic advances have similarly allowed access to diverse symmetrical and unsymmetrically substituted derivatives so that their properties, such as factors controlling liquid crystal behavior, and applications could be interrogated.[14] In the field of discotic liquid crystals, the majority of mesophases are columnar in structure. Most recently we have applied our synthetic refinements to open the way to twinned macrocyclic structures linked through the triphenylene 3,6-positions. Using this approach strained and formally antiaromatic systems can be produced – the links through triphenylene 3,6-sites allows completion of conjugation pathways like in simple 1,2-disubstituted benzenes. However, the links are separated in space preventing destructive pericyclic processes. The twinning geometry, if carefully designed, leads to a void region in the centre of the molecule, such as in twins **6** and **7** (Figure 2). Columnar organization would lead to a void region through the column-centre and columnar mesophase formation is therefore suppressed. Self-organisation into the rare discotic nematic mesophase is then observed.[15]

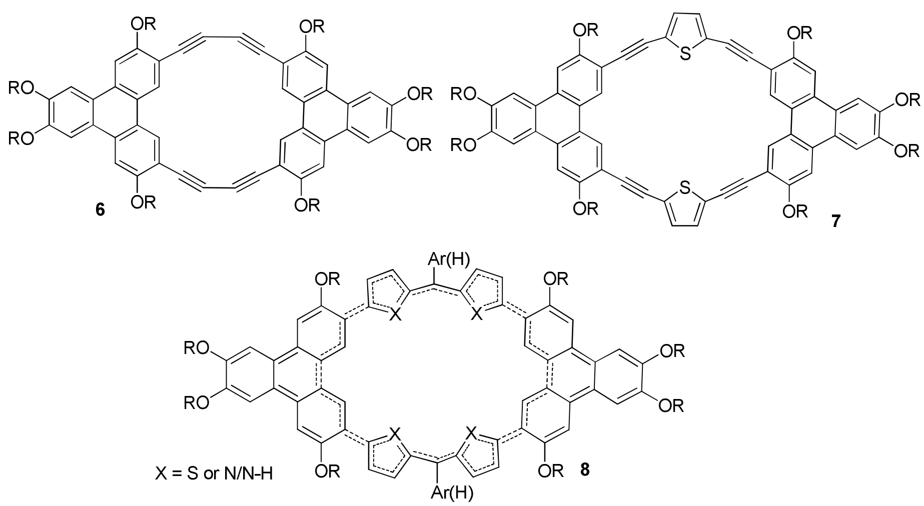
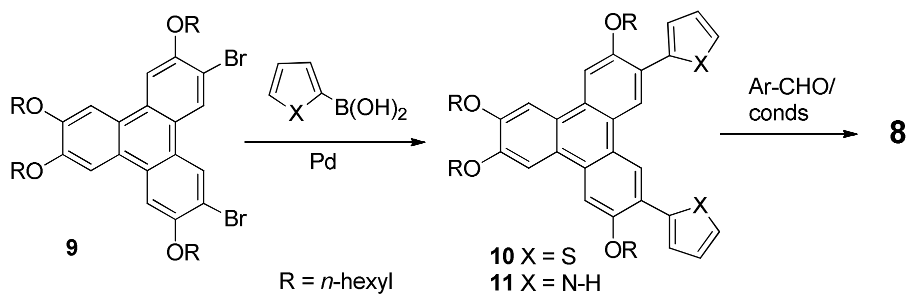


Figure 2. Rigid, nematic twins and the target twinned triphenylenes that have an expanded porphyrin-like core.

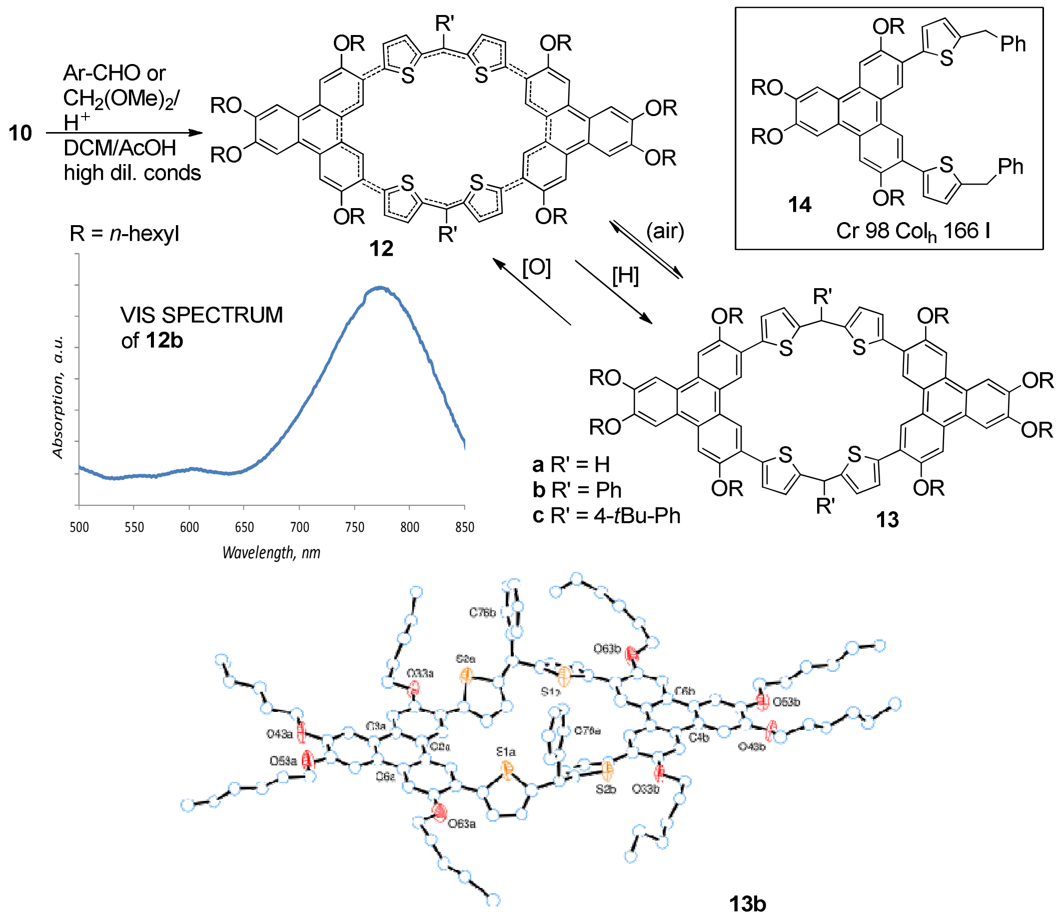
The structural motif therefore appears both useful and versatile, and we recognized that interesting molecular variants could be envisaged through more imaginative choice of linking units. Core structures represented by macrocycle **8** (Figure 2) were conceived; they can be considered direct but distant relatives of porphyrins and are therefore expected to mimic their cousins in some important respects.

Tetrahexyloxytriphenylene dibromide **9**[16] was identified as the key intermediate, and we reasoned that conversion to bis-thiophene and bis-pyrrole derivatives **10** and **11**, *via* Suzuki-Miyaura cross-coupling with appropriate boronic acids, would provide intermediates suitable for macrocyclization/condensation with aldehydes. The overall strategy, shown in Scheme 1, therefore resembles the classic 2+2 synthesis used for preparation of 5,15-substituted porphyrins.[17,18]



Scheme 1. 2+2 Approach to expanded porphyrin twins 8.

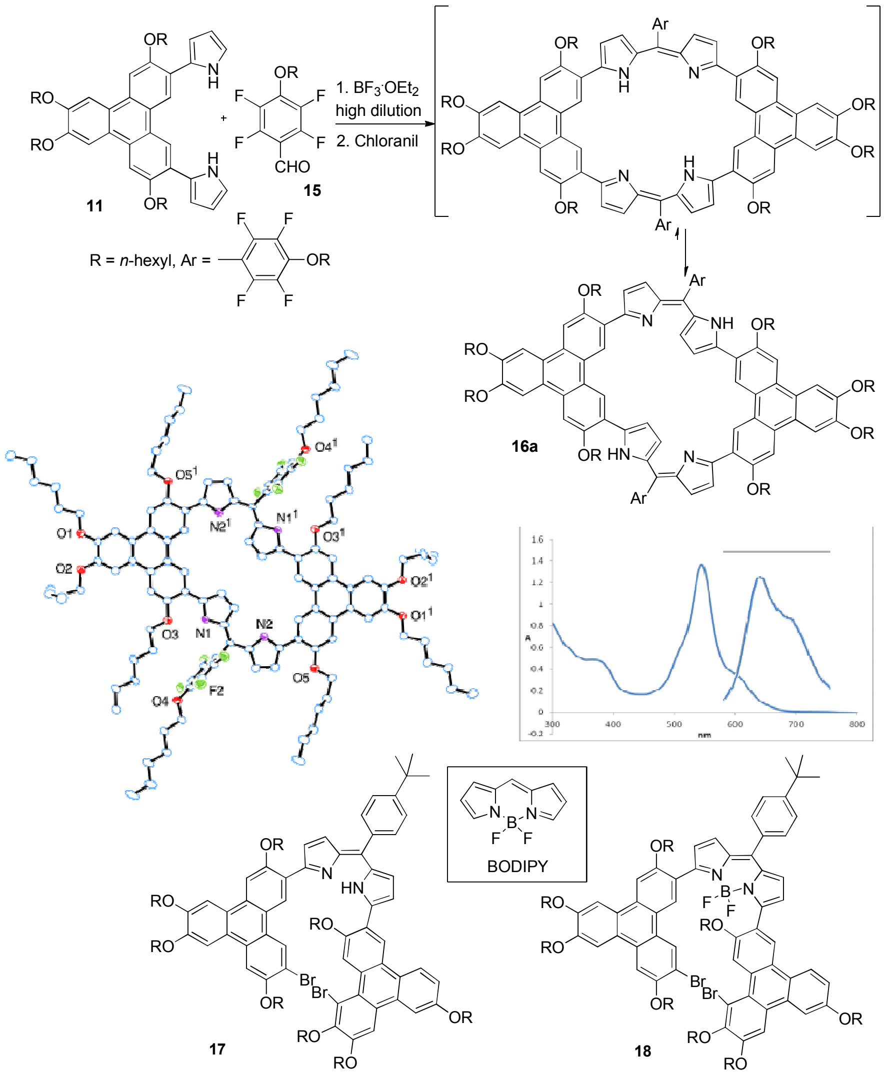
Thiophene derivatives were initially targeted because the precursor bis(2-thiophenyl) triphenylene **10** had been previously prepared for investigation of its liquid crystal properties.[14] The four hexyloxy side chains were retained primarily to confer solubility and aid purification and characterization of the intermediates and final products, but we also recognized that their inclusion could also potentially confer liquid crystallinity on intermediates and final products. Condensation of **10** with simple benzaldehyde derivatives consistently yielded product mixtures that were dark blue in color. The mixtures contained varying amounts of benzyl-substituted products, such as triphenylene **14**, resulting from reduction of intermediate addition adducts. Like its precursor (**10**), this discotic structure shows a wide-range columnar mesophase. Analysis of the crude reaction mixtures by MALDI-MS also showed strong molecular ion peaks corresponding to the conjugated target twinned structure, and a reproducible reaction protocol was developed that involved addition of an appropriate benzaldehyde (or dimethoxymethane) and conc. sulfuric acid in portions over 90 min. to a solution of **10** in dichloromethane/glacial acetic acid. Workup and isolation at this stage gave a blue solid, again showing a molecular ion consistent with the target twinned structure **12**. The product required THF or methanol-rich solvent systems to remove it from silica gel chromatographic columns indicating a highly aggregating, polar and/or charged system. Although freely soluble in organic solvents, the product gave no observable signals in the aromatic region of its ^{1}H NMR spectrum even at elevated temperatures (80 ^{o}C in toluene). EPR spectroscopy showed no free radical, and strong aggregation appears to be the likely cause. Visible spectra are also broad, extending into the near IR region (>800nm), indicating that the neutral, aromatic structure represented by **12** is most accurate, although this is unlikely to be the observed conformation (see later). Simple tlc analysis in non-polar solvents revealed the blue product to be in slow equilibrium with a colorless, non-polar material that returned to blue in air over time. 2D tlc showed reversibility between the two components. The equilibrium is a redox process, and can be driven to the colorless product instantly by simple treatment with hydrazine. Indeed, addition of a drop of hydrazine to the original (blue) NMR sample gives instant bleaching and appearance of strong, well-resolved signals leading to full characterization of these compounds as the expected non-conjugated twins **13**. Crystals suitable for X-ray diffraction were grown for one example under an inert atmosphere and the structure (**13b**), confirming the assignment, is also shown in Scheme 2.



Scheme 2. Synthesis of expanded thiaporphyrin-like twins **12** and the low resolution X-ray crystal structure of reduced derivative **13b** (R' = Phenyl); there are two molecules in the unit cell with very similar conformations of which only one is shown here (see supporting information): inset, absorption spectrum of **12b** and the structure of side-product **14.**

The synthesis of porphyrin-like target structures **8** (X = N/NH) required 3,6-triphenylene bis(2-pyrrole) precursor **11**, most conveniently prepared by cross-coupling between N-Boc protected pyrrole-2-boronic acid[19] and triphenylene dibromide **9**. The intermediate Boc-protected bis-pyrrole could be easily stored but once deprotected it had a very limited shelf-life. In practice, therefore, the deprotected bispyrrole was used immediately.

Macrocycle formation was attempted through condensation with a variety of benzaldehydes using conditions optimized for porphyrin synthesis.[18] Intractable tars were generally produced and, although highly colored materials were obtained, the mixtures could not be effectively separated. High-dilution conditions were therefore again employed for optimization of the reaction. 4-Hexyloxyperfluorobenzaldehyde **15** was selected as the reaction partner, reasoning that ^{1}H NMR spectra of the products would be simplified in the key aromatic region, and its higher molecular weight and low volatility would allow easy control of the required 1:1 stoichiometry. Reproducible macrocyclization was achieved by slow addition (syringe pump) of a 1:1 mixture of dipyrrole **11** and benzaldehyde **15** to a dilute solution of $BF_3.OEt_2$ in dichloromethane. After a further 24 h, chloranil was added and the mixture neutralized (triethylamine). After evaporation, the residue was separated by column chromatography giving a dark purple solid. MALDI-MS gave results (including isotopic distribution) consistent with the expected macrocyclic product. ^{1}H NMR spectra gave well-resolved signals and indicated lower symmetry than expected for the expanded structure depicted in Figure 2. 2D NMR allowed full characterization of the structure, verifying the molecule's preferred lower-symmetry, strain free conformation with pyrroles facing in opposite directions with respect to the core. Crystals suitable for X-Ray diffraction were eventually grown from dichloromethane/methanol. The crystal structure shows a planar core with this same conformation in the solid state, and it is reasonable to presume that the aromatic thiophene analogue, **12**, adopts a similar strain-free arrangement.



Scheme 3. 2+2 Synthetic approach to expanded porphyrin twin **16a,** its crystal structure and absorption and fluorescence (inset) profiles in dichloromethane solvent; open analogues **17** and **18**.

The macrocyclic framework, although formally antiaromatic, maintains resemblance to porphyrin yet it shows an absorption profile that differs significantly from that of its cousins. Closer similarities can perhaps be drawn between structures like **16** and the important BODIPY/dipyrromethene chromophores.[20] The new macrocycle shows its most intense absorption band around 550 nm with a high absorptivity (*ca* 10^5 $M^{-1}cm^{-1}$), similar to typical BODIPY dyes. Unlike BODIPYs, however, macrocyclic derivative **16** shows weak fluorescence ($\phi < 0.05$) with a significant Stokes shift (120 nm) implying reorganization in the excited state. This fluorescence behavior parallels simple .0pyrromethenes. However, dipyrromethenes also generally show low stability in light/air; here the behavior of twin **16**, which displays good thermal and shelf stability, is distinctive. Open dipyrromethene **17** and BODIPY **18** analogues were synthesized to allow direct comparison. Open dipyrromethene **17** has similar λ_{max} (570 nm) to macrocyclic twin **16** and weak fluorescence ($\phi < 0.05$, Stokes shift 70 nm). Solutions degrade appreciably within hours under ambient light and exposed to air. Shelf-stable BODIPY analogue **18** also absorbs at *ca* 570 nm, but has a fluorescence quantum yield ϕ = 0.3. Macrocycles **16** are therefore best described as robust dipyrromethene twins. The molecule is planar and, although a formally antiaromatic π-system can be identified, the absorption spectra bare close resemblance to the open variants suggesting that conjugation effects are localized and there is little or no antiaromatic character. The ^{1}H NMR spectrum of twin **16** is significantly different from its open analogue **17**. β-Pyrrole protons for the open dipyrromethene **17** appear at 5.3 and 6.6 ppm. Significant downfield shifts are observed for the corresponding protons in twin **16**, with one signal observed at around 9 ppm. The shift could be explained by the protons' location inside an antiaromatic system but more likely results from the enforced co-planarity within the macrocyclic system.

The synthesis strategy is general and has been applied to yield further derivatives based on simplified benzaldehydes (**16b** Ar = 4-MeOPh-, **16c** Ar = 4-*n*-hexyloxyPh-, **16d** Ar = 4-tBuPh-). Similar absorption spectra are obtained but NMR evidence suggests aggregation at higher concentrations in some cases. All materials are stable beyond 300 ^oC.

In summary, two interesting new classes of macrocyclic chromophores are reported. The twinning strategy, through triphenylene 3,6-positions, provides a conjugation pathway but preserves the stability of the planar, conjugated conformations. The first macrocycles are formally aromatic in their fully conjugated, oxidized form, showing wide electronic absorption into the near IR region. Reversible reduction yields the colorless, non-conjugated macrocycles that give well-resolved NMR signals. The second class of new macrocyclic chromophore is directly related to porphyrins. In this case the expanded system is formally antiaromatic but the systems show their main absorption around 550 nm, leading to closer comparison to BODIPY/ dipyrromethene-type systems. Unlike BODIPYs, however, the new macrocycles are highly stable in the absence of boron complexation. The motif provides an intriguing chromophore framework where co-planarity of the triphenylene and dipyrromethene is enforced. The enforced conjugation and planarity has dramatic effect on the NMR chemical shifts for pyrrole β-protons, but conversely has almost no effect on their electronic absorption profiles which essentially mirror those of the open dipyrromethene analogues.

4. Experimental Section

Twin 13b (R' = Ph). 3,6,7,10-Tetrakis(hexyloxy)-2,11-bis(2-thiophenyl)triphenylene **10** (0.20 g, 0.25 mmol) and conc. H_2SO_4 (0.15 mL) were dissolved and stirred in a mixture of CH_2Cl_2 (5 mL) and glacial acetic acid (2.5 mL). A solution of benzaldehyde (0.027 g, 0.25 mmol) in CH_2Cl_2 (10 mL) was added in portions over 90 min. and the resulting blue solution was left to stir at room temperature for a further 2 h. Hydrazine (1 mL) was added and the colourless solution obtained was washed with water (2 × 50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic solvent was removed *in vacuo* and the residue purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 3:7) to give the title compound (0.040 g, 18%) as a colorless solid.

$C_{114}H_{136}O_8S_4$. Mp 252 °C; ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ 0.84-1.08 (m, 24 H), 1.26-1.70 (m, 48 H), 1.92-1.97 (m, 16 H), 4.22-4.26 (m, 16 H), 5.97 (s, 2 H), 7.07 (d, J = 3.7 Hz, 4 H), 7.28-7.40 (m, 6 H), 7.50-7.52 (m, 4 H), 7.59 (d, J = 3.7 Hz, 4 H), 7.75 (s, 4 H), 7.84 (s, 4 H), 8.76 (s, 4 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 14.0,15.0, 25.8, 26.9, 28.7, 28.8, 29.2 29.5, 30.6, 31.5, 31.6, 65.7, 67.8, 104.0, 107.4, 122.8, 123.3, 123.5, 124.2, 126.0, 126.4, 126.9, 128.4, 128.6, 128.7, 139.6, 144.3, 147.1, 149.6, 154.1; MS (MALDI-TOF): *m/z* 1762 (M^+, 100%).

Dibenzyl derivative 14 was also isolated from this reaction (0.15g, 6%). It melts into a columnar hexagonal mesophase at 98°C, and then to an isotropic liquid at 166 °C.

^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 0.94 (t, J = 7.2 Hz, 12 H), 1.38-1.45 (m, 16 H), 1.55-1.64 (m, 8 H), 1.91-2.01 (m, 8 H), 4.23-4.28 (m, 12 H), 6.85 (d, J = 3.7 Hz, 2 H), 7.23-7.27 (m, 2 H), 7.31-7.36 (m, 8 H), 7.54 (d, J = 3.7 Hz, 2 H), 7.77 (s, 2 H), 7.85 (s, 2 H), 8.71 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 13.95, 13.98, 22.50, 22.56, 25.8, 26.0, 29.20, 29.28, 31.58, 31.60, 36.2, 68.9, 69.6, 104.5, 107.5, 122.6, 123.0, 123.4, 124.3, 125.3, 125.8, 126.5, 128.6, 128.76, 128.81, 138.4, 140.5, 144.3, 149.7, 154.1. HRMS (APCI ion trap): Calcd. For [$C_{64}H_{77}O_4S_2$]: 973.5251. Found: 973.5258.

Twin 13c (R' = 4-*t*-butylphenyl). Prepared as above using 4-t-butylbenzaldehyde (0.041 g, 0.25 mmol) to give the title compound (0.052 g, 22%) as a colorless solid.

$C_{122}H_{152}O_8S_4$. Mp 168 °C; ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ 0.74-1.08 (m, 24 H), 1.26 (s, 18 H), 1.29-1.48 (m, 48 H), 1.90-1.99 (m, 16 H), 4.22-4.27 (m, 16 H), 5.93 (s, 2 H), 7.06 (d, *J* = 3.7 Hz, 4 H), 7.37-7.45 (m, 8 H), 7.59 (d, *J* = 3.7 Hz, 4 H), 7.78 (s, 4 H), 7.86 (s, 4 H), 8.77 (s, 4 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 13.8, 13.9, 22.4, 22.5, 25.7, 25.9, 29.6, 29.9, 31.3, 31.6, 31.8, 37.3, 68.7, 69.6, 104.4, 107.7, 123.0, 123.6, 124.4, 125.4, 126.2, 12.4, 128.1, 128.3, 128.9, 139.3, 141.0, 147.6, 149.7, 154.3; MS (MALDI-TOF): *m/z* 1874 (M^+, 100%).

Methylene-bridged twin 13a. 3,6,7,10-Tetrakis(hexyloxy)-2,11-(2-thiophene)triphenylene **10** (0.20 g, 0.25 mmol) and dimethoxymethane (0.19 g, 0.25 mmol) were dissolved in dry, degassed CH_2Cl_2 (25 mL). The solution was added at a rate of 2.0 mL / h *via* syringe pump to a stirred solution of dry, degassed CH_2Cl_2 (100 mL) containing $BF_3.OEt_2$ (0.10 mL, 1M) in an atmosphere of argon at room temperature. The mixture was then left to stir for a further 24 h, after which hydrazine (1 mL) was added. The solvents were removed to give a brown residue. The crude product was purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 1:4 and gradually increasing to 1:1) to give the title compound (0.032 g, 16%) as a colorless solid.

$C_{102}H_{128}O_8S_4$. Mp 212 °C; ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ 0.83-0.99 (m, 24 H), 1.26-1.59 (m, 48 H), 1.92-1.99 (m, 16 H), 4.22-4.28 (m, 16 H), 4.51 (s, 4 H), 7.10 (d, *J* = 3.6 Hz, 4 H), 7.58 (d, *J* = 3.6 Hz, 4 H), 7.77 (s, 4 H), 7.85 (s, 4 H), 8.71 (s, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.0, 14.1, 22.6, 22.7, 25.9, 26.0, 29.3, 29.4, 31.7, 31.8, 68.9, 69.7, 104.3, 107.5, 122.5, 122.9, 123.3, 124.3, 125.4, 125.7, 128.6, 138.4, 143.2, 149.5, 153.9; MS (MALDI-TOF): *m/z* 1609 (M^+, 100%).

1-(Diethoxymethyl)-2,3,4,5,6-pentafluorobenzene. 2,3,4,5,6-Pentafluorobenzaldehyde (10.0 g, 0.05 mol), triethyl orthoformate (9.80 g, 0.066 mol) and conc. HCl (0.15 mL) were dissolved in EtOH (30 mL) and the solution was stirred under reflux for 1 h. The mixture was cooled and solid K_2CO_3 (3.0 g, 0.02 mol) was slowly added. The solid residue was then removed by filtration and the filtrate concentrated *in vacuo* to give the title compound as a colorless oil (9.80 g, 71%) that was used without further purification.

^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.26 (t, J = 6.9 Hz, 6 H), 3.54-3.62 (m, 2 H), 3.74-3.82 (m, 2 H), 5.71 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 14.7, 63.5, 96.4, 112.3, 135.8, 139.3, 143.1, 146.5; MS (ES): *m/z* 288.2 ($[M+NH4]^+$, 100%); HRMS (APCI-ion trap): Calcd. For $[C_{11}H_{14}F_5NO_2]^+$: 288.1017. Found: 288.1016.

2,3,5,6-Tetrafluoro-4-hydroxybenzaldehyde. 1-(Diethoxymethyl)-2,3,4,5,6-pentafluorobenzene (9.80 g, 0.036 mol) and powdered KOH (8.13 g, 0.145 mol) were stirred in refluxing *t*-butanol (100 mL) for 6 h. The solution was cooled, H_2O (100 mL) added and the mixture extracted with EtOAc (3×100 mL). The organic phase was discarded and the aqueous layer obtained made acidic using aqueous HCl (2 M). The mixture was then extracted with EtOAc (3×100 mL) and the organic phase obtained dried ($MgSO_4$). The organic solvent was removed *in vacuo* to give the title compound as a white solid (4.75 g, 67%).

Mp 141 °C; ^{1}H NMR (CD_3OD, 400 MHz): δ 10.22 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 91.5, 98.7, 136.1, 139.5, 143.2, 146.5, 182.3; MS (ES): *m/z* 192.7 ($[M-H]^-$, 100%); HRMS (APCI-ion trap): Calcd. For $[C_7HF_4O_2]^-$: 192.9918. Found: 192.9919.

2,3,5,6-Tetrafluoro-4-hexyloxybenzaldehyde 15. 2,3,5,6-Tetrafluoro-4-hydroxybenzaldehyde (2.0 g, 0.01 mol), 1-bromohexane (3.40 g, 0.02 mol) and anhydrous K_2CO_3 (2.84 g, 0.02 mol) were heated in refluxing acetone (50 mL) under nitrogen for 24 h. The solution was cooled, the solid residue filtered off and the filtrate concentrated *in vacuo*. The crude compound was then dissolved in chloroform (20 mL) followed by addition of trifluoroaceic acid (2 mL) and water (2 mL) and the mixture stirred under reflux for 2 h. The mixture was then extracted with CH_2Cl_2 (3×100 mL). The solvent was removed *in vacuo* and the residue purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 3:7) to give the title compound (1.20 g, 42%) as a colorless oil.

^{1}H NMR ($CDCl_3$/TMS, 300 MHz): δ 0.91 (t, J = 6.9 Hz, 3 H), 1.30-1.55 (m, 6 H), 1.75-1.81 (m, 2 H), 4.41 (t, J = 6.4 Hz, 2 H), 10.23 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 13.7, 22.3, 24.9, 31.1, 75.4, 108.8, 138.5, 142.0, 143.2, 144.0, 149.6, 182.2; MS (ES): *m/z* 296.1 ($[M+NH_4]^+$, 100%); HRMS (APCI-ion trap): Calcd. For $[C_{13}H_{14}F_4O_2.NH_4]^+$: 296.1268. Found: 296.1261.

3,6,7,10-Tetrakis(hexyloxy)-2,11-bis[2-(N-Boc-pyrrolyl)]triphenylene. N-Boc-pyrrole-2-boronic acid (5.36 g, 0.025 mol), 2,11-dibromo-3,6,7,10-tetrakis (hexyloxy)triphenylene **9** (2.0 g, 2.50 mmol), Na_2CO_3 (2.69 g, 0.025 mol), PPh_3 (0.21 g, 0.81 mmol) and $PdCl_2$ (0.036 g, 0.20 mmol) were stirred in a refluxing mixture of toluene, EtOH and H_2O (3:3:1 respectively, 50 mL) under nitrogen for 48 h. Water was added and the mixture extracted with CH_2Cl_2 (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown oil which was purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 2:3) to give the title compound (1.50 g, 61%) as a colorless solid.

Mp 134 °C; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 0.88-0.98 (m, 12 H), 1.26-1.66 (m, 42 H), 1.73-1.81 (m, 4 H), 1.94-2.02 (m, 4 H), 4.11 (t, J = 6.5 Hz, 4 H), 4.28 (t, J = 6.6 Hz, 4 H), 6.27-6.29 (m, 4 H), 7.42 (dd, J = 2.7, 2.8 Hz, 2 H), 7.78 (s, 2 H), 7.95 (s, 2 H), 8.46 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 13.9, 14.0, 22.4, 22.5, 25.5, 25.7, 29.1, 29.3, 31.4, 31.5, 68.6, 69.6, 82.8, 103.8, 107.7, 110.3, 114.3, 122.1, 123.0, 124.6, 124.7, 124.9, 129.3, 131.4, 149.6, 149.7, 156.0; MS (ES): *m/z* 976.6 $[(M+NH_4)]^+$, 100%); HRMS (p-NSI-ion trap): Calcd for $C_{60}H_{82}N_2O_8.NH_4$: 976.6409. Found: 976.6401.

3,6,7,10-Tetrakis(hexyloxy)-2,11-bis(2-pyrrolyl)triphenylene 11. 3,6,7,10-Tetrakis(hexyloxy)-2,11-bis[2-(N-Boc-pyrrolyl)]triphenylene (1.20 g, 1.25 mmol) was heated (as a neat solid) at 200 °C under reduced pressure (1mm Hg) for 2 h. The residue obtained was cooled and purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 2:3) to give the pure title compound (0.58 g, 73%) as a white solid that was used immediately in subsequent reactions.

The material forms a columnar hexagonal phase between 82-221 °C; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 0.93-0.98 (m, 12 H), 1.37-1.66 (m, 24 H), 1.92-2.07 (m, 8 H), 4.24 (t, J = 6.5 Hz, 4 H), 4.33 (t, J = 6.6 Hz, 4 H), 6.41 (d, J = 3.2 Hz, 2 H), 6.91-6.97 (m, 4 H), 7.78 (s, 2 H), 7.82 (s, 2 H), 8.82 (s, 2 H), 10.00 (br, 2 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 13.9, 14.0, 22.5, 22.6, 25.7, 25.9, 29.4, 31.5, 31.6, 68.7, 69.6, 104.7, 106.5, 107.4, 109.1, 118.0, 120.6, 120.7, 123.4, 124.2, 127.7, 130.3, 149.5, 153.6; UV-Vis: (CH_2Cl_2) λ_{max} (log ε) 275 (4.56), 317 (4.68), 357 (4.52) nm; Fluor: (CH_2Cl_2) λ_{max} (λ_{exc}) 412 (314) nm; MS (ES): *m/z* 759.5 (M^+, 100%); HRMS (p-NSI-ion trap): Calcd for $C_{50}H_{66}N_2O_4$: 759.5088. Found: 759.5095.

Porphyrin-like Twin 16a (Ar = 2,3,5,6-tetrafluoro-4-hexyloxyphenyl-). 3,6,7,10-Tetrakis(hexyloxy)-2,11-bis(2-pyrrolyl)triphenylene **11** (0.30 g, 0.39 mmol), 2,3,5,6-tetrafluoro-4-hexyloxybenzaldehyde **10** (0.109 g, 0.39 mmol) were dissolved in dry, degassed CH_2Cl_2 (25 mL). The solution was added at a rate of 2.0 mL / h *via* syringe pump to a stirred solution of dry, degassed CH_2Cl_2 (100 mL) containing $BF_3.OEt_2$ (0.10 mL, 1M) in an atmosphere of argon at room temperature. The mixture was then left to stir for a further 24 h, after which chloranil (0.19 g, 0.79 mmol) was added and stirring continued for a further 2 h. The mixture was neutralised with a few drops of triethylamine and the solvents removed to give a dark purple residue. The crude product was purified by column chromatography using silca gel pretreated with triethylamine (eluting with THF / petroleum ether, 1:4 and gradually increasing to 1:1) to give the pure title compound (0.064 g, 16%) as a dark purple solid.

Mp >300 °C; Anal: Calcd. For $C_{126}H_{152}F_8N_4O_{10}$: C, 74.38; H, 7.53; N, 2.75. Found: C, 74.28; H, 7.39; N, 2.84; ^{1}H NMR (CD_2Cl_2/TMS, 400 MHz): δ 0.85-0.98 (m, 30 H), 1.10-1.54 (m, 60 H), 1.74-1.96 (m, 20 H), 4.05-4.19 (m, 16 H), 4.37 (t, J = 6.3 Hz, 4 H), 6.62 (d, J = 4.4 Hz, 2 H), 7.48 (d, J = 4.5 Hz, 2 H), 7.62-7.70 (m, 10 H), 9.00-9.02 (m, 2 H), 9.26 (s, 2 H), 9.96 (s, 2 H, pyrrole NH, disappears with D_2O), 10.15 (s, 2 H); UV-Vis: (CH_2Cl_2) λ_{max} (log ε) 548 (5.13) nm; Fluor: (CH_2Cl_2) λ_{max} (λ_{exc}) 674 (545) nm; MS (MALDI-TOF): *m/z* 2035 cluster, M^++2, 100%).

Porphyrin-like Twin 16b (Ar = 4-methoxyphenyl-). Prepared as above using *p*-anisaldehyde to give the title compound (0.031 g, 18%) as a dark purple solid.

Mp >300 °C; Anal: Calcd. For $C_{116}H_{140}N_4O_{10}$: C, 79.59; H, 8.06; N, 3.20. Found: C, 79.45; H, 7.86; N, 3.24; ^{1}H NMR (CD_2Cl_2/TMS, 400 MHz): δ 0.75-1.12 (m, 24 H), 1.14-1.47 (m, 48 H), 1.80-1.85 (m, 16 H), 3.80 (s, 6 H), 3.84-4.92 (m, 16 H), 6.52 (m, 2 H), 6.92 (d, J = 8.4 Hz, 4 H), 7.23-7.41 (m, 14 H), 7.62 (s, 2 H), 8.85 (s, 2 H), 8.91 (s, 2 H), 9.19 (s, 4 H); UV-Vis: (CH_2Cl_2) λ_{max} (log ε) 536 (5.02) nm; Fluor: (CH_2Cl_2) λ_{max} (λ_{exc}) 653 (536) nm; MS (MALDI-TOF): *m/z* 1751 (cluster, M^++2, 100%).

Porphyrin-like Twin 16c (Ar = 4-hexyloxyphenyl-). Prepared as above using 4-hexyloxybenzaldehyde to give the title compound (0.026 g, 17%) as a dark purple solid.

$C_{126}H_{160}N_4O_{10}$. Mp >300 °C; ^{1}H NMR (CD_2Cl_2/TMS, 400 MHz): δ 0.89-1.02 (m, 30 H), 1.20-1.58 (m, 60 H), 1.77-1.95 (m, 20 H), 3.97-3.99 (m, 16 H), 4.14 (t, J = 6.2 Hz, 4 H), 6.64 (br-d, J = 4.3 Hz, 2 H), 6.99 (d, J = 8.4 Hz, 4 H), 7.32-7.50 (m, 14 H), 7.72 (br-s, 2 H), 8.95 (br-s, 2 H), 9.01 (br-s, 2 H), 10.04 (br-s, 2 H); UV-Vis: (CH_2Cl_2) λ_{max} (log ε) 536 (5.08) nm; Fluor: (CH_2Cl_2) λ_{max} (λ_{exc}) 653 (533) nm; MS (MALDI-TOF): *m/z* 1892 (cluster, M^++2, 100%).

Porphyrin-like Twin 16d (Ar = 4-t-butylphenyl-). Prepared as above using 4-*t*-butylbenzaldehyde to give the title compound (0.018 g, 15%) as a dark purple solid.

$C_{122}H_{152}N_4O_8$. Mp >300 °C; ^{1}H NMR (CD_2Cl_2/TMS, 400 MHz): δ 0.87-0.99 (m, 24 H), 1.22-1.56 (m, 66 H), 1.90-2.13 (m, 16 H), 4.16-4.21 (m, 16 H), 6.76 (d, J = 4.6 Hz, 2 H), 7.47 (d, J = 4.6 Hz, 2 H), 7.52-7.69 (m, 16 H), 7.82 (br-s, 2 H), 9.07 (br-s, 2 H), 9.32 (br-s, 2 H), 10.19 (br-s, 2 H) , 10.23 (br-s, 2 H); UV-Vis: (CH_2Cl_2) λ_{max} (log ε) 537 (5.14) nm; Fluor: (CH_2Cl_2) λ_{max} (λ_{exc}) 653 (533) nm; MS (MALDI-TOF): *m/z* 1804 (cluster, M^++2, 100%).

3,6,7,10-Tetrakis(hexyloxy)-11-bromo-2-[2-(N-BOC-pyrrolyl)triphenylene. N-BOC-pyrrole-2-boronic acid (1.10 g, 4.98 mmol), 2,11-dibromo-3,6,7,10-tetrakis (hexyloxy)triphenylene **9** (2.61 g, 3.32 mmol), CsF (0.75 g, 4.98 mmol), PPh_3 (0.139 g, 0.53 mmol) and $PdCl_2$ (0.023 g, 0.13 mmol) were stirred in a refluxing mixture of toluene, EtOH and H_2O (3:3:1 50 mL) under nitrogen for 24 h. Water was added and the mixture extracted with CH_2Cl_2 (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown oil which was purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 3:7) to give the pure title compound (1.15 g, 40%) as a white solid.

Mp 69 °C; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 0.76-0.88 (m, 12 H), 1.14-1.70 (m, 33 H), 1.86-1.90 (m, 8 H), 4.01-4.20 (m, 8 H), 6.21-6.24 (m, 2 H), 7.34-7.36 (m, 1 H), 7.66 (s, 1 H), 7.72 (s, 1 H), 7.80 (s, 1 H), 7.83 (s, 1 H), 8.28 (s, 1 H), 8.63 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 13.8, 13.9, 22.4, 22.5, 25.5, 25.6, 25.7, 27.5, 29.0, 29.1, 29.3, 31.3, 31.4, 31.5, 68.5, 69.5, 69.6, 103.7, 105.8, 107.4, 107.7, 110.3, 112.7, 114.4, 121.8, 122.2, 124.0, 124.5, 124.7, 125.2, 128.0, 129.0, 129.6, 131.3, 149.5, 149.8, 149.9, 153.8, 156.4; MS (ES): *m/z* 872.4 [$(M+H)]^+$, 100%); HRMS (p-NSI-ion trap): Calcd for $C_{51}H_{71}BrNO_6$: 872.4459. Found: 872.4461.

3,6,7,10-Tetrakis(hexyloxy) -2-bromo-11-(2-pyrrolyl)triphenylene. 3,6,7,10-Tetrakis(hexyloxy)-11-bromo-2-[2-(N-BOC-pyrrolyl)triphenylene (0.12 g, 0.14 mmol) was heated (as neat solid) at 200 °C under reduced pressure (1mm Hg) for 2 h. The residue obtained was cooled and purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 3:7) to give the pure title compound (0.102 g, 96%) as a white solid.

Mesophase behavior I 195 °C Col_h < RT ; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 0.95-0.98 (m, 12 H), 1.41-1.61 (m, 24 H), 1.92-2.05 (m, 8 H), 4.23-4.34 (m, 8 H), 6.39-6.41 (m, 1 H), 6.92-6.95 (m, 2 H), 7.74 (s, 1 H), 7.77 (s, 1 H), 7.80-7.82 (m, 2 H), 8.64 (s, 1 H), 8.68 (s, 1 H), 9.98 (br, 1 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 13.8, 13.9, 22.4, 22.5, 25.6, 25.7, 25.9, 29.1, 29.3, 31.5, 31.6, 68.7, 69.3, 69.5, 104.6, 10.5, 106.7, 107.1, 107.3, 109.1, 112.4, 118.0, 120.4, 120.8, 122.4, 123.6, 124.1, 124.3, 127.5, 127.6, 129.1, 130.0, 149.5, 149.8, 153.7; MS (ES): *m/z* 772.1 [$(M+H)^+$, 100%); HRMS (p-NSI-ion trap):: Calcd for $C_{46}H_{63}BrNO_4$: 772.3935. Found: 772.3930.

Dipyrromethene 17 and BODIPY 18. 3,6,7,10-Tetrakis(hexyloxy)-2-bromo-11-(2-pyrrolyl)triphenylene (0.10 g, 0.13 mmol), 4-*t*-butylbenzaldehyde (0.010 g, 0.065 mmol) and trifluoroacetic acid (1.0 mmol) were dissolved in CH_2Cl_2 (25 mL) and the solution stirred for 1 h in an atmosphere of argon at room temperature. *p*-Chloranil (0.031 g, 0.13 mmol) was added and stirring continued for a further 5 min. The mixture was neutralised with a triethylamine followed by the addition of an excess of $BF_3.OEt_2$ and then left to stir overnight. Water was added and the mixture extracted with CH_2Cl_2 (3×100 mL). The solvent was removed *in vacuo* to leave a blue solid which was purified by column chromatography (eluting with CH_2Cl_2 / petroleum ether, 3:7 and gradually increasing to 2:3, respectively) to give the two fractions as follows:

Fraction 1: BODIPY 18 (0.068g, 60%). $C_{103}H_{133}BBr_2F_2N_2O_8$. Mp 192 °C; ^{1}H NMR ($CD_2Cl_2$/TMS, 400 MHz): δ 0.75-0.85 (m, 24 H), 1.05-1.46 (m, 57 H), 1.73-1.83 (m, 16 H), 4.06-4.15 (m, 16 H), 6.69 (d, J = 4.2 Hz, 2 H), 6.97 (d, J = 4.2 Hz, 2 H), 7.58-7.60 (m, 6 H), 7.68 (s, 2 H), 7.69 (s, 2 H), 7.73 (s, 2 H), 8.46 (s, 2 H), 8.59 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 22.5, 22.6, 25.7, 25.8, 31.5, 31.6, 69.3, 69.4, 69.5, 105.1, 105.6, 107.2, 107.5, 112.8, 121.6, 122.4, 124.2, 124.3, 124.7, 125.4, 128.5, 128.8, 130.7, 149.6, 149.7, 153.4, 153.6, 155.5, 156.1; UV-Vis: (CH_2Cl_2) λ_{max} (log ε) 569 (4.40) nm; Fluor: (CH_2Cl_2) λ_{max} (λ_{exc}) 653 (569) nm; MS (MALDI-TOF): *m/z* 1736 (cluster, M^++2, 100%).

Fraction 2: (17) (0.012 g, 11%). $C_{103}H_{134}Br_2N_2O_8$. Mp 180 °C; ^{1}H NMR (CD_2Cl_2/TMS, 400 MHz): δ 0.78-0.96 (m, 24 H), 1.16-1.48 (m, 57 H), 1.53-1.61 (m, 8 H), 1.73-1.95 (m, 8 H), 3.98 (t, J = 6.3 Hz, 4 H), 4.11 (t, J = 6.3 Hz, 4 H), 4.17 (t, J = 6.5 Hz, 4 H), 4.23 (t, J = 6.5 Hz, 4 H), 5.30 (d, J = 4.2 Hz, 2 H), 6.83 (d, J = 4.2 Hz, 2 H), 7.54-7.61 (m, 6 H), 7.72 (s, 2 H), 7.75 (s, 2 H), 7.79 (s, 2 H), 8.43 (s, 2 H), 9.01 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.7, 13.8, 13.9, 22.4, 22.5, 22.6, 25.5, 25.6, 25.7, 25.8, 29.0, 29.2, 29.3, 31.3 31.4, 31.5, 31.6, 69.1, 69.4, 69.6, 105.4, 107.2, 107.5, 112.8, 118.9, 122.4, 122.5, 123.7, 124.2, 124.3, 124.6, 128.0, 128.8, 130.5, 131.1, 134.9, 139.6, 141.4, 149.8, 151.9, 153.7, 155.9; UV-Vis: (CH_2Cl_2) λ_{max} (log ε) 570 (4.48) nm; Fluor: (CH_2Cl_2) λ_{max} (λ_{exc}) 639 (570) nm; MS (MALDI-TOF): *m/z* 1690 (cluster, M^++2, 100%).

Acknowledgment

Support from The Leverhulme Foundation (HG), EPSRC (IC and the National Crystallography and Mass Spectrometry Services) and the China Scholarship Council (XK) are gratefully acknowledged.

Supporting Information: Characterization spectra for new compounds; X-ray crystal structures. This information is available free of charge via the internet at http://pubs.acs.org/.

References

(1) (a) Kadish, K. M., Smith, K. M., Guilard, R. Eds, *The Porphyrin Handbook*; Academic Press: 2000-2003; Vols. 1-20. (b) Kadish, K. M., Smith, K. M., Guilard, R. Eds, *Handbook of Porphyrin Science*; World Scientific Publishing: 2010-2012; Vols. 1-20.

(2) Sessler, J. L., Weghorn, S. J. Eds, *Expanded, Contracted and Isomeric Porphyrins*, Pergamon, Oxford, 1997.

(3) Kuzuhara, D.; Sakakibara, Y.; Mori, S.; Okujima, T.; Uno, H.; Yamada, H. *Angew. Chem. Int. Ed.* **2013**, *52*, 3360.

(4) Brothers, P. J. *Inorg. Chem*. **2011**, *50*, 12374.

(5) Misra, R.; Chandrasekhar, T. K. *Acc. Chem. Res.* **2008**, *41*, 265-279.

(6) (a) Takeuchi, Y.; Matsuda, A.; Kobayashi, N. *J. Am. Chem. Soc.* **2007**, *129*, 8271. (b) Shimizu, S.; Miura, A.; Nyokong, T.; Kobayashi, N. *J. Am. Chem. Soc.* **2011**, *133*, 17322. (c) Guilleme, J.; Gonzalez-Rodriguez, D.; Torres, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 3506

(7) Matsushita, O.; Derkacheva, V. M.; Muranaka, A.; Shimizu, S.; Uchiyama, M.; Luk'yanets, E. A.; Kobayashi, N. *J. Am. Chem. Soc.* **2012**, *134*, 3411 (and references therein).

(8) Cammidge, A. N.; Chambrier, I.; Cook, M. J.; Hughes, D. L.; Rahman, M.; Sosa-Vargas, L. *Chem. Eur. J.* **2011**, *17*, 3136.

(9) Roznyatovskiy, V. V.; Lee, C-H.; Sessler, J. L. *Chem. Soc. Rev.* **2013**, *42*, 1921.

(10) (a) Saito, S.; Osuka, A. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 4342. (b) Mori, H.; Sung, Y. M.; Lee, B. S.; Kim, D.; Osuka, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 12259. (c) Chmielewski, P. J. *Angew. Chem. Int. Ed.* **2010**, *49*, 1359.

(11) Chang, Y.; Chen, H.; Zhou, Z.; Zhang, Y.; Schütt, C.; Herges, R.; Shen, Z. *Angew. Chem. Int. Ed.* **2012**, *51*, 12800.

(12) Ishida, M.; Kim, S. –J.; Preihs, C.; Ohkubo, K.; Lim, J. M.; Lee, B. S.; Park, J. S.; Lynch, V. M.; Roznyatovskiy, V. V.; Sharma, T.; Pada, P. K.; Lee, C. -H.; Fukuzumi, S.; Kim, D.; Sessler, J. L. *Nat. Chem.* **2013**, *5*, 15

(13) (a) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902. (b) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hagele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem*., Int. Ed. **2007**, *46*, 4832.

(14) Cammidge A. N.; Chausson C.; Gopee H.; Li J.; Hughes D. L. *Chem. Commun.* **2009**, 7375.

(15) (a) Zhang, L.; Gopee, H.; Hughes, D. L.; Cammidge, A. N. *Chem. Commun.* **2010**, 4255. (b) Zhang, L.; Hughes, D. L.; Cammidge, A. N. *J. Org. Chem.* **2012**, 77, 4288.

(16) Cammidge A. N.; Gopee H. *J. Mater. Chem*. **2001**, *11*, 2773.

(17) Brückner, C.; Posakony, J. J.; Johnson, C. K.; Boyle, R. W.; James, B. R.; Dolphin, D. *J. Porphyrins Phthalocyanines*, **1998**, *2*, 455.

(18) Lindsey, J. S. *Acc. Chem. Res*. 2010, 43, 300.

(19) Martina, S.; Enkelmann, V.; Wegner, G.; Schlüter, A-D. *Synthesis*, **1991**, 613.

(20) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**.*107*, 4891.

SYNOPSIS TOC