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Expanded Porphyrin-like Structures Based on Twinned Triphenylenes

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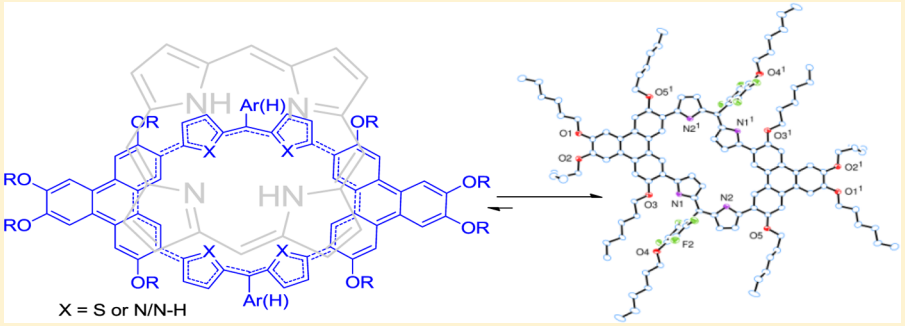
Supporting Information



ABSTRACT: Triphenylene twins are intriguing structures, and those bridged through their 3,6-positions by dipyrromethene units give a new class of macrocycles that can be viewed as rigid, expanded porphyrin derivatives in which coplanarity 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 to electronic engineering, with corresponding applications from medicine to ubiquitous consumer devices.[1] Synthetic breakthroughs have advanced the scope of the 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 hexaphyrins (**2**) but including octaphyrins 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]

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 symmetrically 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 applied our synthetic refinements to open the

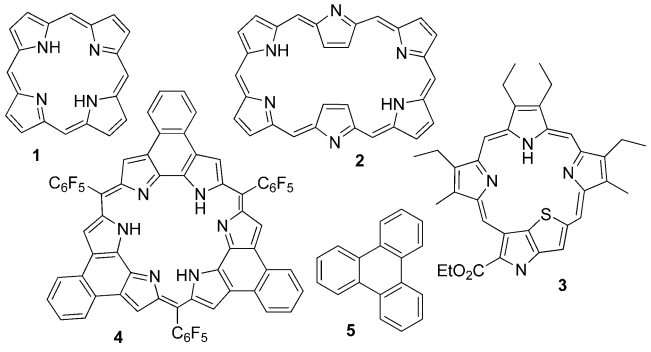


Figure 1. Structures of the parent porphyrin (**1**) and triphenylene (**5**) plus examples of more exotic porphyrinoids (**2**−**4**).

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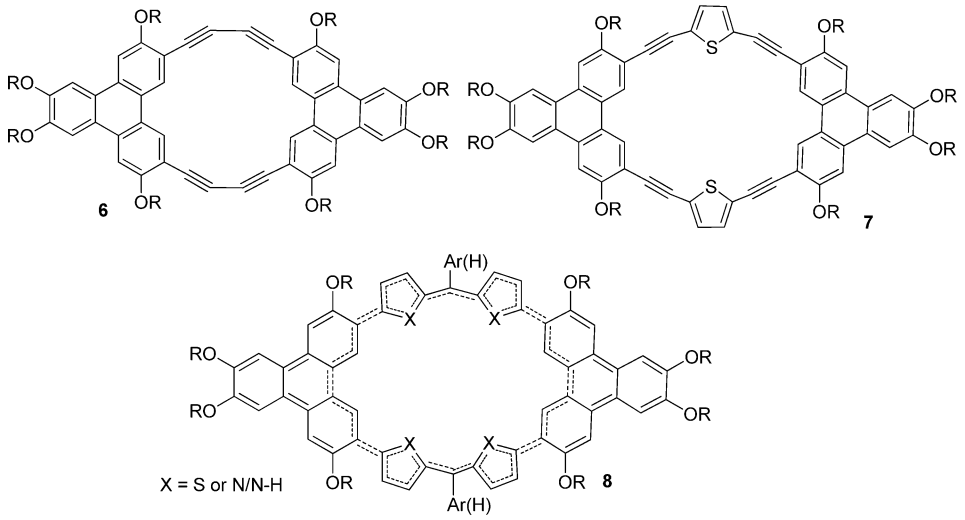


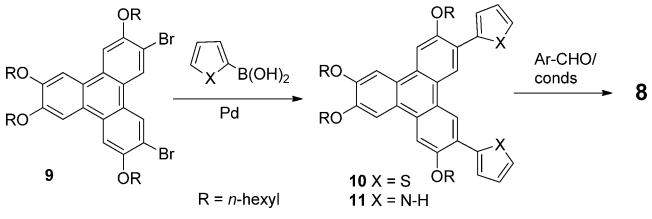
Figure 2. Rigid, nematic twins **6** and **7** and the target twinned triphenylenes **8** that have an expanded porphyrin-like core.

way to twinned macrocyclic structures linked through the triphenylene 3,6-positions. With this approach, strained and formally antiaromatic systems can be produced, as linking through the triphenylene 3,6-sites allows completion of conjugation pathways as 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 center of the molecule, such as in twins **6** and **7** (Figure 2). Columnar organization would lead to a void region through the column center, and columnar mesophase formation is therefore suppressed. Self-organization into the rare discotic nematic mesophase is then observed.[15]

The structural motif therefore appears to be both useful and versatile, and we recognized that interesting molecular variants could be envisaged through a 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 bisthiophene and bispyrrole derivatives **10** and **11**, respectively, 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 the preparation of 5,15-substituted porphyrins.[17,18]

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 concentrated sulfuric acid in portions over 90 min to a solution of **10** in dichloromethane/glacial acetic acid (Scheme 2). 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 °C in toluene). EPR spectroscopy showed no free radicals, and strong aggregation appeared to be the likely cause. The visible spectra (Scheme 2) were also broad, extending into the near-IR region (>800 nm), indicating that the neutral aromatic structure represented by **12** is the most accurate, although this is unlikely to be the observed conformation (see later). Simple TLC analysis in nonpolar solvents revealed the blue product to be in slow equilibrium with a colorless, nonpolar material that returned to blue in air over time. 2D TLC showed reversibility between the two components. The equilibrium is a redox process that 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 gave instant bleaching and the appearance of strong, well-resolved signals, leading to the full characterization of these compounds as the expected nonconjugated twins **13**. Crystals suitable for X-ray diffraction were grown for one example under an inert atmosphere, and the structure of **13b**, confirming the assignment, is also shown in Scheme 2.

Scheme 1. 2 + 2 Approach to Expanded Porphyrin Twins 8



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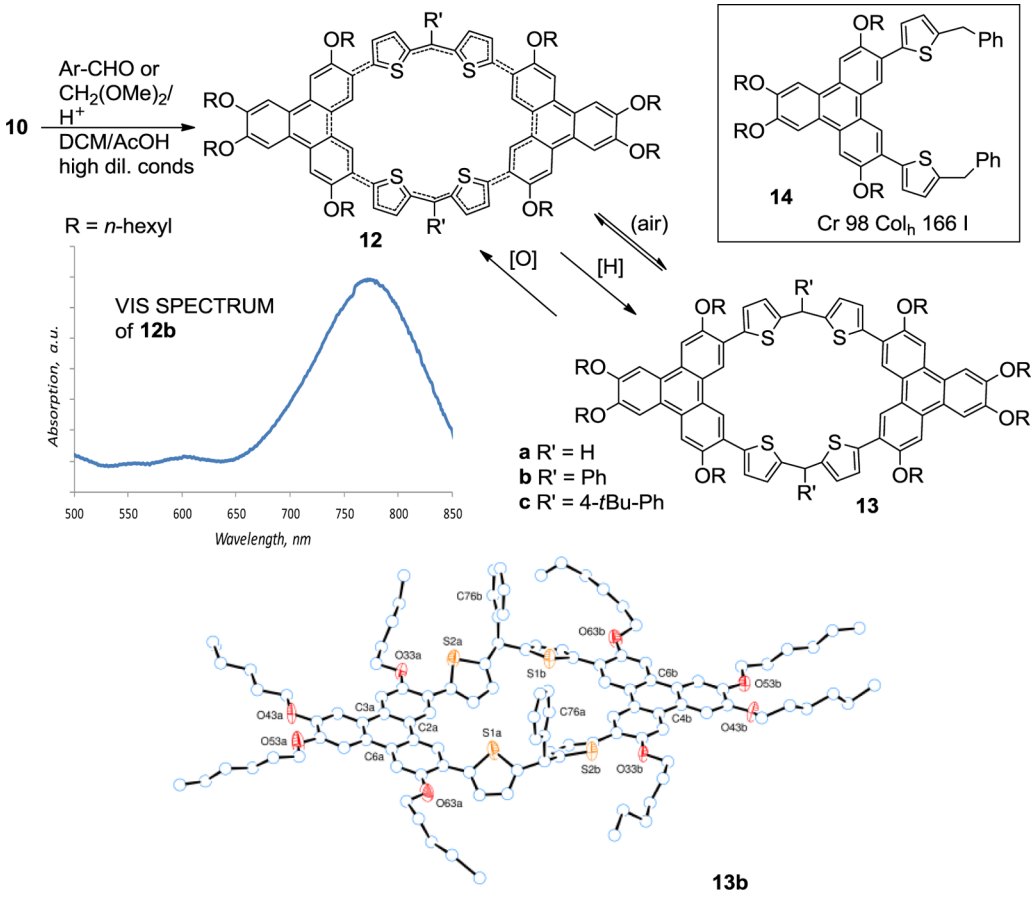
Scheme 2. Synthesis of Expanded Thiaporphyrin-like Twins 12 and the Low-Resolution X-ray Crystal Structure of Reduced Derivative 13b (R′ = Phenyl);[a] The Insets Show the Absorption Spectrum of 12b and the Structure of Side Product 14



[a]In the crystal structure of **13b** there are two molecules in the unit cell with very similar conformations, of which only one is shown here (see the Supporting Information).

The synthesis of porphyrin-like target structures **8** (X = N/NH) required 3,6-triphenylene bis(2-pyrrole) precursor **11**, which was most conveniently prepared by cross-coupling between *N*-Boc-protected pyrrole-2-boronic acid[19] and triphenylene dibromide **9**. The intermediate Boc-protected bispyrrole 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, as we reasoned that the ^{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 $BF_3{\cdot}OEt_2$ in dichloromethane (Scheme 3). After a further 24 h, chloranil was added, and the mixture was neutralized (triethylamine). After evaporation, the residue was separated by column chromatography, giving a dark-purple solid. MALDI-MS gave results (including an isotopic distribution) consistent with the expected macrocyclic product **16a**. ^{1}H NMR spectra exhibited well-resolved signals and indicated lower symmetry than expected for the expanded structure depicted in Figure 2. 2D NMR analysis 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 showed 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.

The macrocyclic framework, although formally antiaromatic, maintains a resemblance to porphyrin yet 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 at 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 (ϕ < 0.05) with a significant Stokes shift (120 nm), implying reorganization in the excited state. This fluorescence behavior parallels that of simple dipyrromethenes. However, dipyrromethenes also generally show low stability in light/air; here the behavior of twin **16**, which displays good thermal and shelf stability, is

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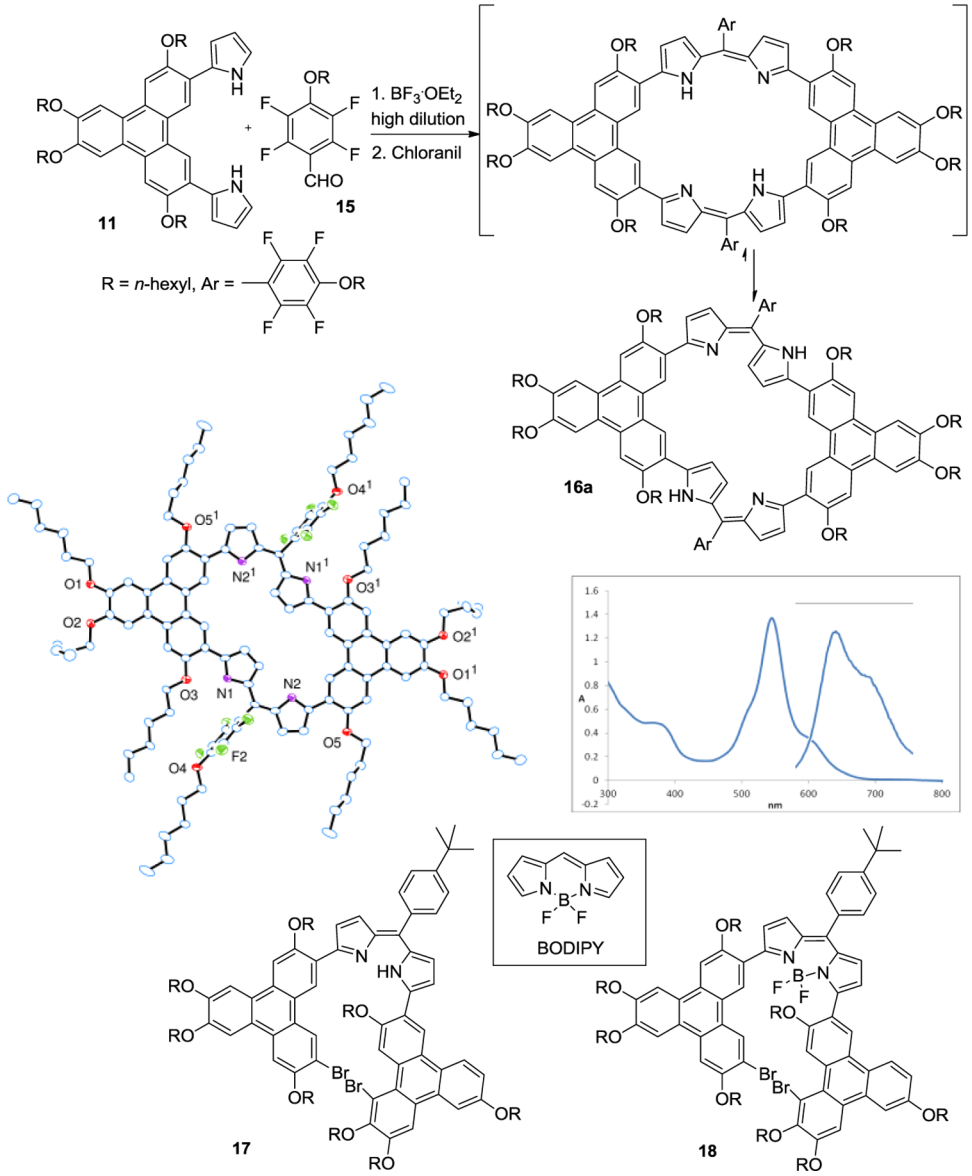
Scheme 3. The 2 + 2 Synthetic Approach to Expanded Porphyrin Twin 16a, Its Crystal Structure and Absorption and (Inset) Fluorescence Profiles in Dichloromethane Solvent, and the Open Analogues 17 and 18



distinctive. The open dipyrromethene and BODIPY analogues **17** and **18**, respectively, were synthesized to allow direct comparison. Open dipyrromethene **17** has a similar λ_{max} (570 nm) as macrocyclic twin **16** and weak fluorescence (ϕ < 0.05, Stokes shift = 70 nm). Solutions degraded appreciably within hours under ambient light and upon exposure to air. Shelf-stable BODIPY analogue **18** also absorbs at ca. 570 nm but has a fluorescence quantum yield of 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 bear a close resemblance to those of the open variants, suggesting that the 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 were 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 coplanarity 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*-hexyloxy-Ph; **16d**, Ar = 4-tBuPh). Similar absorption spectra were obtained, but the NMR evidence suggested aggregation at higher concentrations in some cases. All of these materials are stable beyond 300 °C.

In summary, two interesting new classes of macrocyclic chromophores are reported. The twinning strategy involving links through the 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 colorless nonconjugated macrocycles that give well-resolved NMR signals. The second class of new macrocyclic chromophores is directly related to porphyrins. In this case, the expanded system is formally antiaromatic but the

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systems show their main absorption at 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 coplanarity of the triphenylene and dipyrromethene is enforced. The enforced conjugation and planarity has a dramatic effect on the NMR chemical shifts for the 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 colorless 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 was 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-*tert*-Butylphenyl). Prepared as above using 4-*tert*-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 $BF_3{\cdot}OEt_2$ (0.10 mL, 1 M) under 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 was 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 ($[M + NH_4]^+$, 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 *tert*-butanol (100 mL) for 6 h. The solution was cooled, H_2O (100 mL) was added, and the mixture was extracted with EtOAc (3 × 100 mL). The organic phase was discarded, and the aqueous layer obtained was made acidic using aqueous HCl (2 M). The mixture was then extracted with EtOAc (3 × 100 mL), and the organic phase obtained was 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 was filtered off, and the filtrate was 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 was 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 was 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 $[C_{13}H_{14}F_4O_2{\cdot}NH_4]^+$: 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, 50 mL) under nitrogen for 48 h. Water was added, and the mixture was 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,

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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 $C_{60}H_{82}N_2O_8{\cdot}NH_4$: 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 (1 mm 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 and 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}/nm ($\log[\varepsilon/M^{-1}\ cm^{-1}]$) 275 (4.56), 317 (4.68), 357 (4.52); Fluor (CH_2Cl_2) λ_{max}/nm (λ_{exc}/nm) 412 (314); 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) and 2,3,5,6-tetrafluoro-4-hexyloxybenzaldehyde (**15**) (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 $BF_3{\cdot}OEt_2$ (0.10 mL, 1M) under 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 was continued for a further 2 h. The mixture was neutralized with a few drops of triethylamine, and the solvents were 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}/nm ($\log[\varepsilon/M^{-1}\ cm^{-1}]$) 548 (5.13); Fluor ($CH_2Cl_2$) λ_{max}/nm (λ_{exc}/nm) 674 (545); 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}/nm ($\log[\varepsilon/M^{-1}\ cm^{-1}]$) 536 (5.02); Fluor ($CH_2Cl_2$) λ_{max}/nm (λ_{exc}/nm) 653 (536); 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}/nm ($\log[\varepsilon/M^{-1}\ cm^{-1}]$) 536 (5.08); Fluor ($CH_2Cl_2$) λ_{max}/nm (λ_{exc}/nm) 653 (533); MS (MALDI-TOF) m/z 1892 (cluster, M^+ + 2, 100%).

Porphyrin-like Twin 16d (Ar = 4-*tert*-Butylphenyl). Prepared as above using 4-*tert*-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}/nm ($\log[\varepsilon/M^{-1}\ cm^{-1}]$) 537 (5.14); Fluor ($CH_2Cl_2$) λ_{max}/nm (λ_{exc}/nm) 653 (533); 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 was 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 a neat solid) at 200 °C under reduced pressure (1 mm 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-*tert*-butylbenzaldehyde (0.010 g, 0.065 mmol), and trifluoroacetic acid (1.0 mmol) were dissolved in CH_2Cl_2 (25 mL), and the solution was stirred for 1 h under an atmosphere of argon at room temperature. *p*-Chloranil (0.031 g, 0.13 mmol) was added, and stirring was continued for a further 5 min. The mixture was neutralized with triethylamine followed by the addition of an excess of $BF_3{\cdot}OEt_2$ and then left to stir overnight. Water was added, and the mixture was 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) to give two fractions as follows:

Fraction 1 (BODIPY **18**): (0.068 g, 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,

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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}/nm (log[ε/M^{-1} cm^{-1}]) 569 (4.40); Fluor (CH_2Cl_2) λ_{max}/nm (λ_{exc}/nm) 653 (569); 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}/nm (log[ε/M^{-1} cm^{-1}]) 570 (4.48); Fluor (CH_2Cl_2) λ_{max}/nm (λ_{exc}/nm) 639 (570); MS (MALDI-TOF) m/z 1690 (cluster, M^+ + 2, 100%).

■ ASSOCIATED CONTENT

Supporting Information

Characterization spectra for new compounds and X-ray crystal structures (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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