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Meso-Substituted Liquid Porphyrins

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Abstract: *Meso*-substituted A_4-porphyrins bearing 3,4,5-trialkoxyphenyl substituents are efficiently synthesized and characterized. Porphyrins bearing twelve C10 and C11 alkyl chains turned out to be liquid at room temperature. The remaining porphyrins, bearing C8, C9, C12, and C18 alkyl chains, have low melting points and high solubility in nonpolar solvents. Their differential scanning calorimetry distinctly shows, in most cases, only one phase transition.

Keywords: aldehydes • calorimetry • liquids • optical limiters • porphyrinoids

Introduction

An intrinsic property of planar aromatic systems is their tendency to form stacks and aggregates which eventually results in low solubility, high crystallinity, and high melting point.[1] This also holds true for porphyrins and phthalocyanines.[2] The design and synthesis of porphyrins which are liquids at room temperature is a formidable scientific challenge and to the best of our knowledge, no single solution has been reported. The first porphyrins which displayed liquid crystalline properties were reported by Goodby et al. in 1980.[3] In the following years many porphyrinoids which are liquid crystals[4] as well as liquid phthalocyanines[5] were described in the literature. Complex, dendritic porphyrins with low melting points have also been known for some time.[6] At the same time, liquidity is also a prerequisite to their application as real-world optical limiters.[7] As part of a broader project, we decided to tackle the problem of the design and synthesis of porphyrin-based optical limiters possessing a high two-photon absorption (2PA) cross-section combined with reverse-saturable absorption. Among many different architectures, we focused on *meso*-substituted A_4-porphyrins bearing substituted phenyl groups. Herein, we report the synthesis and characterization of a homologous series of porphyrins with very low melting points.

Our aim was not only to synthesize liquid porphyrins but also to identify patterns of substituents which can subsequently be used in the synthesis of more complex two-photon absorbing porphyrins.[8] For this reason, we focused on electron-donating groups which, suitably placed, are known to increase 2PA.[7b,9] Screening of a variety of different substituent arrangements allowed the identification of the 3,4,5-trialkoxyphenyl moiety as a promising lead. The influence of n-alkyl chains on melting points of various aromatic compounds has been broadly explored,[4c,j,l–o,10] including the 3,4,5-trialkoxyphenyl moiety, which was utilized in the design of liquid crystals.[10b–f,11] The 3,4,5-trialkoxyphenyl structural motive was also often used in conjunction with the studying of dye aggregation,[12,13] self-assembling dendrimers,[14] chiral liquid crystals,[15] and ionic liquid crystals.[11a]

Results and Discussion

Easily available 3,4,5-trihydroxybenzaldehyde[16] (**1**) was alkylated under classical Williamson conditions with alkyl bromides or iodides to give a set of 3,4,5-trialkoxybenzaldehydes **3a–f** (Scheme 1). The alkyl chain length ranged from 8 to 18 carbon atoms. The resulting aldehydes **3a–f** were reacted with pyrrole under Lindsey's co-catalysis conditions[17] to give A_4-porphyrins **4a–f** in 36–53 % yield (Scheme 1). These high yields together with straightforward purification allowed the preparation of porphyrins **4a–f** at a scale of around 200 mg. All porphyrins were highly soluble in organic solvents such as hexanes, diethyl ether, ethyl acetate, and so forth. Residual solvents were removed by drying for 72 h under high vacuum, and allowed the identification of porphyrins which are liquid at room temperature.

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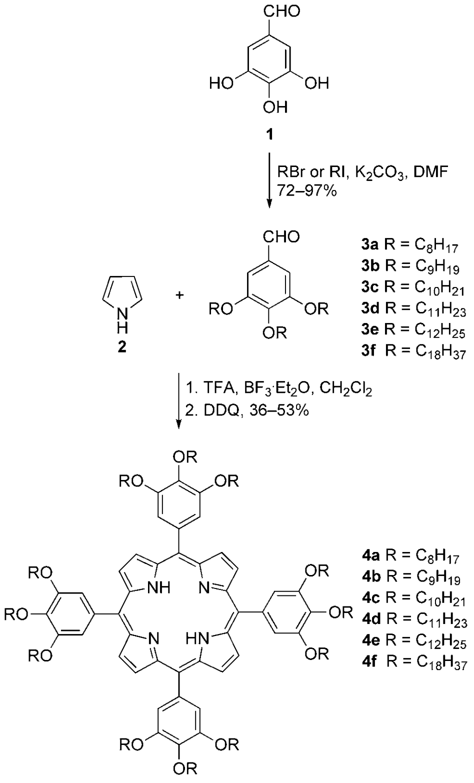

Scheme 1. Synthesis of porphyrins **4a–f**.

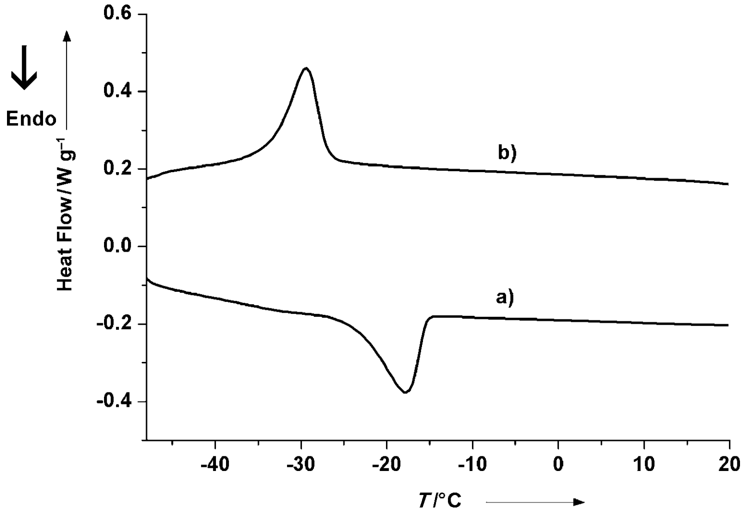

Figure 1. DSC curves for **4d**: a) reheating; and b) the second cooling (heating rate/cooling rate: 5 °C min^{-1}).

Table 1. Calorimetric data for compounds **4a–f**[a].

Compound	n[b]	Transition	T [°C] Onset	Maximum	ΔH [kJ mol^{-1}]
4a	8	Cry[c]→Iso[d]	55.1	56.8	78.1
4b	9	Cry→Iso	26.2	27.3	25.1
4c	10	Cry→Iso	−54.6	−39.7	11.5
4d	11	Cry→Iso	−23.8	−17.8	33.6
4e	12	Cry(I)→Cry(II)	32.0	34.6	47.1
		Cry(II)→Iso	36.4	38.4	7.32
4f	18	Cry→Iso	44.0	46.6	284.9

[a] Temperature and enthalpy changes were obtained by reheating the samples. [b] The length of the alkyl chain. [c] Crystal. [d] Isotropic liquid.

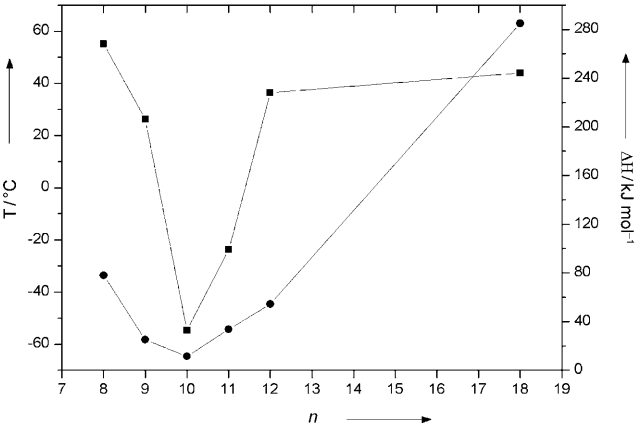

Figure 2. The melting points of porphyrins **4a–4f** (■) and enthalpy of phase transition (●) as a function of alkyl chain length; the phase transition temperatures represent the peak onset in the DSC (n is number of carbon atoms in aliphatic chain).

Subsequently, the thermal behavior of the porphyrins was investigated by differential scanning calorimetry (DSC). An exemplary DSC of porphyrin **4d** is presented in Figure 1. The results obtained from DSC analysis of porphyrins **4a–f** are summarized in Table 1 and Figure 2. All the temperatures represent the peak onset temperature of the DSC curves.

The data presented for **4a** shows that during heating/cooling cycles from 10 °C to 70 °C, a large sharp endothermic peak was observed at ca. 55 °C with almost equal enthalpy changes (ΔH), which can clearly be attributed to fusion of **4a**. However, on cooling from 70 °C no peak was observed, signifying that material stayed in the liquid state until 10 °C. A similar supercooling effect was also observed in the case of porphyrins **4b**, **4c**, and **4e**. Additionally, porphyrin **4e** exhibits the crystal Cry(I)–crystal Cry(II) phase transition, the crystal Cry(II) melts to isotropic liquid at ca. 36 °C. The large enthalpy change for isotropization of **4e** porphyrin and the strong supercooling effect indicate that Cry(II) is a solid crystal rather than liquid crystal. This is also confirmed

Abstract in Polish: Zsyntetyzowano sześć mezo podstawionych porfiryn zawierających podstawniki 3,4,5-trialkoksyfenylowe. Porfiryny z łańcuchami alkilowymi zawierającymi dziesięć i jedenaście atomów węgla są cieczami w temperaturze pokojowej. Pozostałe cztery porfiryny wykazują bardzo dobrą rozpuszczalność w rozpuszczalnikach niepolarnych oraz niskie temperatury topnienia. Badania metodą skaningowej kalorymetrii różnicowej wykazały dla większości porfiryn tylko jedno przejście fazowe.

by polarized optical microscopy (POM). The striking difference between the physical state at room temperature is exemplified by comparison of porphyrins **4a** and **4c** in polarized light (Figure 3).

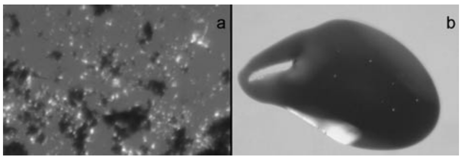

Figure 3. POM of porphyrins **4a** (a) and **4c** (b) at RT.

Porphyrin **4c** melts at −55 °C and it shows only a crystal–isotropic liquid phase transition. An analogous situation occurs also for porphyrins **4a**, **4b**, **4d**, and **4f**. In the case of **4d** and **4f** the degree of supercooling is low, mainly ca. 3 °C for **4d** and 2.5 °C for **4f**. Upon heating both compounds undergo single phase transitions (Cry→Iso) at −24 °C and 44 °C, respectively. Upon cooling **4d** from the melt, a broad exothermic peak was observed at −27 °C, and in the case of **4f** one strong exothermic peak at 41.5 °C is observed followed by two very weak exotherms at 37 °C and 34 °C. The behavior of the compounds in DSC thermograms is very sensitive to the alkoxy chain lengths present in the molecule. Increasing the length of the alkoxy side chains leads to a decrease in the temperature for the Cry→Iso phase transition (porphyrins **4a** to **4c**), exhibiting a minimum for the decyloxy substituted compound **4c** (−55 °C).

Further elongation of the alkyl chain causes an increase in the melting point (porphyrins **4d** to **4f**). The dramatic alkoxy-chain length dependent decrease in melting point for compounds **4a** to **4c** may arise from the disruption of π–π interactions and induction of weak hydrophobic interactions between the porphyrins. The presence of twelve alkyl chains serves as an effective steric stabilizer preventing porphyrin aggregation.

Conclusions

In conclusion, we have identified structural features which allow the synthesis of porphyrin architectures which are liquids at room temperature.[18] 5,10,15,20-Tetrakis[3,4,5-tri(undecyloxy)phenyl]porphyrin and its decyloxy analogue are both liquids at room temperature and have melting points −24 °C and −55 °C, respectively. Considering that liquid porphyrins maintain the same spectroscopic features as their solid analogues, this discovery not only opens the way to design porphyrins possessing such substituents in optical limiting devices but also allows its broader use in other applications where liquidity or very high solubility are desirable.

Experimental Section

General

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. All reported ^{1}H NMR and ^{13}C NMR spectra were collected using a 500 or 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. The UV/Vis absorption spectra were recorded in CH_2Cl_2. The absorption wavelengths are reported in nm with the extinction coefficient in $M^{-1}cm^{-1}$ in brackets. Melting points of aldehydes were determined using a capillary type apparatus. Melting points of porphyrins were determined by means of DSC apparatus. Purge gas is high purity nitrogen. All the temperatures collected represent the peak onset temperature of the DSC curves. The heating rate is given in brackets. The enthalpies (Δ*H*) are the thermodynamics parameters of these temperature variation processes which were estimated from each DSC peak area computed by standard procedure in DSC apparatus. Chromatography was performed on silica (200–400 mesh) or alumina. Dry column vacuum chromatography (DCVC) was performed on preparative thin-layer chromatography silica. The mass spectra were obtained by field desorption MS (FD-MS) or electron impact MS (EI-MS).

Synthesis

3,4,5-Trioctyloxybenzaldehyde (3a). To a solution of 3,4,5-trihydroxybenzaldehyde monohydrate (**1**; 1.12 g, 6.5 mmol) in DMF (40 mL), 1-iodooctane (4.8 mL, 26.6 mmol) was added, followed by K_2CO_3 (2.42 g, 17,5 mmol). The reaction mixture was stirred for 24 h at 160 °C. Subsequently, the mixture was poured into water (100 mL) and extracted with EtOAc (3×30 mL). The organic layers were combined, dried (Na_2SO_4), filtered, and evaporated affording brown oil. The crude product was chromatographed (silica gel, hexanes/CH_2Cl_2 3:1 to 13:6) to obtain pure aldehyde **3a** (2.31 g, 72 %) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87–0.90 (m, 9 H, CH_3), 1.26–1.37 (m, 24 H, CH_2), 1.46–1.51 (m, 6 H, CH_2), 1.73–1.78 (m, 2 H, CH_2), 1.80–1.85 (m, 4 H, CH_2), 4.02–4.07 (m, 6 H, OCH_2), 7.08 (s, 2 H, ArH), 9.83 ppm (s, 1 H, CHO). Other spectral and physical properties concur with published data.[10e]

3,4,5-Trinonyloxybenzaldehyde (3b). To a solution of 3,4,5-trihydroxybenzaldehyde monohydrate (**1**; 1.12 g, 6.5 mmol) in DMF (40 mL), 1-bromononane (5.0 mL, 26.2 mmol) was added, followed by K_2CO_3 (2.42 g, 17,5 mmol) and KI (210 mg, 1.27 mmol). The reaction mixture was stirred for 24 h at 160 °C. Subsequently, the mixture was poured into water (100 mL) and extracted with EtOAc (4×30 mL). The organic layers were combined, dried (Na_2SO_4), filtered, and evaporated affording brown oil. The crude product was chromatographed (silica gel, hexanes/CH_2Cl_2 3:1) to obtain pure aldehyde **3b** (3.01 g, 87 %) as a white solid. M.p.: 35.4–36.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87–0.90 (m, 9 H, CH_3), 1.28–1.37 (m, 30 H, CH_2), 1.45–1.51 (m, 6 H, CH_2), 1.72–1.78 (m, 2 H, CH_2), 1.80–1.85 (m, 4 H, CH_2), 4.02–4.07 (m, 6 H, OCH_2), 7.08 (s, 2 H, ArH), 9.83 ppm (s, 1 H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.1, 22.7, 22.7, 26.0, 26.1, 29.2, 29.3, 29.3, 29.4, 29.5, 29.6, 29.6, 30.3, 31.9, 31.9, 69.2, 73.6, 107.9, 131.4, 143.9, 153.5, 191.3 ppm. Other spectral and physical properties concur with published data.[19]

3,4,5-Tridecyloxybenzaldehyde (3c). To a solution of 3,4,5-trihydroxybenzaldehyde monohydrate (**1**; 1.12 g, 6.5 mmol) in DMF (40 mL), 1-bromodecane (5.5 mL, 26.5 mmol) was added, followed by K_2CO_3 (2.42 g, 17,5 mmol) and KI (180 mg, 1.08 mmol). The reaction mixture was stirred for 24 h at 160 °C. Subsequently, the mixture was poured into water (100 mL) and extracted with EtOAc (3×30 mL). The organic layers were combined, dried (Na_2SO_4), filtered, and evaporated affording brown oil. The crude product was chromatographed (silica gel, hexanes/CH_2Cl_2 3:1 to 13:7) to obtain pure aldehyde **3c** (2.94 g, 79 %) as a white solid. M.p.: 34.6–35.7 °C (lit. m.p.: 33 °C);[13] ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.87–0.89 (m, 9 H, CH_3), 1.27–1.37 (m, 36 H, CH_2), 1.45–1.50 (m, 6 H, CH_2), 1.73–1.77 (m, 2 H, CH_2), 1.80–1.85 (m, 4 H, CH_2), 4.02–4.07 (m, 6 H, OCH_2), 7.08 (s, 2 H, ArH), 9.83 ppm (s, 1 H, CHO). Other spectral and physical properties concur with published data.[20]

3,4,5-Triundecyloxybenzaldehyde (3d). To a solution of 3,4,5-trihydroxybenzaldehyde monohydrate (**1**; 1.14 g, 6.6 mmol) in DMF (40 mL), 1-bromoundecane (5.8 mL, 25.9 mmol) was added, followed by K_2CO_3 (2.42 g, 17,5 mmol) and KI (180 mg, 1.08 mmol). The reaction mixture was stirred for 24 h at 160°C and further allowed to cool down to RT. The product crystallized from the reaction mixture while cooling. The resulting solid was washed with water, dissolved in EtOAc, and dried (Na_2SO_4). Then it was filtered and evaporated to dryness to give a brown solid. Subsequently, the crude product was chromatographed (silica gel, hexanes/CH_2Cl_2 3:1 to 3:2) to obtain pure aldehyde **3d** (3.57 g, 87%) which was recrystallized (EtOH) to give colorless crystals. M.p.: 50.0–50.7°C (EtOH); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.88$ (m, 9H, CH_3), 1.27–1.35 (m, 42H, CH_2), 1.45–1.51 (m, 6H, CH_2), 1.72–1.78 (m, 2H, CH_2), 1.80–1.85 (m, 4H, CH_2), 4.05 (m, 6H, OCH_2), 7.08 (s, 2H, ArH), 9.83 ppm (s, 1H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): $\delta =$ 14.1, 22.7, 26.0, 26.1, 29.3, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 31.9, 31.9, 69.3, 73.6, 107.9, 131.5, 143.9, 153.5, 191.2 ppm; HRMS (EI): *m*/*z* calcd for $C_{40}H_{72}O_4$: 616.5431; found: 616.5418; elemental analysis calcd (%) for $C_{40}H_{72}O_4$: C 77.87, H 11.76; found: C 77.61, H 11.90.

3,4,5-Tridodecyloxybenzaldehyde (3e). To a solution of 3,4,5-trihydroxybenzaldehyde monohydrate (**1**; 4.49 g, 26.1 mmol) in DMF (160 mL), 1-bromododecane (34.0 mL, 141.6 mmol) was added, followed by K_2CO_3 (9.71 g, 70.3 mmol) and KI (660 mg, 3.98 mmol). The reaction mixture was stirred for 15 h at 160°C and further allowed to cool down to RT. The product crystallized from the reaction mixture while cooling. The resulting solid was washed with water, dissolved in EtOAc and dried (Na_2SO_4). Then it was filtered and evaporated to dryness to give a brown solid. Subsequently, the crude product was chromatographed (silica gel, hexanes/CH_2Cl_2 4:1 to 3:7) to obtain pure aldehyde **3e** (15.47 g, 90%) which was recrystallized (EtOAc) to give colorless crystals. M.p.: 50.4–51.3°C (EtOAc) [lit. m.p.: 50°C (propan-2-ol)];[14] ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.88$ (m, 9H, CH_3), 1.26–1.36 (m, 48H, CH_2), 1.45–1.51 (m, 6H, CH_2), 1.72–1.78 (m, 2H, CH_2), 1.80–1.85 (m, 4H, CH_2), 4.02–4.07 (m, 6H, OCH_2), 7.08 (s, 2H, ArH), 9.83 ppm (s, 1H, CHO). Other spectral and physical properties concur with published data.[21]

3,4,5-Trioctadecyloxybenzaldehyde (3f). To a solution of 3,4,5-trihydroxybenzaldehyde monohydrate (**1**; 1.14 g, 6.6 mmol) in DMF (40 mL), 1-bromooctadecane (8.72 g, 26.2 mmol) was added, followed by K_2CO_3 (2.42 g, 17,5 mmol) and KI (180 mg, 1.08 mmol). The reaction mixture was stirred for 22 h at 160°C and further allowed to cool down to RT. The product crystallized from the reaction mixture while cooling. The resulting solid was washed with water, dissolved in $CHCl_3$, and dried (Na_2SO_4). Then it was filtered and evaporated to dryness to give a brown solid. Subsequently, the crude product was chromatographed (silica gel, hexanes/$CHCl_3$ 4:1 to 7:3) to obtain pure aldehyde **3d** (5.86 g, 97%) which was recrystallized (hexanes/EtOAc) to give colorless crystals. M.p.: 73.3–75°C (hexanes/EtOAc) (lit. m.p.: 75–76°C);[15] ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.88$ (m, 9H, CH_3), 1.26–1.36 (m, 84H, CH_2), 1.45–1.59 (m, 6H, CH_2), 1.72–1.78 (m, 2H, CH_2), 1.80–1.85 (m, 4H, CH_2), 4.02–4.07 (m, 6H, OCH_2), 7.08 (s, 2H, ArH), 9.83 ppm (s, 1H, CHO). Other spectral and physical properties concur with published data.[22]

General procedure for porphyrins synthesis: Samples of an aldehyde (0.64 mmol) and pyrrole (56 μL, 0.81 mmol) were dissolved in CH_2Cl_2 (64 mL) at room temperature (in the case of some solid aldehydes, gentle heating to 40°C was necessary). Then TFA (78 μL) and $BF_3{\cdot}Et_2O$ (2.4 μL) were added while stirring. After 2.5 h, a solution of DDQ (110 mg, 0.49 mmol) in THF (6.0 mL) was added, and the reaction mixture was stirred at RT for an additional 1 h. The purification details are described for each case as follows.

5,10,15,20-Tetrakis(3,4,5-trioctyloxyphenyl)porphyrin (4a). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2) and all fractions containing porphyrin **4a** were combined, evaporated to dryness, and chromatographed (silica gel, hexanes/CH_2Cl_2 3:1 to 1:1) to obtain porphyrin **4a** contaminated with a blue-fluorescent compound. Subsequent chromatography (DCVC, silica gel, hexanes/CH_2Cl_2 4:1 to 1:1) afforded pure porphyrin **4a** as a violet solid (124 mg, 36%). $R_f = 0.31$ (silica gel, CH_2Cl_2/hexanes, 9:20); m.p.: 55.1°C (DSC, 5°C min^{-1}); UV/Vis (CH_2Cl_2): λ (ε) = 425 (548000), 518 (24100), 555 (11500), 592 (7200), 649 nm (5800); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.79$ (br s, 2H, NH), 0.82–0.85 (m, 24H, CH_3), 0.92–0.95 (m, 12H, CH_3), 1.24–1.37 (m, 88H, CH_2), 1.43–1.50 (m, 24H, CH_2), 1.67 (m, 8H, CH_2), 1.86 (m, 16H, CH_2), 1.97 (m, 8H, CH_2), 4.08 (t, $J_{H,H} = 6.5$ Hz, 16H, OCH_2), 4.30 (t, $J_{H,H} = 6.5$ Hz, 8H, OCH_2), 7.42 (s, 8H, ArH), 8.93 ppm (s, 8H, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): $\delta = 14.0$, 14.2, 22.6, 22.8, 26.1, 26.3, 29.2, 29.4, 29.5, 29.5, 29.7, 30.6, 31.8, 32.0, 69.4, 73.8, 114.3, 120.2, 137.1, 138.0, 151.2 ppm; HRMS (FD): *m*/*z* calcd for $C_{140}H_{222}N_4O_{12}$: 2151.6884; found: 2151.6714, isotope profiles agree; elemental analysis calcd (%) for $C_{140}H_{222}N_4O_{12}$: C 78.09, H 10.39, N 2.60; found: C 77.89, H 10.47, N 2.60.

5,10,15,20-Tetrakis(3,4,5-trinonyloxyphenyl)porphyrin (4b). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2) and all fractions containing porphyrin **4b** were combined, evaporated to dryness, and chromatographed (silica gel, hexanes/CH_2Cl_2 4:1 to 3:2) to obtain porphyrin **4b** contaminated with a blue-fluorescent compound. Subsequent chromatography (DCVC, silica gel, hexanes/CH_2Cl_2 4:1 to 1:1) afforded pure porphyrin **4b** as an amorphous dark violet solid (138 mg, 37%). $R_f = 0.37$ (silica gel, CH_2Cl_2/hexanes, 9:20); m.p.: 26.2°C (DSC, 1°C min^{-1}); UV/Vis (CH_2Cl_2): λ (ε) = 425 (567000), 518 (25100), 555 (12000), 592 (6900), 649 nm (6900); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.79$ (br s, 2H, NH), 0.82–0.85 (m, 24H, CH_3), 0.91–0.94 (m, 12H, CH_3), 1.23–1.41 (m, 112H, CH_2), 1.45–1.52 (m, 24H, CH_2), 1.66 (m, 8H, CH_2), 1.86 (m, 16H, CH_2), 1.97 (m, 8H, CH_2), 4.08 (t, $J_{H,H} =$ 6.5 Hz, 16H, OCH_2), 4.29 (t, $J_{H,H} = 6.5$ Hz, 8H, OCH_2), 7.41 (s, 8H, ArH), 8.93 ppm (s, 8H, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): $\delta = 14.1$, 14.2, 22.6, 22.8, 26.1, 26.3, 29.2, 29.4, 29.5, 29.5, 29.6, 29.8, 29.8, 30.6, 31.9, 32.0, 69.4, 73.8, 114.3, 120.2, 137.1, 138.0, 151.2 ppm; LRMS (FD): *m*/*z* calcd for $C_{152}H_{246}N_4O_{12}$: 2319.9; found: 2319.8, isotope profiles agree; elemental analysis calcd (%) for $C_{152}H_{246}N_4O_{12}$: C 78.64, H 10.68, N 2.41; found: C 78.43, H 10.70, N 2.38.

5,10,15,20-Tetrakis(3,4,5-tridecyloxyphenyl)porphyrin (4c). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2) and all fractions containing porphyrin **4c** were combined, evaporated to dryness, and chromatographed (silica gel, hexanes/CH_2Cl_2 9:1 to 3:2) to obtain porphyrin **4c** contaminated with a blue-fluorescent compound. Subsequent chromatography (DCVC, silica gel, hexanes/CH_2Cl_2 3:1 to 3:2) afforded pure porphyrin **4c** as a dark violet oil (156 mg, 39%). $R_f =$ 0.41 (silica gel, CH_2Cl_2/hexanes, 9:20); m.p.: −54.6°C (DSC, 10°C min^{-1}); UV/Vis (CH_2Cl_2): λ (ε) = 425 (523000), 518 (23200), 555 (11000), 593 (7000), 649 nm (5800); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta =$ −2.79 (br s, 2H, NH), 0.82–0.84 (m, 24H, CH_3), 0.90–0.92 (m, 12H, CH_3), 1.22–1.42 (m, 136H, CH_2), 1.45–1.52 (m, 24H, CH_2), 1.66 (m, 8H, CH_2), 1.86 (m, 16H, CH_2), 1.97 (m, 8H, CH_2), 4.08 (t, $J_{H,H} = 6.5$ Hz, 16H, OCH_2), 4.29 (t, $J_{H,H} = 6.5$ Hz, 8H, OCH_2), 7.41 (s, 8H, ArH), 8.93 ppm (s, 8H, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): $\delta = 14.1$, 14.1, 22.6, 22.7, 26.2, 26.3, 29.3, 29.4, 29.5, 29.5, 29.5, 29.6, 29.8, 29.8, 29.9, 30.6, 31.9, 32.0, 69.4, 73.8, 114.3, 120.2, 137.1, 138.0, 151.2 ppm; LRMS (FD): *m*/*z* calcd for $C_{164}H_{270}N_4O_{12}$: 2488.1; found: 2488.2, isotope profiles agree; elemental analysis calcd (%) for $C_{164}H_{270}N_4O_{12}$: C 79.11, H 10.93, N 2.25; found: C 78.94, H 10.99, N 2.21.

5,10,15,20-Tetrakis(3,4,5-triundecyloxyphenyl)porphyrin (4d). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2) and all fractions containing porphyrin **4d** were combined, evaporated to dryness, and chromatographed (silica gel, hexanes/CH_2Cl_2 9:1 to 3:2) to obtain porphyrin **4d** contaminated with a blue-fluorescent compound. Subsequent chromatography (DCVC, silica gel, hexanes/CH_2Cl_2 4:1 to 13:7) afforded pure porphyrin **4d** as a violet oil (227 mg, 53%). $R_f = 0.48$ (silica gel, CH_2Cl_2/hexanes, 9:20); m.p.: −23.8°C (DSC, 5°C min^{-1}); UV/Vis (CH_2Cl_2): λ (ε) = 425 (412000), 518 (18300), 555 (8400), 591 (5500), 649 nm (4400); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.79$ (br s, 2H, NH), 0.82–0.85 (m, 24H, CH_3), 0.88–0.92 (m, 12H, CH_3), 1.22–1.34 (m, 160H, CH_2), 1.46–1.52 (m, 24H, CH_2), 1.64–1.70 (m, 8H, CH_2), 1.86 (m, 16H, CH_2), 1.94–2.00 (m, 8H, CH_2), 4.08 (t, $J_{H,H} = 6.5$ Hz, 16H, OCH_2), 4.29 (t, $J_{H,H} = 6.5$ Hz, 8H, OCH_2), 7.42 (s, 8H, ArH), 8.93 ppm (s, 8H, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): $\delta = 14.0$, 14.1, 22.6, 22.7, 26.2, 26.3, 29.3, 29.5, 29.6, 29.6, 29.6, 29.8, 29.8, 29.8, 29.9, 30.6, 31.9, 32.0, 69.4, 73.8, 114.4, 120.2, 137.1, 138.1, 151.2 ppm;

LRMS (FD): m/z calcd for $C_{176}H_{294}N_4O_{12}$:2656.2; found: 2656.2, isotope profiles agree; elemental analysis calcd (%) for $C_{176}H_{294}N_4O_{12}$: C 79.52, H 11.15, N 2.11; found: C 79.26, H 11.21, N 2.06.

5,10,15,20-Tetrakis(3,4,5-tridodecyloxyphenyl)porphyrin (4e). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2) and all fractions containing porphyrin **4e** were combined and evaporated to dryness. Two repetitive column chromatography (silica gel, hexanes/CH_2Cl_2 2:3 to 1:1) afforded pure porphyrin **4e** as a violet solid (209 mg, 46%). $R_f = 0.52$ (silica gel, CH_2Cl_2/hexanes, 9:20); m.p.: 36.4°C (DSC, 1°C min^{-1}); UV/Vis (CH_2Cl_2): λ (ε) = 425 (437000), 518 (21300), 554 (9900), 592 (6500), 649 nm (5600);^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.79$ (brs, 2H, NH), 0.83–0.85 (m, 24H, CH_3), 0.88–0.91 (m, 12H, CH_3), 1.22–1.34 (m, 184H, CH_2), 1.46–1.52 (m, 24H, CH_2), 1.67 (m, 8H, CH_2), 1.86 (m, 16H, CH_2), 1.97 (m, 8H, CH_2), 4.08 (t, $J_{H,H} = 6.4$ Hz, 16H, OCH_2), 4.30 (t, $J_{H,H} = 6.5$ Hz, 8H, OCH_2), 7.42 (s, 8H, ArH), 8.94 ppm (s, 8H, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): $\delta =$ 14.1, 22.6, 26.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 29.6, 29.7, 29.8, 29.8, 29.8, 31.9, 32.0, 69.4, 73.8, 114.4, 120.2, 137.1, 138.1, 151.2 ppm; LRMS (FD): m/z calcd for $C_{188}H_{318}N_4O_{12}$:2824.4; found: 2824.3, isotope profiles agree; elemental analysis calcd (%) for $C_{188}H_{318}N_4O_{12}$: C 79.89, H 11.34, N 1.98; found: C 79.82, H 11.22, N 1.87.

5,10,15,20-Tetrakis(3,4,5-trioctadecyloxyphenyl)porphyrin (4f). The reaction mixture was passed through a short pad of alumina (Al_2O_3, CH_2Cl_2) and all fractions containing porphyrin **4f** were combined and evaporated to dryness. The resulting solid was then chromatographed (silica gel, hexanes/CH_2Cl_2 3:1 to 3:2) to obtain pure porphyrin **4f** (302 mg, 49%) which was recrystallized (hexanes/acetone) providing dark violet crystals. $R_f = 0.67$ (silica gel, CH_2Cl_2/hexanes, 9:20); m.p.: 44.0°C (DSC, 1°C min^{-1}); UV/Vis (CH_2Cl_2): λ (ε) = 425 (450000), 518 (19400), 555 (8800), 592 (5700), 649 nm (4600);^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.79$ (brs, 2H, NH), 0.85–0.89 (m, 36H, CH_3), 1.21–1.34 (m, 328H, CH_2), 1.46–1.52 (m, 24H, CH_2), 1.67 (m, 8H, CH_2), 1.86 (m, 16H, CH_2), 1.97 (m, 8H, CH_2), 4.08 (t, $J_{H,H} = 6.4$ Hz, 16H, OCH_2), 4.29 (t, $J_{H,H} = 6.5$ Hz, 8H, OCH_2), 7.41 (s, 8H, ArH), 8.93 ppm (s, 8H, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): $\delta = 14.1$, 14.1, 22.7, 22.7, 26.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 29.7, 29.8, 29.8, 29.8, 29.8, 29.9, 31.9, 31.9, 69.4, 73.8, 114.4, 120.2, 137.1, 138.1, 151.3 ppm; LRMS (FD): m/z calcd for $C_{260}H_{462}N_4O_{12}$: 3833.6; found: 3833.4, isotope profiles agree; elemental analysis calcd (%) for $C_{260}H_{462}N_4O_{12}$: C 81.40, H 12.14, N 1.46; found: C 81.17, H 12.16, N 1.45.

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