Supporting Information

For

Nanosized π -Conjugated Molecules Based on Truxene and Porphyrin: Synthesis and High Fluorescence Quantum Yields

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Scheme 1:

Reagents and conditions: (a) 4-formylbenzeneboronic acid, $\text{Pd}(\text{PPh}_3)_4$, THF, reflux; (b) arylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, THF, reflux; (c) NBS, $\text{CH}_2\text{Cl}_2/\text{acetic acid}$, $0\text{ }^\circ\text{C}$; (d) 4-thiophenboronic acid, $\text{Pd}(\text{PPh}_3)_4$, THF, reflux;

$\text{R} = n\text{-C}_6\text{H}_{13}$

General Methods.

All reactions were performed under a nitrogen atmosphere unless stated otherwise. All commercially available chemicals were used as received unless stated otherwise. Tetrahydrofuran (THF) was distilled over sodium and benzophenone; pyrrole was distilled over CaH_2 . ^1H and ^{13}C NMR spectra were recorded on a Mercury plus 200 MHz or 300 MHz or Bruker 500 MHz using CDCl_3 as solvent in all cases. UV-vis spectra were recorded on PerkinElmer Lambda 35 UV-vis spectrometer. PL spectra were carried out on PerkinElmer LS 55 Luminescence Spectrometer. Fluorescence quantum yields (Φ_F) of the samples in THF were measured by using tetraphenylporphyrin (TPP, $\Phi_F = 0.11$ in toluene¹) as a standard. All solutions of sample were measured at 10^{-6} M. All films of sample were spin-coated at 1000 r/s for 1 minute and the solution concentration is 10mg/mL. MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) MS spectra were recorded in Bruker BIFLEX III. Structures were optimized by Dreiding force field⁵ implemented with a commercial package Cerius² (the diameter of the 2-6 are 4.4 nm, 5.0 nm, 4.3 nm 5.2 nm and 5.0 nm, correspondingly).

Tr: truxene; Th: thiophen; Flu: Fluorene; Por: Porphyrin

Experimental Section.

2-Bromo-9,9-dihexylfluorene, 9,9-dihexylfluorene-2-boronic acid,² 5,10,15-tribromotruxene³ were prepared according to literature procedures. The catalyst precursor $\text{Pd}(\text{PPh}_3)_4$ was prepared according to the literature² and stored under nitrogen in a Schlenk tube.

7: To the mixture of 5,10,15-tribromotruxene (10.8g 0.01mmol), 4-formyl-benzeneboronic acid (1.65g, 0.011mmol) and Na_2CO_3 (16.5mL, 2M in distilled water) in THF was added $\text{Pd}(\text{PPh}_3)_4$. After degassed, the mixture was refluxed overnight, then quenched with aqueous NH_4Cl solution. The aqueous layer was extracted twice with CH_2Cl_2 , the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of solvent in vacuum, the crude product was purified by column chromatograph on silica gel with elutant (hexane/EtOAc) to give white solids

(2.15g, yield: 70%). ^1H NMR (CDCl_3 , 300 Hz, ppm, δ): 10.10 (Ar-CHO, 1H, s), 8.44-8.41 (Tr-H, 1H, d, $J = 8.4$ Hz), 8.24-8.21 (Tr-H, H, d, $J = 8.4$ Hz), 8.21-8.18 (Tr-H, H, d, $J = 8.4$ Hz), 8.04-8.01 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.93-7.90 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.72-7.70 (Tr-H, 2H, m), 7.60-7.51 (Tr-H, 4H, m), 2.95-2.85 (CH_2 , 6H, m), 2.15-2.01 (CH_2 , 6H, m), 0.92-0.86 (CH_2 , 36H, m), 0.624-0.606 (CH_2 , CH_3 , 30H, m). ^{13}C NMR (CDCl_3 , 75 MHz, ppm, δ): 191.89, 155.90, 155.85, 154.39, 147.12, 145.59, 145.11, 144.87, 140.39, 138.94, 138.90, 137.90, 137.77, 137.66, 137.55, 135.11, 130.34, 129.34, 127.57, 125.90, 125.62, 125.49, 125.01, 120.98, 120.79, 55.95, 36.82, 31.43, 29.37, 23.86, 22.23, 13.86. MALDI-TOF, m/z : Calcd, 1106.6. Found: 1214 ($[\text{M}+\text{Ag}]^+$), 1022 (M^+-85).

General procedure for the synthesis of aldehyde derivatives 7, 8, 9, 10, 11, 12 by Suzuki-Miyaura cross coupling reaction (SMCC).

To the mixture of aldehyde (**7** or **13**) (1 eq), boronic acid (4-8 eq) and Na_2CO_3 (12-24 eq) dissolved in THF and distilled water was added $\text{Pd}(\text{PPh}_3)_4$. After degassed, the reaction mixture was refluxed overnight then quenched with aqueous NH_4Cl solution. The aqueous layer was extracted twice with CH_2Cl_2 , and the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of solvent in vacuo, the crude product was purified by column chromatograph on silica gel with elutant (hexane/EtOAc).

8: yield: 86% (0.97g). ^1H NMR (CDCl_3 , 300 Hz, ppm, δ): 10.11 (Ar-CHO, 1H, s), 8.49-8.46 (Tr-H, 1H, d, $J = 8.4$ Hz), 8.43-8.40 (Tr-H 2H, m) 8.04-8.01 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.95-7.92 (Ar -H, 2H, d, $J = 8.4$ Hz), 7.74-7.64 (Tr-H, Ar-H, 10H, m), 7.34-7.31 (Ar-H, 4H, d, $J = 8.4$ Hz), 3.04-2.99 (CH_2 , 6H, m), 2.45 (Ar- CH_3 , 6H, s), 2.19-2.16 (CH_2 , 6H, m), 0.91-0.88 (CH_2 , 36H, m), 0.62-0.57 (CH_2 , CH_3 , 30H, m). ^{13}C NMR (CDCl_3 , 125 Hz, ppm, δ): 191.80, 154.58, 154.24, 154.13, 147.34, 145.56, 145.30, 145.02, 141.04, 139.21, 139.14, 138.41, 138.31, 138.21, 137.65, 137.40, 136.93, 135.07, 130.31, 129.53, 127.53, 126.91, 125.47, 125.03, 124.95, 124.79, 120.76, 120.45, 120.40, 55.81, 37.18, 37.06, 31.47, 29.49, 23.94, 22.26, 21.12, 13.89.

MALDI-TOF, m/z : Calcd, 1130.8. Found: 1238 ($[M+Ag]^+$), 1046 (M^+-85).

9: yield: 75% (1.70g). 1H NMR ($CDCl_3$, 500 Hz, ppm, δ): 10.11 (Ar-CHO, 1H, s), 8.51-8.45 (Tr-H, 3H, m), 8.04-8.02 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.95-7.93 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.87-7.86 (Ar-H, 4H, d, $J = 8.4$ Hz), 7.77-7.73 (Ar-H, Tr-H, 10H, m), 7.71-7.69 (Ar-H, 4H, d, $J = 8.4$ Hz), 7.51-7.48 (Ar-H, 4H, m), 7.40-7.37 (Ar-H, 2H, m), 3.07-3.06 (CH_2 , 6H, m), 2.34-2.14 (CH_2 , 6H, m), 0.97-0.90 (CH_2 , 36H, m), 0.64-0.61 (CH_2 , CH_3 , 30H, m). ^{13}C NMR ($CDCl_3$, 125 Hz, ppm, δ): 191.92, 154.58, 154.35, 154.27, 147.36, 145.69, 145.49, 145.26, 140.97, 140.77, 140.20, 140.07, 139.56, 138.66, 138.26, 138.18, 137.73, 137.47, 135.08, 130.35, 128.85, 127.57, 127.43, 127.36, 127.05, 125.52, 125.09, 124.99, 124.91, 120.80, 120.50, 55.89, 37.09, 31.49, 29.50, 23.97, 22.28, 13.90. MALDI-TOF, m/z : Calcd, 1254.8. Found: 1362 ($[M+Ag]^+$), 1170 (M^+-85).

10: yield: 84% (0.75g). 1H NMR ($CDCl_3$, 500 Hz, ppm, δ): 10.12 (Ar-CHO, 1H, s), 8.49-8.48 (Tr-H, 1H, d, $J = 8.4$ Hz), 8.40-8.38 (Tr-H, 2H, d, $J = 8.4$ Hz), 8.05-8.03 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.95-7.93 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.75-7.71 (Tr-H, 6H, m), 7.49-7.48 (Th-H, 2H, d, $J = 3.6$ Hz), 7.34-7.33 (Th-H, 2H, d, $J = 4.8$ Hz), 7.17-7.15 (Th-H, 2H, dd, $J = 3.6$ Hz, $J = 4.8$ Hz), 3.04-2.96 (CH_2 , 6H, m), 2.21-2.13 (CH_2 , 6H, m), 0.97-0.85 (CH_2 , 36H, m), 0.63-0.58 (CH_2 , CH_3 , 30H, m). ^{13}C NMR ($CDCl_3$, 125 Hz, ppm, δ): 191.89, 154.53, 154.39, 147.30, 145.47, 145.39, 145.19, 144.84, 140.84, 139.65, 138.11, 137.72, 137.50, 135.09, 132.56, 130.33, 128.09, 127.56, 125.51, 124.97, 124.60, 124.18, 122.93, 120.78, 119.32, 55.81, 37.09, 31.46, 29.47, 23.96, 22.25, 13.87. MALDI-TOF, m/z : Calcd, 1114.8; Found: 1222 ($[M+Ag]^+$), 1030 (M^+-85).

11: yield: 70% (1.41g). 1H NMR ($CDCl_3$, 300 Hz, ppm, δ): 10.11 (Ar-CHO, 1H, s), 8.50-8.48 (Tr-H, 1H, d, $J = 8.4$ Hz), 8.41-8.38 (Tr-H, 2H, m), 8.05-8.02 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.95-7.92 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.76-7.02 (Tr-H, 6H, m), 7.40-7.39 (Th-H, 2H, d, $J = 3.6$ Hz), 7.28-7.23 (Th-H, 6H, m), 7.07-7.04 (Th-H, 2H, dd, $J = 3.6$

Hz, $J = 4.8$ Hz), 3.04-2.96 (CH₂, 6H, m), 2.21-2.13 (CH₂, 6H, m), 0.97-0.85 (CH₂, 36H, m), 0.63-0.50 (CH₂, CH₃, 30H, m). ¹³C NMR (CDCl₃, 75 Hz, ppm, δ): 191.81, 154.48, 154.42, 154.37, 147.21, 145.46, 145.42, 145.25, 143.50, 140.74, 139.73, 138.04, 137.74, 137.50, 136.48, 135.06, 132.21, 130.29, 127.85, 127.51, 125.51, 124.99, 124.64, 124.30, 123.82, 123.56, 123.54, 120.75, 118.95, 55.84, 37.05, 31.42, 29.42, 23.93, 22.22, 13.84. MALDI-TOF, m/z : Calcd, 1278.7; Found: 1386 ([M+Ag]⁺), 1194 (M⁺-85).

12: yield: 78% (2.52g). ¹H NMR (CDCl₃, 300 Hz, ppm, δ): 10.11 (Ar-CHO, 1H, s), 8.53-8.49 (Tr-H, 3H, m), 8.05-8.02 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.96-7.93 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.86-7.74 (Tr-H, Flu-H, 14H, m), 7.41-7.32 (Flu-H, 6H, m), 3.08-2.96 (CH₂, 6H, m), 2.28-2.08 (CH₂, 14H, m), 1.111-0.587 (110H, m). ¹³C NMR (CDCl₃, 75 Hz, ppm, δ): 191.85, 154.59, 154.38, 154.29, 151.49, 150.95, 147.33, 145.63, 145.43, 145.11, 141.02, 140.80, 140.45, 139.99, 139.63, 139.40, 139.36, 138.30, 138.20, 137.72, 137.43, 135.07, 130.34, 127.55, 127.03, 126.80, 125.95, 125.52, 125.28, 125.04, 124.95, 122.88, 121.18, 120.79, 120.50, 119.95, 119.73, 55.89, 55.84, 55.18, 40.50, 37.10, 31.54, 31.49, 29.74, 29.56, 29.50, 29.42, 24.04, 23.79, 22.59, 22.31, 14.01, 13.91. MALDI-TOF, m/z : Calcd, 1615.2; Found: 1722 ([M+Ag]⁺), 1530 (M⁺-85).

13: NBS (0.307g, 1.72mmol) was added in portion to a solution of 10 (1.75g, 1.57mmol) in a mixture of CH₂Cl₂ (20 mL) and acetic acid (20 mL) at 0 °C. The mixture was stirred for 0.5h, and added another portion of NBS (0.307g, 1.72mmol) then stirred for another 0.5h again. The result mixture was poured into water and extracted with CH₂Cl₂, the combined organic layers was washed with H₂O, saturated NaHCO₃ and brine, then dried over MgSO₄, after removing solvents in vacuo, the resulting residue was purified by column chromatograph on silica gel with elutant (hexane/EtOAc) to give yellow solids (1.80g, yield: 90%). ¹H NMR (CDCl₃, 300 Hz, ppm, δ): 10.11 (Ar-CHO, 1H, s), 8.47- 8.44 (Tr-H, 1H, d, $J = 8.4$ Hz), 8.38-8.34 (Tr-H, 2H, m), 8.05-8.02 (Ar-H, 2H, d, $J = 8.4$ Hz), 7.94-7.91 (Ar-H, 2H, d, $J = 8.4$

Hz), 7.74- 7.71 (Tr-H, 2H, m), 7.62-7.58 (Tr-H, 4H, m), 7.22-7.20 (Th-H, 2H, d, $J = 3.6$ Hz), 7.11-7.09 (Th-H, 2H, d, $J = 3.6$ Hz), 2.93-2.81 (CH₂, 6H, m), 2.15-2.03 (CH₂, 6H, m), 0.92-0.86 (CH₂, 36H, m), 0.624-0.606 (CH₂, CH₃, 30H, m). ¹³C NMR (CDCl₃, 50 MHz, ppm, δ): 191.82, 154.46, 147.21, 146.27, 145.72, 145.52, 145.45, 140.66, 139.97, 137.96, 137.83, 137.63, 135.11, 133.85, 131.83, 130.88, 130.33, 127.55, 125.57, 125.02, 123.83, 123.04, 120.79, 118.96, 111.14, 55.88, 37.03, 31.43, 29.42, 23.93, 22.23, 13.86. MALDI-TOF, m/z : Calcd, 1270.5; Found: 1377 ([M+Ag]⁺), 1186 (M⁺-85).

General procedure for Lindsey Condensation of Porphyrins Derivatives 1-6.

A solution of aldehyde (6, 7, 8, 9, 10, 11, or 12) (0.45 mmol), pyrrole (0.45 mmol) and ethanol (1 mL) in dry CH₂Cl₂ (112 mL) was degassed three times and stirred at room temperature for 45 min in the absence of light. The condensation was initiated by addition of BF₃•Et₂O in CH₂Cl₂ (0.15 mmol) followed by addition of another BF₃•Et₂O in CH₂Cl₂ (0.15 mmol) and CH₂Cl₂ (340 mL) after overnight. After stirred overnight again, DDQ (1 equivalents) was added, and the reaction mixture heated under reflux for 4 h. After addition of triethylamine (0.5 mmol), the reaction was stirred for 45 min, concentrated and chromatographed on silica gel with PE: CH₂Cl₂ to yield the purple solids.

1: yield: 30% (201 mg). ¹H NMR (CDCl₃, 300 Hz, ppm, δ): 9.10 (Por-H, 8H, s), 8.58-8.55 (Tr-H, 4H, d, $J = 8.4$ Hz), 8.47-8.45 (Tr-H, 8H, d, $J = 8.4$ Hz), 8.32-8.22 (Ar-H, 16H, m), 8.06-8.03 (Tr-H, 8H, m), 7.64-7.53 (Tr-H, 16H, m), 3.11-2.87 (CH₂, 24H, m), 2.29-2.02 (CH₂, 24H, m), 1.00-0.85 (CH₂, 144H, m), 0.70-0.55 (CH₂, CH₃, 120H, m), -2.55 (Por-H, 2H, s). ¹³C NMR (CDCl₃, 75 Hz, ppm, δ): 156.03, 155.92, 154.47, 145.66, 144.99, 144.59, 141.25, 140.32, 139.59, 139.13, 139.05, 138.85, 138.30, 137.67, 137.50, 135.28, 129.34, 125.89, 125.54, 125.39, 125.14, 120.92, 120.68, 120.06, 56.09, 55.95, 37.12, 36.88, 31.54, 31.49, 29.70, 29.56, 29.49, 29.42, 24.05, 23.92, 22.33, 22.29, 13.94, 13.92. MALDI-TOF, m/z : Calcd, 4627.5; Found: 4626 (M⁺), 4542 (M⁺-85).

2: yield: 30% (160 mg). ^1H NMR (CDCl_3 , 300 Hz, ppm, δ): 9.08 (Por-H, 8H, s), 8.62-8.59 (Tr-H, 4H, d, $J=8.4$ Hz), 8.49-8.45 (Tr-H, 8H, m), 8.45-8.42 (Ar-H, 8H, d, $J=8.4$ Hz), 8.24-8.22 (Ar-H, 8H, d, $J=8.4$ Hz), 8.07-8.02 (Tru-H, 8H, m), 7.71-7.67 (Tr-H, Ar-H, 32H, m), 7.35-7.32 (Ar-H, 16H, d, $J=8.4$ Hz), 3.14-3.05 (CH_2 , 24H, m), 2.45 (Ar- CH_3 , 24H, s), 2.34-2.19 (CH_2 , 24H, m), 1.00-0.85 (CH_2 , 144H, m), 0.70-0.64 (CH_2 , CH_3 , 120H, m), -2.54 (Por-H, 2H, s). ^{13}C NMR (CDCl_3 , 125 Hz, ppm, δ): 154.65, 154.29, 145.26, 145.18, 145.10, 141.15, 140.53, 140.19, 139.40, 139.03, 138.53, 138.20, 138.05, 136.95, 135.25, 129.66, 129.55, 126.96, 125.36, 125.17, 124.92, 120.65, 120.48, 120.10, 55.96, 55.82, 37.22, 37.11, 31.59, 31.56, 31.51, 29.60, 29.54, 24.04, 23.97, 22.34, 21.16, 13.94. MALDI-TOF, m/z : calcd, 4717.3; found: 4717 (M^+).

3: yield: 25% (147 mg). ^1H NMR (CDCl_3 , 300 Hz, ppm, δ): 9.10 (Por-H, 8H, s), 8.65-8.62 (Tr-H, 4H, d, $J=8.4$ Hz), 8.55-8.49 (Tr-H, 8H, m), 8.47-8.45 (Ar-H, 8H, d, $J=8.4$ Hz), 8.27-8.24 (Ar-H, 8H, d, $J=8.4$ Hz), 8.10-8.05 (Tru-H, 8H, m), 7.90-7.87 (Ar-H, 16H, dd, $J=1.2$ Hz, $J=8.4$ Hz), 7.79-7.76 (Ar-H, Tr-H, 32H, m), 7.72-7.70 (Ar-H, 16H, dd, $J=1.2$ Hz, $J=8.4$ Hz), 7.53-7.48 (Ar-H, 16H, m), 7.42-7.37 (Ar-H, 8H, m), 3.22-3.15 (CH_2 , 24H, m), 2.22-2.18 (CH_2 , 24H, m), 1.28-0.92 (CH_2 , 144H, m), 0.73-0.56 (CH_2 , CH_3 , 120H, m), -2.46 (Por-H, 2H, s). ^{13}C NMR (CDCl_3 , 75 Hz, ppm, δ): 154.67, 154.42, 145.38, 141.23, 140.81, 140.29, 140.31, 140.16, 140.06, 139.78, 138.60, 138.21, 135.29, 129.09, 128.87, 127.81, 127.59, 127.47, 127.37, 127.08, 125.48, 125.41, 125.23, 125.09, 125.04, 120.71, 120.56, 120.15, 56.05, 37.28, 31.62, 29.66, 24.13, 22.40, 14.00. MALDI-TOF, m/z : Calcd, 5213.8; Found: 5214 (M^+).

4: yield: 20% (147 mg). ^1H NMR (CDCl_3 , 500 Hz, ppm, δ): 9.13 (Por-H, 8H, s), 8.65-8.63 (Tr-H, 4H, d, $J=8.4$ Hz), 8.49-8.48 (Ar-H, 8H, d, $J=8.4$ Hz), 8.45-8.43 (Tr-H, 4H, d, $J=8.4$ Hz), 8.29-8.27 (Ar-H, 8H, d, $J=8.4$ Hz), 8.12-8.08 (Tru-H, 8H, m), 7.78-7.75 (Tr-H, 16H, m), 7.53-7.52 (Th-H, 8H, m), 7.38-7.36 (Th-H, 8H, m),

7.20-7.18 (Th-H, 8H, m), 3.12-3.06 (CH₂, 24H, m), 2.37-2.20 (CH₂, 24H, m), 1.08-0.94 (CH₂, 144H, m), 0.71-0.51 (CH₂, CH₃, 120H, m), -2.53 (Por-H, 2H, s). ¹³C NMR (CDCl₃, 75 Hz, ppm, δ): 154.62, 154.46, 145.29, 145.19, 144.95, 141.20, 140.47, 140.01, 139.85, 138.62, 138.09, 135.26, 132.50, 128.11, 125.46, 125.37, 125.17, 125.00, 124.58, 124.18, 122.93, 120.68, 120.10, 119.36, 55.98, 55.88, 37.16, 31.59, 31.56, 29.58, 29.53, 24.05, 22.35, 13.94. MALDI-TOF, *m/z*: Calcd, 4653.3; Found: 4654(M⁺).

5: yield: 18% (114 mg). ¹H NMR (CDCl₃, 300 Hz, ppm, δ): 9.13 (Por-H, 8H, s), 8.66-8.63 (Tr-H, 4H, d, *J* = 8.4 Hz), 8.50-8.48 (Ar-H, H, d, *J* = 8.4 Hz), 8.48-8.43 (Tru-H, 8H, m), 8.29-8.27 (Ar-H, 8H, d, *J* = 8.4 Hz), 8.12-8.08 (Tr-H, 8H, m), 7.76-7.74 (Tr-H, 16H, m), 7.45-7.43 (Th-H, 8H, m), 7.31-7.26 (Th-H, 24H, m), 7.11-7.08 (Th-H, 8H, m), 3.23-3.03 (CH₂, 24H, m), 2.36-2.23 (CH₂, 24H, m), 0.99-0.80 (CH₂, 144H, m), 0.71-0.48 (CH₂, CH₃, 120H, m), -2.51 (Por-H, 2H, s). ¹³C NMR (CDCl₃, 75 Hz, ppm, δ): 154.53, 145.35, 145.19, 143.60, 141.22, 140.45, 139.95, 138.67, 138.18, 138.03, 137.59, 136.50, 135.32, 132.18, 127.92, 125.47, 125.02, 124.69, 124.32, 123.85, 123.58, 120.69, 120.16, 118.99, 55.98, 55.89, 37.13, 37.94, 31.58, 31.55, 29.61, 24.03, 22.71, 22.37, 22.33, 14.00. 13.98. MALDI-TOF, *m/z*: Calcd, 5310.2; Found: 5310(M⁺).

6: yield: 15% (129 mg). ¹H NMR (CDCl₃, 300 Hz, ppm, δ): 9.11 (Por-H, 8H, s), 8.66-8.64 (Tr-H, 4H, d, *J* = 8.4 Hz), 8.54-8.52 (Tr-H, 8H, m), 8.48-8.45 (Ar-H, 8H, d, *J* = 8.4 Hz), 8.27-8.25 (Ar-H, 8H, d, *J* = 8.4 Hz), 8.11-8.06 (Ar-H, 8H, m), 7.91-7.76 (Tr-H, Flu-H, 48H, m), 7.38-7.25 (Flu-H, 24H, m), 3.17-3.11 (CH₂, 24H, m), 2.35-2.33 (CH₂, 24H, m), 2.28-2.09 (CH₂, 32H, m), 1.10-0.67 (CH₂, 440H, m), -2.53 (Por-H, 2H, s). ¹³C NMR (CDCl₃, 75 Hz, ppm, δ): 154.70, 154.45, 154.29, 151.52, 150.98, 145.35, 145.22, 141.22, 140.84, 140.46, 140.08, 139.58, 138.60, 135.25, 135.33, 127.04, 126.84, 126.00, 125.30, 122.90, 121.24, 120.56, 120.00, 119.76, 55.92, 55.21, 40.54, 37.17, 37.70, 31.60, 31.53, 30.17, 29.77, 29.64, 24.11, 23.82, 22.63, 22.38, 14.02. MALDI-TOF, *m/z*: Calcd, 6656.6; Found: 6657(M⁺).

References:

1. Seybold, P.; Gouterman, M. *J. Molecular Spectrosc.* **1969**, *31*, 1.
2. Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.
3. Pei, J.; Wang, J.-L.; Cao, X.-Y.; Zhou, X.-H.; Zhang, W.-B. *J. Am. Chem. Soc.* **2003**, *125*, 9944.
4. Clouston, D. *Inorg. Synth.* 1972, *13*, 121.
5. Stephen L. M.; Barry D. O.; William A. G. III. *J. Phys. Chem.* **1990**; *94*, 8897.

Figure S1. Normalized absorbance (left) and fluorescence (right) spectra of **1** in solution and film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

Figure S2. Normalized absorbance (left) and fluorescence (right) spectra of **2** in solution and film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

Figure S3. Normalized absorbance (left) and fluorescence (right) spectra of **3** in solution and film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

Figure S4. Normalized absorbance (left) and fluorescence (right) spectra of **4** in solution and film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

Figure S5. Normalized absorbance (left) and fluorescence (right) spectra of **5** in solution and film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

Figure S6. Normalized absorbance (left) and fluorescence (right) spectra of **6** in solution and film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

Figure S7. PL, PLE, and absorption spectra of **1** in solution. The spectra have been normalized for ease of comparison.

Figure S8. PL, PLE, and absorption spectra of **2** in solution. The spectra have been normalized for ease of comparison.

Figure S9. PL, PLE, and absorption spectra of **3** in solution. The spectra have been normalized for ease of comparison.

Figure S10. PL, PLE, and absorption spectra of **4** in solution. The spectra have been normalized for ease of comparison.

Figure S11. PL, PLE, and absorption spectra of **5** in solution. The spectra have been normalized for ease of comparison.

Figure S12. PL, PLE, and absorption spectra of **6** in solution. The spectra have been normalized for ease of comparison.

Figure S13. Normalized absorbance (left) and fluorescence (right) spectra of **8-12** in solution at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

Table S1. Molecular weights and optical properties of porphyrins **1-6**.

Cmps.	abs. λ_{max} /nm		emis. λ_{max} /nm		ΦF	molecular weight
	solution	film	solution	film		
1	315, 425	317, 433	371, 429, 640	365, 440, 647	0.19	4627
2	328, 425	325, 433	348, 444, 640	357, 446, 651	0.27	4717
3	334, 425	332, 433	390, 445, 640	649	0.26	5213
4	340, 425	340, 433	365, 427, 640	654	0.24	4653
5	375, 425	377, 434	400, 428, 640	650	0.23	5310
6	341, 426	339, 433	380, 426, 640	648	0.30	6656

Figure S14. Dreiding force field optimized geometry for **2** (the diameter of **2** is 4.4 nm).

Figure S15. Dreiding force field optimized geometry for **3** (the diameter of **3** is 5.0 nm).

Figure S16. Dreiding force field optimized geometry for **4** (the diameter of **4** is 4.3 nm).

Figure S17. Dreiding force field optimized geometry for **5** (the diameter of **5** is 5.2 nm).

Figure S18. Dreiding force field optimized geometry for **6** (the diameter of **6** is 5.0 nm).

Figure S19: ¹H Spectra for 1

Figure S20: ^{13}C Spectra for 1

Figure S21: MALDI-TOF Mass Spectroscopy for 1

Figure S22: ^1H Spectra for 2

Figure S23: ^{13}C Spectra for 2

Figure S25: ^1H Spectra for 3

Figure S26: ^{13}C Spectra for 3

Figure S27: MALDI-TOF Mass Spectroscopy for 3

Figure S30: MALDI-TOF Mass Spectroscopy for 4

Figure S31: ^1H Spectra for 5

Figure S32: ^{13}C Spectra for 5

Figure S33: MALDI-TOF Mass Spectroscopy for 5

Figure S34: ^1H Spectra for 6

S38

Figure S36: MALDI-TOF Mass Spectroscopy for 6

Archive directory: /export/home/vmar1/vmar1/s/data
 Sample directory: /export/home/vmar1/vmar1/s/data
 File: PROTON
 Pulse Sequence: szpu1

Figure S37: ^1H Spectra for 7

Figure S38: ¹³C Spectra for 7

Figure S39: MALDI-TOF Mass Spectroscopy for 7

Figure S40: ^1H Spectra for 8

Figure S41: ^{13}C Spectra for 8

Figure S42: MALDI-TOF Mass Spectroscopy for 8

Figure S43: ^1H Spectra for 9

Figure S45: MALDI-TOF Mass Spectroscopy for 9

Figure S46: ^1H Spectra for 10

Figure S47: ^{13}C Spectra for 10

Figure S48: MALDI-TOF Mass Spectroscopy for 10

Figure S49: ^1H Spectra for 11

Figure S50: ^{13}C Spectra for 11

Figure S51: MALDI-TOF Mass Spectroscopy for 11

Figure S52: ^1H Spectra for 12

Figure S53: ^{13}C Spectra for 12

Figure S55: ^1H Spectra for **13**

Figure S56: ^{13}C Spectra for 13

Figure S57: MALDI-TOF Mass Spectroscopy for 13