

Supporting Information

Energy Transfer Pathways and Triplet Lifetime Manipulation in a Zinc Porphyrin / F8BT Hybrid Polymer

Jordan Shaikh,[†] David M E Freeman,^{†,§} Hugo Bronstein,^{†,‡} and Tracey M Clarke.^{†,*}

[†] Department of Chemistry, University College London, Christopher Ingold Building, London, WC1H 0AJ, United Kingdom

[§] Department of Chemistry, Imperial College London, Exhibition Road, London, UK SW7 2AZ

[‡] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

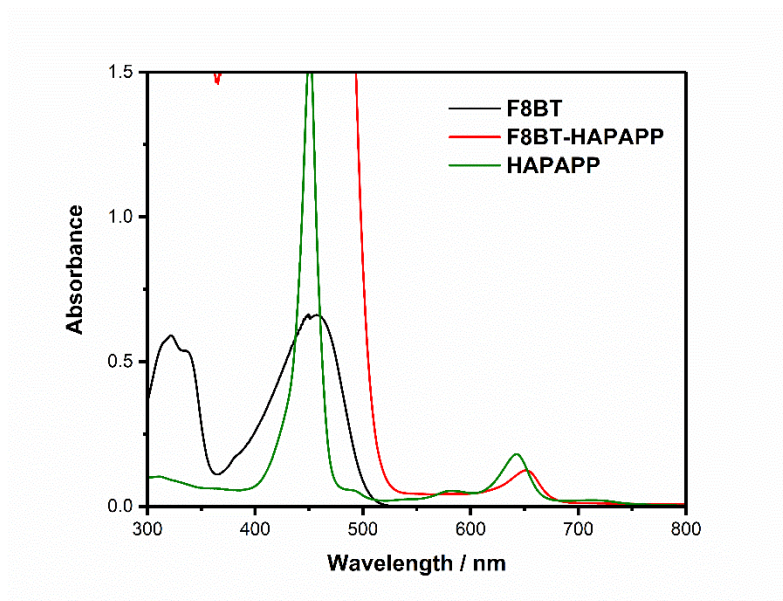


Figure S1. Steady state absorption spectra of F8BT, F8BT-HAPAPP and HAPAPP, in chlorobenzene solution. Concentrations were 68 $\mu\text{g/mL}$, 0.65 mg/mL and 34 $\mu\text{g/mL}$ for F8BT, F8BT-HAPAPP and HAPAPP respectively. These concentrations were for transient absorption measurements, such that excitation at the Q-band would excite similar ground state absorbance. The relatively high concentration of F8BT-HAPAPP was necessary due to the low absorbance of the Q-band (because of the low concentration of HAPAPP inside the polymer chain, and subsequent low porphyrin transient signals). Note that lower concentrations of F8BT-HAPAPP were also checked for concentration / quenching effects – none were observed for this range of concentrations.

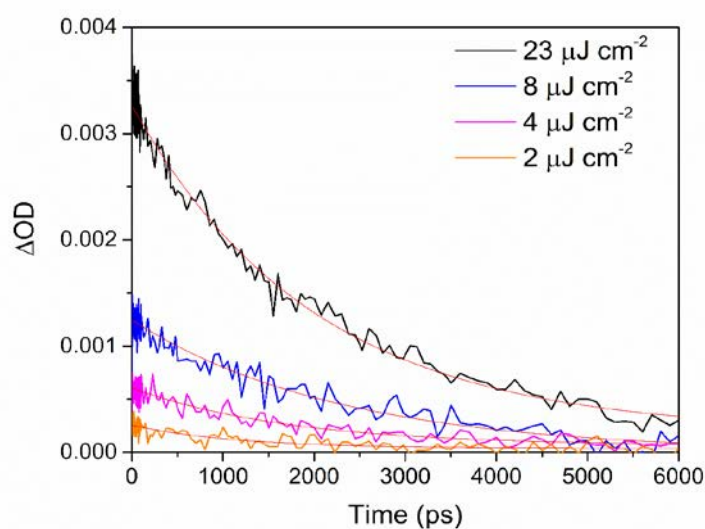


Figure S2. Picosecond transient absorption decay kinetics of F8BT excited at 518 nm, with a probe wavelength of 940 nm. Sample was in chlorobenzene degassed with argon (3.4 mg/mL). The red lines are monoexponential fits.

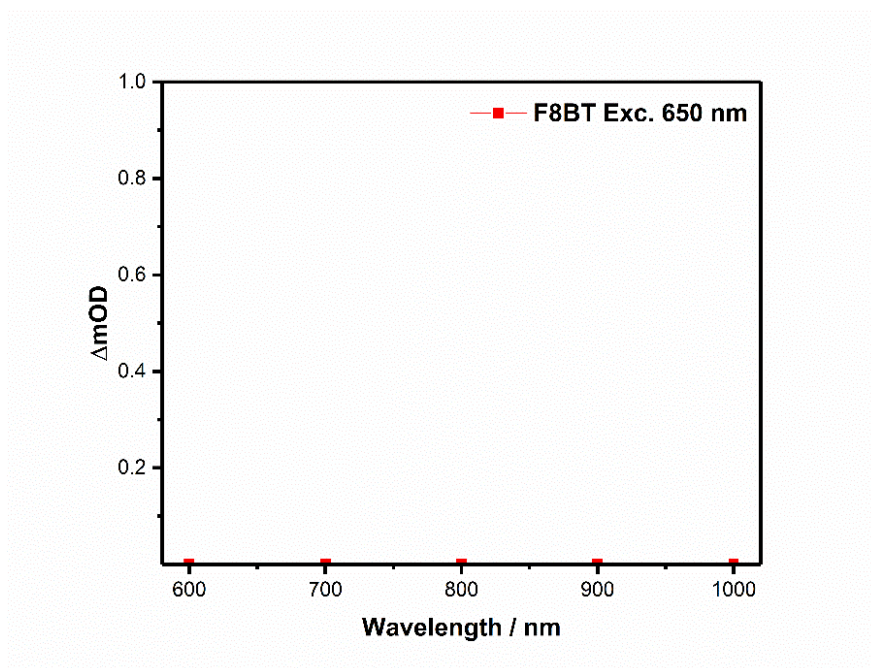


Figure S3. μ s TAS spectrum of F8BT in chlorobenzene solution ($68 \mu\text{g/mL}$), obtained with a pump wavelength of 650 nm and at an excitation density of $12 \mu\text{J cm}^{-2}$. Spectrum recorded at 1 μ s. No spectral response is observed at this excitation wavelength.

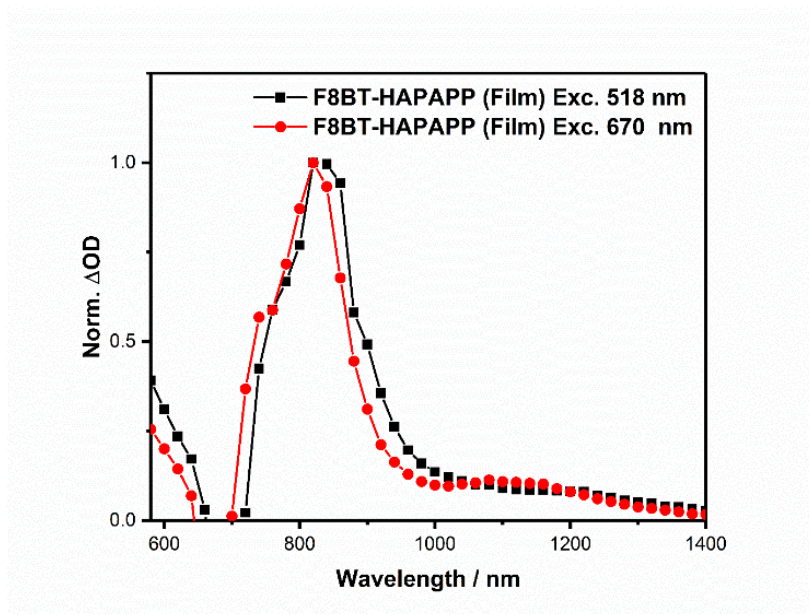


Figure S4. Microsecond transient absorption of F8BT-HAPAPP thin film. Spectra taken at 10 μ s. Spectra are normalised to their respective peak maxima. Energy densities of 15 and $3 \mu\text{J cm}^{-2}$ were used for excitation at 518 and 670 nm respectively. The same triplet energy transfer from F8BT to the HAPAPP as seen in the solution appears to occur in the thin film as well.

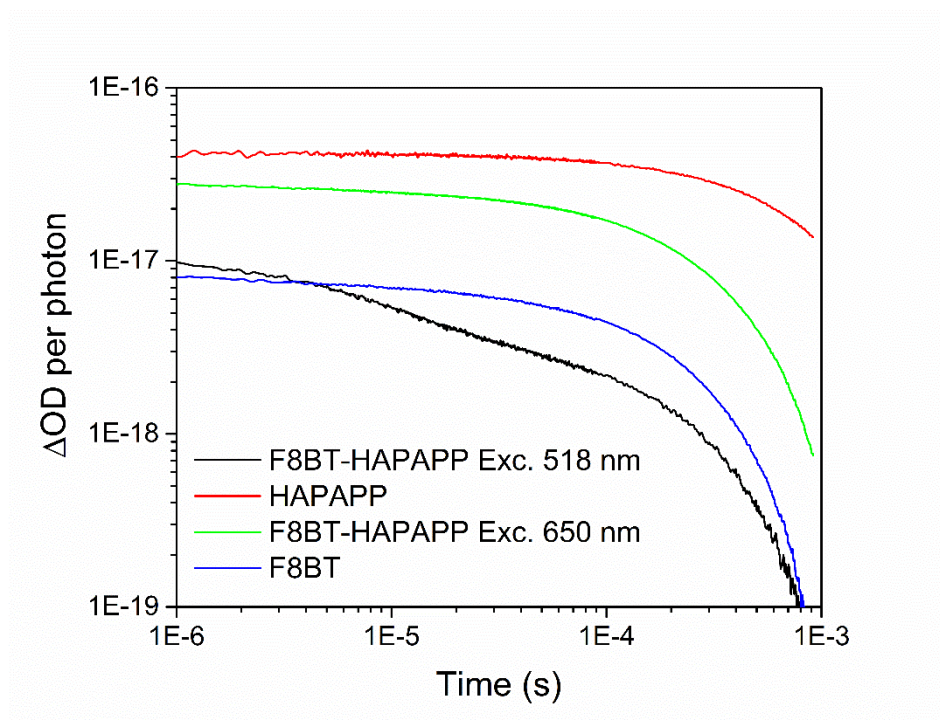


Figure S5. Microsecond transient absorption kinetics of the different samples corrected for photons absorbed. The excitation wavelengths for the controls are 460 nm for F8BT and 640 nm for HAPAPP. The excitation density used was approximately $7 \mu\text{J cm}^{-2}$.

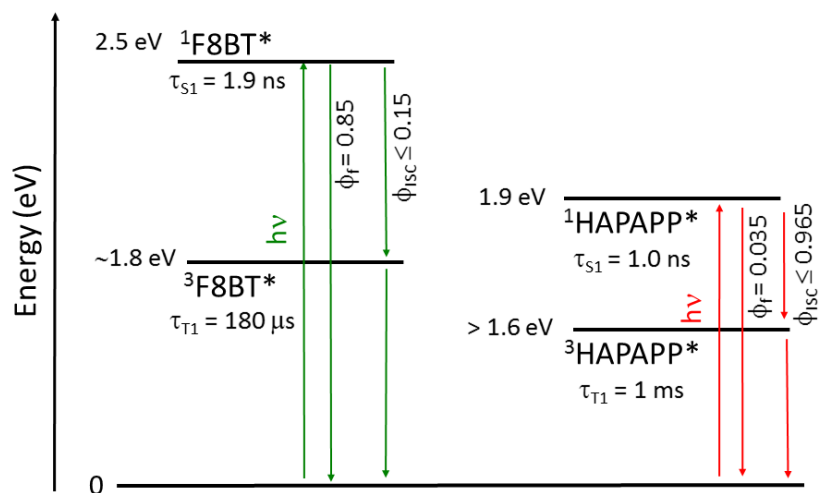


Figure S6. State diagram for the proposed photophysical mechanisms in the control F8BT and HAPAPP solutions (not to scale). Since the S_1 - T_1 gap of conjugated polymers is usually invariant at (approximately) 0.7 eV, the F8BT T_1 energy is approximately 1.8 eV, since analysis of the steady state absorbance and emission spectrum suggest the S_1 state to be at 2.5 eV in solution. Internal conversion is not shown.

Table S1. Selected TD-DFT results for HAPAPP and an F8BT-HAPAPP model using B3LYP/6-31G(d)

Molecule	State	Transition	Coefficient
HAPAPP	T ₁	HOMO→LUMO	0.70
F8BT-HAPAPP	T ₁	HOMO→LUMO	0.68
F8BT-HAPAPP	T ₁	HOMO→LUMO+2	-0.12

Synthesis

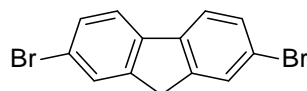
Reagents and Solvents: All reagents and solvents were used as received. MeOH, CH₂Cl₂ and *n*-hexane were HiPerSolv grade. Et₂O and EtOAc were GPR grade. Pet 40-60 refers to BDH AnalaR petroleum spirit 40-60 °C. All other chemicals were used as supplied unless otherwise indicated.

Experimental techniques: All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise indicated. Air and moisture sensitive reagents were transferred by syringe. Reactions performed at temperatures other than rt were recorded as silicon oil bath temperatures. The phrase “concentrated *in vacuo*” refers to rotary evaporation. Brine refers to an aqueous solution of NaCl. Column chromatography was carried out using BDH (40-60 μm) silica gel and analytical thin layer chromatography was carried out using Merck Kieselgel aluminium-backed plates coated with silica gel. If necessary, components were visualised using combinations of ultra-violet light and potassium permanganate.

Characterisation: ¹H NMR spectra were recorded at 300 MHz on a Bruker AMX300 spectrometer, at 500 MHz on a Bruker Avance 500 spectrometer, or at 600 MHz on a Bruker Avance 600 spectrometer in the stated solvent using residual protic solvent CHCl₃ (δ = 7.26 ppm, s), DMSO (δ = 2.56 ppm, qn) or pyridine (δ = 8.74 ppm, s; 7.58 ppm, s; 7.22 ppm, s) as the internal standard. Chemical shifts are quoted in ppm using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet; br, broad or a combination of these. The coupling constants (*J*) are measured in Hertz. ¹³C NMR spectra were recorded at 75 MHz on a Bruker AMX300 spectrometer, at 125 MHz on a Bruker Avance 500 spectrometer or at 150 MHz on a Bruker Avance 600 spectrometer in the stated solvent using the central reference of CHCl₃ (δ = 77.0 ppm, t), DMSO (δ = 39.52 ppm, septet) as the internal standard. Chemical shifts are reported to the nearest 0.1 ppm. UV-visible spectra were recorded, at room temperature, on a Thermo Unicam UV500 spectrometer, in CH₂Cl₂ solutions at concentrations of ~10⁻⁵ M. Thin films of polymers were spin coated from CH₂Cl₂ solutions of 10 mg/mL on a Laurell spin coater at 2000 rpm for 30 s. Mass spectra was obtained from the mass spectrometry service at

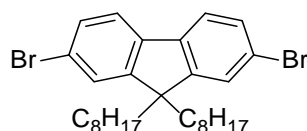
the Department of Chemistry, University College London. Number-average (M_n) and weight-average (M_w) molecular weights were determined against a polystyrene standard using an Agilent Technologies 1200 series GPC in chlorobenzene at 80 °C.

2,7-dibromo-9H-fluorene



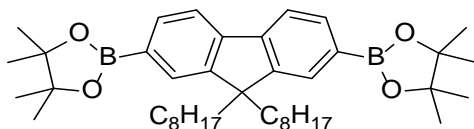
To a solution of fluorene (9.97 g, 60.0 mmol) and I_2 (1.52 g, 6.0 mmol) in CH_2Cl_2 (120 mL) at 0 °C in the absence of light was added a solution of Br_2 (6.50 mL, 126.0 mmol) in CH_2Cl_2 (24 mL) over 10 min. The reaction mixture was stirred at rt for 6 h. The reaction was quenched with Na_2SO_3 solution and the organic product was extracted with CH_2Cl_2 (100 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated *in vacuo*. The resultant white powder was recrystallised from EtOAc to yield the product as white crystals (10.18 g, 31.4 mmol, 52%). 1H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 2H, CH_2CCH), 7.60 (d, J = 8.1 Hz, 2H, $CBrCHCH$), 7.50 (d, J = 8.1 Hz, 2H, $CBrCHCH$), 3.87 (s, 2H, CH_2); MS (Cl^+) m/z 322, 324 and 326 (M)⁺. All spectroscopic data is in accordance with literature values.¹

2,7-dibromo-9,9-dioctyl-9H-fluorene



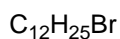
2,7-dibromofluorene (4.0 g, 12.34 mmol) and 1-bromooctane (6.40 mL, 37.04 mmol) in a 1:1 mixture of 13 M NaOH solution and toluene (60 mL) were degassed. Tetrabutylammonium bromide (40 mg, 0.12 mmol) was added and the reaction was heated to reflux for 18 h. The reaction was allowed to cool, the organic layer separated and the aqueous washed with CH_2Cl_2 (2 x 50 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated *in vacuo* to yield a yellow solid which was recrystallized from EtOH to give off white crystals (4.24 g, 7.74 mmol, 63%). 1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.9 Hz, 2H, $CBrCHCH$), 7.45 (m, 4H, CH_2CCH + $CBrCHCH$), 1.95 – 1.86 (m, 4H, $C(CH_2CH_2C_5H_{10}CH_3)_2$), 1.27 – 1.17 (m, 4H, $C(CH_2CH_2C_5H_{10}CH_3)_2$), 1.17 – 1.00 (m, 16H, $C(CH_2CH_2C_5H_{10}CH_3)_2$), 0.83 (t, J = 7.2 Hz, 6H, $C(CH_2CH_2C_5H_{10}CH_3)_2$), 0.64 – 0.53 (m, 4H, $C(CH_2CH_2C_5H_{10}CH_3)_2$); MS (El^+) m/z 546, 548 and 550 (M)⁺. All spectroscopic data is in accordance with literature values.²

2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



2,7-dibromo-9,9-dioctyl-9H-fluorene (1.0 g, 1.82 mmol) in THF (40 mL) was stirred under argon at -78 °C. 2.5 M n-butyllithium (1.28 mL, 3.82 mmol) was added slowly and the reaction was stirred at -78 °C for a further 2 h. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.11 mL, 5.46 mmol) was added and the reaction mixture was allowed to warm to rt and stirred for 64 h. H₂O (50 mL) was added and the organic product was extracted with Et₂O (2 x 50 mL). The organic fractions were dried over MgSO₄, and concentrated *in vacuo* and the product was recrystallized from acetone (631 mg, 0.98 mmol, 54%). ¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 7.5 Hz, 2H, CBCHCH), 7.74 (s, 2H, C(C₈H₁₇)₂CCH), 7.72 (d, *J* = 7.5 Hz, 2H, CBCHCH), 2.02 – 1.96 (m, 4H, C(CH₂C₆H₁₂CH₃)₂), 1.38 (s, 24H, OC(CH₃)₂), 1.23 – 0.95 (m, 24H, C(CH₂C₆H₁₂CH₃)₂), 0.80 (t, *J* = 7.3 Hz, 6H, C(CH₂C₆H₁₂CH₃)₂); MS (EI⁺) *m/z* 640, 642 and 644 (M)⁺. All spectroscopic data is in accordance with literature values.³

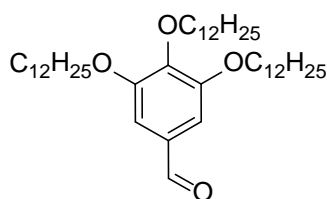
1-Bromododecane



NBS (28.7 g, 161.00 mmol) was added in portions to 1-Dodecanol (20.0 g, 107.34 mmol) and PPh₃ (42.2 g, 161.00 mmol) in CH₂Cl₂ (500 mL) at 0 °C. The reaction mixture was stirred for 2 h. The reaction mixture was quenched with saturated Na₂SO₃ solution (300 mL), the product was extracted with CH₂Cl₂ (3 x 250 mL), dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified *via* column chromatography (SiO₂, Eluent hexane) and was isolated as a colourless liquid (23.39 g, 101.87 mmol, 95%). ¹H NMR (600 MHz, CDCl₃) δ 3.41 (t, *J* = 6.9 Hz, 2H, BrCH₂CH₂CH₂C₈H₁₆CH₃), 1.90 – 1.82 (m, 2H, BrCH₂CH₂CH₂C₈H₁₆CH₃), 1.46 – 1.38 (m, 2H, BrCH₂CH₂CH₂C₈H₁₆CH₃), 1.35 – 1.21 (m, 16H,

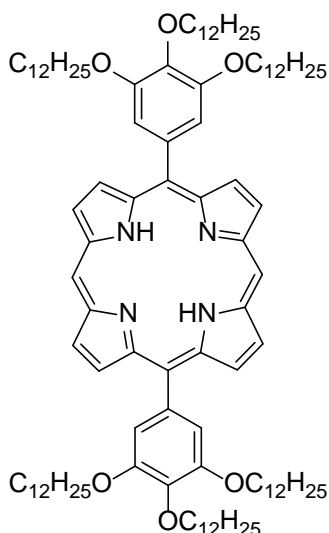
BrCH₂CH₂CH₂C₈H₁₆CH₃), 0.88 (t, *J* = 7.1 Hz, 3H, BrCH₂CH₂CH₂C₈H₁₆CH₃); MS (EI⁺) *m/z* 248, 250 (M)⁺. All spectroscopic data is in accordance with literature values.⁴

3,4,5-tris(dodecyloxy)benzaldehyde



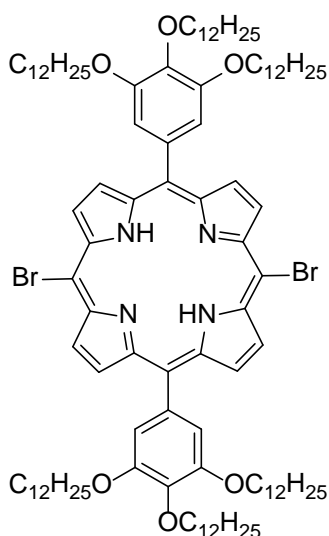
1-bromododecane (5.0 g, 20.15 mmol), 3,4,5-Trihydroxybenzaldehyde monohydrate (578 mg, 3.36 mmol), K₂CO₃ (1.39 g, 10.06 mmol) and KI (33 mg, 0.20 mmol) were dissolved in DMF (20 mL). The reaction mixture was heated at 70 °C for 18 h. The product was extracted with CHCl₃ (40 mL) from brine (40 mL) and the organic layer was further washed with brine (3 x 40 mL). The organic layer was dried over MgSO₄, concentrated *in vacuo* and the product was recrystallised from CHCl₃/MeOH (1.27 g, 1.93 mmol, 57%). ¹H NMR (600 MHz, CDCl₃) δ 9.83 (s, 1H, COH), 7.08 (s, 2H, CHCCOH), 4.07 – 4.02 (m, 6H, OCH₂CH₂CH₂(C₇H₁₄)CH₃), 1.86 – 1.80 (m, 4H, *meta*OCH₂CH₂CH₂(C₇H₁₄)CH₃), 1.78 – 1.72 (m, 2H, *para*OCH₂CH₂CH₂(C₇H₁₄)CH₃), 1.51 – 1.45 (m, 6H, OCH₂CH₂CH₂(C₇H₁₄)CH₃), 1.39 – 1.22 (m, 42H, OCH₂CH₂CH₂(C₇H₁₄)CH₃), 0.88 (t, *J* = 7.0 Hz, 9H, OCH₂CH₂CH₂(C₇H₁₄)CH₃); MS (CI⁺) *m/z* 659 (M[+H])⁺. All spectroscopic data is in accordance with literature values.⁵

5,15-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrin



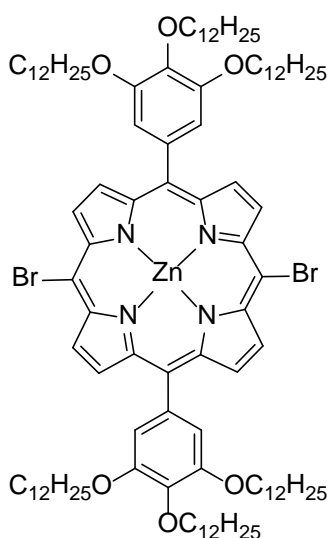
3,4,5-tris(dodecyloxy)benzaldehyde (742 mg, 1.13 mmol), dipyrromethane (165 mg, 1.13 mmol) and CH_2Cl_2 (400 mL) were degassed with argon for 10 min. Trifluoroacetic acid (0.03 mL, 0.34 mmol) was added and the reaction mixture was stirred at rt under argon in the dark for 2 h. DDQ (385 mg, 1.70 mmol) was added and the reaction mixture was stirred for a further 1 h. The reaction mixture was passed through a plug of silica using CH_2Cl_2 as eluent and concentrated *in vacuo*. The crude product was further purified *via* column chromatography (SiO_2 , Eluent Hexane: CHCl_3 (9:1 to 1:4)) and washed with MeOH and acetone to yield a thick oil (150 mg, 0.096 mmol, 8%). ^1H NMR (600 MHz, CDCl_3) δ 10.31 (s, 2H, NHCCH), 9.39 (d, $J = 4.5$ Hz, 4H, NCCHCH), 9.19 (d, $J = 4.5$ Hz, 4H, NCCHCH), 7.48 (s, 4H, OCCH), 4.32 (t, $J = 6.5$ Hz, 4H, $\text{NCCCCHC(OC}_{12}\text{H}_{25})\text{COCH}_2\text{C}_{11}\text{H}_{23}$), 4.14 (t, $J = 6.4$ Hz, 8H, $\text{NCCCCHC(OCH}_2\text{C}_{11}\text{H}_{23})\text{COC}_{12}\text{H}_{25}$), 2.03 – 1.96 (m, 4H, $\text{NCCCCHC(OC}_{12}\text{H}_{25})\text{COCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$), 1.93 – 1.87 (m, 8H, $\text{NCCCCHC(OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21})\text{COC}_{12}\text{H}_{25}$), 1.72 – 1.65 (m, 4H, $\text{NCCCCHC(OC}_{12}\text{H}_{25})\text{COC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19}$), 1.55 – 1.18 (m, 104H, $\text{NCCCCHC(OC}_{12}\text{H}_{25})\text{COC}_3\text{H}_6\text{C}_8\text{H}_{16}\text{CH}_3$ and $\text{NCCCCHC(OC}_2\text{H}_4\text{C}_9\text{H}_{18}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$), 0.91 (t, $J = 7.0$ Hz, 6H, $\text{NCCCCHC(OC}_{12}\text{H}_{25})\text{COC}_{11}\text{H}_{22}\text{CH}_3$), 0.85 (t, $J = 7.0$ Hz, 12H, $\text{NCCCCHC(OC}_{11}\text{H}_{22}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$), -3.12 (s, 2H, NH); MS (TOF LD^+) m/z 1568 (M) $^+$.

Country	Year	Population (millions)	GDP (billions of USD)	Urban population (%)	Population growth (%)	GDP growth (%)	Urban population growth (%)	Population growth (%)	GDP growth (%)	Urban population growth (%)
China	1990	1150	100	30	1.5	8.5	1.5	1.5	8.5	1.5
China	2000	1250	1000	40	1.2	8.5	1.2	1.2	8.5	1.2
China	2010	1350	5800	50	0.5	11.5	0.5	0.5	11.5	0.5
India	1990	850	100	25	1.8	5.5	1.8	1.8	5.5	1.8
India	2000	1000	500	30	1.5	7.5	1.5	1.5	7.5	1.5
India	2010	1150	1800	35	1.2	9.5	1.2	1.2	9.5	1.2
USA	1990	250	6000	75	0.5	3.5	0.5	0.5	3.5	0.5
USA	2000	270	10000	78	0.4	4.5	0.4	0.4	4.5	0.4
USA	2010	290	14000	80	0.3	5.5	0.3	0.3	5.5	0.3



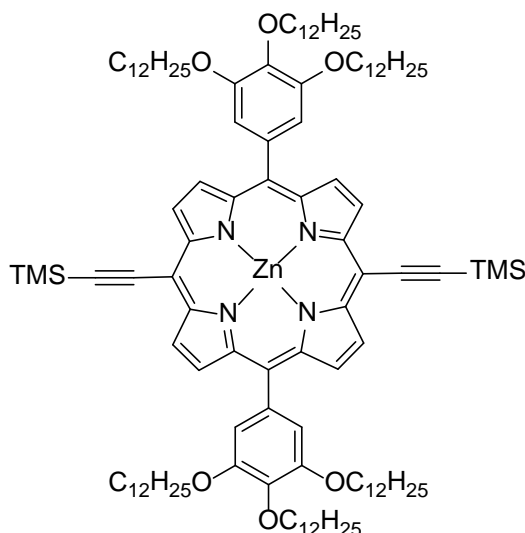
To a solution of 5,15-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrin (150 mg, 0.10 mmol) in CHCl_3 (15 mL) was added NBS (43 mg, 0.24 mmol) and pyridine (0.1 mL) and the reaction mixture was stirred for 2 h at rt under argon in the dark. The reaction mixture was concentrated *in vacuo* and purified *via* column chromatography (SiO_2 , Eluent Hexane: CHCl_3 (8:1 to 0:1)) to yield the product as a thick oil (165 mg, 0.10 mmol, quant) which was taken into the next reaction without further purification. ^1H NMR (300 MHz, CDCl_3) δ 9.61 (d, J = 4.6 Hz, 4H, NCCHCH), 8.95 (d, J = 4.7 Hz, 4H, NCCHCH), 7.37 (s, 4H, OCCH), 4.30 (t, J = 6.5 Hz, 4H, NCCCCHC(OC₁₂H₂₅)COCH₂C₁₁H₂₃), 4.10 (t, J = 6.2 Hz, 8H, NCCCCHC(OCH₂C₁₁H₂₃)COC₁₂H₂₅), 2.02 – 1.85 (m, 12H, NCCCCHC(OC₁₂H₂₅)COCH₂CH₂C₁₀H₂₁ and NCCCCHC(OCH₂CH₂C₁₀H₂₁)COC₁₂H₂₅), 1.53 – 1.18 (m, 108H, NCCCCHC(OC₁₂H₂₅)COC₂H₄C₉H₁₈CH₃ and NCCCCHC(OC₂H₄C₉H₁₈CH₃)COC₁₂H₂₅), 0.95 – 0.80 (m, 18H, CH₃), -2.72 (s, 2H, NH); MS (TOF LD⁺) m/z 1726 (M)⁺.

5,15-dibromo-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato zinc (II)



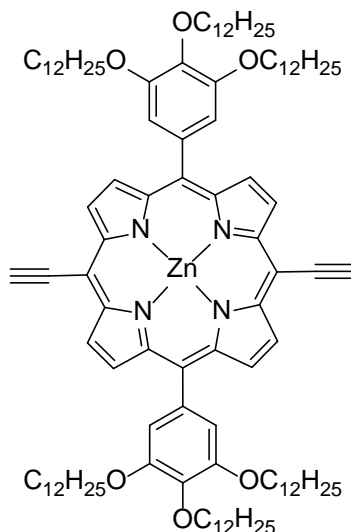
5,15-dibromo-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrin (165 mg, 0.10 mmol) and $\text{Zn}(\text{OAc})_2$ (351 mg, 1.912 mmol) were stirred in CH_2Cl_2 (30 mL) for 18 h at rt in the dark. The reaction mixture was concentrated *in vacuo* and purified *via* column chromatography (SiO_2 , Eluent Hexane: CHCl_3 (8:1 to 0:1)) to yield the product as a thick oil (100 mg, 0.06 mmol, 58%). ^1H NMR (600 MHz, CDCl_3) δ 9.74 (d, $J = 4.6$ Hz, 4H, NCCHCH), 9.07 (d, $J = 4.6$ Hz, 4H, NCCHCH), 7.38 (s, 4H, OCCH), 4.31 (t, $J = 6.6$ Hz, 4H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COCH}_2\text{C}_{11}\text{H}_{23}$), 4.10 (t, $J = 6.6$ Hz, 8H, $\text{NCCCCHC}(\text{OCH}_2\text{C}_{11}\text{H}_{23})\text{COC}_{12}\text{H}_{25}$), 2.02 – 1.96 (m, 4H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$), 1.91 – 1.85 (m, 8H, $\text{NCCCCHC}(\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21})\text{COC}_{12}\text{H}_{25}$), 1.71 – 1.65 (m, 4H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19}$), 1.53 – 1.46 (m, 8H, $\text{NCCCCHC}(\text{OC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19})\text{COC}_{12}\text{H}_{25}$), 1.45 – 1.17 (m, 96H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COC}_3\text{H}_6\text{C}_8\text{H}_{16}\text{CH}_3$ and $\text{NCCCCHC}(\text{OC}_3\text{H}_6\text{C}_8\text{H}_{16}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$), 0.91 (t, $J = 7.1$ Hz, 6H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COC}_{11}\text{H}_{22}\text{CH}_3$), 0.85 (t, $J = 7.0$ Hz, 12H, $\text{NCCCCHC}(\text{OC}_{11}\text{H}_{22}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$); MS (TOF LD^+) m/z 1790 (M) $^+$.

5,15-bis((trimethylsilyl)ethynyl)-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato zinc (II)



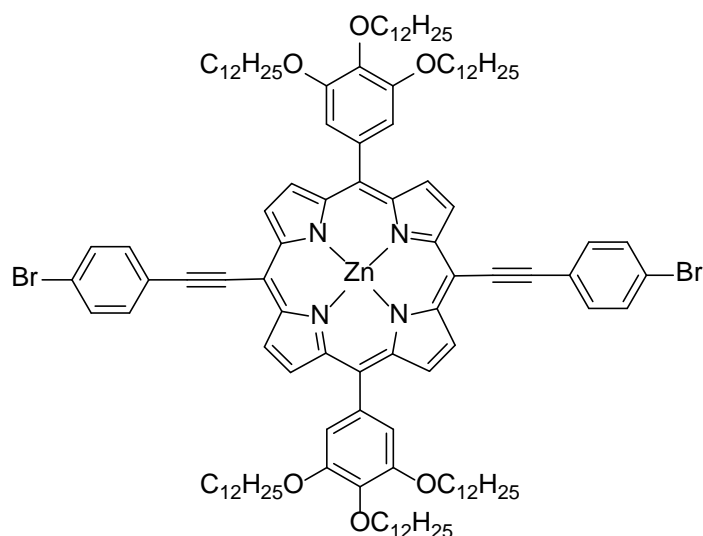
A mixture of triethylamine (30 mL) and THF (10 mL) was degassed with argon for 30 min before the addition of 5,15-dibromo-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato zinc (II) (100 mg, 0.06 mmol). Trimethylsilylacetylene (17 μ L, 0.12 mmol), Pd(PPh₃)₂Cl₂ (4 mg, 0.006 mmol) and CuI (2 mg, 0.011 mmol) were added, the reaction mixture was further degassed for 10 min at 0 °C and then allowed to warm to rt and stirred for 18 h under argon in the dark. The reaction mixture was concentrated *in vacuo* and purified *via* column chromatography (SiO₂, Eluent Hexane:CHCl₃ (8:1 to 0:1)) to yield the product as a thick oil (92 mg, 0.05 mmol, 90%). ¹H NMR (600 MHz, CDCl₃) δ 9.70 (d, *J* = 4.5 Hz, 4H, NCCHCH), 9.03 (d, *J* = 4.5 Hz, 4H, NCCHCH), 7.39 (s, 4H, OCCH), 4.31 (t, *J* = 6.5 Hz, 4H, NCCCCCHC(OC₁₂H₂₅)COCH₂C₁₁H₂₃), 4.11 (t, *J* = 6.4 Hz, 8H, NCCCCCHC(OCH₂C₁₁H₂₃)COC₁₂H₂₅), 2.02 – 1.95 (m, 4H, NCCCCCHC(OC₁₂H₂₅)COCH₂CH₂C₁₀H₂₁), 1.92 – 1.85 (m, 8H, NCCCCCHC(OCH₂CH₂C₁₀H₂₁)COC₁₂H₂₅), 1.72 – 1.64 (m, 4H, NCCCCCHC(OC₁₂H₂₅)COC₂H₄CH₂C₉H₁₉), 1.52 – 1.46 (m, 8H, NCCCCCHC(OC₂H₄CH₂C₉H₁₉)COC₁₂H₂₅), 1.46 – 1.17 (m, 96H, NCCCCCHC(OC₁₂H₂₅)COC₃H₆C₈H₁₆CH₃ and NCCCCCHC(OC₃H₆C₈H₁₆CH₃)COC₁₂H₂₅), 0.90 (t, *J* = 6.9 Hz, 6H, NCCCCCHC(OC₁₂H₂₅)COC₁₁H₂₂CH₃), 0.84 (t, *J* = 7.0 Hz, 12H, NCCCCCHC(OC₁₁H₂₂CH₃)COC₁₂H₂₅), 0.61 (s, *J* = 5.8 Hz, 18H, SiCH₃); MS (TOF LD⁺) *m/z* 1824 (M)⁺.

5,15-diethynyl-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato zinc (II)



5,15-bis((trimethylsilyl)ethynyl)-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato zinc (II) (46 mg, 0.025 mmol) was dissolved in CH_2Cl_2 (20 mL), a 1.0 M solution of TBAF in THF was added (0.1 mL, 0.1 mmol) was added and the reaction mixture was stirred for 18 h at rt under argon in the dark. The reaction mixture was concentrated *in vacuo* and purified *via* column chromatography (SiO_2 , Eluent Hexane: CH_2Cl_2 (8:1 to 0:1)) to yield the product as a thick oil (42 mg, 0.025 mmol, quant). ^1H NMR (600 MHz, CDCl_3) δ 9.75 (d, J = 4.6 Hz, 4H, NCCHCH), 9.07 (d, J = 4.6 Hz, 4H, NCCHCH), 7.40 (s, 4H, OCCH), 4.31 (t, J = 6.7 Hz, 4H, $\text{NCCCCCHC(OC}_{12}\text{H}_{25})\text{COCH}_2\text{C}_{11}\text{H}_{23}$), 4.20 (s, 2H, $\text{C}\equiv\text{CH}$), 4.11 (t, J = 6.5 Hz, 8H, $\text{NCCCCCHC(OCH}_2\text{C}_{11}\text{H}_{23})\text{COC}_{12}\text{H}_{25}$), 2.02 – 1.96 (m, 4H, $\text{NCCCCCHC(OC}_{12}\text{H}_{25})\text{COCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$), 1.92 – 1.85 (m, 8H, $\text{NCCCCCHC(OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21})\text{COC}_{12}\text{H}_{25}$), 1.72 – 1.65 (m, 4H, $\text{NCCCCCHC(OC}_{12}\text{H}_{25})\text{COC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19}$), 1.53 – 1.46 (m, 8H, $\text{NCCCCCHC(OC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19})\text{COC}_{12}\text{H}_{25}$), 1.46 – 1.18 (m, 96H, $\text{NCCCCCHC(OC}_{12}\text{H}_{25})\text{COC}_3\text{H}_6\text{C}_8\text{H}_{16}\text{CH}_3$ and $\text{NCCCCCHC(OC}_3\text{H}_6\text{C}_8\text{H}_{16}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$), 0.91 (t, J = 7.0 Hz, 6H, $\text{NCCCCCHC(OC}_{12}\text{H}_{25})\text{COC}_{11}\text{H}_{22}\text{CH}_3$), 0.85 (t, J = 7.1 Hz, 12H, $\text{NCCCCCHC(OC}_{11}\text{H}_{22}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$).

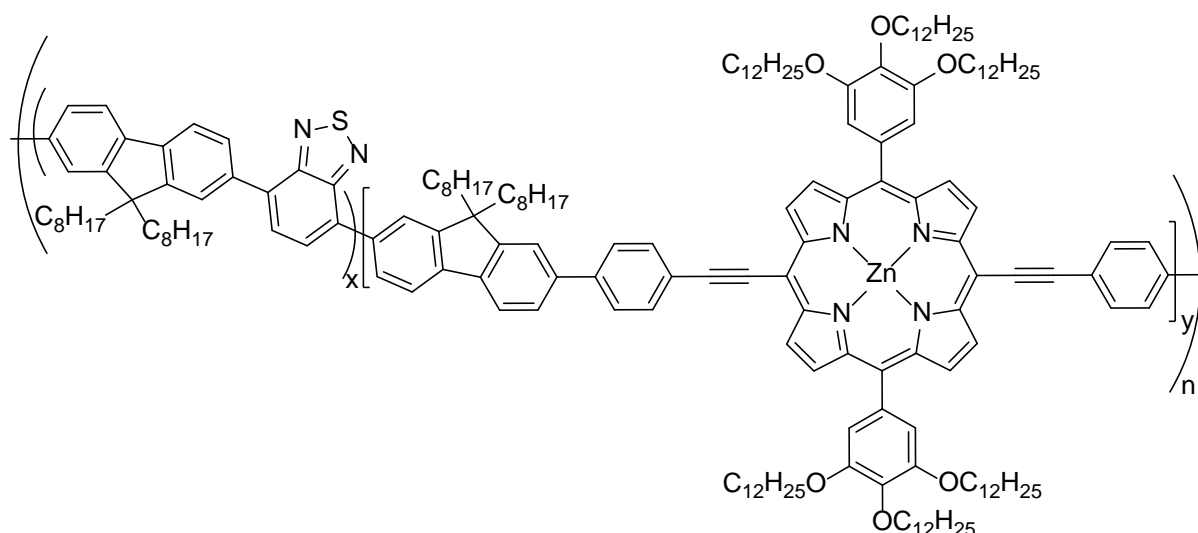
5,15-bis((4-bromophenyl)ethynyl)-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrin



5,15-diethynyl-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato zinc (II) (53 mg, 0.032 mmol), triethylamine (30 mL) and THF (10 mL) were degassed with argon for 30 min. 1-bromo-4-iodobenzene (20 mg, 0.070 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2 mg, 0.003 mmol) and CuI (1 mg, 0.005 mmol) were added and the reaction mixture was stirred for 18 h at rt under argon in the dark. The reaction mixture was concentrated *in vacuo* and purified *via* column chromatography (SiO_2 , Eluent Hexane: Et_2O (1:0 to 9:1)) to yield the product as a thick oil (13 mg, 0.007 mmol, 20%). ^1H NMR (600 MHz, CDCl_3) δ 9.75 (d, J = 4.6 Hz, 4H, NCCHCH), 9.07 (d, J = 4.6 Hz, 4H, NCCHCH), 7.90 (d, J = 8.3 Hz, 4H, BrCCHCH), 7.72 (d, J = 8.3 Hz, 4H, BrCCHCH), 7.42 (s, 4H, OCCH), 4.32 (t, J = 6.6 Hz, 4H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COCH}_2\text{C}_{11}\text{H}_{23}$), 4.12 (t, J = 6.5 Hz, 8H, $\text{NCCCCHC}(\text{OCH}_2\text{C}_{11}\text{H}_{23})\text{COC}_{12}\text{H}_{25}$), 2.03 – 1.96 (m, 4H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$), 1.93 – 1.86 (m, 8H, $\text{NCCCCHC}(\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21})\text{COC}_{12}\text{H}_{25}$), 1.74 – 1.66 (m, 4H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19}$), 1.53 – 1.47 (m, 8H, $\text{NCCCCHC}(\text{OC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19})\text{COC}_{12}\text{H}_{25}$), 1.41 – 1.18 (m, 96H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COC}_3\text{H}_6\text{C}_8\text{H}_{16}\text{CH}_3$ and $\text{NCCCCHC}(\text{OC}_3\text{H}_6\text{C}_8\text{H}_{16}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$), 0.91 – 0.82 (m, 18H, $\text{NCCCCHC}(\text{OC}_{12}\text{H}_{25})\text{COC}_{11}\text{H}_{22}\text{CH}_3$ and $\text{NCCCCHC}(\text{OC}_{11}\text{H}_{22}\text{CH}_3)\text{COC}_{12}\text{H}_{25}$); ^{13}C NMR (151 MHz, CDCl_3) δ 151.3, 151.0, 150.3, 133.1, 132.1,

114.4, 69.5, 50.7, 32.1, 32.0, 30.7, 30.0, 29.9, 29.8, 29.6, 29.5, 26.5, 26.3, 22.9, 22.8, 14.3, 14.2; UV (chlorobenzene) λ_{max} 453; MS (TOF LD⁺) m/z 1988 (M)⁺.

F8BT-HAPAPP – **Poly-2,7-(9,9-dioctylfluorene-*alt*-4,7-2,1,3-benzothiadiazole)-*ran*-2,7-(9,9-dioctylfluorene-*alt*-4',4''-5,15-bis(phenylethynyl)-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato Zinc (II))**



A polymer was synthesised with a weight percentage of 5% porphyrin to benzothiadiazole moiety ($x:y = 19:1$).

A solution of 4,7-dibromo-2,1,3-benzothiadiazole (53 mg, 0.181 mmol), 9,9-Dioctyl-9H-fluorene-2,7-diboronic acid bis(pinacol) ester (118 mg, 0.183 mmol) and 5,15-bis((4-bromophenyl)ethynyl)-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrinato zinc (II) (4.5 mg, 0.002 mmol) in toluene (4 mL) and a separate solution of 20% tetraethylammonium hydroxide in water (3 mL) were degassed for 30 min. Pd(OAc)₂ (1 mg, 0.005 mmol) and PPh₃ (5 mg, 0.019 mmol) were added to the organic solution which was again degassed for 30 min. The aqueous solution was added to the organic and the reaction mixture was stirred under argon at 110 °C for 18 h. The reaction was allowed to cool and the product was precipitated from MeOH and filtered. The polymer product was then washed with acetone and hexane and extracted with CHCl₃. The polymer was then concentrated *in vacuo* to a small volume and precipitated from MeOH (20 mg, 20%). UV (chlorobenzene) λ_{max} 469; GPC (PS): $M_n = 10000$, $M_w = 15000$, PDI = 1.5.

References

1. Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R., Self-Encapsulation of Poly-2,7-fluorenes in a Dendrimer Matrix. *Journal of the American Chemical Society* **2001**, *123* (29), 6965-6972.
2. Li, Q.; Guo, H.; Ma, L.; Wu, W.; Liu, Y.; Zhao, J., Tuning the photophysical properties of N⁺NPt(ii) bisacetylides complexes with fluorene moiety and its applications for triplet-triplet-annihilation based upconversion. *Journal of Materials Chemistry* **2012**, *22* (12), 5319-5329.
3. Kim, J.-H.; Kim, H. U.; Mi, D.; Jin, S.-H.; Shin, W. S.; Yoon, S. C.; Kang, I.-N.; Hwang, D.-H., Introduction of Perylene Units for Enhanced Interchain Interaction in Conjugated Polymers for Organic Photovoltaic Devices. *Macromolecules* **2012**, *45* (5), 2367-2376.
4. Cahiez, G.; Gager, O.; Moyeux, A.; Delacroix, T., Efficient Procedures to Prepare Primary and Secondary Alkyl Halides from Alkanols via the Corresponding Sulfonates under Mild Conditions. *Advanced Synthesis & Catalysis* **2012**, *354* (8), 1519-1528.
5. Balasaravanan, R.; Duraimurugan, K.; Sivamani, J.; Thiagarajan, V.; Siva, A., Synthesis and photophysical properties of triphenylamine-based multiply conjugated star-like molecules. *New Journal of Chemistry* **2015**, *39* (9), 7472-7480.