

Supporting Information

EXPERIMENTAL SECTION

All chemicals were purchased from commercial suppliers and used without purification. Solvents, such as toluene, THF, and CH_2Cl_2 , were freshly distilled. Column chromatography was performed with Activated alumina. NMR spectra were recorded on JEM LA400 FT-NMR spectrometer operating at 399.65MHz for ^1H in CDCl_3 solution. Chemical shifts were relative to internal TMS. IR spectra were obtained on a JASCO FS-420 spectrometer as KBr pellets. UV-Vis spectra and fluorescence spectra were measured on a JASCO V-570 and a JASCO FP-750. The calorimetric data were obtained on a Seiko DSC 220 at a scanning rate of 10 °C / min under flow of nitrogen. MALDI-TOF mass spectra were obtained on a PerSeptive Biosystems Voyager-DE-Pro spectrometer with dithranol as matrix. GPC analyses were carried out with a JASCO HPLC system (pump 1580, UV-detector 1575, refractive index-detector 930) with Showa Denko GPC KF-804L column (8.0 x 300 mm, polystyrene standards, $M = 900\text{--}400000$ g/mol) in THF as an eluent at 35°C (1.0ml min^{-1}). Melting points were recorded using a Shibata MEL-270 melting point apparatus and are corrected.

1: A mixture of pyrrole (2.0 ml, 1.59×10^{-2} mol) and 3, 5-dibromobenzaldehyde (4.2g, 1.59×10^{-2} mol) in 25ml of propionic acid refluxed for 48hr. The residue resulting from evaporation was purified using column chromatography on activated alumina by eluting with CHCl_3 . Yield: 11%. MALDI-TOF-MS (Dithranol): $m/z = 1238$ ($[\text{M}+\text{H}]^+$, 100) calcd for $\text{C}_{44}\text{H}_{22}\text{N}_4\text{Br}_8$: 1237.5.

5: A Schlenk flask was charged with **1** (0.18 g, 4.32×10^{-4} mol) and $\text{Pd}(\text{PPh}_3)_4$ (0.03g, 2.60×10^{-5} mol) under Ar atmosphere. Solutions of **2** (1.35g, 1.44×10^{-3} mol) in THF (6 ml) and Na_2CO_3 (2.0 M, 7 ml) in H_2O was prepared and deoxygenated with a stream of Ar. These solutions and deoxygenated toluene were added to the reaction vessel, and the mixture was refluxed under Ar for 72 hr. The reaction mixture was poured into a mixture of H_2O and diethylether. The aqueous phase was washed with ether, and the organic phases were combined and washed with 1 M NaOH aqueous

solution and brine. The crude product was purified using column chromatography on activated alumina by eluting with CHCl_3 / n-hexane (1 : 9 v/v), and resulting material was recrystallized from 2-methoxyethanol. Yield 57%. ^1H NMR (CDCl_3 , 400MHz): δ = 9.04 (8H, d, Pyrrole), 8.48 (8H, d, Ph), 8.25 (4H, s, Ph), 7.86 (16H, d, Ph), 7.54 (16H, d, Ph), 1.37 (s, 36H, $-\text{C}(\text{CH}_3)_3$). MALDI-TOF-MS (Dithranol): m/z = 1672 ($[\text{M}+\text{H}]^+$, 100) calcd for $\text{C}_{124}\text{H}_{126}\text{N}_4$: 1670.9.

6: Yield 24%. ^1H NMR (CDCl_3 , 400MHz): δ = 9.11 (8H, d, Pyrrole), 8.62 (8H, d, Ph), 8.42 (4H, s, Ph), 8.03 (16H, d, Ph), 7.80 (8H, s, Ph), 7.61 (32H, d, Ph), 7.40 (32H, d, Ph), 1.37 (s, 144H, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (CDCl_3): δ = 150.5, 142.7, 142.4, 142.0, 141.7, 140.6, 138.3, 132.5, 129.1, 127.1, 126.9, 125.7, 125.4, 125.2, 34.5, 31.3. MALDI-TOF-MS (Dithranol): m/z = 3337 ($[\text{M}+\text{H}]^+$, 100) calcd for $\text{C}_{252}\text{H}_{254}\text{N}_4$: 3335.9.