Electronic Supplementary Information for


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Synthetic considerations. Reagents were purchased commercially and generally used without further purification. N-Methylquinolinium hexafluorophosphate was prepared by a literature procedure (K.P. Dockery, J.P. Dinnocenzo, S. Farid, J.L. Goodman, I.R. Gould and W.P. Todd, J. Am. Chem. Soc. 1997, 119, 1876). Toluene-diisopropylamine mixtures used for polymerization reactions were degassed by vigorous sparging with argon before use. Melting points were recorded on a Laboratory Devices Inc. Mel-Temp II and are uncorrected. NMR spectra were recorded on Varian INOVA 500 MHz spectrometers and referenced to the $^1$H resonance of internal Me$_4$Si or the $^{13}$C resonance of the solvent. High-resolution mass spectra were recorded on a Bruker Daltonics Apex II 3T FT-ICR instrument. HPLC analyses were carried out on a Dynamax 250×9.5 column using degassed EtOAc/C$_2$H$_6$ eluents at a 4 ml/min flow rate. Compound elution was monitored at 265 nm.

Mononitrotetra(octyloxy)calix[4]arene 2. Silica-supported HNO$_3$ was prepared by stirring a suspension of 40 g silica gel in 100 ml of 8 N HNO$_3$ for 3 h. The silica was recovered by filtration and air-dried overnight before use. Calix[4]arene tetraoctyl ether (reference 8 in the main text) (1.00 g, 1.15 mmol) was dissolved in 40 ml CH$_2$Cl$_2$ and treated with ca. 1 g of HNO$_3$-SiO$_2$. A purple color developed immediately. After 50 min TLC analysis (9:1 hexanes/EtOAc) indicated complete consumption of 7. After removal of the silica by filtration, the reaction mixture was washed with aqueous NaHCO$_3$ and saturated NaCl solution. The organic phase was separated, dried over anhydrous MgSO$_4$, and filtered through a small pad of silica gel. The oil remaining after concentration of the eluate was chromatographed on silica gel (elution with 3% EtOAc/hexanes) to provide 365 mg (35%) of 8 as an oily orange solid. $^1$H NMR (CDCl$_3$, ppm): 0.89 (m, 12H), 1.30 (m, 4H), 1.88 (m, 8H), 3.16 (d, 2H, 14.0 Hz), 3.19 (d, 2H, 14.0 Hz), 3.75 (t, 2H, 6.5 Hz), 3.84-3.92 (m, 4H), 3.92-4.02 (m, 2H), 4.41 (d, 2H, 14 Hz), 4.46 (d, 2H, 14 Hz), 6.23 (br s, 2H), 6.83 (t, 1H, 7.5 Hz), 6.93 (t, 2H, 8.3 Hz), 7.11 (s, 1H). $^{13}$C NMR (CDCl$_3$, ppm): 14.32, 22.91, 22.91, 22.94, 26.32, 26.60, 26.77, 29.71, 29.78, 29.90, 29.93, 30.04, 30.20, 30.44, 30.60, 30.69, 31.16, 31.31, 32.16, 32.18, 32.19, 75.34, 75.39, 75.71, 121.87, 122.61, 123.41, 127.89, 129.70, 129.65, 134.18, 135.17, 136.19, 136.87, 142.73, 156.04, 157.41, 161.66, 163.15. HRMS: [C$_{60}$H$_{87}$NO$_6$] requires 917.6528, found 917.6501.

Monoaminotetra(octyloxy)calix[4]arene 3. For a related procedure, see C.-C. Zeng, Q.-Y. Zheng, Y.-L. Tang and Z.-T. Huang, Tetrahedron 2003, 59, 2539. Nitro compound 2 (129 mg, 0.14 mmol) was dissolved in EtOH containing ca. 5% EtOAc to promote
solubility. 2 g of SnCl2 were added and the reaction mixture heated at reflux under argon overnight. The reaction mixture was concentrated to dryness, re-dissolved in CH2Cl2 and washed with 1 N NaOH followed by saturated NaCl solution. The organic phase was dried over anhydrous MgSO4 and filtered, and the solvent was removed under reduced pressure to afford a dark red oil that was used without further purification (86 mg, 69%).

1H NMR (CDCl3, ppm): 0.89 (app t, 12H, 6.0 Hz), 1.25-1.40 (br m, 40H), 1.89 (m, 8H), 3.02 (d, 2H, 13.5 Hz), 3.14 (d, 2H, 13.5 Hz), 3.78 (t, 2H, 7.5 Hz), 3.86 (m, 6H), 4.36 (d, 2H, 13.0 Hz), 4.44 (d, 2H, 13.5 Hz), 5.94 (s, 2H), 6.54-6.65 (m, 9H). 13C NMR (CDCl3, ppm): 14.34, 22.95, 26.54, 26.60, 26.66, 29.87, 29.88, 30.16, 30.52, 30.57, 30.58, 31.19, 31.23, 31.25, 32.22, 71.19, 75.34, 75.37, 75.40, 115.57, 121.72, 121.99, 122.05, 128.23, 128.24, 128.28, 128.29, 135.38, 135.44, 135.58, 140.47, 149.99, 156.80, 156.89. HRMS: [C60H89NO4+H] requires 888.6864, found 888.6881.

Calix[4]arene monomer 5. A solution of 4 (reference 2 in the main text) (161 mg, 0.40 mmol) in CH2Cl2 was added dropwise over 30 min to an ice-cold solution of 3 (353 mg, 0.40 mmol) in 40 ml CH2Cl2 containing 1 ml Et3N. The reaction mixture was allowed to stir overnight while warming to room temperature, then was poured into dilute HCl. The organic phase was separated, washed with water and saturated NaCl solution, and dried over anhydrous MgSO4. The residue remaining after concentration to dryness was subjected to column chromatography (6:1 hexanes/EtOAc) and the product recrystallized from a CHCl3-MeOH-hexane mixture, yielding 103 mg (21%) of a cream-colored solid. M.p. 100º dec. HPLC: 4.3 min (10% EtOAc/C7H16). 1H NMR (CDCl3, ppm): 0.89 (m, 12H), 1.30-1.42 (m, 40H), 1.89 (m, 8H), 2.40 (s, 3H), 3.15 (d, 2H, 13.0 Hz), 3.17 (d, 2H, 14.0 Hz), 3.84 (t, 2H, 7.0 Hz), 3.90 (m, 6H), 3.44 (app d, 4H, 13.5 Hz), 6.53 (m, 3H), 6.63-6.75 (m, 8H), 6.89 (s, 1H), 7.72 (s, 1H), 7.83 (s, 1H). 13C NMR: major peaks at 14.34, 22.95, 26.52, 26.65, 29.89, 30.19, 30.54, 32.21, 75.40, 100.00, 120.92, 122.21, 128.21, 128.61, 135.39, 157.09. HRMS: [C68H93NO5I2+Na] requires 1280.5035, found 1280.5075.

2,5-Diiodo-4-methylbenzoic acid, (4-hexyloxy)phenylamide (7). A solution of 4 (418 mg, 1.03 mmol) in CH2Cl2 was added dropwise to an ice-cold solution of 4-hexyloxyaniline (203 mg, 1.05 mmol) in a mixture of 20 ml CH2Cl2 and 4 ml Et3N. After stirring for 8 hr under argon, the reaction mixture was washed with 1 N NaOH followed by 1 N HCl and saturated NaCl solution. The organic layer was dried over anhydrous MgSO4, filtered, and concentrated to dryness. The residue remaining was recrystallized from hot EtOH to give 16 as pale pink plates (208 mg, 37%). M.p. 162-164º. 1H NMR (CDCl3, ppm): 0.91 (m, 3H), 1.33-1.37 (m, 4H), 1.78 (m, 2H), 2.41 (s, 3H), 3.95 (t, 2H, 6.8 Hz), 6.89 (app dd, 2H, 2.0 Hz, 6.5 Hz), 7.44 (s, 1H), 7.50 (app dd, 2H, 2.0 Hz, 6.5 Hz), 7.73 (s, 1H), 7.90 (s, 1H). 13C NMR (CDCl3, ppm): 14.27, 22.83, 25.92, 27.70, 29.43, 31.80, 68.53, 92.25, 100.80, 115.08, 122.13, 130.37, 138.58, 140.63, 141.22, 145.60, 156.72, 165.44. HRMS: [C20H23NO2I2-H] requires 561.9745, found 561.9729.

Polymer synthesis. PPEs were synthesized by standard methods. In a typical synthesis, monomer 7 (17 mg, 0.018 mmol), 2,5-diethynyl-1,4-bis(hexadecyloxy)benzene (see T.M. Swager, C.J. Gil and M.S. Wrighton, J. Phys. Chem. 1995, 99, 4886) (11 mg, 0.018
mmol), Pd(PPh₃)₄ and CuI (catalytic amounts) were dissolved in freshly degassed 4:1 toluene/diisopropylamine (2 ml) under argon and stirred at 60º overnight. The reaction mixture was diluted with a small quantity of CH₂Cl₂, washed with saturated NaHCO₃ and NaCl solutions, dried over anhydrous MgSO₄ and concentrated. Slow addition of the concentrated CH₂Cl₂ solution to MeOH resulted in the precipitation of the PPE 8 as a yellow solid. Polymer 6 was prepared by analogous method from monomer 5 and without precipitation into MeOH. GPC data was measured from filtered THF solutions versus polystyrene standards. ¹H NMR data for 6 (CDCl₃, ppm): broad peaks at 0.9, 1.3, 1.6, 1.9, 3.2, 3.8, 4.4, 6.2-7.0. For 8 (CDCl₃, ppm): broad peaks at 1.0, 1.3, 1.6, 2.5, 3.5, 4.0, 4.9, 7.0, 7.6.

Fluorescence studies. Fluorescence spectra were measured on a Spex Fluorolog 2 fluorimeter in quartz cuvettes. Fluorescence lifetimes were measured in the frequency domain using phase modulation at 10 frequencies between 10 and 220 MHz and referenced to a colloidal-silica standard (τ = 0). For Stern-Volmer quenching studies, quenchers were dissolved in solutions equal in polymer concentration to the assay solution. Lifetime Stern-Volmer studies showed consistent τ values in each case (0.55 ± 0.02 ns) regardless of quencher concentration.