Electronic Supporting Information for:

Self-Assembly of Amphiphilic Poly(phenylene ethynylene)s in Water - Potassium Dodecanoate - Decanol Lyotropic Liquid Crystals

*Jean Bouffard, Timothy M. Swager**

Department of Chemistry, Massachusetts Institute of Technology,

77 Massachusetts Ave., Cambridge, Massachusetts 02139, USA

tswager@mit.edu

Table of Contents:

I. Detailed Experimental Procedures and Characterization Data **S2-S17**

II. Self-Assembly in Lyotropic LC and Spectroscopy **S18-S28**

III. ^{1}H- and ^{13}C-NMR Spectra **S29-S43**

IV. References and Notes **S44**

I. EXPERIMENTAL SECTION

Materials

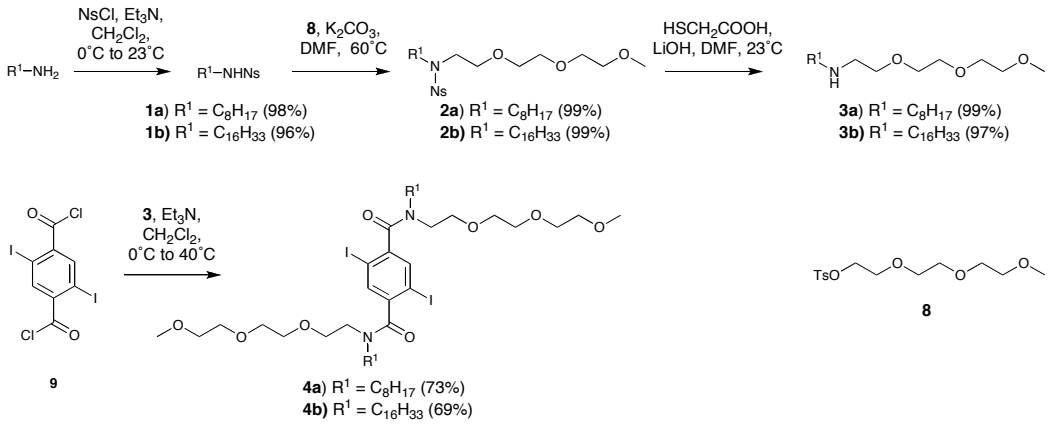
All solvents were of ACS reagent grade or better unless otherwise noted. Anhydrous tetrahydrofuran, toluene and dichloromethane were dried on a solvent column purification system. *N*,*N*-Dimethylformamide was dried by storage over 4Å molecular sieves for 48h, followed by vacuum distillation and storage over 3Å molecular sieves for a minimum of 48h prior to use. Potassium dodecanoate was recrystallized thrice from EtOH prior to use. Silica gel (40-63 μm) was obtained from SiliCycle Inc. Tri(ethylene glycol) monomethyl ether tosylate (**8**),[1] 2,5-diiodobenzene-1,4-dicarbonyl dichlorode (**9**),[2] 2,2'-(2,5-diiodo-1,4-phenylene)bis(oxy)diethanoic acid (**10**),[3] 2,5-diiodo-N^1,N^1,N^4,N^4-tetraoctylbenzene-1,4-dicarbamide (**11**)[2] and polymers **P1a**, **b**[4] were prepared according to literature procedures or slight modifications thereof. All other reagents, compounds and chemicals were obtained from commercial suppliers and used without further purification.

General methods, instrumentation and measurements

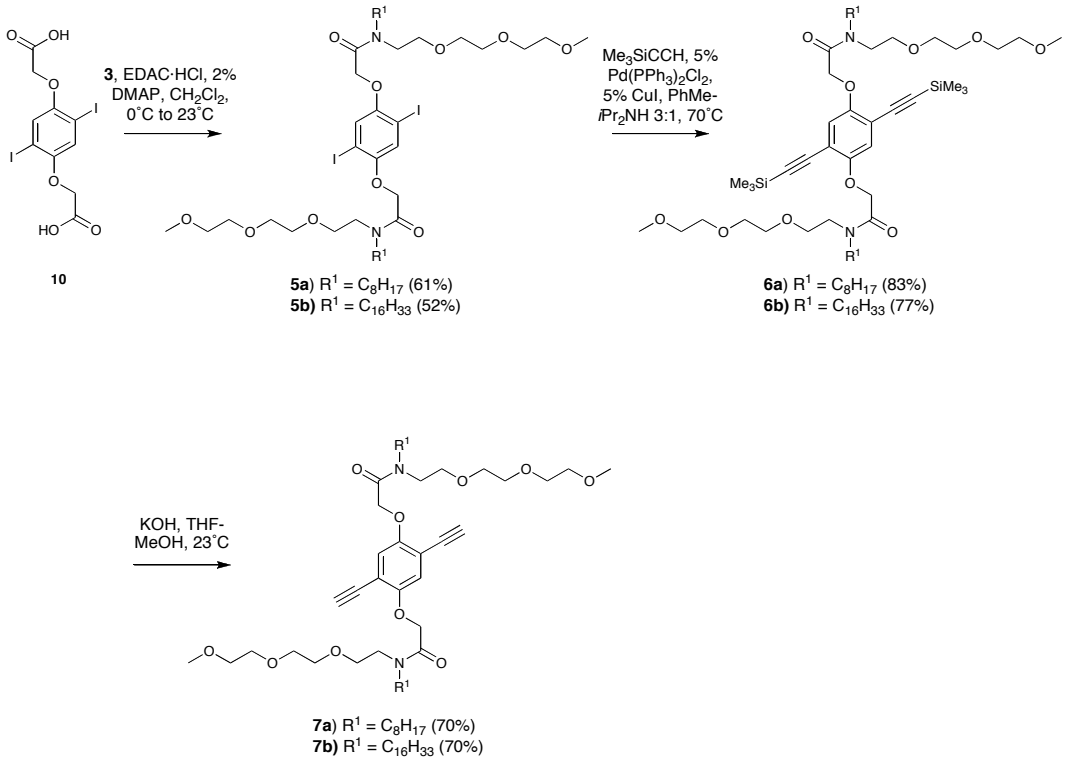
Synthetic manipulations that required an inert atmosphere (where noted) were carried out under nitrogen or argon using standard Schlenk techniques or in an inert-atmosphere glovebox. NMR (^{1}H and ^{13}C) spectra were recorded on 300 and 500 MHz spectrometers. The chemical shift data for each signal are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0, and referenced to the residual solvent resonances. Splitting patterns are denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). High-resolution mass spectra (HR-MS) were obtained at the MIT Department of Chemistry Instrumentation Facility using electron impact ionization (EI) with a voltage of 70 V or electrospray ionization (ESI). Melting point (m.p.) determination was performed using open capillaries and are reported uncorrected. Polymer molecular weights were determined in THF solutions on an Agilent 1100 series HPLC/GPC system with three PLgel columns (10^3, 10^4, 10^5 Å) in series against narrow polystyrene standards. Polymer thin films were spin cast from ~1 mg/mL $CHCl_3$ solutions on microscope coverslips using an EC101DT photoresist spinner

(Headway Research, Inc.) at a 1000 rpm rate for 60 s. UV-Vis spectra of solutions and thin films were recorded with an Agilent 8453 diode array spectrophotometer. Fluorescence spectra of films and solutions were recorded on a Jobin Yvon Horiba SPEX Fluorolog fluorimeter (model FL-12, 450 W xenon lamp) using either front-face (films) or right angle detection (solutions). Langmuir-Blodgett experiments were performed using a Nima 102M trough equipped with a fused silica (quartz) window for *in situ* spectroscopy following previously reported procedures.[4-5] Langmuir monolayers were spread on a >18 MΩ cm^{-1} water subphase (purified on a Milipore water purifier) from spectroscopic-grade chloroform solutions of polymers (~1 mg/mL). Solvent was allowed to evaporate 5-10 mins, and the monolayers were mechanically annealed by 5 cycles of compression-decompression before spectroscopic measurements. Absorption spectra of Langmuir monolayers were acquired using a Cary 50 UV-Vis spectrophotometer with fiber optics linking to the air-water interface. Fluorescence spectra of Langmuir monolayers were recorded a Jobin Yvon Horiba SPEX Fluorolog fluorimeter (model FL-12, 450 W xenon lamp) using fiber optics linking to the air-water interface.

Scheme S1: Preparation of Amphiphilic Monomers **4a**, **b**.



Scheme S2: Preparation of Amphiphilic Monomers **7a**, **b**.



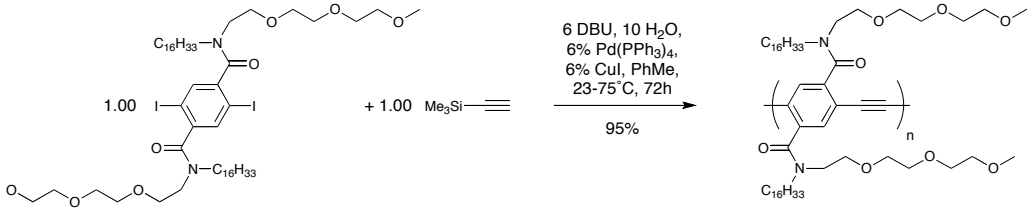
10

5a) $R^1 = C_8H_{17}$ (61%)
5b) $R^1 = C_{16}H_{33}$ (52%)

6a) $R^1 = C_8H_{17}$ (83%)
6b) $R^1 = C_{16}H_{33}$ (77%)

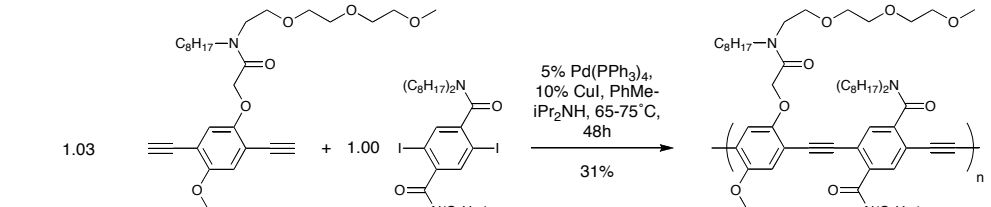
7a) $R^1 = C_8H_{17}$ (70%)
7b) $R^1 = C_{16}H_{33}$ (70%)

Scheme S3: Preparation of Amphiphilic Polymers **P2** and **P3**.

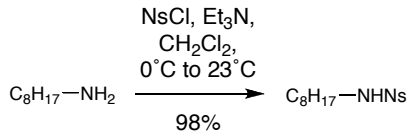


4b

P2

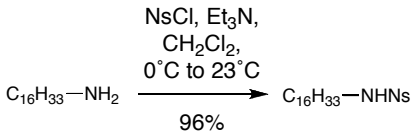


7a **11** **P3**



1a

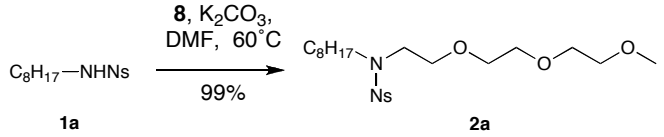
2-Nitro-*N*-octylbenzenesulfonamide (1a). To a stirred solution of *n*-octylamine (12.9 g, 100 mmol) in CH_2Cl_2 (150 mL) and Et_3N (15 mL) at 0˚C was added 2-nitrobenzenesulfonyl chloride (22.2 g, 100 mmol) by portions. After stirring for ca. 15 mins. at 0˚C, the mixture was stirred at room temperature for ca. 1 h, and then quenched by the addition of aq. 2N HCl. Extraction with CH_2Cl_2, washing with brine, drying over anh. $MgSO_4$ followed by evaporation of the solvents under reduced pressure affords sulfonamide **1a** as a pale beige solid (30.89 g, 98%). m. p. 68-69˚C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.14 (dd, 1H, *J* = 4.5, 3.0 Hz), 7.86 (m, 1H), 7.75 (m, 2H), 5.27 (t, 1H, *J* = 6.0 Hz), 3.09 (q, 2H, *J* = 6.3 Hz), 1.50 (m, 2H), 1.22 (m, 10H), 0.86 (t, 3H, *J* = 6.9 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 148.2, 133.8, 133.7, 133.0, 131.2, 125.5, 44.0, 31.8, 29.6, 29.2, 29.1, 26.6, 22.7, 14.2; HR-MS (ESI): calc for $C_{14}H_{22}N_2O_4S$ $[M+H]^+$ 315.1373, found 315.1379.



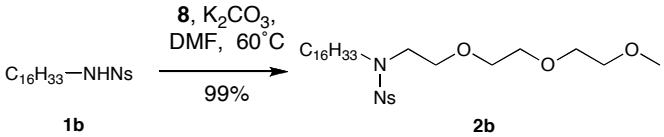
1b

2-Nitro-*N*-hexadecylbenzenesulfonamide (1b). To a stirred solution of *n*-hexadecylamine (24.1 g, 100 mmol) in CH_2Cl_2 (180 mL) and Et_3N (15 mL) at 0˚C was added 2-nitrobenzenesulfonyl chloride (22.2 g, 100 mmol) by portions. After stirring for ca. 15 mins. at 0˚C, the mixture was stirred at room temperature for ca. 1 h, and then quenched by the addition of aq. 2N HCl. Extraction with CH_2Cl_2, washing with brine, drying over anh. $MgSO_4$ followed by evaporation of the solvents under reduced pressure affords sulfonamide **1b** as off-white flakes (40.03 g, 96%). m. p. 91-92˚C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.14 (m, 1H,), 7.86 (m, 1H), 7.75 (m, 2H), 5.27 (t, 1H, *J* = 5.5 Hz), 3.09 (q, 2H, *J* = 6.0 Hz), 1.51 (m, 2H), 1.22 (m, 26H), 0.88 (t, 3H, *J* = 7.0 Hz); ^{13}C-NMR

(125 MHz, $CDCl_3$): δ = 148.2, 133.9, 133.7, 133.0, 131.3, 125.5, 44.1, 32.1, 29.86, 29.85, 29.83, 29.78, 29.70, 29.68, 29.6, 29.5, 29.2, 26.6, 22.9, 14.3; HR-MS (ESI): calc for $C_{22}H_{38}N_2O_4S$ $[M+H]^+$ 427.2631, found 427.2644.

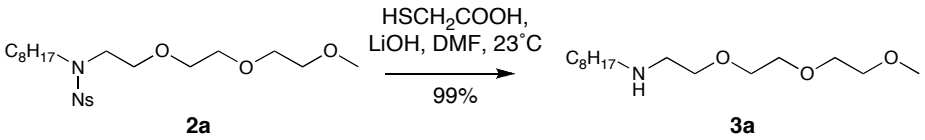


***N*-(3,6,9-Trioxadecyl)-2-nitro-*N*-octylbenzenesulfonamide (2a).** Sulfonamide **1a** (31.4 g, 100 mmol), tri(ethylene glycol) monomethyl ether tosylate (**8**) (32.5 g, 102 mmol) and potassium carbonate (41.4 g, 300 mmol) were added to a Schlenk flask equipped with a magnetic stirrer. Contents were evacuated and back-filled with argon 5 times, and dry DMF (100 mL) was then added. The reaction mixture was stirred at 60˚C for ca. 16 h, cooled to room temperature, and then poured in water (ca. 500 mL). Extraction with diethyl ether, washing with brine, drying over anh. $MgSO_4$ and evaporation of the solvents under reduced pressure affords sulfonamide **2a** as a yellow oil (45.51 g, 99%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.00 (m, 1H), 7.69-7.62 (m, 2H), 7.61-7.58 (m, 1H), 3.60-3.48 (m, 12H), 3.34-3.29 (m, 5H), 1.52 (m, 2H), 1.25-1.17 (m, 10H), 0.83 (t, 3H, *J* = 6.6 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ =148.1, 133.9, 133.4, 131.8, 130.6, 124.2, 72.0, 70.60, 70.57, 70.5, 69.7, 59.1, 48.8, 46.7, 31.8, 29.2 (2), 28.1, 26.6, 22.7, 14.2; HR-MS (ESI): calc for $C_{21}H_{36}N_2O_7S$ $[M+Na]^+$ 483.2135, found 483.2130.



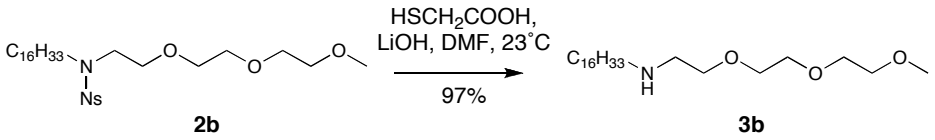
***N*-(3,6,9-Trioxadecyl)-2-nitro-*N*-hexadecylbenzenesulfonamide (2b).** Sulfonamide **1b** (42.7 g, 100 mmol), tri(ethylene glycol) monomethyl ether tosylate (**8**) (32.5 g, 102 mmol) and potassium carbonate (41.4 g, 300 mmol) were added to a Schlenk flask equipped with a magnetic stirrer. Contents were evacuated and back-filled with argon 5

times, and dry DMF (125 mL) was then added. The reaction mixture was stirred at 60°C for ca. 16 h, cooled to room temperature, and then poured in water (ca. 500 mL). Extraction with diethyl ether, washing with brine, drying over anh. $MgSO_4$ and evaporation of the solvents under reduced pressure affords sulfonamide **2b** as a yellow oil (57.0 g, 99%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.01 (m, 1H), 7.69-7.63 (m, 2H), 7.61-7.58 (m, 1H), 3.61-3.49 (m, 12H), 3.35-3.30 (m, 5H), 1.53 (m, 2H), 1.25-1.20 (m, 26H), 0.85 (t, 3H, *J* = 6.3 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ =148.2, 134.0, 133.4, 131.8, 130.7, 124.2, 72.0, 70.62, 70.60, 69.7, 59.1, 48.8, 46.7, 32.0,29.8, 29.6, 29.5, 29.3, 28.2, 26.6, 22.8, 14.2; HR-MS (ESI): calc for $C_{29}H_{52}N_2O_7S$ $[M+H]^+$ 573.3568, found 573.3540.



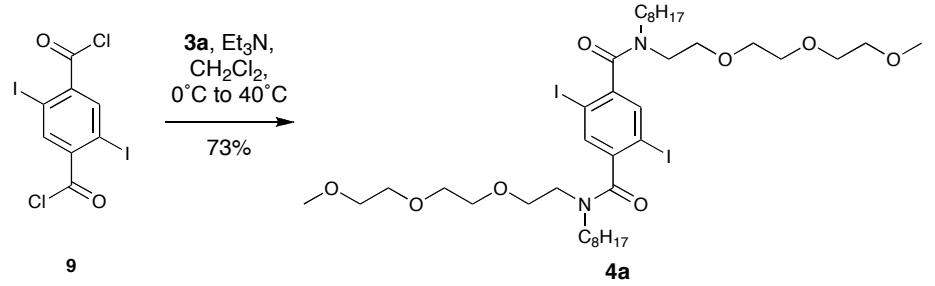
2a **3a**

***N*-(3,6,9-Trioxadecyl)-octan-1-amine (3a).** A solution of sulfonamide **2a** (45.5 g, 99 mmol) and $LiOH{\cdot}H_2O$ (17 g, 405 mmol) in DMF (100 mL) is degassed by bubbling nitrogen through for ca. 15 minutes. To this solution is then added thioglycolic acid (14 mL, 202 mmol), and the resulting mixture is stirred at room temperature for 1 h. The mixture is then poured in water (ca. 500 mL), extracted with Et_2O, washed with sat. aq. $NaHCO_3$, dried over anh. $MgSO_4$, and the solvents are evaporated under reduced pressure to afford the secondary amine **3a** as pale yellow oil (27.9 g, 99%). ^{1}H-NMR (300 MHz, $3CDCl_3$): δ = 3.55-3.45 (m, 10H), 3.26 (s, 3H), 2.66 (t, 2H, *J* = 4.8 Hz), 2.48 (t, 2H, *J* = 6.9 Hz), 1.37 (m, 3H), 1.16 (m, 10H), 0.76 (t, 3H, *J* = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 71.9, 70.6, 70.49, 70.46, 70.3, 59.0, 50.0, 49.3, 31.8, 30.2, 29.5, 29.2, 27.4, 22.6, 12.0; HR-MS (ESI): calc for $C_{15}H_{33}NO_3$ $[M+H]^+$ 276.2533, found 276.2522.



2b **3b**

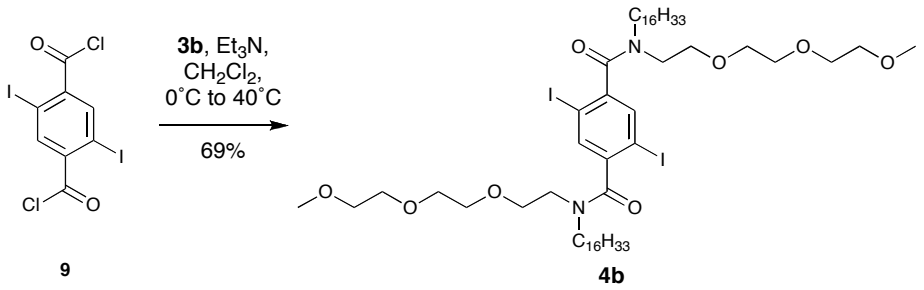
***N*-(3,6,9-Trioxadecyl)-hexadecan-1-amine (3b).** A solution of sulfonamide **2b** (57 g, 100 mmol) and $LiOH{\cdot}H_2O$ (17 g, 405 mmol) in DMF (100 mL) is degassed by bubbling nitrogen through for ca. 15 minutes. To this solution is then added thioglycolic acid (14 mL, 202 mmol), and the resulting mixture is stirred at room temperature for 1 h. The mixture is then poured in water (ca. 500 mL), extracted with Et_2O, washed with sat. aq. $NaHCO_3$, dried over anh. $MgSO_4$, and the solvents are evaporated under reduced pressure to afford the secondary amine **3b** as a pale brown oil (37.8 g, 97%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.65-3.53 (m, 10H), 3.37 (s, 3H), 2.77 (t, 2H, *J* = 5.4 Hz), 2.58 (t, 2H, *J* = 7.5 Hz), 1.60 (br, 1H), 1.47 (m, 2H), 1.24 (m, 26H), 0.87 (t, 3H, *J* = 6.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 72.1, 70.8, 70.7, 70.5, 59.2, 50.3, 49.5, 32.1, 30.3, 29.9, 29.8, 29.5, 27.6, 22.9, 14.3; HR-MS (ESI): calc for $C_{23}H_{49}NO_3$ $[M+H]^+$ 388.3785, found 388.3780.



9 **4a**

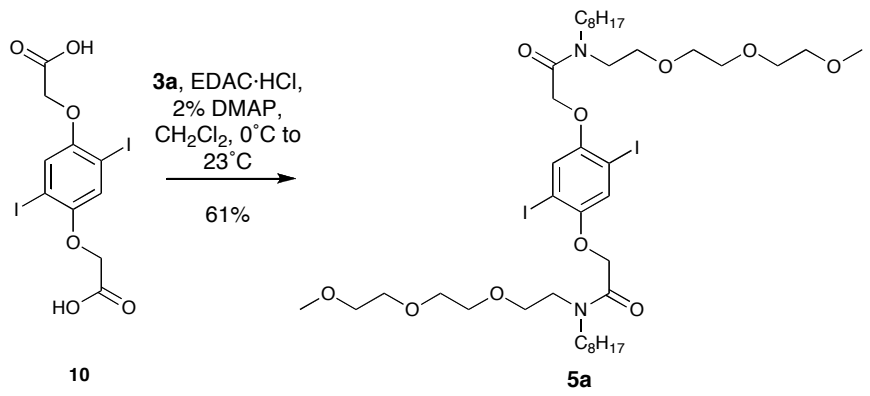
2,5-Diiodo-*N*^{1},*N*^{4}-bis(3,6,9-Trioxadecyl)-*N*^{1},*N*^{4}-dioctylbenzene-1,4-dicarbamide (4a). To a stirred solution of amine **3a** (1.50 g, 5.5 mmol) and Et_3N (1 mL) in CH_2Cl_2 (30 mL) at 0°C is added diacid dichloride **9** (908 mg, 2.0 mmol) by portions. The mixture is stirred overnight as it slowly warms up from 0°C to room temperature, and is then refluxed for ca. 7 h. The mixture is then cooled to room temperature, solvents are evaporated under reduced pressure and the residue is submitted to a 2N aq. HCl / EtOAc workup. The crude product is purified by column chromatography on silica gel using 1:1 CH_2Cl_2 : EtOAc (v/v) as the mobile phase to afford diiodide **4a** as a viscous oil (1359 mg,

73%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.65 (s, 0.5 H), 7.62 (s, 0.5 H), 7.59 (s, 0.5 H), 7.56 (s, 0.5 H), 4.00-3.70 (m, 4H), 3.67-3.64 (m, 10H), 3.57-3.55 (m, 7H), 3.50-3.40 (m, 2H), 3.39 (s, 6H), 3.38-3.00 (m, 5H), 1.69-1.15 (m, 26H), 0.90-0.86 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 168.9, 168.8, 144.33, 144.26, 144.2, 144.1, 138.5, 138.3, 137.5, 137.2, 92.8, 92.7, 92.6, 72.1, 72.0, 70.8, 70.73, 70.68, 70.6, 68.9, 68.7, 59.2, 50.0, 48.2, 45.3, 44.5, 32.0, 31.8, 29.5, 29.4, 29.3, 28.6, 27.4, 27.0, 26.7, 22.8, 14.27, 14.25; HR-MS (ESI): calc for $C_{38}H_{66}I_2N_2O_8$ $[M+Na]^+$ 955.2801, found 955.2817.

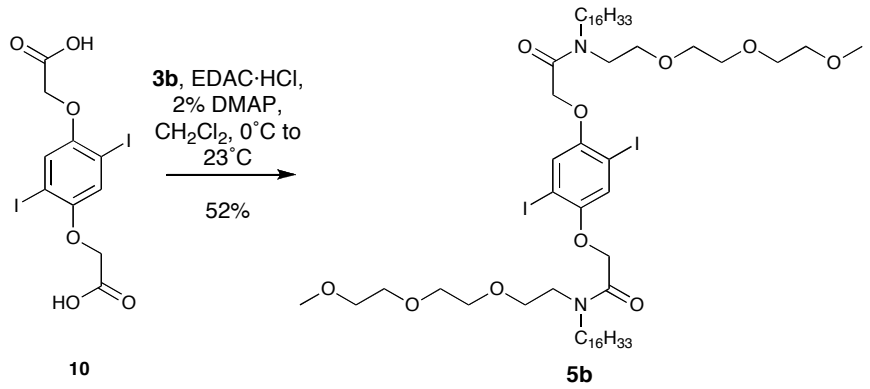


9 **4b**

2,5-Diiodo-*N*^{1},*N*^{4}-bis(3,6,9-Trioxadecyl)-*N*^{1},*N*^{4}-hexadecylbenzene-1,4-dicarbamide (4b). To a stirred solution of amine **3b** (2.20 g, 5.7 mmol) and Et_3N (1 mL) in CH_2Cl_2 (30 mL) at 0˚C is added diacid dichloride **9** (908 mg, 2.0 mmol) by portions. The mixture is stirred overnight as it slowly warms up from 0˚C to room temperature, and is then refluxed for ca. 7 h. The mixture is then cooled to room temperature, solvents are evaporated under reduced pressure and the residue is submitted to a 2N aq. HCl / EtOAc workup. The crude product is purified by column chromatography on silica gel using 1:1 CH_2Cl_2 : EtOAc (v/v) as the mobile phase to afford diiodide **4b** as a viscous oil that slowly solidifies upon refrigeration (1599 mg, 69%). m. p. 28.5-29.5˚C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.65 (s, 0.5 H), 7.62 (s, 0.5 H), 7.59 (s, 0.5 H), 7.56 (s, 0.5 H), 4.00-3.70 (m, 4H), 3.67-3.64 (m, 10H), 3.57-3.55 (m, 7H), 3.50-3.40 (m, 2H), 3.39 (s, 6H), 3.38-3.00 (m, 5H), 1.69-1.15 (m, 60H), 0.90-0.87 (td, 6H, *J* = 7.5, 1.0 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 168.84, 168.77, 144.33, 144.25, 144.2, 144.1, 138.5, 138.3, 137.5, 137.2, 92.8, 92.7, 92.5, 72.1, 72.0, 70.8, 70.73, 70.67, 70.6, 68.9, 68.7, 59.2, 50.0, 48.2, 45.3, 44.5, 32.0, 29.84, 29.80, 29.65, 29.60, 29.5, 28.6, 27.4, 27.0, 26.7, 22.8, 14.3; HR-MS (ESI): calc for $C_{54}H_{98}I_2N_2O_8$ $[M+Na]^+$ 1179.5305, found 1179.5302.

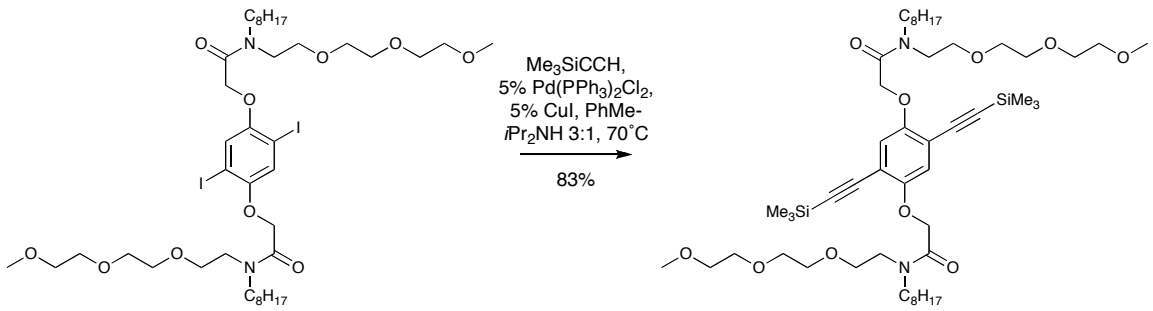


2,2'-(2,5-Diiodo-1,4-phenylene)bis(oxy)bis(*N*-(3,6,9-trioxadecyl)-*N*-octylethanamide) (5a). A stirred, sonicated suspension of diiodo diacid **10** (478 mg, 1.0 mmol), secondary amine **3a** (550 mg, 2.0 mmol) and 4-dimethylaminopyridine (DMAP, 2-3 mg, 0.02 mmol) in CH_2Cl_2 (5 mL) is cooled to 0˚C, and *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDAC, 422 mg, 2.2 mmol) is then added by portions. The resulting mixture is stirred overnight as it slowly warms up to room temperature. The mixture is then poured in aq. 2N HCl, extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$ and the solvents are evaporated under reduced pressure. The resulting residue is purified by column chromatography on silical gel using progressively more polar 1:1 to 1:3 CH_2Cl_2 : EtOAc (v/v) as the mobile phase to afford diiodide **5a** as a pale oil (606 mg, 61%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.20 (s, 1H), 7.16 (s, 1H), 4.78 (d, 2H, *J* = 10.5 Hz), 4.65 (d, 2H, *J* = 8.0 Hz), 3.63-3.57 (m, 17H), 3.53-3.47 (m, 9H), 3.37-3.33 (m, 10H), 1.56-1.51 (m, 4H), 1.27-1.22 (m, 22H), 0.86-0.83 (m, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.4, 167.3, 166.9, 166.8, 152.9, 152.8, 152.7, 152.6, 123.7, 123.6, 123.2, 123.1, 86.2, 86.0, 85.9, 85.8, 72.00, 71.96, 70.84, 70.81, 70.68, 70.63, 70.60, 70.54, 69.1, 69.0, 68.9, 68.8, 59.2, 48.8, 47.1, 46.2, 46.0, 31.89, 31.86, 29.48, 29.45, 29.34, 29.0, 27.5, 27.0, 22.7, 14.2; HR-MS (ESI): calc for $C_{40}H_{70}I_2N_2O_{10}$ $[M+Na]^+$ 1015.3012, found 1015.3047.



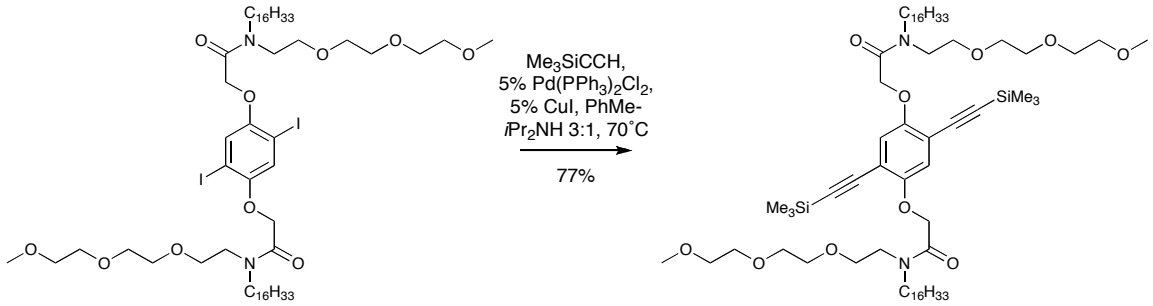
10 **5b**

2,2'-(2,5-Diiodo-1,4-phenylene)bis(oxy)bis(*N*-(3,6,9-trioxadecyl)-*N*-hexadecylethanamide) (5b). A stirred, sonicated suspension of diiodo diacid **10** (1434 mg, 3.0 mmol), secondary amine **3b** (2328 mg, 6.0 mmol) and 4-dimethylaminopyridine (DMAP, 7-8 mg, 0.06 mmol) in CH_2Cl_2 (15 mL) is cooled to 0˚C, and *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDAC, 1267 mg, 6.6 mmol) is then added by portions. The resulting mixture is stirred overnight as it slowly warms up to room temperature. The mixture is then poured in aq. 2N HCl, extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$ and the solvents are evaporated under reduced pressure. The resulting residue is purified by column chromatography on silical gel using progressively more polar 1:1 to 1:3 CH_2Cl_2 : EtOAc (v/v) as the mobile phase to afford diiodide **5b** as a pale oil that slowly solidifies upon refrigeration (1881 mg, 52%). m. p. 58-59°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.21 (s, 1H), 7.17 (s, 1H), 4.79 (d, 2H, *J* = 5.7 Hz), 4.66 (d, 2H, *J* = 4.5 Hz), 3.64-3.47 (m, 25H), 3.37-3.33 (m, 10H), 1.56-1.51 (m, 4H), 1.27-1.22 (m, 54H), 0.86-0.83 (t, 6H, *J* = 6.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.42, 167.37, 166.9, 166.8, 153.0, 152.9, 152.7, 152.6, 123.7, 123.6, 123.2 (2), 86.2, 86.1, 86.0, 85.9, 72.04, 72.00, 70.88, 70.85, 70.70, 70.67, 70.63, 70.57, 69.1 (2), 69.0, 68.9, 59.2, 48.8, 47.2, 46.3, 46.0, 32.0, 29.83, 29.79, 29.74, 29.56, 29.5, 29.0, 27.6, 27.0, 22.8, 14.3; HR-MS (ESI): calc for $C_{56}H_{102}I_2N_2O_{10}$ $[M+Na]^+$ 1239.5516, found 1239.5544.



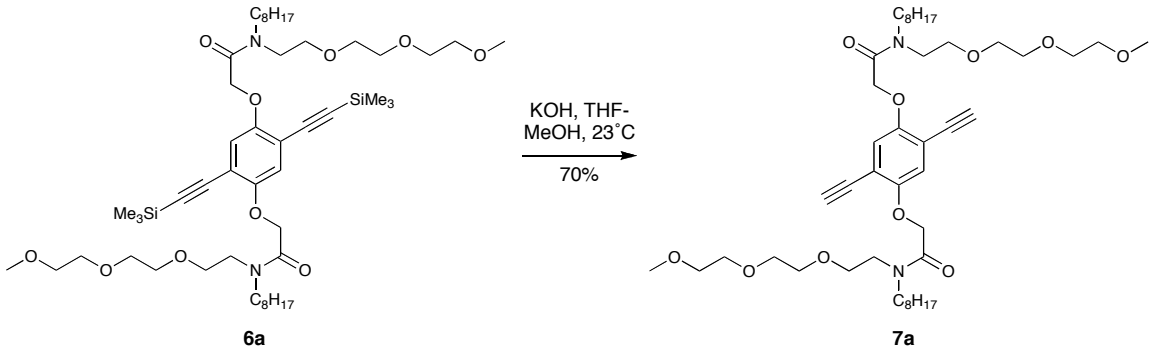
5a **6a**

2,2'-(2,5-Bis(trimethylsilylethynyl)-1,4-phenylene)bis(oxy)bis(*N*-(3,6,9-trioxadecyl)-*N*-octylethanamide) (6a). Diiodide **5a** (993 mg, 1.0 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (35 mg, 0.05 mmol) and copper(I) iodide (10 mg, 0.05 mmol) are placed in a Schlenk flask equipped with a magnetic stirrer. Contents are evacuated and back-filled with argon 5 times, and a degassed, premixed solution of PhMe (3 mL) and *i*Pr_2NH (1 mL) is added, followed by trimethylsilylacetylene (0.42 mL, 3.0 mmol). After 5 more quick vacuum / backfill cycles, the mixture is stirred at 70˚C for ca. 16 h. The mixture is then cooled to room temperature, diluted with ethyl acetate, and ca. 10 g of silica gel are added. Solvents are evaporated under reduced pressure, and the crude product immobilized on silica gel is purified by column chromatography on silica gel using progressively more polar 3:1 to 1:1 CH_2Cl_2 : EtOAc (v/v) as the mobile phase to afford **6a** as a pale brown oil that solidifies upon refrigeration (778 mg, 83%). m. p. 55-56˚C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.97 (s, 1H), 6.92 (s, 1H), 4.77 (d, 2H, *J* = 6.5 Hz), 4.68 (d, 2H, *J* = 5.0 Hz), 3.63-3.49 (m, 28H), 3.37-3.33 (m, 10H), 1.56-1.51 (m, 4H), 1.27-1.22 (m, 22H), 0.87-0.84 (td, 6H, *J* = 7.0, 1.5 Hz), 0.22 (d, 18H, *J* = 2.0 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.9, 167.8, 167.54, 167.49, 153.8, 153.6, 119.1, 119.0, 118.24, 118.20, 114.73, 114.70, 114.3, 101.2, 101.02, 100.95, 100.82, 100.79, 100.69, 100.65, 100.5, 72.1, 72.0, 70.9, 70.8, 70.74, 70.69, 70.6, 69.51, 69.48, 69.4, 69.3, 69.2, 69.0, 59.21, 59.19, 49.0, 47.1, 46.5, 46.4, 46.1, 31.96, 31.91, 29.52, 29.50, 29.4, 29.1, 27.6, 27.10, 27.05, 23.0, 22.8, 14.27, 14.26, 0.14, 0.12; HR-MS (ESI): calc for $C_{50}H_{88}N_2O_{10}Si_2$ $[M+Na]^+$ 955.5870, found 955.5897.



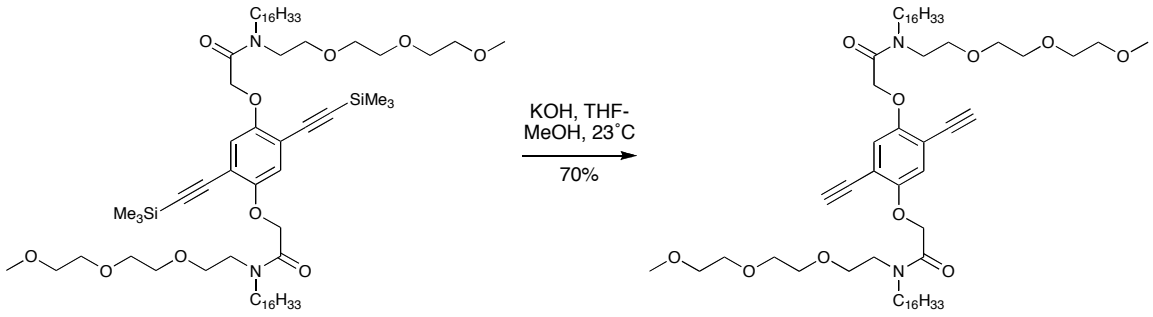
5b **6b**

2,2'-(2,5-Bis(trimethylsilylethynyl)-1,4-phenylene)bis(oxy)bis(*N*-(3,6,9-trioxadecyl)-*N*-hexadecylethanamide) (6b). Diiodide **5b** (1217 mg, 1.0 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (35 mg, 0.05 mmol) and copper(I) iodide (10 mg, 0.05 mmol) are placed in a Schlenk flask equipped with a magnetic stirrer. Contents are evacuated and back-filled with argon 5 times, and a degassed, premixed solution of PhMe (3 mL) and *i*Pr_2NH (1 mL) is added, followed by trimethylsilylacetylene (0.42 mL, 3.0 mmol). After 5 more quick vacuum / backfill cycles, the mixture is stirred at 70˚C for ca. 16 h. The mixture is then cooled to room temperature, diluted with ethyl acetate, and ca. 10 g of silica gel are added. Solvents are evaporated under reduced pressure, and the crude product immobilized on silica gel is purified by column chromatography on silica gel using progressively more polar 3:1 to 1:1 CH_2Cl_2 : EtOAc (v/v) as the mobile phase to afford **6b** as a pale brown oil (888 mg, 73%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.97 (s, 1H), 6.93 (s, 1H), 4.78 (d, 2H, *J* = 6.0 Hz), 4.69 (d, 2H, *J* = 4.5 Hz), 3.63-3.49 (m, 28H), 3.37-3.33 (m, 10H), 1.56-1.50 (m, 4H), 1.27-1.22 (m, 62H), 0.89-0.86 (t, 6H, *J* = 7.0), 0.23 (d, 18H, *J* = 1.5 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.9, 167.6, 167.5, 153.9, 153.6, 119.1, 119.0, 118.3, 114.7, 114.3, 101.2, 101.0, 100.8, 100.7, 100.5, 72.10, 72.05, 70.92, 70.86, 70.77, 70.71, 70.6, 69.5, 69.35, 69.26, 69.2, 69.1, 59.2, 48.9, 47.2, 46.5, 46.1, 32.1, 29.9, 29.85, 29.81, 29.78, 29.61, 29.55, 29.2, 27.6, 27.2, 27.1, 22.9, 14.3, 0.16, 0.15; HR-MS (ESI): calc for $C_{66}H_{120}N_2O_{10}Si_2$ $[M+Na]^+$ 1179.8374, found 1179.8388.



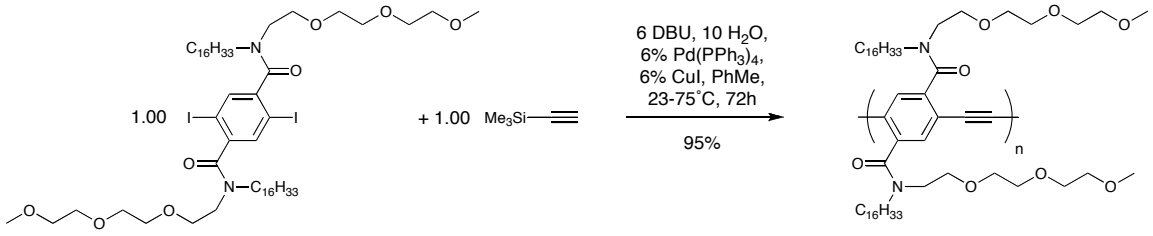
6a **7a**

2,2'-(2,5-Diethynyl-1,4-phenylene)bis(oxy)bis(*N*-(3,6,9-trioxadecyl)-*N*-octylethanamide) (7a). A solution of protected monomer **6a** (729 mg, 0.78 mmol) in THF (20 mL) is degassed by bubbling nitrogen through for ca. 15 mins. To this solution is added a methanolic solution of KOH (2 mL, 1 g KOH / 10 mL MeOH), and the resulting mixture is stirred at room temperature for 1 h. Contents are then poured in sat aq. NaCl, extracted with Et_2O and the solvents are evaporated under reduced pressure. The resulting residue is purified by column chromatography on silical gel using progressively more polar 3:1 to 1:3 CH_2Cl_2 : EtOAc (v/v) to afford **7a** as a pale brown oil that slowly solidifies upon refrigeration (432 mg, 70%). m. p. 50-51˚C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.96 (dd, 2H, *J* = 8.0, 2.5 Hz), 4.83 (d, 2H, *J* = 9.0 Hz), 4.71 (d, 2H, *J* = 7.0 Hz), 3.63-3.56 (m, 18H), 3.56-3.49 (m, 9H), 3.38-3.33 (m, 12H), 1.57-1.51 (m, 4H), 1.27-1.22 (m, 22H), 0.88-0.84 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.64, 167.60, 167.21, 167.16, 154.0, 153.84, 153.78, 153.6, 118.5, 118.10, 118.07, 113.68, 113.65, 113.40, 113.35, 83.5, 83.44, 83.37, 83.3, 79.7, 79.6, 79.5, 79.4, 72.1, 72.0, 70.9, 70.8, 70.72, 70.69, 70.67, 70.6, 69.30, 69.26, 69.2, 68.6, 68.5, 68.4, 68.2, 59.19, 59.18, 48.8, 47.0, 46.3, 46.1, 31.95, 31.92, 29.52, 29.49, 29.41, 29.39, 29.0, 27.5, 27.07, 27.04, 22.8, 14.3; HR-MS (ESI): calc for $C_{44}H_{72}N_2O_{10}$ $[M+Na]^+$ 811.5079, found 811.5079.



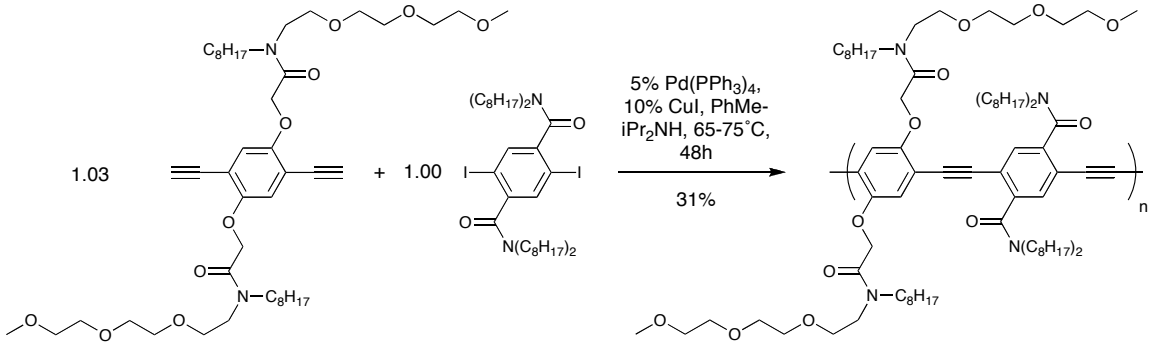
6b **7b**

2,2'-(2,5-Diethynyl-1,4-phenylene)bis(oxy)bis(*N*-(3,6,9-trioxadecyl)-*N*-hexadecylethanamide) (7b). A solution of protected monomer **6b** (843 mg, 0.73 mmol) in THF (20 mL) is degassed by bubbling nitrogen through for ca. 15 mins. To this solution is added a methanolic solution of KOH (2 mL, 1 g KOH / 10 mL MeOH), and the resulting mixture is stirred at room temperature for 1 h. Contents are then poured in sat aq. NaCl, extracted with Et_2O and the solvents are evaporated under reduced pressure. The resulting residue is purified by column chromatography on silical gel using progressively more polar 3:1 to 1:3 CH_2Cl_2 : EtOAc (v/v) to afford **7b** as an off-white solid (515 mg, 70%). m. p. 66.5-68.5˚C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.96 (dd, 2H, *J* = 7.5, 2.0 Hz), 4.83 (d, 2H, *J* = 8.5 Hz), 4.71 (d, 2H, *J* = 7.0 Hz), 3.63-3.55 (m, 18H), 3.54-3.49 (m, 9H), 3.38-3.32 (m, 12H), 1.57-1.50 (m, 4H), 1.27-1.22 (m, 60H), 0.86 (t, 6H, *J* = 7.0 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.62, 167.58, 167.2, 167.1, 154.0, 153.83, 153.77, 153.6, 118.5, 118.09, 118.06, 113.7, 113.6, 113.4, 113.3, 83.5, 83.43, 83.36, 83.3, 79.7, 79.6, 79.5, 79.3, 72.1, 72.0, 70.9, 70.8, 70.71, 70.68, 70.66, 70.6, 69.29, 69.26, 69.2, 68.6, 68.5, 68.3, 68.2, 59.18, 59.16, 48.8, 47.0, 46.3, 46.1, 32.1, 29.9, 29.81, 29.76, 29.7, 29.6, 29.5, 29.0, 27.5, 27.09, 27.07, 22.8, 14.3; HR-MS (ESI): calc for $C_{60}H_{104}N_2O_{10}$ $[M+Na]^+$ 1035.7589, found 1035.7698.



4b **P2**

Polymer P2. To a Schlenk equipped with a magnetic stirring bar are added monomer **4b** (266.9 mg, 0.231 mmol), tetrakis(triphenylphosphine)palladium(0) (16 mg, 0.014 mmol) and copper(I) iodide (5 mg, 0.014 mmol). Contents are evacuated and back-filled with argon 5 times, and degassed PhME (4 mL) is added, followed by DBU (0.25 mL, 1.4 mmol), trimethylsilylacetylene (32.6 μL, 0.231 mmol), and water (42 μL, 2.3 mmol). The resulting mixture is stirred under argon at room temperature for ca. 16 h, followed by ca. 8 h at 50˚C, ca. 16 h at 65˚C and finally ca. 24 h at 75 ˚C.[6] The mixture is then cooled to room temperature, and precipitated in an excess of methanol and isolated by centrifugation. The polymer is redissolved in dichloromethane and filtered on a short plug of silica gel and eluted with more dichloromethane. Concentration of the solution followed by reprecipitation from methanol affords polymer **P2** as a rubbery yellow-brown solid (204 mg, 95%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.40 (s, 2H), 3.73-3.50 (m, 24H), 3.38-3.35 (m, 8H), 3.18 (br, 2H), 1.65-1.16 (m, 56H), 0.89-0.83 (m, 6H); GPC (THF vs. PS): Mn = 19 900, Mw = 35 900.



7a **11** **P3**

Polymer P3. To a Schlenk equipped with a magnetic stirring bar are added monomer **7a** (81.3 mg, 0.103 mmol), monomer **11** (86.5 mg, 0.100 mmol), tetrakis(triphenylphosphine)palladium(0) (6 mg, 0.005 mmol) and copper(I) iodide (2 mg, 0.010 mmol). Contents are evacuated and back-filled with argon 5 times, and a degassed, premixed solution of PhMe (3 mL) and *i*Pr_2NH (1 mL) is added. The resulting mixture is stirred under argon at room temperature for ca. 30 minutes, followed by ca. 16 h at 65˚C and ca. 24 h at 75 ˚C. The mixture is then cooled to room temperature, and precipitated in an excess of methanol and isolated by centrifugation. The polymer is redissolved in dichloromethane and filtered on a short plug of silica gel and eluted with more dichloromethane. Concentration of the solution followed by reprecipitation from methanol affords polymer **P3** as a rubbery yellow-green solid (43 mg, 31%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.46 (s, 2H), 7.05 (s, 2H), 4.80-4.70 (br, 4H), 3.63-3.48 (m, 28H), 3.38-3.35 (m, 12H), 3.18 (br, 4H), 1.65-1.52 (12H), 1.26-1.16 (m, 60H), 0.89-0.83 (m, 18H); GPC (THF vs. PS): Mn = 60 300, Mw = 141 700.

II. SELF-ASSEMBLY IN LYOTROPIC LC AND SPECTROSCOPY

Preparation of Lyotropic Liquid Crystal Samples

The lyotropic liquid crystal samples were prepared according to literature procedures.[7] Potassium dodecanoate (recrystallized thrice from EtOH) was thoroughly mixed with D_2O (and with KCl in the case of **LLC-2**) with the help of a vortex shaker. To this was then added n-decanol, following once more by thoroughly mixing with the help of a vortex shaker. For samples containing polymer **P2** or **P3** a solution of the polymer in 1-decanol (~1 mg/mL) was used instead of pure 1-decanol. Samples were allowed to settle for a minimum of 24h before taking measurements. The specific compositions of the lyotropic liquid crystal mixtures are presented in **Table S1** below. The resulting mixtures are moderately viscous and quasi-transparent / translucent though light scattering. Polymers **P2** and **P3** do not precipitate from these mixtures – solid polymer aggregates are visible neither to the naked eye nor to the microscope – and the samples remain highly fluorescent to the naked eye under UV irradiation (**Figure S1**).

Table S1: Composition of the Lyotropic Liquid Crystal Mixtures.

	Assigned Phases*	**Composition (% w/w)**			
		D_2O	Potassium Dodecanoate	n-Decanol	KCl
LLC-1	Calamitic Nematic	67.5	26.2	6.3	-
LLC-2	Nematic (undefined)	60.0	30.0	6.0	4.0
LLC-3	Discotic Nematic	69.0	24.8	6.2	-

* As previously assigned in the literature for LLCs of identical compositions.[7]

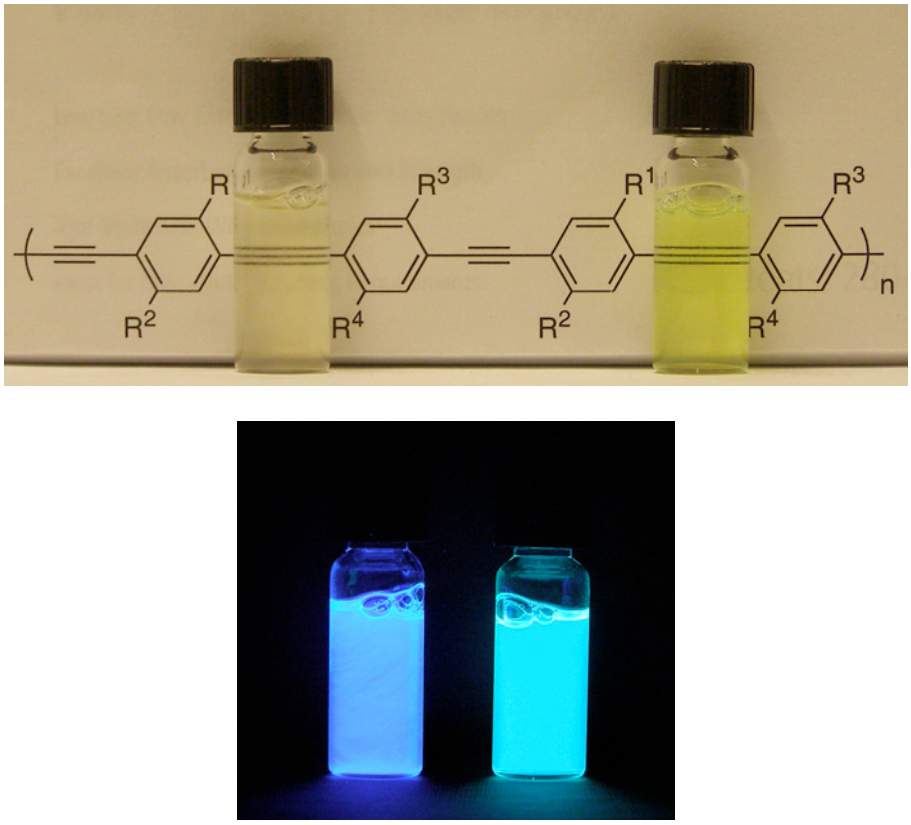


Figure S1: Photographs of **P2** (left) and **P3** (right) in D_2O-$C_{11}H_{23}COOK$-$C_{10}H_{21}OH$ Lyotropic Liquic Crystal mixtures under ambient light (top) and under UV irradiation (bottom)

Measurements with Lyotropic Liquid Crystal Samples

For spectroscopic measurements, due the scattering and highly absorbing nature of the samples, a fused silica (quartz) cell with a narrow optical path (0.1 cm) was used. Absorption spectra are presented after baseline correction. For LLC samples, fluorescence spectra were recorded by front-face ($\theta \simeq 22.5^{\circ}$) detection. Optical textures were obtained form thin films of the LLC samples placed between a microscope slide and a glass coverslip under cross-polarizers.

Spectra of P2 and P3 in solution

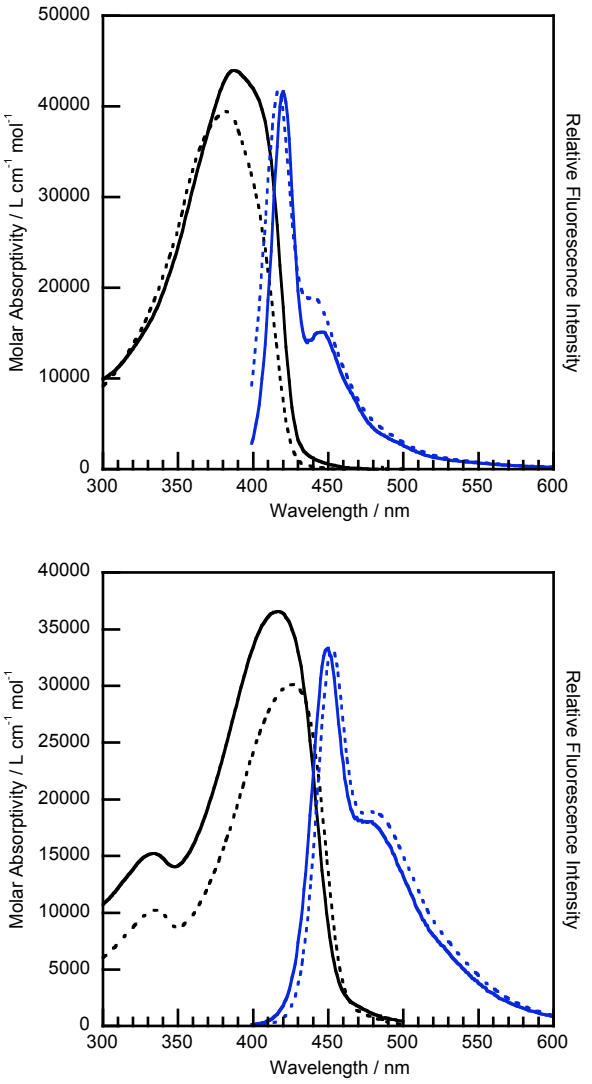


Figure S2: Absorption (black) and normalized fluorescence emisison (blue) spectra of **P2** (top) and **P3** (bottom) in chloroform (plain) and 1-decanol (dashed) solution.

Langmuir-Blodgett Experiments with P2 and P3 at the Air-Water Interface

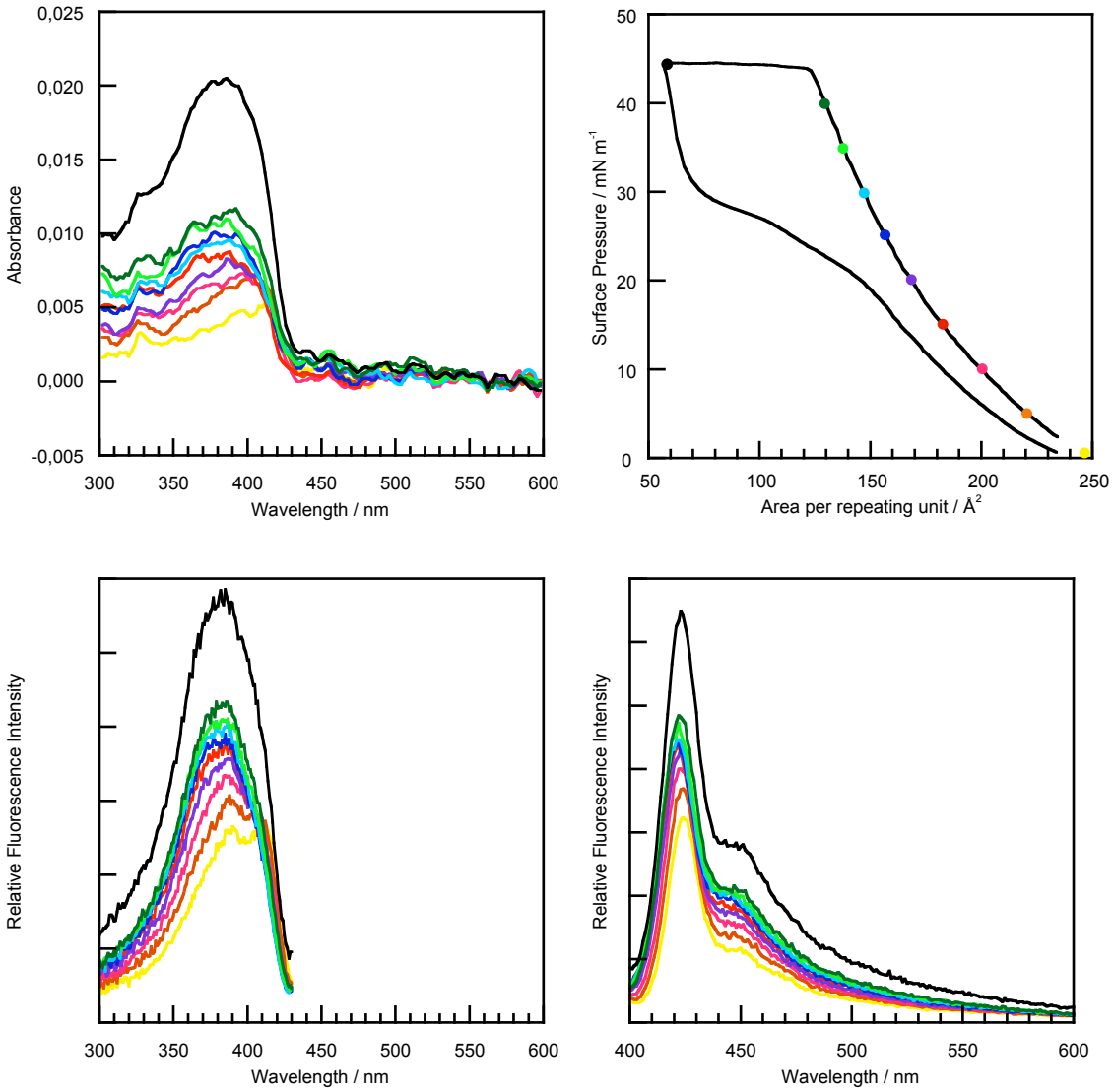


Figure S3: Absorption (top left), fluorescence excitation (bottom left) and emission (bottom right) of monolayers of **P2** at the Air-Water interface. The different curves were acquired at the surface pressure indicated by the color code on the pressure-area isotherm (top right). Spectra with black curves were acquired after folding into multilayers.

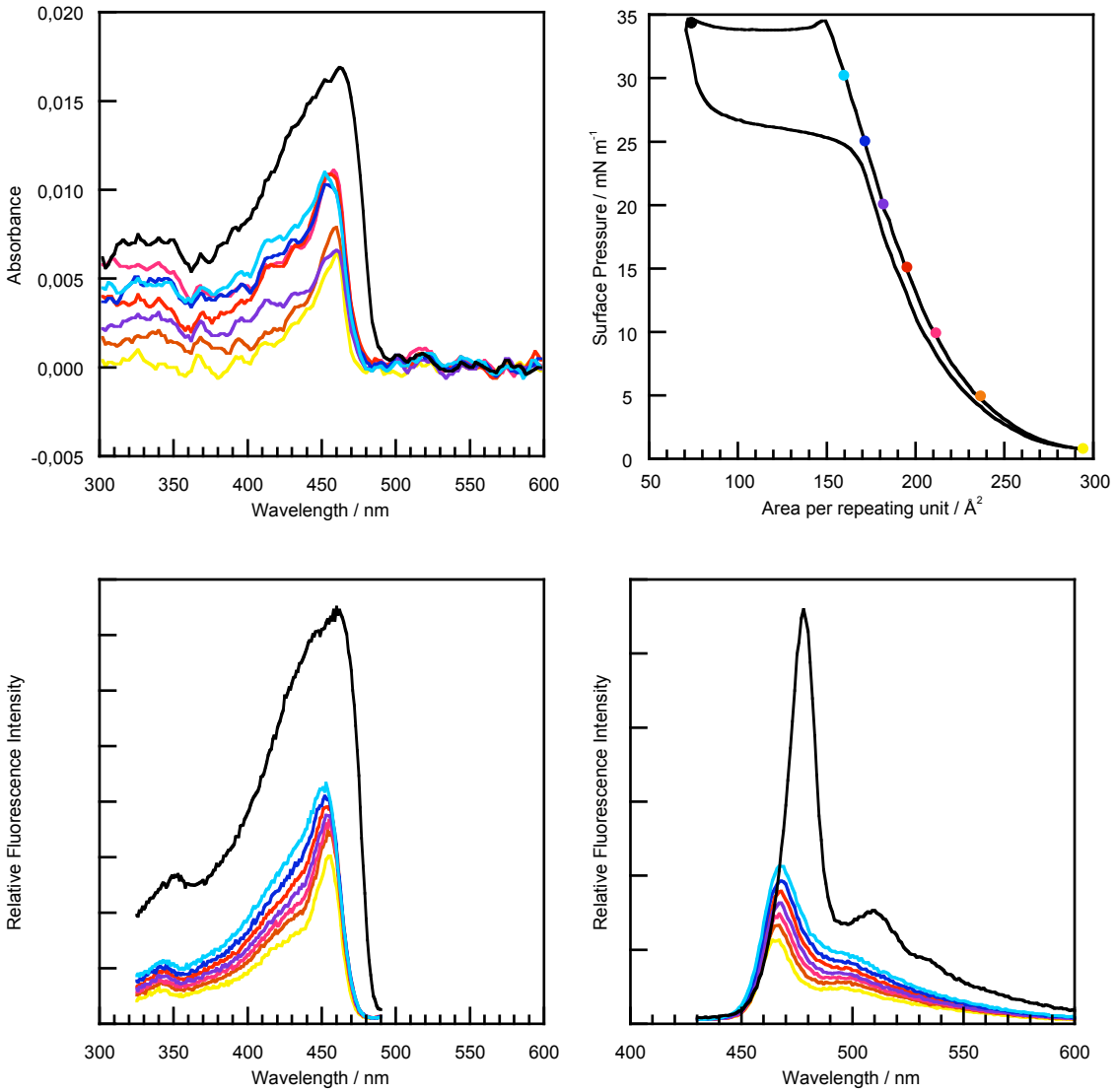


Figure S4: Absorption (top left), fluorescence excitation (bottom left) and emission (bottom right) of monolayers of **P3** at the Air-Water interface. The different curves were acquired at the surface pressure indicated by the color code on the pressure-area isotherm (top right). Spectra with black curves were acquired after folding into multilayers.

Comparative Spectra of P2 and P3 in Lyotropic Liquid Crystal

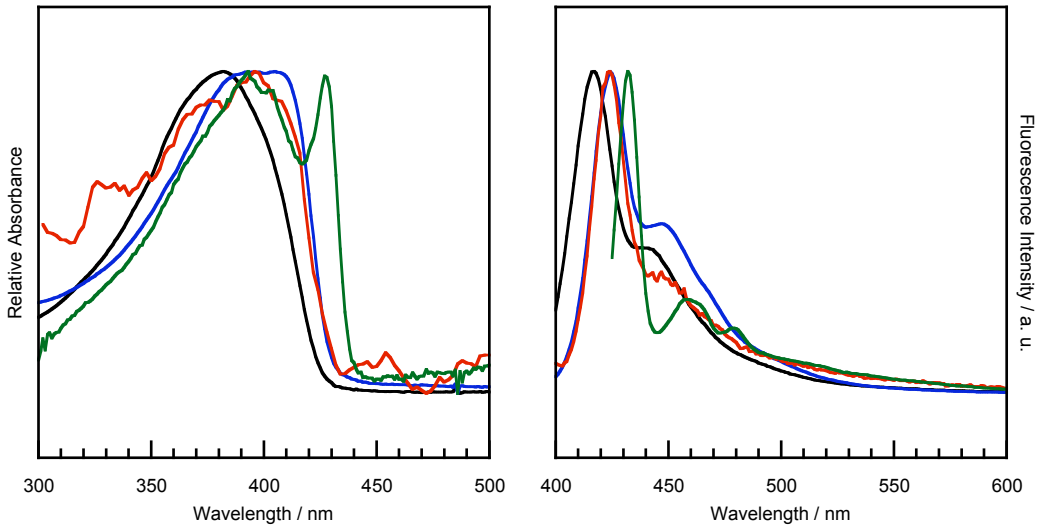


Figure S5: Normalized absorption (left) and fluorescence emission (right) spectra of **P2** in 1-decanol (black), Langmuir monolayers at the air-water interface (red), **LLC-1** (blue) and thin solid films (green).

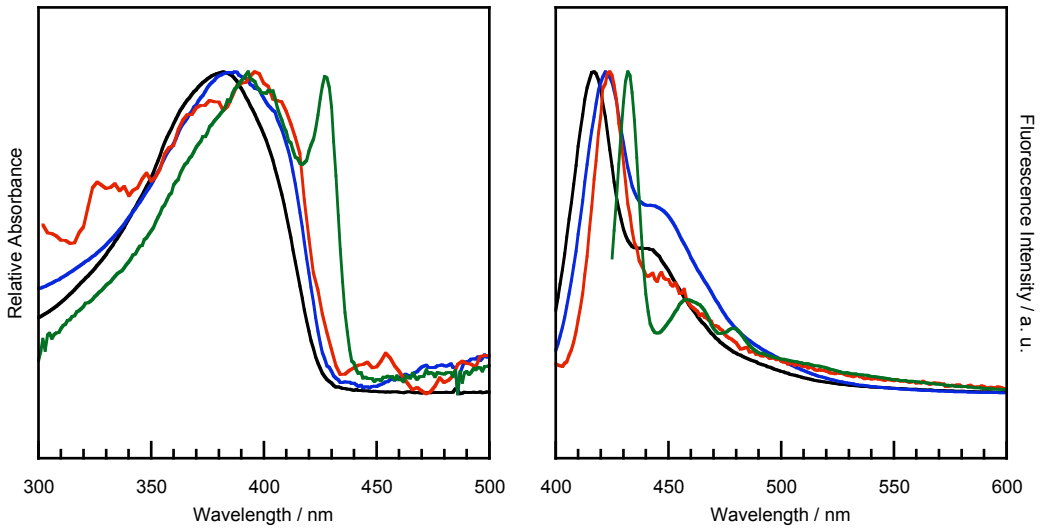


Figure S6: Normalized absorption (left) and fluorescence emission (right) spectra of **P2** in 1-decanol (black), Langmuir monolayers at the air-water interface (red), **LLC-2** (blue) and thin solid films (green).

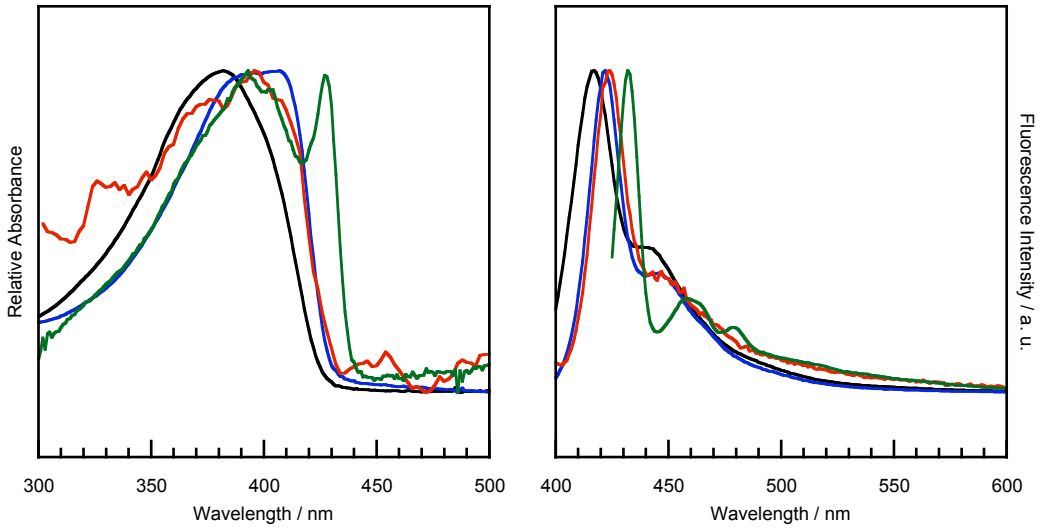


Figure S7: Normalized absorption (left) and fluorescence emission (right) spectra of **P2** in 1-decanol (black), Langmuir monolayers at the air-water interface (red), **LLC-3** (blue) and thin solid films (green).

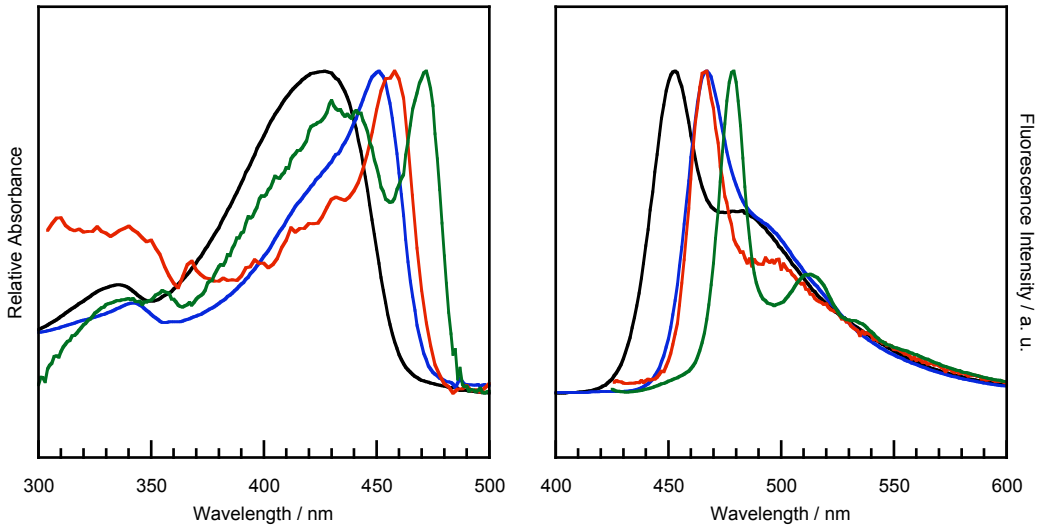


Figure S8: Normalized absorption (left) and fluorescence emission (right) spectra of **P3** in 1-decanol (black), Langmuir monolayers at the air-water interface (red), **LLC-1** (blue) and thin solid films (green).

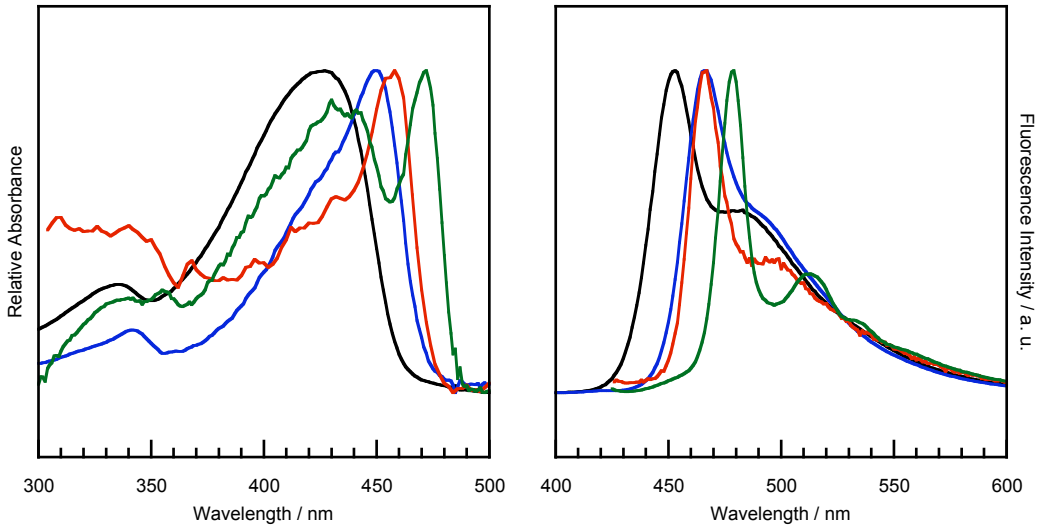


Figure S9: Normalized absorption (left) and fluorescence emission (right) spectra of **P3** in 1-decanol (black), Langmuir monolayers at the air-water interface (red), **LLC-2** (blue) and thin solid films (green).

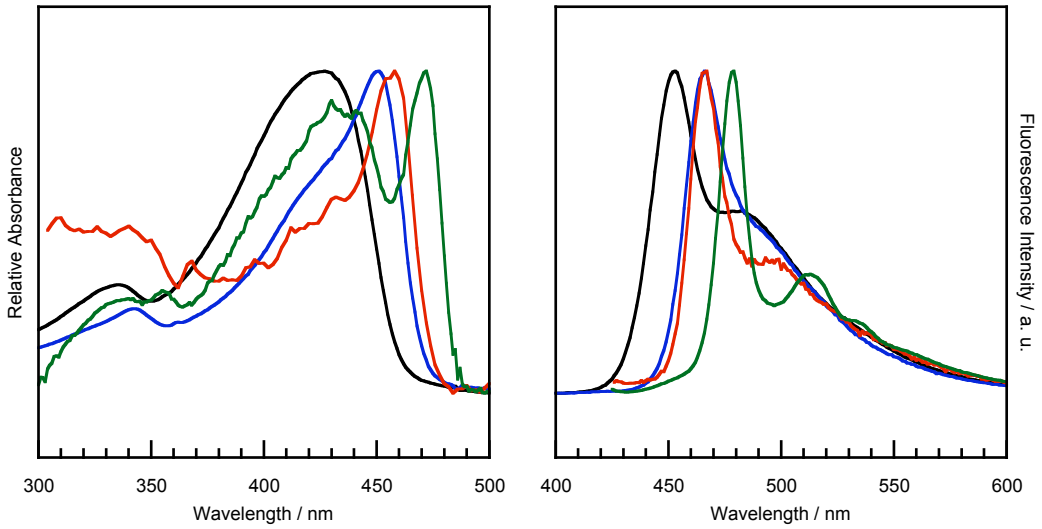


Figure S10: Normalized absorption (left) and fluorescence emission (right) spectra of **P3** in 1-decanol (black), Langmuir monolayers at the air-water interface (red), **LLC-3** (blue) and thin solid films (green).

Table S2: Summary of photophysical properties for **P2** and **P3**.

	P2			P3		
	$\lambda_{max,\ abs}$ (nm)	$\lambda_{max,\ em}$ (nm)	Φ_f	$\lambda_{max,\ abs}$ (nm)	$\lambda_{max,\ em}$ (nm)	Φ_f
$CHCl_3$	387	420	0.23[a]	417	450	0.21[a]
$C_{10}H_{21}OH$	382	417	-	427	453	-
Air-Water Interface	406	424	-	460	467	-
LLC-1	405	424	-	451	467	-
LLC-2	387	422	-	449	467	-
LLC-3	407	422	-	451	466	-
Thin Solid Film	393, 432*	432	0.08[b]	440, 472*	479	0.07[b]

* Aggregation peak. [a] Against quinine sulfate in 1N H_2SO_4 ($\Phi_f = 0.546$, $\lambda_{ex} = 366$ nm).[8] [b] Against perylene in PMMA ($\Phi_f = 0.87$, $\lambda_{ex} = 412$ nm).[9]

Optical Textures of P2 and P3 in Lyotropic Liquid Crystal

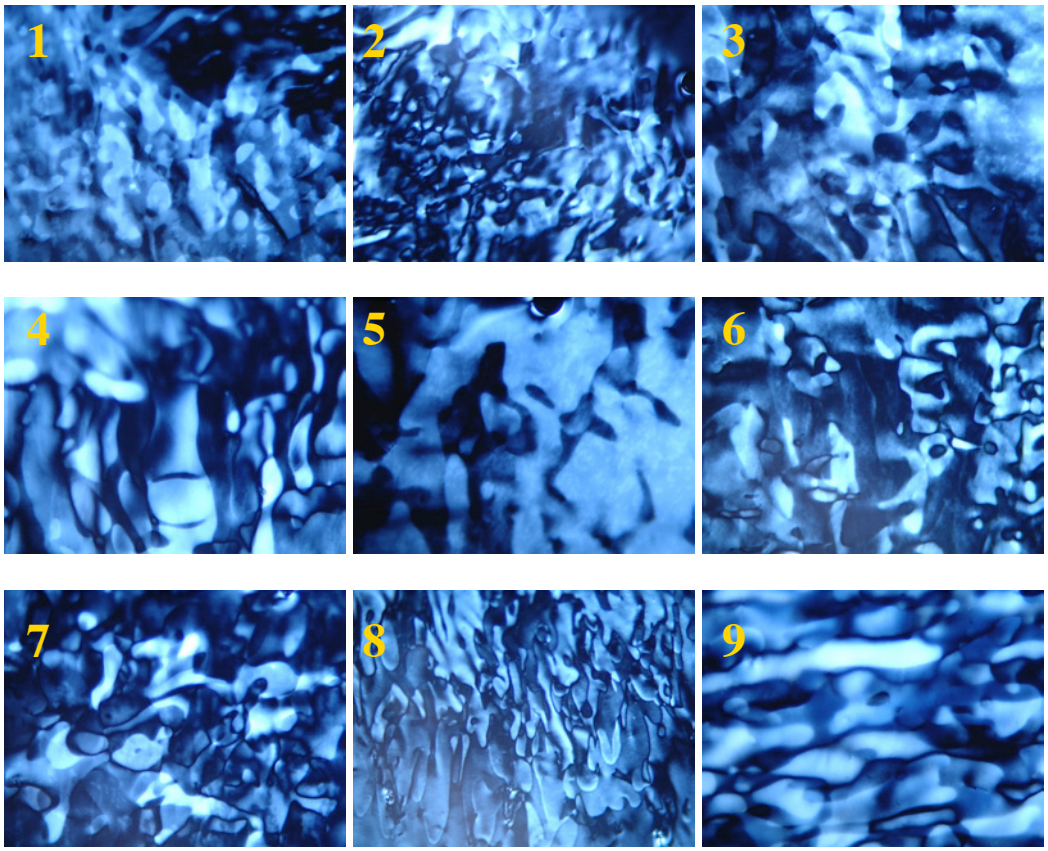


Figure S11: Optical micrographs of **LLC-1** (1-2), **P2** in **LLC-1** (3-7) and **P3** in **LLC-1** (8-9) under cross-polarizers (100 X magnification).

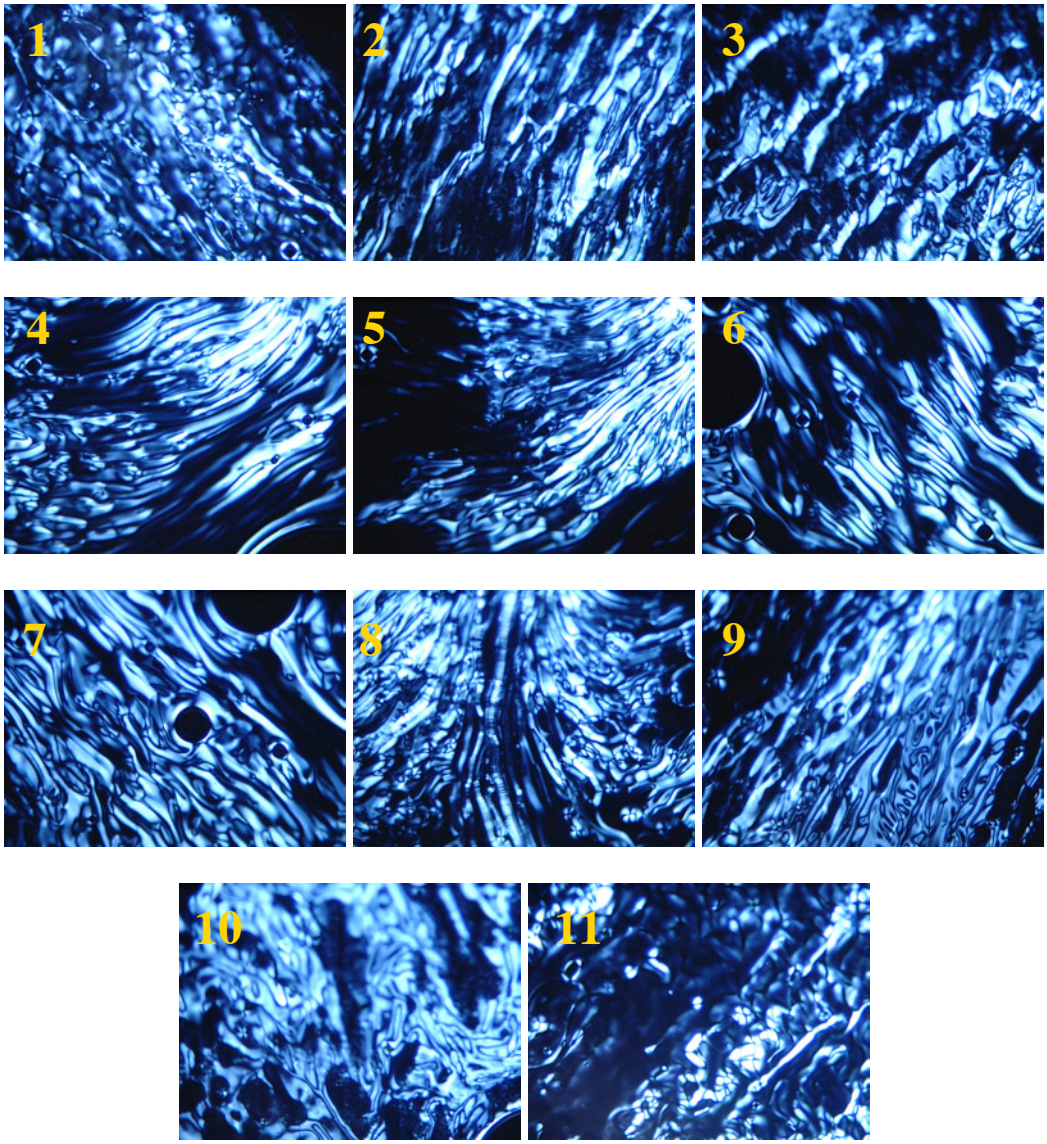


Figure S12: Optical micrographs of **LLC-2** (1-3), **P2** in **LLC-2** (4-7) and **P3** in **LLC-2** (8-11) under cross-polarizers (100 X magnification).

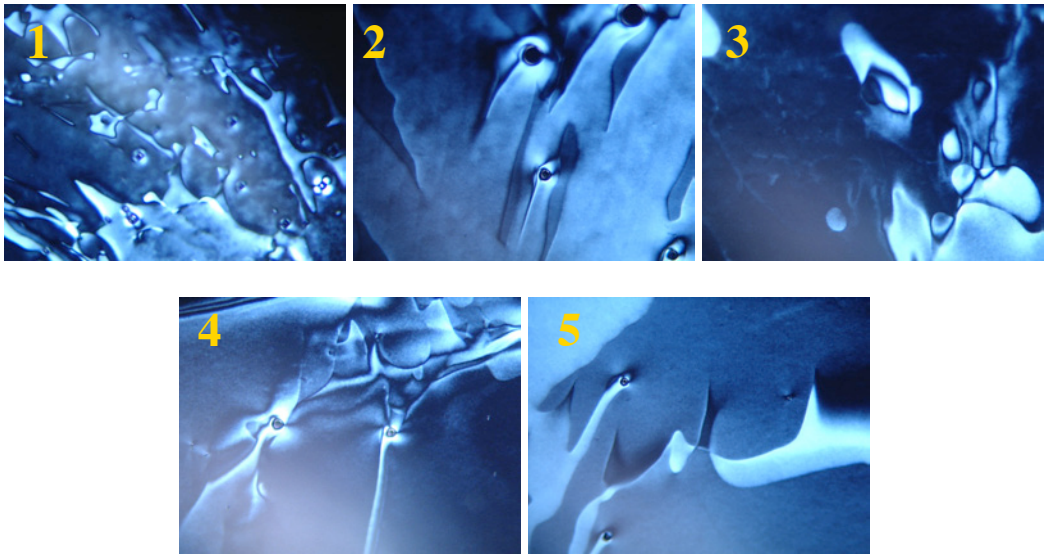


Figure S13: Optical micrographs of **LLC-3** (1), **P2** in **LLC-3** (2-3) and **P3** in **LLC-3** (4-5) under cross-polarizers (100 X magnification).

III. ^{1}H- AND ^{13}C-NMR SPECTRA

Figure S14. ^{1}H-NMR Spectrum of **1a** in $CDCl_3$ (300 MHz).

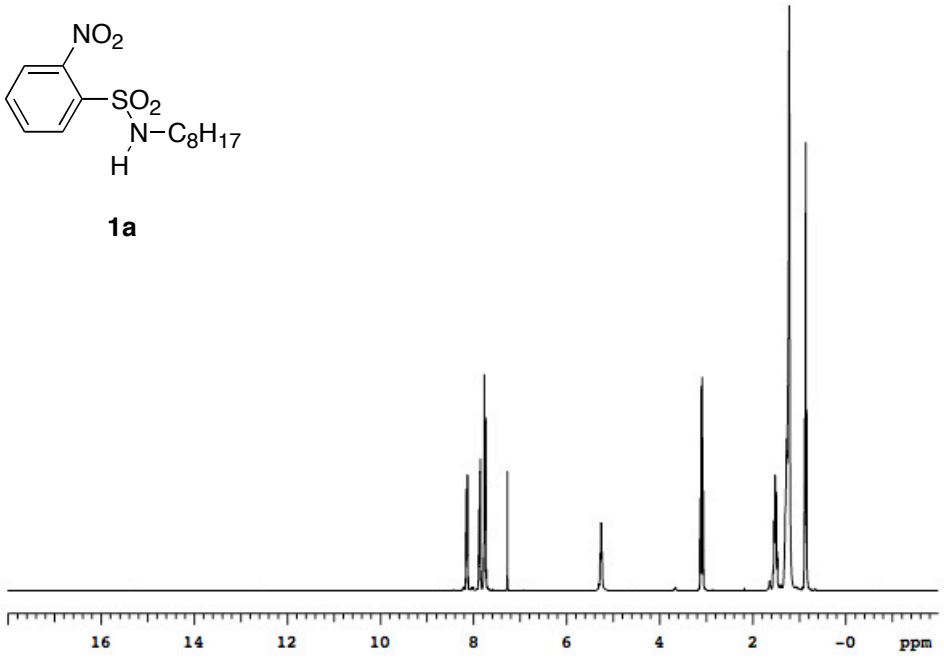


Figure S15. ^{13}C-NMR Spectrum of **1a** in $CDCl_3$ (125 MHz).

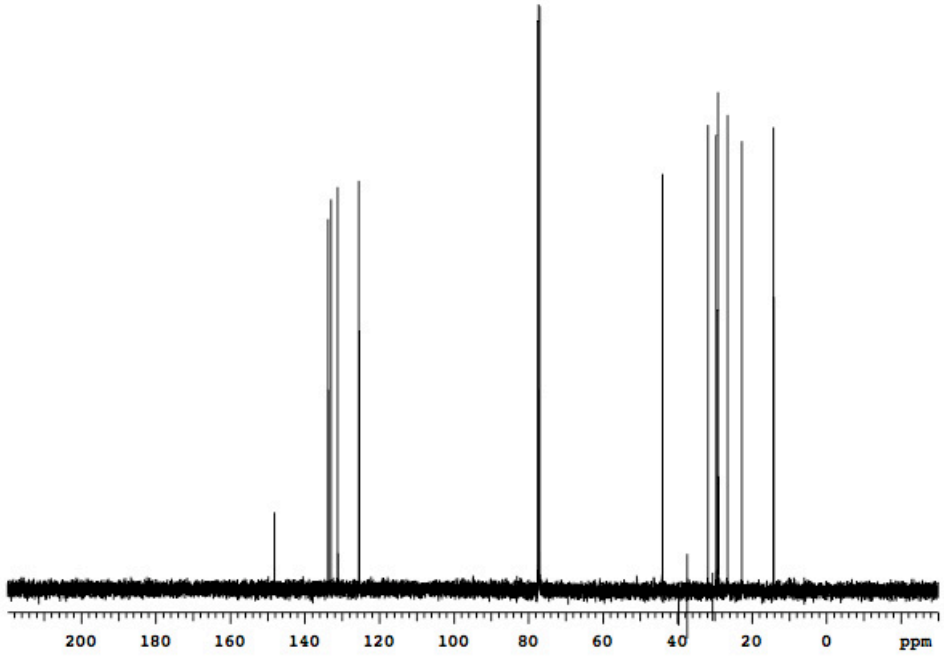


Figure S16. ^{1}H-NMR Spectrum of **1b** in $CDCl_3$ (500 MHz).

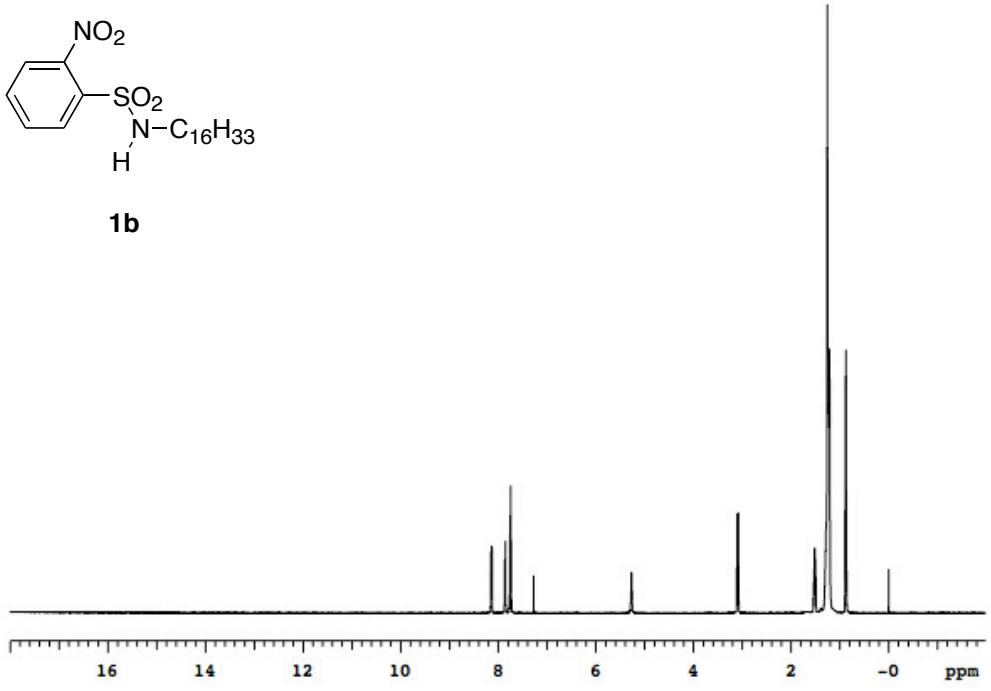


Figure S17. ^{13}C-NMR Spectrum of **1b** in $CDCl_3$ (125 MHz).

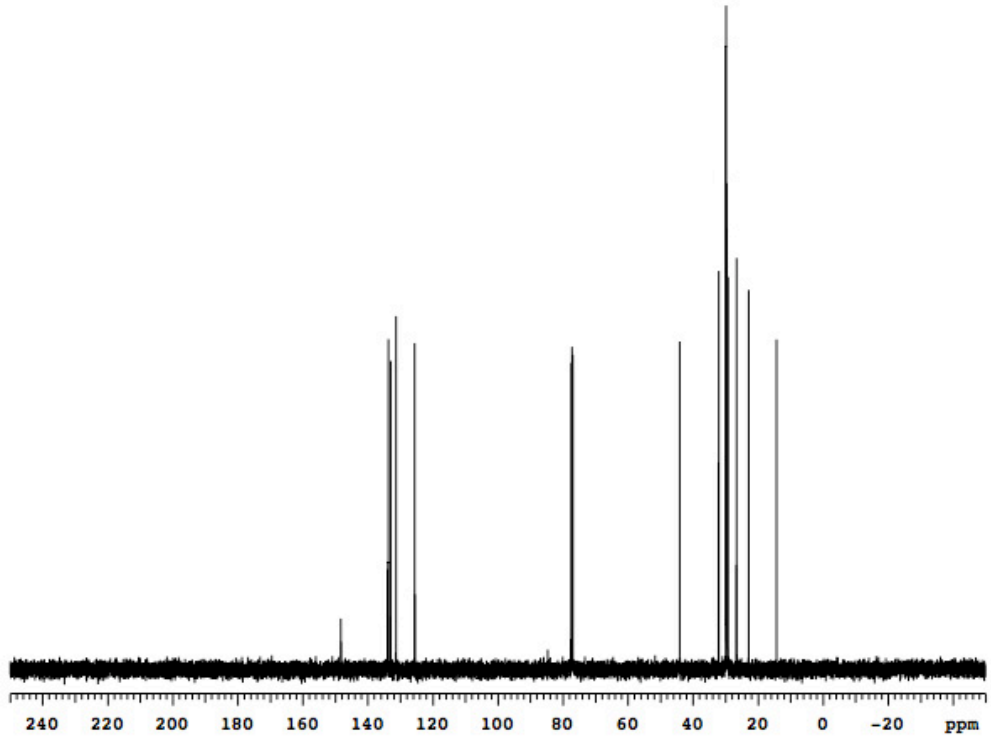


Figure S18. ^{1}H-NMR Spectrum of **2a** in $CDCl_3$ (300 MHz).

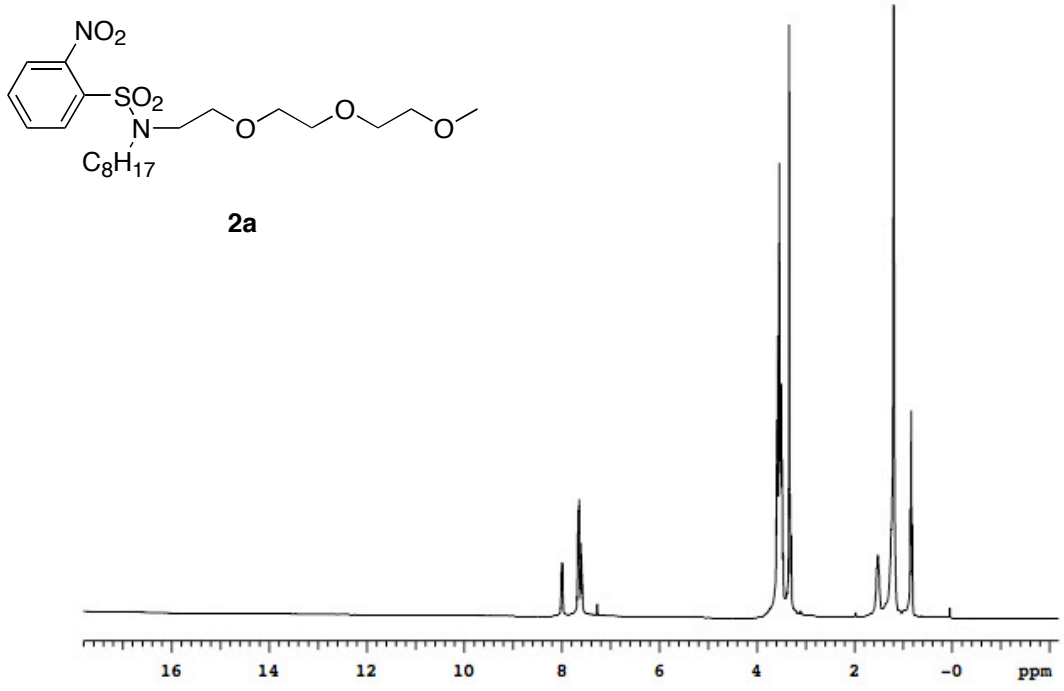


Figure S19. ^{13}C-NMR Spectrum of **2a** in $CDCl_3$ (75 MHz).

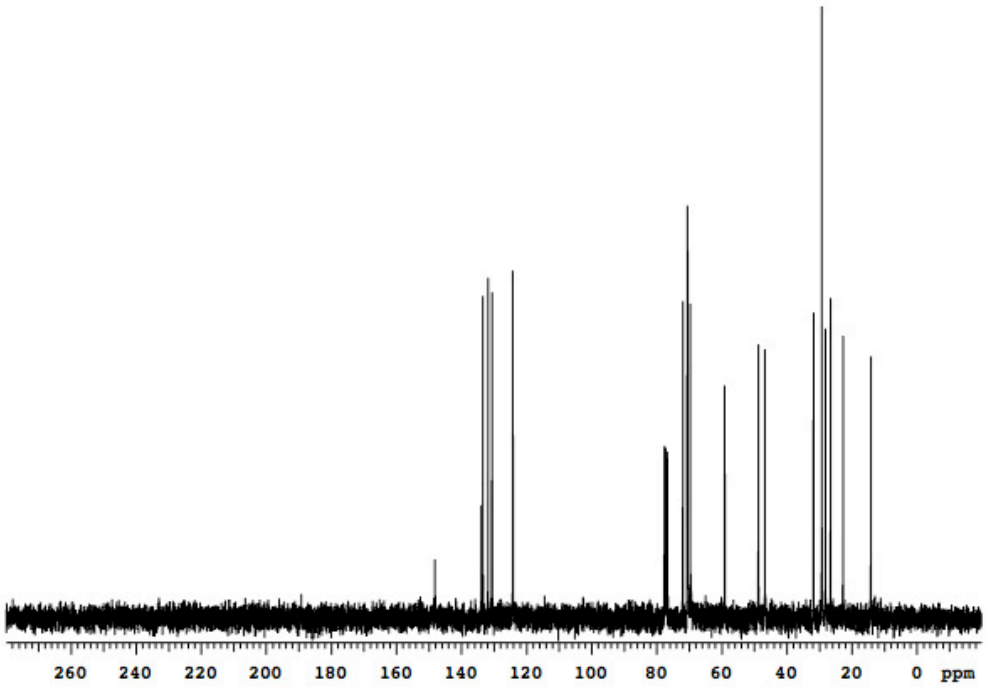


Figure S20. ^{1}H-NMR Spectrum of **2b** in $CDCl_3$ (300 MHz).

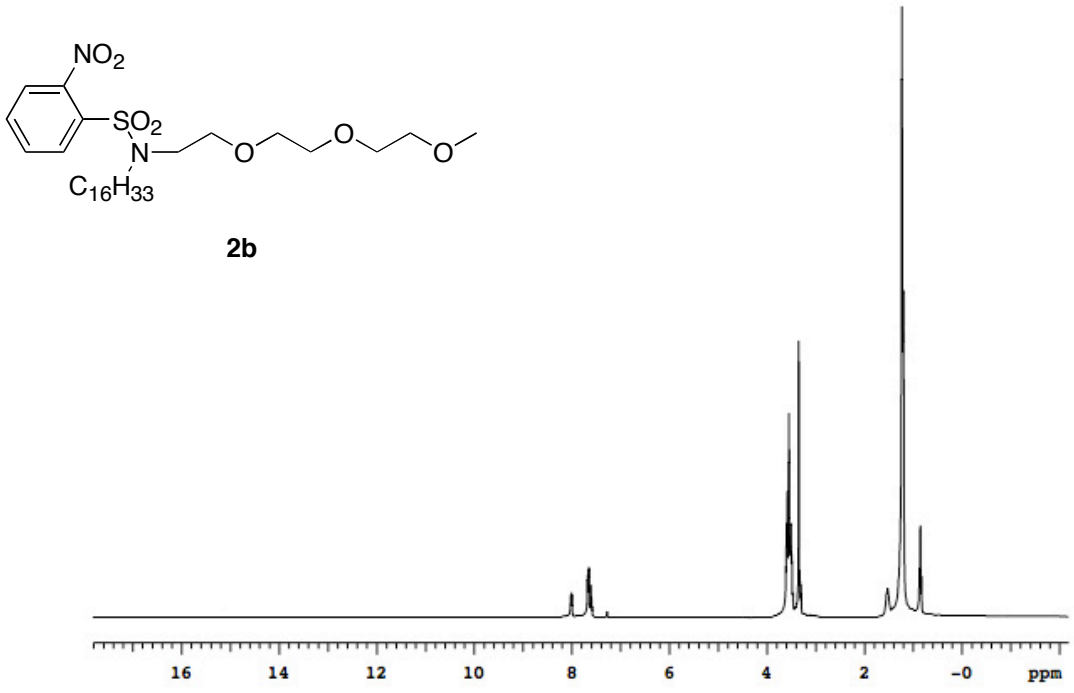


Figure S21. ^{13}C-NMR Spectrum of **2b** in $CDCl_3$ (75 MHz).

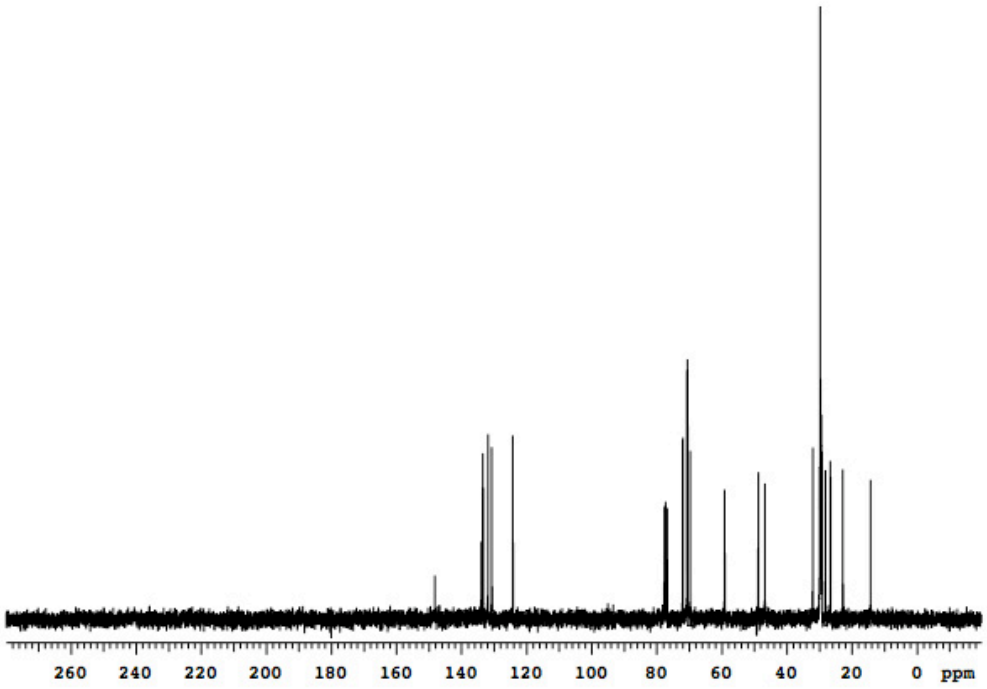


Figure S22. ^{1}H-NMR Spectrum of **3a** in $CDCl_3$ (300 MHz).

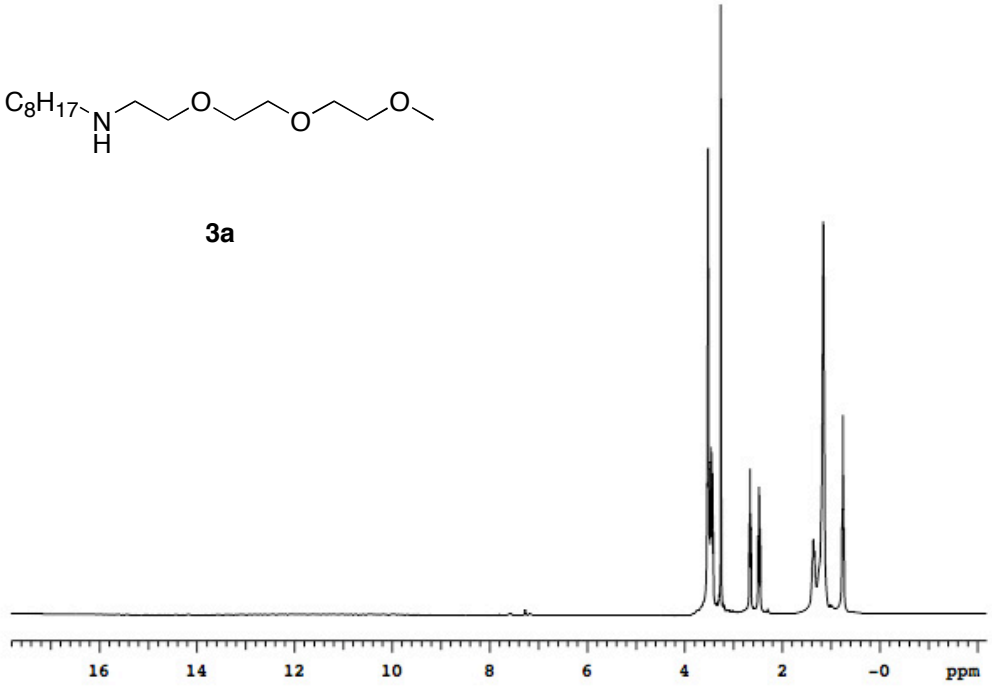


Figure S23. ^{13}C-NMR Spectrum of **3a** in $CDCl_3$ (75 MHz).

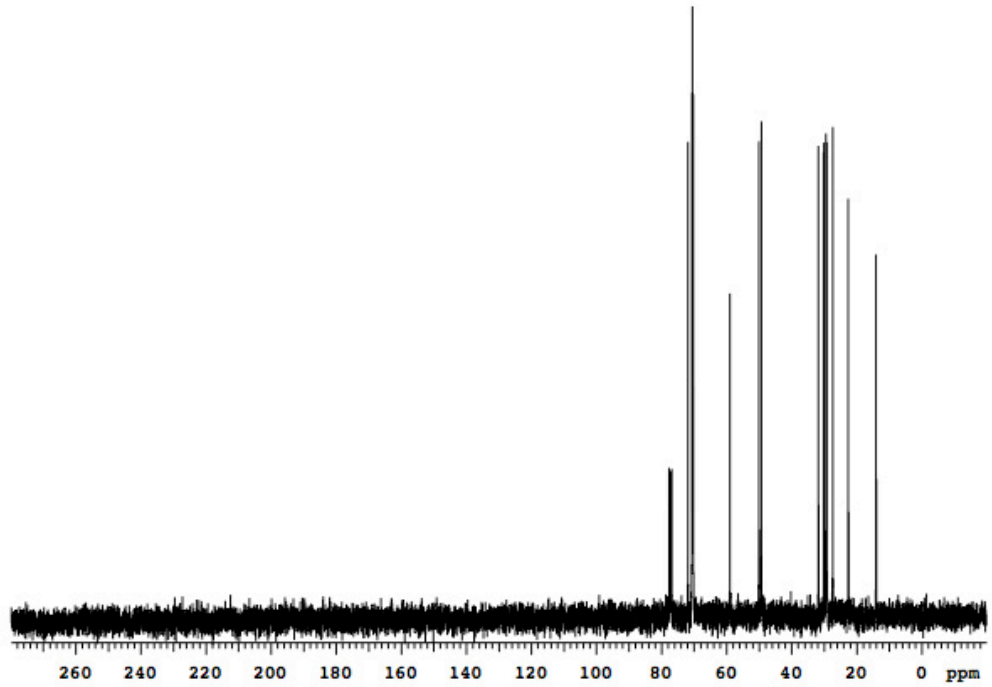


Figure S24. ^{1}H-NMR Spectrum of **3b** in $CDCl_3$ (300 MHz).

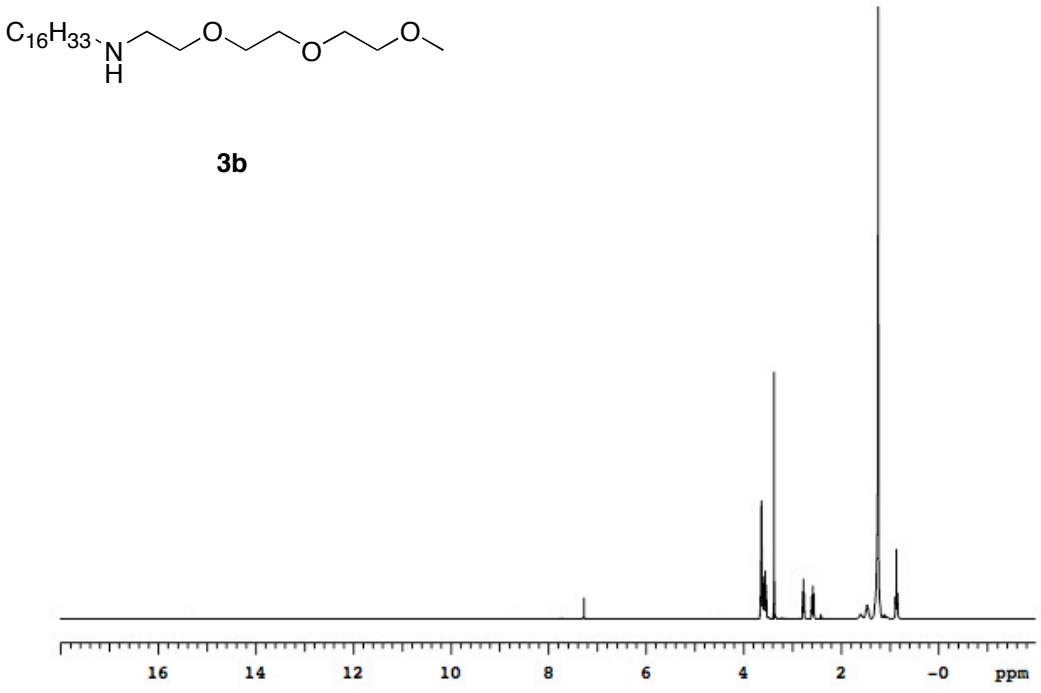


Figure S25. ^{13}C-NMR Spectrum of **3b** in $CDCl_3$ (75 MHz).

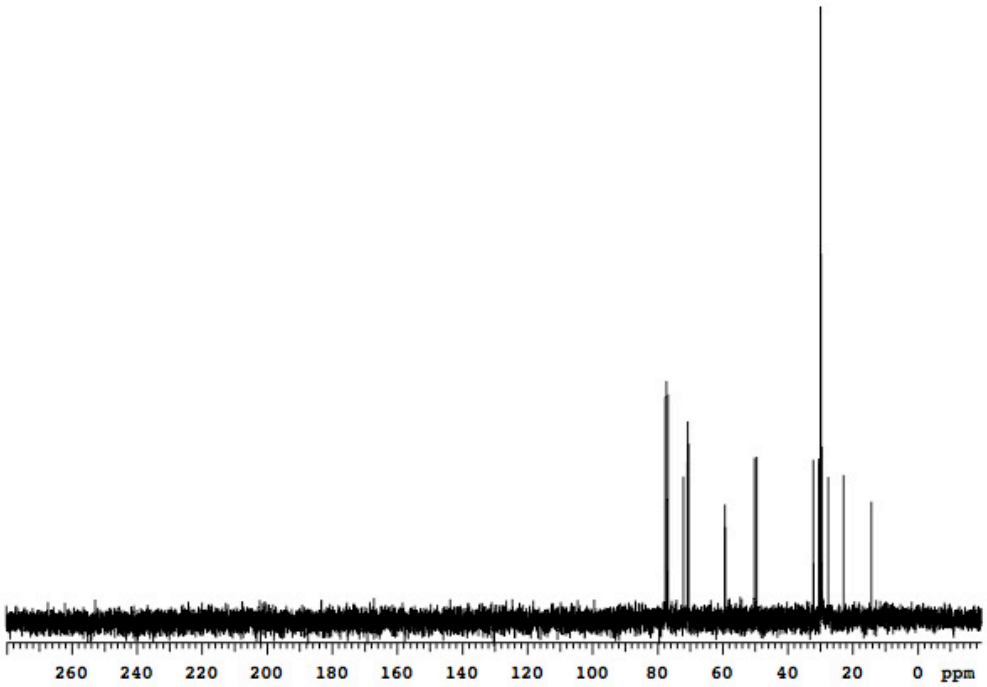


Figure S26. ^{1}H-NMR Spectrum of **4a** in $CDCl_3$ (500 MHz).

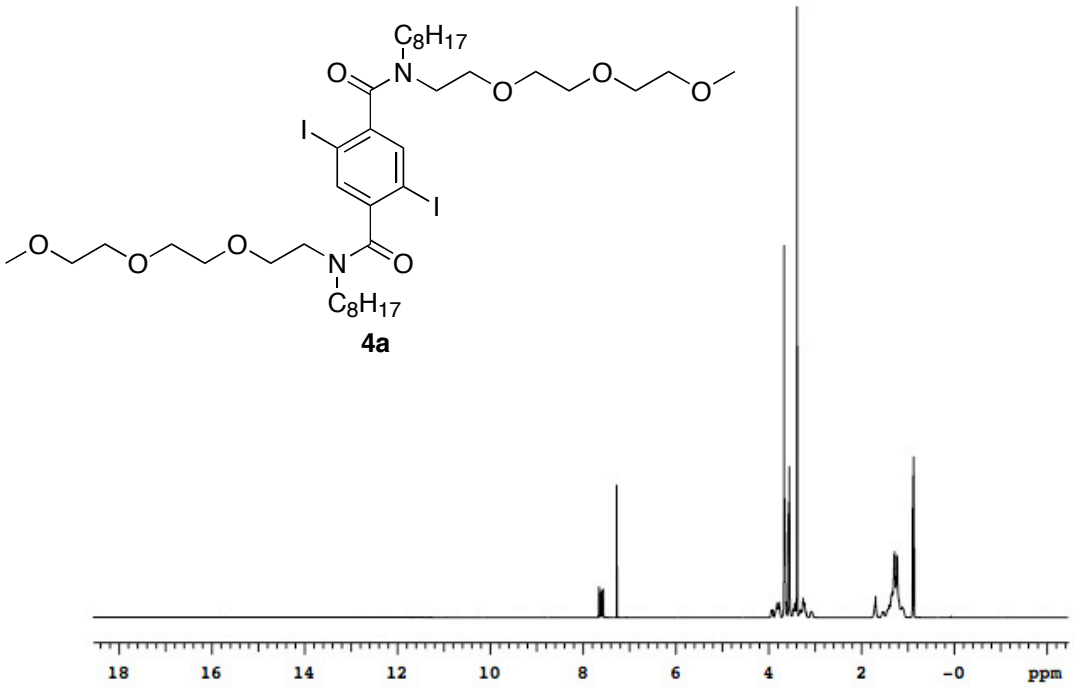


Figure S27. ^{13}C-NMR Spectrum of **4a** in $CDCl_3$ (125 MHz).

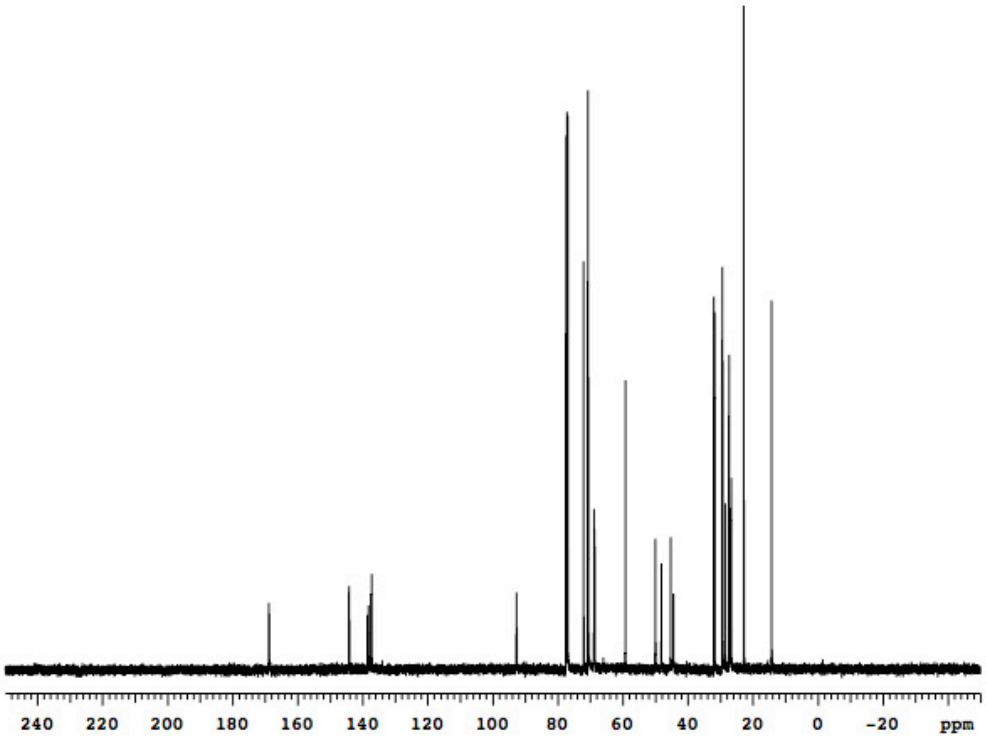


Figure S28. ^{1}H-NMR Spectrum of **4b** in $CDCl_3$ (500 MHz).

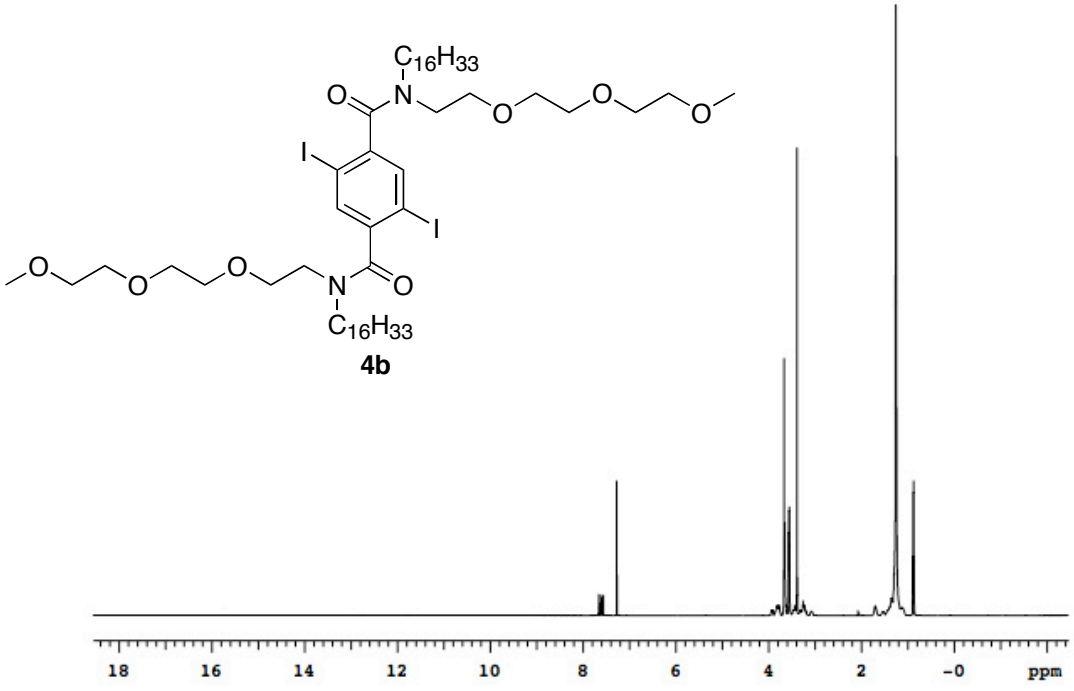


Figure S29. ^{13}C-NMR Spectrum of **4b** in $CDCl_3$ (125 MHz).

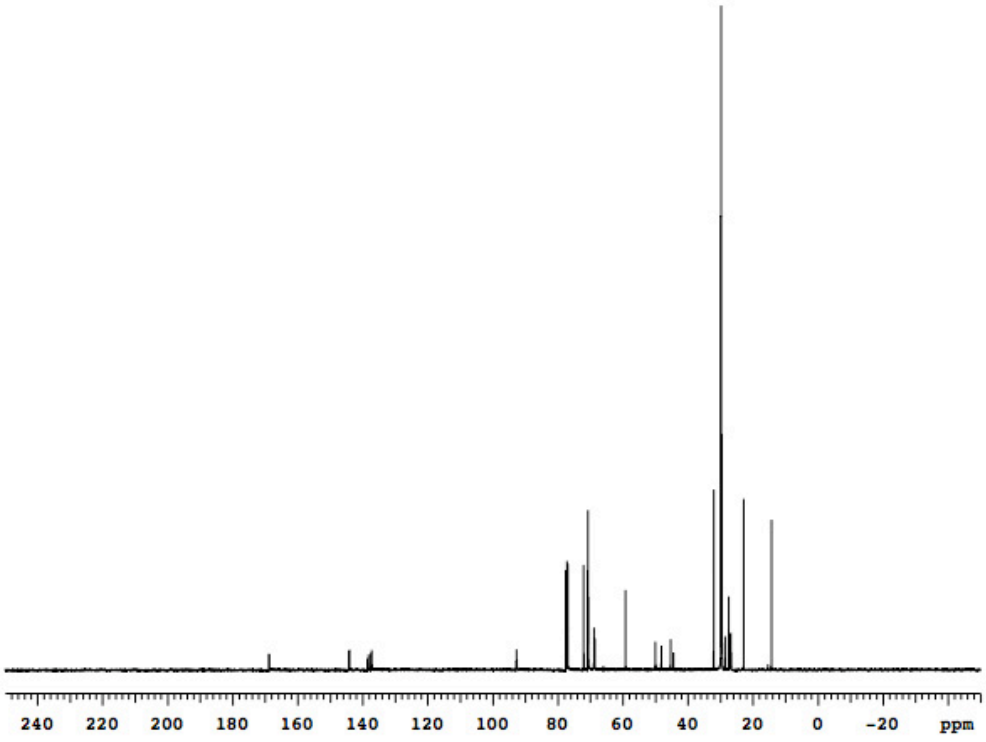
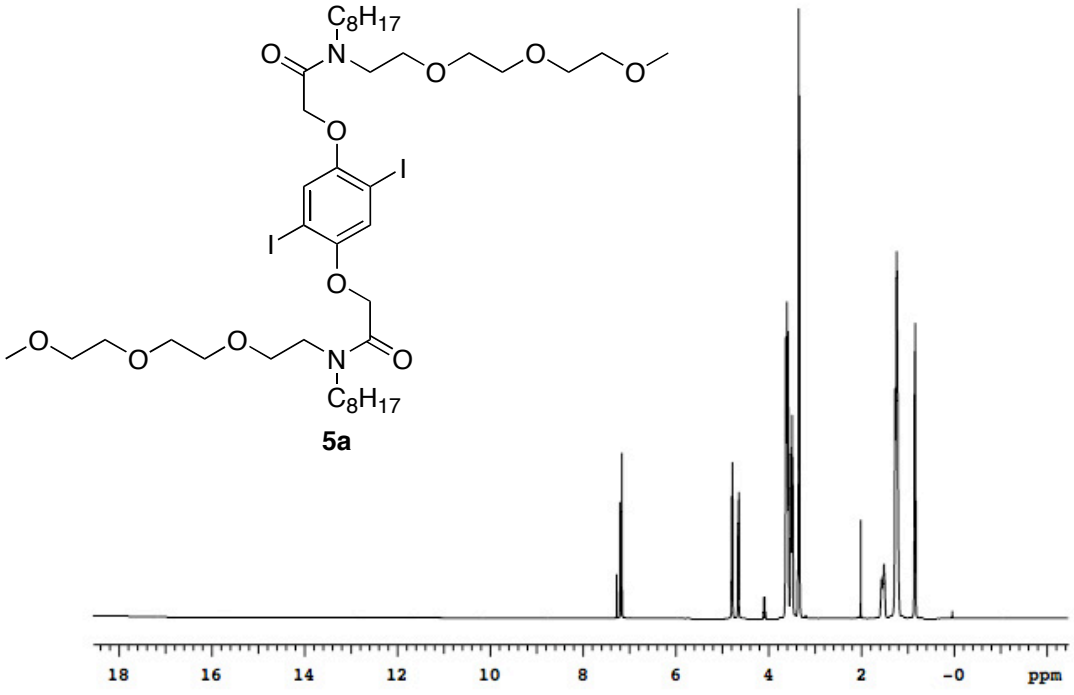


Figure S30. ^{1}H-NMR Spectrum of **5a** in $CDCl_3$ (500 MHz).



5a

Figure S31. ^{13}C-NMR Spectrum of **5a** in $CDCl_3$ (125 MHz).

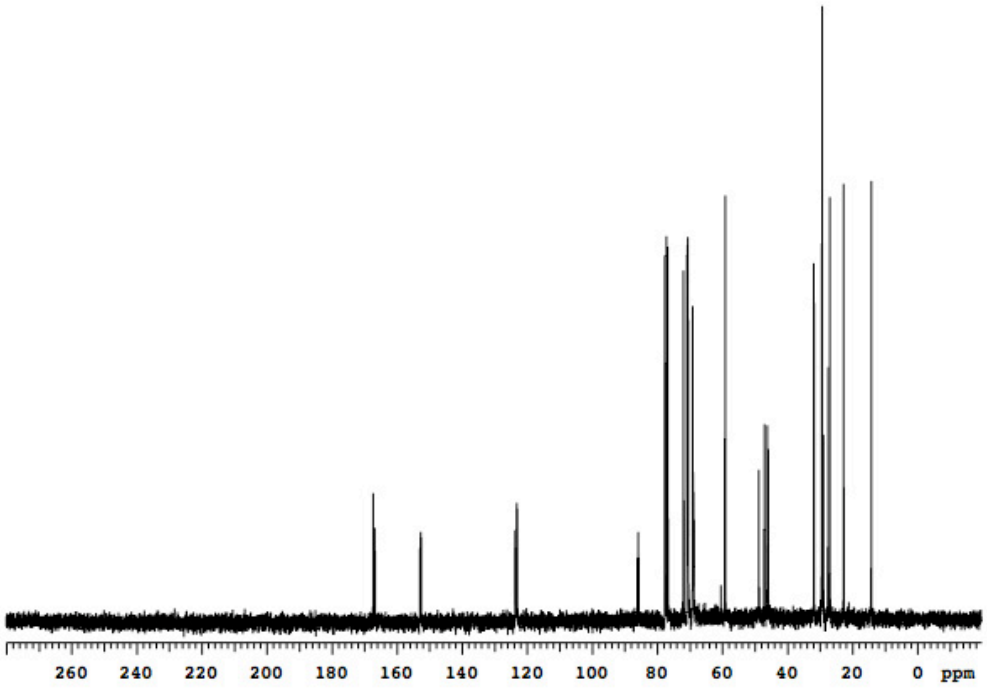
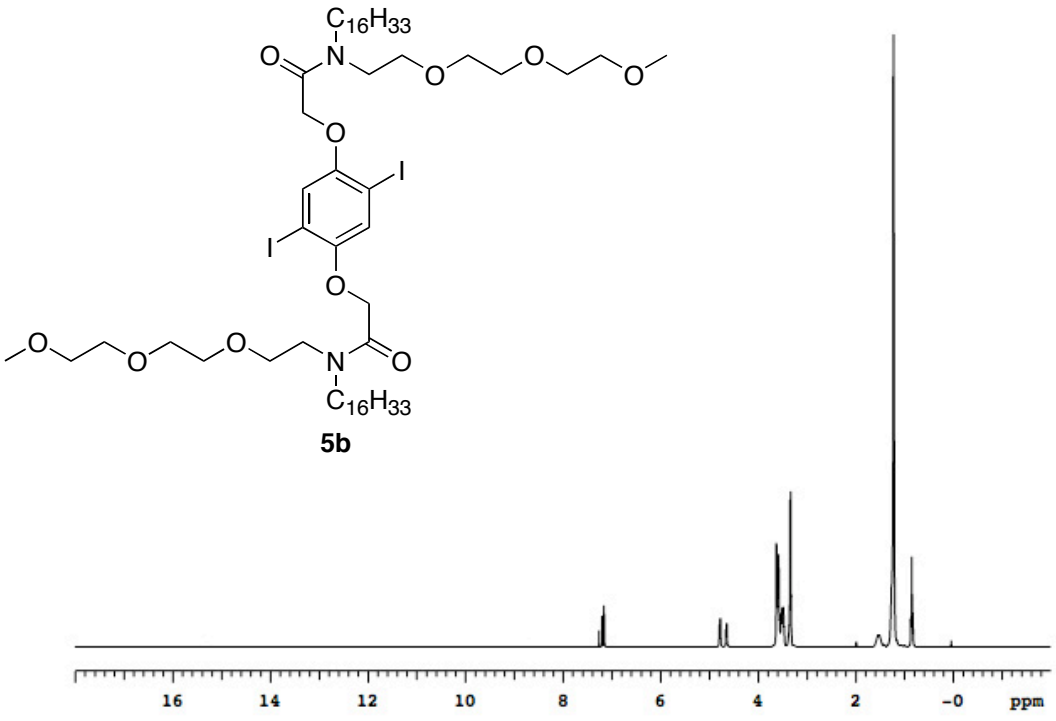


Figure S32. ^{1}H-NMR Spectrum of **5b** in $CDCl_3$ (300 MHz).



5b

Figure S33. ^{13}C-NMR Spectrum of **5b** in $CDCl_3$ (75 MHz).

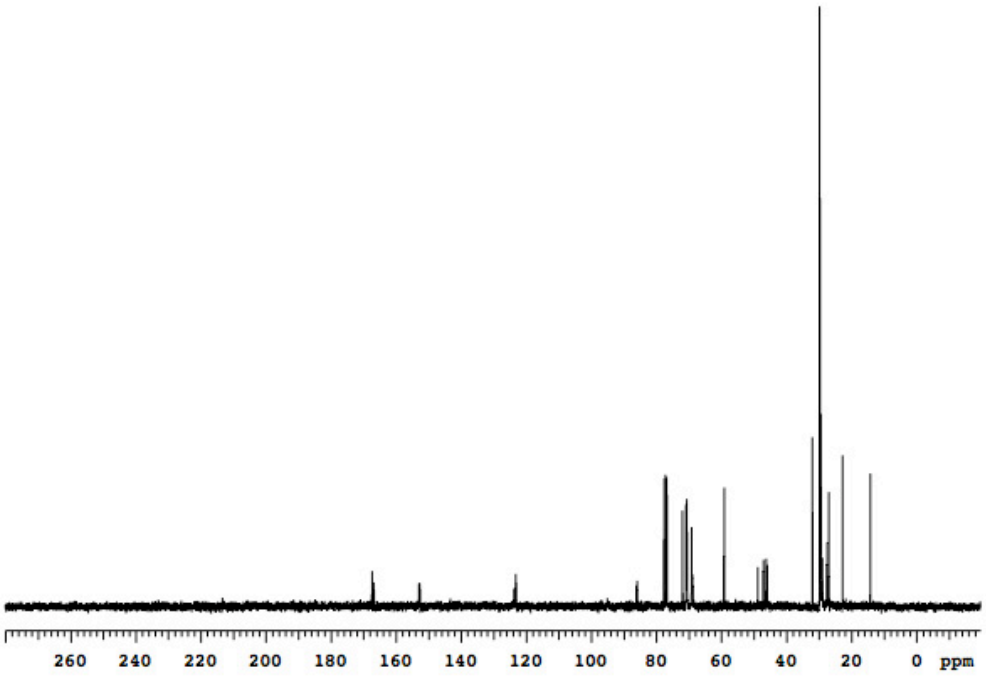
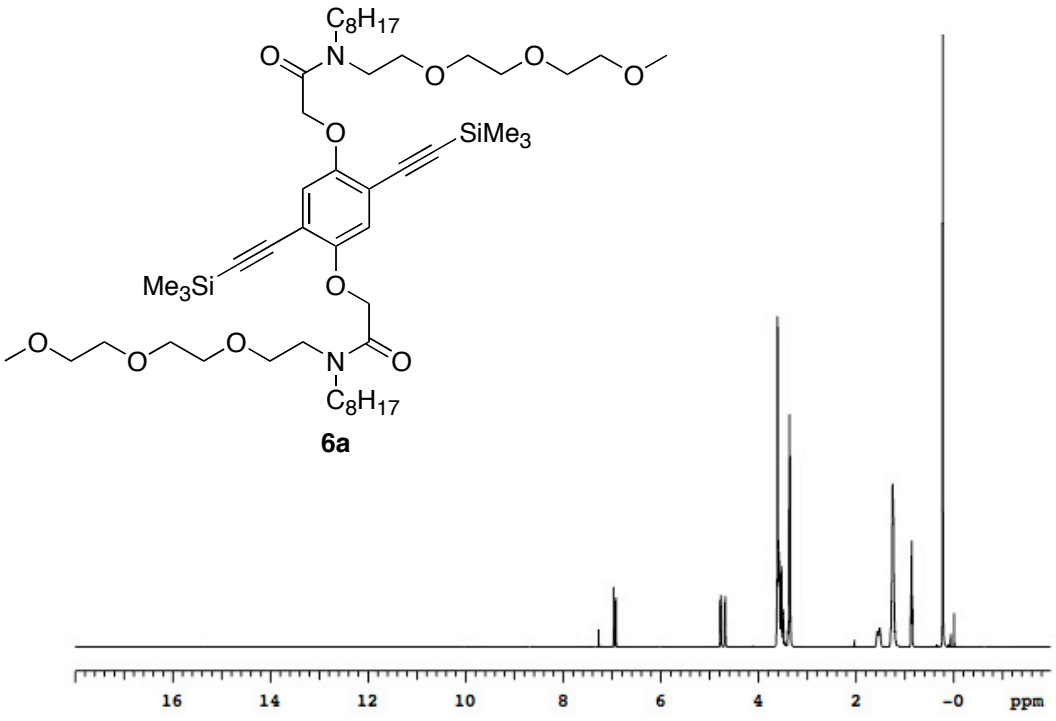


Figure S34. ^{1}H-NMR Spectrum of **6a** in $CDCl_3$ (500 MHz).



6a

Figure S35. ^{13}C-NMR Spectrum of **6a** in $CDCl_3$ (125 MHz).

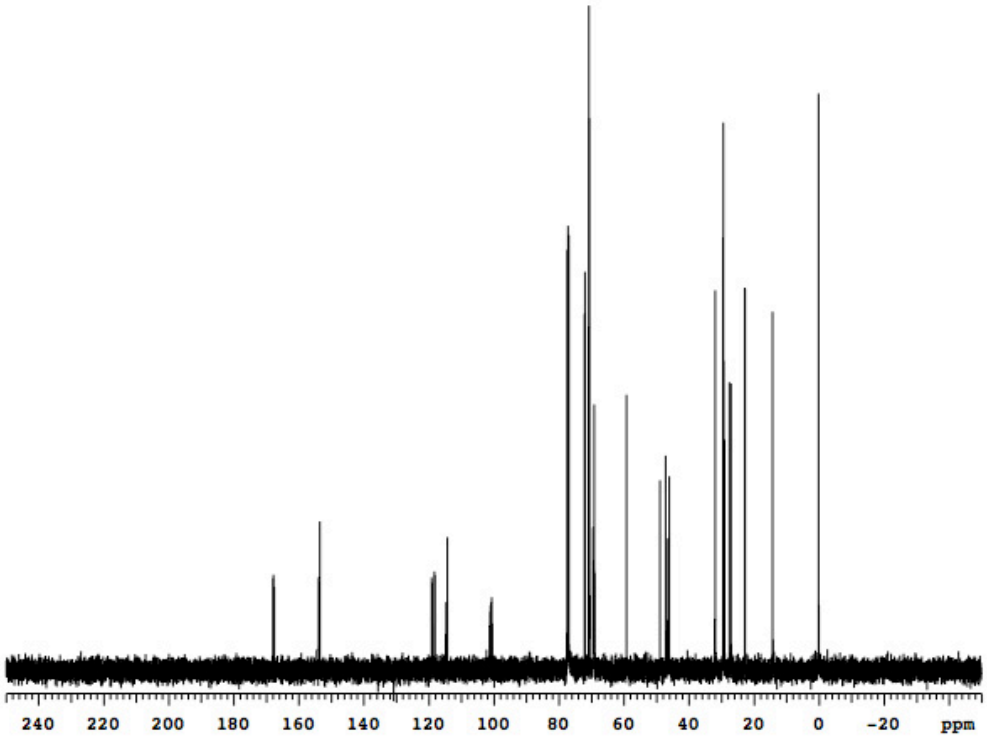
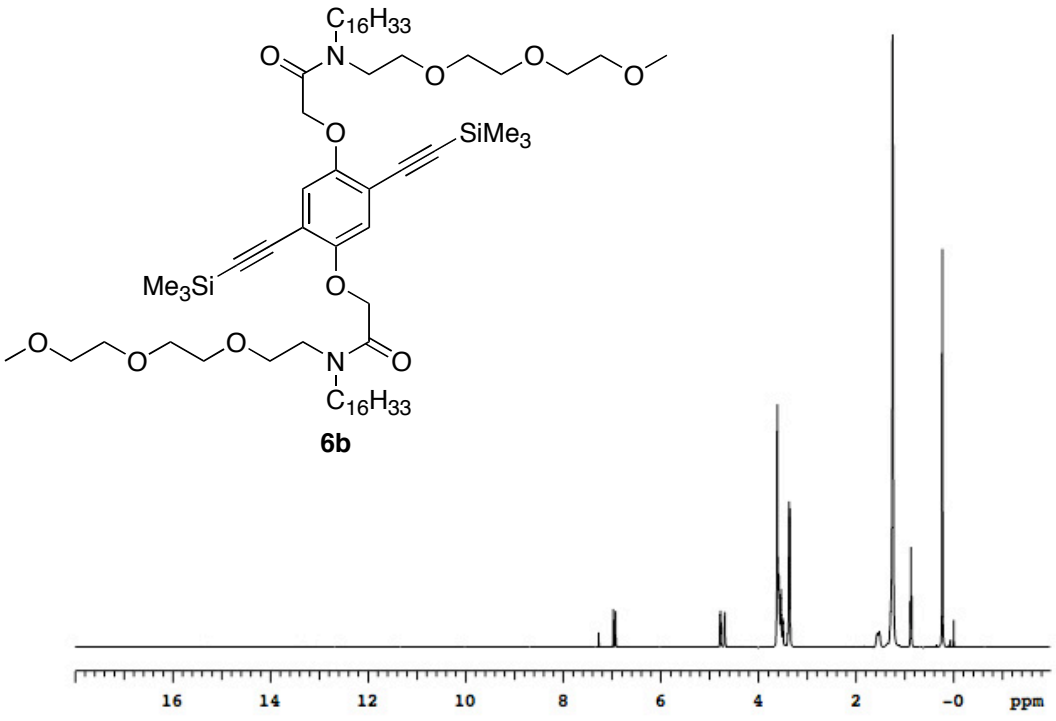


Figure S36. ^{1}H-NMR Spectrum of **6b** in $CDCl_3$ (500 MHz).



6b

Figure S37. ^{13}C-NMR Spectrum of **6b** in $CDCl_3$ (125 MHz).

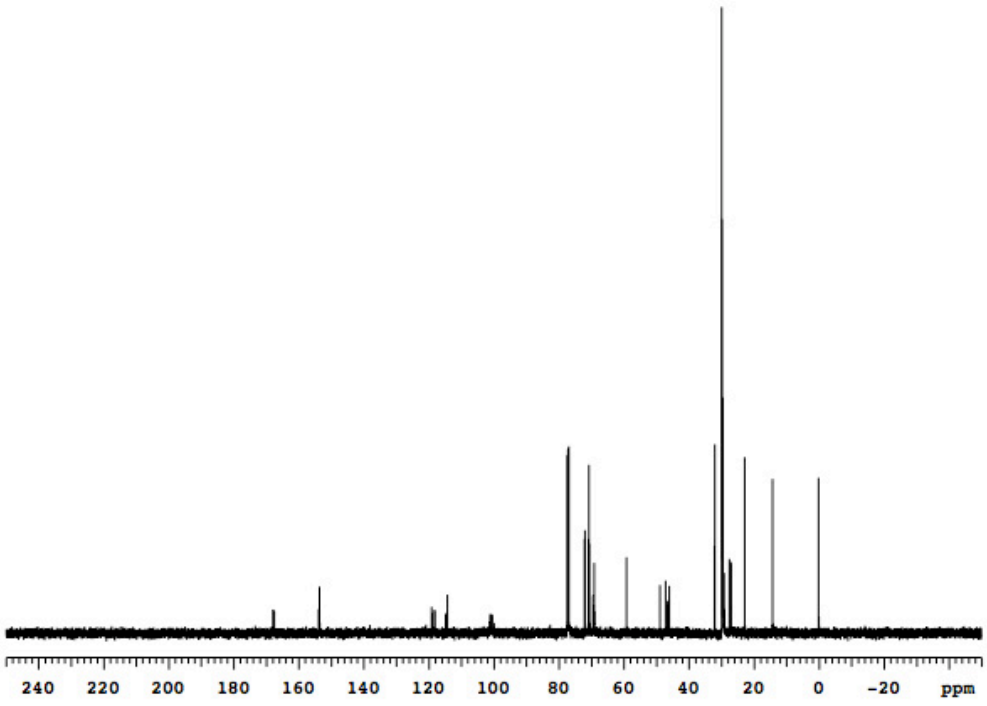
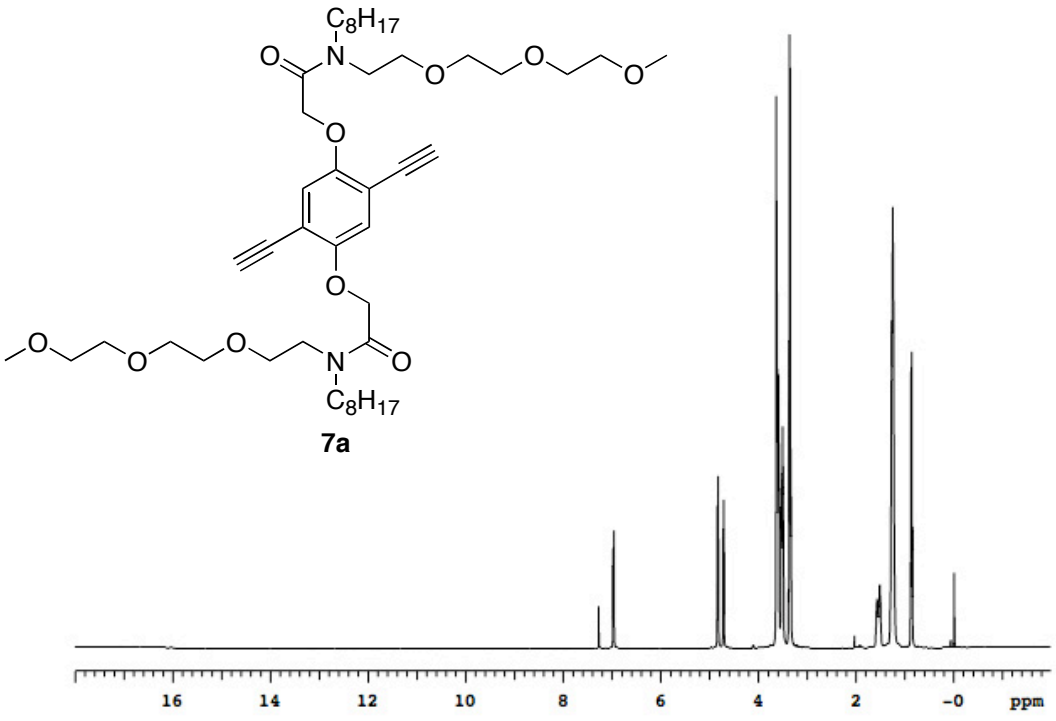


Figure S38. ^{1}H-NMR Spectrum of **7a** in $CDCl_3$ (500 MHz).



7a

Figure S39. ^{13}C-NMR Spectrum of **7a** in $CDCl_3$ (125 MHz).

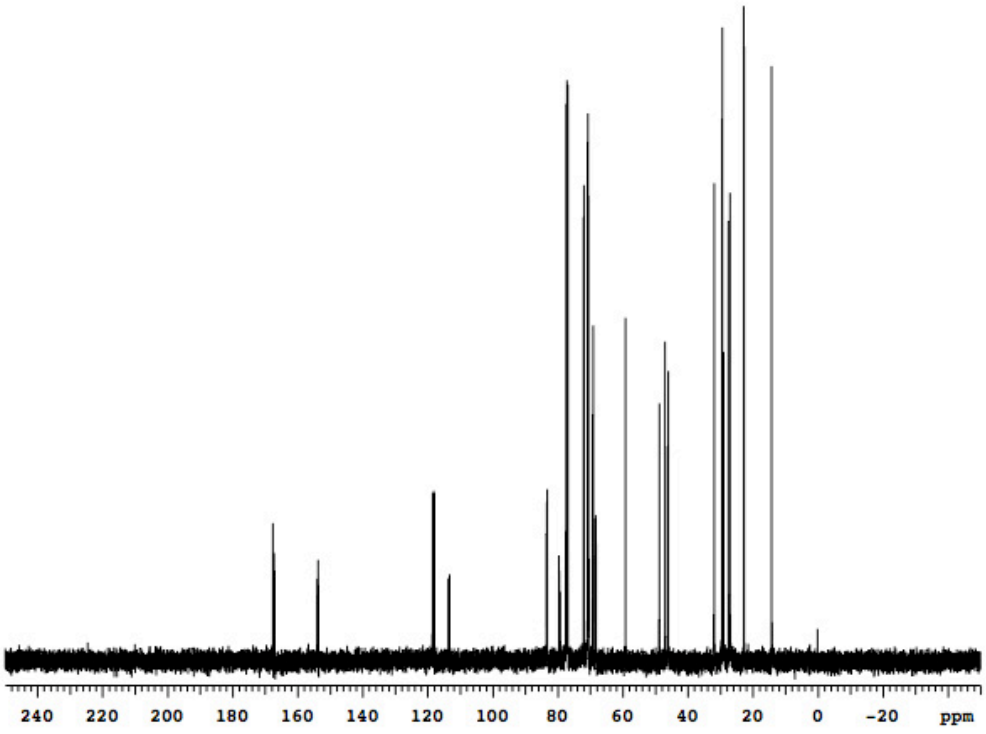
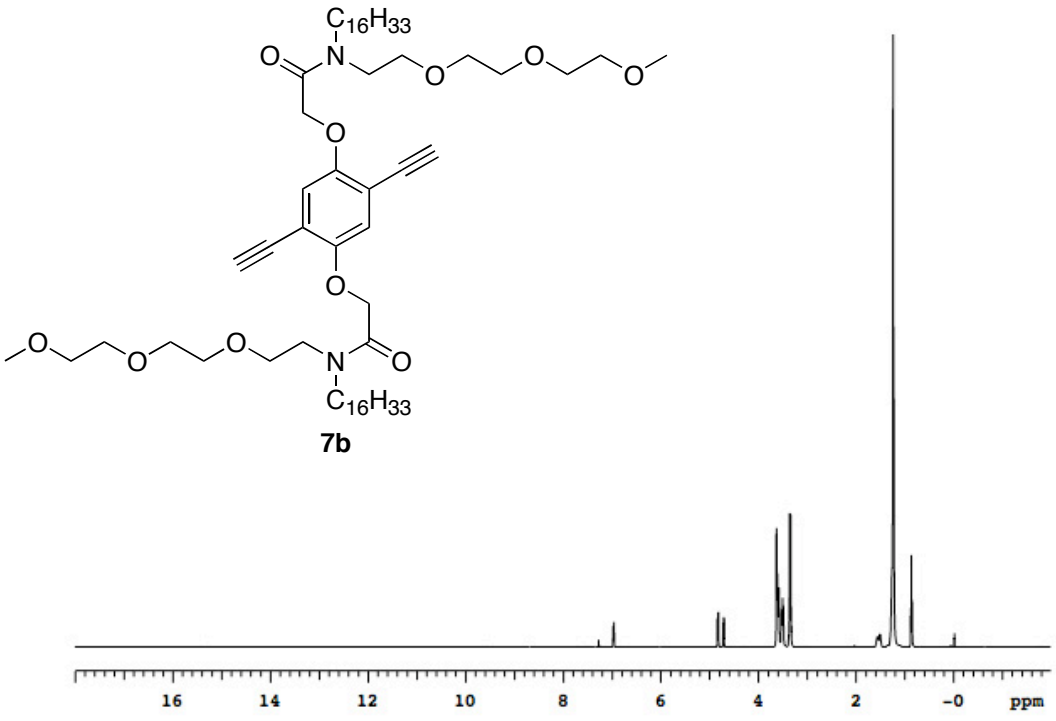


Figure S40. ^{1}H-NMR Spectrum of **7b** in $CDCl_3$ (500 MHz).



7b

Figure S41. ^{13}C-NMR Spectrum of **7b** in $CDCl_3$ (125 MHz).

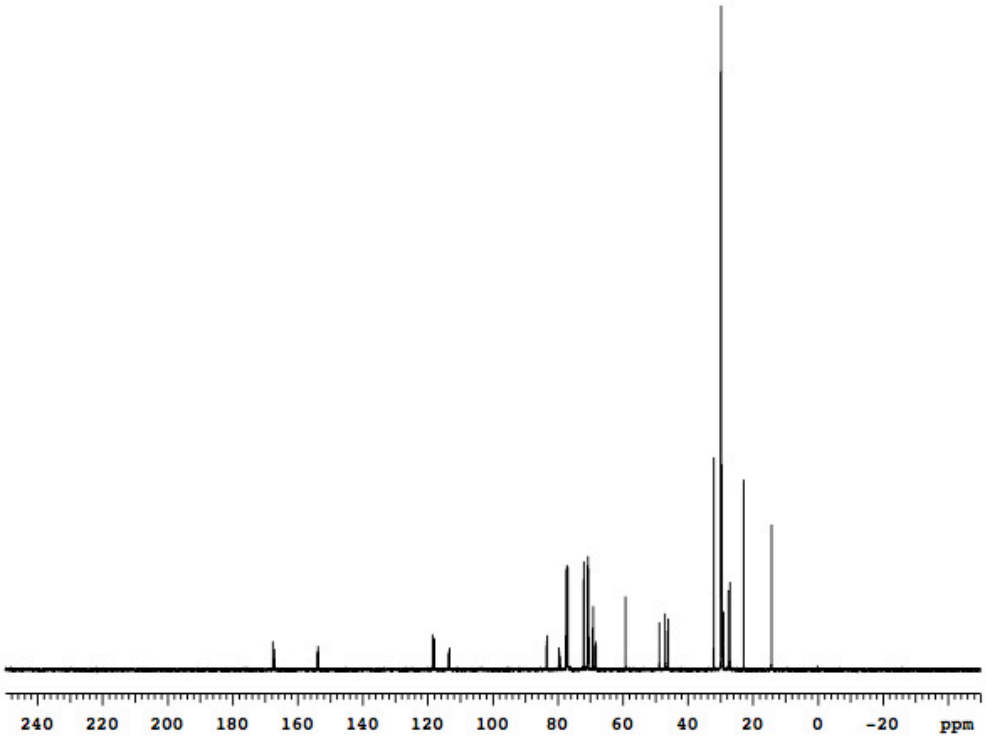


Figure S42. ^{1}H-NMR Spectrum of **P2** in $CDCl_3$ (500 MHz).

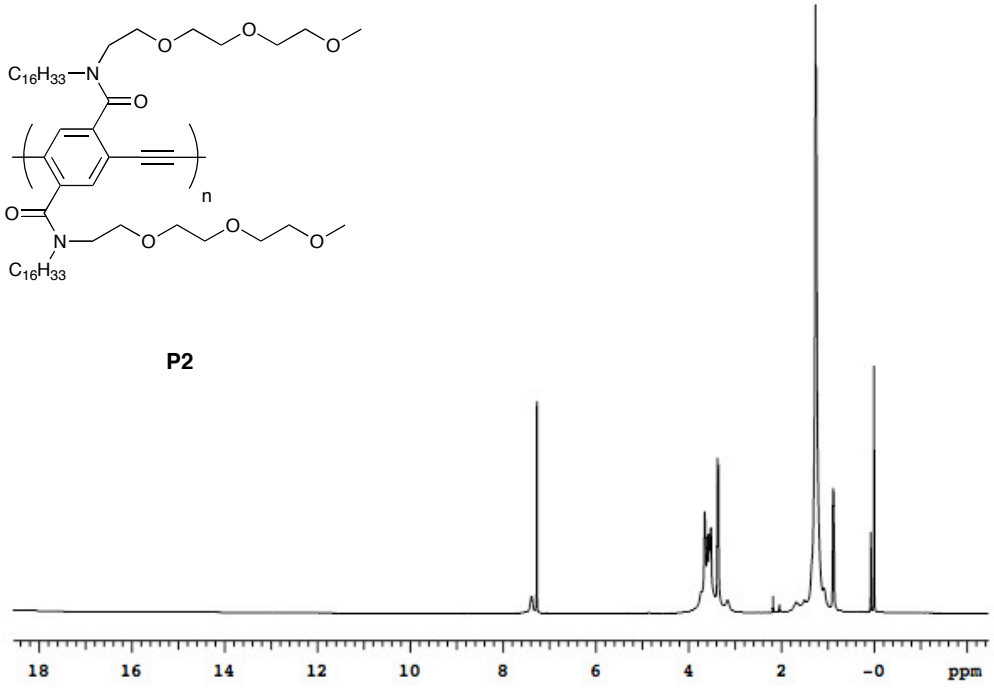
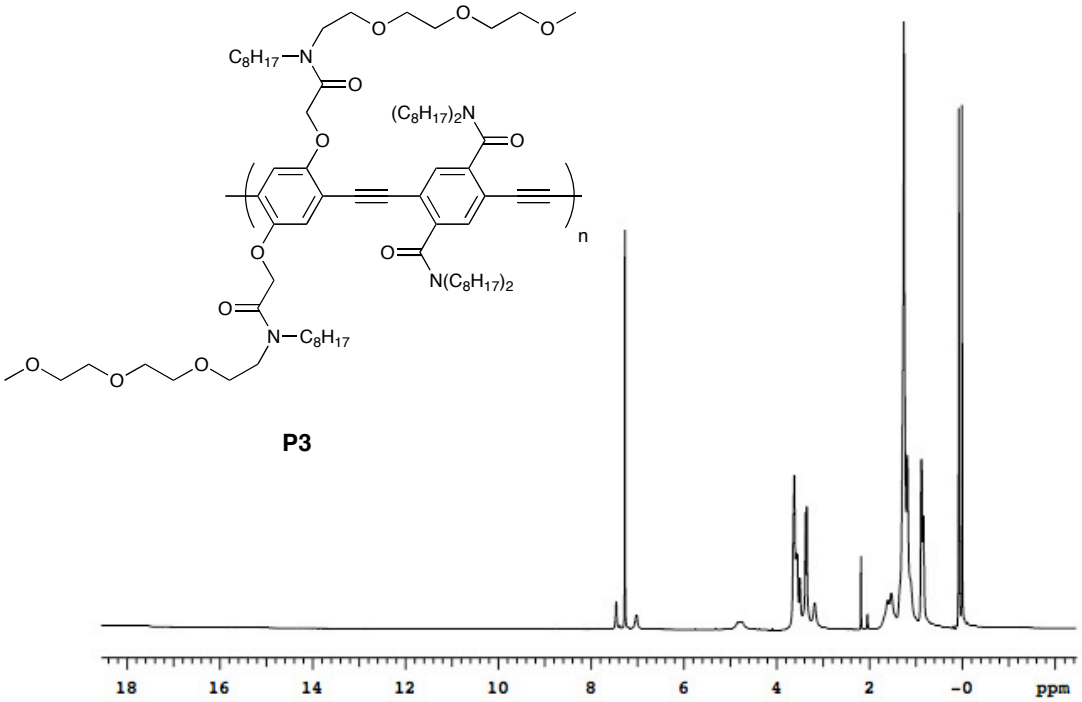


Figure S43. ^{1}H-NMR Spectrum of **P3** in $CDCl_3$ (500 MHz).



IV. REFERENCES AND NOTES

[1] Lee, M.; Oh, N.-K. *J. Mater. Chem.* **1996**, *6*, 1079-1086.
[2] (a) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 7017-7018. (b) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593-12602.
[3] Kuroda, K.; Swager, T. M. *Chem. Commun.* **2003**, 26-27.
[4] a) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030-1034. b) Kim, J.; Levitsky, I. A.; McQuade, D. T.; Swager, T. M. **2002**, *124*, 7710-7718.
[5] Zheng, J.; Swager T. M. *Macromolecules*, **2006**, *39*, 6781-6783.
[6] a) Khan, A.; Hecht, S. *Chem. Commun.* **2004**, 300-301. b) Khan, A.; Müller, S.; Hecht, S. *Chem. Commun.* **2005**, 584-586.
[7] a) Hendrikx, Y.; Charvolin, J.; Rawlso, M.; Liébert, L.; Holmes, M. C. *J. Phys. Chem.* **1983**, *87*, 3991-3999. b) Yu, L. J.; Saupe, A. *Phys. Rev. Lett.* **1980**, *45* 1000-1003. c) Figueiredo Neto, A. M.; Liébert, L; Galerne, Y. *J. Phys. Chem.* **1985**, *89*, 3737-3739. d) Galerne, Y.; Marcerou, J. P. *Phys. Rev. Lett.* **1983**, *51*, 2109-2111.e) Lacerda Santos, M. B.; Galerne, Y.; Durand, G. *Phys. Rev. Lett.* **1984**, *53*, 787-790. f) Long, R. C. Jr. *J. Magnet. Res.* **1973**, *12*, 216-217.
[8] (a) Olmsted, J., III *J. Phys. Chem.* **1979**, *83*, 2581-2584. (b) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991-1024. (c) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229-235. (d) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251-3260. (e)
[9] Melhuish, W. H. *J. Opt. Soc. Am.* **1964**, *52*, 183-186.