SUPPORTING INFORMATION

Bent-core liquid crystal phases promoted by azo-containing molecules: From monomers to side-chain polymers

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S1. Experimental section.

Materials and techniques

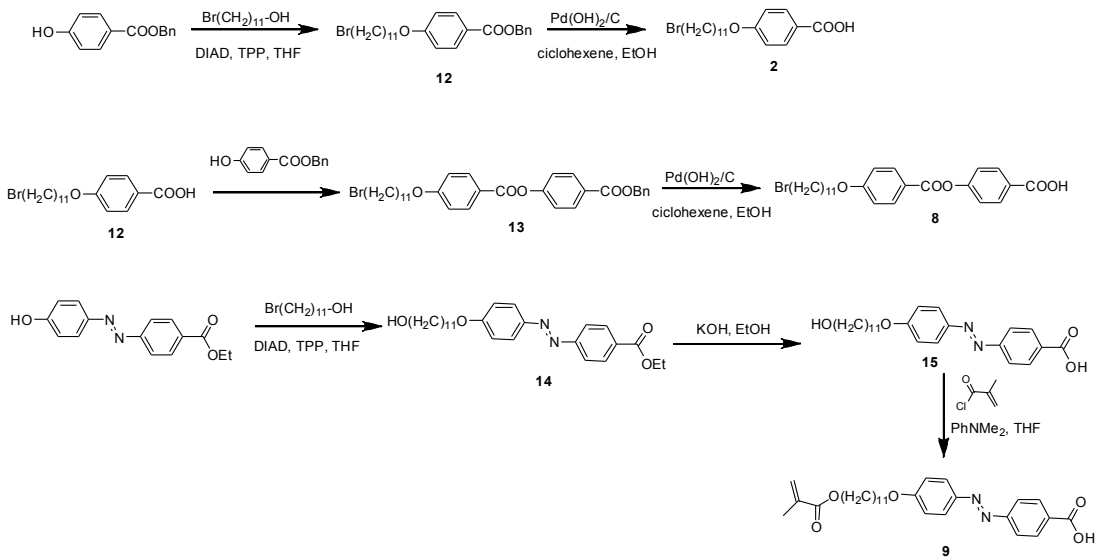
All commercial reagents were used as purchased. Solvents were purified and rigorously dried over appropriate drying agents and distilled prior to use. All atmosphere-sensitive reactions were carried out under dry argon using standard Schlenk techniques. Analytical TLC was performed on 60F 254, 60A-15 μm silica gel polyester plates (SDS). Column chromatography was carried out under flash conditions using 60 Å silica gel (SDS). Silica gel type 7749 (with gypsum, Merck) was used for centrifugal force mediated preparative thin layer chromatography in conjunction with a Chromatotron from Harrison Research Europe, model 8924. The compositions of the synthesized compounds were determined by elemental analysis performed on a PERKIN-ELMER 240C CHNS elemental analyzer. FT-IR spectra were obtained on a THERMONICOLET Avatar 360 spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer or a Bruker Avance 300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 analyzer. Mass spectrometry studies (FAB+, MALDI+) were performed with VG AutoSpec EBE and Microflex (MALDI-ToF) spectrometers. UV-vis absorption spectra were measured with a UV4-200 from ATI-Unicam using 10^{-4} to 10^{-5} M solutions in THF.

The mesophase identification was based on microscopic examination of the textures formed by samples between two glass plates. NIKON and OLYMPUS BH-2 polarizing microscopes equipped with a LINKAM THMS600 hot stage were used. The temperatures and enthalpies of the phase transitions were determined by calorimetric measurements performed with DSC TA Instrument Q-20 and Q-2000 systems. Thermogravimetric analysis (TGA) was performed on a TA Q5000IR instrument at a heating rate of 10 ºC/min under a nitrogen atmosphere. Molecular dimensions were

estimated by molecular modeling (ChemSketch3D). The X-ray investigations on non-oriented samples were carried out in Lindemann capillary tubes (diameter: 0.9 or 1 mm) using a PINHOLE (ANTON-PAAR) film camera.

Polarization measurements were carried out using commercial cells with ITO electrodes coated with polyimide (LINKAM, 5 μm). An HP3245A function generator plus an amplifier supplied the triangular wave voltage and the current was recorded using an IO tech 488/6A multimeter. All the equipment was controlled with a Fujitsu S-325 generator and a Tektronix TDS 310 oscilloscope.

Synthesis of the benzoic acids



Scheme S1. *Synthetic routes followed to prepare the different benzoic acids used.*

The preparation of intermediates **1**, **7** and **10** and benzoic acids **5** and **6** has been reported previously [(a) G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl, C. Tschierske, *Angew. Chem. Int. Ed.* 2002, **41**, 2408. (b) C. L. Folcia, I. Alonso, J. Ortega, J. Etxebarria, I. Pintre, M.B. Ros. *Chem. Mater.* 2006, **18**, 4617, (c) I. C.

Pintre, N. Gimeno, J. L. Serrano, M. B. Ros, I. Alonso, C. L. Folcia, J. Ortega, J. Etxebarria, *J. Mater. Chem.* 2007, **17**, 2219]

Benzyl 4-(11-bromoundecyloxy)benzoate (12). Diisopropylazodicarboxylate (DIAD) (94.94 g, 23.9 mmol) was added dropwise to a solution of benzyl 4-hydroxybenzoate (5.00 g, 21.7 mmol), 1-bromo-11-hydroxyundecane (5.56 g, 21.7 mmol) and triphenylphosphine (6.32 g, 23.9 mmol) in dry THF (50 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h. The solvent was evaporated and the residue was suspended in a mixture of hexanes/ethyl acetate (7/3) (100 mL). The precipitate was filtered off through a pad of Celite® and the solvent was evaporated to yield a brown liquid, which was purified by flash chromatography in silica gel using dichloromethane as eluent. **Yield:** 9.72 g of a brown oil (97%). **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm**: 8.02 (d, J = 8.8 Hz, 2H), 7.47-7.43(m, 2H), 7.42-7.31 (m, 3H), 6.90 (d, J = 8.8 Hz, 2H), 5.34 (s, 2H), 4.01 (t, J = 6.8 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.91-1.74 (m, 4H), 1.50-1.23 (m, 14H). **^{13}C-NMR, APT, (100 MHz, $CDCl_3$), δ, ppm**: 166.2, 163.0, 136.3, 131.7, 128.5, 128.1, 128.0, 122.2, 114.0, 68.1, 66.3, 34.0, 32.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 28.1, 25.9. **FTIR (neat, NaCl), cm^{-1}:** 2926, 2852, 1711, 1605, 1510, 1252, 1164, 1100.

4-(11-Bromoundecyloxy)benzoic acid (2). Compound **12** (19.2 g) was dissolved in ethanol (300 mL) and cyclohexene (150 mL) and $Pd(OH)_2/C$ (20% wt) (1.9 g) was added. The mixture was stirred at 80 ºC for 12 h under an argon atmosphere. The reaction mixture was filtered through a pad of Celite® and washed with THF. The solvent was evaporated the compound was crystallized from ethanol. **Yield.** 10.9 g of a white solid (71%). **Mp.** 116-117 ºC. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm**: 8.05 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.89-1.77 (m, 4H), 1.49-1.25 (m, 14H). **^{13}C-NMR, APT, (100 MHz, $CDCl_3$), δ, ppm**:

171.8, 163.7, 132.3, 121.4, 114.2, 68.3, 34.1, 32.9, 29.5, 29.5, 29.4, 29.3, 29.1, 28.8, 28.2, 26.0. **FTIR (neat, KBr), cm^{-1}:** 2932, 2852, 2560, 2538, 1668, 1605, 1576, 1428, 1292, 1255, 1169.

Benzyl 4-(11-bromoundecyloxy)benzoyloxybenzoate (13). Compound **2** (2.3 g, 6.19 mmol) was mixed with benzyl 4-hydroxybenzoate (1.43 g, 6.19 mmol) and DMAP (0.08 g, 0.06 mmol) in dry dichloromethane (60 mL) under argon. The reaction mixture was cooled (ice bath) and dicyclohexylcarbodiimide (DCC) (1.55 g, 7.43 mmol) was added. The cooled mixture was stirred for 1 h and then at room temperature for 24 h. The resulting precipitate was filtered off and the solvent was evaporated to dryness. The product was crystallized from ethanol. Yield 2.87 g of a white solid (80%). **Mp.** 62 ºC. **^{1}H-NMR (400 MHz, CDCl3), δ, ppm:** 8.15 (d, J = 8.6 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H), 7.47-7.31 (m, 5H), 7.29 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 5.38 (s, 2H), 4.04 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.9 Hz, 2H), 1.91-1.76 (m, 4H), 1.50-1.25 (m, 14 H). **FTIR (neat, KBr), cm^{-1}:** 2922, 2853, 1736, 1715, 1603, 1510, 1256, 1204, 1158.

4-[4'-(11-Bromoundecyloxy)benzoyloxy]benzoic acid (8). Compound **13** (2.8 g, 4.81 mmol) was dissolved in ethanol (36 mL) and cyclohexene (18 mL). $Pd(OH)_2/C$ (20% wt) (1.9 g) was added and the mixture stirred at 80 ºC for 6 h under argon. The reaction mixture was filtered through a pad of Celite® and this was washed with THF. The solvent was evaporated and the compound was crystallized from ethanol. **Yield.** 2.04 g of a white solid (87%). **Mp.** Cr 134 ºC SmC 183 ºC N 214 ºC Is (decomposition). **^{1}H-NMR (400 MHz, CDCl3), δ, ppm:** 8.18 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.92-1.76 (m, 4H), 1.54-1.22 (m, 14H). **FTIR (neat, KBr), cm^{-1}:** 3200-2200, 1733, 1687, 1603, 1255, 1208, 1159.

Ethyl 4-[4'-(11-hydroxyundecyloxy)phenylazo]benzoate (14). A stirred mixture of ethyl 4-[4'-(hydroxyphenylazo)benzoate] (2.0 g, 7.4 mmol), dry K_2CO_3 (1.02 g, 14.8 mmol) and KI (0.040 g) in dry acetone (60 mL) was heated under reflux under an argon atmosphere. 1-Bromo-11-hydroxyundecane (2.23 g, 8. 88 mmol) was added dropwise and the mixture was stirred and heated under reflux for 24 h. The mixture was cooled down to room temperature and poured into 100 mL of water. The product was extracted into a mixture of hexanes/ethyl acetate (1/1) and the organic phase was dried over magnesium sulfate. After evaporating the solvent, the product was purified by crystallization in ethanol. **Yield.** 3.00 g of orange solid (92%). **Mp.** Cr 108 ºC SmA 122 ºC I. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.17 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 3.68-3.60 (m, 2H), 1.87-1.77 (m, 2H), 1.55-1.20 (m, 19H). **FTIR (Nujol, NaCl), cm^{-1}:** 3565, 3404, 2921, 2851, 1716, 1703, 1604, 1501, 1290, 1259, 1141.

4-[4'-(11-Hydroxyundecyloxy)phenylazo]benzoic acid (15). Compound **14** (3.96 g, 8.99 mmol) was dissolved in ethanol (110 mL) and KOH (3.92 g, 62.9 mmol) was added. The mixture was stirred at 78 ºC for 21 h and then allowed to cool down to rt. Water (135 mL) and HCl were added to give an acidic pH. The resulting orange solid was filtered off, washed with water and crystallized from isopropanol. **Yield.** 4.41 g of an orange solid (68%). Mp. Cr 196 ºC M 226 ºC I. **^{1}H-NMR (400 MHz, DMSO-d6), δ, ppm:** 13.18 (bs, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.9 Hz, 2H), 4.31 (bs, 1H), 4.08 (t, 6.5 Hz, 2H), 3.36 (t, J = 6.5 Hz, 2H), 1.78-1.69 (m, 2H), 1.46-1.20(m, 16H). **FTIR (neat, KBr), cm^{-1}:** 3475, 3386, 3200-2300, 1693, 1603, 1584, 1502, 1256,1141.

4-[4'-(11-Methacryloyloxyundecyloxy)phenylazo]benzoic acid (9). Compound **15** (2.15 g, 5.21 mmol), N,N-dimethylaniline (0.80 mL, 6.25 mmol) and a small amount of 2,6-di-*tert*-butyl-4-methylphenol were dissolved in dry THF (140 mL). The reaction mixture was stirred at 65 ºC under argon and then methacryloyl chloride (0.88 mL, 7.82 mmol) was added dropwise. The reaction mixture was stirred for 24 h and then cooled in an ice bath before being added to an acid solution (0.24 mL of c. HCl in 400 mL of water). The resulting solid was filtered off and washed thoroughly with water, hexanes and hot isopropanol. **Yield.** 0.69 g of an orange solid (28%). **Mp.** Cr 129 ºC M (thermal polymerization). **^{1}H-NMR (400 MHz, CDCl3), δ, ppm:** 8.24 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 6.11-6.08 (m, 1H), 5.56-5.53 (m, 1H), 4.14 (t, 6.5 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 1.94 (s, 3H), 1.89-1.75 (m, 2H), 1.74-1.20 (m, 16H). **IR (Nujol, NaCl), cm^{-1}:** 3300-2300, 1717, 1680, 1602, 1502, 1292, 1249, 1144.

3'-Benzyloxy-4-[4"-(11-bromoundecyloxybenzoyloxy)]biphenyl (3). 4-(11-Bromoundecyloxy)benzoic acid **2** (2.83 g, 7.6 mmol), 3'-benzyloxy-4-(hydroxy)biphenyl **(1)** (2.30 g, 8.3 mmol) and dimethylaminopyridine (DMAP) (0.09 g, 0.8 mmol) were stirred in dry dichloromethane (75 mL) under an argon atmosphere. Dicyclohexylcarbodiimide (DCC) (2.08 g, 10.0 mmol) was added and the mixture was cooled in an ice bath and stirred for 30 min. The ice bath was removed and the mixture was stirred for 20 h at room temperature. The solid was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography using dichloromethane as eluent. **Yield.** 4.1 g of a white solid (86%). **Mp.** 91-92 ºC. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.16 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.50-7.45 (m, 2H), 7.44-7.38 (m, 2H), 7.37-7.33 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.23-7.17 (m, 2H), 7.01-6.96 (m, 3H), 5.13 (s, 2H), 4.05 (t, J = 6.4 Hz, 2H), 3.42 (t, J =

6.8 Hz, 2H), 1.92-1.76 (m, 4H), 1.52-1.23 (m, 14H). **^{13}C-NMR, (100 MHz, $CDCl_3$), δ, ppm:** 172.4, 165.0, 163.6, 159.2, 150.6, 142.0, 138.6, 132.3, 129.9, 128.7, 128.2, 128.1, 127.6, 122.1, 119.9, 119.2, 114.3, 113.9, 113.6, 70.1, 68.3, 34.1, 32.9, 29.5, 29.5, 29.5, 29.4, 29.1, 29.1, 28.8, 28.2, 26.0. **FTIR (neat, KBr), cm^{-1}:** 1728, 1604, 1506, 1470, 1260, 1165.

3'-Benzyloxy-4-[4"-(11-bromoundecyloxybenzoyloxy)]biphenyl (4). Compound **3** (4.1 g, 4.81 mol) was dissolved in ethanol (88 mL) and cyclohexene (72 mL). $Pd(OH)_2$/C (20% wt, 0.41 g) was added and the mixture was stirred at 80 ºC for 24 h under an argon atmosphere. The reaction mixture was filtered through a pad of Celite® and this was washed with THF. The solvent was evaporated and the crude product was purified by crystallization from ethanol. **Yield.** 3.1 g of a white solid (87 %). **Mp.** 114-115 ºC. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.11 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.25-7.20 (m, 1H), 7.20 (d, J = 8.8 Hz, 2H), 7.11-7.06 (m, 1H), 6.97-6.95 (m, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.79-6.74 (m, 1H), 4.00 (t, J = 6.4 Hz, 2H), 3.36 (t, J = 6.8 Hz, 2H), 1.86-1.72 (m, 4H), 1.48-1.21 (m, 14H). **^{13}C-NMR, (100 MHz, $CDCl_3$), δ, ppm:** 165.3, 163.7, 156.0, 150.6, 142.1, 138.4, 132.4, 129.9, 128.2, 122.1, 121.4, 119.6, 114.4, 114.3, 114.0, 68.4, 34.2, 32.9, 29.5, 29.5, 29.4, 29.3, 29.1, 28.8, 28.2, 26.0. **FTIR (neat, KBr), cm^{-1}:** 3407, 1721, 1604, 1509, 1475, 1255, 1166.

4'-Hydroxy-3-4"-[4"'-(11-bromoundecyloxy)benzoyloxy]benzoyloxybiphenyl (11).

(A) Dicyclohexylcarbodiimide (DCC) (1.51 g, 7.3 mmol) was added to a cooled (ice bath) mixture of compound **8** (2.77 g, 5.6 mmol), 4'-benzyloxy-3-(hydroxy)biphenyl **10** (1.30 g, 4.7 mmol) and DMAP (0.06 g, 0.05 mmol) in dry dichloromethane (100 mL) under an argon atmosphere. The cooled mixture was stirred for 1 h and then at room

temperature for 16 h. The precipitate was filtered off and the solvent was evaporated to dryness. The product was crystallized from ethanol. **Yield.** 2.64 g of a white solid (75%). **Mp.** 123 ºC. **^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm:** 8.30 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.49-7.32 (m, 10H), 7.20-7.13 (m, 1H), 7.05 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 5.12 (s, 2H), 4.06 (t, J = 6.5 Hz, 2H), 3.41 (d, J = 6.8 Hz, 2H), 1.92-1.77 (m, 4H), 1.54-1.25 (m, 14H). **IR (neat, KBr), cm^{-1}:** 2925, 2853, 1732, 1606, 1514, 1275, 1214, 1175, 1164.

(B) The Bn-compound (2.2 g, 2.9 mmol) was dissolved in ethanol (50 mL) and cyclohexene (16 mL). $Pd(OH)_2/C$ (20% wt, 0.44 g) was added and the mixture was stirred at 80 ºC for 24 h under argon. The reaction mixture was filtered through a pad of Celite® and this was washed with THF. The solvent was evaporated and the crude product was purified by crystallization from ethanol. **Yield.** 1.34 g of a white solid (70%). **Mp.** 111 ºC. **^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm:** 8.30 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 7.53-7.44 (m, 4H), 7.41-4.35 (m, 3H), 7.19-7.13 (m, 1H), 6.99 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.91 (s, 1H), 4.06 (t, J = 6.6 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.92-1.77 (m, 4H), 1.53-1.24 (m, 14H). **FTIR (neat, KBr), cm^{-1}:** 3431, 2922, 2853, 1738, 1723, 1605, 1510, 1257, 1203, 1159.

Synthesis of the bent-core precursors and monomers.

The preparation of the different monomers was approached using different synthetic pathways depending on the number of aromatic rings and the chemical nature of the structures (Schemes 2, 3 and 4 in the main text).

Compound E5Br. Acid **5** (1.35 g, 3.0 mmol) was mixed with biphenol **4** (1.60 g, 3.0 mmol) and DMAP (0.04 g, 0.03 mmol) in dry dichloromethane (110 mL) under an argon atmosphere. The reaction mixture was cooled (ice bath) and

dicyclohexylcarbodiimide (DCC) (0.74 g, 3.6 mmol) was added. The cooled mixture was stirred for 1 h and then at room temperature for 24 h. The resulting precipitate was filtered off and the solvent was evaporated to dryness. The crude product was purified by flash chromatography using dichloromethane as eluent and crystallized from ethyl acetate. **Yield.** 2.00 g of a white solid (67%). **Mp.** Cr 84 ºC SmCP 92 ºC I. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.33 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 4H), 7.68 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 5.0 Hz, 2H), 7.49-7.47 (m, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.25-7.22 (m, 1H), 7.05 (d, J = 9 Hz, 2H), 7.01 (d, J = 9 Hz, 2H), 4.08 (t, J = 6.5 Hz, 4H), 3.44 (t, J = 6.9 Hz, 2H), 1.86 (m, 6H), 1.60-1.23 (m, 38H), 0.91 (t, J = 6.8 Hz, 3H). **^{13}C-NMR, (100 MHz, $CDCl_3$), δ, ppm:** 164.9, 164.5, 164.4, 163.9, 163.6, 155.4, 151.3, 150.9, 142.2, 137.8, 132.4, 132.3, 131.9, 129.9, 128.3, 126.9, 124.7, 122.2, 122.1, 121.5, 121.0, 120.6, 120.4, 114.4, 114.3, 68.4, 68.3, 34.1, 32.8, 31.9, 29.7, 29.7, 29.6, 29.60, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 28.8, 28.2, 26.0, 22.7, 14.1. **IR (neat, KBr), cm^{-1}:** 2919, 1730, 1605, 1509, 1285, 1252, 1168. **MS (MALDI+): m/z:** 997 $(M+Na)^+$. **UV-vis ($CHCl_3$, $1.24 \cdot 10^{-5}$ M):** λ_{max}: 271 nm ($\varepsilon = 67.500 \cdot 10^3$ $M^{-1}cm^{-1}$).

Compound E5M. Compound **E5Br** (1.40 g, 1.4 mmol), tetrabutylammonium bromide (0.93 g, 0.5 mmol) and a small amount of 2,6-di-*tert*-butyl-4-methylphenol were dissolved in a mixture of chloroform/water (3/6). Sodium methacrylate (0.47g, 4.4 mmol) was added and the mixture was stirred at 70 ºC for 8 h. After cooling, the mixture was extracted with dichloromethane and the organic phase was washed with water and dried over magnesium sulfate. The product was purified by flash chromatography using dichloromethane as eluent and crystallized from ethyl acetate. **Yield.** 0.70 g of a white solid (50%). **Mp.** 79 ºC. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.30 (d, J = 9.0 Hz, 2H), 8.16 (d, J = 9.0 Hz, 4H), 7.66 (d, J = 8.7 Hz, 2H),

7.53-7.49 (m, 2H), 7.47-7.44 (m, 1H), 7.39 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 7.25-7.20 (m, 1H), 7.01 (d, J = 9 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 6.11-6.08 (m, 1H), 5.54 (dq, J = 1.8 Hz, J = 1.8 Hz, 1H), 4.14 (t, J = 6.9 Hz, 2H), 4.09-4.01 (m, 4H), 1.98-1.92 (m, 3H), 1.90-1.76 (m, 4H), 1.74-1.61 (m, 2H), 1.53-1.19 (m, 36H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C-NMR, (100 MHz, $CDCl_3$), δ, ppm:** 167.5, 164.9, 164.5, 164.3, 163.8, 163.6, 155.4, 151.3, 150.8, 14.1, 137.7, 136.5, 132.4, 132.3, 131.8, 129.8, 128.2, 126.8, 125.1, 124.7, 122.2, 122.1, 121.4, 120.9, 120.5, 120.4, 114.4, 114.3, 68.4, 68.3, 64.8, 31.9, 29.7, 29.7, 29.7, 29.6, 29.5, 29.5, 29.5, 29.5, 29.3, 29.3, 29.2, 29.1, 29.1, 28.6, 26.0, 22.7, 18.3, 14.1. **FTIR (neat, KBr), cm^{-1}:** 2922, 2851, 1731, 1605, 1511, 1255, 1208, 1065. **MS (MALDI+): m/z:** 1003 $(M + Na)^+$. **UV-vis ($CHCl_3$, $1.04 \cdot 10^{-5}$ M):** λ_{max}: 271 nm ($\varepsilon = 62.019 \cdot 10^3$ $M^{-1}cm^{-1}$).

Compound A5Br. *(A)* Oxalyl chloride (0.88 g, 6.7 mmol) was added to a suspension of benzoic acid **6** (1.46 g, 3.3 mmol) in dry toluene (110 mL). A few drops of DMF were added and the reaction mixture was stirred at room temperature under an argon atmosphere for 16 h. The solvent was evaporated and the residue was dried under vacuum. The product was used in the next step without further purification.

(B) The acid chloride (1.50 g, 3.3 mmol) was dissolved in dry dichloromethane and added to a solution of biphenol **4** in the same solvent. Triethylamine (0.65 mL, 4.7 mmol) was added and the mixture was stirred overnight. After this time, the solvent was evaporated and the crude product was purified first by flash chromatography using dichloromethane as eluent and then by crystallization from ethyl acetate. **Yield.** 1.4 g of an orange solid (53%). **Mp.** 96 ºC. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.37 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 9.0 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.6-7.51 (m, 2H), 7.50-7.47 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.27-7.21 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 4.10-

4.01 (m, 4H), 3.54 (t, J = 6.9 Hz, 0.6H), 3.41 (t, J = 6.9 Hz, 2H), 1.91-1.77 (m, 6H), 1.56-1.23 (m, 3H), 0.89 (t, J = 6.3 Hz, 3H). **^{13}C-NMR, (100 MHz, $CDCl_3$), δ, ppm:** 164.9, 164.7, 163.5, 162.4, 155.8, 151.3, 150.8, 146.8, 142.1, 137.7, 132.3, 131.2, 130.3, 129.8, 128.2, 125.3, 124.7, 122.5, 122.2, 121.4, 120.5, 120.4, 114.7, 114.2, 68.4, 68.3, 34.1, 32.8, 30.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.4, 29.3, 29.3, 29.1, 29.1, 28.7, 28.1, 25.9, 25.9, 22.7, 14.0. **FTIR (neat, KBr), cm^{-1}:** 2919, 1730, 1604, 1503, 1250, 1210, 1181. **MS (MALDI+): m/z:** 959 $(M + 1)^+$. **UV-vis ($CHCl_3$, $1.01 \cdot 10^{-5}$ M):** λ_{max}: 267 nm ($\varepsilon = 43.366 \cdot 10^3$ $M^{-1}cm^{-1}$), λ_{max}: 366 nm ($\varepsilon = 26.534 \cdot 10^3$ $M^{-1}cm^{-1}$).

Compound A5M. Compound **A5Br** (1.50 g, 1.6 mmol), tetrabutylammonium bromide (1.01 g, 3.1 mmol) and a small amount of 2,6-di-*tert*-butyl-4-methylphenol were dissolved in a mixture of chloroform/water (3/6). Sodium methacrylate (0.47g, 4.4 mmol) was added and the mixture was stirred at 70 ºC for 24 h. After cooling, the mixture was extracted with dichloromethane and the organic phase was washed with water and dried over magnesium sulfate. The product was purified by flash chromatography using dichloromethane as eluent and crystallization from ethyl acetate. **Yield.** 0.8 g of an orange solid. **Mp.** 95 ºC. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.36 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.55-7.50 (m, 2H), 7.49-7.46 (m, 1H), 7.29 (d, J = 8.7 Hz, 2H), 7.27-7.21 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.10 (m, 1H), 5.54 (dqdc, J = 1.8 Hz, J = 1.8 Hz, 1H), 4.14 (t, J = 6.9 Hz, 2H), 4.1-4.01 (m, 4H), 1.95 (m, 3H), 1.90-1.76 (m, 4H), 1.74-1.61 (m, 2H), 1.53-1.21 (m, 36H), 0.89 (t, J = 6.6 Hz, 3H). **^{13}C-NMR, (100 MHz, $CDCl_3$), δ, ppm:** 167.5, 165.0, 164.7, 163.6, 162.5, 155.8, 151.3, 150.8, 146.9, 142.2, 137.7, 136.5, 132.3, 131.2, 130.3, 129.9, 128.2, 125.3, 125.1, 124.7, 122.5, 122.2, 121.4, 120.5, 120.4, 114.8,

114.3, 68.5, 68.3, 64.8, 31.9, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 28.6, 26.0, 25.9, 22.7, 18.3, 14.1. **FTIR (neat, KBr), cm^{-1}:** 2919, 1730, 1604, 1501, 1472, 1272, 1251, 1175, 1081. **MS (MALDI+): m/z:** 987 $(M + Na)^{+\cdot}$. **UV-vis ($CHCl_3$, $1.26 \cdot 10^{-5}$ M):** λ_{max}: 267 nm ($\varepsilon = 40.793 \cdot 10^3$ $M^{-1}cm^{-1}$), λ_{max}: 366 nm ($\varepsilon = 25.396 \cdot 10^3$ $M^{-1}cm^{-1}$).

Compound 6EBr. Acid **8** (1.00 g, 2.20 mmol) was mixed with biphenol **7** (0.42 g, 1.14 mmol) and DMAP (0.01 g, 0.09 mmol) in dry dichloromethane (45 mL) under an argon atmosphere. The reaction mixture was cooled in an ice bath and dicyclohexylcarbodiimide (DCC) (0.26 g, 1.22 mmol) was added. The cooled mixture was stirred for 30 minutes and then at room temperature for 24 h. The resulting precipitate was filtered off and the solvent was evaporated to dryness. The product was purified by flash chromatography using dichloromethane as eluent and crystallization from ethyl acetate. **Yield.** 0.52 g of a white solid (54%). **Mp.** Cr 94 ºC SmC_AP_A 133 ºC Colr-I. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.31 (d, J = 8.7 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 8.9 Hz, 4H), 7.67 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 5.0 Hz, 2H), 7.48-7.45 (m, 1H), 7.39 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.25-7.21 (m, 1H), 6.99 (d, J = 8.9 Hz, 4H), 4.06 (t, J = 6.5 Hz, 4H), 3.41 (t, J = 6.8 Hz, 2H), 1.90-1.79 (m, 6H), 1.53-1.24 (m, 36H), 0.88 (t, J = 6.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$), δ, ppm:** 164.4, 164.4, 164.3, 163.8, 155.4, 151.3, 150.6, 142.0, 138.0, 132.4, 131.8, 129.8, 128.3, 126.8, 126.7, 124.6, 122.1, 122.0, 120.9, 120.6, 120.4, 114.4, 68.3, 68.2, 34.0, 32.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.0, 28.7, 28.2, 25.9, 22.7, 14.1. **FTIR (neat, KBr), cm^{-1}:** 2923, 2853, 1733, 1603, 1512, 1255, 1205, 1161. **EA** for $C_{65}H_{75}BrO_{10}$: calc.: 71.22 %C, 6.90 %H; found: 70.90 %C, 6.95 %H. **MS (MALDI +):** m/z: 1119.3 $(M + Na)^+$, 645.3, 491.0, 355.0.

Compound 6EM. Compound **E6Br** (0.80 g, 0.73 mmol), tetrabutylammonium bromide (0.47 g, 1.46 mmol) and a small amount of 2,6-di-*tert*-butyl-4-methylphenol were dissolved in a mixture of chloroform/water (3/6). Sodium methacrylate (0.24 g, 2.19 mmol) was added and the mixture was stirred at 70 ºC for 24 h. After cooling, the mixture was extracted with dichloromethane and the organic phase was washed with water and dried over magnesium sulfate. The product was purified by flash chromatography using dichloromethane as eluent and crystallization from ethyl acetate. **Yield.** 0.48 g of a white solid (60%). **Mp.** Bx 53 ºC $SmCP_A$ 131 ºC I. **^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm:** 8.31 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.9 Hz, 4H), 7.67 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 5.0 Hz, 2H), 7.48-7.45 (m, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.25-7.20 (m, 1H), 6.99 (d, J = 8.9 Hz, 4H), 6.11-6.09 (m, 1H), 5.56-5.53 (m, 1H), 4.14 (t, J = 6.7 Hz, 2H), 4.05 (t, J = 6.5 Hz, 4H), 1.94 (s, 3H), 1.89-1.77 (m, 4H), 1.73-1.61 (m, 2H), 1.54-1.20 (m, 36H), 0.88 (t, J = 6.6 Hz, 3H). **^{13}C-NMR (75 MHz, $CDCl_3$), δ, ppm:** 164.49, 164.47, 164.33, 163.83, 155.44, 151.34, 150.65, 142.07, 138.03, 132.44, 131.86, 129.89, 128.34, 126.85, 126.81, 125.17, 124.72, 122.15, 122.10, 120.95, 120.65, 120.46, 114.43, 68.40, 64.84, 31.95, 29.68, 29.62, 29.58, 29.53, 29.51, 29.39, 29.26, 29.11, 28.63, 26.00, 22.72, 18.37, 14.16. **FTIR (neat, KBr), cm^{-1}:** 2921, 2851, 1734, 1605, 1511, 1257, 1204, 1163. **EA for $C_{69}H_{80}O_{12}$:** Calc. 75.25 %C, 7.32 %H; found: 75.25 %C, 7.24 %H. **MS (MALDI +):** m/z: 1123.6 $(M + Na)^+$, 513.2, 491.2, 451.2, 359.3.

Compound 6AM. *(A)* Oxalyl chloride (0.35 g, 2.73 mmol) was added to a suspension of benzoic acid **9** (0.65 g, 1.36 mmol) in dry dichloromethane (65 mL). A few drops of DMF were added and the reaction mixture was stirred at room temperature under an argon atmosphere overnight. The solvent was evaporated and the residue was

dried under vacuum. The product was used in the next step without further purification. *(B)* The acid chloride (1.18 g, 2.37 mmol) was dissolved in dry dichloromethane and added to a solution of biphenol **7** (0.71g, 1.14 mmol) in the same solvent. Triethylamine (0.22 mL, 1.6 mmol) was added and the mixture was stirred for 23 h. After this time, the solvent was evaporated and the crude product was purified first by flash chromatography using dichloromethane/hexanes (9/1) as eluent and then by crystallization from ethyl acetate. **Yield.** 0.57 g of an orange solid (46%). **Mp.** Cr 109 ºC Col_r 139 ºC I. **^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm:** 8.36 (d, J = 8.6 Hz, 2H), 8.31 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 5.0 Hz, 2H), 7.48-7.45 (m, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.25-7.20 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 6.11-6.09 (m, 1H), 5.56-5.53 (m, 1H), 4.14 (t, J = 6.7 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 1.94 (s, 3H), 1.89-1.77 (m, 4H), 1.73-1.61 (m, 2H), 1.54-1.22 (m, 36H), 0.88 (t, J = 6.6 Hz, 3H). **^{13}C-NMR (75 MHz, $CDCl_3$), δ, ppm:** 164.7, 164.4, 164.3, 163.8, 162.4, 155.8, 155.4, 151.3, 150.6, 146.8, 142.0, 140.0, 132.4, 131.8, 131.20, 130.3, 129.8, 128.3, 126.8, 125.3, 125.1, 124.7, 122.5, 122.1, 122.0, 120.9, 120.6, 120.4, 114.8, 114.4, 68.4, 68.3, 64.8, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.6, 26.0, 25.9, 22.7, 18.3, 14.1. **FTIR (neat, KBr), cm^{-1}:** 2920, 2851, 1733, 1604, 1511, 1502, 1475, 1287, 1274, 1255, 1163. **EA** for $C_{68}H_{80}N_2O_{10}$: 75.25 %C, 7.43 %H, 2.58 %N; found: 74.95 %C, 7.45 %H, 2.62 %N. **MS (MALDI +):** m/z: 1107.5 $(M + Na)^+$, 1085.6 $(M + 1)^+$, 645.3, 491.1, 463.3, 347.2. **UV-vis ($CHCl_3$, 5.1·10^{-5} M):** λ_{max}: 264 nm (ε = 58.235·103 $M^{-1}cm^{-1}$), λ_{max}: 364 nm (ε = 31.002·103 $M^{-1}cm^{-1}$).

Compound Br6A. *(A)* Oxalyl chloride (0.53 g, 4.0 mmol) was added to a suspension of benzoic acid **6** (0.88 g, 2.0 mmol) in dry toluene (20 mL). A few drops of

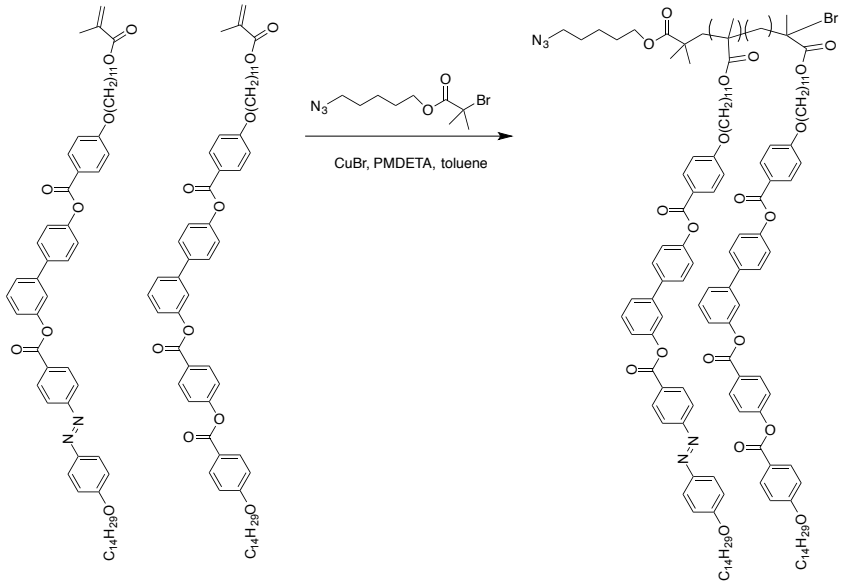
DMF were added and the reaction mixture was stirred at room temperature under an argon atmosphere for 16 h. The solvent was evaporated and the residue was dried under vacuum. The product was used in the next step without further purification.

(B) The acid chloride (0.91 g, 2.0 mmol) was dissolved in dry dichloromethane and added to a solution of biphenol **11** in the same solvent. Triethylamine (0.33 mL, 2.33 mmol) was added and the reaction mixture was stirred for 20 h. After this time, the solvent was evaporated and the crude product was purified first by flash chromatography using dichloromethane as eluent and then by crystallization from ethyl acetate. **Yield.** 1.17 g of an orange solid (65%) **Mp.** Cr 111 ºC SmC_AP_A 139 ºC I. **^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm:** 8.36 (d, J = 8.5 Hz, 2H), 8.32 (d, J = 8.6 Hz, 2H), 8.17 (d, J = 8.7 Hz, 2H), 7.99 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 4.6 Hz, 2H), 7.50-7.46 (m, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.25-7.21 (m, 1H), 7.03 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.05 (t, J = 6.0 Hz, 4H), 3.54 (t, J = 6.7 Hz, 0.5H), 3.41 (d, J = 6.8 Hz, 1.5H) 1.91-1.73 (m, 6H), 1.54-1.20 (m, 36H), 0.89 (t, J = 6.5 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$), δ, ppm:** 164.6, 164.4, 164.2, 163.7, 162.4, 155.7, 155.3, 151.2, 150.6, 146.7, 141.9, 137.9, 132.3, 131.7, 131.1, 130.2, 129.8, 128.2, 126.7, 125.2, 124.6, 122.4, 122.0, 122.0, 120.8, 120.5, 120.3, 114.7, 114.3, 68.3, 68.2, 33.9, 32.7, 32.5, 31.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.0, 28.8, 28.6, 28.0, 26.8, 25.9, 25.9, 22.6, 14.0. **FTIR (neat, KBr), cm^{-1}:** 2920, 1850, 1732, 1604, 1510, 1475, 1275, 1254, 1171. **MS (MALDI+):** m/z: 1081.5 $(M + 1)^+$ (Br-compound), 1035.6 (M^+) (Cl-compound), 422.2, 353.0.

Compound M6A. The mixture obtained above (0.30 g), tetrabutylammonium bromide (0.22 g, 0.67 mmol) and a small amount of 2,6-di-*tert*-butyl-4-methylphenol were dissolved in a mixture of chloroform/water (6/12). Sodium methacrylate (0.11 g,

1.04 mmol) was added and the mixture was stirred at 70 ºC for 48 h. After cooling, the mixture was extracted with dichloromethane and the organic phase was washed with water and dried over magnesium sulfate. The product was purified by flash chromatography using dichloromethane/hexanes (9/1) as eluent and by crystallization from ethyl acetate. **Yield.** 0.20 g of an orange solid (65%). **Mp.** Cr 106 ºC SmCP 130 ºC I. **^{1}H-NMR (300 MHz, $CDCl_3$), δ, ppm:** 8.36 (d, J = 8.4 Hz, 2H), 8.31 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 8.9 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 4.6 Hz, 2H), 7.48-7.45 (m, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.25-7.20 (m, 1H), 7.03 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 9.1 Hz, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.14 (t, J = 6.5 Hz, 2H), 4.06 (t, J = 6.5 Hz, 4H), 1.95 (s, 3H), 1.89-1.77 (m, 4H), 1.73-1.61 (m, 2H), 1.54-1.22 (m, 36H), 0.88 (t, J = 6.6 Hz, 3H). **^{13}C-NMR (75 MHz, $CDCl_3$), δ, ppm:** 167.6, 164.7, 164.5, 164.3, 163.8, 162.5, 155.8, 155.4, 151.3, 150.7, 146.9, 142.1, 138.0, 136.6, 132.4, 131.8, 131.3, 130.3, 129.9, 128.3, 126.8, 125.3, 125.2, 124.7, 122.5, 122.1, 122.1, 121.0, 120.6, 120.5, 114.8, 114.4, 68.5, 68.4, 64.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.6, 26.0, 25.9, 22.7, 18.4, 14.1. **FTIR (neat, KBr), cm^{-1}:** 2920, 2850, 1732, 1604, 1510, 1502, 1474, 1286, 1254, 1171. **EA** for $C_{68}H_{80}N_2O_{10}$: Calc. 75.25 %C, 7.43 %H, 2.58 %N; found: 75.21 %C, 7.48 %H, 2.64 %N. **MS (MALDI +):** m/z: 1107.5 $(M + Na)^+$, 938.5. **UV-vis ($CHCl_3$, $5.2 \cdot 10^{-5}$ M):** λ_{max}: 264 nm ($\varepsilon = 58.980 \cdot 10^3$ $M^{-1}cm^{-1}$), λ_{max}: 364 nm ($\varepsilon = 31.150 \cdot 10^3$ $M^{-1}cm^{-1}$).

Synthesis of polymer P-(E5M +A5M) by ATRP.



Scheme S2. *Synthetic route followed to synthesize the polymer* ***P-(E5M+A5M)*** *by ATRP.*

To a Schlenk tube charged with CuBr (10 mg, 0.07 mmol) and monomers **E5M** (165 g, 0.17 mmol) and **A5M** (165 g, 0.17 mmol) under an argon atmosphere was added distilled toluene (2 mL) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) (14 μL, 0.07 mmol), Finally, the initiator 5-azidopentyl 2-bromo-2-methylpropanoate (10 mg, 0.04 mmol) was added. Oxygen was removed by successive pump-thaw cycles by applying vacuum and backfilling with argon. The polymerization was carried out at 80 ºC for 24 h. The Cu(I) complex was removed by treatment with the acidic ion exchange resin DowexVR Marathon MSC. The resin was filtered off and the solution was poured into cold methanol to isolate the polymer as an orangish solid, which was dried under vacuum. **Yield.** 50%. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.28, 8.13, 7.95, 7.61, 7.48, 7.44, 7.36, 7.23, 6.96, 4.12, 1.81, 1.62, 1.57, 1.46, 1.31, 1.26, 0.88. **FTIR (KBr disk, cm^{-1}):** 2920, 2851, 1729, 1604, 1510, 1473, 1253, 1175, 1075. **SEC (THF) Mw:** 15,700, Mw/Mn: 1.13.

S2. MS of compound Br6A

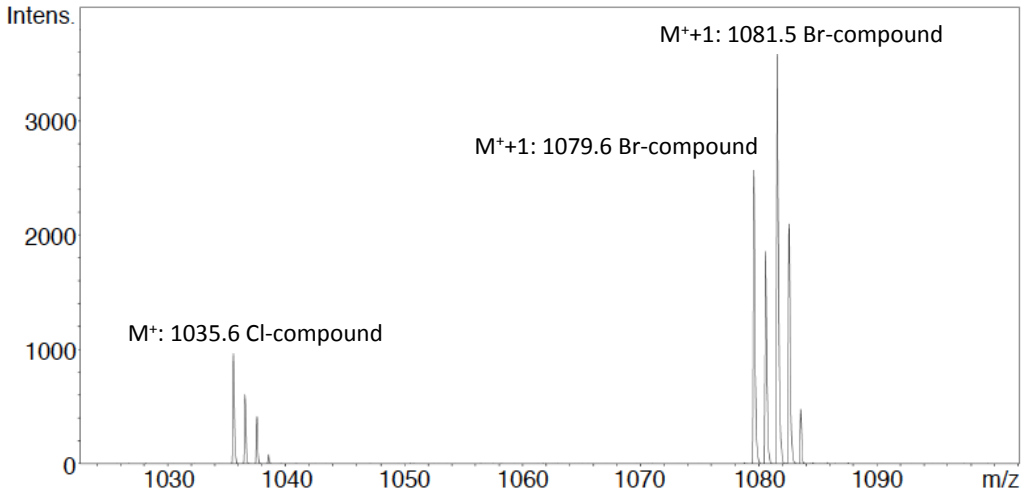


Figure S1. *Mass spectra of mixture of compounds obtained in the synthesis of compound* ***Br6A,*** *showing the presence of chloro- and bromo-derivatives.*

S3. Thermal properties of the photopolymerizable mixtures.

Mixture (10% molar in AZO-component)	**Phase Transition Temperature (ºC) and Enthalpy (kJ/mol)**
6EM+6AM	B_x 49.7 [4.5] $SmCP_A$ 129.8 [20.2] Is Is 129.4 [20.0] $SmCP_A$ 49.8 [2.7] B_x
6EM+M6A	B_x 49.4 [4.4] $SmCP_A$ 129.6 [19.6] Is Is 129.7 [19.7] $SmCP_A$ 49.2 [2.9] B_x

S4. ^{1}H-NMR studies of polymer P-M6A.

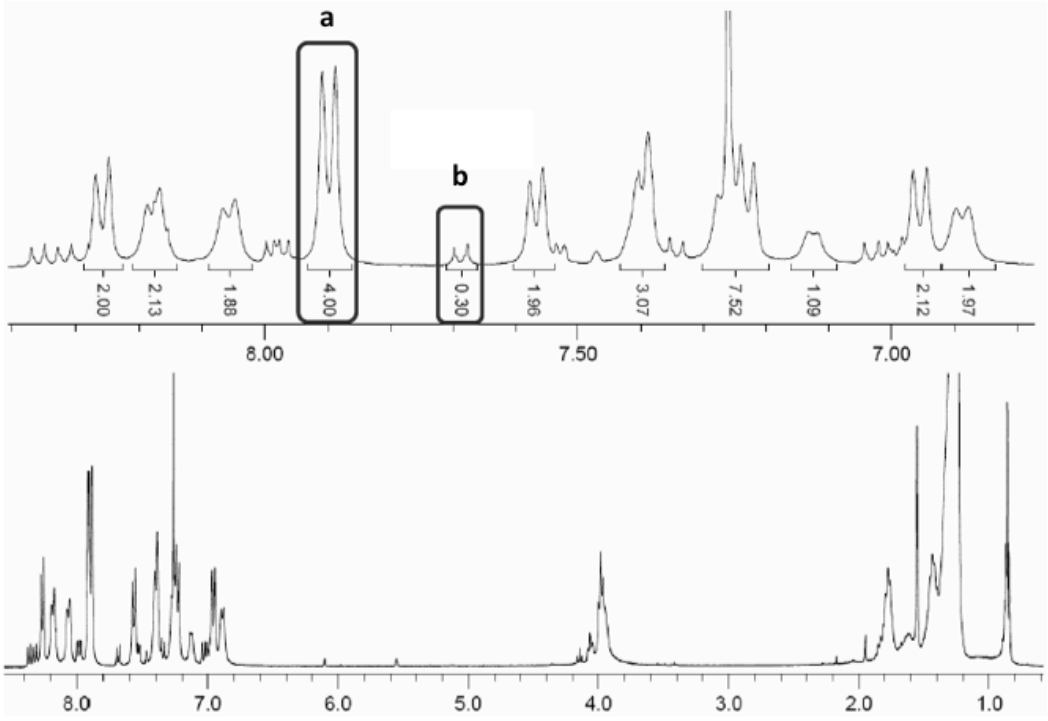


Figure S2. *^{1}H-NMR spectrum of the polymer* ***P-M6A*** *(bottom) and detail of the ^{1}H-NMR spectrum of the same compound (top) of an in situ photopolymerized sample. Ratio between the integrals of protons* ***a*** *(polymer) and* ***b*** *(monomer) was used to calculate degree of conversion.*

S5. DSC thermograms and POM images of representative monomers and polymers.

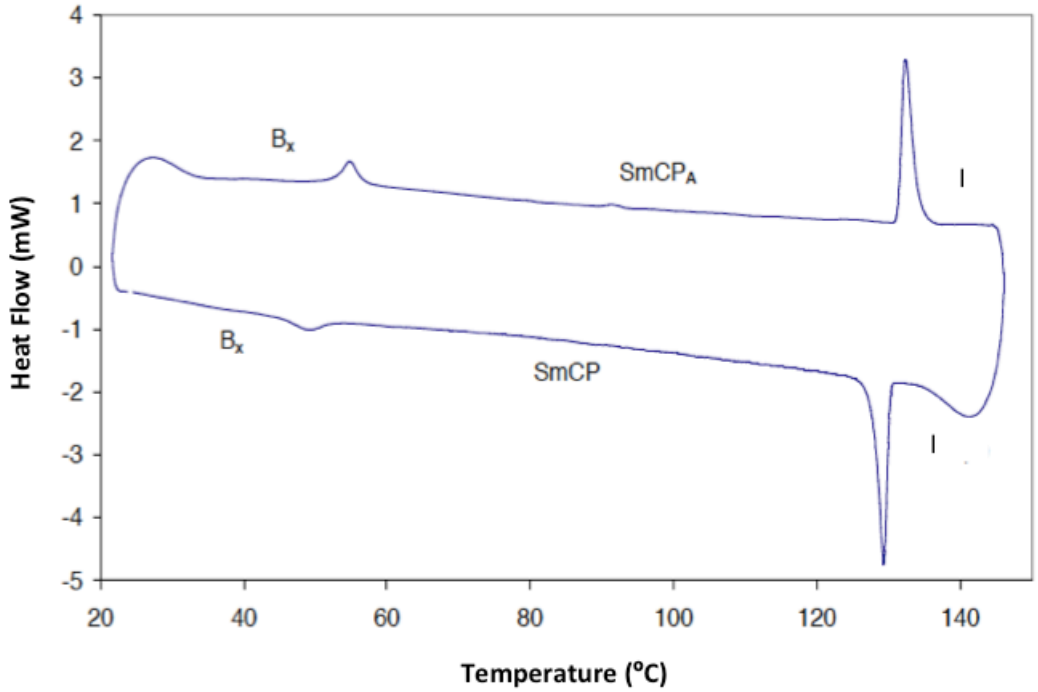


Figure S3. *DSC thermogram corresponding to the second heating scan and cooling of monomer* ***E6M*** *at a rate of at 10 ºC/min.*

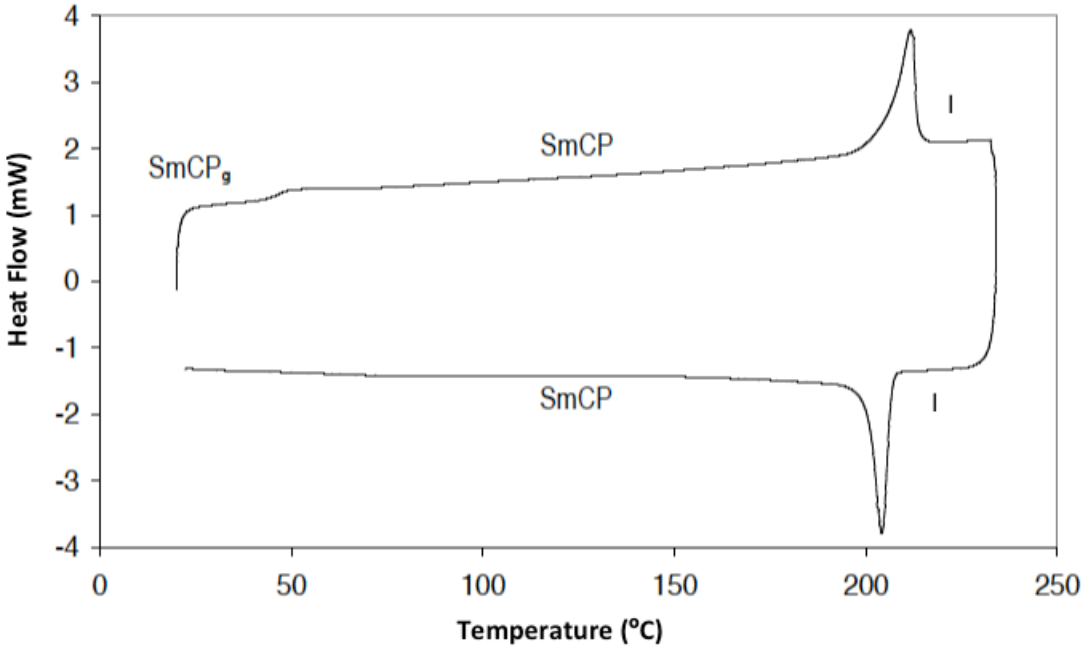


Figure S4. *DSC thermogram of the third heating scan and cooling of the copolymer* ***P-(E6M+6AM)*** *at 20 ºC/min.*

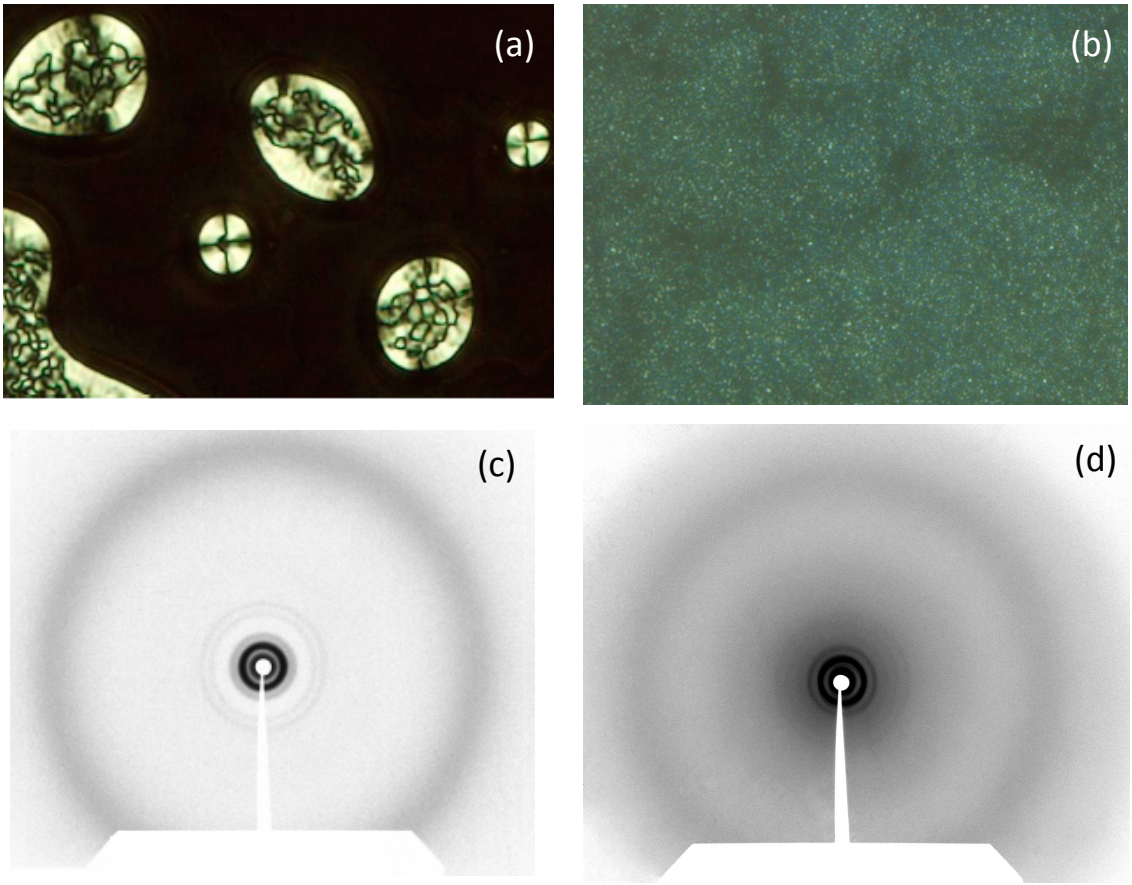


Figure S5. *Textures: (a) of the SmCP phase of* ***P-(E6M+6AM)*** *on cooling from the isotropic liquid and (b) of the SmCP phase of* ***P-(E5M+A5M)*** *at 100 ºC.*

X-ray diffractograms: (c) of ***P-(E6M+M6A)*** *in the SmCP glassy phase at r.t., after cooling down from the mesophase and (d) of* ***P-(E5M+A5M)*** *in the SmCP mephase at 100 ºC.*