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SUPPORTING INFORMATION
For

TTF-BASED BENT-CORE LIQUID CRYSTALS

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Content list

General

NMR experiments were performed on a Bruker ARX-300 MHz and a Bruker AV-400 MHz spectrometer. Infrared spectra for all the complexes were obtained using a Nicolet Avatar 360 (FTIR) spectrophotometer in the 400-4000 cm^{-1} spectral range. Microanalyses were performed with a LECO CHNS-932 microanalyser. Mass spectrometry performed with a Microflex (MALDI-ToF). UV-Vis measurements were taken using an ATI Unicam UV4 spectrophotometer.

Mesomorphic properties were studied by optical microscopy using an Olympus BH2 microscope with crossed polarizers. The microscope was connected to a Linkam THMS 600 hot stage and an Olympus DP-12 camera. Transition temperatures were determined by differential scanning calorimetry (DSC) using either a TA2910 differential calorimeter or a DSC Q1000 calorimeter of TA Instruments. Thermogravimetric analysis were performed using a TGA Q5000 thermobalance of TA Instruments. Each apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g) using a scanning rate of 10 °C/min in most cases. X-ray measurements on nonoriented samples were performed using a small-angle goniometer equipped with a high temperature attachment, a linear position-sensitive detector of 4º of angular range, and an angular resolution better than 0.01º. Monochromatic Cu-$K\alpha$ radiation was used. The samples were held in Lindemann glass capillaries (0.5 mm diameter).

Polarization measurements were carried out using commercial cells with ITO electrodes coated with polyimide (Linkam, 5 μm). The triangular wave voltage was supplied by a HP3325A function generator plus an amplifier and the current was

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recorded by a HP3458A digital multimeter. All the equipment was interfaced to a microcomputer.

SHG measurements were also carried out in Linkam cells of thickness 5 μm. The measurements were performed with an experimental set-up described in detail elsewhere.[1] The fundamental light was a Q-switched Nd-YAG laser (wavelength 1064 nm) with a pulse width of 6 ns and a frequency of 5 Hz. A square-wave electric field synchronized with the laser pulse was applied to the sample.

Conductivity studies were carried out using the same cells by measuring the electrical resistance of the sample as a function of temperature. For measuring the sample resistance a 10 MΩ resistor was set in parallel to the sample and the equivalent resistance was measured by using a HP 34401A multimeter. To study the photoconductivity the sample was illuminated with a halogen lamp ELC-403 Electro-lite Co. The irradiation on the sample was about 50 mW cm^{-2} in the wavelength range 340–380 nm.

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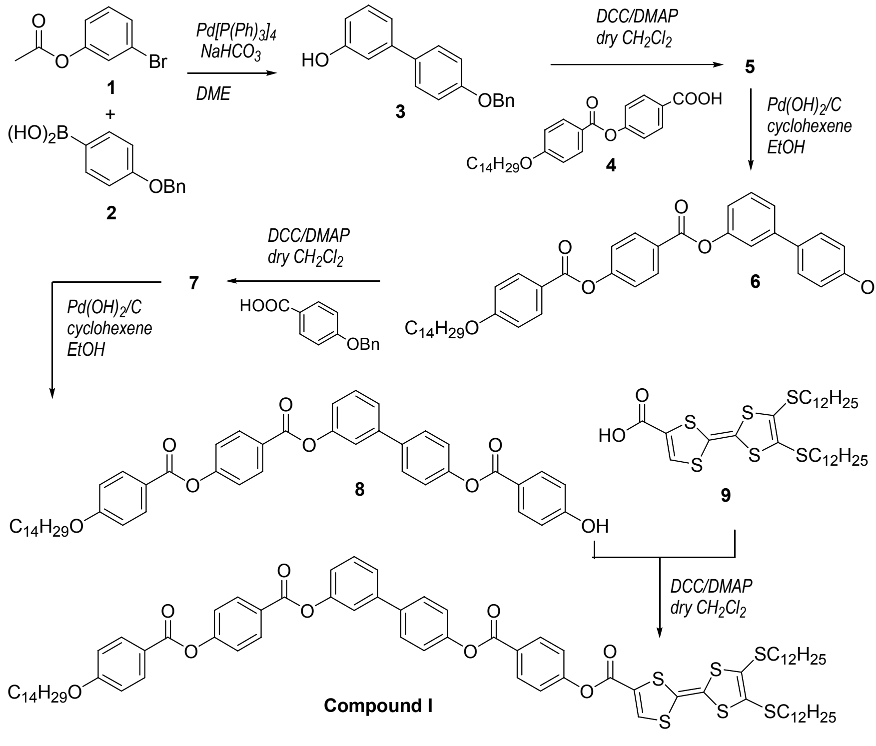
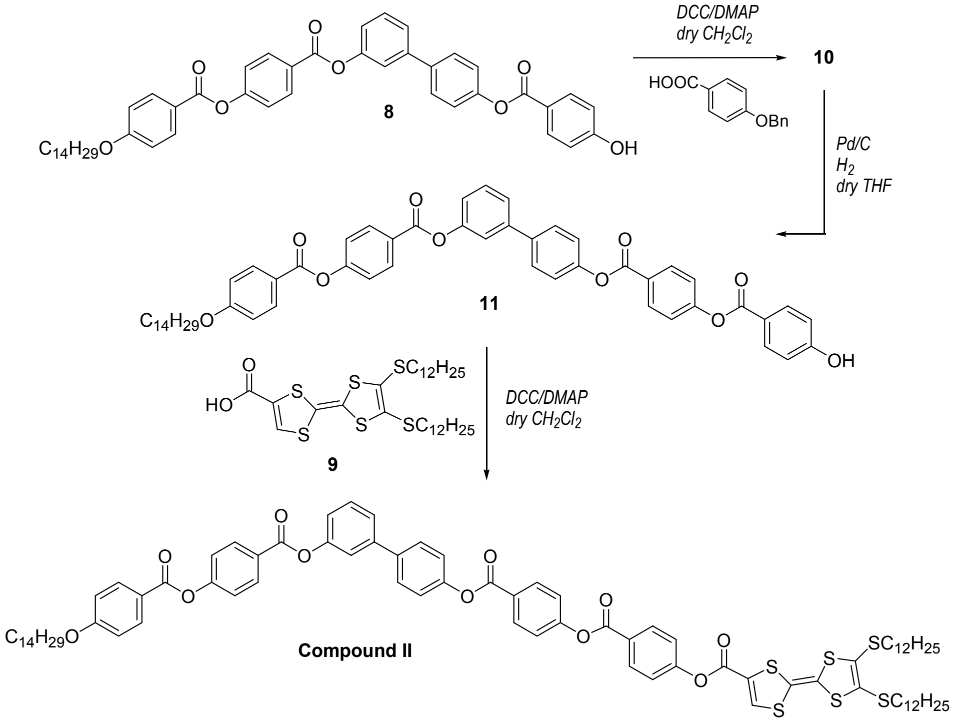
[1] N. Pereda, C. L. Folcia, J. Etxebarria, J. Ortega and M. B. Ros, *Liq. Cryst.*, **1998**, *24*, 451.

Synthesis and structural characterization of compounds I, II and I.

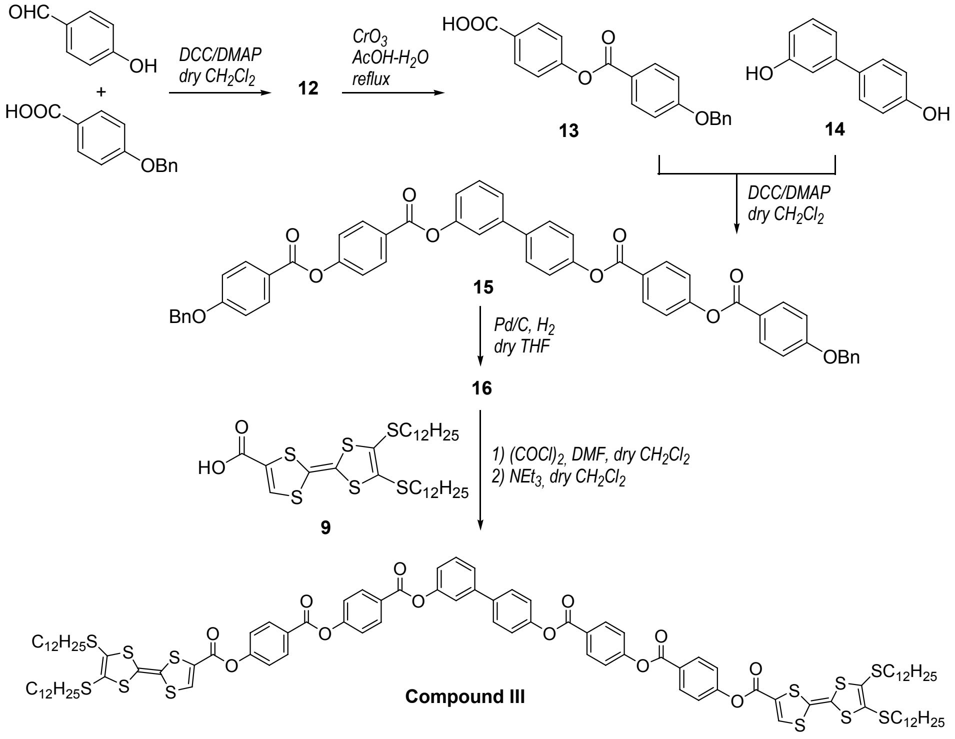
Synthetic routes to compounds I, II and III are in Schemes S1, S2 and S3.



Scheme S1. Synthetic scheme for the synthesis of compound **I**.



Scheme S2. Synthetic scheme for the synthesis of compound **II**.



Scheme S3. Synthetic scheme for the synthesis of compound **III**.

Organic starting materials were purchased from Sigma-Aldrich, Fluka and Lancaster and used as delivered. Solvents were purified and dried by standard methods.

In all cases, synthetic methods reported in the literature for the same compounds (**1-6**[2], **9**[3] and **14**[4]) or adapted to the aimed ones have been followed. Experimental details as well as their structural characterization are included.

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[2] N. Gimeno; M. B. Ros, J. L. Serrano, M. R. de la Fuente, *Angew. Chem. Inter. Ed.,* **2004,** *43*, 5235.

[3] M.M.S. Abdel-Mottaleb, E. Gomar-Nadal, M. Surin, H. Uji-I, W. Mamdouh, J. Veciana, V. Lemaur, C. Rovira, J. Cornil, R. Lazzaroni, D.B. Amabilino, S. De Feyter, F.C. De Schryver, *J. Mater. Chem.*, **2005**, *15*, 4601.

[4] a) D. Shen, A. Pegenau, S. Diele, I. Wirth, C. Tschierske, *J. Am. Chem. Soc.* **2000**, *122*, 1593-. b) C.L: Folcia, I. Alonso, J. Ortega, J. Etxebarria, I. Pintre, M. B. Ros, *Chem. Mater.*, **2006**, *18*, 4617.

3-[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]-4′-[4′-benzyloxybenzoyloxy]biphenyl (7).

A mixture of 3.0 g of 3-[4-(4-n-tetradecyloxybenzoyloxy)benzoyloxy]biphenyl-4′-ol (6) (4.8 mmol), 1.35 g of p-benzyloxybenzoic acid (5.8 mmol) and 0.071 mg of DMAP (0.5 mmol) in 120 mL of dry dichloromethane, was cooled in an ice/water bath and 1.32 g of dicyclohexylcarbodiimide DCC (6.3 mmol) was added under an argon atmosphere. After 30 min, the reaction mixture was allowed to stir at room temperature overnight. The precipitate was filtered off and the solvent was evaporated. After purification by flash chromatography on silica gel using dichloromethane as solvent, the yield was 90%. Mp 190.1 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.5 Hz, 2H), 8.20-8.14 (m, 4H), 7.65 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 4.9 Hz, 2 H), 7.50-7.30 (m, 8H), 7.29 (d, J = 8.6 Hz, 2H), 7.25-7.20 (m, 1H), 7.08 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 9.1 Hz, 2H), 5.17 (s, 1H), 4.06 (t, J = 6.6 Hz, 2H), 1.87-1.76(m, 2H), 1.53-1.43 (m, 2H), 1.42-1.22 (m, 20H), 0.88 (t, J = 6.8 Hz, 3H). IR (neat, KBr): 2919, 2850, 1731, 1605, 1510, 1257, 1160 cm^{-1}.

3-[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]-4′-[4′-hydroxybenzoyloxy]biphenyl (8).

To a mixture of the benzyl ether (1.56 g, 1.88 mmol) and cyclohexene (25 mL) in ethanol (160 mL), Pd(OH)2/C (20%, 0.310 g) was added in small portions, under an argon atmosphere. The mixture was heated under reflux for 21 h, filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the resulting solid was used without further purification. Yield: 92%. Mp 198.5 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.8 Hz, 2H), 8.20-8.10 (m, 4H), 7.65 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 5.1 Hz, 2H), 7.46-7.43 (m, 1H), 7.38 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 7.25-7.20 (m, 1H), 6.99 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.45 (s_a, 1H), 4.05 (t, J = 6.5 Hz, 2H), 1.89-1.77 (m, 2H), 1.50-1.20 (m, 22H), 0.88 (t, J = 6.6 Hz, 3H). IR (neat, KBr). 3390, 2921, 2852, 1740, 1728, 1699, 1606, 1511, 1284, 1255, 1203, 1159 cm^{-1}.

3-[4’’-(4’’’-n-tetradecyloxybenzoyloxy)benzoyloxy]-4’-[4^{iv}-(5^{v},6^{v}-bis-n-dodecilthia-2^{v}-tetrathiafulvalenylcarbonyloxy)benzoyloxy] biphenyl (I).

A catalytic amount of dimethylaminopyridine DMAP (0.002 g, 0.015 mmol) was added under an argon atmosphere to a mixture of 0.160 g of 3-[4’’-(4’’’-n-tetradecyloxybenzoyloxy) benzoyloxy]-4’-(4^{iv}-hydroxybenzoyloxy)biphenyl (**8**) (0.216 mmol), 0.100 g of (2-tetrathiafulvalenyl)acetic acid (**9**) (0.154 mmol) and 0.045 g of dicyclohexylcarbodiimide DCC (0.216 mmol) in 25 mL of dry dichloromethane. The reaction mixture was stirred at room temperature overnight. After 22 hours the solvent was evaporated and the red solid was purified by half-pressure chromatography on silica gel using dichloromethane-hexane (8:2) as solvent and by recrystallization from ethyl acetate (43% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.35-8.25 (m, 4H), 8.16 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.63 (s, 1H), 7.52 (d, J = 5.13 Hz, 2H), 7.48-7.44 (m, 1H), 7.38 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.6, 2H), 7.25-7.20 (m, 1H), 7.00 (d, J = 8.9 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 2.87-2.78 (m, 4H), 1.89-1.76 (m, 2H), 1.70-1.58 (m, 4H), 1.58-1.20 (m, 58H), 0.93-0.84 (m, 9H). ^{13}C-NMR (300 MHz, $CDCl_3$) δ 164.70, 164.55, 164.43, 164.05, 157.16, 155.66, 154.54, 151.56, 150.77, 142.24, 138.34, 135.17, 132.64, 132.17, 132.06, 130.11, 128.71, 128.57, 127.71, 127.65, 127.38, 127.06, 124.92, 122.35, 122.24, 121.87, 121.17, 120.88, 120.68, 114.65, 111.68, 110.94, 68.62, 36.60, 32.15, 29.99, 29.96, 29.90, 29.88, 29.83, 29.78, 29.75, 29.58, 29.35, 29.31, 28.74, 26.20, 22.92, 14.35. IR (neat, KBr): 2921, 2851, 1737, 1606, 1512, 1470, 1266, 1207, 1163, 1071 cm^{-1}. AE for $C_{78}H_{100}O_9S_6$ (calculated: 68.18% C, 7.34% H, 14.0% S) found 68.12% C, 7.54% H, 13.89% S. EM (MALDI +): m/z: 1372.8. UV-vis (CH_2Cl_2, $2.3\cdot10^{-5}$ M): $\lambda_{máx}$: 264 nm (ε: $74.17\cdot10^3$ $M^{-1}cm^{-1}$), $\lambda_{máx}$: 324 nm (ε: $15.75\cdot10^3$ $M^{-1}cm^{-1}$), $\lambda_{máx}$: 456 nm (ε: $2.36\cdot10^3$ $M^{-1}cm^{-1}$).

3-[4”-(4’’’-*n*-tetradecyloxybenzoyloxy)benzoyloxy]-4’-[4^{iv}-(4^{v}-benzyloxybenzoyloxy)benzoyloxy]biphenyl (10).

A mixture of 0.700 g of 3-[4’’-(4’’’-n-tetradecyloxybenzoyloxy)benzoyloxy]-4’-(4^{iv}-hydroxybenzoyloxy)biphenyl (**8**) (0.942 mmol), 0.263 g of p-benzyloxybenzoic acid (1.13 mmol) and 0.009 mg of DMAP (0.094 mmol) in 75 mL of dry dichloromethane, was cooled in an ice/water bath and 0.236 g of dicyclohexylcarbodiimide DCC (1.13 mmol) was added under an argon atmosphere. After 30 min, the reaction mixture was allowed to stir at room temperature overnight. The precipitate was filtered off and the solvent was evaporated. After purification by half-pressure chromatography on silica gel using a mixture of dichloromethane-hexane (8:2) as solvent, a white solid was obtained in a 92 % yield. Mp 221° C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.6 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H), 8.18 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 5.3 Hz, 2H), 7.48-7.36 (m, 10H), 7.32 (d, J = 8.6 Hz, 2H), 7.25-7.20 (m, 1H), 7.08 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 5.18 (s, 2H), 4.06 (t, J = 6.6 Hz, 2H), 1.88-1.78 (m, 2H), 1.53-1.43 (m, 2H), 1.41-1.20 (m, 20H), 0.88 (t, J = 6.8 Hz, 3H). IR (neat, KBr) 2921, 2851, 1734, 1606, 1511, 1263, 1205, 1163 cm^{-1}.

3-[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]-4´-[4^{iv}-(4^{v}-hydroxybenzoyloxy) benzoyloxy]biphenyl (11).

Pd/C 20% wt. (0.150 g, 30% wt.) was added to a suspension of **10** (0.500 g, 0.525 mmol) in dry THF and mechanically stirred at room temperature under hydrogen atmosphere (ca. 30 psi) in a low pressure hydrogenator. After 24 hours the Pd/C was filtered off filtered through a pad of Celite ® and the solvent was evaporated to give a white solid purified by recrystallization from ethanol. 84% yield. Mp 198° C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 9.1 Hz, 2H), 8.29 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.9 Hz, 2H), 7.52 (d, J = 5.0 Hz, 2H), 7.47-7.45 (m, 1H), 7.39 (d, J = 8.9 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.25-7.20 (m, 1H), 6.99 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.70 (s, 1H), 4.06 (t, J = 6.6 Hz, 2H), 1.87-1.77 (m, 2H), 1.53-1.43 (m, 2H), 1.41-1.20 (m, 20H), 0.88 (t, J = 6.9 Hz, 3H). IR (neat, KBr) 3396, 2923, 2853, 1741, 1739, 1700, 1607, 1512, 1286, 1256, 1205, 1161 cm^{-1}.

3-[4’’-(4’’’-n-tetradecyloxybenzoyloxy)benzoyloxy]-4’-{4^{iv}-[4^{v}-(5^{vi},6^{vi}-bis-n-dodeciltia-2^{vi}-tetrathiafulvalenylcarbonyloxy)benzoyloxy]benzoyloxy}biphenyl (II).

A mixture of 3-[4’’-(4’’’-n-tetradecyloxybenzoyloxy) benzoyloxy]- 4´-[4^{iv}-(4^{v}-hydroxybenzoyloxy)benzoyloxy]biphenyl (**11**) (0.186 g, 0.216 mmol), 0.100 g of (2-tetrathiafulvalenyl)acetic acid (**9**) (0.154 mmol), 0.051 g of DCC (0.246 mmol) and 0.002 g of DMAP (0.022 mmol) in 17 mL of dry dichloromethane was stirred overnight at room temperature. After 16 hours the solvent was evaporated and the solid purified by half-pressure chromatography on silica gel using dichloromethane-hexane (8:2) as solvent and by recrystallization from ethyl acetate to give rise to a dark-red product in 50% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.9 Hz, 2H), 8.31 (d, J = 8.9 Hz, 2H), 8.28 (d, J = 9.1 Hz, 2H), 8.16 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 8.9 Hz, 2H), 7.63 (s, 1H), 7.52 (d, J = 4.8 Hz, 2H), 7.47-7.45 (m, 1H), 7.39 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.36-7.30 (m, 4H), 7.25-7.20 (m, 1H), 6.99 (d, J = 9.0 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 2.86-2.79 (m, 4H), 1.87-1.77 (m, 2H), 1.69-1.57 (m, 4H), 1.57-1.20 (m, 58H), 0.92-0.83 (m, 9H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 164.52, 164.39, 164.36, 163.84, 163.66, 156.92, 155.44, 155.05, 154.54, 151.34, 150.61, 142.05, 138.09, 135.14, 132.45, 132.06, 131.97, 131.87, 129.92, 128.47, 128.37, 127.48, 127.20, 127.08, 127.01, 126.84, 124.74, 122.17, 122.10, 122.04, 121.80, 120.94, 120.48, 114.44, 111.53, 110.67, 68.41, 36.39, 31.96, 29.79, 29.76, 29.69, 29.62, 29.57, 29.40, 29.16, 29.11, 28.55, 26.01, 22.73, 14.17. IR (neat, KBr): 2923, 2852, 1739,1605, 1512, 1469, 1266, 1207, 1162, 1067 cm^{-1}. AE for $C_{85}H_{104}O_{11}S_6$ (calculated: 68.33% C, 7.02% H, 12.88% S) found 68.23% C, 7.07% H, 12.72% S. EM (MALDI +): m/z: 1493.6. UV-vis (CH_2Cl_2, $2.8\cdot10^{-5}$ M): $\lambda_{máx}$: 264 nm (ε: $88.10\cdot10^3$ M^{-1}cm^{-1}), $\lambda_{máx}$: 324 nm (ε: $16.56\cdot10^3$ M^{-1}cm^{-1}), $\lambda_{máx}$: 464 nm (ε: $2.69\cdot10^3$ M^{-1}cm^{-1}).

4-(4’-benzyloxybenzoyloxy)benzaldehyde (12).
The synthetic method followed was analogous to the method of compound 10, using 1.87 g of 4-benzyloxybenzoic acid (8.02 mmol), 1.00 g of 4-hydroxybenzaldehyde (8.02 mmol), 2.05 g of DCC (9.63 mmol), 0.10 g of DMAP (0.80 mmol) and 85 mL of dry dichloromethane. Purification was carried out by recrystallization from ethanol. A white solid was obtained in 82% yield. Mp: 156ºC (199.8ºC decomposes). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.16 (d, J = 9.0 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H), 7.24-7.17 (m, 7H), 7.08 (d, J = 9.0 Hz, 2H), 5.17 (s, 2H). IR (neat, KBr) 1727, 1708, 1603, 1510, 1278, 1254, 1207, 1156 cm^{-1}.

4-(4’-benzyloxybenzoyloxy)benzoic acid (13).
To a suspension of 2.0 g of aldehyde 12 (6 mmol) 24 mL of acetic acid 90% were slowly added 1.20 g of chromium (VI) oxide (12 mmol) dissolved in 10 mL of acetic acid 60%. The system was heated at reflux for 8 hours and then the reaction mixture, after addition of 10 mL of water, was cooled and kept in a refrigerator for two days before the solid was filtered off and washed with water. Purification was carried out washing the solid with dichloromethane and by recrystallization from ethanol giving rise to a white solid in 68% yield. Mp: 196.5ºC decomposes. ^{1}H-NMR (400 MHz, DMSO-d6): δ 8.10 (d, J = 8.9 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 6.9 Hz, 2H), 7.44-7.32 (m, 5H), 7.22 (d, J = 9.0 Hz, 2H), 5.25 (s, 2H). IR (neat, KBr) 3250-2400, 1725, 1696, 1607, 1514, 1432, 1274, 1266, 1211, 1162 cm^{-1}.

3,4’-Bis[4”-(4’’’-benzyloxybenzoyloxy)benzoyloxy]biphenyl (15).
The synthetic method followed was analogous to the method of compound 10 and 12, using 0.449 g of 13 (1.29 mmol), 0.100 g of 3,4’-dihydroxybiphenyle (14) (0.54 mmol), 0.291 g of DCC (1.40 mmol), 0.013 g of DMAP (0.11 mmol) and 40 mL of dry dichloromethane. Purification was carried out by half-pressure chromatography on silica gel using dichloromethane as solvent. A white solid was obtained in 85% yield. Mp: Is 219.6º C mesophase 200.2º C Cryst. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.9 Hz, 2H), 8.30 (d, J = 8.9 Hz, 2H), 8.18 (d, J = 8.5 Hz, 4H), 7.67 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 4.9 Hz, 2H), 7.47-7.34 (m, 15H), 7.32 (d, J = 8.7 Hz,

2H), 7.25-7.20 (m, 1H), 7.09 (d, J = 8.9 Hz, 4H), 5.18 (s, 4H). IR (neat, KBr) 1735, 1604, 1511, 1269, 1203, 1162 cm^{-1}.

3,4'-Bis[4"-(4'''-hydroxybenzoyloxy)benzoyloxy]biphenyl (16).
The synthetic method followed was analogous to the method of compound 11, using 0.330 g of 15 (0.39 mmol), 0.099 g of Pd/C 20% wt. and 10 mL of dry THF. Purification was performed by recrystallization from ethanol. 71% yield. Mp: 229.6ºC. ^{1}H-NMR (400 MHz, DMSO-d^6): δ 8.26 (d, J = 8.7 Hz, 2H), 8.24 (d, J = 8.7 Hz, 2H), 8.02 (d, J = 8.7 Hz, 4H), 7.83 (d, J = 8.7 Hz, 2H), 7.71-7.66 (m, 2H), 7.59 (t, J = 8.1 Hz, 1H), 7.52 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.36-7.31 (m, 1H), 6.95 (d, J = 8.7 Hz, 4H). IR (neat, KBr) 3435, 1733, 1728, 1604, 1514, 1271, 1204, 1161 cm^{-1}.

3,4'-Bis{4"-[4'''-(5^{vi},6^{vi}-bis-n-dodeciltia-2^{vi}-tetrathiafulvalenylcarbonyloxy) benzoyloxy]benzoyloxy}biphenyl (III).
The acid chloride of **9** was prepared using 0.400 g of it (0.62 mmol), oxalyl chloride (0.163 g, 0.11 mL, 1.23 mmol), 35 mL of dry dichloromethane and 5 drops of dimethylformamide. The mixture was stirred under argon atmosphere and room temperature for 15 hours, the solvent was evaporated and the solid dried with a vacuum plump. Then it was put into reaction with **16** (0.171 g, 0.26 mmol), triethylamine (0.10 mL, 0.74 mmol), and 35 mL of dry dichloromethane. After 46 hours the solvent was evaporated and the dark-red solid purified by half-pressure chromatography on silica gel using dichloromethane as solvent. A glassy material was obtained after removal of the solvent by vacuum. Yield 16%. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.35-8.25 (m, 8H), 7.72 (d, J = 8.9 Hz, 2H), 7.67 (s, 2H), 7.60-7.53 (m, 2H), 7.52-7.48 (m, 1H), 7.43 (d, J = 8.9 Hz, 2H), 7.42 (d, J = 9.0 Hz, 2H), 7.38-7.32 (m, 6H), 7.26 (dt, J_d =7.5 Hz, J_t = 2.0 Hz, 1H), 2.84 (t, J = 7.4 Hz, 4H), 2.83 (t, J = 7.1 Hz, 8H), 1.67-1.58 (m, 8H), 1.45-1.2 (m, 72H), 0.91-0.85 (m, 12H). IR (neat, KBr) 2925, 2852, 1738, 1604, 1507, 1467, 1266, 1206, 1161 cm^{-1}. AE for $C_{102}H_{126}O_{12}S_{12}$ (calculated: 63.51% C, 6.58% H, 19.95% S) found 63.82% C, 6.79% H, 19.30% S. EM (MALDI +): m/z: 1928.9, 579.2, 226.6. UV-vis (CH_2Cl_2, $2.2\cdot10^{-5}$ M): $\lambda_{máx}$: 252 nm (ε: $71.48\cdot10^3$ M^{-1}cm^{-1}), $\lambda_{máx}$: 324 nm (ε: $23.77\cdot10^3$ M^{-1}cm^{-1}), $\lambda_{máx}$: 464 nm (ε: $4.65\cdot10^3$ M^{-1}cm^{-1}).

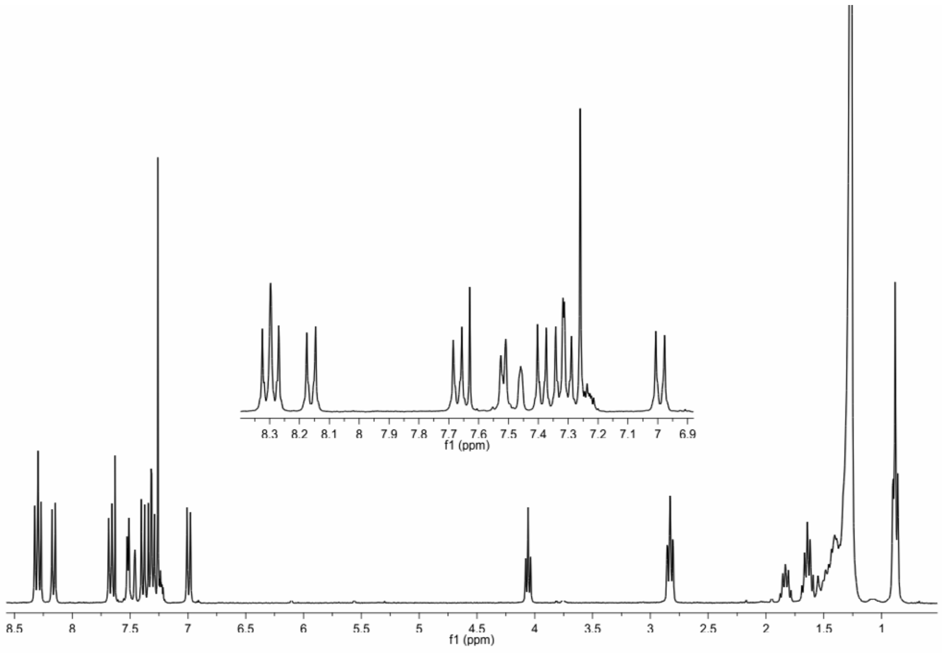


Figure S1: ^{1}H-NMR of compound **I** (400 MHz, CDCl$_3$).

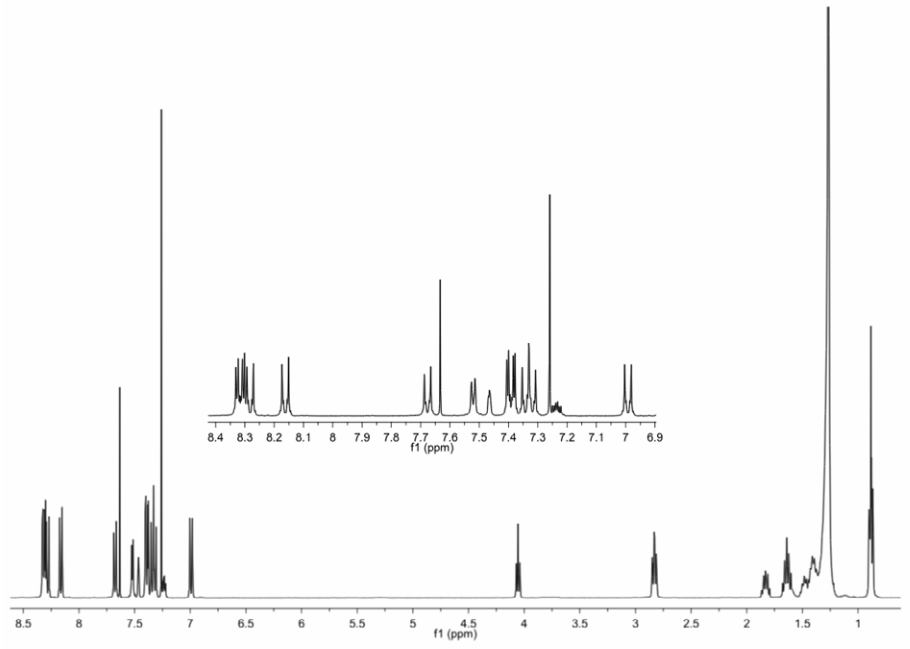


Figure S2: ^{1}H-NMR of compound **II** (400 MHz, CDCl$_3$).

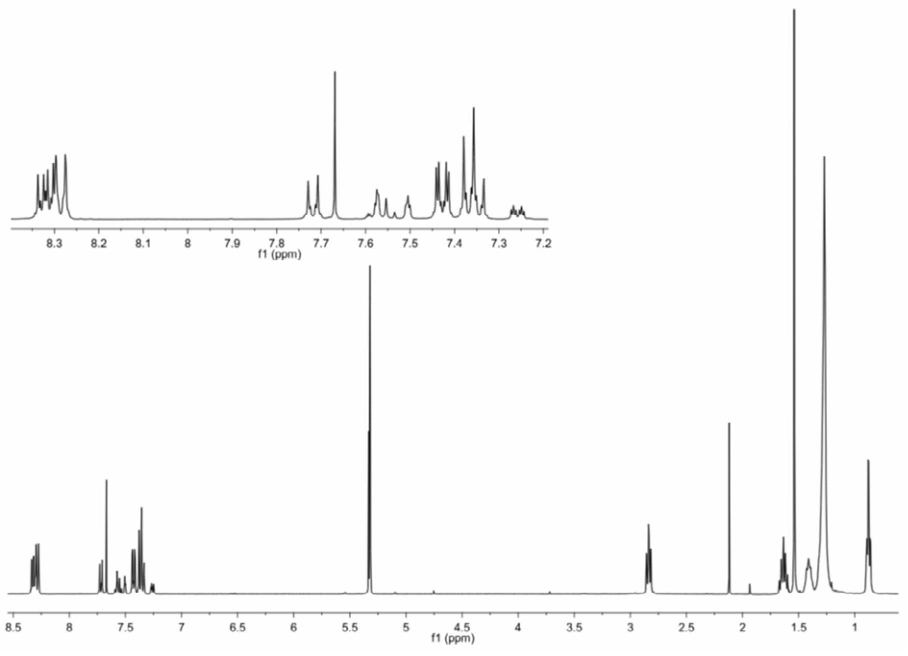
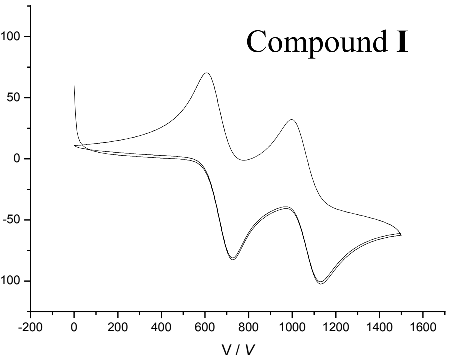


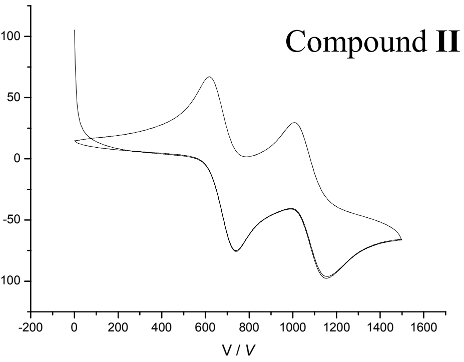
Figure S3: ^{1}H- NMR of compound **III** (400 MHz, CD_2Cl_2).

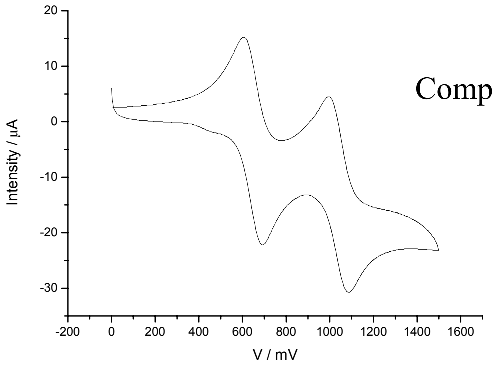
Cyclic voltammograms

The cyclic voltammograms were performed on a Potentiostat-Galvanostat 263A from EG&G Princeton Applied Research, using a standard three electrode cell with Pt-electrodes and an Ag/AgCl electrode in 3M KCl solution with a double salt bridge as a reference. The solvent was dried (CaH_2 and distilled) CH_2Cl_2 containing 0.1 M $[NBu_4][PF_6]$, as a supporting electrolyte.

Compound	$E_{1/2}(0/\cdot+)$ / V	$E_{1/2}(\cdot+/2+)$ / V
I	0.66	1.07
II	0.67	1.07
III	0.65	1.05

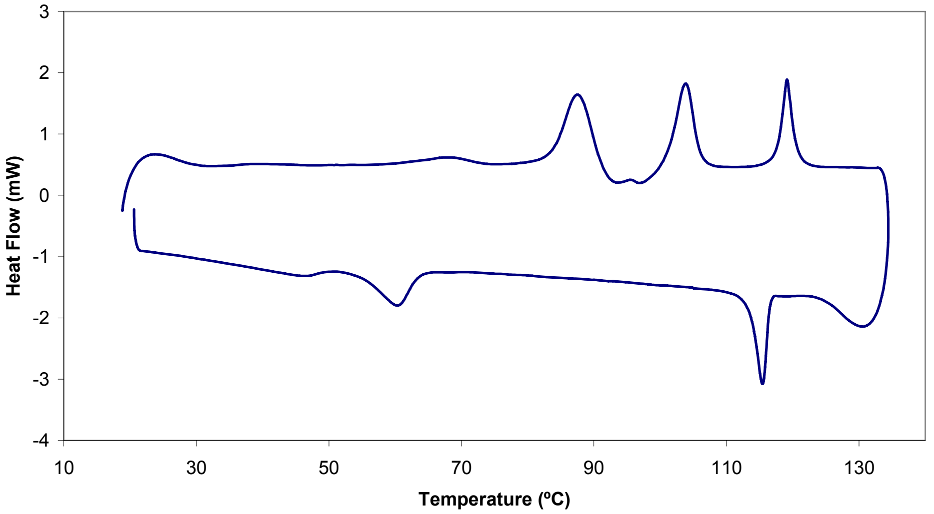




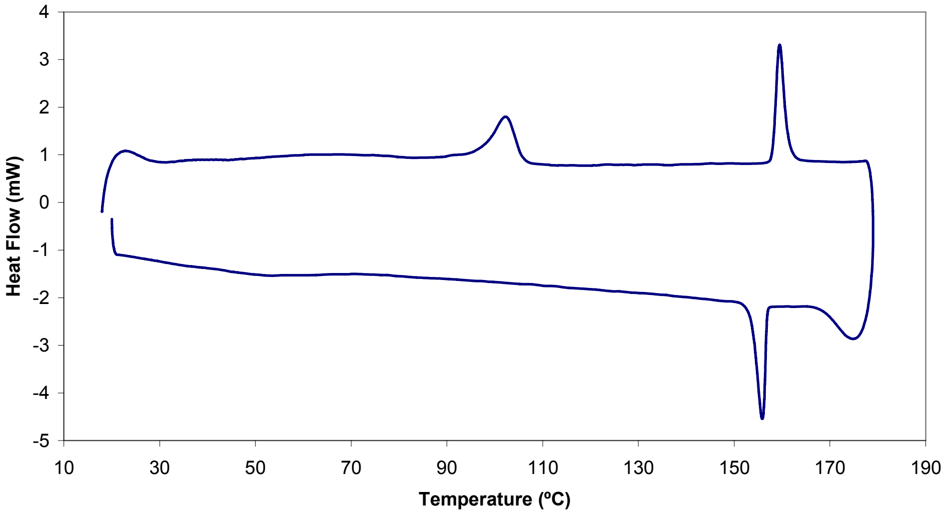


DSC thermograms

First heating and cooling scans (10 ºC/min) of compound **I.**



First heating and cooling scans (10 ºC/min) of compound **II.**



First heating and cooling scans (10 ºC/min) of compound **III.**

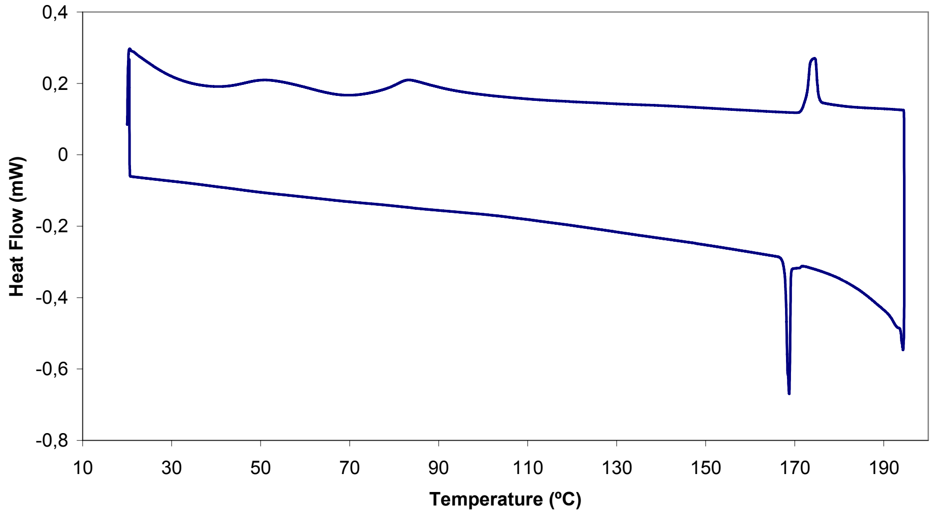


Figure S4. Schematic representations used for bent-shaped molecules (top). Schematic representations of the different molecular packing proposed for compounds **I**, **II** with and without field and **III** (bottom).

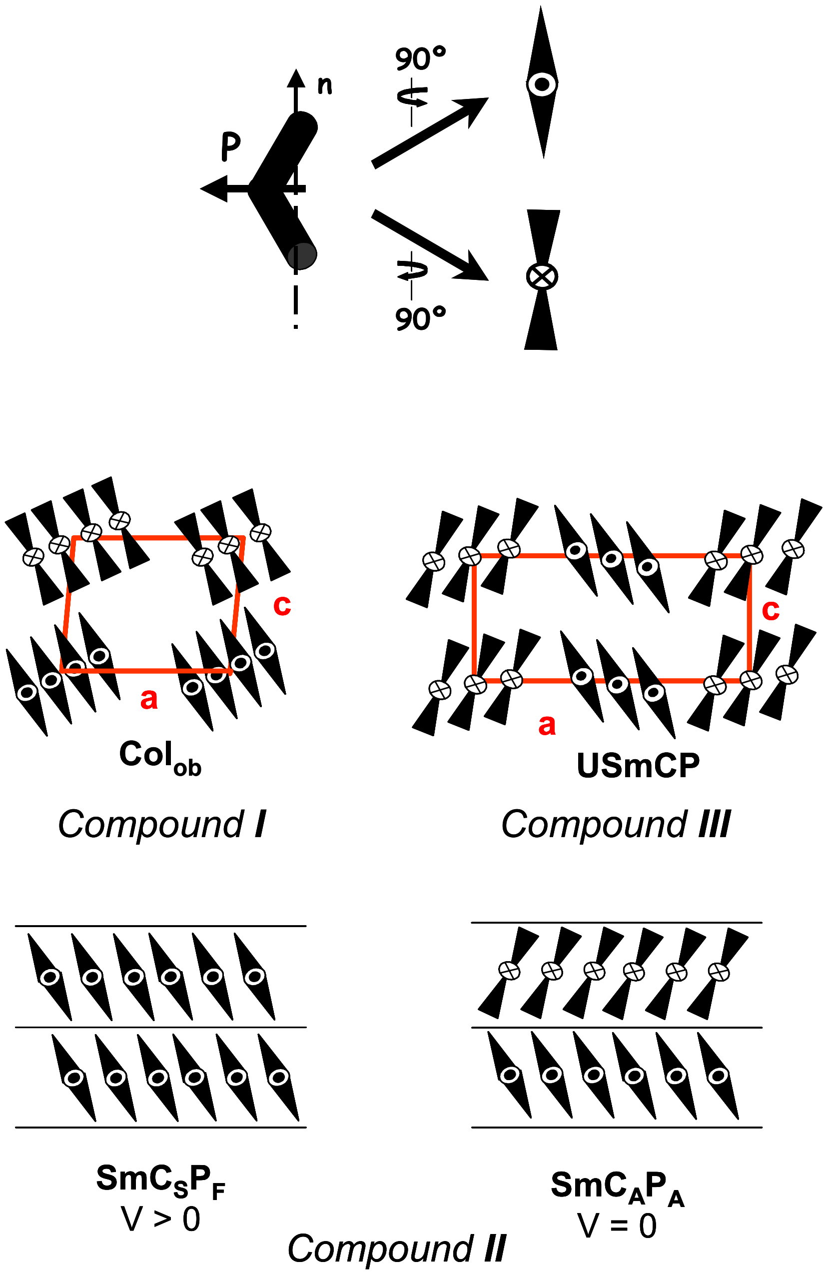


Figure S5. Temperature dependence of the electrical conductivity of **II** in its three phases.

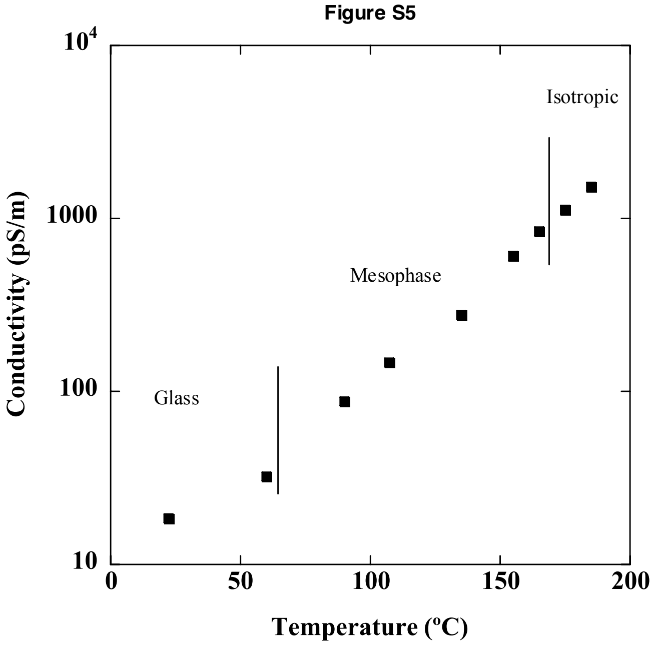


Figure S6. Electrical conductivity of **II** in the isotropic phase (solid squares) and in the mesophase (open squares) in the dark (OFF) and under illumination (ON).