Supplementary Information

Synthesis, mesomorphism and electronic properties of nonaflate and cyano substituted pentyloxy and 3-methylbutyloxy triphenylenes

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Content

1. Synthesis and characterization

1,2-di(pentyloxy)benzene (1a), 1,2-di(3-methylbutyloxy)benzene (1b), 1-(pentyloxy)-2-methyloxybenzene (6a) and 1-(3-methylbutyloxy)-2-methyloxybenzene (6b)

Finely powdered and dried potassium carbonate (31.0 g, 230 mmol for **1** and 16.0 g, 120 mmol for **6**) was added to a solution of catechol (10.0 g, 91 mmol) or guaiacol, (10.0 g, 80 mmol)] and 1-bromopentane (34.0 g, 230 mmol for **1** and 18.0 g, 120 mmol for **6**) or 1-bromo-3-methylbutane (34.0 g, 230 mmol for **1** and 18.0 g, 120 mmol for **6**) in DMF (125 mL or 15 mL) under argon and stirred at 80 ºC for 10 days or 1 day, respectively. The same volume of diethyl ether was added to the reaction mixtures at room temperature, precipitated salts were filtered off and the organic filtrated was extracted with deionized water and dried over magnesium sulfate. Evaporation of the solvent gave compounds **6** as pale yellow oils that were subject to vacuum distillation to remove remaining DMF (b.p. about 80 ºC at 0.8 mm Hg) and other impurities. Compounds **6a** (13.4 g, 86%) and **6b** (15.0 g, 95%) were obtained as colourless oils (b.p. about 110 ºC at 1 mbar). Crude compounds **1a** and **1b** were obtained as brown oils and filtered through a short column of neutral aluminum oxide (CH_2Cl_2/hexane 1:9) to give pale yellow oils that were distilled under vacuum to give **1a** (19.4 g, 85%) and **1b** (15.5 g, 68%) as colourless oils (b.p. about 150 ºC at 1 mbar).

1a TLC R_f: 0.65 (CH_2Cl_2-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 6.87 (4 H, m, arom. H), 3.98 (4 H, t, OCH_2, *J* 6.6 Hz), 1.87 (2 H, m, $CH(CH_3)_2$), 1.81 (4 H, m, CH_2), 1.50-1.37 (8 H, m, CH_2), 0.92 (6 H, d, CH_3, *J* 6.9 Hz).

1b (Found: C, 76.70; H, 10.50; $C_{16}H_{26}O_2$ requires C, 76.75%; H, 10.47%; O, 12.78%); TLC R_f: 0.65 (CH_2Cl_2-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 6.91 (4 H, s, arom. H), 4.04 (4 H, t, OCH_2, *J* 6.8 Hz), 1.87 (2 H, m, $CH(CH_3)_2$), 1.73 (4 H, m, CH_2), 0.96 (6 H, d, CH_3, *J* 6.6 Hz); δ_C (75 MHz, $CDCl_3$) 149.8, 148.9, 121.1 (2C), 113.5, 112.2, 67.7, 56.2, 38.2, 25.3, 22.8.

6a TLC R_f: 0.50 (CH_2Cl_2-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 6.90 (4 H, s, arom. H), 4.00 (2 H, t, OCH_2, *J* 6.2 Hz), 3.82 (3 H, s, OCH_3), 1.82 (2 H, m, CH_2), 1.5-1.4 (4 H, m, CH_2), 0.98 (3 H, t, CH_3, *J* 6.4 Hz).

6b (Found: C, 74.15; H, 9.39; $C_{12}H_{18}O_2$ requires C, 74.19%; H, 9.34%; O, 16.47%); TLC R_f: 0.50 (CH_2Cl_2-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 6.89 (4 H, s, arom. H), 4.04 (2 H, t, OCH_2, *J* 6.7 Hz), 3.86 (3 H, s, OCH_3), 1.82 (1 H, m, $CH(CH_3)_2$), 1.73 (2 H, m, CH_2), 0.98 (6 H, d, CH_3, *J* 6.6 Hz); δ_C (75 MHz, $CDCl_3$) 149.5, 121.2, 114.3, 112.2, 67.9, 56.2, 38.3, 25.4, 22.8.

2,3,6,7,10,11–hexakis-(pentyloxy)triphenylene (2a), 2,3,6,7,10,11–hexakis-(3-methylbutyloxy)triphenylene (2b), 2,6,10-trimethyloxy-3,7,11-tris-(pentyloxy)triphenylene (7a,s), 2,6,11-trimethyloxy-3,7,10-tris-(pentyloxy)triphenylene (7a,ns), 2,6,10-trimethyloxy-3,7,11-tris-(3-methylbutyloxy)triphenylene (7b,s), 2,6,11-trimethyloxy-3,7,10-tris-(3-methylbutyloxy)triphenylene (7b,ns).

Iron(III) chloride (90 mmol) was slowly added (over 5 min) *via* a solid addition funnel to a stirred solutions of **1a**, **1b**, **6a**, or **6b** (25 mmol) in nitromethane or dichloromethane/nitromethane 1:1 (100 mL) at 0 ºC under argon. The reaction mixture was stirred for another 5 min after completion of the addition and then quenched by the addition of dry methanol (25 mL) *via* a syringe. Subsequent addition of methanol and water precipitated the crude products as pale purple solids, which were purified by column chromatography on basic aluminum oxide with CH_2Cl_2/hexane 1:1 as mobile phase. A small amount (100 mg) of the product mixtures of **7a,s/7a,ns** and **7b,s/7b,ns** were separated by preparative TLC on silica with diethyl ether/hexane 1:1 as mobile phase for analysis.

2a (4.9 g, 6.6 mmol); yield: 80%; TLC R_f: 0.30 (toluene-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.85 (6 H, s, arom. H), 4.24 (12 H, t, OCH_2, *J* 6.5 Hz), 1.96 (12 H, m, CH_2), 1.58 (12 H, m, CH_2), 1.48 (12 H, m, CH_2), 0.99 (18 H, t, CH_3, *J* 6.3 Hz); δ_C (75 MHz, $CDCl_3$) 149.4, 124.1, 107.9, 70.1, 29.5, 28.8, 22.9, 14.5.

2b (3.0 g, 4.0 mmol); yield: 49%; TLC R_f: 0.36 (toluene-hexane 1:1); (Found: C, 77.40; H, 9.91; $C_{48}H_{72}O_6$ requires: C, 77.38%; H, 9.74%); δ_H (300 MHz, $CDCl_3$) 7.87 (6 H, s), 4.29 (12 H, t, OCH_2, *J* 6.7 Hz), 1.94-2.03 (6 H, m, $CH(CH_3)_2$), 1.83-1.89 (12 H, m, CH_2), 1.06 (36 H, d, CH_3, *J* 6.5 Hz); δ_C (75 MHz, $CDCl_3$) 149.2, 123.8, 107.5, 68.3, 38.3, 25.5, 22.9; HRCI MS: calc. *m/z* 744.5329 ($C_{48}H_{72}O_6$), found *m/z* 744.5339 (M^+).

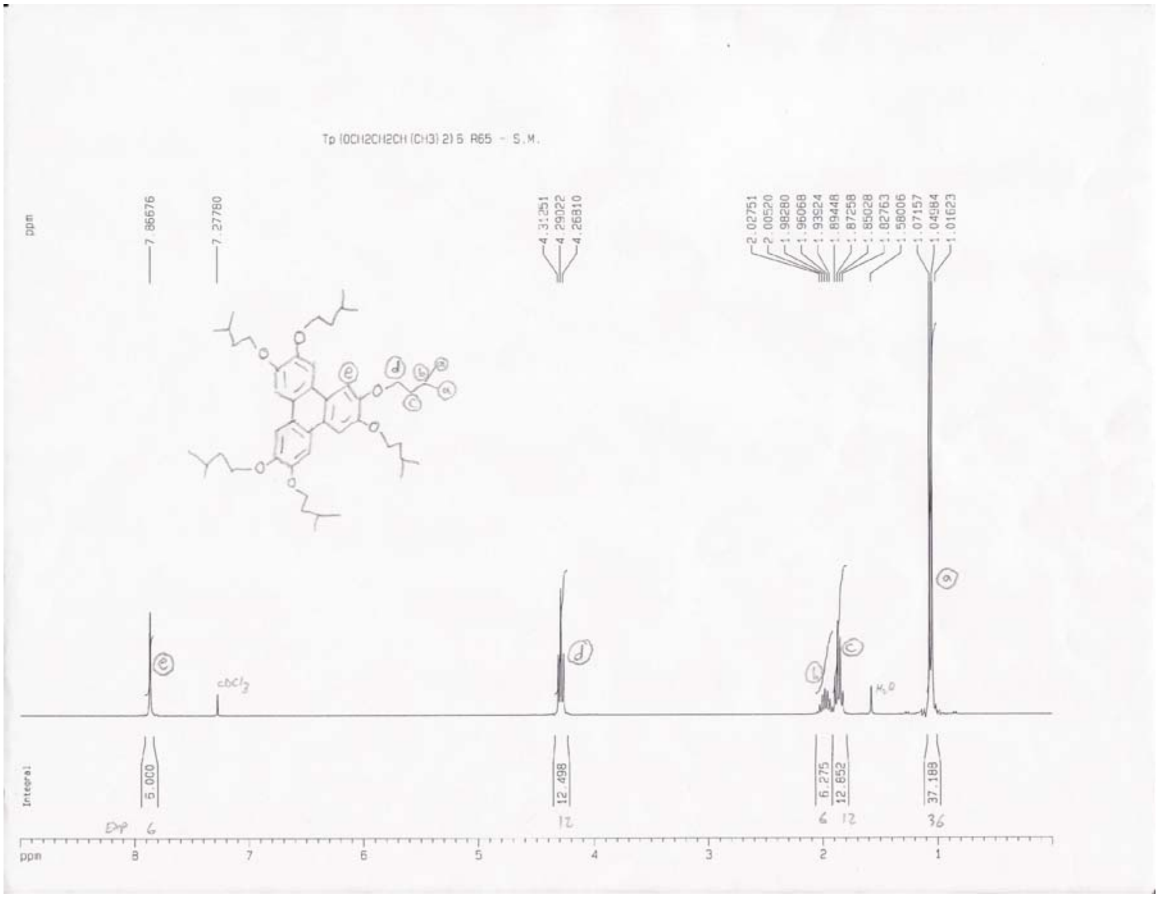

*Figure ESI-1: ^{1}H-NMR of **2b** in CDCl$_3$*

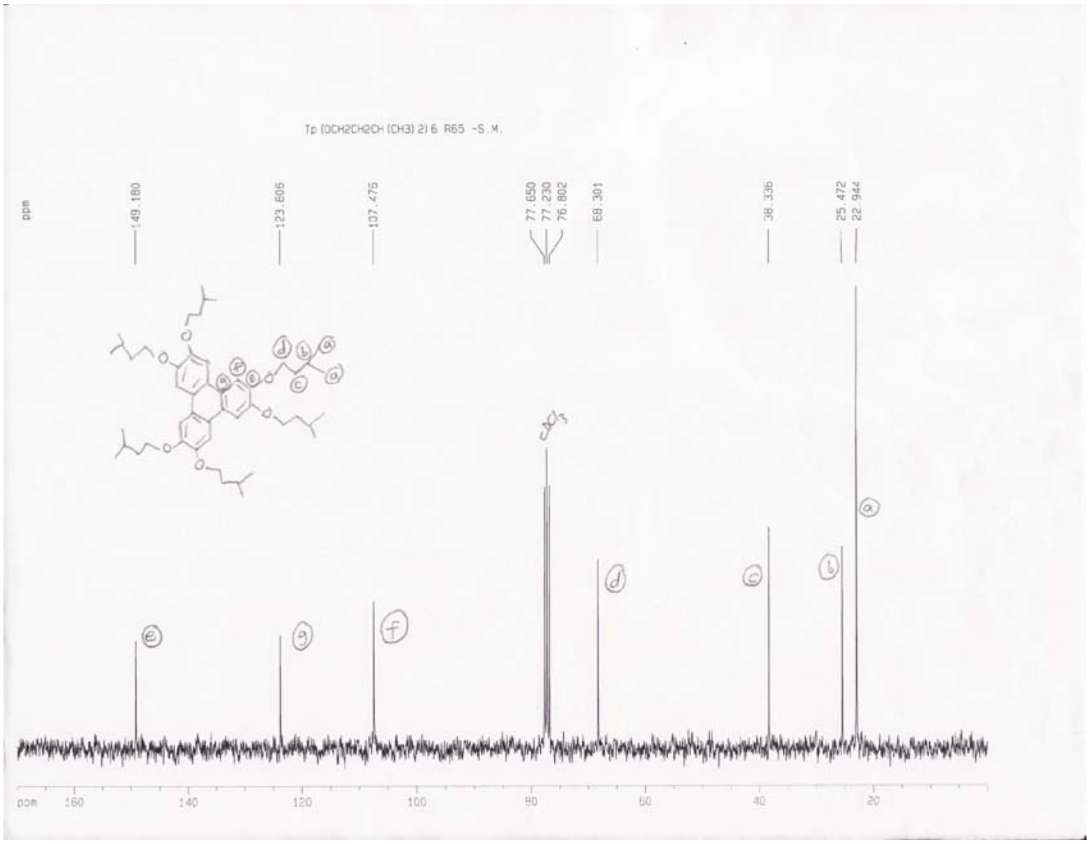

*Figure ESI-2: ^{13}C-NMR of **2b** in $CDCl_3$*

7a,s (0.66 g, 1.17 mmol); yield: 14%; TLC R_f: 0.55 (diethyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.87 (3 H, s, arom. H), 7.84 (3 H, s, arom. H), 4.28 (6 H, t, OCH_2, *J* 6.8 Hz), 4.12 (9 H, s, OCH_3), 2.01 (6 H, m, CH_2), 1.6-1.4 (12 H, m, 2 CH_2), 0.99 (9 H, t, CH_3, *J* 7.1 Hz).

7a,ns (1.9 g, 3.3 mmol); yield: 40%; TLC R_f: 0.36 (diethyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.86-7.83 (6 H, m, arom. H), 4.28 (6 H, t, OCH_2, *J* 6.8 Hz), 4.12 (9H, s, OCH_3), 2.02 (6 H, m, CH_2), 1.57 (6 H, m, CH_2), 1.49 (6 H, m, CH_2), 0.99 (9 H, t, CH_3, *J* 6.7 Hz); δ_C (75 MHz, $CDCl_3$) 149.9, 149.1, 123.9, 107.0, 105.7, 70.0, 56.9, 29.6, 28.9, 23.2, 14.7.

7b,s (0.57 g, 0.99 mmol); yield: 12%; (Found: C, 74.83; H, 8.14; $C_{36}H_{48}O_6$ requires: C, 74.97%; H, 8.39%); TLC R_f: 0.51 (diethyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.88 (3 H, s, arom. H), 7.84 (3 H, s, arom. H), 4.32 (6 H, t, OCH_2, *J* 6.7 Hz), 4.12 (9 H, s, OCH_3), 1.95-1.86 (9 H, m, $CH(CH_3)_2$ and CH_2), 1.06 (18 H, d, CH_3, *J* 6.3 Hz); δ_C (75 MHz, $CDCl_3$) 149.9, 149.1, 124.0, 123.9, 106.9, 105.7, 68.4, 56.9, 38.6, 25.8, 23.4.

7b,ns (1.7 g, 3.0 mmol); yield: 36%; (Found: C, 74.91; H, 8.26; $C_{36}H_{48}O_6$ requires: C, 74.97%; H, 8.39%); TLC R_f: 0.31 (dietheyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.88-7.84 (6 H, m, arom. H), 4.32 (6 H, t, OCH_2, *J* 6.7 Hz), 4.12 (9H, s, OCH_3), 1.95-1.86 (9 H, m, $CH(CH_3)_2$ and CH_2), 1.06 (18 H, d, CH_3, *J* 6.3 Hz); δ_C (75 MHz, $CDCl_3$) 150.2, 149.2, 124.2, 107.1, 105.9, 68.6, 57.1, 38.8, 26.1, 23.6.

2-methyloxy-3,6,7,10,11-pentapentyloxytriphenylene (8a, mixture with **2a)**

Iron(III) chloride (13.6 g, 84 mmol) was slowly added (over 5 min) *via* a solid addition funnel to a stirred solution of 2 equivalents **1a** (4.0 g, 16 mmol) and 1 equivalent **6a** (1.5 g, 8 mmol) in dichloromethane/nitromethane 1:1 (100 mL) at 0 ºC under argon. The reaction mixture was stirred for another 5 min after completion of the addition and then quenched by the addition of dry methanol (25 mL) *via* a syringe. Subsequent addition of methanol and water precipitated the crude products as pale purple solids, which were purified by column chromatography on basic aluminum oxide with toluene/hexane 1:1 as mobile phase. The product mixture (3.58 g) of **2a** (1.86 g, 2.49 mmol, 31%) and

8a (1.32 g 1.92 mmol, 24%) (about 1.3 to 1 molar ratio based on ^{1}H-NMR) was obtained as a white solid and was subjected to selective methylether cleavage without separation to give a mixture of **2a** and **3a** that was more easily separated by column chromatography than the mixture of **2a** and **8a**.

2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene (3a)

Method 1: Boroncatechol bromide (0.4 g, 2.0 mmol) was slowly added via a solid addition funnel to a solution of **2a** (1.0 g, 1.3 mmol) in dichloromethane (20 mL) at 0 °C under argon over a period of 10 minutes. The reaction mixture was stirred at 25 °C and monitored by TLC on silica (toluene/hexane 1:1) to avoid the formation di-hydroxy and tri-hydroxy triphenylene derivatives. A reaction time of 5 days has been found to give maximum yields of **3a** with no higher cleaved products detected. The reaction mixture was poured into $HCl_{aq.}$ (20 mL, 0.1 M), extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic phase was dried over $MgSO_4$, filtered and evaporated. A pale purple solid was obtained as crude product mixture that was separated and purified by column chromatography on silica gel with diethyl ether/hexane 1:6 to give unreacted **2a** (262 mg, 26%) and **3a** (424 mg, 47%) as white and off-white solids, respectively.

Method 2: Butyl lithium (1.58 M in hexane, 2.4 mL, 3.8 mmol) was added to a solution of diphenyl phosphine (0.70 g, 3.8 mmol) in THF (30 mL) under argon to give a bright orange solution. A solution of a 1.3:1 mixture of **2a** (1.8 g, 2.4 mmol) and **8a** (1.3 g 1.9 mmol) in THF (10 mL) was added under argon via a transfer needle and the combined solution was stirred at room temperature for 2 days. Aqueous HCl (0.1 M, 20 mL) was added to quench the reaction and the product mixture was extracted with diethyl ether. The combined organic phase was washed with water, dried over $MgSO_4$, filtered and evaporated. Purification and separation of the isomers was achieved by column chromatography on silica as described in method 1, except that methyl diphenyl phosphine was first removed with toluene/hexane 1:2, to give pure compound **3a** (1.07 g, 1.59 mmol, 84% with regard to **8a**) and unreacted **2a** (1.58 g, 2.12 mmol).

TLC R_f: 0.12 (toluene-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.98 (1 H, s, arom. H), 7.85 - 7.84 (4 H, m, arom. H), 7.79 (1 H, s, arom. H), 5.92 (1 H, s, OH), 4.35 - 4.20(10 H, m, OCH_2, *J* 6.7 Hz), 1.97 (10 H, m, CH_2), 1.6-1.4 (20 H, m, 2 CH_2), 0.99 (15 H, m, CH_3); δ_C (75 MHz, $CDCl_3$) 149.2, 148.9, 145.9, 145.4, 124.1, 123.9, 123.4, 123.1, 107.5, 106.7 104.5, 70.0, 69.8, 69.3, 29.3, 29.2, 28.5, 22.7, 14.2.

2-nonaflyl-3,6,7,10,11-pentapentyloxytriphenylene (4a)

Nonafluorobutanesulfonyl fluoride (0.313 g, 1.036 mmols) was added dropwise to a solution of 2-hydroxy-3,6,7,10,11-pentapentyloxy triphenylene (0.200 g, 0.296 mmols) and triethylamine (0.105 g, 1.036 mmols) in DMF (10 mL) at 0˚C. The mixture was stirred at room temperature under argon for 2 days until no mono-hydroxy triphenylene was detected by TLC. CH_2Cl_2 (20 mL) was added to the solution and the organic layer was extracted with water to remove DMF and ammonium salts. The organic phase was dried over $MgSO_4$, filtered, evaporated, and the residue was dissolved in hexane and passed through a short column of silica gel (CH_2Cl_2-hexane 1:2). The off-white solid was recrystallized from methanol to give the product as white crystals (207 mg, 0.217 mmols, 73%).

Found: C, 58.92; H, 6.48; $C_{47}H_{61}F_9O_8S$ requires C, 58.98%; H, 6.42%); TLC R_f 0.60 (diethyl ether-hexane 1:6); IR (KBr) 1352 cm^{-1} (S=O); δ_H (300 MHz, $CDCl_3$) 8.20 (1 H, s), 7.89 (1 H, s), 7.83 (1 H, s), 7.71 (2 H, s), 7.59 (1 H, s), 4.11–4.30 (10 H, m), 1.94 (10 H, m), 1.43 - 1.56 (20 H, m), 0.97 (15 H, t)**;** δ_C (75 MHz, $CDCl_3$) 150.2, 149.8, 124.2, 123.6, 109.4, 108.7, 108.2, 107.9, 106.6, 70.2, 68.9, 29.7, 28.8, 28.0, 23.2, 22.2, 15.2, 14.3 ($CF_{2,3}$ groups are not resolved because of low intensity due to coupling); δ_F (282 MHz, $CDCl_3$) -80.9 (3 F, t, 9.6 Hz, CF_3), -110.0 (2 F, t, 13.8 Hz, SCF_2), -121.1 (2 F, m, CF_2), -126.2 (2 F, m, CF_2); HRCI MS: calc. *m/z* 956.3943 ($C_{47}H_{61}F_9O_8S$), found m/z 956.3401 (M^+).

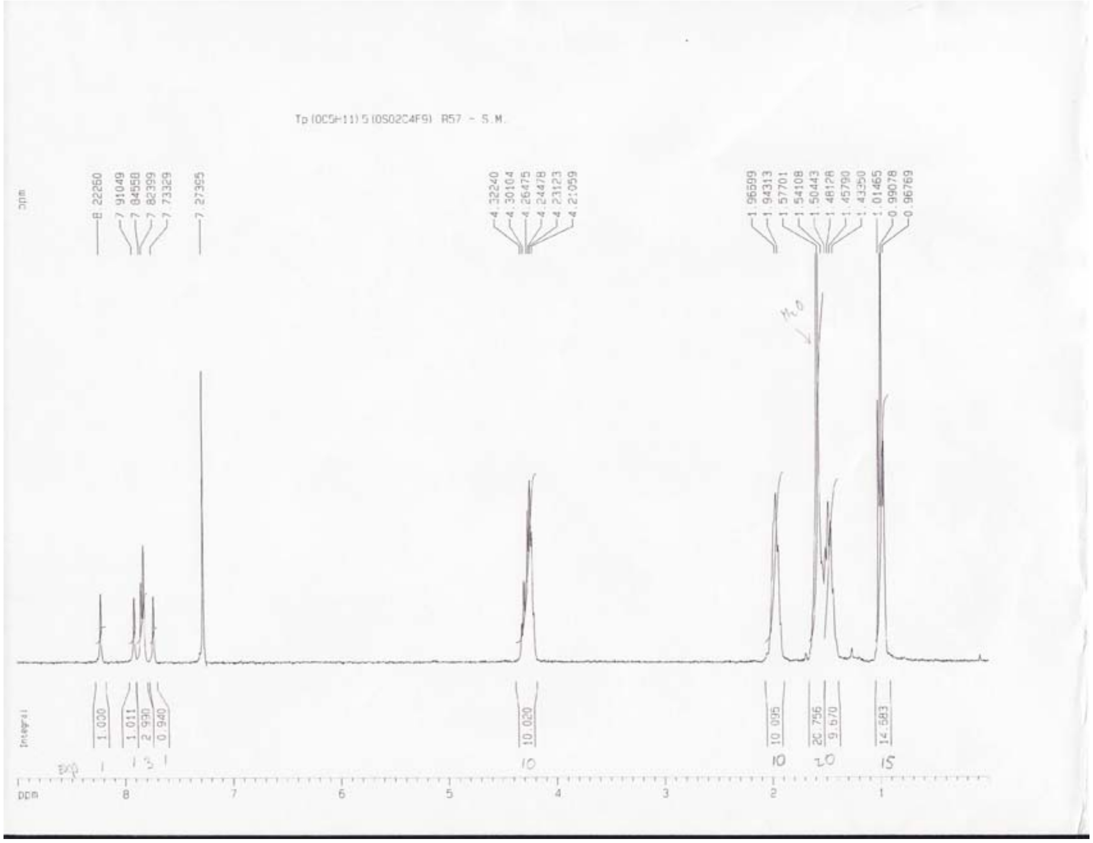

*Figure ESI-3: ^{1}H-NMR of **4a** in CDCl$_3$*

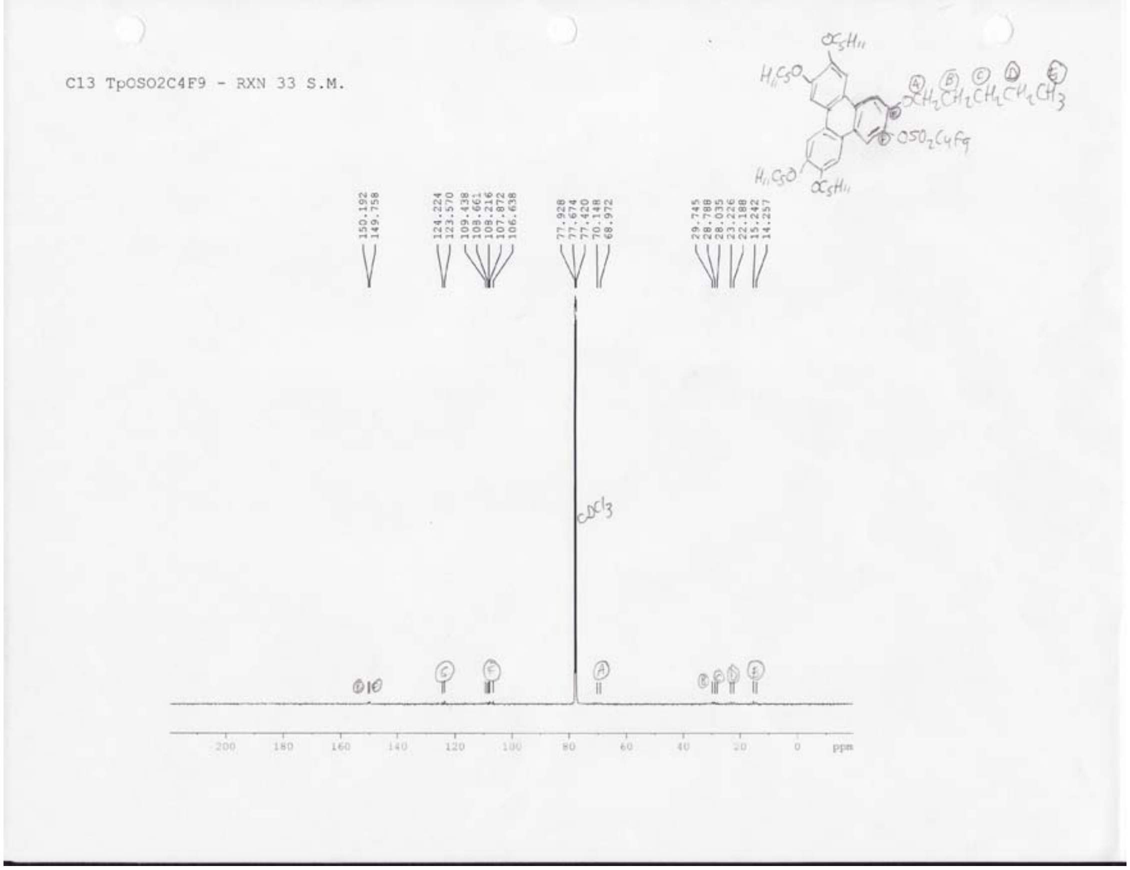

*Figure ESI-4: ^{13}C-NMR of **4a** in CDCl$_3$*

2-cyano-3,6,7,10,11-pentapentyloxytriphenylene (5a)

A solution of **4a** (300 mg, 0.314 mmols) in dry DMF (15 mL) was heated to 85 °C under argon. $Pd(PPh_3)_4$ (0.061 g, 0.0525 mmols) and $Zn(CN)_2$ (74 mg, 0.627 mmols) were added in 5 portions *via* a solid addition funnel over 35 min. All starting material **4a** was consumed after 7 days based on TLC (CH_2Cl_2/hexane 1:1, $R_f = 0.48$ (**4a**) and 0.23 (**5a**)). Water was added to quench the reaction and the product was extracted with CH_2Cl_2. The combined organic phase was evaporated and the residual crude product was purified by preparative TLC (CH_2Cl_2/hexane 2:1) followed by precipitation from acetone/methanol to give **5a** as fine pale yellow crystals (139 mg, 0.204 mmols, 65%).

(Found: C, 76.98; H, 9.14; N, 2.07; $C_{44}H_{61}NO_5$ requires C, 77.27%; H, 8.99%; N, 2.05%); IR (KBr) 2227 cm^{-1} (C≡N); δ_H (300 MHz, $CDCl_3$) 8.68 (1 H, s), 7.85 (1 H, s), 7.81 (4 H, s), 4.21-4.31 (10 H, m), 1.96 (10 H, m), 1.46-1.57 (20 H, m), 1.00 (15 H, m); δ_C (75 MHz, $CDCl_3$) 157.6, 151.2, 149.9, 149.5, 149.0, 133.7, 129.9, 126.4, 123.2, 122.7, 122.0, 117.3, 108.4, 107.5, 106.6, 106.0, 104.7, 101.3, 70.1, 70.0, 69.4, 29.8, 29.2, 29.1, 28.8, 28.4, 28.3, 22.6, 14.1; HRCI MS: calc. *m/z* 683.4550 ($C_{44}H_{61}NO_5$), found m/z 683.4554 (M^+).

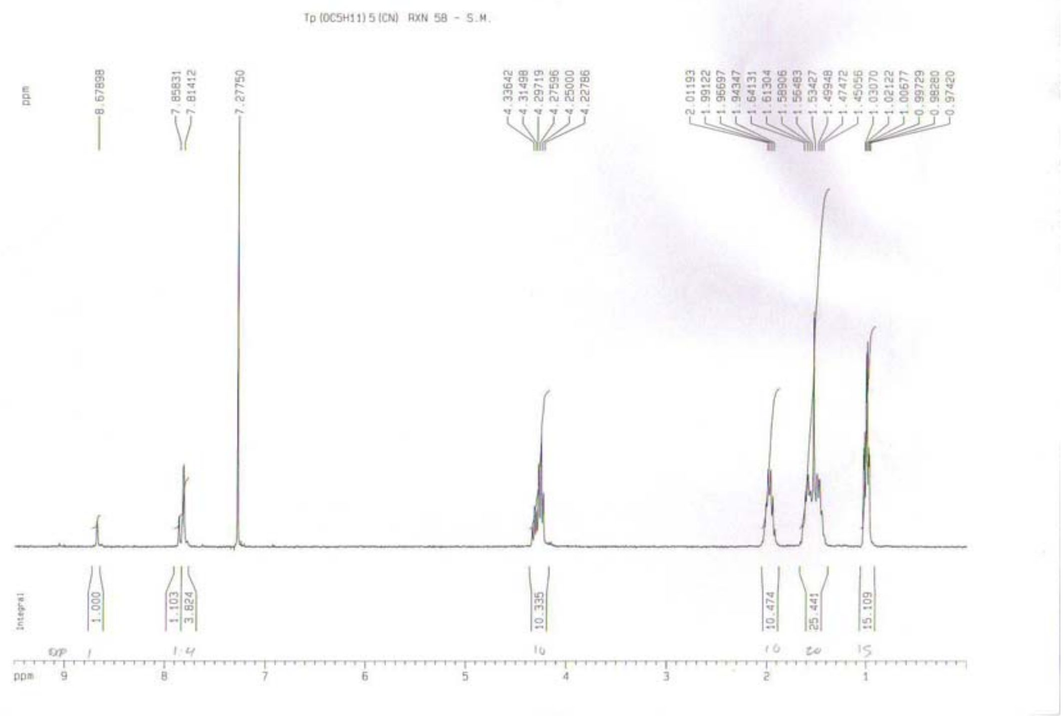

*Figure ESI-5: ^{1}H-NMR of **5a** in CDCl$_3$*

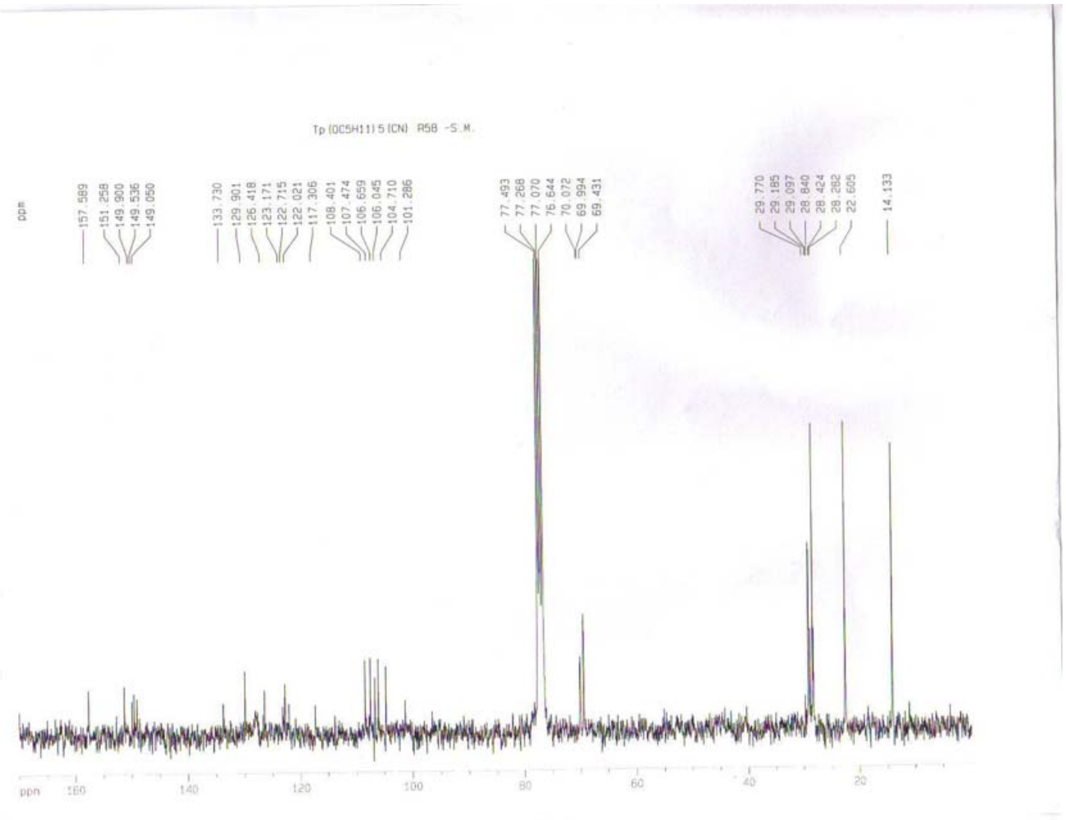

*Figure ESI-6: ^{13}C-NMR of **5a** in CDCl$_3$*

2,6,10-trihydroxy-3,7,11-tris-(pentyloxy)triphenylene (9a,s), 2,6,11-trihydroxy-3,7,10-tris-(pentyloxy)triphenylene (9a,ns), 2,6,10-trihydroxy-3,7,11-tris-(3-methylbutyloxy)triphenylene (9b,s), 2,6,11-trihydroxy-3,7,10-tris-(3-methylbutoxy)triphenylene (9b,ns)

Method 1: A solution of **1a** (2.00 g, 8.0 mmol) in CH_2Cl_2/nitromethane 1:1 (100 mL) was purged with argon for 20 minutes before 3.0 equivalents of $FeCl_3$ (7.78g, 48.0 mmol) were added slowly over 10 minutes using a solid addition funnel under argon. The mixture was allowed to stir for 3 days at room temperature and the progress of the phenolic group formation was monitored by TLC (diethyl ether-hexane 1:1). Dry methanol (10 mL) was added to quench the reaction and the crude product was precipitated by further addition of methanol (50 mL). The crude product mixture was purified and separated by column chromatography (silica gel, CH_2Cl_2) to yield **9a,s** (1.11 g, 2.08 mmol, 26%) and **9a,ns** (1.19 g, 2.24 mmol, 28%) as off-white solids.

Method 2: A solution of butyl lithium in hexane (1.58 M, 1.59 mL, 12 mmol) was added to a solution of diphenylphosphine (2.3 g, 13 mmol) in THF (30 mL) under argon to give a bright orange solution. A solution of the mixtures **7a,s/ns** (ratio 1:5) or **7b,s/ns** (ratio 1:3) (1.00 g, 1.73 mmol) in THF (10 mL) was added under argon *via* a transfer needle and the combined solution was stirred at room temperature for 3-4 days. The progress of the reaction was monitored by TLC (diethyl ether-hexane 1:2) to ensure full conversion of the starting materials. Aqueous HCl (0.1 M, 40 mL) was added to quench the reaction and the product mixture was extracted with diethyl ether. The combined organic phase was extracted with water, dried over $MgSO_4$, filtered and evaporated. Purification and separation was achieved by column chromatography on silica by first eluting methyl diphenylphosphine with toluene/hexane 1:2 and then **9a/b,s** followed by **9a/b,ns** with diethyl ether/hexane 1:1 to yield **9a,s** (74 mg, 0.14 mmol, 48% regarding **7a,s**), **9a,ns**, (527 mg, 0.98 mmol, 68% regarding **7a,ns**) (65% overall), **9b,s** (112 mg, 0.20 mmol, 46% regarding **7b,s**) and **9b,ns** (462 mg, 0.86 mmol, 66% regarding **7b,ns**) (61% overall) as white solids.

Method 3: A solution of bromo catechol borane (1.15 g, 5.79 mmol for **2a** or 2.11 g, 10.63 mmol for **2b**) in CH_2Cl_2 (10 mL) was added to a solution of **2a** or **2b** (1.20 g, 1.61 mmol) in CH_2Cl_2 (20 mL) at 0 ºC under argon. The reaction mixture was stirred at room temperature for 13 days (having followed the reaction progress via TLC), filtered, quenched with 0.1 M $HCl_{aq.}$ and extracted with CH_2Cl_2 (3 x 30 mL), dried over $MgSO_4$, filtered and concentrated. The products were purified and separated by column chromatography (silica, diethyl ether/hexane 1:2 to 1:1 gradient) to yield **9a,s** (439 mg, 0.82 mmol, 51%), **9a,ns**, (241 mg, 0.45 mmol, 28%), **9b,s** (155 mg, 0.29 mmol, 18%) and **9b,ns** (155 mg, 0.29 mmol, 18%) as white solids.

Method 4: A solution of 9-borabicyclo[3.3.1]nonyl bromide (9-BBN-Br) in CH_2Cl_2 (1.0 M, 6.2 mL, 6.2 mmol for **2a** or 8.7 mL, 8.7 mmol for **2b**) was added to a solution of **2a** or **2b** (1.00 g, 1.34 mmol) in CH_2Cl_2 (20 mL) at 0 ºC under argon. The reaction mixture was stirred at room temperature (**2a**) or 35 ºC (**2b**) for 6 days and the progress of the cleavage was monitored by TLC (silica, diethyl ether/hexane 1:1). CH_2Cl_2 (15 mL) was added to the solution and the reaction mixture was washed with water and extracted with CH_2Cl_2 (3 x 30 mL), dried over $MgSO_4$, filtered and concentrated. The products were purified and separated by column chromatography (silica, diethyl ether/hexane 1:2 to 1:1 gradient) to yield **9a,s** (272 mg, 0.51 mmol, 38%), **9a,ns**, (337 mg, 0.63 mmol, 47%), **9b,s** (64 mg, 0.12 mmol, 9%) and **9b,ns** (244 mg, 0.46 mmol, 34%) as white solids.

9a,s: TLC R_f: 0.25 (diethyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.91 (3 H, s, arom. H), 7.79 (3 H, s, arom. H), 5.88 (3H, s, OH), 4.26 (6 H, t, OCH_2, *J* 6.5 Hz), 1.94 (6 H, m, CH_2), 1.6-1.4 (12 H, m, 2 CH_2), 0.98 (9 H, t, CH_3, *J* 7.0 Hz); δ_C (75 MHz, $CDCl_3$) 146.3, 145.8, 124.4, 123.4, 107.5, 105.1, 69.5, 29.5, 28.8, 23.0, 14.6.

9a,ns: TLC R_f: 0.11 (diethyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.92-7.71 (6 H, m, arom. H), 5.89 (3 H, s, OH), 4.29-4.22 (6 H, m, OCH_2), 1.94 (6 H, m, CH_2), 1.6-1.4 (12 H, m, 2 CH_2), 0.97 (9 H, t, CH_3, *J* 6.8 Hz); δ_C (75 MHz, $CDCl_3$) 146.6, 146.1, 145.9, 124.5, 123.6, 108.4, 108.1, 107.9, 105.0, 104.8, 69.8, 29.6, 28.9, 23.2, 14.7.

9b,s: TLC R_f: 0.50 (diethyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.94 (3 H, s, arom. H), 7.83 (3 H, s, arom. H), 5.90 (3 H, s, OH), 4.32 (6 H, t, OCH_2, *J* 6.6 Hz), 1.83-1.99 (9 H, m, CH_2 and CH), 1.07

(18 H, d, CH_3, *J* 6.3 Hz); δ_C (75 MHz, $CDCl_3$) 145.8, 145.3, 123.9, 122.9, 107.0, 104.6, 67.5, 38.1, 25.2, 22.7; HRCI MS: calc. *m/z* 534.2981 ($C_{33}H_{42}O_6$), found *m/z* 534.2981 (M^+).

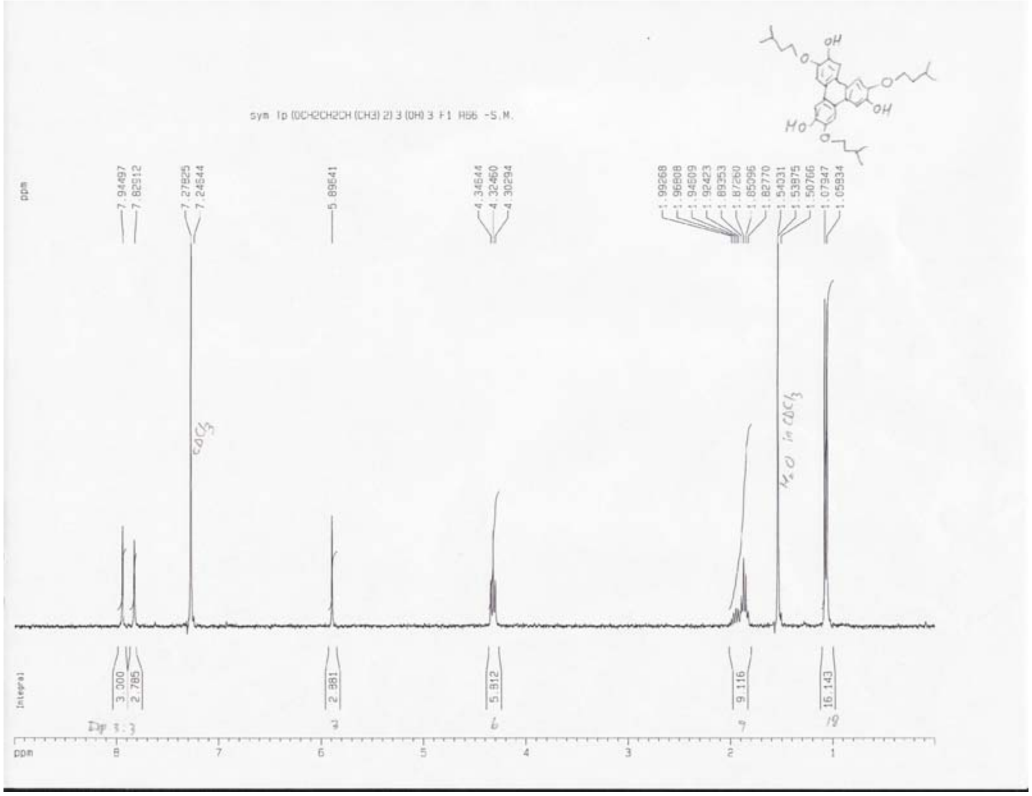

*Figure ESI-7: ^{1}H-NMR of **9b,s** in $CDCl_3$*

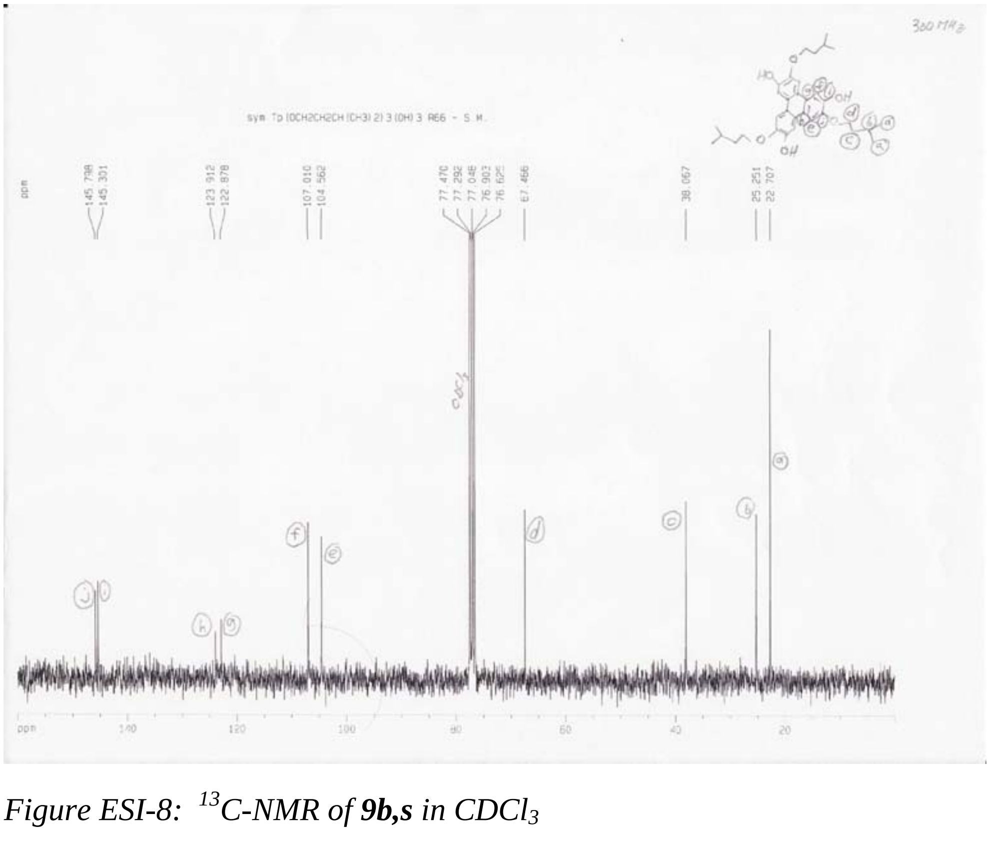

*Figure ESI-8: ^{13}C-NMR of **9b,s** in $CDCl_3$*

9b,ns: TLC R_f: 0.26 (diethyl ether-hexane 1:1); δ_H (300 MHz, $CDCl_3$) 7.96 (2 H, s, arom. H), 7.94 (1 H, s, arom. H), 7.81 (1 H, s, arom. H), 7.77 (1 H, s, arom. H), 7.76 (1 H, s, arom. H), 5.88 (1 H, s, OH), 5.86 (1 H, s, OH), 5.83 (1 H, s, OH), 4.30-4.37 (6 H, m, OCH_2), 1.85-2.00 (9 H, m, CH_2 and CH), 1.05-1.09 (18 H, m, CH_3); δ_C (75 MHz, $CDCl_3$) 146.2, 146.1, 145.9, 145.6, 145.5, 145.4, 124.2, 124.1, 124.0, 123.1, 123.0, 107.9, 107.6, 107.5, 104.6, 104.4, 104.2, 67.7, 38.2, 25.4, 22.9; HRCI MS: calc. *m/z* 534.2981 ($C_{33}H_{42}O_6$), found *m/z* 534.2983 (M^+).

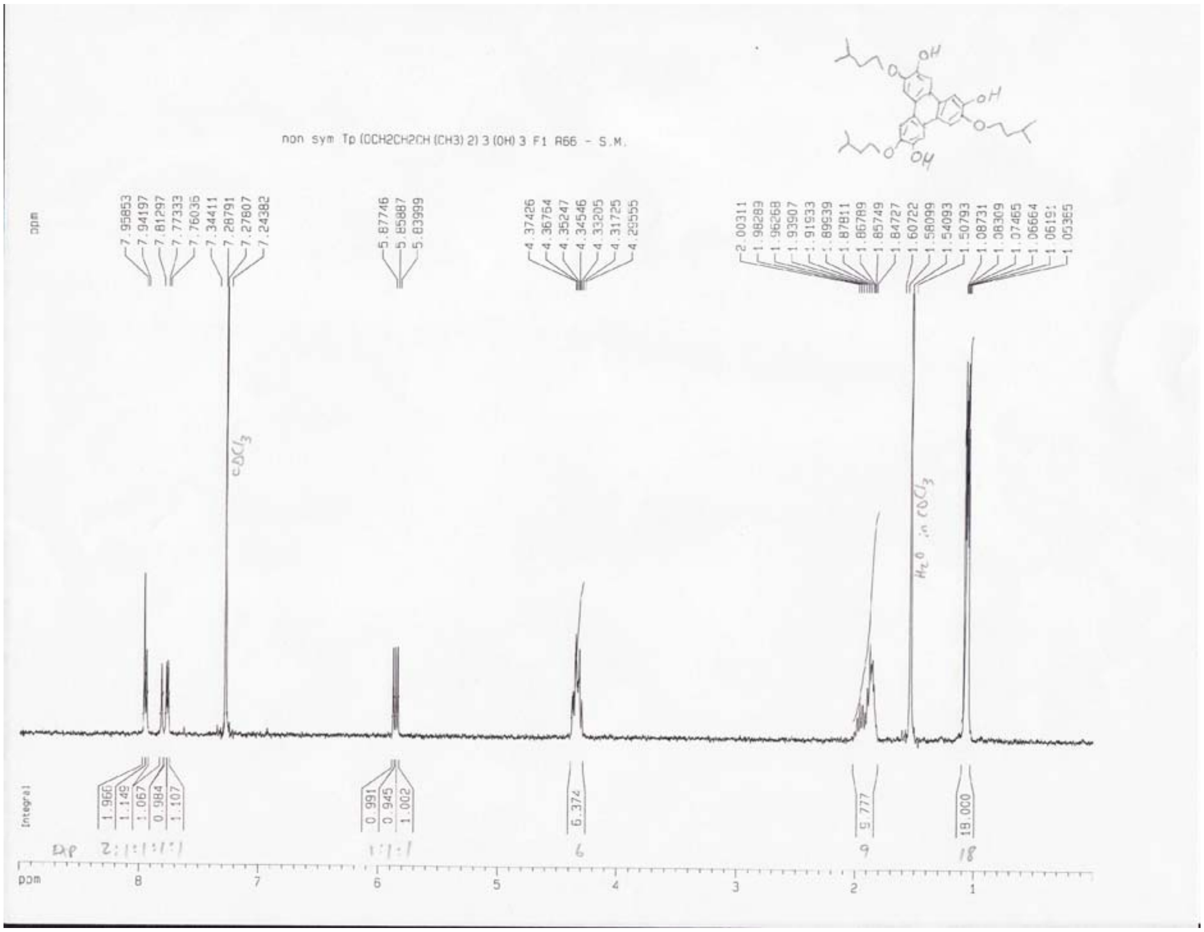

*Figure ESI-9: ^{1}H-NMR of **9b,ns** in $CDCl_3$*

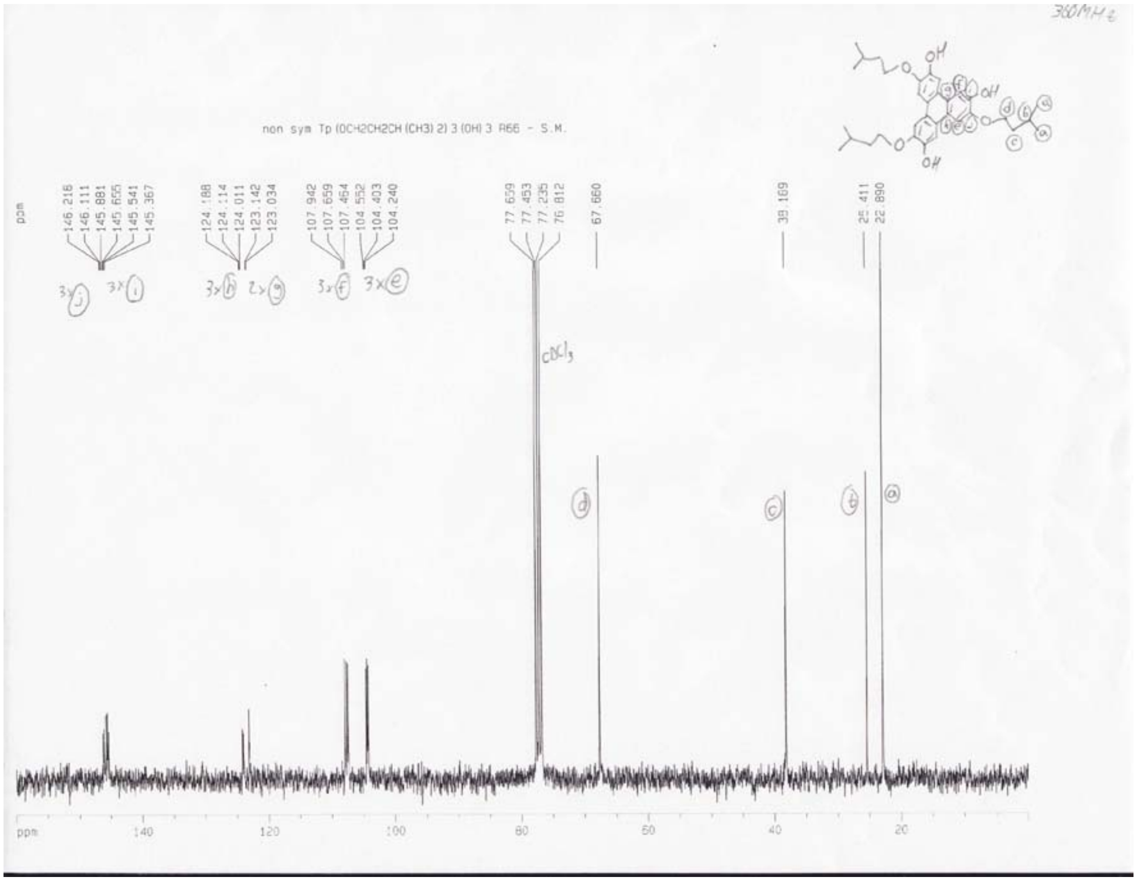

*Figure ESI-10: ^{13}C-NMR of **9b,ns** in $CDCl_3$*

2,6,10-trinonaflyl-3,7,11-tripentyloxytriphenylene (10a,s), 2,7,11-trinonaflyl-3,6,10-tripentyloxy-triphenylene (10a,ns), 2,6,10-trinonaflyl-3,7,11-tris(3-methylbutoxy)triphenylene (10b,s), 3,6,11-trinonaflyl-2,7,10–tris(3-methylbutoxy)triphenylene (10b,ns)

Nonafluorobutanesulfonylfluoride (1.27 g, 4.21 mmol) was added dropwise to a stirred solution of trihydroxy-trialkyloxytriphenylenes **9a,s**, **9a,ns**, **9b,s** or **9b,ns** (0.250 g, 0.468 mmol) and triethylamine (0.426 g, 4.21 mmol) in 20 mL CH_2Cl_2 at 0 ^{o}C under argon. The reaction mixture was stirred at room temperature for 3-5 days and the progress of the conversion was monitored by TLC (CH_2Cl_2/hexane, 1:2). The fully converted reaction mixture was poured into water (100 mL), extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic layers were washed with 0.01 M HCl_{aq} (10 mL) and water (3 x 20 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated to give the crude product as a slightly purple solid, which was precipitated from a saturated solution in acetone by the addition of methanol to give the analytically pure product as a white solid.

10a,s: (394 mg 0.285 mmol); yield: 61%; (Found: C, 38.99; H, 3.02; $C_{45}H_{39}F_{27}O_{12}S_3$ requires: C, 39.14%; H, 2.85%); TLC R_f: 0.78 (diethyl ether-hexane 1:5); IR (KBr) 1355 cm^{-1} (S=O); δ_H (300 MHz, $CDCl_3$) 8.24 (3 H, s) 7.81 (3 H, s), 4.31 (6 H, t, *J* 6.5 Hz), 1.99 (6 H, m), 1.43–1.63 (12 H, m), 0.99 (9 H, t, *J* 7.1 Hz); δ_C (75 MHz, $CDCl_3$) 150.6, 138.8, 129.9, 121.3, 117.2, 106.1, 69.3, 28.3, 27.7, 22.1, 13.7 (carbons bonded to F are not resolved); δ_F (282 MHz, $CDCl_3$) -80.8 (9 F, t, 9.6 Hz, CF_3), -109.7 (6 F, t, 14.1 Hz, SCF_2), -120.9 (6 F, m, CF_2), -126.1 (6 F, m, CF_2); HRESI MS: calc. *m/z* 1398.1516 $(C_{45}H_{39}F_{27}O_{12}S_3+NH_4)^+$, found *m/z* 1398.1260 $(M+NH_4)^+$.

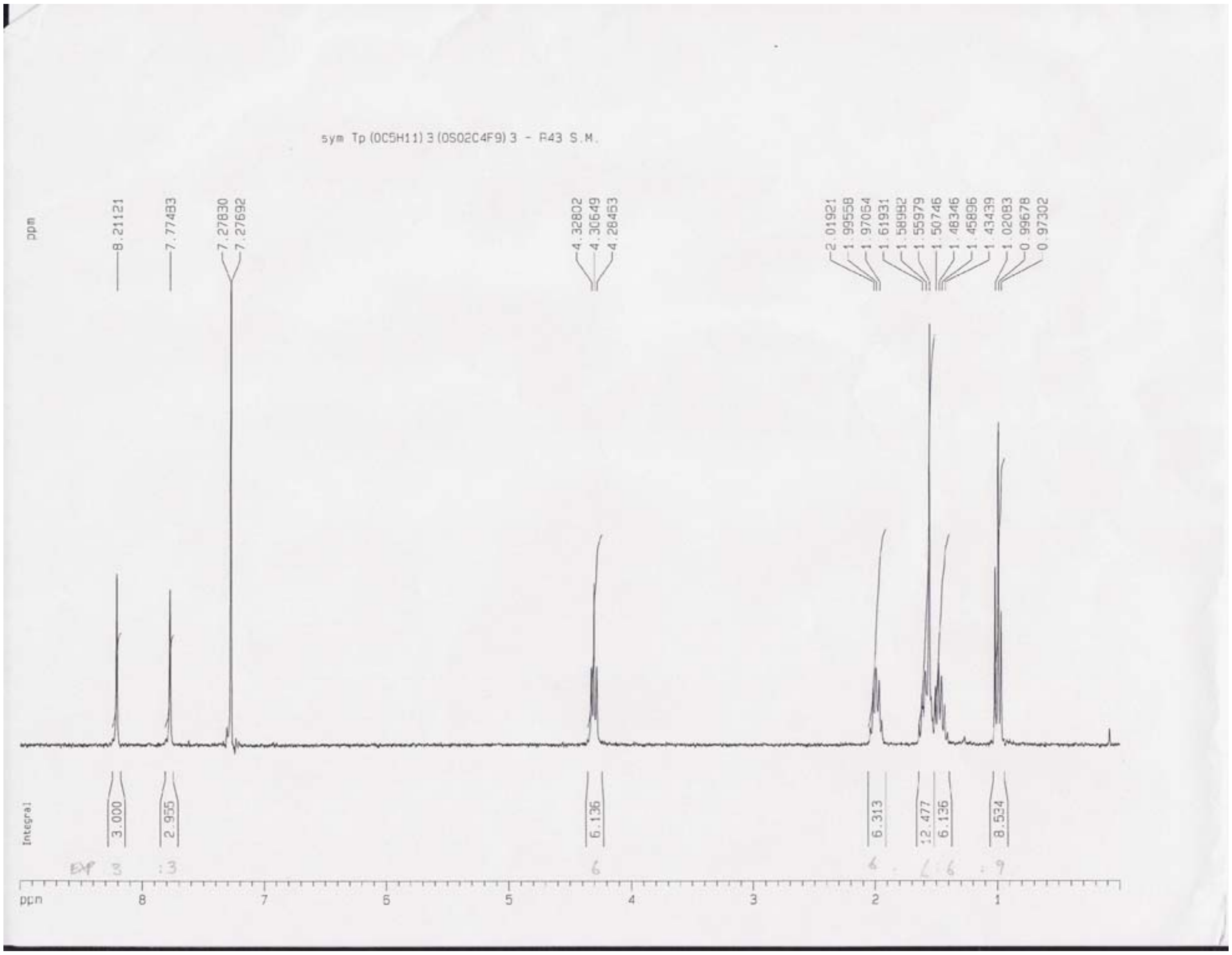

*Figure ESI-11: ^{1}H-NMR of **10a,s** in $CDCl_3$*

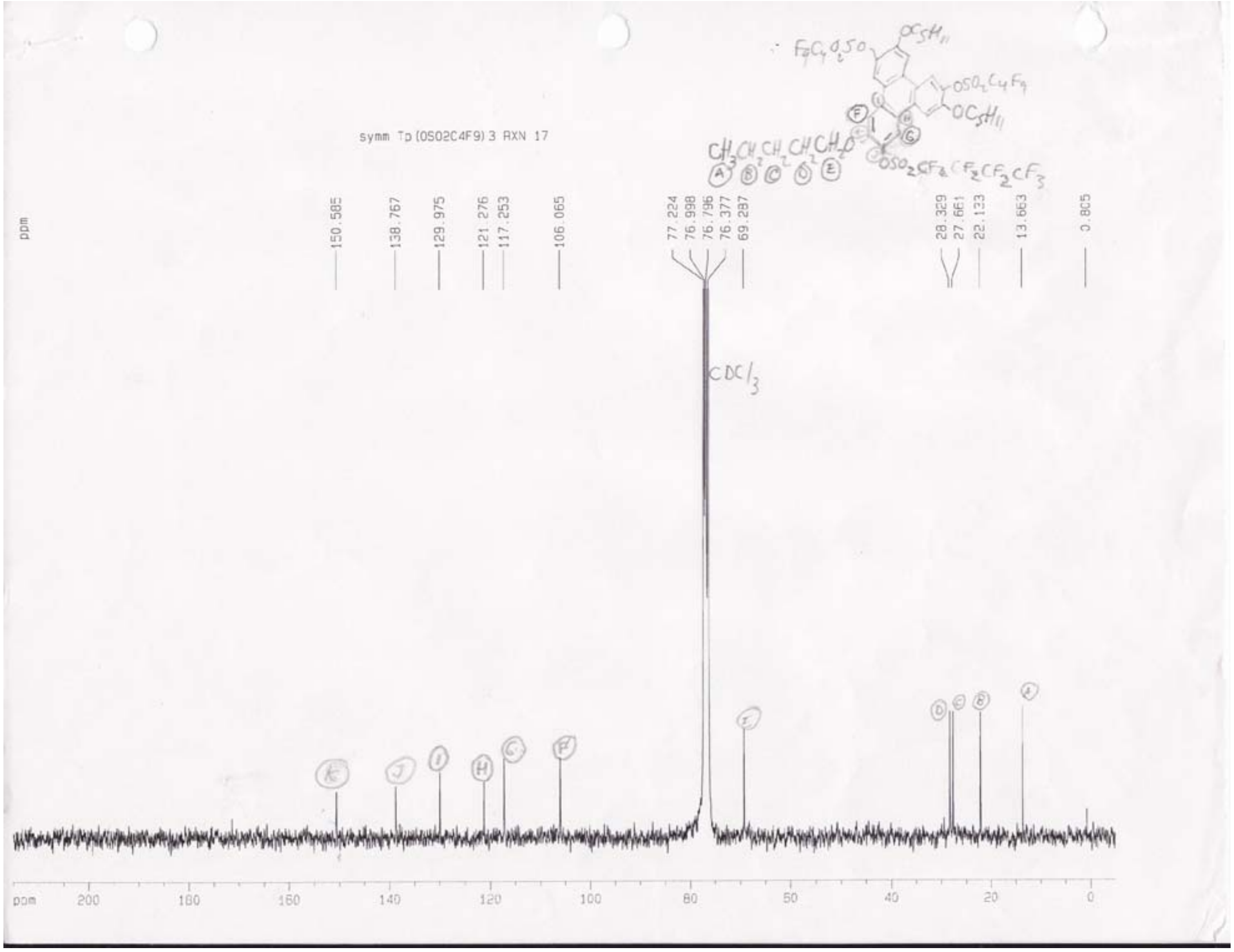

*Figure ESI-12: ^{13}C-NMR of **10a,s** in $CDCl_3$*

10a,ns: (427 mg, 0.309 mmol); yield: 66%; (Found: C, 39.06; H, 2.87; $C_{45}H_{39}F_{27}O_{12}S_3$ requires: C, 39.14%; H, 2.85%); TLC R_f: 0.56 (diethyl ether-hexane 1:5); IR (KBr) 1354 cm^{-1} (S=O); δ_H (300 MHz, $CDCl_3$) 8.28 (1 H, s) 8.14 (1 H, s), 8.11 (1 H, s), 7.93 (1 H, s), 7.91 (1 H, s), 7.82 (1 H, s), 4.31 (6 H, m), 2.00 (6 H, m), 1.44-1.61 (12 H, m), 1.00 (9 H, t); δ_C (75 MHz, $CDCl_3$) 158.6,157.9, 157.6, 133.4, 131.5, 130.9, 130.1, 128.6, 128.4, 122.5, 122.2, 120.2, 114.9, 114.6, 104.7, 104.6, 104.2, 103.7, 103.5, 102.5, 68.8, 27.7, 27.2, 21.4, 13.0; δ_F (282 MHz, $CDCl_3$) -79.9 (3 F, t, CF_3), -81.1 (6 F, t, CF_3), -109.8 (2 F, t, SCF_2), -110.1 (4 F, t, SCF_2), -121.0 (2 F, m, CF_2), -121.2 (4 F, m, CF_2), -126.1 (2 F, m, CF_2), -126.4 (4 F, m, CF_2); HRESI MS: calc. *m/z* 1398.1516 ($C_{45}H_{39}F_{27}O_{12}S_3$+$NH_4$), found *m/z* 1398.1372 $(M+NH_4)^+$.

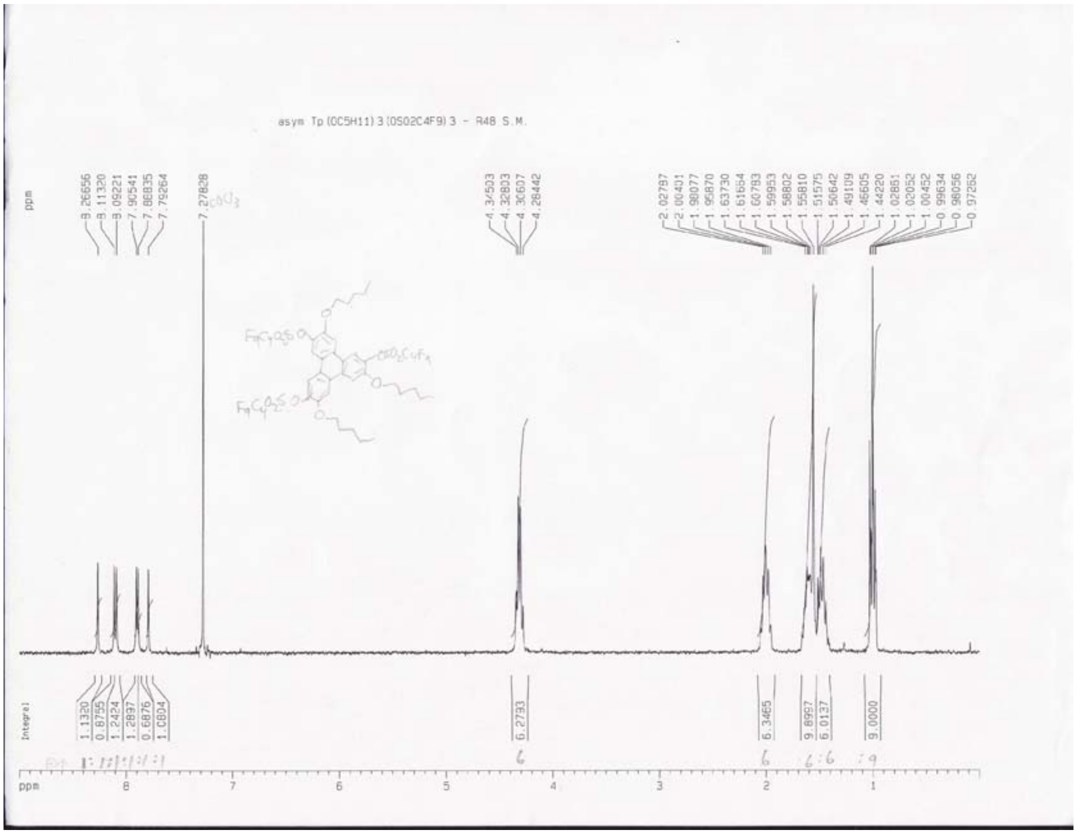

Figure ESI-13: ^{1}*H-NMR of* ***10a,ns*** *in* $CDCl_3$

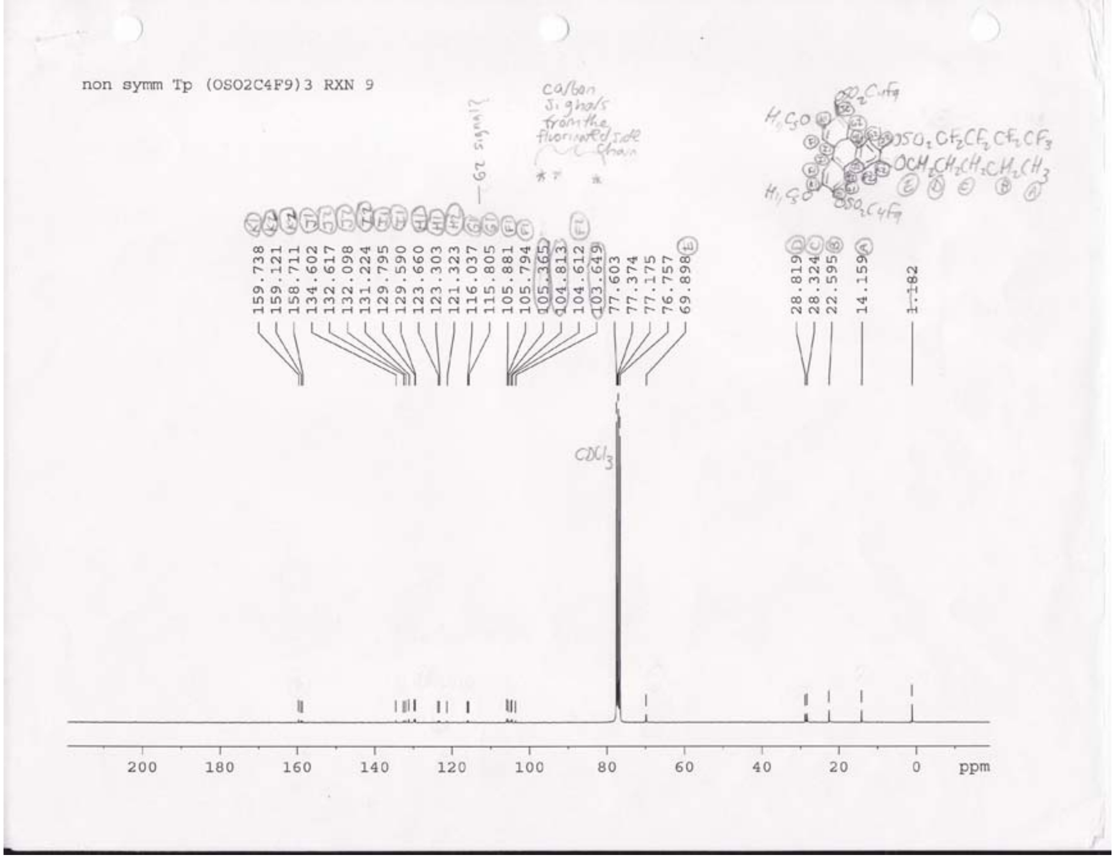

Figure ESI-14: ^{13}*C-NMR of* ***10a,ns*** *in* $CDCl_3$

10b,s: (0.055 g, 0.103 mmol); yield: 74%; (Found: C, 39.06; H, 3.03; $C_{45}H_{39}F_{27}O_{12}S_3$ requires: C, 39.14%; H, 2.85%); TLC, R_f: 0.78 (diethyl ether-hexane 1:5); δ_H (300 MHz, $CDCl_3$) 8.13 (3 H, s), 7.68 (3 H, s), 4.29 (6 H, t, *J* 6.5 Hz), 1.92-2.00 (3 H, m), 1.83-1.90 (6 H, m), 1.02 (18 H, d, *J* 6.5 Hz); δ_C (75 MHz, $CDCl_3$) 150.9, 139.1, 130.3, 121.6, 117.5, 106.3, 68.1, 37.7, 25.0, 22.6; δ_F (282 MHz, $CDCl_3$) -80.9 (9 F, t, CF_3, *J* 9.3 Hz), -109.8 (6 F, t, SCF_2, *J* 13.8 Hz), -121.0(6 F, m, CF_2), -126.2 (6 F, m, CF_2).

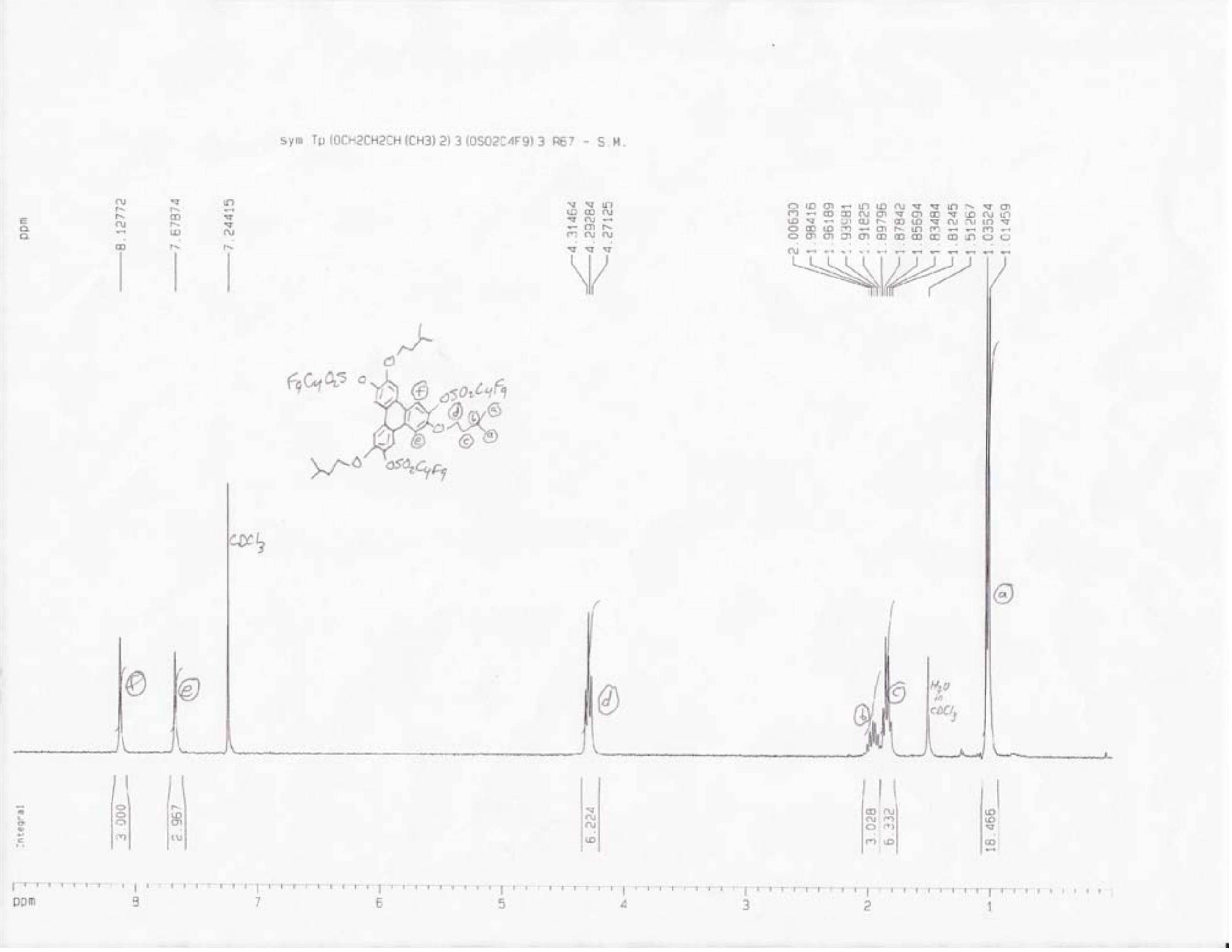

*Figure ESI-15: ^{1}H-NMR of **10b,s** in $CDCl_3$*

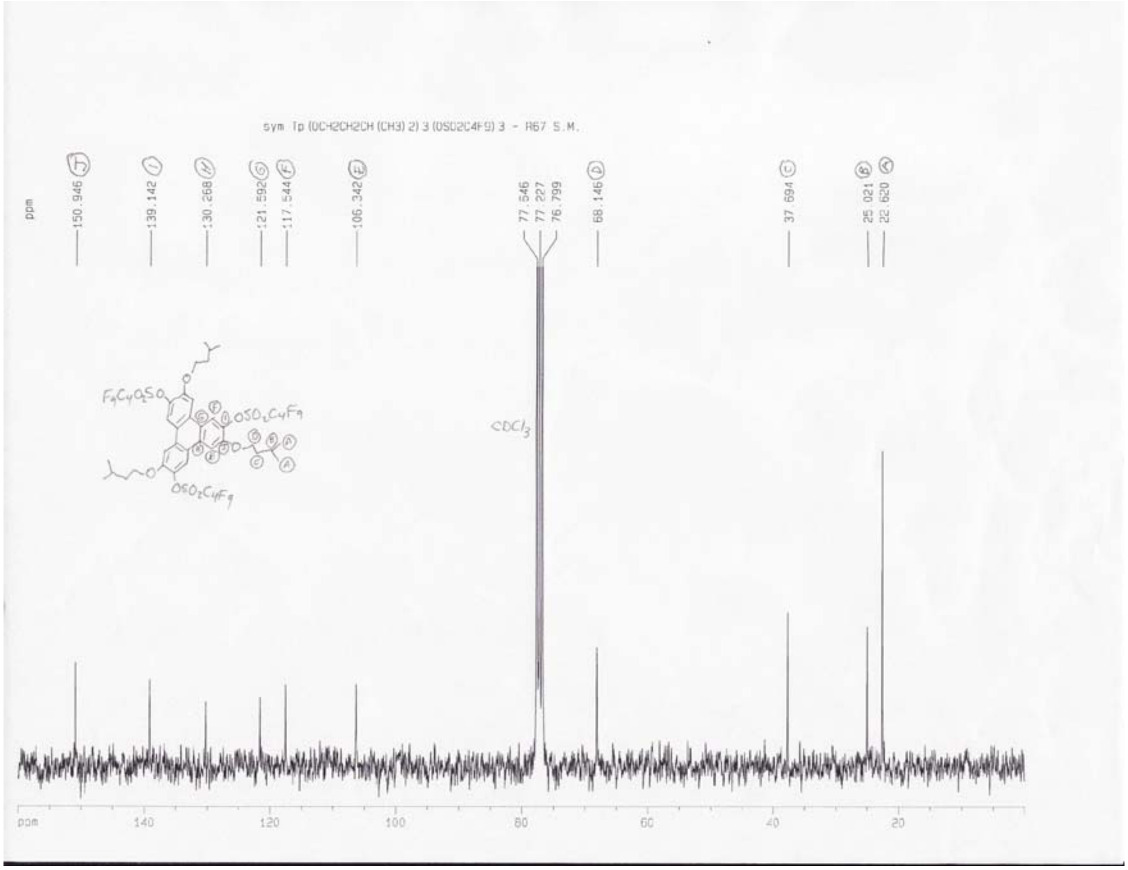

Figure ESI-16: ^{13}*C-NMR of* ***10b,s*** *in CDCl*$_3$

10b,ns: (0.364 g, 0.681 mmol); yield: 94%; (Found: C, 39.28; H, 2.76; $C_{45}H_{39}F_{27}O_{12}S_3$ requires: C, 39.14%; H, 2.85%); TLC R_f 0.56 (diethyl ether-hexane 1:5); δ_H (300 MHz, $CDCl_3$) 8.30 (1 H, s), 8.15 (1 H, s), 8.13 (1 H, s), 7.96 (1 H, s), 7.94 (1 H, s), 7.84 (1 H, s), 4.33-4.38 (6 H, m), 1.88-2.04 (9 H, m), 1.05-1.08 (18 H, m); δ_C (75 MHz, $CDCl_3$) 151.2, 151.1, 150.8, 140.7, 140.3, 140.1, 130.4, 129.4, 129.0, 124.0, 123.5, 122.5, 119.6, 118.2, 117.2, 117.1, 115.3, 110.5, 107.6, 106.8, 68.5, 38.1, 25.3, 23.1, 23.0; δ_F (282 MHz, $CDCl_3$) -80.7 (3 F, t, CF_3, *J* 8.5 Hz), -80.9 (6 F, t, CF_3, *J* 8.5 Hz), -109.6 (2 F, t, SCF_2, *J* 14.1 Hz), -109.9 (4 F, t, SCF_2, *J* 14.1 Hz), -120.9 (2 F, m, CF_2), -121.0 (4 F, m, CF_2), -126.0 (2 F, m, CF_2), -126.2 (4 F, m, CF_2).

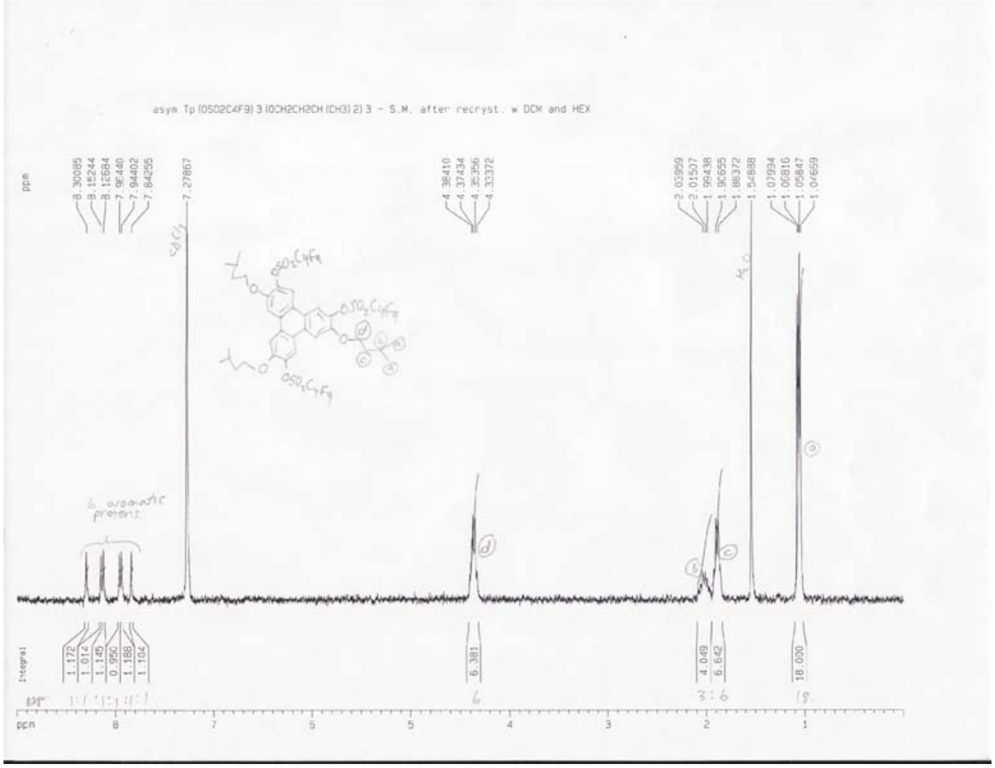

Figure ESI-17: ^{1}*H-NMR of* ***10b,ns*** *in* $CDCl_3$

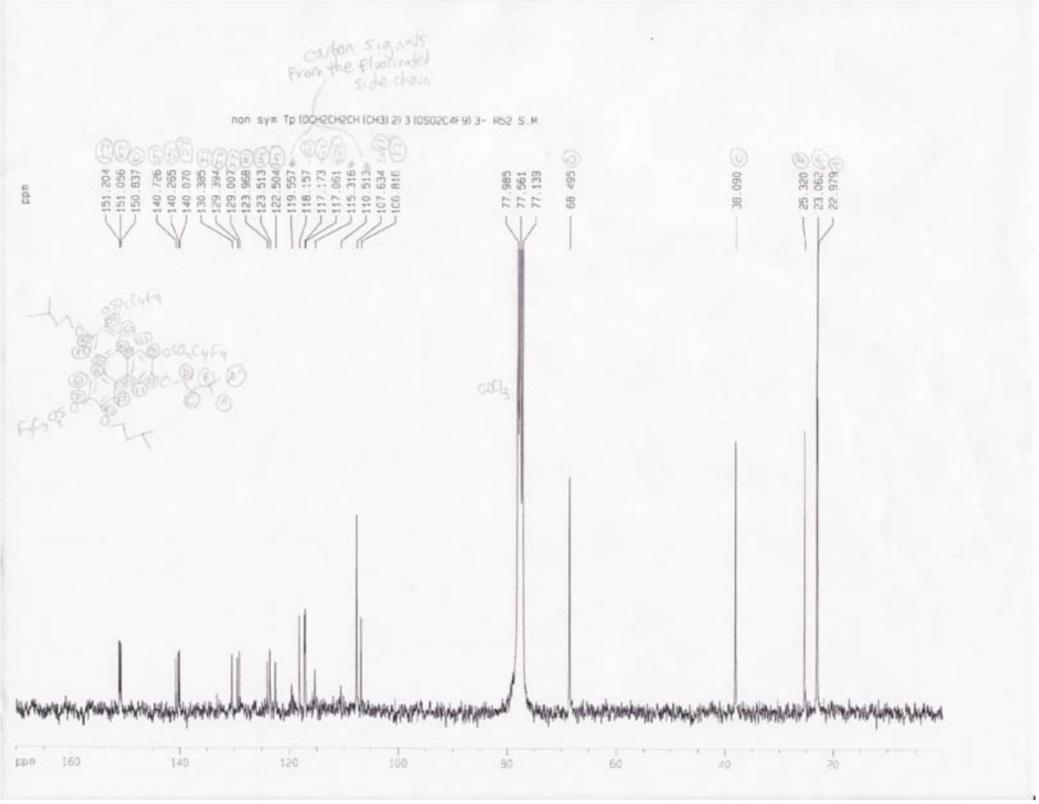

Figure ESI-18: ^{13}*C-NMR of* ***10b,ns*** *in* $CDCl_3$

2,6,10-tricyano-3,7,11-tripentyloxytriphenylene (11a,s), **2,6,11-tricyano-3,7,10-tripentyloxytriphenylene (11a,ns)**, **2,7,11-tricyano-3,6,10-tris(3-methylbutoxy)triphenylene (11b,ns)**

A solution of **10a,s**, **10a,ns**, or **10b,ns** (0.100 g, 0.072 mmols) in 20 mL dry, deoxygenated DMF (saturated with argon) was heated to 85˚C under argon. Pd(PPh$_3$)$_4$ (0.0293 g, 0.02534 mmols) and Zn(CN)$_2$ (0.0340 g, 0.2897 mmols) were added in 5 portions, in solid addition funnels, over 35 min. The reaction mixture was stirred at 85 ˚C for 6-7 days until no starting material and intermediate products were detected by TLC (CH_2Cl_2-hexane 1:1 and ethyl acetate-hexane 1:3). before separating with water and CH_2Cl_2. The organic phase was evaporated and the crude product was precipitated from acetone by the addition of ethanol to give the product as white crystals (**11a,s**) or pale yellow crystals (**11a,ns** and **11b,ns**).

11a,s: (22 mg, 0.040 mmols); yield: 55%; TLC R$_f$: 0.30 (CH_2Cl_2/hexane 1:1); IR (KBr) 2227 cm^{-1} (C≡N); δ_H (300 MHz, $CDCl_3$) 8.70 (3 H, s, arom. H), 7.83 (3 H, s, arom. H), 4.36 (6 H, t, OCH_2, *J* 6.4 Hz), 2.03 (6 H, m, CH_2), 1.48-1.61 (12 H, m, CH_2), 1.01 (9 H, t, CH_3, *J* 7.2 Hz); δ_C (75 MHz, $CDCl_3$) 160.6, 135.6, 131.6, 121.5, 116.7, 105.2, 103.6, 70.4, 29.2, 28.7, 27.3, 23.0, 14.6; HRCI MS: calc. *m/z* 561.2991 ($C_{36}H_{39}N_3O_3$), found m/z 561.2997 (M^+).

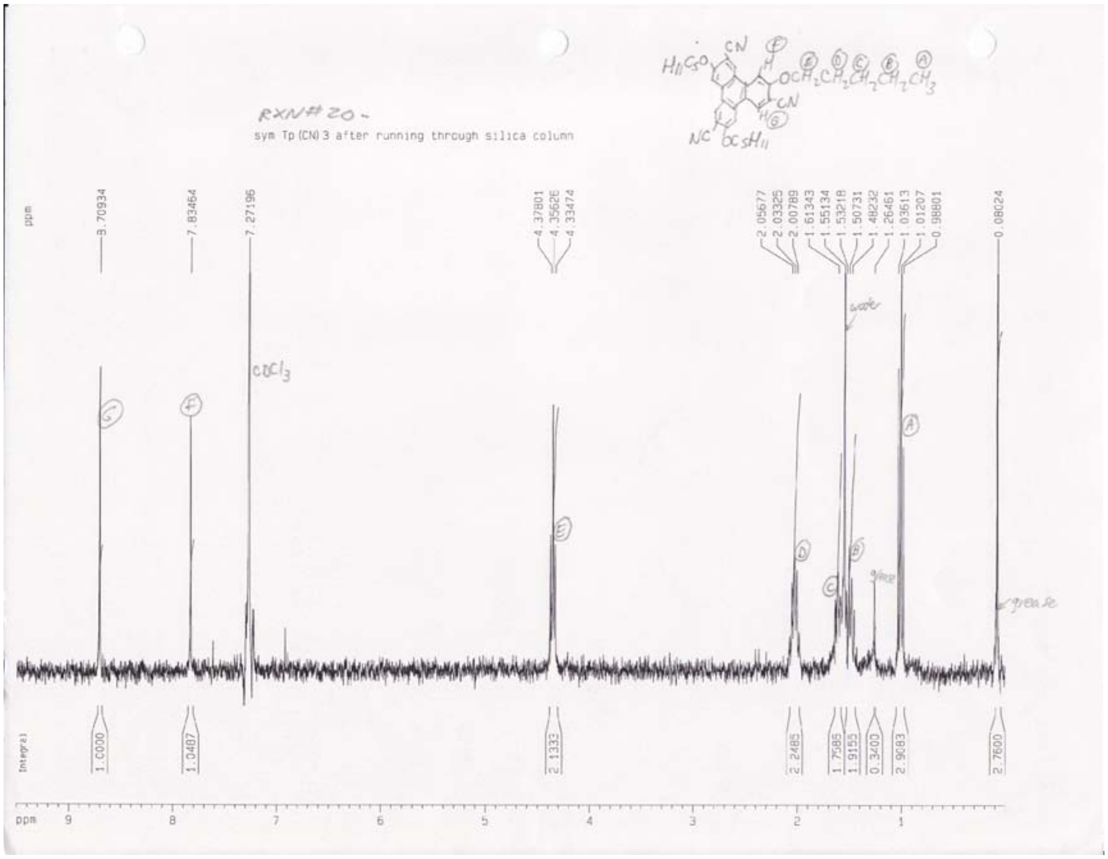

Figure ESI-19: ^{1}*H-NMR of* ***11a,s*** *in* $CDCl_3$

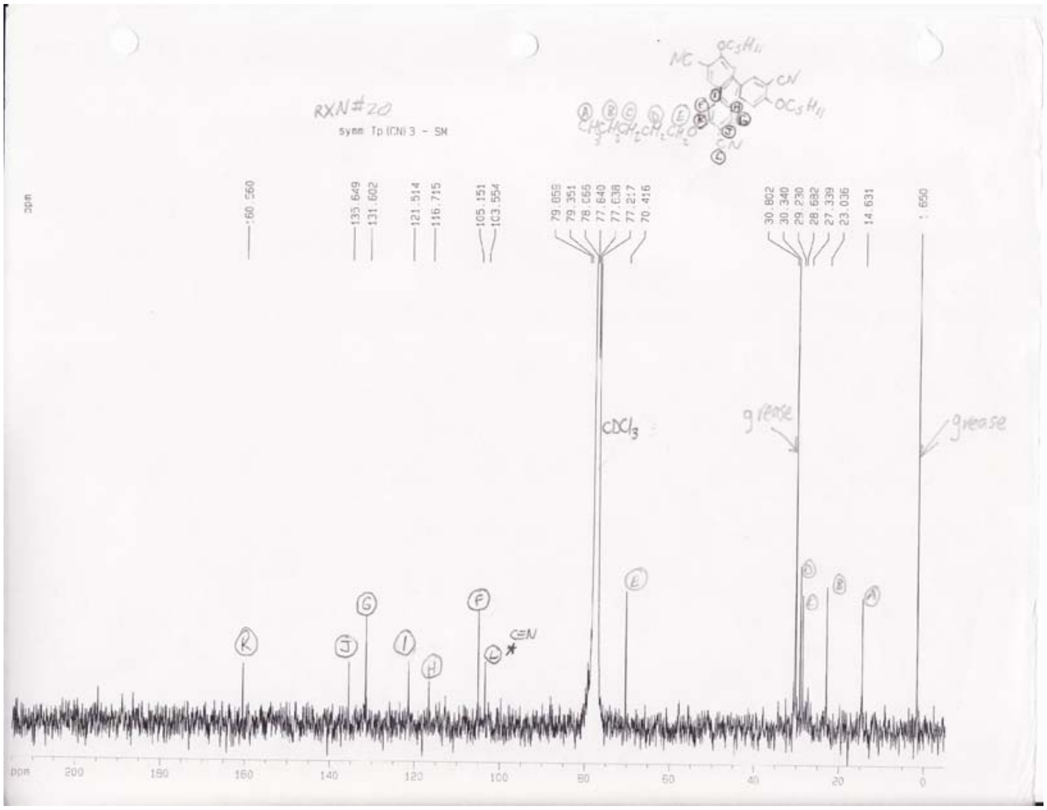

Figure ESI-20: ^{13}*C-NMR of* ***11a,s*** *in* $CDCl_3$

11a,ns: (39 mg, 0.068 mmol); yield: 95%; TLC R_f: 0.24 (CH_2Cl_2/hexane 1:1); IR (KBr) 2228 cm^{-1} ($C\equiv N$); δ_H (300 MHz, $CDCl_3$) 8.76 (1 H, s), 8.64 (1 H, s, arom. H), 8.60 (1 H, s, arom. H), 7.86 (1 H, s, arom. H), 7.82 (1 H, s, arom. H), 7.80 (1 H, s, arom. H), 4.34 (6 H, m, OCH_2), 1.99 (6 H, m, CH_2), 1.47-1.64 (12 H, m, CH_2), 1.00 ppm (9 H, t, CH_3); δ_C (75 MHz, $CDCl_3$) 159.7, 159.0, 158.6, 134.5, 132.5, 132.0, 131.1, 129.6, 129.4, 123.5, 123.1, 121.1, 116.0, 115.9, 115.8, 105.7, 105.6, 105.2, 104.7, 104.4, 103.4, 69.8, 29.8, 28.8, 28.3, 28.2, 22.6, 14.2; HRCI MS: calc. *m/z* 561.2991 ($C_{36}H_{39}N_3O_3$), found m/z 561.2979 (M^+).

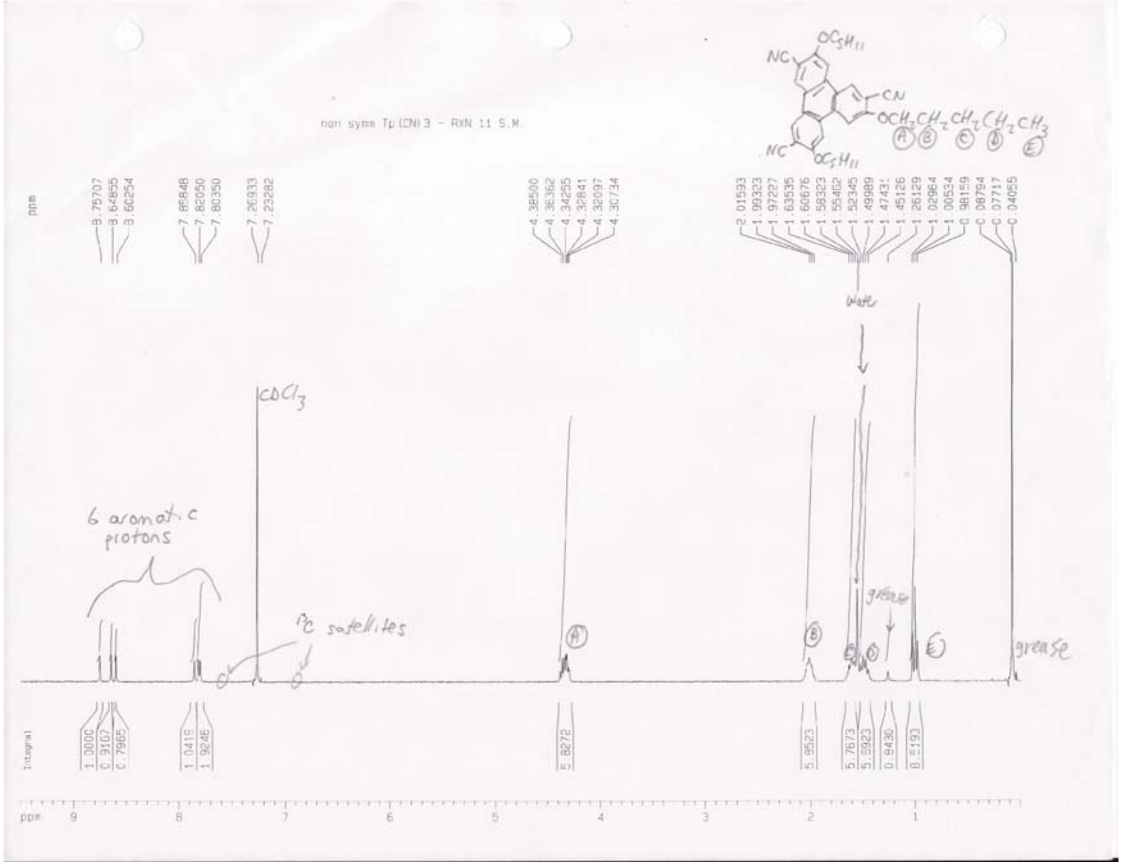

*Figure ESI-21: ^{1}H-NMR of **11a,ns** in $CDCl_3$*

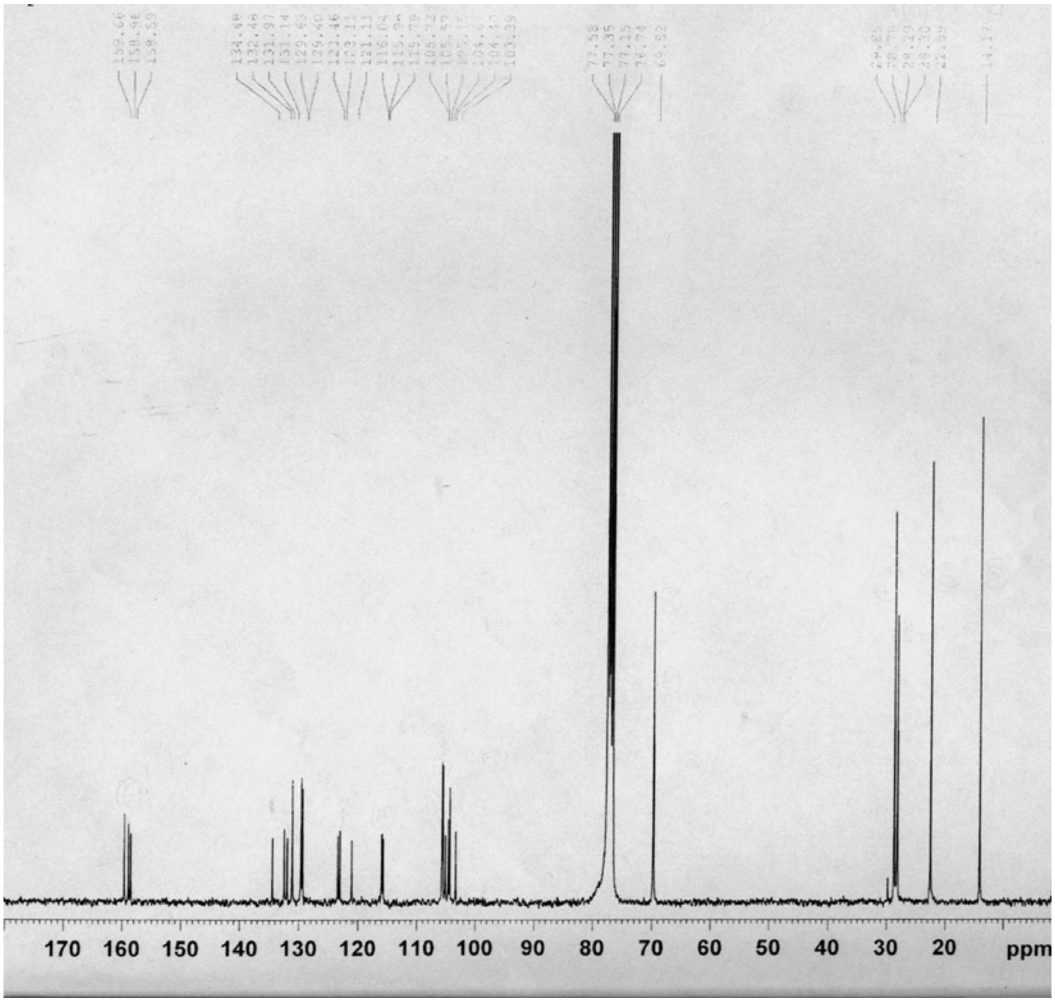

*Figure ESI-22: ^{13}C-NMR of **11a,ns** in $CDCl_3$*

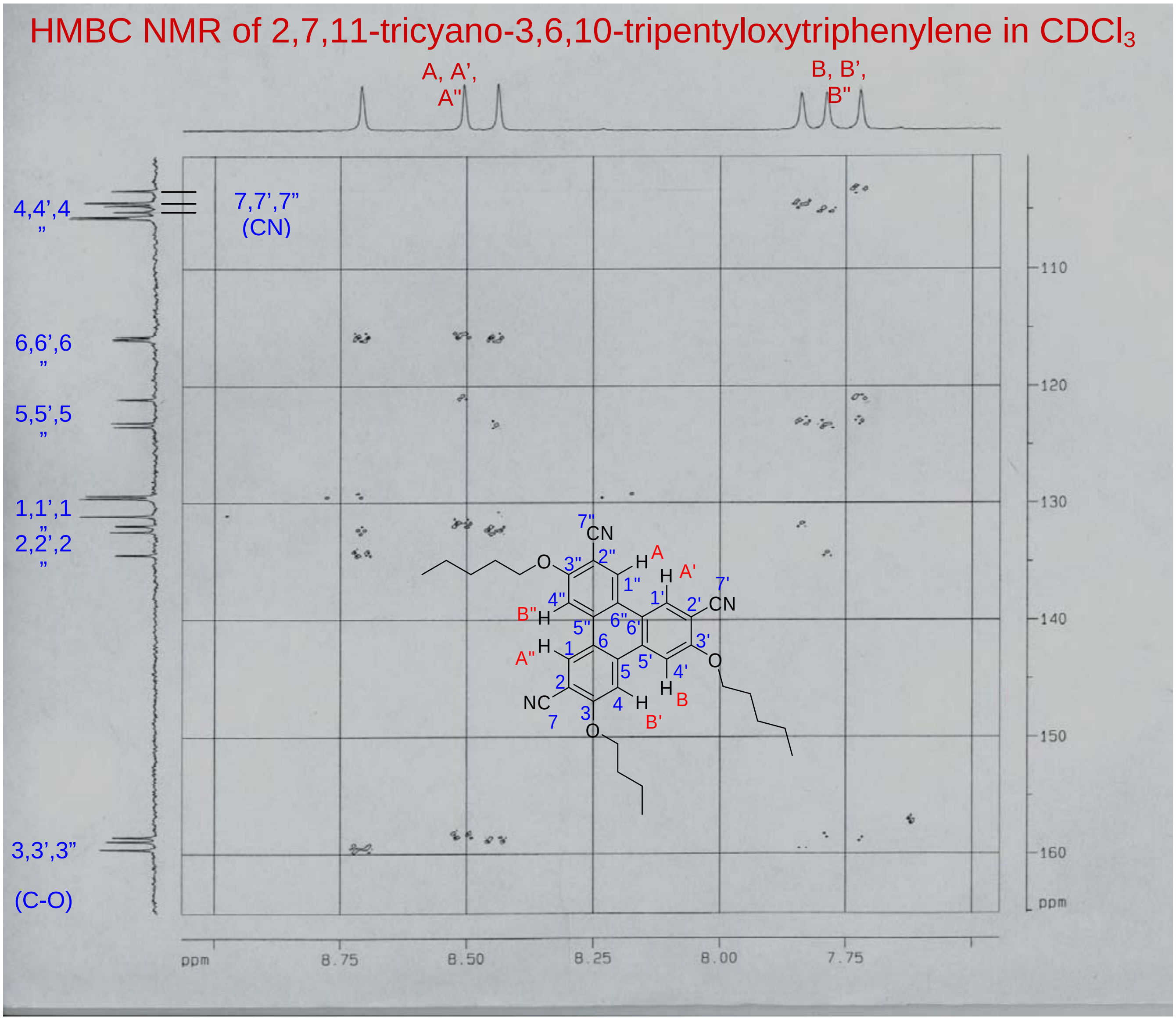

Figure ESI-23: HMBC H,C-NMR of ***11a,ns*** *in CDCl$_3$. Assignment: Carbons 3 are used as an entry point due to their characteristic chemical shift as well as carbons 1 and 4 because of there attachment to protons A and B. Carbons 1 and 4 give higher intensity peaks due to the NOE and were also identified in an HMQC experiment (not shown). Carbons 4 and attached protons B are more shielded than carbons 1 and protons A because they are ortho to the ether and meta to the cyano groups. Carbons 5 and 6 are assigned based on their visible coupling to protons A (^{2}J C-6) but not B (^{3}J C-6) and B (^{2}J C-5) but not A (^{3}J C-5). Carbons 2 couple with protons A (^{2}J) and barely with protons B (^{3}J) but, to our surprise, carbons 3 couple with protons A (^{3}J) and hardly with protons B (^{2}J). Similarly, carbons 7 couple with protons B (^{4}J) but not visibly with protons A (^{3}J).*

11b,ns: (0.175 g, 0.127 mmol); yield: 77%; TLC R_f: 0.25 (CH_2Cl_2/hexane 1:1); IR (KBr) 2228 cm^{-1} (C≡N); δ_H (300 MHz, $CDCl_3$) 8.78 (1 H, s, arom. H), 8.68 (1 H, s, arom. H), 8.63 (1 H, s, arom. H), 7.89 (1 H, s, arom. H), 7.85 (1 H, s, arom. H), 7.83 (1 H, s, arom. H), 4.37-4.41 (6 H, m, OCH_2), 1.99-2.06 (3 H, m, CH_2), 1.90-1.95 (6 H, m, CH_2), 1.07-1.10 (18 H, m, CH_3); δ_C (75 MHz, $CDCl_3$) 159.7, 159.1, 158.7, 134.6, 132.6, 132.1, 131.3, 129.9, 129.6, 123.7, 123.3, 121.3, 116.1, 116.0, 115.9, 105.8, 105.7, 105.3, 104.8, 104.6, 103.6, 68.3, 68.2, 68.1, 37.8, 37.7, 25.3, 22.8; HRCI MS: calc. *m/z* 561.2991 ($C_{36}H_{39}N_3O_3$), found *m/z* 561.2993 (M^+).

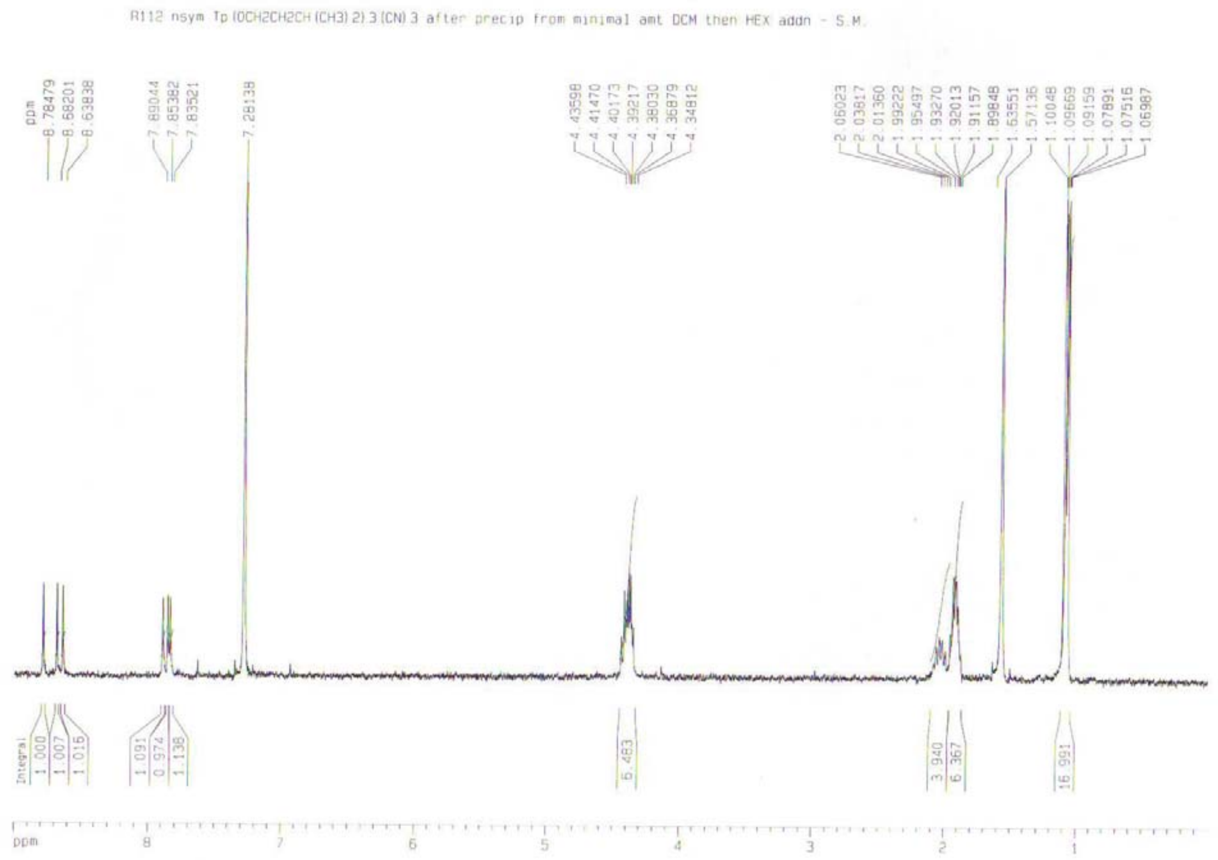

*Figure ESI-24: ^{1}H-NMR of **11b,ns** in $CDCl_3$*

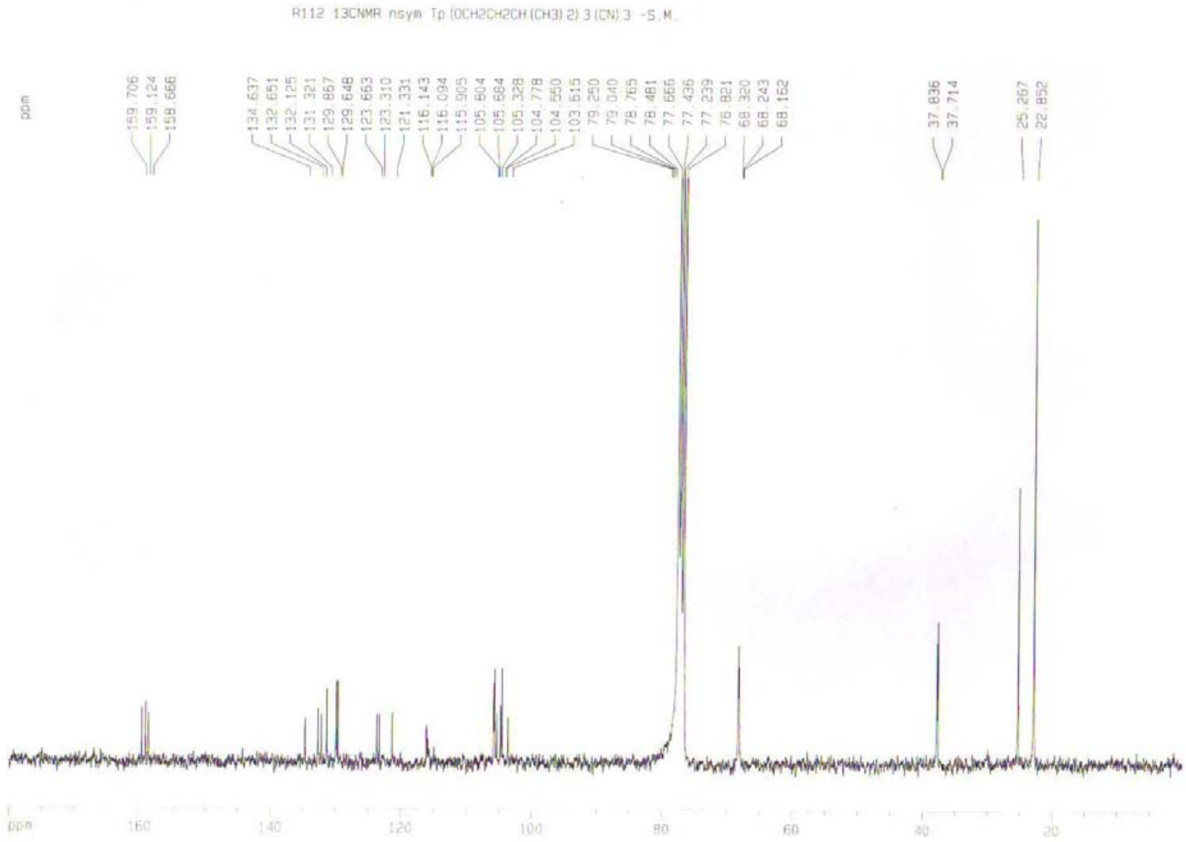

*Figure ESI-25: ^{13}C-NMR of **11b,ns** in CDCl$_3$*

2. **Mesomorphism**

Table ESI-1. Transitions temperatures (°C, peak temperature) and enthalpies (kJ/mol) of the 2nd heating run and the 1st cooling run determined by DSC (10 °C/min).

Compound	**Phase transition temperatures (ºC) heating/cooling**	**ΔH (kJ/mol) heating/cooling**	**Temp. range (ºC) of LC phases heating/cooling**	**Phase assignment**
2a	66.6 / 44.7	-20.93 / 19.56	54.3 / 74.2	Cr – Col$_h$
	120.9 / 118.9	-5.27 / 5.10		Col$_h$ – Iso
2b	130.7 / 126.4	-17.30 / 18.68		Cr – Iso
4a	-57 (T$_g$) / n. o.		>136 (Col$_{hp}$)	T$_g$ (Col$_{hp}$)
	79.7 / n. o.	-0.11 / n. o.	109.8 / n. o. (Col$_h$)	Col$_{hp}$ – Col$_h$
	189.5 / 181.7	-12.98 / 18.68		Col$_h$ – Iso
5a	51.7 / 15.1	-16.20 / 13.21	176.6 / 199.8	Cr – Col$_h$
	228.3 / 214.9	-8.29 / 9.27		Col$_h$ – Iso
7a,s	146		-	Cr – Iso
7a,ns	118		-	Cr – Iso
7b,s	144.3 / 109.5	-22.05 / 9.96	-	Cr – Iso
7b,ns	118.2 / 89.8	-15.37 / 12.59	-	Cr – Iso
10a,s	156.1 / 146.8	-10.12 / 7.54	36.2 / 41.8	Cr – Col$_{hp}$
	192.3 / 188.6	-5.76 / 6.24		Col$_{hp}$ – Iso
10a,ns	133.0 / 129.7	-7.53 / 6.77	42.7 / 43.7	Cr – Col$_h$
	175.7 / 173.4	-5.56 / 5.71		Col$_h$ – Iso
10b,s	137.6 / 97.1	-20.98 / 3.08	16.0 / 53.3	Cr – Col$_h$
	153.6 / 150.4	-4.04 / 4.36		Col$_h$ – Iso
10b,ns	152.4	-48.86	- / 21.2 (monotropic)	Cr – Iso
	135.4	4.91		Iso – Col$_h$
	114.2	31.28		Col$_h$ – Cr
11a,s	220 / n. o.			T$_g$
	345.7 / 341.1	-16.29 / 13.66		Col$_{hc}$ – Iso
11a,ns	293.0 / 279.3	-24.06 / 24.43		Col$_{hc}$ – Iso
11b,ns	265.4 / 252.9	-17.64 / 14.34		Col$_{hc}$ – Iso

[a] Observed only in the 1st heating run because the sample started to decompose at about 190 °C. [b] This transition is broad in the 1st heating run with two maxima at 66.3 °C and 88.6 °C. [c] A broad transition at 155 °C (-7.75 kJ/mol) was only observed in the first heating run. [d] A broad transition at 122 °C (-12.83 kJ/mol) was only observed in the first heating run.

Table ESI-2. X-ray diffraction data of compounds **1** as fibers and **2** as aligned thin films on Kapton foil derived from 2-D diffraction patterns

Comp.	d / Å (hk) or (br = broad peak of amorphous material)	lattice parameters/Å	(T / ºC)
2a	17.4 (10), 10.09 (11), 8.75 (20), 4.6 (br)[a], 3.55 (001);	a = 20.1	70
4a	18.2 (100), 9.07 (200), 6.85 (210), 4.93 (211), 4.9 (br)[a], 4.11 (311), 3.54 (002), 3.48 (102);	a,c = 21.0,7.08	20
	18.3 (10), 9.10 (20), 6.91 (210), 4.96 (211), 4.8 (br)[a], 4.14 (311), 3.57 (002), 3.53 (102);	a,c = 21.1,7.14	75
	18.3 (10), 9.10 (20), 6.91 (21), 4.8 (br)[a], 3.61 (001)	a = 21.1	125
	18.3 (10), 10.48 (11), 9.10 (20), 6.91 (21), 4.8 (br)[a], 3.65 (001)	a = 21.1	160
5a	16.95 (10), 9.81 (11), 8.50 (20), 4.4 (br)[a], 3.52 (001)	a = 19.57	110
10a,s	18.1 (100), 10.79 (110), 9.01 (200), 7.01 (210), 6.15 (111), 5.14 (211), 5.1 (br)[a,b], 4.66 (400), 4.26 (311), 3.74 (002), 3.68 (102)	a,c = 20.9,7.48	20
	18.7 (100), 10.83 (110), 9.35 (200), 7.09 (210), 6.37 (111), 5.27 (211), 5.1 (br)[a,b], 4.71 (400), 4.30 (311), 3.94 (002), 3.85 (102)	a,c = 21.6,7.88	170
	18.5 (10), 10.76 (11), 9.26 (20), 6.99 (210), 6.41 (111), 5.30 (211), 5.2 (br)[a,b], 3.95 (002), 3.87 (102)		
	18.5 (10), 10.72 (11), 9.26 (20), 6.97 (210), 6.41 (111), 5.35 (211), 5.2 (br)[a,b], 3.97 (002), 3.91 (102)	a,c = 21.4,7.90	180
		a,c = 21.4,7.93	185
10a,ns	18.4 (10), 10.73 (11), 9.25 (20), 7.12 (21), 5.2 (br)[a,b], 3.88 (001)	a = 21.2	145
10b,s	17.9 (10), 10.29 (11), 6.75 (21), 5.1 (br)[b], 5.21 (22), 4.4 (br)[a], 3.78 (001)	a = 20.7	145
10b,ns	19.27, 13.79, 12.80, 11.69, 11.18, 9.84, 7.42, 6.68, 5.91, 5.52, 5.17, 4.77, 4.47, 4.32, 3.86, 3.54 (crystalline phase, not $\mathrm{Col_h}$)[c]	not solved	155
11a,s	17.4 (10), 10.35 (11), 8.89 (20), 6.71 (21), 5.89 (30), 4.9 (br)[a], 3.57 (001)	a = 20.1	20
11a,ns	20.8 (10), 10.43 (20), 8.87, 8.49, 7.09, 6.59, 5.57, 5.21, 4.43, 4.11, 3.51, 3.37;		25
	21.3 (10), 10.73 (20), 9.37, 7.34, 6.65, 5.59, 5.24, 4.91, 4.59, 4.25, 4.16, 3.59, 3.46, 3.20;		200
	20.8 (10), 11.82 (11), 10.38 (20), 9.27, 7.39, 6.78, 5.58, 5.37, 5.23, 4.83, 4.57, 4.46, 4.29, 4.15, 3.74, 3.55, 3.47, 3.30, 3.19, 3.08;	(a = 24.0)[d]	30 cool
11b,ns	19.4 (10), 9.65 (20), 8.25, 6.83, 6.13, 5.60, 5.12, 4.84, 4.79, 4.69, 3.88, 3.53, 3.19, 3.05, 2.86, 2.82, 2.66;		150
	19.1 (10), 10.81 (11), 9.34 (20), 7.02, 6.44, 6.09, 5.09, 4.69, 4.06, 3.96, 3.60, 3.51, 3.21, 3.05, 2.86, 2.82, 2.66;	(a = 22.0)[d]	225

[a] Typical "halo" of aliphatic chains in the molten state; [b] Packing distance of perfluorinated chains; [c] Monotropic $\mathrm{Col_h}$ phase could not be measured by XRD because crystallization occurred during the measurements; [d] These values are based on a hexagonal lattice but many of the observed reflections could not be assigned and, therefore, the assignment is questionable.

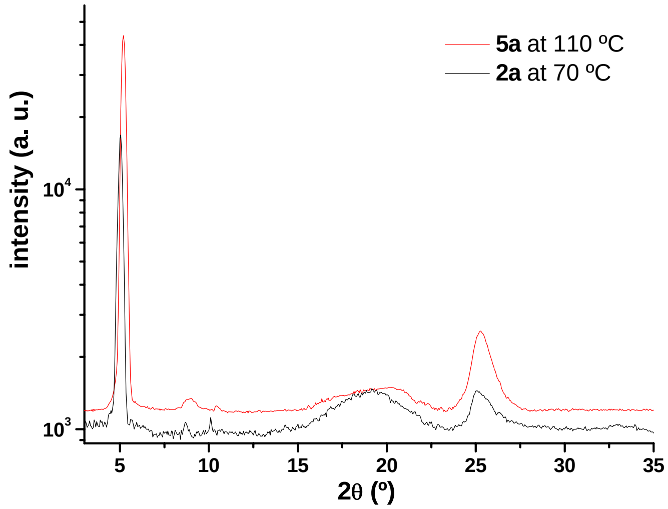

Figure ESI-26. XRD patterns of **2a** and **5a** in their Col_h phases.

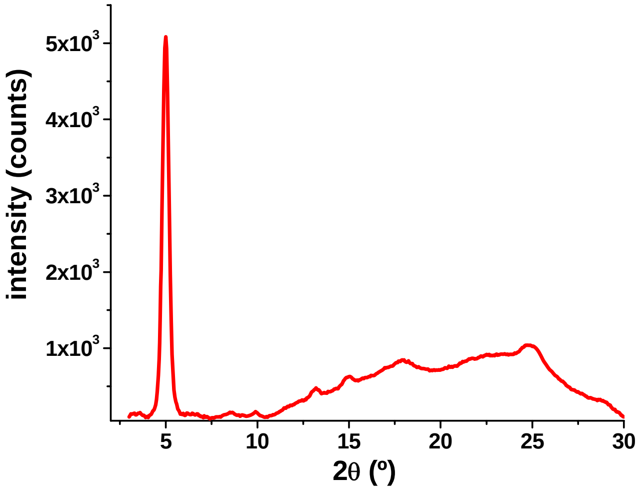

Figure ESI-27. XRD pattern of **11a,s** at 20 ºC

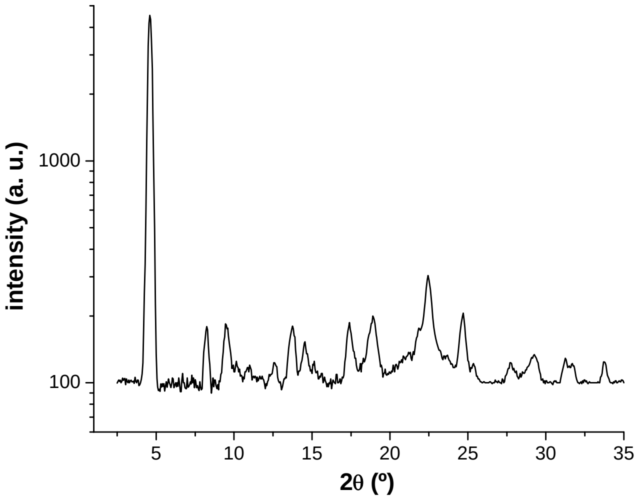

Figure ESI-28. XRD pattern of **11b,ns** at 225 ºC

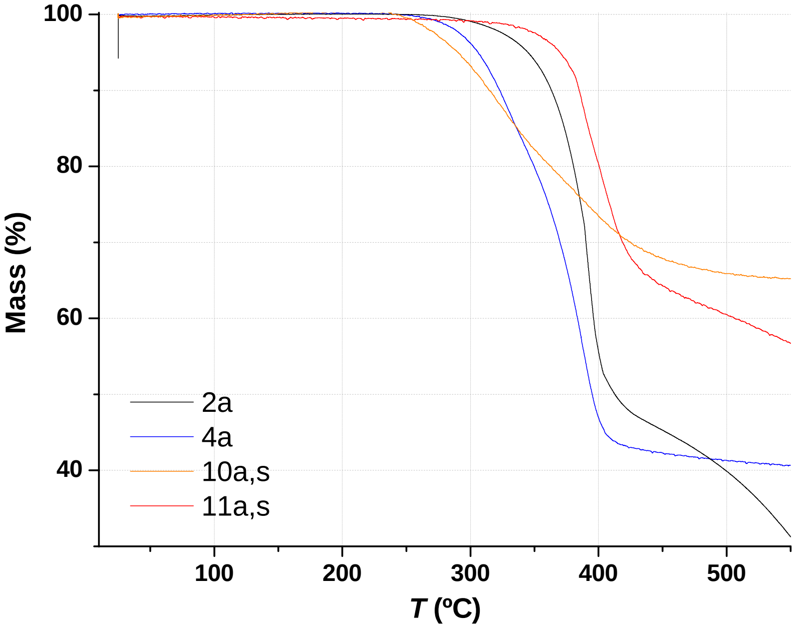

Figure ESI-29. TGA curves of **2a**, **4a**, **10a,s** and **11a,s** at 5 ºC/min under He

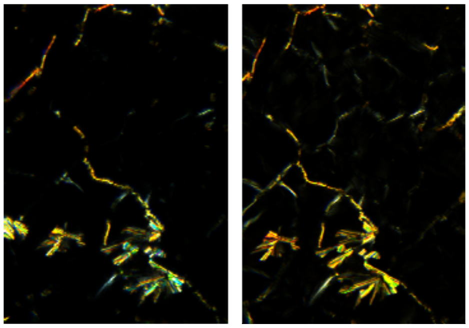

Figure ESI-30. Photomicrographs (crossed polarizers, imaged areas are 0.6 x 0.84 mm) of compound **4a** sandwiched between clean glass slides on cooling from its isotropic phase at 105 ºC (left, fan-shaped and homeotropic areas of its Col_{ho} phase) and at 30 ºC (right, fan-shaped and homeotropic areas of its Col_{hp} phase). A reversible transition between Col_{ho} phase and Col_{hp} phase is detected as subtle increase in birefringence especially at the boundaries between domains and best observed at the boundaries between homeotropic domains.

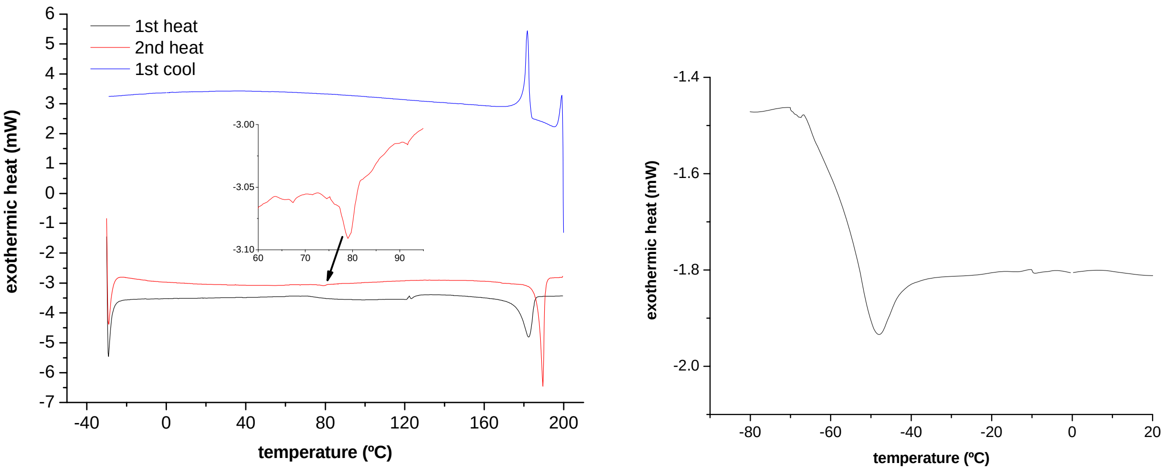

Figure ESI-31. DSC graphs of **4a** run at 5 ºC/min under N_2. Measurements between -30 ºC and 200 ºC with enlarged transition between Col_{hp} and Col_h phases (left) and glass transition detected by a low temperature heating run (right)

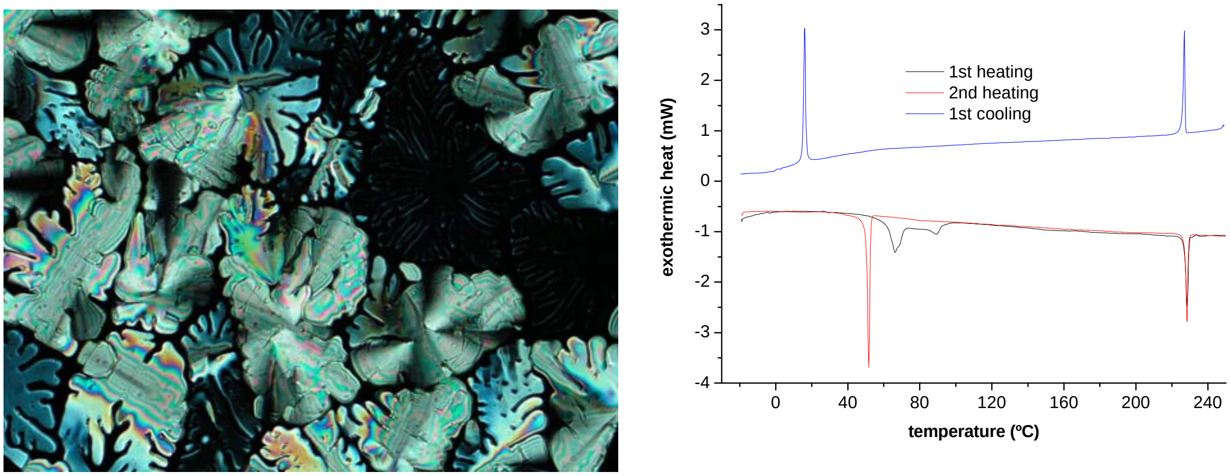

Figure ESI-32. Photomicrograph (crossed polarizers, imaged area is 1.8 x 1.3 mm) of compound **5a** sandwiched between clean glass slides on cooling from its isotropic phase at 228 ºC; shown are fan-shaped and homeotropic areas of the Col_{ho} phase as well as characteristic dendritic growth patterns (left). DSC graphs of **5a** run at 5 ºC/min under N_2 (right).

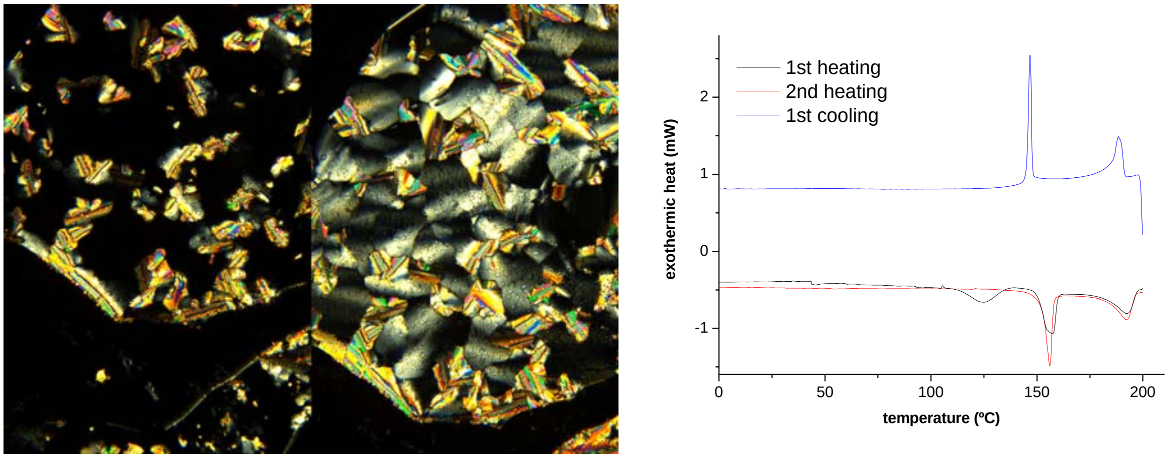

Figure ESI-33. Photomicrographs (crossed polarizers, imaged areas are 0.7 x 1.0 mm) of compound **10a,s** sandwiched between clean glass slides on cooling from its isotropic phase at 185 ºC; shown are fan-shaped and homeotropic areas of the $\mathrm{Col_{hp}}$ phase as well as a areas with no compound (left) and the same area after slightly shifting the top glass slide (centre). After shifting the top glass slide the previously homeotropically aligned areas are tilted in the direction of the shear force. DSC graphs of **10a,s** run at 5 ºC/min under N_2 (right).

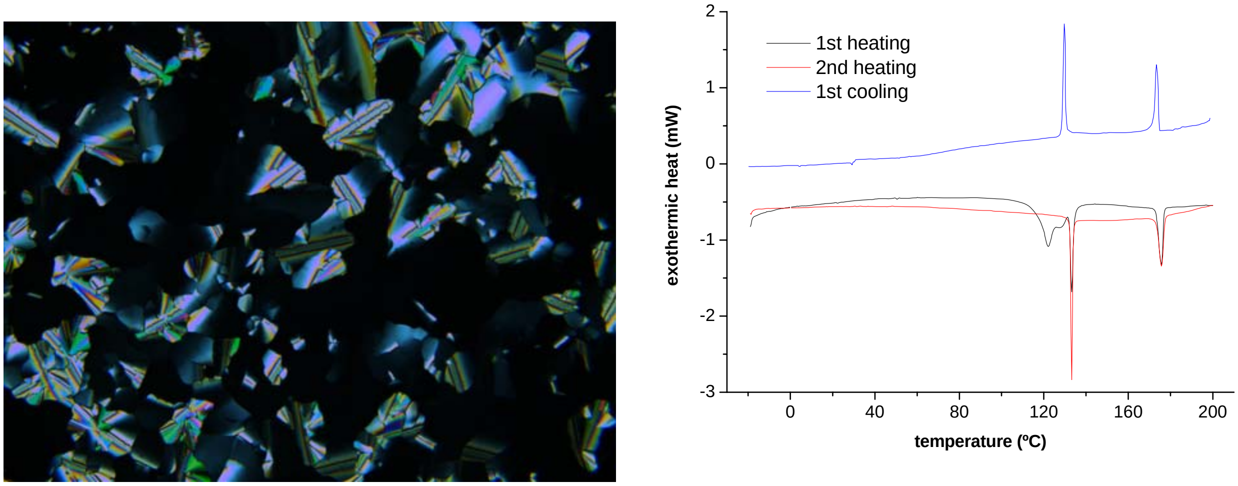

Figure ESI-34. Photomicrograph (crossed polarizers, image area is 1.4 x 1.1 mm) of compound **10a,ns** sandwiched between clean glass slides on cooling from its isotropic phase at 150 ºC (left); shown are fan-shaped and homeotropic areas of the $\mathrm{Col_{ho}}$ phase. DSC graphs of **10a,ns** run at 5 ºC/min under N_2 (right).

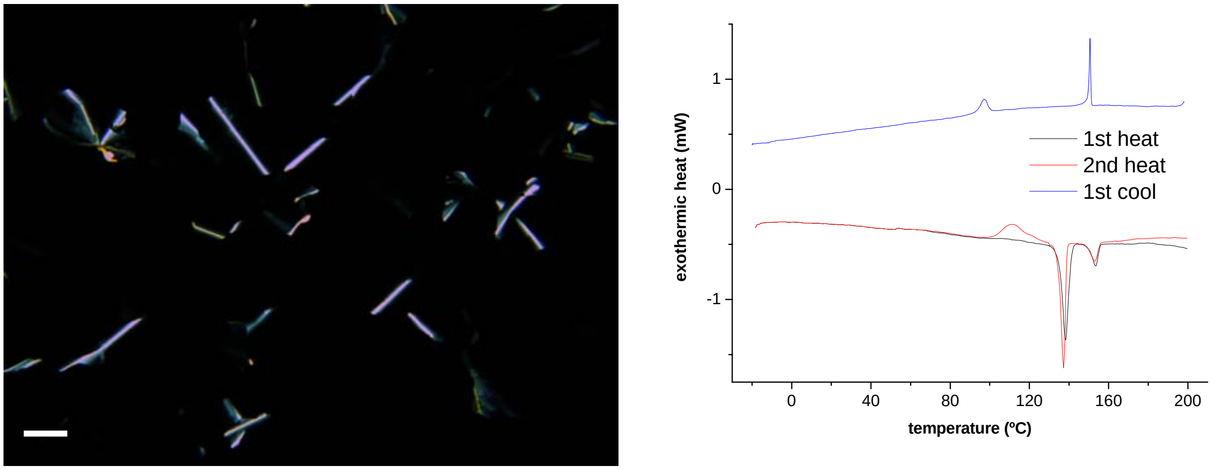

Figure ESI-35. Photomicrograph (crossed polarizers, image area is 1.4 x 1.1 mm) of compound **10b,s** sandwiched between clean glass slides on cooling from its isotropic phase at 142 ºC (left); shown are fan-shaped and homeotropic areas of the $\mathrm{Col_{ho}}$ phase. This compound aligns preferentially homeotropically even at a relatively fast cooling rate of 5 ºC/min. DSC graphs of **10b,s** run at 5 ºC/min under N_2 (right). Cold crystallization precedes melting in the 2nd heating run.

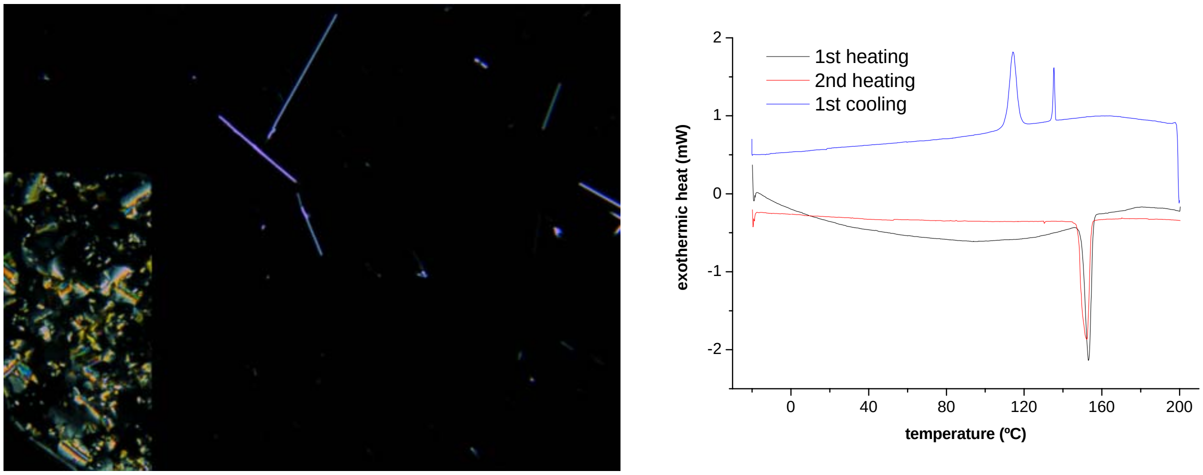

Figure ESI-36. Photomicrograph (crossed polarizers, width of area 1.4 μm) of compound **10b,ns** sandwiched between clean glass slides on cooling from its isotropic phase at 128 ºC (left); shown are fan-shaped and homeotropic areas of the $\mathrm{Col_{ho}}$ phase. This compound aligns preferentially homeotropically even at a relatively fast cooling rate of 5 ºC/min although fan-shaped areas are observed at the edges of the sample when cooled at 5 ºC/min (insert). DSC graphs of **10b,ns** run at 5 ºC/min under N_2 (right).

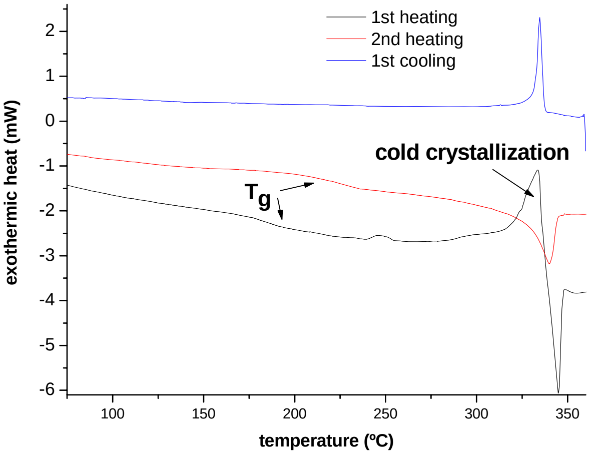

Figure ESI-37. DSC graphs of **11a,s** run at 5 ºC/min under N_2. Slow decomposition occurs during the DSC runs at temperatures above 300 ºC.

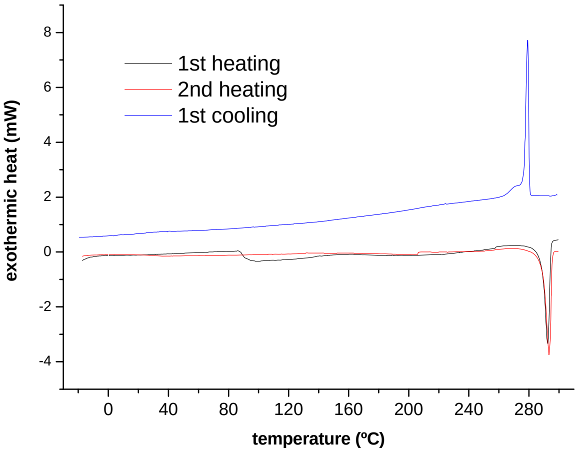

Figure ESI-38. DSC graphs of **11a,ns** run at 5 ºC/min under N_2. A broad transition between 80-120 ºC is unique to the first heating run.

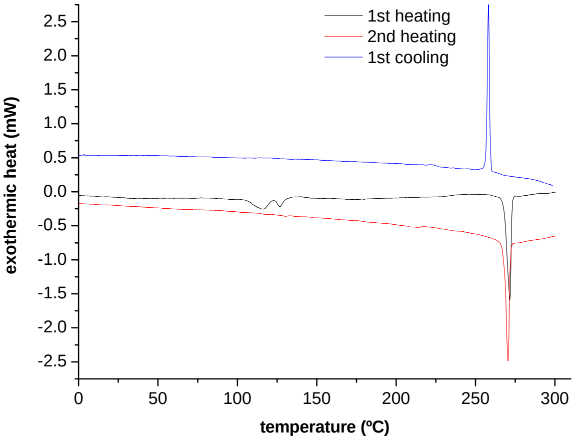

Figure ESI-39. DSC graphs of **11b,ns** run at 5 ºC/min under N_2. Two transitions at 120 ºC and 130 ºC are unique to the first heating run.

3. Time-of-Flight Charge Carrier Mobility Measurements

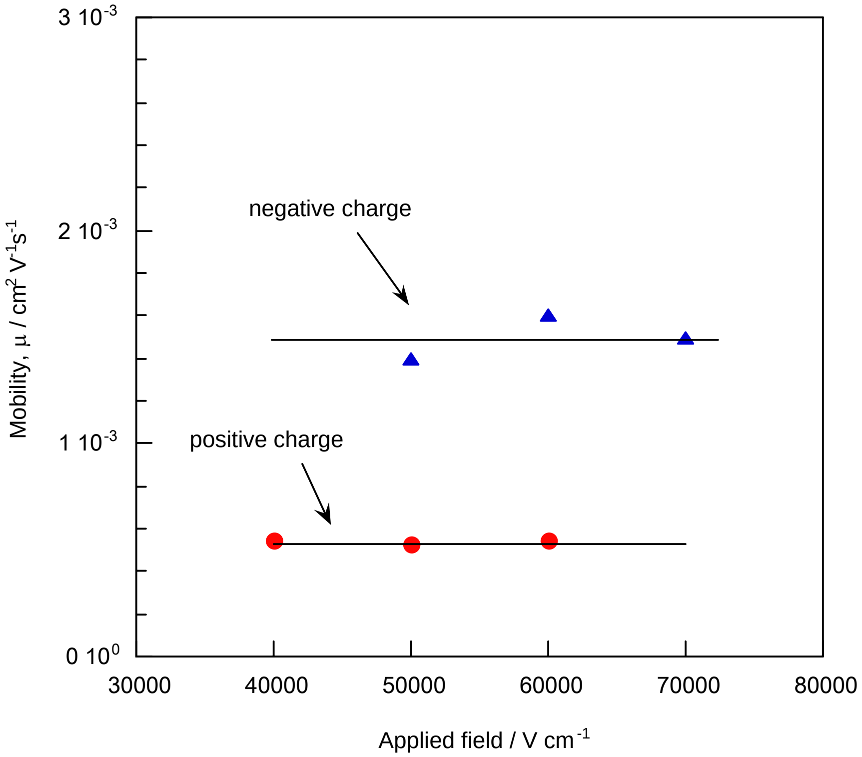

Figure ESI-40. Applied field dependence of carrier mobility for **4a** (Col$_{hp}$ phase at 25 °C)

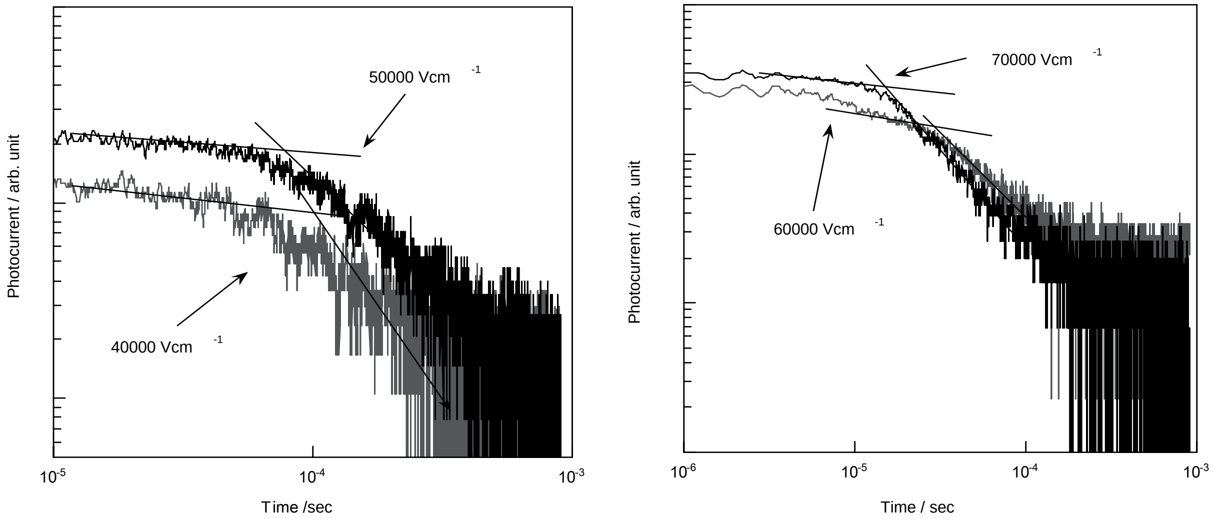

Figure ESI-41. Double logarithmic plots of photocurrent decay curves for the positive (left) and negative (right) charges in compound **4a** (Col$_{ph}$ phase at 25 °C)

4. Cyclic Voltammetry

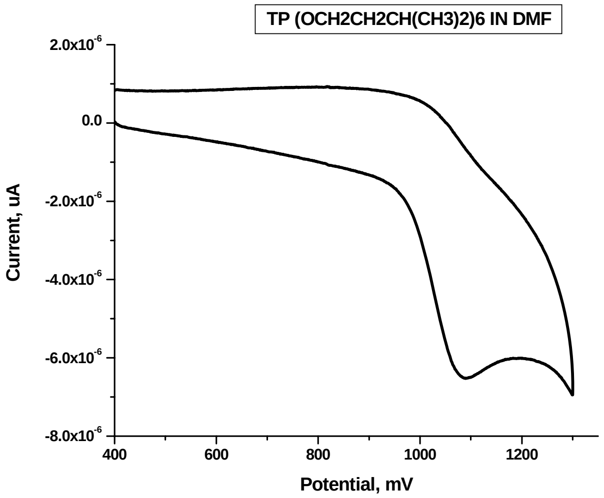

Figure ESI-42. Cyclic voltammogram of **2b** in DMF (7.8 x 10^{-4} M) (glassy carbon working electrode, 0.1 M TBAPClO$_4$ electrolyte, 20 ºC, scan rate = 100 mVs^{-1})

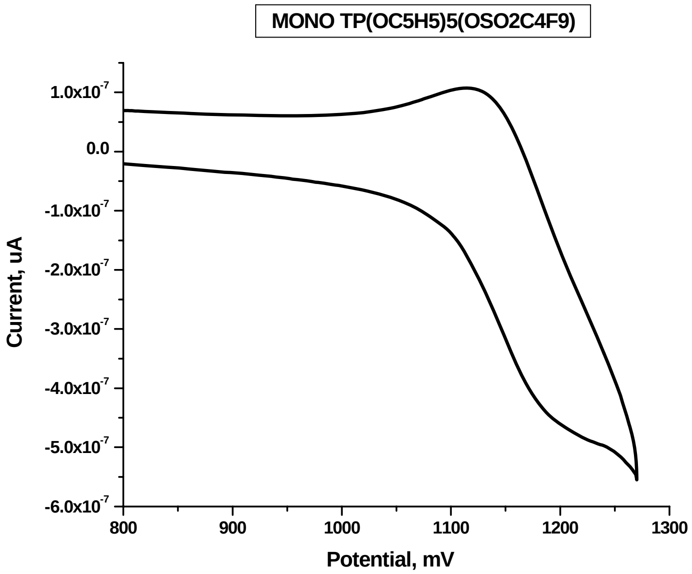

Figure ESI-43. Cyclic voltammogram of **4a** in CH$_2$Cl$_2$ (5.6 x 10^{-4} M) (glassy carbon working electrode, 0.1 M TBAPClO$_4$ electrolyte, 20 ºC, scan rate = 100 mVs^{-1})

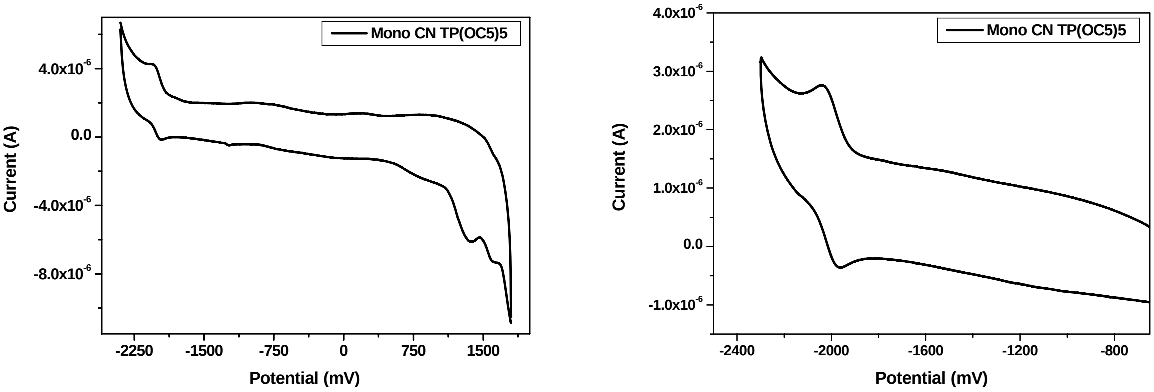

Figure ESI-44. Cyclic voltammogram of **5a** in CH_3CN (8.2 x 10^{-4} M) (glassy carbon working electrode, 0.1 M $TBAPClO_4$ electrolyte, 20 ºC, scan rate = 100 mVs^{-1})

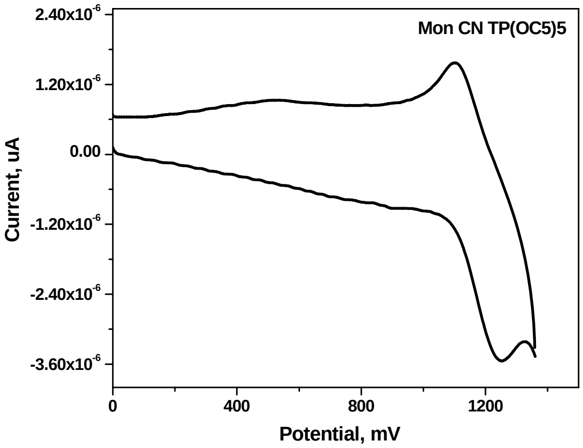

Figure ESI-45. Cyclic voltammogram of **5a** in CH_2Cl_2 (8.0 x 10^{-4} M) (working electrode = glassy carbon, electrolyte = 0.1 M $TBAPClO_4$, 20 ºC, scan rate = 100 mVs^{-1})

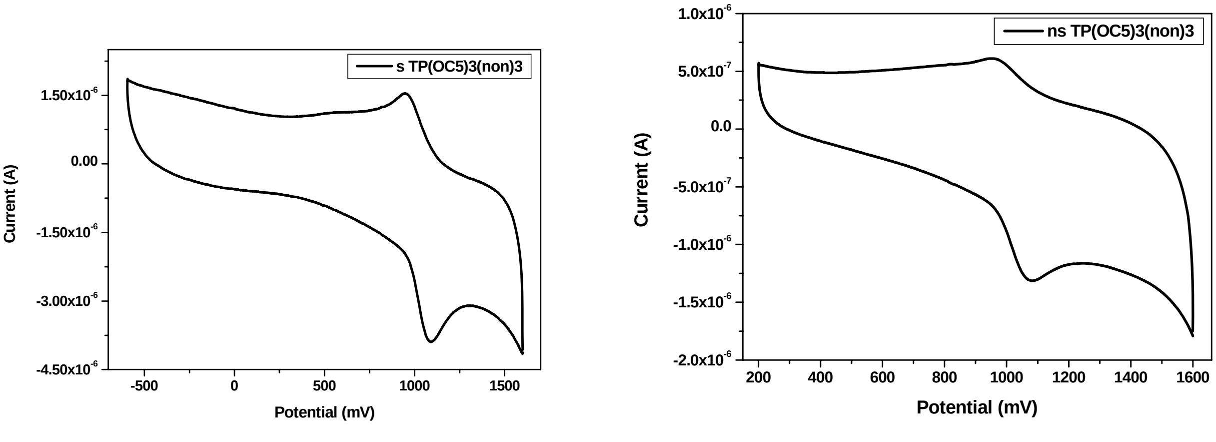

Figure ESI-46. Cyclic voltammograms of **10a,s** (5.2 x 10^{-4} M) (left) and **10a,ns** (7.8 x 10^{-4} M) (right) in CH_3CN (working electrode = glassy carbon, electrolyte = 0.1 M $TBAPClO_4$, 20 ºC, scan rate = 100 mVs^{-1})

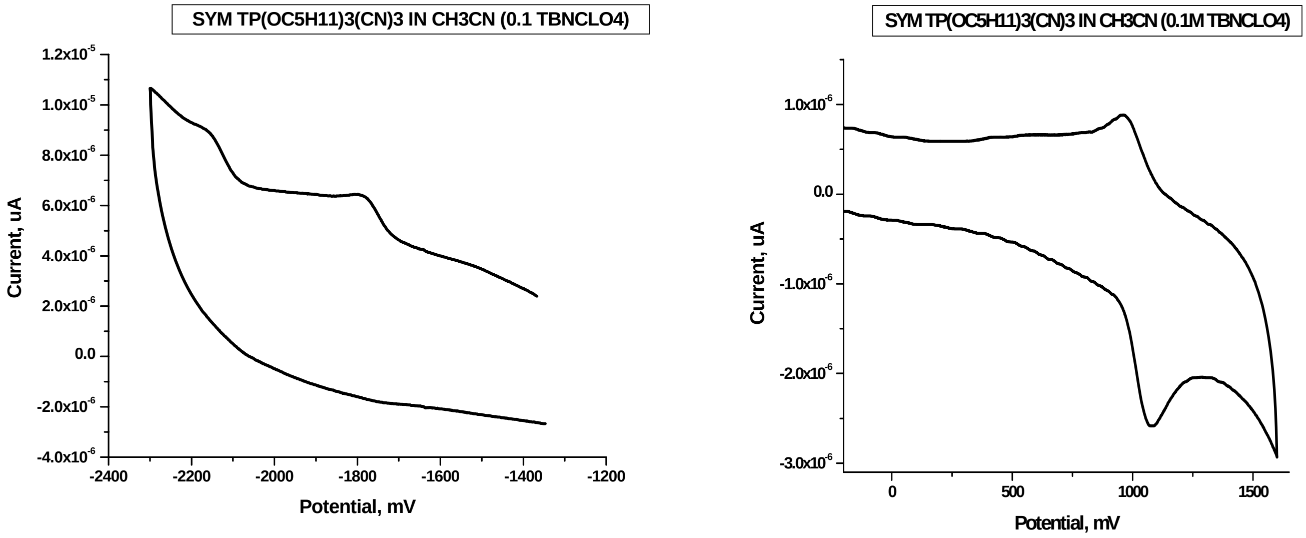

Figure ESI-47. Cyclic voltammograms of **11a,s** (5.1 x 10^{-4} M) in CH_3CN (working electrode = glassy carbon, electrolyte = 0.1 M $TBAPClO_4$, 20 ºC, scan rate = 100 mVs^{-1})

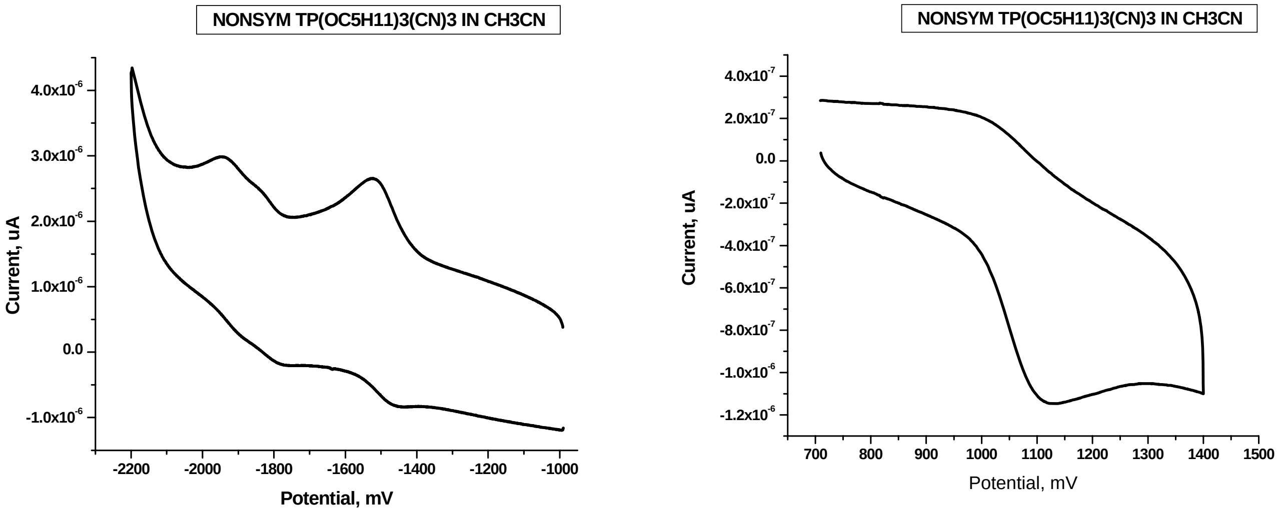

Figure ESI-48. Cyclic voltammograms of **11a,ns** (1.0 x 10^{-3} M) in CH_3CN (working electrode = glassy carbon, electrolyte = 0.1 M $TBAPClO_4$, 20 ºC, scan rate = 100 mVs^{-1})

5. UV-Vis Spectroscopy

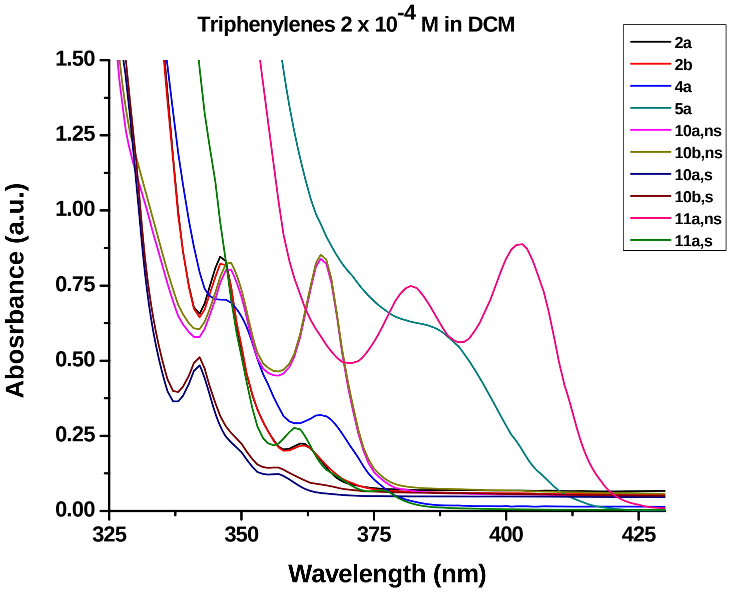

Figure ESI-49. UV-VIS spectra of stated triphenylenes derivatives in CH_2Cl_2 (2 x 10^{-4} molar)

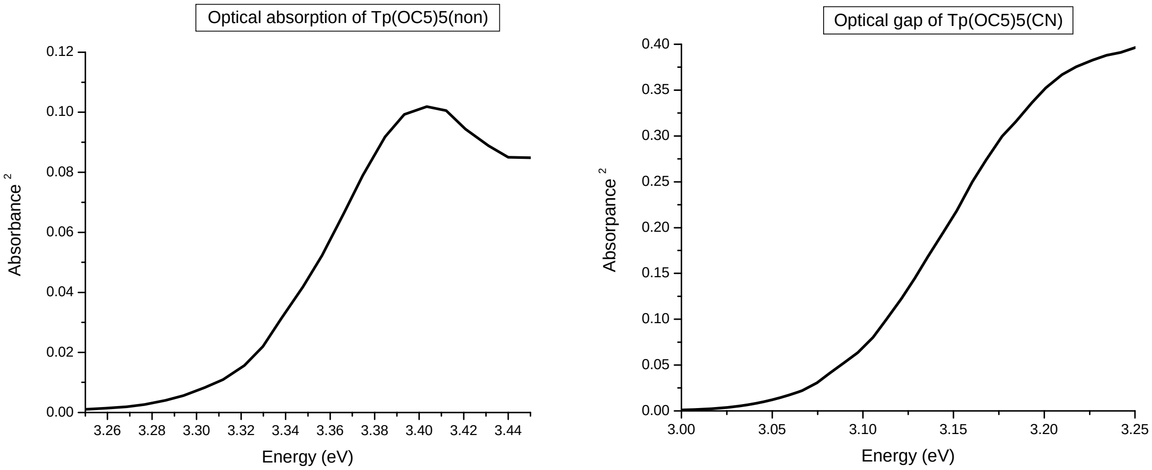

Figure ESI-50. UV-VIS spectra plotted versus eV for the determination of the optical band gaps. Shown are the on-sets of absorption for **4a** (left) and **5a** (right) in CH_2Cl_2 (2 x 10^{-4} molar)

6. Computational studies

Table ESI-3. Comparison of HOMO-LUMO gap energies measured by UV-VIS spectroscopy in solution (optical H-L gap) and calculated (in vacuum) at different levels of theory.

TP	**Optical H-L gap (± 0.05)**	**DFT- B88LYP- 6-31g****	**DFT- B88LYP- DZVP**	**DFT- B3LYP- 6-31g***	**DFT- LSDA - 3-21g**	**DFT- DVW- 6-31G***
2a	3.70	3.15	3.12	4.54	3.19	3.19
4a	3.32	2.50	2.86	4.38	2.88	3.33
5a	3.08	2.51	2.47	4.05	2.55	2.52
10a,ns	3.35	2.78	2.96	4.04	2.89	2.54
10a,s	3.64	3.20	3.22	4.42	2.99	3.22
11a,ns	3.01	2.39	2.36	3.93	2.42	2.89
11a,s	3.54	2.91	2.88	4.19	3.01	2.95

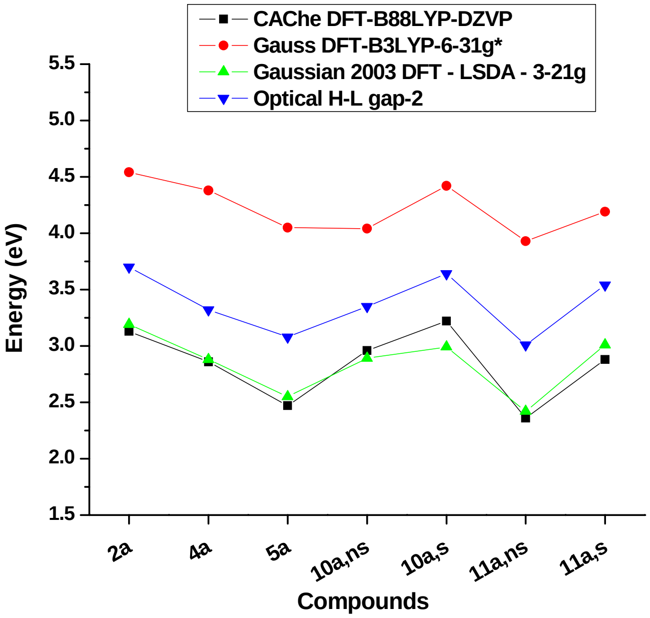

Figure ESI-51. Graphical comparison of calculated HOMO-LUMO gaps and the measured optical HOMO-LUMO gap in CH_2Cl_2 solution.