Supplementary Material (ESI) for Chemical Communications

Supporting information for:

Electroaactive C_3-symmetric discotic liquid-crystalline triindoles

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SYNTHETIC AND CHARACTERIZATION DETAILS

General

NMR spectra were recorded at 23°C. Solvents were purified and dried using standard procedures. Chromatography purifications were carried out by using a gradient of eluents on a Biotage Sp1 flash chromatography system. All reactions were carried out under Ar.

2,3,7,8,12,13-Hexabromo-5,10,15-tris-(4-methoxybenzyl)-10,15-dihydro-5*H*-5,10,15-triaza-diindeno[1,2-a;1',2'-c]fluorene (2)

A mixture of **1** (812 mg, 1 mmol) and NaH (66 mg, 1.65 mmol, 60% in mineral oil) in dry THF (15 mL) was stirred at room temperature for 15 min. Then, *p*-metoxybenzyl chloride (475 mL, 3.5 mmol) was added and the mixture was stirred for 3 h. The mixture was diluted with EtOAc and washed with 10% aqueous HCl and with saturated aqueous NaCl solution, dried (Na_2SO_4) and evaporated. The residue was triturated with CH_3CN to give **1** as a white solid (1.049 mg, 89 %): mp 248ºC (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 3H), 7.50 (s, 3H), 7.29 (d, J = 9.0 Hz, 6 H), 7.01 (d, J = 8.9 Hz, 6 H), 5.78 (s, 6H), 3.86 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 159.50, 141.18, 140.00, 127.95, 127.25, 125.84, 123.18, 119.13, 116.01, 115.05, 105.08, 102.200, 55.43, 50.69; MALDI-TOF MS *m/z* 1172-1185 [M^++1]. HR-MALDI-MS *m/z* calcd for. $C_{48}H_{33}N_3{}^{79}Br_6$ 1172.76166, found 1172.76575.

2,3,7,8,12,13-Hexakis-(*p*-tolylethynyl)-5,10,15-tris-(4-methoxybenzyl)-10,15-dihydro-5*H*-5,10,15-triaza-diindeno[1,2-a;1',2'-c]fluorene (3)

A mixture of **2** (117 mg, 0.1 mmol), $PdCl_2$(dppf) (44 mg, 0.06 mmol) CuI (6 mg, 0.03 mmol) and *p*-tolylacetylene (0.151 mL, 1.2 mmol) was stirred in 4mL of a dry degassed 1:1 mixture of THF:Et_3N at 110 °C for 12 h in a closed vessel.

The black suspension was partitioned between H_2O and CH_2Cl_2, washed with a saturated aqueous solution of KF, and dried (Na_2SO_4). The solvent was evaporated and the residue was triturated with CH_3CN to give **3** as a white solid (101 mg, 73%) mp >300; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.16 (s, 3H), 7.46-7.40 (m, 15H), 7.36 (d, J = 8.0 Hz, 6 H), 7.18-7.11 (m, 12H), 7.02 (d, J = 8.6 Hz, 6 H), 5.95 (s, 6H), 3.78 (s, 9H), 2.39 (s, 9H), 2.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 159.24, 141.00, 140.77, 138.26, 137.86, 131.51, 131.40, 129.09, 127.54, 125.66, 122.61, 120.94, 120.72, 120.52, 118.46, 114.90, 113.47, 103.28, 93.22, 91.41, 88.79, 88.71, 55.26, 51.00, 21.55; MALDI-TOF MS *m/z* 1390 [M^++1], 1269, 1148. HR-MALDI-MS *m/z* calcd for. $C_{102}H_{75}N_3O_3$ 1389.58298, found 1389.57935

2,3,7,8,12,13-Hexakis-(4-pentylphenylethynyl)-5,10,15-tris-(4-methoxybenzyl)- 10,15-dihydro-5*H*-5,10,15-triaza-diindeno[1,2-a;1',2'-c]fluorene (4)

A mixture of **2** (117 mg, 0.1 mmol), $PdCl_2$(dppf) (44 mg, 0.06 mmol) CuI (6 mg, 0.03 mmol) and 1-ethynyl-4-pentylbenzene (0.180mL, 1.2 mmol) was stirred in 4mL of a dry degassed 1:1 mixture of THF: Et_3N at 110 °C for 12 h in a closed vessel.

The black suspension was partitioned between H_2O and CH_2Cl_2, washed with a saturated aqueous solution of KF, and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (hexane → CH_2Cl_2 /hexane 66%) to give **4** as a white solid (94 mg, 68%): mp 223ºC (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 3H), 7.48-7.36 (m, 21H), 7.16 (d, J = 9.9 Hz, 6 H), 7.13 (d, J = 10.1 Hz, 6 H), 7.01 (d, J = 8.9 Hz, 6 H), 5.94 (s, 6H), 3.76 (s, 9H), 2.62 (q, J= 16.1 Hz, 8.9 Hz, 12 H), 1.67-1.57 (m, 12H) ,1.38-1.31 (m, 24H), 0.91 (q, J= 14.5 Hz, 6.9 Hz, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.08, 143.14, 142.78, 140.81, 140.49, 131.57, 131.47, 129.11, 128.39, 127.44, 125.60, 122.32, 121.28, 120.82, 120.55, 118.32, 114.82, 113.30, 103.11, 93.24, 91.38, 88.97, 88.90, 55.20, 50.85, 35.99,

31.64, 31.58, 31.08, 30.97, 29.74, 22.62, 22.59, 14.13, 14.10; MALDI-TOF MS *m/z* 1727 [M^++1], 1606, 1485. HR-MALDI-MS *m/z* calcd for. $C_{126}H_{123}N_3O_3$ 1725.95590 found 1725.95520

2,3,7,8,12,13-Hexakis-(dec-1-ynyl)-5,10,15-tris-(4-methoxybenzyl)-10,15-dihydro-5*H*-5,10,15-triaza-diindeno[1,2-a;1',2'-c]fluorene (5)

A mixture of **2** (117 mg, 0.1 mmol), $PdCl_2$(dppf) (44 mg, 0.06 mmol) CuI (6 mg, 0.03 mmol) and 1-decyne (1.2 mmol) was stirred in 4mL of a dry degassed 1:1 mixture of THF: Et_3N at 110 °C for 24 h in a closed vessel.

The black suspension was partitioned between H_2O and CH_2Cl_2, washed with a saturated aqueous solution of KF, and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (hexane → CH_2Cl_2 /hexane 66%) to give **5** as a white solid (91 mg, 60%): mp 95ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06 (s, 3H), 7.29 (s, 3H), 7.29 (d, *J* = 8.5 Hz, 6 H), 6.93 (d, *J* = 8.6 Hz, 6 H), 5.90 (s, 6H), 3.80 (s, 9H), 2.45-2.35 (m, 12H), 1.61-1.56 (m, 12H), 1.46 (br m, 6H), 1.28 (br m, 54H), 0.90-0.86 (m, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 159.00, 140.53, 140.22, 129.25, 127.47, 125.73, 122.04, 121.12, 118.81, 114,52, 113.41, 102.98, 93.32, 91.29, 80.38, 79.98, 55.22, 50.64, 32.03, 31.98, 31.45, 30.23, 29.73, 29.40, 29.36, 29.33, 29.31, 29.21, 29.07, 22.76, 22.72, 19.85, 19.70, 14.16, 14.15; MALDI-TOF MS *m/z* 1523 [M^++1], 1386 . HR-MALDI-MS *m/z* calcd for. $C_{108}H_{135}N_3O_3$ 1522.04675 found 1522.04980

2,3,7,8,12,13-Hexakis-(decyl)-5,10,15-tris-(4-methoxybenzyl)-10,15-dihydro-5*H*-5,10,15-triaza-diindeno[1,2-a;1',2'-c]fluorene (6)

A mixture of **5** (150 mg, 0.1 mmol), $HCOONH_4$ (378mg, 6 mmol) and 10% Pd/C (28 mg, 0.03mmol) in EtOAc (10 mL) was heated under refluxing conditions for 30 min. The mixture was filtered through Celite and the filtrate was diluted with Et_2O, washed with 10% aqueous HCl and with saturated aqueous NaCl solution, dried (Na_2SO_4) and evaporated. The residue was chromatographed (hexane → CH_2Cl_2 /hexane 50%) give **6** as an orange

glassy solid (112 mg, 73%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74 (s, 3H), 7.49 (d, J = 8.5 Hz, 6 H), 6.99 (d, J = 7.0 Hz, 6 H), 6.97 (s, 3H), 5.90 (s, 6H), 3.84 (s, 9H), 2.61(br m, 6H), 2.35(br m, 6H), 1.53 (br m, 6H), 1.28-1.25 (m, 90H), 0.91-0.85 (m, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 158.88, 140.80, 139.48, 136.09, 132.74, 130.94, 127.70, 122.16, 121.51, 114.37, 110.48, 103.09, 55.23, 50.91, 33.22, 33.11, 32.26, 31.95, 31.76, 29.83, 29.72, 29.65, 29.56, 29.43, 29.36, 22.70, 14.11; MALDI-TOF MS *m/z* 1547 [M^++1]. HR-MALDI-MS *m/z* calcd for. $C_{108}H_{159}N_3O_3$ 1546.23694 found 1546.23760

2,3,7,8,12,13-hexakis-(decyl)-10,15-dihydro-5*H*-5,10,15-triaza-diindeno[1,2-a;1',2'-c]fluorene (7)

To a colourless solution of **6** (77 mg, 0.05 mmol) in CH_2Cl_2 (2 mL), $AlCl_3$ (20 mg, 0.15 mmol) was added and the mixture was stirred for 30 min at room temperature. The mixture was partitioned between H_2O and Et_2O, washed and dried (Na_2SO_4). The solvent was evaporated, the residue chromatographed (hexane → CH_2Cl_2 /hexane 30%) and the pure compound triturated with CH_3CN to give **3** as a white solid (32mg, 54%)

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.57 (s, 3H), 7.85 (s, 3H), 7.46 (s, 3H), 2.83 (br m, 12H), 1.73 (br m, 12H), 1.28 (br m, 84H), 0.86 (br m, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.18, 135.90, 134.09, 132.80, 121.72, 119.42, 110.93, 101.32, 33.51, 32.50, 31.92, 30.12, 29.68, 29.36, 22.68, 14.10; MALDI-TOF MS *m/z* 1186 [M^+]. HR-MALDI-MS *m/z* calcd for. $C_{84}H_{135}N_3$ 1186.06604 found 1186.06505.

X-RAY DIFFRACTION DATA DETAILS

The mesophases of compounds **6** and **7** were studied by X-ray diffraction at high temperatures. The patterns of both compounds were similar and contain a set of three or four sharp, strong maxima at small angles and a broad, diffuse halo at large angles (Table 2). The small-angle maxima correspond to reciprocal spacings that are in the ratio 1 : √3 : 2 (: √7) and can be indexed, respectively, as the (1 0), (1 1), (2 0) and (2 1) reflections from a two-dimensional hexagonal lattice. In addition, the diffuse halo mainly arises from the conformationally-disordered hydrocarbon chains and confirms the mesomorphic nature of these phases. Therefore the mesophases are hexagonal columnar (Col_h).

Table S1. X-ray data for the mesophases of compounds **6** and **7**.

Compound	**T (ºC)**	**Mesophase**	***h k l***	d_{obs} **(Å)**	D_{calc} **(Å)**	**Lattice constant (Å)**
6	**95**	Col_h	1 0 0	21.1	21.0	a = 24.2
			1 1 0	12.1	12.1	
			2 0 0	10.4	10.5	
			4.6[a]			
7	**90**	Col_h	1 0 0	23.3	23.3	a = 26.9
			1 1 0	13.4	13.45	
			2 0 0	11.7	11.65	
			2 1 0	8.8	8.8	
			4.6[a]			

[a] diffuse maximum