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Syntheses of new 'large core' discogens based on the triphenylene, azatriphenylene and hexabenztrinaphthylene nuclei

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We have synthesized new discogens based on polyphenylated triphenylene, polyphenylated azatriphenylene and hexabenztrinaphthylene. A procedure for the extension of the aromatic core by Suzuki coupling is described, which minimizes competitive reductive dehalogenation.

1. Introduction

The formation of a columnar phase is favoured by molecules with a large width to length anisotropy, generally achieved by using a flat aromatic core with flexible side chains. Many different cores and side chain combinations which produce discotic liquid crystalline (LC) materials have been investigated [1], but traditionally the phthalocyanines and triphenylenes are the most studied. This has provided an insight into how one can control the supramolecular structure/stability of the mesophase and its electronic properties by careful molecular engineering [2]. Here we describe new classes of discogen based on polyphenylated azatriphenylene (**1**) and polyphenylated triphenylene (**2**) nuclei, and a method for the synthesis of the novel, large core 'hexabenztrinaphthylene' (**4**) which has 13 fused benzene rings. The synthesis of the polyphenylated triphenylenes requires a modification of the Suzuki coupling protocol that allows efficient polyarylation without competitive reduction of the aryl halide.

2. Results

Azatriphenylenes of the general type **1** (figure 1) were systematically investigated by Praefcke's group some years ago [3]. He showed that none of those compounds with six alkyl or six alkoxy chains (including compound **1a**) were mesogenic. However, the new derivative **1b** with 12 hexyloxy substituents gives Cr₁ 98 Cr₂ 147 Col₁ 150 Col₂ 194 I (°C). It is the first mesogenic trisquinoxaline of its type. The optical texture of the higher temperature columnar phase is shown in figure 2 and is typical of a columnar mesophase on cooling from the isotropic liquid. The phase formed between 150 and

194°C is probably rectangular columnar; low angle X-ray diffraction shows sharp reflections corresponding to column–column separations of 21.1 and 23.7 Å with an intracolumnar distance of 3.5 Å. The equivalent all-carbon isoelectronic hexaphenyltriphenylenes **2** show somewhat similar behaviour. As with the quinoxalines made by Praefcke, those with six side chains **2a–d** are non-mesogenic. However, in this series, the system **2e**, which is the equivalent of **1b**, gives a single columnar phase between 65 and 135°C, the optical texture of this phase is shown in figure 3. The single mesophase has a hexagonal structure with a column–column separation of 25.8 Å; the wide angle region shows the separation of the cores to be 3.5 Å.

Synthesis of the azatriphenylenes **1** involves a straightforward condensation of hexa-aminobenzene† with the appropriate benzil, but to make the hexakis(4-alkoxyphenyl)triphenylenes **2** a variation on the normal Suzuki reaction conditions had to be employed (figure 4) [4].

The conditions required for this type of polyarylation are more demanding than those for simple aryl–aryl coupling. Under standard Suzuki coupling conditions (0.3 mol % Pd(0) as Pd(PPh₃)₄, toluene, water, Na₂CO₃, reflux under argon for 24 h) the reaction of the appropriate arylboronic acid with hexabromotriphenylene gave the product **2** contaminated with the reduction product **3**. Competitive reduction under these reaction conditions is a well-known problem [5]. Ordinarily it is not significant since it often amounts to only 1–2% and the by-product is usually easily removed. However, in this case the by-product is very difficult to remove and the 'error is cumulative' giving 5–12% of the reduction

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† The trinitrotriaminobenzene used in the synthesis of hexa-aminobenzene was a gift from the Royal Ordnance PLC, and is gratefully acknowledged.

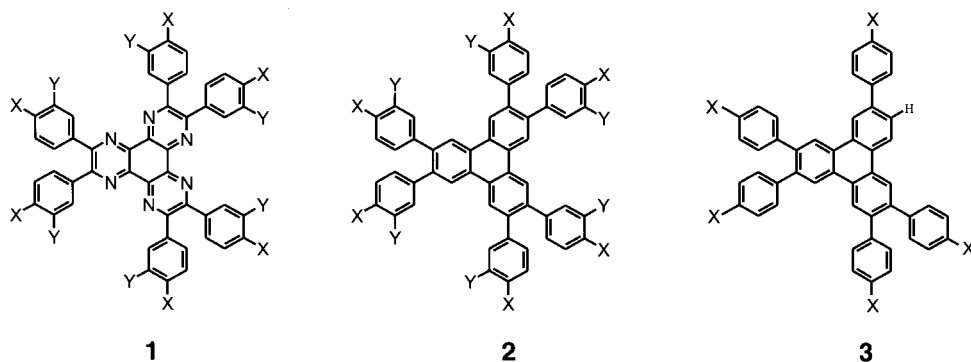


Figure 1. Structures of the compounds **1** and **2** and the reduction by-product **3**. **1a** $X = C_9H_{19}$, $Y = H$; **1b** $X = OC_6H_{13}$, $Y = OC_6H_{13}$; **2a** $X = C_9H_{19}$, $Y = H$; **2b** $X = C_{12}H_{25}$, $Y = H$; **2c** $X = OC_6H_{13}$, $Y = H$; **2d** $X = OC_{11}H_{23}$, $Y = H$; **2e** $X = OC_6H_{13}$, $Y = OC_6H_{13}$. **3a–e** as **2a–e**.

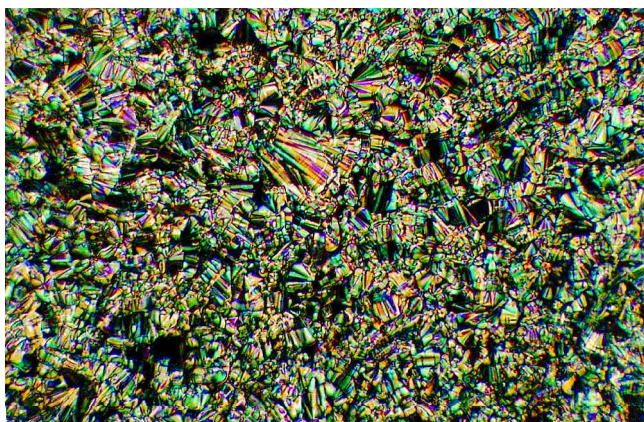


Figure 2. Optical texture of **1b** at 190°C when viewed through crossed polarizing filters (200× magnification).



Figure 3. Optical texture of **2e** at 120°C when viewed through crossed polarizing filters (200× magnification).

product **3**. To overcome this problem we have modified the Suzuki protocol to minimize reduction. To this end, a stronger base was used to improve the rate of meta-thesis of the boronic acid species and DME was used to give a homogeneous reaction medium [6]. In order

to prevent excessive de-borylation of the boronic acid starting material, the less labile pinacol ester **7** was used. The boronic ester is also easier to purify than the acid and is more stable with respect to temperature, pH and oxygen.

These modifications improved the yield and purity of **2** giving a product in which the by-product **3** could no longer be detected by 1H NMR. The pioneering work of the Mullen group suggested that oxidative cyclization of compounds **1** and **2** should yield systems with exceptionally large aromatic cores [7]. Indeed, Mullen has used this approach in the synthesis of large core discogens.‡ The conversion of **2e** to the novel ‘hexabenz-trinaphthylene’ **4** was achieved by us using DCM/ $FeCl_3$, followed by a reductive methanol work-up and excellent yields were obtained (86%, 4 h at 25°C). This is a new type of polynuclear aromatic core [8]. Molecular modelling suggests that it is non-planar with a propeller-like geometry.

X-Ray diffraction analysis in the columnar phase (200°C) shows sharp diffractions corresponding to a rectangular columnar arrangement with column–column separations of 27.5 and 24.5 Å and an intracolumnar separation of 3.6 Å. The 1H NMR spectrum of **4** showed three 6H singlets at 7.5, 8.2 and 9.5 ppm. No large core products were obtained from **1** and **2a–2d** under equivalent conditions. Attempts to couple these substrates using other oxidants ($AlCl_3$, $AlCl_3/Cu(triflate)_2$, $AlCl_3/CuCl$, $FeCl_3/DCM/MeNO_2$) also failed. In each case unreacted starting material was obtained.

The new, ‘clean’ polyphenylation procedure described in this paper, together with the $FeCl_3/MeOH$ coupling protocol [9] will enable discotics to be synthesized with

‡ Since completing our own work we have discovered that Prof. Mullen has independently discovered discogens based upon this nucleus. Since published: YATABE, T., HARBISON, M. A., DIEDRICHBRAND, J., WAGNER, M., MÜLLEN, K., SAMORI, P., and RABE, J. P., 2000, *J. Mater. Chem.*, **7**, 1519–1527.

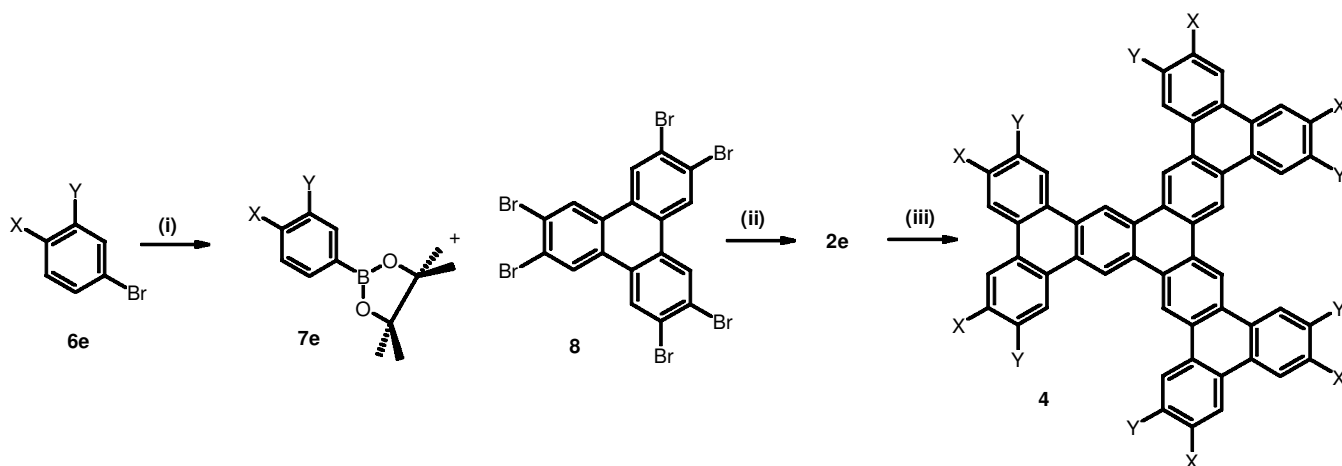


Figure 4. Synthesis of the polyphenylated triphenylene **2e** ($X = Y = \text{OC}_6\text{H}_{13}$) and hexabenztrinitraphthylene **4**. (i) 1. BuLi (1.6M in hexanes)/THF – 78°C, 2. $\text{B}(\text{O}^i\text{Pr})_3$ /THF – 78°C, 3. HCl(aq.) 1M., 4. pinacol/THF. (ii) Pd(PPh₃)₄, DME, H₂O, Ba(OH)₂·H₂O, 80°C, 1–3 days. (iii) 1. FeCl₃/DCM, 2. CH₃OH.

even larger nuclei. These extended pi-systems should prove useful, since many are coloured and some give better matching of the molecular energy levels to electrode work functions, leading to better hole or electron injection [10, 11].

3. Experimental

3.1. General details

The transition temperatures and X-ray diffraction data for compounds **1**, **2** and **4** are summarized in the table. The thermal behaviour of all the materials was investigated by polarizing optical microscopy (Olympus BH-2 microscope with a Linkam hot stage) and differential scanning calorimetry (Perkin-Elmer DSC 7, 2–3 mg samples in closed Al pans) with heating and cooling scans performed at 10°C min⁻¹. Peak values are given in the table together with the transition enthalpies (ΔH) in kJ mol⁻¹. X-ray diffraction experiments were performed at room temperature (on the crystalline phase) and, for those compounds with mesomorphic properties,

at a temperature towards the upper limit of the columnar phase. The diffraction pattern was collected on film using a pinhole camera consisting of a Philips generator and tubes, nickel filtered CuK_α radiation of wavelength $\lambda = 0.154$ nm, and a Lindemann sample tube (1.5 mm inner diameter) to plate distance of 135.5 mm.

¹H and ¹³C NMR spectra were acquired on a 400 MHz Bruker AM400 NMR spectrometer, and chemical shifts are reported in δ units—ppm, relative to Me₄Si (TMS). COSY and HMQC NMR experiments were run as necessary, to assign any ambiguous peaks in the ¹H or ¹³C spectra. Mass spectra were recorded on a VG Autospec instrument and all peaks > 20% were routinely recorded unless stated; FAB+ refers to the caesium atom bombardment method of ionization. UV/Vis (250–600 nm, 1 cm path length quartz cell) were recorded on a Perkin-Elmer Lambda series 2 spectrometer; the extinction coefficients ϵ are given in units of dm³ mol⁻¹ cm⁻¹. FTIR spectra were recorded using a Perkin-Elmer 1760X FTIR spectrometer in the range 4000–600 cm⁻¹, as a liquid film or nujol mull between polished NaCl disks.

Table 1. Summary of the phase behaviour and unit cell parameters for the compounds **1**, **2** and **4**.

Compound	Phase transitions for DSC heating scan/°C (kJ mol ⁻¹) ^a	X-ray diffraction analysis ^b
1a	Cr 71 (34.3) I	hex (30.5, 3.6), $T = 25$,
1b	Cr ₁ 98 (32.0) Cr ₂ 147 (6.7) Col ₁ 150 (10.2) Col _r 194 (31.8) I	rec (23.7, 21.1, 3.5), $T = 190$
2a	Cr 59 (27.0) I	hex (29.6, 3.6), $T = 25$
2b	Cr 36.50 (8.5) I	
2c	Glass 101 (– 37) Cr ₁ 147 (5.1) Cr ₂ 153 (37.2) I	rec (22.1, 16.8, 3.6), $T = 25$, 135
2d	Cr 66.0 (23.5) I	
2e	Cr 64.7 (1.3) Col _h 135.2 (12.5) I	hex (25.8, 3.5), $T = 120$
4	Cr 100 (28.2) Col _r > 400 (dec) I	rec (27.5, 24.5, 3.6), $T = 200$

^a Some of the materials investigated have double melting points upon first heating, probably due to the existence of different crystal polymorphs. Only peaks that remained on subsequent heating runs are recorded in the table.

^b The diffraction pattern was recorded at the temperature T (°C), hex = hexagonal ($a/\text{Å}$, $c/\text{Å}$), rec = rectangular ($a/\text{Å}$, $b/\text{Å}$, $c/\text{Å}$), where a and b represent the column–column separations and c is the intracolumnar distance.

Chemicals and solvents (AR grade) were obtained from Sigma-Aldrich and, unless mentioned, were used without further purification. Column chromatographic separations were performed on silica gel (Merck, Kieselgel 9385 Type 60). Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Whatman AL SIL G/UV plates). Petroleum ether refers to the petroleum fraction boiling at 40–60°C, and this was double distilled before use.

The synthesis of boronic acids [12] and of 2,3,6,7,10,11-hexabromotriphenylene [13] are reported elsewhere. General syntheses of the azatriphenylene-based discogens are given elsewhere [3]. We also employed a modification in the synthesis of the substituted benzil [14], an intermediate in the production of **1**, which gave much higher yields than the method previously reported in [3].

3.2. General synthesis of boronic esters (**7**)

The boronic acid (**6a–e**, 1 mmol) [12] was weighed into a clean, dry round bottomed flask fitted with a reflux condenser and a gas bubbler. Pinacol (distilled, 1.1 mol) was added in 5 ml of dry, distilled THF. The reaction mixture was heated at reflux under nitrogen for at least 1 h until TLC (using dichloromethane) indicated the reaction was complete. Removal of the solvent yielded the crude product (**7a–e**), which was purified by flash column chromatography (1:1 dichloromethane/petroleum ether as eluant). All spectra were in excellent agreement with the proposed structures, and elemental analysis results (C, H) were within 0.3% of the predicted values.

3.3. General synthesis of

hexakis(4-alkoxyphenyl)triphenylenes (2)

2,3,6,7,10,11-Hexabromotriphenylene [13] (**8**, 1 mmol) was added to a mixture of ethylene glycol-1,2-dimethyl ether (DME) (50 ml) and water (2 ml). Argon was bubbled through the suspension for 15 min before tetrakis-triphenylphosphine palladium(0) was added (0.3–3 mol % Pd per reaction site). The boronic ester (7 mmol) was added carefully under a stream of argon and stirring was continued for 10 min. Finally barium hydroxide monohydrate (7 mmol) was added. The mixture was heated to 80°C and stirred under argon until TLC (toluene) indicated the reaction was complete (1–3 days). Cool water was added to the reaction mixture and the organic phase was extracted with dichloromethane. The combined extracts were washed with water and dried over magnesium sulphate. The dry organic phase was passed through a short silica column and the solvent removed to give the crude product as a straw coloured oil. Flash column chromatography (using a gradient elution of petroleum ether followed by 1:1

dichloromethane/petroleum ether) was used to purify the product and (where possible) it was precipitated from ether (–30°C for 14 days–2 months!) or recrystallized from ethanol.

3.4. Synthesis of hexabenztriphthylene (**4**) [11]

Compound **2e** (0.1 g, 5.3×10^{-5} mol) was stirred in dry, distilled dichloromethane (10 ml). Iron (III) chloride (anhydrous, 0.22 g, 8.3×10^{-4} mol) was then added carefully. A stream of nitrogen through the reaction mixture helped to remove the hydrogen chloride produced (which can act as a dealkylating agent). After 4 h, methanol (HPLC, 5 ml) was added, followed by dichloromethane (10 ml) and water (5 ml). The aqueous layer was shaken with dichloromethane (2×5 ml) and the combined organic extracts were washed with water (4×5 ml). Drying and removal of the solvent left compound **4** as a dark brown solid. This was purified by flash column chromatography using dichloromethane/petroleum ether (1:3) as the eluting solvent. After removal of the solvent, a light brown powder remained; this was recrystallized from hot toluene and a small amount of ethanol was added to promote aggregation of the gelatinous precipitate which formed on cooling. Compound **4** was obtained pure as a yellow solid.

3.5. Analysis of compounds

3.5.1. **1a**: 2,3,6,7,10,11-Hexakis(4-*n*-nonylphenyl)-dipyrazino[2,3-*f*:2',3'-*h*]quinoxaline

Yield 20%. Elemental analysis: C 84.9, H 9.4; $C_{102}H_{136}N_6$ requires C 84.5, H 9.5, N 5.8%. IR (Nujol): $\nu_{\max} = 2360$ (C=C), 1913 cm^{-1} (C=N). UV/Vis ($\sim 1\ \mu\text{M}$ in CH_2Cl_2): $\lambda_{\max} = 380\text{ nm}$ ($\epsilon = 7.9 \times 10^4$). $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C, TMS): $\delta = 0.90$ (t, $^3J(\text{H,H}) = 7\text{ Hz}$, 18H; $6 \times -\text{CH}_3$), 1.31 (m, 72H, $6 \times -(\text{CH}_2)_6-$), 1.59 (m, 12H, $6 \times -\text{CH}_2\text{CH}_2-\text{Ar}$), 2.73 (t, $^3J(\text{H,H}) = 7\text{ Hz}$, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{Ar}$), 7.20 (d, $^3J(\text{H,H}) = 8.02\text{ Hz}$, 12H; $6 \times 2\text{ CH}$), 7.14 (d, $^3J(\text{H,H}) = 8.02\text{ Hz}$, 12H; $6 \times 2\text{ CH}$). $^{13}\text{C NMR}$ (75 MHz, $^1\text{H}\{\text{BB}\}$ and DEPT, CDCl_3 , 25°C, TMS): $\delta = 14.52$ (CH_3), 23.08 (CH_2), 29.60 (CH_2), 29.73 (CH_2), 29.92 (CH_2), 29.99 (CH_2), 31.63 (CH_2), 32.30 (CH_2), 36.21 (CH_2), 128.86 (phenyl CH), 130.59 (phenyl CH), 136.55 (quinoxaline $\text{C}_{2a,2b,6a,6b,10a,10b}$), 139.51 (phenyl C), 144.76 (phenyl C), 154.28 (quinoxaline $\text{C}_{2,3,6,7,10,11}$). MS (FAB+): m/z (%): 1448(100) [M^+], 1348(44), 1248(15), 204(30).

3.5.2. **1b**: 2,3,6,7,10,11-Hexakis(3,4-dihexyloxyphenyl)-dipyrazino[2,3-*f*:2',3'-*h*]quinoxaline

Yield 66%. Elemental analysis: C 75.95, H 9.4, N 4.35; $C_{120}H_{174}N_6O_{12}$ requires C 76.2, H 9.3, N 4.4%. IR (Nujol): $\nu_{\max} = 2358$ (C=C), 1912 cm^{-1} (C=N). UV/Vis ($\sim 1\ \mu\text{M}$ in CH_2Cl_2): $\lambda_{\max} = 275\text{ nm}$ ($\epsilon = 6.5 \times 10^4$), 415 nm ($\epsilon = 7.5 \times 10^4$). $^1\text{H NMR}$ (300 MHz, CDCl_3 ,

25°C, TMS): $\delta = 0.91$ (t, $^3J(\text{H,H}) = 7$ Hz, 18H; $6 \times -\text{Me}$), 0.92 (t, $^3J(\text{H,H}) = 7$ Hz, 18H; $6 \times -\text{Me}$), 1.34 (m, 24H, $6 \times -(\text{CH}_2)_2-$), 1.35 (m, 24H; $6 \times -(\text{CH}_2)_2-$), 1.46 (m, 24H; $12 \times -\text{CH}_2\text{CH}_2-\text{OAr}$), 1.75 (t, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{OAr}$), 1.85 (t, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{OAr}$), 6.88 (d, $^3J(\text{H,H}) = 8.02$ Hz, 6H; $6 \times \text{CH}$, phenyl C_5), 7.45 (d, $^4J(\text{H,H}) = 2.01$ Hz, 6H; $6 \times \text{CH}$, phenyl C_6), 7.51 (dd, $^3J(\text{H,H}) = 8.02$ Hz, $^4J(\text{H,H}) = 2.01$ Hz, 6H; $6 \times \text{CH}$, phenyl C_2). ^{13}C NMR (75 MHz, $^1\text{H}\{\text{BB}\}$ and DEPT, CDCl_3 , 25°C, TMS): $\delta = 14.00$ ($12 \times \text{CH}_3$), 22.60 ($12 \times \text{CH}_2$), 25.70 ($12 \times \text{CH}_2$), 29.15 ($6 \times \text{CH}_2$), 29.19 ($6 \times \text{CH}_2$), 29.15 ($6 \times \text{CH}_2$), 29.20 ($6 \times \text{CH}_2$), 31.6 ($12 \times \text{CH}_2$), 69.15 ($6 \times \text{CH}_2$), 69.24 ($6 \times \text{CH}_2$), 113.13 (phenyl CH), 115.72 (phenyl CH), 123.35 (phenyl CH), 131.47 (phenyl C), 138.68 (quinoxaline $\text{C}_{3a,3b,7a,7b,11a,11b}$), 148.72 (phenyl C), 150.39 (phenyl C), 154.28 (quinoxaline $\text{C}_{1,2,5,6,9,10}$). MS (FAB+): m/z (%): 1892(10) [$\text{M}^+ + 2$].

3.5.3. **2a**: 2,3,6,7,10,11-Hexakis-(4-*n*-nonylphenyl)-triphenylene

Yield 88%, white solid. Elemental analysis: C 89.9, H 10.2; $\text{C}_{108}\text{H}_{144}$ requires C 89.9, H 10.1%. IR (Nujol) $\nu_{\text{max}} = 1909 \text{ cm}^{-1}$ (C=C). UV/Vis ($\sim 1 \mu\text{M}$ in CH_2Cl_2): $\lambda_{\text{max}} = 389 \text{ nm}$ ($\epsilon = 1 \times 10^6$). ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): $\delta = 0.81$ (t, $^3J(\text{H,H}) = 7$ Hz, 18H; $6 \times -\text{CH}_3$), 1.20 (m, 72H; $6 \times -(\text{CH}_2)_6-$), 1.55 (m, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{Ar}$), 2.53 (t, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{Ar}$), 7.02 (d, $^3J(\text{H,H}) = 8.0$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl $\text{C}_{3,6}$), 7.15 (d, $^3J(\text{H,H}) = 8.0$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl $\text{C}_{2,5}$), 8.61 (s, 6H; $6 -\text{CH}-$, triphenylene). ^{13}C NMR (75 MHz, $^1\text{H}\{\text{BB}\}$ and DEPT, CDCl_3 , 25°C, TMS): $\delta = 14.53$ (CH_3), 23.10 (CH_2), 29.73 (CH_2), 29.76 (CH_2), 29.96 (CH_2), 30.02 (CH_2), 31.82 (CH_2), 32.33 (CH_2), 36.04 (CH_2), 125.85 (C, triphenylene $\text{C}_{1,4,5,8,9,12}$), 128.40 (CH, phenyl $\text{C}_{2,6}$), 129.22 (C, triphenylene $\text{C}_{4a,4b,8a,8b,12a,12b}$), 130.34 (CH, phenyl $\text{C}_{3,5}$), 139.27 (C, phenyl C_4), 140.24 (C, phenyl C_1), 141.76 (C, triphenylene $\text{C}_{2,3,6,7,10,11}$). MS (FAB+): m/z (%): 1442(100) [M^+], 1370(10), 1329(15), 1239(35).

3.5.4. **2b**: 2,3,6,7,10,11-Hexakis-(4-*n*-dodecylphenyl)-triphenylene

Yield 78%, white solid. Elemental analysis: C 89.1, H 10.5; $\text{C}_{126}\text{H}_{180}$ requires C 89.3, H 10.5%. IR (Nujol): $\nu_{\text{max}} = 1909 \text{ cm}^{-1}$ (C=C). UV/Vis ($\sim 1 \mu\text{M}$ in CH_2Cl_2): $\lambda_{\text{max}} = 390 \text{ nm}$ ($\epsilon = 1.9 \times 10^5$). ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): $\delta = 0.91$ (t, $^3J(\text{H,H}) = 7$ Hz, 18H; $6 \times -\text{CH}_3$), 1.30 (m, 84H; $6 \times -(\text{CH}_2)_7-$), 1.33 (m, 12H; $6 \times -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{Ar}$), 1.34 (m, 12H; $6 \times -\text{CH}_2\text{CH}_2\text{CH}_2-\text{Ar}$), 1.65 (m, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{Ar}$), 2.63 (t, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{Ar}$), 7.12 (d, $^3J(\text{H,H}) = 8.2$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl $\text{C}_{3,5}$), 7.27 (d, $^3J(\text{H,H}) = 8.2$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl

$\text{C}_{2,6}$), 8.71 (s, 6H; $6 \times -\text{CH}-$, triphenylene). ^{13}C NMR (75 MHz, $^1\text{H}\{\text{BB}\}$ and DEPT, CDCl_3 , 25°C, TMS): $\delta = 14.53$ (CH_3), 23.11 (CH_2), 29.75 (CH_2), 29.79 (CH_2), 29.97 (CH_2), 30.08 (CH_2), 30.12 ($2 \times \text{CH}_2$), 30.81 ($2 \times \text{CH}_2$), 32.34 (CH_2), 36.04 (CH_2), 125.87 (CH, triphenylene $\text{C}_{1,4,5,8,9,12}$), 128.38 (CH, phenyl $\text{C}_{2,6}$), 129.22 (C, triphenylene $\text{C}_{4a,4b,8a,8b,12a,12b}$), 130.35 (CH, phenyl $\text{C}_{3,5}$), 139.28 (C, phenyl C_4), 140.25 (C, phenyl C_1), 1421.74 (C, triphenylene $\text{C}_{2,3,6,7,10,11}$). MS (FAB+): m/z (%): 1694(75) [M^+], 1552(10), 57(100).

3.5.5. **2c**: 2,3,6,7,10,11-Hexakis-(4-*n*-hexyloxyphenyl)-triphenylene

Yield 66%, white solid. Elemental analysis: C 83.8, H 8.65; $\text{C}_{90}\text{H}_{108}\text{O}_6$ requires C 84.0, H 8.5%. IR (Nujol): $\nu_{\text{max}} = 1908 \text{ cm}^{-1}$ (C=C). UV/Vis ($\sim 1 \mu\text{M}$ in CH_2Cl_2): $\lambda_{\text{max}} = 308 \text{ nm}$ ($\epsilon = 1.43 \times 10^5$). ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): $\delta = 0.85$ (t, $^3J(\text{H,H}) = 7$ Hz, 18H; $6 \times -\text{CH}_3$), 1.28 (m, 24H; $6 \times -(\text{CH}_2)_2-$), 1.40 (m, 12H; $6 \times -\text{CH}_2\text{CH}_2\text{CH}_2-\text{OAr}$), 1.72 (quint, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2\text{CH}_2-\text{OAr}$), 3.89 (t, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{OAr}$), 6.76 (d, $^3J(\text{H,H}) = 8.8$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl $\text{C}_{3,5}$), 7.16 (d, $^3J(\text{H,H}) = 8.8$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl $\text{C}_{2,6}$), 8.56 (s, 6H; $6 \times -\text{CH}-$, triphenylene). ^{13}C NMR (75 MHz, $^1\text{H}\{\text{BB}\}$ and DEPT, CDCl_3 , 25°C, TMS): $\delta = 14.46$ (CH_3), 23.02 (CH_2), 26.16 (CH_2), 29.68 (CH_2), 30.98 (CH_2), 32.02 (CH_2), 68.39 (CH_2), 114.48 (CH, phenyl $\text{C}_{3,5}$), 125.73 (CH, triphenylene $\text{C}_{1,4,5,8,9,12}$), 129.08 (C, triphenylene $\text{C}_{4a,4b,8a,8b,12a,12b}$), 131.51 (CH, phenyl $\text{C}_{2,6}$), 134.29 (C, phenyl C_1), 139.81 (C, triphenylene $\text{C}_{2,3,6,7,10,11}$), 158.46 (C, phenyl C_4). MS (FAB+): m/z (%): 1285(28) [M^+], 1108(10), 109(25), 69(100).

2.5.6. **2d**: 2,3,6,7,10,11-Hexakis-(4-*n*-undecyloxyphenyl)-triphenylene

Yield 77%, pale yellow solid. Elemental analysis: C 84.8, H 10.2; $\text{C}_{120}\text{H}_{168}\text{O}_6$ requires C 84.5, H 9.9%. IR (Nujol): $\nu_{\text{max}} = 2300 \text{ cm}^{-1}$ (C=C); UV/Vis ($\sim 1 \mu\text{M}$ in CH_2Cl_2): $\lambda_{\text{max}} = 307 \text{ nm}$ ($\epsilon = 1.6 \times 10^5$). ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): $\delta = 0.92$ (t, $^3J(\text{H,H}) = 7$ Hz, 18H; $6 \times -\text{CH}_3$), 1.31 (m, 84H; $6 \times -(\text{CH}_2)_7-$), 1.60 (m, 12H; $6 \times -\text{CH}_2\text{CH}_2\text{CH}_2-\text{OAr}$), 1.82 (quint, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2\text{CH}_2-\text{OAr}$), 3.99 (t, $^3J(\text{H,H}) = 7$ Hz, 12H; $6 \times -\text{CH}_2\text{CH}_2-\text{OAr}$), 6.90 (d, $^3J(\text{H,H}) = 8.5$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl $\text{C}_{3,5}$), 7.28 (d, $^3J(\text{H,H}) = 8.5$ Hz, 12H; $6 \times 2 -\text{CH}-$, phenyl $\text{C}_{2,6}$), 8.66 (s, 6H; $6 \times -\text{CH}-$, triphenylene). ^{13}C NMR (75 MHz, $^1\text{H}\{\text{BB}\}$ and DEPT, CDCl_3 , 25°C, TMS): $\delta = 14.54$ (CH_3), 23.11 (CH_2), 26.50 (CH_2), 29.76 (CH_2), 29.77 (CH_2), 29.86 (CH_2), 29.87 (CH_2), 30.03 (CH_2), 30.04 (CH_2), 32.33 (CH_2), 68.39 (CH_2), 114.48 (CH, phenyl $\text{C}_{3,5}$), 125.74 (CH, triphenylene $\text{C}_{1,4,5,8,9,12}$), 129.09 (C, triphenylene $\text{C}_{4a,4b,8a,8b,12a,12b}$), 131.52 (CH, phenyl

C_{2,6}), 134.29 (C, phenyl C₁), 139.82 (C, triphenylene C_{2,3,6,7,10,11}), 158.47 (C, phenyl C₄). MS (FAB+): *m/z*(%): 1705(70) [M⁺], 1459(100), 1305(35), 79(30), 502(35), 423(40).

3.5.7. **2e**: 2,3,6,7,10,11-Hexakis-(3,4-*n*-dihexyloxy-phenyl)triphenylene

Yield 40%, white solid. Elemental analysis: C 80.2, H 9.5; C₁₂₆H₁₈₀O₁₂ requires C 80.2, H 9.6%. IR (Nujol): ν_{\max} = 2350 cm⁻¹ (C=C). UV/Vis (~1 μ M in CH₂Cl₂): λ_{\max} = 281 nm (ϵ = 1.5 × 10⁵), 320 nm (ϵ = 1.2 × 10⁵). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ = 0.84 (t, ³*J*(H,H) = 7 Hz, 18H; 6 × -CH₃), 0.84 (t, ³*J*(H,H) = 7 Hz, 18H; 6 × -CH₃), 1.27 (m, 24H; 6 × -(CH₂)₂-), 1.28 (m, 24H; 6 × -(CH₂)₂-), 1.42 (m, 24H; 6 × 2 × -CH₂CH₂CH₂-OAr), 1.74 (m, 12H; 6 × -CH₂CH₂CH₂-OAr), 1.78 (m, 12H; 6 × -CH₂CH₂CH₂-OAr), 3.95 (t, ³*J*(H,H) = 7 Hz, 12H; 6 × -CH₂CH₂-OAr), 3.98 (t, ³*J*(H,H) = 7 Hz, 12H; 6 × -CH₂CH₂-OAr), 6.86 (d, ³*J*(H,H) = 9.0 Hz, 6H; 6 × -CH-, phenyl C₅), 6.98 (dd, ³*J*(H,H) = 9.0 Hz, ⁴*J*(H,H) = 2 Hz, 6H; 6 × -CH-, phenyl C₆), 7.00 (d, ⁴*J*(H,H) = 2 Hz, 6H; 6 × -CH-, phenyl C₂), 8.60 (s, 6H; 6 × -CH-, triphenylene). ¹³C NMR (75 MHz, ¹H{BB} and DEPT, CDCl₃, 25°C, TMS): δ = 14.43 (CH₃), 23.03 (CH₂), 26.13 (CH₂), 29.72 (CH₂), 32.02 (CH₂), 69.93 (CH₂), 113.58 (CH, phenyl C₂), 114.59 (CH, phenyl C₅), 119.70 (CH, phenyl C₆), 125.10 (CH, triphenylene C_{1,4,5,8,9,12}), 129.13 (C, triphenylene C_{4a,4b,8a,8b,12a,12b}), 134.76 (C, phenyl C₁), 148.87 (CH, phenyl C₄), 149.67 (C, phenyl C₃), 162 (C, triphenylene C_{2,3,6,7,10,11}). MS (FAB+): *m/z*(%): 1894(10) [M⁺], 554(100), 470(10), 310(50), 218(25).

3.5.8. **4**: 2,3,8,9,12,13,18,19,22,23,28,29 dodecakis-(hexyloxy)hexabenz[*a,c,k,m,v,w*]trinaphthylene

Yield 86%. Elemental analysis: C 80.2, H 9.6; C₁₂₆H₁₇₄O₁₂ requires C 80.4, H 9.4%. IR (Nujol): ν_{\max} = 2360 cm⁻¹ (C=C); UV/Vis (~1 μ M in CH₂Cl₂): λ_{\max} = 377 nm (ϵ = 9.4 × 10⁴), 356 nm (ϵ = 1.4 × 10⁵), 325 nm (ϵ = 1.2 × 10⁵), 290 nm (ϵ = 8.0 × 10⁴), 266 nm (ϵ = 7.6 × 10⁴). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ = 0.93 (t, ³*J*(H,H) = 7 Hz, 18H; 6 × -CH₃), 0.98 (t, ³*J*(H,H) = 7 Hz, 18H; 6 × -CH₃), 1.42 (m, 24H; 6 × -(CH₂)₂-), 1.43 (m, 24H; 6 × -(CH₂)₂-), 1.97 (m, 24H; 6 × 2 × -CH₂CH₂CH₂-OAr), 2.02 (m, 24H; 6 × 2 × -CH₂CH₂CH₂-OAr), 4.22 (t, ³*J*(H,H) = 7 Hz, 12H; 6 × -CH₂CH₂-OAr), 4.34 (t, ³*J*(H,H) = 7 Hz, 12H; 6 × -CH₂CH₂-OAr), 7.55 (s, 6H; hexabenztri-

naphthylene C_{1,10,11,20,21,30}), 8.21 (s, 6H; hexabenztrinaphthylene C_{4,7,14,17,24,27}), 9.53 (s, 6H; hexabenztrinaphthylene C_{5,6,15,16,25,26}). ¹³C NMR (75 MHz, ¹H{BB} and DEPT, CDCl₃, 25°C, TMS): δ = 14.54 (2 × CH₃), 23.18 (2 × CH₂), 26.47 (CH₂), 26.70 (CH₂), 30.02 (CH₂), 30.35 (CH₂), 32.29 (CH₂), 32.45 (CH₂), 69.60 (CH₂), 69.82 (CH₂), 107.14 (CH, phenyl C₂), 108.17 (CH, phenyl C₅), 117.12 (CH triphenylene C_{1,4,5,8,9,12}), 124.05 (C, phenyl C₁), 124.96 (CH, phenyl C₆), 128.31 (C, triphenylene C_{2,3,6,7,10,11}), 128.45 (C, triphenylene C_{4a,4b,8a,8b,12a,12b}), 149.30 (C, phenyl C₄), 150.22 (C, phenyl C₃). MS (FAB+): *m/z*(%): 1885(1) [M⁺], 424(15), 305(10), 176(30), 55(100).

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