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Introduction of bis-discotic and bis-calamitic mesogenic addends to C_{60}

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The synthesis and characterization of four C_{60} Bingel cyclopropanation adducts incorporating bis-biphenylene (three adducts) and bis-triphenylene (one adduct) moieties are described. The thermal analysis (POM and DSC) of these materials reveals that they are not liquid crystalline. However, two of the precursor bis-biphenylene malonate esters possess monotropic mesophases. Furthermore, each of the corresponding C_{60} adducts is miscible in the melts of the precursor malonate ester, and at low dopings, retains the liquid crystalline monotropic mesophases of the precursor.

1. Introduction

C_{60} has received a great deal of interest [1], since it was first discovered [2] and then made available in gram scale quantities [3]. The chemistry of C_{60} is being explored by many research groups throughout the world, and the physical properties of these derivatives are being rigorously investigated by a host of chemists [4], and physicists [5], in a quest to discover technological applications [6], of which many have been proposed in the years since this molecular allotrope of carbon was discovered.

One area of C_{60} research which has not been investigated in detail, is the introduction of mesogenic moieties onto the C_{60} framework [7]. To our knowledge a few publications describe the introduction of calamitic units [8], but there are no examples of the introduction of discotic moieties. Here, we report four C_{60} derivatives in which either the classic alkoxybiphenyl calamitic moiety (**1a–c**) or the hexa-alkoxytriphenylene discotic moiety (**2**) has been introduced onto the C_{60} core (figure 1).

2. Synthesis

The synthesis of compounds **1a–c** was achieved via a series of reactions (scheme 1) starting with the mono-alkylation of commercially available biphenyl-4,4′-diol, under basic conditions (K_2CO_3) with *n*-bromobutane, *n*-bromohexane, and *n*-bromo-octane, respectively, affording white crystalline solids **3a–c**. Similar conditions were then used to perform a second alkylation on the free hydroxyl group of compounds **3a–c**, with the dibromide **4**, affording the malonyl esters **5a–c**. The dibromide **4** was previously synthesized by the bis-esterification of malonyl dichloride with 1-bromoheptan-7-ol. The Bingel cyclopropanation reaction [9] was then carried out under standard conditions with **5a–c** and C_{60} to afford the addends **1a–c**, as brown solids.

The synthesis of compound **2** (scheme 2) was achieved via the alkylation of the monohydroxytriphenylene **6**, with the dibromide **4**, to afford the triphenylene dimer **7**, which underwent a Bingel cyclopropanation with C_{60} to afford **2** as a brown solid.

3. Results and discussion

3.1. *Thermal analysis by polarizing optical microscopy*

The final C_{60} adducts, **1a–c** and **2**, as well as all the novel precursor compounds containing biphenyl (**5a–c**) and discotic (**7**) mesogenic moieties were examined by polarizing optical microscopy (POM), to establish if any displayed thermotropic liquid crystalline behaviour. Of these compounds, only the biphenyl dimers **5a** and **5b** displayed any liquid crystalline mesophase textures, and these were monotropic in nature. The textures were smectic-like and very similar for the monotropic phases M_1 and M_2, but classification has not been possible. The monotropic mesophase texture for **5a** is illustrated in figure 2. Interestingly, the bis-triphenylene derivative **7** does not display a mesophase despite the fact that similar structures, containing ethylene ($-(CH_2)_2-$) to pentylene ($-(CH_2)_5-$) spacers between the two ester moieties do [10]. Furthermore, doping the dimer **7** with

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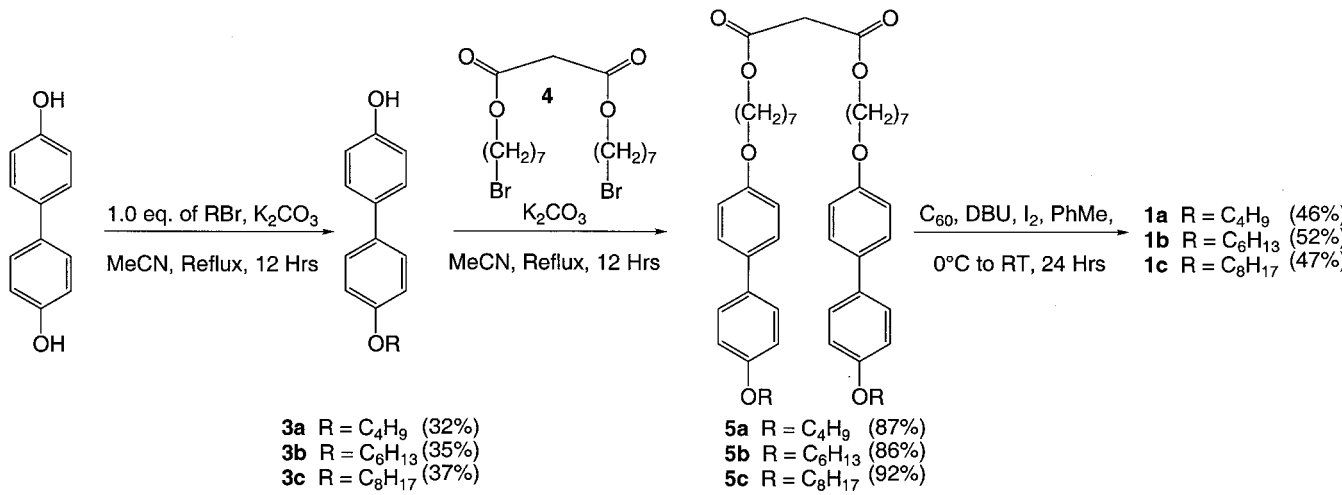
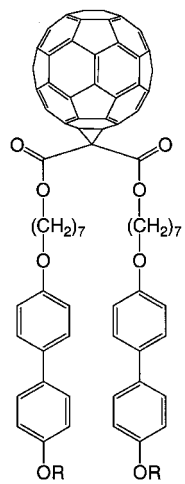


Scheme 1. Synthesis of the bis-biphenyl derivatives **1a–c**.



1a R = C_4H_9
1b R = C_6H_{13}
1c R = C_8H_{17}

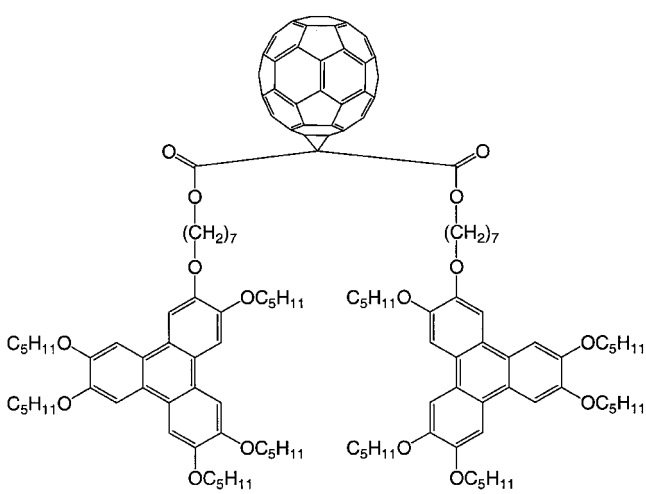


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Figure 1. Molecular structures of the C_{60} adducts.

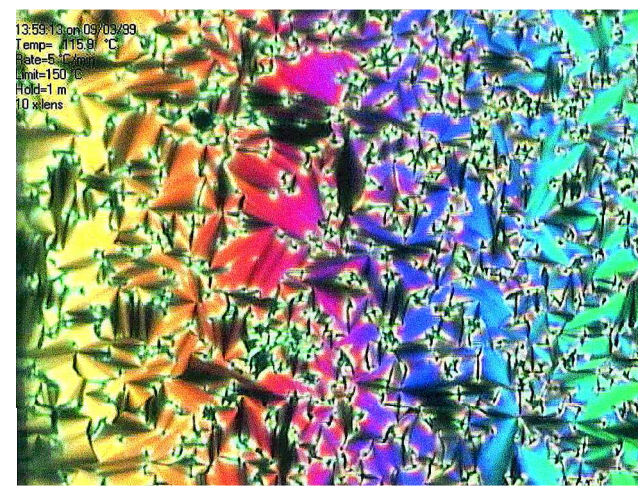
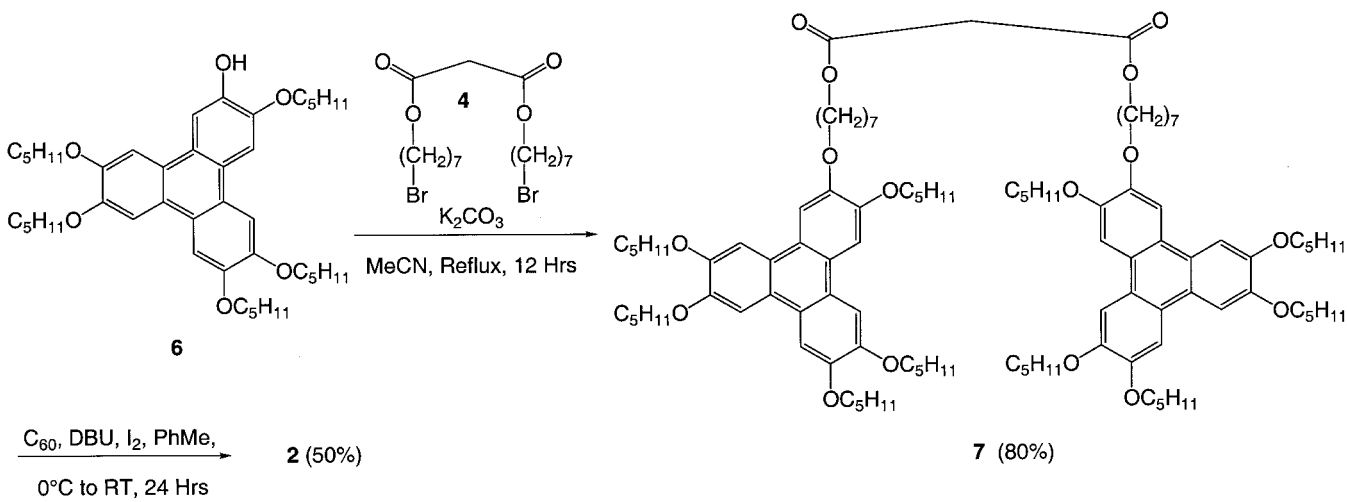


Figure 2. Polarizing optical micrograph of the monotropic mesophase texture of **5a**.

TNF, by a contact preparation experiment using POM, yielded no birefringent liquids. Additionally, doping **2** with TNF induced no mesophase.

3.2. *Differential scanning calorimetry*

The dimers **5a–c** and **7** were thermally characterized by differential scanning calorimetry (DSC). The DSC traces of **5a–c** are illustrated in figure 3, and table 1 summarizes the data. It is worth noting a few points about the thermal analysis of these samples. Firstly, the Cr → I transitions for **5a–c** occur at 128.1, 124.3, and 121.2°C, respectively, as might be expected for a homologous series of compounds with an increasing number of ethylene units in the side chains. However, the thermodynamic data for **5a** and **5b** are not comparable to **5c**. The enthalpy and entropy of melting for **5a** and **5b** are approximately half that of **5c**. This result suggests that



Scheme 2. Synthesis of the bis-triphenylene derivative **2**.

the molecular packing in the solid state is similar for **5a** and **5b**, but different for **5c**, where there must be much increased molecular associations. Thus, **5a** and **5b** display monotropic liquid crystalline mesophases, whereas **5c** does not.

The DSC analysis of compounds **1a–c** and **2** revealed no unusual behaviour. The data are tabulated in table 2.

3.3. *A doping study*

A possible use of the C_{60} moiety is in photovoltaic devices, where it may be doped into conducting liquid crystalline polymers [4–6]. Thus, we have investigated the miscibility of **1b** in the monotropic phases of **5b**. The DSC traces of **1b**, **5b**, **1b**:**5b** 1:6 (w/w), and **1b**:**5b** 1:1 (w/w) are illustrated in figures 4(*a–c*) and the data are tabulated in table 3. Points to note are that the DSC traces of the mixtures are not additive traces of the pure components, and these as such are miscible. More interestingly the 1:6 mixture, figure 4(*c*) still retains the monotropic mesophases, at slightly reduced temperatures and enthalpies, as might be expected for a eutectic mixture. The 1:1 mixture, figure 4(*d*), would still appear to be miscible, but does not have a monotropic mesophase.

4. Conclusions

Four Bingel cyclopropanation C_{60} adducts, three incorporating bis-biphenlene derivatives (**1a–c**) and one incorporating a bis-triphenylene derivative (**2**), have been achieved. None of these derivatives are liquid crystalline. The two shorter chain bis-biphenylene precursor malonate esters (**5a–b**) do, however, possess monotropic mesophases. The longer chain derivative of these two (**5b**) is miscible with the parent C_{60} adduct (**1b**) and at low

Table 1. Enthalpy and entropy data for phase changes in compounds **5a–c** and **7** as identified by DSC analysis. Cr = crystalline phase; M = mesophase; I = isotropic liquid.

Compound	Transition	Onset/°C	Peak/°C	ΔH/kJ mol^{-1}	ΔS/kJ K^{-1} mol^{-1}
5a	Cr → I	128.1	130.1	75.2 ± 11.6	186.8 ± 28.7
	I → M_1	123.7	122.8	−14.7 ± 2.3	−37.0 ± 5.7
	M_1 → M_2	117.5	116.7	−4.7 ± 0.7	−12.0 ± 1.8
	M_2 → Cr	104.5	103.3	−8.9 ± 1.4	−23.7 ± 3.6
5b	Cr → I	124.3	126.4	72.6 ± 10.4	181.7 ± 26.0
	I → M_1	119.6	119.0	−15.4 ± 2.2	−39.3 ± 5.6
	M_1 → M_2	110.9	110.2	−5.6 ± 0.8	−14.7 ± 2.1
	M_2 → Cr	103.5	102.1	−19.8 ± 2.8	−52.9 ± 7.6
5c	Cr_1 → Cr_2	113.5	115.2	5.37 ± 0.3	13.8 ± 0.8
	Cr_2 → I	121.2	124.5	141.4 ± 8.3	355.8 ± 21.0
	I → Cr_2	111.7	110.6	−143.2 ± 8.4	−373.2 ± 22.0
7	Cr_1 → Cr_2	18.4	26.0	16.8 ± 0.4	56.1 ± 1.4
	Cr_2 → I	29.7	33.5	14.9 ± 0.4	48.6 ± 1.2
	I → Cr_2	14.6	13.3	− 32.7 ± 0.8	−114.0 ± 2.9

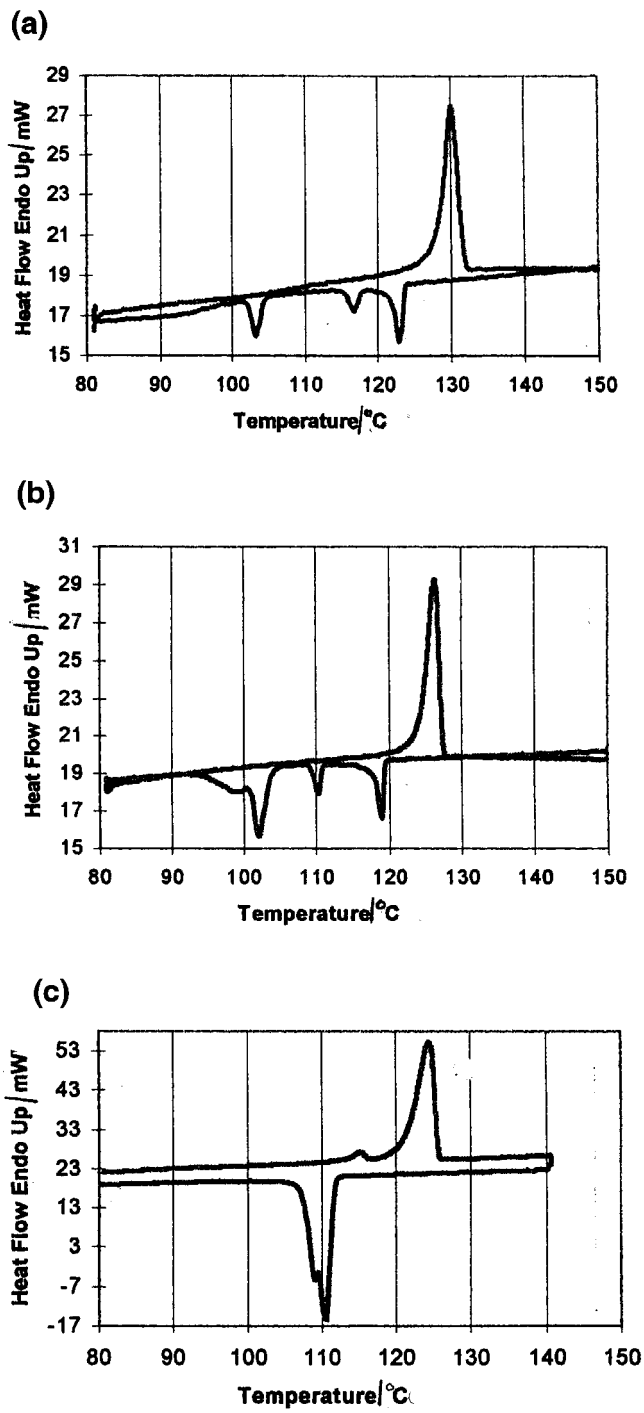


Figure 3. DSC traces (second heating and cooling run) of (*a*) **5a**, (*b*) **5b**, (*c*) **5c**.

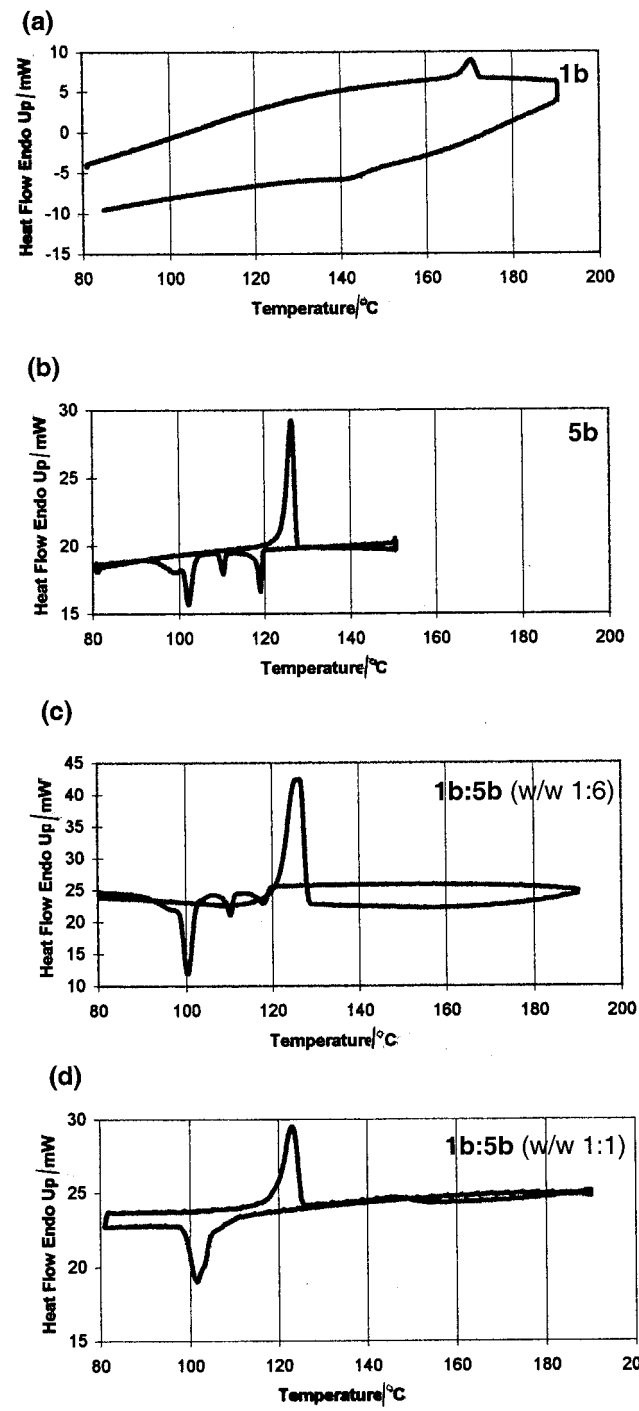


Figure 4. DSC traces (second heating and cooling run) of (*a*) **1b**, (*b*) **5b**, (*c*) **1b** : **5b** (1 : 6 w/w) and **1b** : **5b** (1 : 1 w/w).

dopings (14 wt %) can maintain the monotropic mesophases. It would appear from our results and the literature [8] that to induce liquid crystallinity, at least in calamitic C_{60} adducts, more than one bis-cyclopropanation is required. Thus, we are currently synthesizing multiple adducts of C_{60} bearing the the bis-discotic moieties **7**, in order to induce mesophase behaviour in C_{60}. Such multicomponent mesomorphic C_{60} compounds and liquid crystalline eutectic mixtures containing C_{60} may have potential applications in optoelectronic materials.

Table 2. Enthalpy and entropy data for phase changes in compounds **1a–c** and **2** as identified by DSC analysis. Cr = crystalline phase; M = mesophase; I = isotropic liquid.

Compound	Transition	Onset/°C	Peak/°C	ΔH/kJ mol^{-1}	ΔS/kJ K^{-1} mol^{-1}
1a	Cr → Cr	115.0	122.6	−12.8 ± 0.8	−32.5 ± 2.0
	Cr → I	180.1	183.2	40.1 ± 2.5	88.0 ± 5.5
1b	$Cr_1 \rightarrow Cr_2$	147.8	151.7	−31.0 ± 2.9	−74.7 ± 7.1
	$Cr_2 \rightarrow I$	167.6	170.6	32.6 ± 3.1	73.6 ± 7.0
1c	Cr → I	144.1	148.3	50.6 ± 3.1	121.4 ± 7.4
2	$Cr_1 \rightarrow Cr_2$	68.0	68.6	0.12 ± 0.03	0.35 ± 0.1
	$Cr_2 \rightarrow I$	58.0	58.4	0.21 ± 0.05	0.63 ± 0.2
	I → Cr	34.0	34.5	0.20 ± 0.05	−0.65 ± 0.2

Table 3. Enthalpy and entropy data for phase changes for mixtures of **1b** and **5b** as identified by DSC analysis. Cr = crystalline phase; M = mesophase; I = isotropic liquid.

Mixture **1b**:**5b**	Transition	Onset/°C	Peak/°C	ΔH/kJ mol^{-1}	ΔS/kJ K^{-1} mol^{-1}
1:6	Cr → I	121.7	125.8	75.5 ± 2.4	189.3 ± 6.0
	$I \rightarrow M_1$	119.4	118.0	−4.3 ± 0.1	−11.1 ± 0.4
	$M_1 \rightarrow M_2$	—	110.3	−4.1 ± 0.1	−10.7 ± 0.3
	$M_2 \rightarrow Cr$	102.3	100.3	−29.4 ± 0.9	−78.7 ± 2.5
1:1	Cr → I	167.6	123.2	37.4 ± 2.8	94.4 ± 7.0
	I → Cr	147.8	101.5	−29.0 ± 2.2	−77.5 ± 5.7

5. Experimental

5.1. *General procedures*

All chemicals were purchased from the Aldrich Chemical Co. and were used as received. K_2CO_3 was oven-dried before use. Dry CH_2Cl_2 was prepared by distillation over CaH_2 under a N_2 atmosphere. PhMe was dried over Na/benzophenone and distilled under N_2. Thin layer chromatography was carried out on aluminium sheets coated with Merck 5554 Kieselgel 60 F254. Developed plates were air dried and scrutinized under a UV lamp, and where appropriate developed over iodine. Electron impact mass spectrometry (EIMS) and liquid secondary ion mass spectrometery (LSIMS) were carried out on VG Prospec and VG ZabSpec instruments, respectively. ^{1}H NMR spectra were recorded on a Bruker AC300 spectrometer operating at 300 MHz using the deuteriated solvent as the lock and the residual solvent as the internal reference. ^{13}C NMR spectra were recorded on a Bruker AC300 spectrometer operating at 75 MHz and using the PENDANT pulse sequence. Deuteriated solvent was used as the lock and the residual solvent as the internal reference. Polarizing optical microscopy experiments were carried out using an Olympus BX40 optical microscope with crossed polarizers equipped with a Linkam LT350 hot stage. DSC results were recorded on a Perkin Elmer 7 Series thermal analysis system. All samples were heated and cooled in a double cycle, at a rate of 10°C min^{-1}.

5.2. *4′-Butoxybiphenyl-4-ol (**3a**)*

To a solution of 4,4′-biphenol (3.00 g, 16.1 mmol) dissolved in MeCN (50 ml) was added K_2CO_3 (2.67 g, 19.3 mmol). After slow addition of a solution of 1-bromobutane (2.21 g, 16.1 mmol) in MeCN (5 ml), a $CaCl_2$ guard tube was fitted and the mixture heated under reflux for 12 h. After cooling, the solid residue was filtered off; this consisted of an inorganic component and a white crystalline solid, later characterized as the bis-alkylated product (0.60 g). The filtrate was added to H_2O (100 ml) and extracted with EtOAc (3 × 50 ml). The organic layers were recombined, washed with brine (30 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* yielding a mixture of the mono- and bis-alkylated products. These products were subjected to silica gel column chromatography (hexane/EtOAc, 6/1, mono-alkylated $R_f = 0.21$, bis-alkylated $R_f = 0.79$). 4′-Butoxybiphenyl-4-ol was obtained as a white crystalline solid after concentration *in vacuo* (1.25 g, 32%). *m/z* (EIMS) 242 ([M]$^+$, 68%), 186 ([M-C_4H_9]$^+$, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7$ Hz, 3H), 1.45–1.53 (m, 3H), 1.73–1.82 (m, 2H), 3.98 (t, $J = 7$ Hz, 2H), 6.85–6.97 (m, 4H), 7.38–7.48 (m, 4H). ^{13}C NMR (75 MHz, CD_3OCD_3): $\delta = 14.0$, 19.8, 32.0, 52.2, 68.1, 115.5, 116.4, 127.7, 128.0, 134.1, 157.3, 159.0.

5.3. *4′-Hexyloxybiphenyl-4-ol (**3b**)*

The synthetic and purification procedure for **3a** was followed, using the same molar equivalents based

on 1-bromohexane (2.66 g, 16.1 mmol). Column eluent: hexane/EtOAc, 6/1, mono-alkylated $R_f = 0.43$, bis-alkylated $R_f = 0.96$. 4′-Hexyloxybiphenyl-4-ol was obtained as a white crystalline solid after concentration *in vacuo* (1.51 g, 35%). *m/z* (EIMS) 270 ($[M]^+$, 12%), 187 ($[M\text{-}C_6H_{13}]^+$, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7$ Hz, 3H), 1.35–1.50 (m, 7H), 1.80 (m, 2H), 3.98 (t, $J = 6$ Hz, 2H), 6.85–6.97 (m, 4H), 7.39–7.50 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 25.8, 29.3, 31.6, 56.6, 68.1, 114.8, 115.6, 127.7, 128.0, 133.8, 154.6, 158.3.

5.4. *4′-Octyloxybiphenyl-4-ol (**3c**)*

The synthetic and purification procedure for **3a** was followed, using the same molar equivalents based on 1-bromooctane (3.11 g, 16.1 mmol). Column eluent: hexane/EtOAc, 6/1, mono-alkylated $R_f = 0.44$, bis-alkylated $R_f = 0.94$. 4′-Octyloxybiphenyl-4-ol was obtained as a white crystalline solid after concentration *in vacuo* (1.77 g, 37%). *m/z* (EIMS) 298 ($[M^+]$, 50%), 186 ($[M\text{-}C_8H_{17}]^+$, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7$ Hz, 3H), 1.23–1.50 (m, 11H), 1.73–1.83 (m, 2H), 3.98 (t, $J = 7$ Hz, 2H), 6.85–6.97 (m, 4H), 7.40–7.48 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$, 22.7, 26.1, 29.3, 29.3, 29.4, 31.9, 56.6, 68.1, 114.8, 115.6, 127.7, 128.0, 133.9, 154.6, 158.3.

5.5. *Malonic acid bis(7-bromoheptyl) ester (**4**)*

A solution of malonyl dichloride (1.25 ml, 12.8 mmol) in dry CH_2Cl_2 (5 ml) was added dropwise by syringe to a stirred solution of 7-bromoheptan-1-ol (5 g, 25.6 mmol) and pyridine (2.69 g, 34.9 mmol) in dry CH_2Cl_2 (30 ml) at 0°C under a N_2 atmosphere. The solution turned first dark brown, then violet, then indigo. The reaction mixture was stirred for 22 h allowing it to warm to room temperature, after which time the solvent was removed *in vacuo*. The residue was dissolved in EtOAc (50 ml) and washed with H_2O (2 × 50 ml), then brine (30 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was subjected to silica gel column chromatography (hexane/EtOAc, 10/1, $R_f = 0.38$), yielding a clear viscous oil after concentration *in vacuo* (2.34 g, 40%). *m/z* (EIMS) 458 ($[M]^+$, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$–1.50 (m, 12H), 1.61–1.70 (m, 4H), 1.80–1.90 (m, 4H), 3.36–3.42 (m, 6H), 4.12 (t, $J = 7$ Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.6$, 28.0, 28.4, 32.7, 33.9, 41.7, 56.8, 65.6, 166.7.

5.6. *Malonic acid bis[7-(4′-butoxybiphenyl-4-yloxy)heptyl] ester (**5a**)*

To a solution of 4′-butoxybiphenyl-4-ol (**3a**) (0.46 g, 1.9 mmol) dissolved in MeCN (25 ml) was added K_2CO_3 (2.86 g, 20.7 mmol). After slow addition of a solution of malonic acid bis(7-bromoheptyl) ester (**4**) (0.29 g, 0.63 mmol) in MeCN (25 ml), a $CaCl_2$ guard tube was fitted and the mixture heated under reflux for 24 h. After cooling, H_2O (40 ml) was added to dissolve the inorganic residue, and the reaction mixture extracted with $CHCl_3$ (3 × 20 ml). The organic layers were recombined and washed with brine (20 ml), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* yielding an off-white solid which was purified by silica gel column chromatography ($CHCl_3$, $R_f = 0.20$). Yield of **5a** 87%. *m/z* (LSIMS) 780 ($[M]^+$, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7$ Hz), 1.37–1.52 (m, 20H), 1.53–1.85 (m, 8H), 3.38 (s, 2H), 3.93–4.00 (m, 8H), 4.15 (t, $J = 7$ Hz, 4H), 6.90–6.95 (m, 8H), 7.42–7.47 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.0$, 19.3, 25.8, 26.0, 28.5, 29.0, 29.3, 31.4, 41.7, 56.7, 65.6, 67.8, 67.9, 114.7, 114.8, 127.7, 127.7, 133.3, 133.4, 158.2, 158.3, 166.8.

5.7. *Malonic acid bis[7-(4′-hexyloxybiphenyl-4-yloxy)heptyl] ester (**5b**)*

The synthetic and purification procedure for **5a** was followed, using 4′-hexyloxybiphenyl-4-ol (**3b**) (0.50 g, 1.85 mmol) and malonic acid bis(7-bromoheptyl) ester (**4**) (0.282 g, 0.62 mmol); column eluent $CHCl_3$, $R_f = 0.23$; Yield of **5b** 0.44 g, 86%. *m/z* (LSIMS) 836 ($[M]^+$, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7$ Hz, 6H), 1.29–1.67 (m, 28H), 1.73–1.85 (m, 8H), 3.38 (s, 2H), 3.93–4.00 (m, 8H), 4.13 (t, $J = 7$ Hz, 4H), 6.90–6.95 (m, 8H), 7.42–7.47 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 25.8, 26.0, 28.5, 29.0, 29.2, 29.3, 31.6, 41.7, 56.6, 65.6, 67.9, 68.1, 114.7, 114.8, 127.7, 127.7, 133.3, 133.4, 158.2, 158.3, 166.8.

5.8. *Malonic acid bis[7-(4′-octoxybiphenyl-4-yloxy)heptyl] ester (**5c**)*

The synthetic and purification procedure for **5a** was followed, using 4′-octoxybiphenyl-4-ol (**3c**) (0.50 g, 1.68 mmol) and malonic acid bis(7-bromoheptyl) ester (**4**) (0.256 g, 0.56 mmol); column eluent $CHCl_3$, $R_f = 0.25$; yield of **5c** 0.46 g, 87%. *m/z* (LSIMS) 892 ($[M]^+$, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 7$ Hz, 6H), 1.25–1.71 (m, 36H), 1.72–1.84 (m,8H), 3.38 (s, 2H), 3.94–4.00 (m, 8H), 4.15 (t, $J = 7$ Hz, 4H), 6.90–6.94 (m, 8H), 7.42–7.48 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$, 22.7, 25.8, 26.0, 26.1, 28.5, 29.0, 29.3, 29.3, 29.4, 29.4, 31.9, 41.7, 56.7, 65.6, 67.9, 68.1, 114.7, 114.8, 127.7, 133.3, 133.4, 158.2, 158.3, 166.8.

5.9. *3′H-Cyclopropa[1,9][5,6]-fullerene-C_{60}-IH-3′,3′-dicarbonyldi(4′-butyloxy-4-heptyloxybipheny l) ester (**1a**)*

Solutions of iodine (35.20 mg, 0.14 mmol), 1,8-diazobicyclo(5.4.0)undec-7-ene (DBU) (42.30 mg, 0.28 mmol)

and malonic acid bis[7-(4′-butyloxybiphenyl-4-yloxy)-heptyl] ester (**5a**) (108.4 mg, 0.14 mmol) in degassed, dry PhMe (2, 5 and 2 ml, respectively) were added to a stirred solution of C_{60} (200 mg, 0.28 mmol) in degassed PhMe (200 ml) at 0°C under a N_2 atmosphere. The mixture was allowed to warm to room temperature and stirred overnight, then filtered through a silica gel plug in a sintered glass filter funnel, eluting initially with PhMe to remove excess of C_{60} and then eluting the products with CH_2Cl_2/MeOH (20/1). The second fraction was concentrated *in vacuo* yielding a dark brown solid which was further purified by silica gel column chromatography (hexane/CH_2Cl_2, 1/1, $R_f = 0.32$) to yield product **1a** as a brown solid (95 mg, 46%). *m/z* (LSIMS) 1500 ($[M]^+$, 90%), 720 ($[C_{60}]^+$, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7$ Hz), 1.41–1.55 (m, 16H), 1.73–1.89 (m, 12H), 3.94–4.01 (m, 8H), 4.51 (t, $J = 7$ Hz, 4H), 6.89–6.95 (m, 8H), 7.42–7.47 (m, 8H). No ^{13}C NMR spectral data were recorded due to insufficient solubility in $CDCl_3$, CD_3OCD_3, d_6-DMSO, MeOD or d_6-benzene. Elemental analysis: $C_{109}H_{62}O_8$ requires C 87.29, H 4.17%; found C 87.88, H 4.86%.

5.10. *3′H-Cyclopropa[1,9][5,6]-fullerene-C_{60}-IH-3′,3′-dicarbonyldi(4′-hexyloxy-4-heptyloxybiphenyl) ester (**1b**)*

The synthetic and purification procedure for **1a** was followed, using the same molar equivalents and malonic acid bis[7-(4′-hexyloxybiphenyl-4-yloxy)heptyl] ester (**5b**) (116.2 mg, 0.14 mmol); column eluent: hexane/CH_2Cl_2, 1/1, $R_f = 0.37$; brown solid (112 mg, 52%). *m/z* (LSIMS) 1556 ($[M]^+$, 53%), 720 ($[C_{60}]^+$, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7$ Hz, 6H), 1.30–1.55 (m, 28H), 1.73–1.85 (m, 8H), 3.92–4.00 (m,8H), 4.50 (t, $J = 7$ Hz, 4H), 6.89–6.95 (m, 8H), 7.40–7.43 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 25.8, 26.0, 26.1, 29.0, 29.3, 29.3, 21.7, 56.7, 56.7, 67.4, 67.9, 68.1, 71.7, 114.7, 114.8, 127.7, 127.7, 133.3, 133.4, 139.0, 141.0, 141.9, 142.2, 143.0, 143.0, 143.1, 143.9, 144.6, 144.7, 144.9, 145.0, 145.2, 145.3, 145.4, 158.2, 163.8. Elemental analysis: $C_{113}H_{70}O_8$ requires C 87.23, H 4.54%; found C 86.95, H 4.59%.

5.11. *3′H-Cyclopropa[1,9][5,6]-fullerene-C_{60}-IH-3′,3′-dicarbonyldi(4′-octyloxy-4-heptoxybiphenyl) ester (**1c**)*

The synthetic and purification procedure for **1a** was followed, using the same molar equivalents and malonic acid bis[7-(4′-octoxybiphenyl-4-yloxy)heptyl] ester (**5c**) (124 mg, 0.14 mmol); column eluent: hexane/CH_2Cl_2, 1/1, $R_f = 0.42$; brown solid (105 mg, 47%). *m/z* (LSIMS) 1612 ($[M]^+$, 52%), 720 ($[C_{60}]^+$, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 7$ Hz, 6H), 1.25–1.59 (m, 32H), 1.72–1.90 (m, 12H), 3.93–4.00 (m, 8H), 4.51 (t, $J = 7$ Hz, 4H), 6.89–6.94 (m, 8H), 7.42–7.47 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.3$, 22.9, 26.2, 26.3, 29.2, 29.4, 29.5, 29.5, 29.6, 32.0, 67.6, 68.1, 68.3, 71.8, 114.9, 114.9, 114.9, 119.3, 127.9, 127.9, 133.4, 133.6, 139.2, 141.2, 142.1, 142.4, 143.2, 143.2, 143.3, 144.1, 144.8, 144.8, 144.9, 145.1, 145.3, 145.4, 145.4, 158.2, 163.8. Elemental analysis: $C_{113}H_{70}O_8$ requires C 87.17, H 4.88%; found C 87.19, H 4.86%.

5.12. *2-Hydroxy-3,6,7,10,11-pentapentyloxy-triphenylene (**6**)*

The synthetic route to this product is described in [11]; analysis was as described therein.

5.13. *Malonic acid bis[7-(3,6,7,10,11-pentakis-pentlyloxytriphenylene-2-yloxy)heptyl] ester (**7**)*

To a solution of 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene (882.9 mg, 1.31 mmol) **6** and (200 mg, 0.43 mmol) **4** in MeCN (50 ml) was added K_2CO_3 (180.7 mg, 1.31 mmol). The mixture was heated under reflux for 12 h. After cooling, the solid residue was filtered off and washed with Et_2O. The filtrate was concentrated *in vacuo* and the resulting solid taken up in Et_2O (50 ml) and washed with H_20 (3 × 50 ml) and brine (50 ml). The organic layer was dried ($MgSO_4$), filtered and the filtrate concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2, $R_f = 0.52$) affording a white solid (300 mg, 42%). *m/z* (LSIMS) 1645 ($[M+H]^+$, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7$ Hz, 30H), 1.49–1.51 (m, 52H), 1.71 (m, 4H), 1.98 (m, 4H), 3.49 (s, 2H), 4.15 (t, $J = 6.5$ Hz, 4H), 4.23 (m, 24H), 7.85 (s, 12H).

5.14. *3′H-Cyclopropa[1,9][5,6]-fullerene-C_{60}-IH-3′,3′-dicarbonyldi(2-heptyloxy-3,6,7,10,11-pentapentyloxytriphenylene) ester (**2**)*

Solutions of iodine (35.2 mg, 0.14 mmol), 1,8-diazobicyclo(5.4.0)undec-7-ene (DBU) (42.2 mg, 0.28 mmol) and bis(2-heptyloxy-3,6,7,10,11-pentapentyloxytriphenylene) malonate (**5c**) (124 mg, 0.14 mmol) in degassed dry PhMe (2, 5 and 2 ml, respectively) were added to a stirred solution of C_{60} (200 mg, 0.28 mmol) in degassed PhMe (200 ml) at 0°C under a N_2 atmosphere. The mixture was allowed to warm to room temperature and stirred overnight, then filtered through a silica gel plug in a sintered glass filter funnel, eluting initially with PhMe to remove excess of C_{60} and then eluting the products with CH_2Cl_2/MeOH (20/1). The second fraction was concentrated *in vacuo* yielding a dark brown solid which was further purified by silica gel column chromatography (hexane/CH_2Cl_2, 1/1, $R_f = 0.42$) to yield product (**2**) as a brown solid (105 mg, 47%). (LSIMS) 2364 ($[M]^+$, 52%), 720 ($[C_{60}]^+$, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (m, 30H), 1.40–1.64 (bm, 56H), 1.80–2.00

(bm, 24H), 4.21 (m, 24H), 4.50 (t, $J = 7$ Hz, 4H), 7.80 (overlapping singlets, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 163.6$, 149.0, 148.9, 145.2, 144.9, 144.9, 144.8, 144.6, 144.4, 144.2, 143.5, 142.8, 142.7, 141.9, 141.6, 140.7, 138.8, 123.7, 123.6, 107.6, 107.5, 107.4, 71.6, 69.7, 69.6, 67.2, 29.6, 29.5, 29.4, 29.1, 29.0, 28.6, 28.3, 26.2, 26.0, 22.5, 14.1. Elemental analysis: $C_{163}H_{150}O_{16}$ requires C 82.81, H 6.34%; found C 82.74, H 6.51%.

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