

# Thermotropic behaviour of covalent fullerene adducts displaying 4-cyano-4'-oxybiphenyl mesogens

2 PERKIN

Nicola Tirelli,<sup>\*a</sup> Francesca Cardullo,<sup>b</sup> Tilo Habicher,<sup>b</sup> Ulrich W. Suter<sup>c</sup> and François Diederich<sup>\*b</sup>

<sup>a</sup> Department of Materials, Institute for Biomedical Engineering, ETH-Zentrum, Moussonstr. 18, CH-8044 Zürich, Switzerland

<sup>b</sup> Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, 8092 Zürich, Switzerland

<sup>c</sup> Department of Materials, Institut für Polymere, ETH-Zentrum, Universitätstrasse 6, CH-8092 Zürich, Switzerland

Received (in Cambridge, UK) 28th September 1999, Accepted 16th November 1999

The synthesis of the covalent fullerene derivatives **2**, **3** and **4** with an increasing number (2, 4 and 6) of 4-cyano-4'-oxybiphenyl mesogenic groups is described. The thermotropic behaviour of these compounds was investigated and compared with the liquid crystalline properties of the non-fullerene containing precursors **6** and **9**, and the  $D_{2h}$ -symmetric tetrakis(methano)fullerene **1** bearing eight long alkyl chains instead of mesogenic groups. Tetrakis(methano)fullerene **1** without and methanofullerene **2** with two mesogenic groups only showed an amorphous phase with glass transition temperatures  $T_g = 27$  and  $50$  °C, respectively. Samples of hexakis(methano)-fullerene **3** with four mesogenic groups obtained by slow crystallisation gave a nematic mesophase on the first heating (Cr 85 N 157 I) that disappeared after isotropisation. No mesogenic behaviour could be recovered for **3** in successive thermal cycles. Unlike **3**, the fullerene dendrimer **4** with six 4-cyano-4'-oxybiphenyl groups showed mesogenic properties independent of the thermal history: low intensity first order phase transitions were recorded in the DSC and confirmed by optical microscopy analysis. Owing to the lack of a characteristic texture, the unambiguous identification of the mesophase was not possible. The effect of the introduction of mesogens onto  $C_{60}$  on the stability of the mesophases and on the preservation of liquid crystalline properties is discussed with respect to the number of mesogenic moieties per fullerene sphere.

## Introduction

The supramolecular chemistry of  $C_{60}$  and its covalent derivatives<sup>1</sup> is receiving, at present, considerable attention due to the peculiar physical and chemical properties of the fullerene sphere, such as electronic absorption bands which extend throughout the entire UV/VIS spectral region, strong electron acceptor character, ability to sensitise the formation of singlet oxygen, and conductivity upon doping with alkali metals.<sup>2</sup> An important aspect for practical applications, such as use in optoelectronic devices, is that the fullerene units may be well-ordered in molecular assemblies and supramolecular arrays.<sup>3,4</sup> Particularly attractive is the possibility of conjugating the fullerene with a source of liquid crystalline organisation,<sup>5,6</sup> which could allow i) study of the influence of an orientation effect on the physical properties of this unique chromophore, ii) correlation of the mesomorphic properties of fullerene adducts with their chemical and geometrical characteristics, such as degree and pattern of addition and iii) development of novel materials for use in liquid-crystal technology.

In the present paper, we report one of the first contributions<sup>6</sup> on the thermotropic behaviour of  $C_{60}$  derivatives. In our laboratories, highly symmetric methanofullerene adducts, bearing long alkyl chains without (**1**) or with (**2**, **3** and **4**) mesogenic groups (Fig. 1), were synthesised, and their liquid crystallinity investigated by means of differential scanning calorimetry (DSC) and optical microscopy.

## Results and discussion

### Synthesis

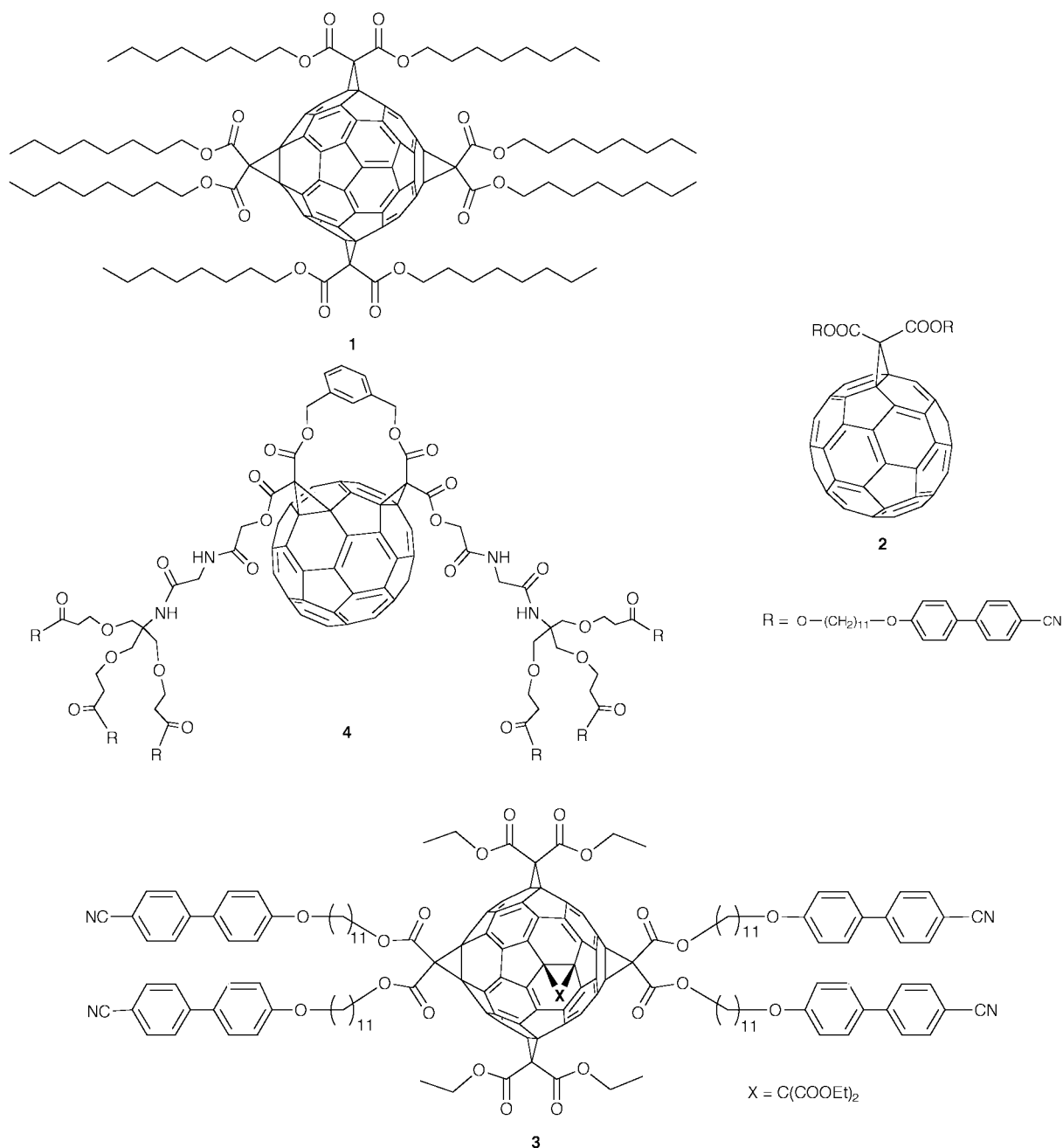
The  $D_{2h}$ -symmetric tetrakis(methano)fullerene **1** displaying

eight alkyl chains was prepared as described earlier.<sup>7</sup> For the synthesis of **2** and **3**, malonate **6** was synthesised in 32% yield by esterification of alcohol **5**<sup>8</sup> with malonyl dichloride in the presence of pyridine (Scheme 1). The corresponding 2-iodo-malonate, prepared *in situ* from **6** and  $I_2$ , was reacted in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in a *Bingel*-type reaction<sup>9-11</sup> with  $C_{60}$  or tetrakis(methano)fullerene **7**<sup>7</sup> to yield **2** and **3**, respectively. Attempts to transform **7** with **5** into the corresponding tetrakis-adduct bearing eight 4-cyano-4'-oxybiphenyl units failed under the transesterification conditions which yielded **1** ( $Cs_2CO_3$ , THF).

In the synthesis of fullerene dendrimer **4**, the dendritic wedge **9** was obtained in 68% yield by reacting the tris(acyl halide), prepared from triacid **8**<sup>10</sup> with the mesogenic alcohol **5** (Scheme 2). Deprotection of the amine function at the focal point gave dendron **10**. Surprisingly, the coupling of this wedge with the fullerene core **13** failed, presumably due to the steric hindrance of the amine group of the dendron. The introduction of a glycine spacer at the focal point of the dendritic wedge was achieved under peptide coupling conditions using *O*-(benzotriazol-1-yl)- $N,N,N',N'$ -tetramethyluronium tetrafluoroborate (TBTU) in the presence of  $NEt_3$ . Deprotection of the resulting **11** with HBr in acetic acid gave the more reactive dendron **12** in only 33% yield, owing to some decomposition of the product under the reaction conditions. Finally, coupling of **12** with fullerenedicarboxylic acid **13**<sup>10</sup> using dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBt) afforded **4** in 68% yield.

### Thermotropic behaviour of the fullerene derivatives

Self-organised multilayer films of fullerenes were reported to form from long-chain alkyl esters.<sup>12</sup> We therefore investigated



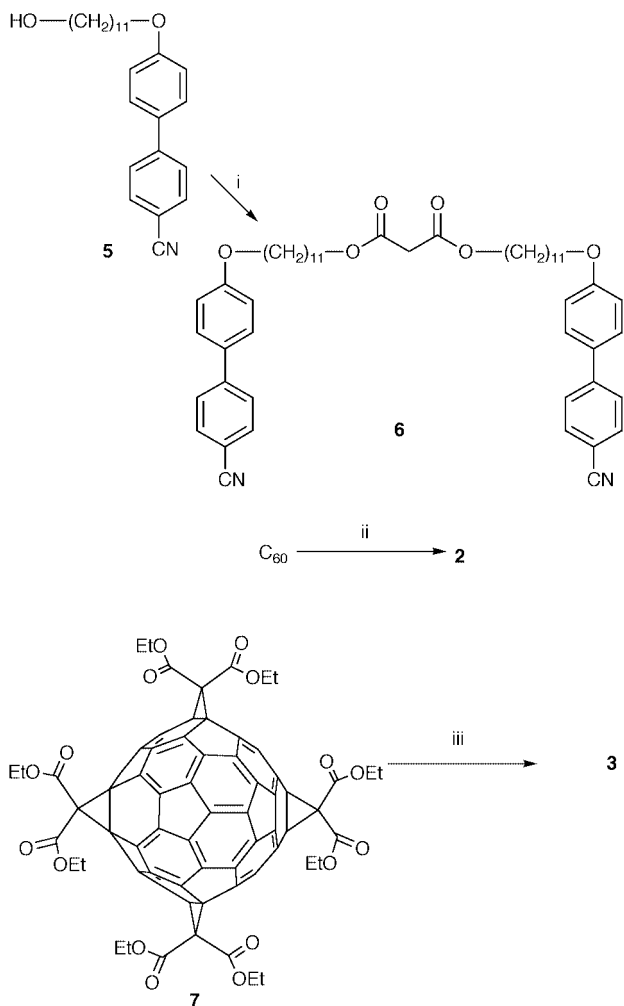
**Fig. 1** Molecular structures of  $C_{60}$  adducts investigated. In **3**, the sixth addend  $C(COOEt)_2$  on the backface of the carbon sphere in an *equatorial* position of the pseudo-octahedral addition pattern has been omitted for clarity.

the liquid crystalline behaviour of the  $D_{2h}$ -symmetric tetrakis(methano)fullerene **1**. It was thought that **1** would possibly arrange in stacks of fullerene spheres with radially organised alkyl chains. However, **1** did not show any well-defined three-dimensional organisation; even after annealing at different temperatures, only an amorphous phase with a glass transition temperature ( $T_g$ ) of 27 °C was obtained. This result, together with the absence in the literature of any evidence for fullerene-based mesogenic self-organisation, suggested that for achieving an orientation effect,  $C_{60}$  units should be coupled to well-known mesogenic groups.

Fullerene-benzoate adducts were shown to only lead to non-crystalline materials.<sup>13</sup> On the other hand, fullerene derivatives bearing cholesterol groups were reported to exhibit thermotropic liquid-crystalline properties.<sup>6</sup> In our work, the influence of the 4-cyano-4'-oxybiphenyl mesogen on the thermotropic properties of the novel fullerene derivatives was investigated. The mesogenic precursor **6** showed a distinct monotropic liquid-crystalline behaviour on cooling, exhibiting a nematic

phase (N) between an isotropic (I) and a crystalline one (Cr) (I 80 N 58 Cr), while on heating no mesophase was recorded (Cr 105 I).

The fullerene derivatives **2** and **3** exhibited markedly different phase behaviours. The monoadduct **2** showed only a glass transition temperature at  $T_g = 50$  °C, independent of the thermal and solidification history. On the other hand, samples of **3** obtained by very slow crystallisation from a  $CH_2Cl_2$ -hexane mixture gave a nematic mesophase on the first heating (Cr 85 N 157 I), that disappeared after isotropisation to leave a completely amorphous material with a  $T_g = 107$  °C; no mesogenic behaviour could be recovered. The first heating showed two features suggesting that the starting material itself was not completely crystalline: i) the  $\Delta H$  value of the crystal-nematic transition was too low ( $6.1 \text{ J g}^{-1}$ ,  $2.2 \text{ mJ mol}^{-1}$ ) compared to that of the nematic-isotropic one ( $9.5 \text{ J g}^{-1}$ ,  $3.4 \text{ mJ mol}^{-1}$ ); ii) a  $T_g$  at 110 °C was observed; above this temperature, the amorphous material too could be organised into the nematic phase.



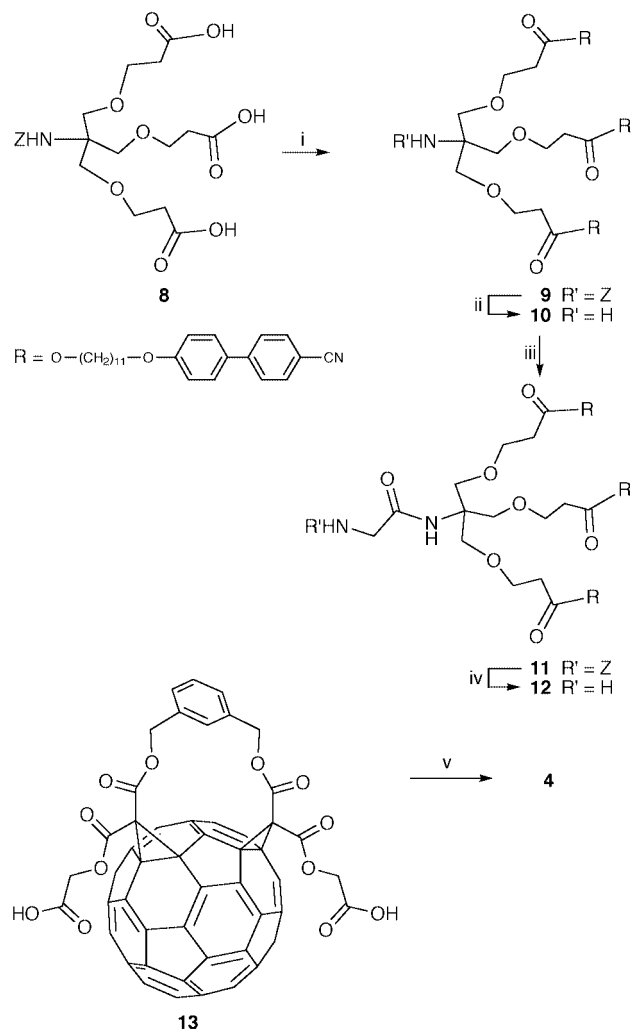
**Scheme 1** Synthesis of methanofullerene **2** and hexakis(methano)-fullerene **3**. i,  $(\text{ClOC})_2\text{CH}_2$ , pyridine,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 3 h, 32%; ii, **6**,  $\text{I}_2$ , DBU, PhMe, 5 h, 45%; iii, **6**,  $\text{I}_2$ , DBU,  $\text{CH}_2\text{Cl}_2$ , 2 h, 9%.

A first tentative interpretation could link these observations to the number of mesogenic groups per fullerene: dense packing of the mesogens in **2** is likely to be hindered by the dimensions of the  $\text{C}_{60}$  moieties. In **3**, with a double density of mesogenic groups and a higher degree of functionalisation on the sphere, this effect is clearly weaker, and a slow crystallisation process can give rise to ordered mesophases.

In order to test the influence of increased mesogen density, the dendritic fullerene derivative **4** was studied. The precursor **9** showed a nematic phase between  $48$  and  $63^\circ\text{C}$  (Fig. 2a), recovered upon cooling below  $58^\circ\text{C}$ , without giving rise to a crystalline phase. In successive thermal cycles, the heating gave a broad exothermic transition between  $23$  and  $42^\circ\text{C}$ , that led to a reproducible crystalline content (about 20%, assuming a starting content of 100%). The other transitions remained unchanged (Fig. 3).

The phase behaviour of **4** was more puzzling; the starting material was obtained only as a mostly amorphous solid (almost no birefringence), with a glass transition temperature at  $T_g = 36^\circ\text{C}$ . On the other hand, repeated heating-cooling cycles showed the development of first-order transitions: a broad one at  $T = 33^\circ\text{C}$ , upon heating, and at  $T = 16^\circ\text{C}$  upon cooling ( $\Delta H = 4.9 \text{ J g}^{-1}$ ,  $1.2 \text{ mJ mol}^{-1}$ ) was easily recorded in the DSC (Fig. 4).

Optical microscope analysis showed the existence of a second transition (at  $T = 70^\circ\text{C}$  on heating and  $T = 45^\circ\text{C}$  on cooling) and identified it as an isotropisation; DSC analysis did not unambiguously confirm it, due to its extremely low intensity. The phase present at intermediate temperatures showed

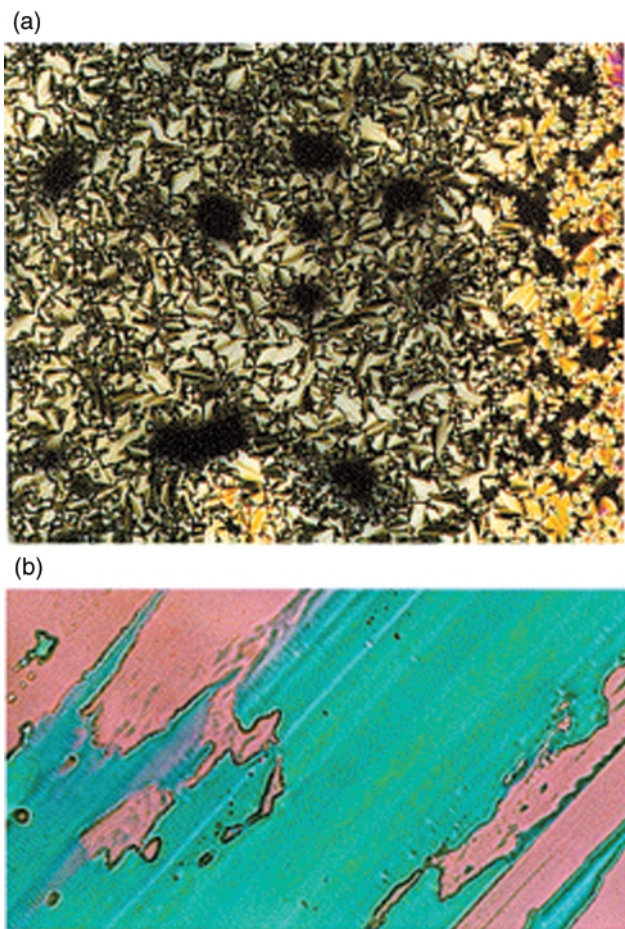


**Scheme 2** Synthesis of bis(methano)fullerene **4**. i, 1)  $\text{SOCl}_2$ ,  $50^\circ\text{C}$ , 2 h; 2) **5**,  $\text{CH}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ , 24 h, 68%; ii,  $\text{HBr-HOAc}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ , 4 h, 52%; iii, Z-glycine (Z = benzyloxycarbonyl), TBTU,  $\text{NEt}_3$ , THF,  $0$  to  $20^\circ\text{C}$ , 15 h, 62%; iv,  $\text{HBr-HOAc}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ , 5 h, 33%; v, **12**, DCC, HOBT, THF,  $0$  to  $20^\circ\text{C}$ , 30 h, 68%.

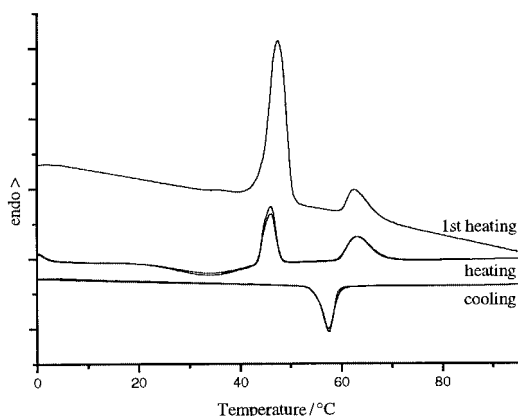
liquid-like rheology and birefringence; however, a precise identification was not possible, due to the lack of characteristic textures; shear or pressure did not change the sample appearance. A picture of the birefringent material before isotropisation is shown in Fig. 2b. Unlike the other fullerene derivatives functionalised with mesogenic groups reported herein, for **4** the formation of mesophases was shown to be possible independent of the thermal history of the sample. However, the very low intensities of the transitions indicated the mainly amorphous character of this material.

## Conclusions

The novel fullerene adducts **3** and **4** exhibit mesogenic properties. Comparison with precursors **6** and **9**, respectively, or similar compounds with (**2**) or without (**1**) mesogenic moieties showed that the formation of liquid-crystalline phases could only be achieved with well-known mesogens and an appropriate balance of their number per fullerene unit. As a general indication, the  $\text{C}_{60}$  structure was shown neither to directly exhibit a mesogenic order, nor to enhance the one coming from otherwise active mesogens. Indeed, a certain tendency to increase the amorphous character on linking the  $\text{C}_{60}$  spheres to liquid-crystalline precursors was observed. It is probable that this is a consequence of the poorer order within the mesophases. Finally, the possibility of densely packing the mesogens was



**Fig. 2** Cross-polarised microscopy (25 $\times$ ) pictures obtained from samples of (a) dendritic wedge **9** at 55  $^{\circ}\text{C}$  and (b) fullerene dendrimer at 40  $^{\circ}\text{C}$ , after shear.



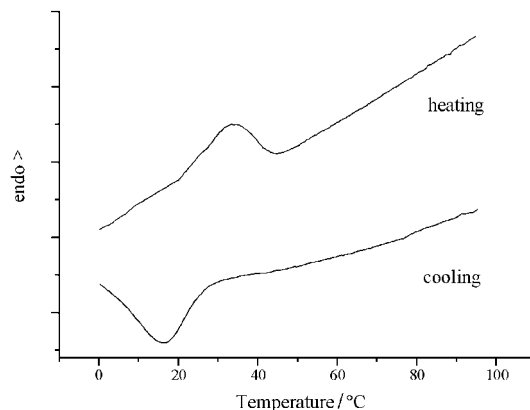
**Fig. 3** DSC traces on heating and cooling of **9**.

shown to be more important than symmetry considerations of the isolated molecules for the preservation of liquid-crystalline order.

## Experimental

### General

Reagents and solvents were purchased reagent-grade and used without further purification, except for THF which was distilled in the presence of Na. Fullerene soot extract was purchased from MER Corporation, Tucson, Arizona (AZ) 85706, USA. All reactions were performed in standard glassware. Evaporation and concentration *in vacuo* were done at water aspirator pressure, and compounds were dried at  $10^{-2}$  Torr. Column



**Fig. 4** DSC traces on heating and cooling of **4**.

chromatography (CC): SiO<sub>2</sub> 60 (230–400 mesh, 0.040–0.063 mm) from E. Merck. TLC glass plates coated with SiO<sub>2</sub> 60 F<sub>254</sub> from E. Merck; visualisation by UV light. UV/Vis spectra: Varian Cary-5 spectrophotometer. Melting points: Büchi Melting Point B-540, uncorrected. IR spectra: Perkin-Elmer 1600-FTIR. NMR Spectra: Bruker AM 500 and Varian Gemini 300 or 200 spectrometers at 298 K, with solvent peaks as reference. FABMS: VG ZAB 2SEQ instrument, 3-nitrobenzyl alcohol as matrix; MALDI-TOFMS: measured with reflectron detection in the positive or negative ion mode, acceleration voltage 15–20 kV, on a Bruker REFLEX spectrometer; matrices are 2,5-dihydroxybenzoic acid (DBH, 0.1 M in MeCN–EtOH–H<sub>2</sub>O 50:45:5),  $\alpha$ -cyano-4-hydroxycinnamic acid (CCA, 0.1 M in MeCN–EtOH–H<sub>2</sub>O 50:45:5) or anthracene-1,8,9-triol (dithranol, 0.05 M in CHCl<sub>3</sub>–MeOH 1:1). Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich. The thermal characterisation was accomplished using a Perkin-Elmer DSC 7 calorimeter at 10  $^{\circ}\text{C min}^{-1}$  both on heating and cooling. A Zeiss microscope with Neofluan (25 $\times$ ) lens, Mettler FP80 temperature controller and FP82 hot stage was used for the microscope analysis.

### Bis[11-(4'-cyanobiphenyl-4-yloxy)undecyl] 1,2-methano[60]-fullerene-61,61-dicarboxylate (**2**)

To a solution of C<sub>60</sub> (216 mg, 0.300 mmol), I<sub>2</sub> (93.5 mg, 0.368 mmol) and **6** (200 mg, 0.250 mmol) in PhMe (110 ml) at 20  $^{\circ}\text{C}$  was added DBU (127 mg, 0.837 mmol). After 5 h, flash chromatography (SiO<sub>2</sub>, PhMe–hexane 3:1, then PhMe) yielded a wine-red solution. Evaporation of the solvents and drying gave **2** (172 mg, 45%) as a dark-red solid:  $T_g = 50$   $^{\circ}\text{C}$  (DSC) [Found: C, 87.84; H, 3.98; N, 1.85; O, 6.33. Calc. for C<sub>111</sub>H<sub>60</sub>N<sub>2</sub>O<sub>6</sub> (1517.72): C, 87.71; H, 4.01; N, 1.78; O, 6.20%];  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 2222 (CN), 1739 (C=O);  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 259 (124400), 326 (sh, 46100), 393 (sh, 3300), 401 (sh, 1950), 412 (sh, 1200), 426 (1200), 491 (1300), 688 (200);  $\delta_{\text{H}}$  (200 MHz, CDCl<sub>3</sub>) 1.21–1.62 (28 H, m), 1.63–1.98 (8 H, m), 4.00 (4 H, t,  $J$  6.4), 4.50 (4 H, t,  $J$  6.4), 6.98 (4 H, dm,  $J$  8.7), 7.52 (4 H, dm,  $J$  8.7), 7.60–7.72 (8 H, m);  $\delta_{\text{C}}$  (125.8 MHz, CDCl<sub>3</sub>) 25.92, 26.00, 28.54, 29.13, 29.18, 29.31, 29.43, 29.50, 52.50, 67.35, 68.10, 71.68, 110.01, 115.07, 118.93, 126.96, 128.23, 131.16, 132.44, 138.89, 140.82, 141.80, 142.07, 142.86, 142.89, 142.96, 143.75, 144.48, 144.54, 144.56, 144.74, 145.04, 145.07, 145.13, 145.16, 145.33, 159.75, 163.50;  $m/z$  (FABMS) 1517 (M<sup>+</sup>, 100), 720 (C<sub>60</sub><sup>+</sup>, 15%).

### Octaethyl tetrakis[11-(4'-cyanobiphenyl-4-yloxy)undecyl] 1,2:18,36:22,23:27,45:31,32:55,60-hexakis(methano)[60]-fullerene-61,61,62,62,63,63,64,64,65,65,66,66-dodecarboxylate (**3**)

To a solution of tetrakis-adduct **7** (10.0 mg, 7.39  $\mu\text{mol}$ ), I<sub>2</sub> (12.2 mg, 0.048 mmol) and **6** (35.4 mg, 0.044 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (21

ml) was added DBU (16.3 mg, 0.107 mmol). After stirring the mixture for 2 h, it was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with sat. aq. NaCl solution (3×) and then dried (MgSO<sub>4</sub>). Flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) followed by preparative TLC (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) afforded a bright yellow solution of the product. Concentration gave **3** (2 mg, 9%) as a yellow solid: [C 85 N 157 I] (DSC);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2222 (CN), 1750 (C=O);  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 282 (109000), 338 (sh, 32900), 381 (sh, 4700), 437 (sh, 630), 450 (sh, 310);  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 1.21–1.40 (48 H, m), 1.31 (24 H, t, *J* 7.1), 1.41–1.52 (8 H, m), 1.63–1.73 (8 H, m), 1.76–1.83 (8 H, m), 3.99 (8 H, t, *J* 6.5), 4.24 (8 H, t, *J* 6.8), 4.32 (16 H, q, *J* 7.1), 6.98 (8 H, dm, *J* 8.7), 7.51 (8 H, dm, *J* 8.7), 7.63 (8 H, dm, *J* 8.6), 7.68 (8 H, dm, *J* 8.6);  $\delta_{\text{C}}$  (125.8 MHz, CDCl<sub>3</sub>) 14.05, 25.83, 26.07, 28.45, 29.21, 29.26, 29.42, 29.51, 29.54, 29.56, 45.42, 45.54, 62.80, 66.99, 68.21, 69.12, 69.18, 110.13, 115.12, 119.05, 127.07, 128.31, 131.30, 132.56, 141.15, 141.17, 145.29, 145.80, 159.85, 163.77, 163.80, 163.92; *m/z* (FABMS) (M<sup>+</sup>, 100), 2788 ([M – C(CO<sub>2</sub>Et)<sub>2</sub>]<sup>+</sup>, 9), 2582 ([M – O(CH<sub>2</sub>)<sub>11</sub>OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>CN]<sup>+</sup>, 8), 2150 ([M – C(CO<sub>2</sub>(CH<sub>2</sub>)<sub>11</sub>OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>]<sup>+</sup>, 5%).

**Bis{[({[tris[2-([11-(4'-cyanobiphenyl-4-yloxy)undecyloxy]carbonyl)ethoxy)methyl]methyl]amino)carbonyl]methyl}endo,endo-(*m*-phenylenedimethyl) 1,2:7,21-bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate (**4**)**

To a stirred solution of **13**<sup>10</sup> (12.70 mg, 0.0111 mmol), **12** (40 mg, 0.0278 mmol) and HOBt (6.1 mg, 0.0445 mmol) in THF (10 ml) was added DCC (9.2 mg, 0.0445 mmol) at 0 °C. The resulting mixture was allowed to warm to 20 °C over a period of 5 h. After a total of 30 h the solvent was removed *in vacuo* and the resulting residue purified by column chromatography (SiO<sub>2</sub>, hexane–EtOAc 3:1) followed by gel permeation chromatography (Biobeads SX-1, PhMe) to give **4** (30 mg, 68%) as a red glassy solid:  $\nu_{\max}$ (neat)/cm<sup>-1</sup> 2224 (CN), 1733 (C=O), 1667 (C=O);  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 267 (157400), 297 (187400), 375 (11600), 411 (sh, 3750), 437 (3350), 464 (2800);  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 1.27–1.37 (72 H, m), 1.42–1.50 (12 H, m), 1.58–1.63 (12 H, m), 1.77–1.82 (12 H, m), 2.53 (12 H, t, *J* 6.2), 3.67 (12 H, t, *J* 6.2), 3.68 (12 H, s), 3.96 (4 H, d, *J* 5.0), 3.99 (12 H, t, *J* 6.6), 4.07 (12 H, t, *J* 6.8), 4.82 (2 H, d, *J*<sub>AB</sub> 14.9), 4.88 (2 H, d, *J*<sub>AB</sub> 14.9), 5.40 (2 H, d, *J*<sub>AB</sub> 13.1), 5.90 (2 H, d, *J*<sub>AB</sub> 13.1), 6.42 (2 H, s), 6.96–7.00 (14 H, m), 7.33–7.35 (2 H, m), 7.39–7.43 (1 H, m), 7.50–7.53 (12 H, m), 7.57 (1 H, br s), 7.61–7.69 (24 H, m);  $\delta_{\text{C}}$  (125.8 MHz, CDCl<sub>3</sub>) 25.92, 26.04, 28.64, 29.23, 29.27, 29.38, 29.51 (2×), 29.54, 34.79, 42.53, 48.70, 60.11, 64.56, 64.79, 66.81, 66.89, 67.99, 68.18, 69.19, 70.39, 110.08, 115.11, 119.04, 124.49, 127.05, 127.17, 128.30, 128.72, 131.27, 132.54, 134.26, 136.00, 136.46, 136.70, 138.22, 140.13, 141.08, 141.34, 142.28, 142.58, 143.41, 143.64, 143.83, 144.08, 144.25, 144.31, 144.47, 144.71, 145.01, 145.26, 145.29, 145.32, 145.43, 145.57, 145.66, 145.73, 145.80, 146.14, 147.39, 147.54, 147.59, 148.43, 159.82, 161.73, 162.84, 165.84, 167.68, 171.69; *m/z* (MALDI-TOFMS) 3981 (M<sup>+</sup>, [<sup>13</sup>C<sub>3</sub><sup>12</sup>C<sub>249</sub>H<sub>236</sub>O<sub>36</sub>N<sub>10</sub>]<sup>+</sup>; calc. 3981).

**Bis(4'-cyanobiphenyl-4-yloxyundecyloxy) malonate (**6**)**

Malonyl dichloride (193 mg, 1.369 mmol) was added to a solution of **5**<sup>8</sup> (1.00 g, 2.736 mmol) and pyridine (216 mg, 2.730 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) at 0 °C. After stirring at 20 °C for 3 h, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with 0.1 M HCl solution (2×), sat. aq. NaHCO<sub>3</sub> solution (2×), sat. aq. NaCl solution (2×), H<sub>2</sub>O, dried (MgSO<sub>4</sub>) and the solvent evaporated. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) gave **6** (353 mg, 32%) as a white solid: mp 105 °C (DSC) [Found: C, 76.38; H, 8.01; N, 3.53; O, 12.27. Calc. for C<sub>51</sub>H<sub>62</sub>N<sub>2</sub>O<sub>6</sub> (799.06): C, 76.66; H, 7.82; N, 3.51; O, 12.01%];  $\nu_{\max}$ (neat)/cm<sup>-1</sup> 2222 (CN), 1749 (C=O);  $\delta_{\text{H}}$  (200 MHz, CDCl<sub>3</sub>) 1.21–1.58 (28 H, m), 1.58–1.75 (4 H, m), 1.75–1.96 (4 H, m), 3.39 (2 H, s), 4.02 (4 H, t, *J* 6.4), 4.16 (4 H, t, *J* 6.9), 7.01 (4 H, dm, *J* 8.7), 7.55 (4 H, dm, *J* 8.7),

7.62–7.74 (8 H, m);  $\delta_{\text{C}}$  (50.3 MHz, CDCl<sub>3</sub>) 25.67, 25.93, 28.34, 29.10, 29.26, 29.36, 41.61, 65.60, 68.13, 110.04, 115.12, 119.12, 127.09, 128.36, 131.31, 132.61, 145.34, 159.91, 166.80; *m/z* (FABMS) 799 (M<sup>+</sup>, 100%).

**Benzyl *N*-tris[2-([11-(4'-cyanobiphenyl-4-yloxy)undecyloxy]carbonyl)ethoxy)methyl]methylcarbamate (**9**)**

A solution of **8** (1.00 g, 2.12 mmol) in SOCl<sub>2</sub> (5 ml) was stirred at 50 °C for 2 h. After evaporation to dryness, a solution of **5** (3.49 g, 9.55 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (80 ml) was added and the mixture stirred at 20 °C for 24 h. Column chromatography (SiO<sub>2</sub>, PhMe–EtOH 95:5) yielded **9** (2.20 g, 68%) as a white solid: [C 48 N 63 I] (DSC) [Found: C, 73.94; H, 7.83; N, 3.69. Calc. for C<sub>93</sub>H<sub>116</sub>N<sub>4</sub>O<sub>14</sub> (1513.98): C, 73.78; H, 7.72; N, 3.70; O, 14.80%];  $\nu_{\max}$ (neat)/cm<sup>-1</sup> 2220 (CN), 1729 (C=O);  $\delta_{\text{H}}$  (200 MHz, CDCl<sub>3</sub>) 1.27–1.52 (42 H, m), 1.57–1.69 (6 H, m), 1.76–1.89 (6 H, m), 2.55 (6 H, t, *J* 6.4), 3.68 (6 H, s), 3.70 (6 H, t, *J* 6.2), 4.02 (6 H, t, *J* 6.2), 4.08 (6 H, t, *J* 6.6), 5.07 (2 H, s), 5.28 (1 H, s), 6.96–7.05 (6 H, m), 7.32–7.40 (5 H, m), 7.50–7.58 (6 H, m), 7.63–7.73 (12 H, m);  $\delta_{\text{C}}$  23.42, 23.58, 26.15, 26.79, 26.92, 27.04, 32.53, 56.31, 62.24, 63.70, 64.43, 65.77, 67.04, 107.73, 112.78, 116.74, 124.74, 125.57, 125.98, 126.11, 128.96, 130.23, 134.46, 142.99, 152.80, 157.56, 169.28; *m/z* (FABMS) 1514 (M<sup>+</sup>, 35), 1470 ([M – CO<sub>2</sub>]<sup>+</sup>, 100), 1406 ([M – PhCH<sub>2</sub>O]<sup>+</sup>, 50%).

**Tris[2-([11-(4'-cyanobiphenyl-4-yloxy)undecyloxy]carbonyl)ethoxy)methyl]methylamine (**10**)**

To a solution of **9** (1.30 g, 0.859 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added HBr in acetic acid (30%, 3 ml). The resulting mixture was stirred at 20 °C for 4 h, quenched with sat. aq. NaHCO<sub>3</sub> (75 ml) and extracted twice with CH<sub>2</sub>Cl<sub>2</sub> (150 ml). The organic layers were dried (MgSO<sub>4</sub>), filtered and evaporated to dryness. The resulting residue was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>–MeOH–PhMe 20:1:1) to give **10** (0.62 g, 52%) as a white solid: mp 71 °C [Found: C, 74.09; H, 8.12; N, 3.98. Calc. for C<sub>85</sub>H<sub>110</sub>N<sub>4</sub>O<sub>12</sub> (1379.84): C, 73.99; H, 8.04; N, 4.06; O, 13.91%];  $\nu_{\max}$ (neat)/cm<sup>-1</sup> 2228 (CN), 1732 (C=O);  $\delta_{\text{H}}$  (200 MHz, CDCl<sub>3</sub>) 1.27–1.53 (42 H, m), 1.57–1.71 (6 H, m), 1.76–1.89 (6 H, m), 2.57 (6 H, t, *J* 6.4), 3.34 (6 H, s), 3.71 (6 H, t, *J* 6.5), 4.02 (6 H, t, *J* 6.6), 4.09 (6 H, t, *J* 6.9), 6.97–7.04 (6 H, m), 7.51–7.58 (6 H, m), 7.63–7.73 (12 H, m);  $\delta_{\text{C}}$  (75.5 MHz, CDCl<sub>3</sub>) 25.95, 26.10, 28.69, 29.29, 29.32, 29.45, 29.58, 35.14, 56.13, 64.80, 67.02, 68.31, 72.92, 110.27, 115.32, 119.32, 127.31, 128.55, 131.51, 132.80, 145.56, 160.11, 171.98; *m/z* (FABMS) 1381 (MH<sup>+</sup>, 100%).

**Benzyl *N*-[tris[2-([11-(4'-cyanobiphenyl-4-yloxy)undecyloxy]carbonyl)ethoxy)methyl]methylamino]carbonyl]methylcarbamate (**11**)**

To a solution of **10** (0.50 g, 0.362 mmol) and *Z*-glycine (*Z* = benzyloxycarbonyl; 84 mg, 0.399 mmol) in THF (10 ml) were added TBTU (128 mg, 0.399 mmol) and NEt<sub>3</sub> (44 mg, 0.435 mmol). The resulting suspension was stirred at 0 °C for 1 h and then allowed to warm to 20 °C over a period of 5 h. After a total of 15 h the solvent was removed *in vacuo* and the resulting residue purified by multiple column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>–MeOH 99:1; then SiO<sub>2</sub>, PhMe–EtOAc 5:1) to give **11** (0.35 g, 62%) as a white solid: mp 59 °C [Found: C, 71.43; H, 7.94; N, 4.21. Calc. for C<sub>95</sub>H<sub>119</sub>N<sub>5</sub>O<sub>15</sub>·2EtOH (1663.17): C, 71.50; H, 7.94; N, 4.21; O, 16.35%];  $\nu_{\max}$ (neat)/cm<sup>-1</sup> 2226 (CN), 1725 (C=O), 1675 (C=O) cm<sup>-1</sup>;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.26–1.40 (36 H, m), 1.42–1.51 (6 H, m), 1.56–1.65 (6 H, m), 1.75–1.85 (6 H, m), 2.52 (6 H, t, *J* 6.3), 3.67 (6 H, t, *J* 6.0), 3.69 (6 H, s), 3.86 (2 H, d, *J* 5.0), 4.00 (6 H, t, *J* 6.6), 4.07 (6 H, t, *J* 6.6), 5.12 (2 H, s), 5.57 (1 H, br t), 6.38 (1 H, s), 6.96–7.01 (6 H, m), 7.30–7.36 (5 H, m), 7.50–7.55 (6 H, m),

7.62–7.70 (12 H, m);  $\delta_{\text{C}}$  (75.5 MHz,  $\text{CDCl}_3$ ) 25.95, 26.08, 28.67, 29.30, 29.43, 29.56, 29.59, 34.95, 44.75, 60.02, 64.83, 66.96, 68.03, 68.26, 69.25, 110.19, 115.30, 119.27, 127.23, 128.17, 128.25, 128.51, 128.70, 131.37, 132.76, 136.82, 145.46, 156.72, 160.12, 169.18, 172.06;  $m/z$  (FABMS) 1571 ( $\text{M}^+$ , 55), 1133 (100%).

### 2-Amino-*N*-tris{2-([11-(4'-cyanobiphenyl-4-yloxy)undecyloxy]-carbonyl)ethoxy)methyl}methylacetamide (**12**)

To a solution of **11** (0.30 g, 0.191 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was added HBr in acetic acid (30%, 1 ml). The resulting mixture was stirred at 20 °C for 5 h, quenched with sat. aq.  $\text{NaHCO}_3$  (75 ml) and extracted twice with  $\text{CH}_2\text{Cl}_2$  (150 ml). The organic layers were dried ( $\text{MgSO}_4$ ), filtered and evaporated to dryness. The resulting residue was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ -MeOH-PhMe 91:4:5). Although the product seemed to decompose partially on the column, pure **12** (0.09 g, 33%) could be isolated as a white solid: mp 70 °C;  $\nu_{\text{max}}$ (neat)/ $\text{cm}^{-1}$  2221 (CN), 1733 (C=O), 1668 (C=O);  $\delta_{\text{H}}$  (200 MHz,  $\text{CDCl}_3$ ) 1.27–1.52 (42 H, m), 1.56–1.70 (6 H, m), 1.75–1.88 (6 H, m), 2.55 (6 H, t,  $J$  6.2), 3.27 (2 H, s), 3.71 (6 H, t,  $J$  6.2), 3.74 (6 H, s), 4.01 (6 H, t,  $J$  6.6), 4.08 (6 H, t,  $J$  6.9), 6.97–7.02 (6 H, m), 7.51–7.55 (6 H, m), 7.61–7.72 (12 H, m);  $\delta_{\text{C}}$  (75.5 MHz,  $\text{CDCl}_3$ ) 25.49, 25.61, 28.22, 28.85, 28.98, 29.11, 34.60, 45.07, 58.98, 64.25, 66.41, 67.74, 68.76, 109.64, 114.69, 118.69, 126.66, 127.93, 130.85, 132.15, 144.88, 159.42, 171.23, 172.43;  $m/z$  (FABMS) 1437 ( $\text{MH}^+$ , 100%).

### Acknowledgements

This work was supported by the Swiss National Science Foundation and a Kekulé doctoral fellowship from the “Stipendienfonds des Verbandes der Deutschen Chemischen Industrie” (T. H.).

### References

- (a) A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994; (b) F. Diederich and C. Thilgen, *Science (Washington)*, 1996, **271**, 317; (c) A. Hirsch (Vol. Ed.), *Fullerenes and Related Structures*, *Top. Curr. Chem.*, 1999, **199**, pp. 1–246.
- F. Diederich and M. Gómez-López, *Chem. Soc. Rev.*, 1999, **28**, 263.
- C. A. Mirkin and W. B. Caldwell, *Tetrahedron*, 1996, **52**, 5113.
- F. Cardullo, F. Diederich, L. Echegoyen, T. Habicher, N. Jayaraman, R. M. Leblanc, J. F. Stoddart and S. Wang, *Langmuir*, 1998, **14**, 1955.
- (a) N. S. Sariciftci, U. Lemmer, D. Vacar, A. J. Heeger and R. A. J. Janssen, *Adv. Mater.*, 1996, **8**, 651; (b) H. Ono and N. Kawatsuki, *Jpn. J. Appl. Phys., Part 1*, 1997, **36**, 6444.
- (a) T. Chuard and R. Deschenaux, *Helv. Chim. Acta*, 1996, **79**, 736; (b) R. Deschenaux, M. Even and D. Guillon, *Chem. Commun.*, 1998, 537; (c) T. Chuard and R. Deschenaux, *Chimia*, 1998, **52**, 547.
- F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht and M. Gross, *Helv. Chim. Acta*, 1997, **80**, 343.
- (a) A. C. Griffin and S. R. Vaidya, *Mol. Cryst. Liq. Cryst.*, 1989, **173**, 85; (b) Z. Komiya and R. R. Schrock, *Macromolecules*, 1993, **26**, 1393; (c) A. W. Hall, D. Lacey, J. S. Hill and D. G. McDonnell, *Supramol. Sci.*, 1994, **1**, 21; (d) M. Ungerank, B. Winkler, E. Eder and F. Stelzer, *Macromol. Chem. Phys.*, 1995, **196**, 3623.
- (a) C. Bingel, *Chem. Ber.*, 1993, **126**, 1957; (b) C. Bingel, presentation at the conference ‘New Perspectives in Fullerene Chemistry and Physics’, Rome (Italy), 1994.
- J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon and M. Gross, *Helv. Chim. Acta*, 1997, **80**, 2238.
- X. Camps and A. Hirsch, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1595.
- H. Murakami, Y. Watanabe and N. Nakashima, *J. Am. Chem. Soc.*, 1996, **118**, 4484.
- S. Ravaine, F. Vicentini, M. Mauzac and P. Delhaes, *New J. Chem.*, 1995, **19**, 1.

Paper a907824j