

## Liquid-Crystalline Mixed [5:1]Hexa-adducts of [60]Fullerene

Preliminary Communication

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A liquid-crystalline mixed [5:1]hexa-adduct of [60]fullerene was synthesized by addition of two different malonate derivatives onto  $C_{60}$ . The hexa-adduct derivative **2** was prepared by a stepwise synthetic procedure (fullerene  $\rightarrow$  mono-adduct of  $C_{60}$   $\rightarrow$  hexa-adduct of  $C_{60}$ ). Cyanobiphenyl and octyloxybiphenyl derivatives were selected as mesogens. The malonate derivatives showed either a monotropic nematic phase or a monotropic smectic A phase, and the hexa-adduct derivative gave rise to an enantiotropic smectic A phase.

**Introduction.** – [60]fullerene-containing thermotropic liquid crystals represent an interesting family of supramolecular materials, as they combine the optical and electrochemical properties of [60]fullerene ( $C_{60}$ ) with the self-organizing behavior of liquid crystals [1]. Covalent functionalization of  $C_{60}$  [1–6] and formation of supramolecular complexes [7] can lead to mesomorphic materials that display a variety of mesophases, including nematic, chiral nematic, smectic A, smectic B, columnar, and cubic phases. Furthermore, the association of  $C_{60}$  with various donor moieties, such as oligophenylenevinylene (OPV) [2f], ferrocene [2d,h,n], or tetrathiafulvalene (TTF) [2i] was achieved with the aim to elaborate liquid-crystalline dyads for applications in solar-cell technology and for the development of supramolecular switches.

The versatile chemistry of  $C_{60}$  prompted us to design liquid-crystalline hexa-adducts to explore the behavior of mesogens in a spherical environment. The first hexa-adduct of  $C_{60}$  was synthesized previously from malonate **1** (see *Scheme* below), which gave rise to a smectic A phase [2c]. Recently, we described a chiral hexa-adduct of  $C_{60}$ , which was prepared from a laterally-branched optically active mesogen. A chiral nematic phase was observed [2m]. Besides our work, other mesomorphic hexa-adducts of  $C_{60}$  were reported. *Diederich* and co-workers described a hexa-adduct containing eight Et groups and four mesogenic cyanobiphenyl units. This compound afforded a nematic phase during the first heating run [3]. *Felder-Flesch et al.* reported two hexa-adducts of  $C_{60}$  containing either twelve mesogenic cholesterol units, or ten mesogenic cholesterol units and two non-mesogenic groups. Both compounds showed a smectic A phase [6]. In all the above-mentioned cases, the observed liquid-crystalline properties are in

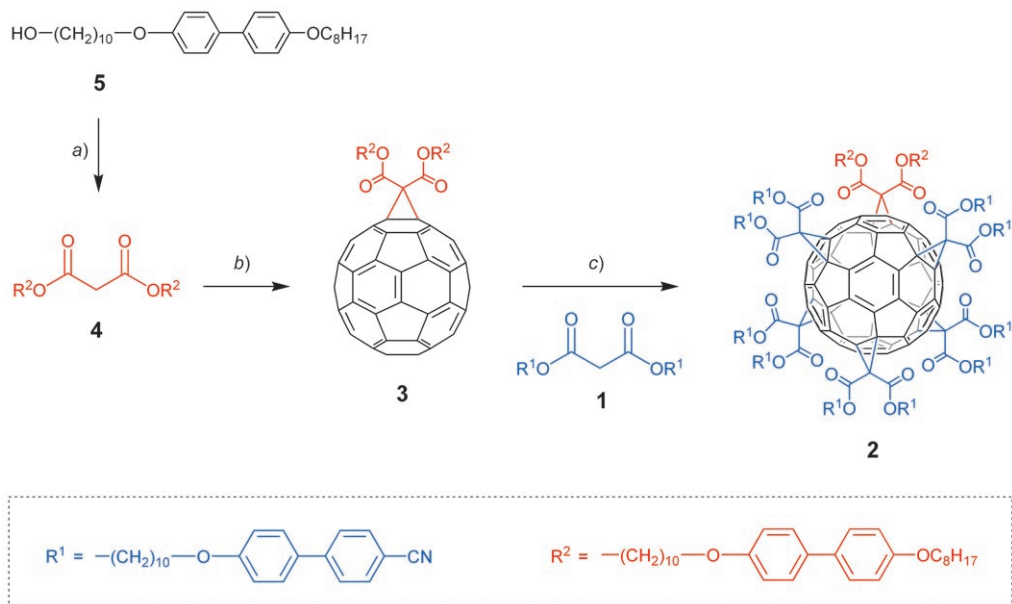
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agreement with the nature of the mesogens and the structure of the hexa-adduct materials.

The search for new hexa-adducts of  $C_{60}$  prompted us to design mixed fullerene derivatives, *i.e.*, fullerenes that carry two different mesogens. The addition of two mesogens (or more in case of other addition patterns) onto  $C_{60}$  could be an elegant means for the design of fullerene-containing liquid crystals with tailor-made properties. For synthetic purposes, we focused our attention first on the [5:1] addition pattern. Indeed, mixed [5:1]hexa-adducts of  $C_{60}$  can be prepared by poly-addition of a malonate derivative onto readily available mono-adducts of  $C_{60}$ . The addition of the two malonates will follow a stepwise synthetic approach. As a first example, we selected cyanobiphenyl and octyloxybiphenyl derivatives as mesomorphic promoters.

Herein, we report the synthesis, characterization, liquid-crystalline behavior, and supramolecular organization of the mixed [5:1]hexa-adduct **2**, and the synthesis and thermal properties of the mono-adduct **3**, which was used in the preparation of **2**. The synthesis and liquid-crystalline properties of the malonate **1** were already reported [2c].

*Scheme*



a) Malonyl dichloride,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ , r.t., 24 h; 79%. b)  $C_{60}$ ,  $\text{I}_2$ , 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, r.t., 19 h; 51%. c) 1. 9,10-Dimethylantracene (DMA), toluene, r.t., 2 h; 2. compound **1**,  $\text{CBr}_4$ , DBU, r.t., overnight; 7%.

**Results and Discussion.** – 1. *Synthesis.* The synthesis of **2** and **3** is described in the *Scheme*. Briefly, malonate **4** was prepared in 79% yield by esterification of malonyl dichloride with alcohol **5**. The latter was obtained by analogy to the synthesis of cyanobiphenyl derivatives used for the preparation of **1** [2c]. Subsequent functional-

ization of  $C_{60}$  with **4** via *Bingel* addition [8] led to mono-adduct **3** in 51% yield. Finally, following the methodology developed by *Hirsch et al.* [9], the desired hexa-adduct **2** was obtained in 7% yield by addition of the malonate **1** [2c] to the methanofullerene **3**. All compounds were purified by column chromatography and/or by semi-preparative HPLC, as described in the *Exper. Part*.

**2. Material Properties.** The thermal and liquid-crystalline properties of compounds **2–4** were investigated by polarized optical microscopy (POM) in combination with differential scanning calorimetry (DSC). The experimental phase-transition temperatures and enthalpies are reported in the *Table*. The malonate derivative **4** gave rise to a monotropic smectic A phase, as identified by POM from the observation of typical focal-conic and homeotropic textures. The mono-adduct **3** was found to be non-mesomorphic. This behavior is consistent with previous results, and is attributed to steric effects resulting from the presence of the three-dimensional  $C_{60}$  unit, which acts as a non-mesomorphic dopant [2c,m].

Table. Phase-Transition Temperatures ( $T$ ) and Associated Enthalpy Changes ( $\Delta H$ ) for Compounds **1–4**

Compound	$T$ [°] <sup>a)</sup>	$\Delta H$ [kJ/mol]	Transition <sup>b)</sup>	$T_g$ [°] <sup>c)</sup>
<b>1</b> <sup>d)</sup>	87	2.7	(I → N)	–
	57	50	(N → Cr)	–
<b>2</b>	151	55.5	SmA → I	80
<b>3</b>	112	43.1	Cr → I	–
<b>4</b>	115	21.6	(I → SmA)	–
	114	12.3	(SmA → Cr)	–
	111	37.7	(Cr → Cr')	–

<sup>a)</sup> Transition temperatures are given at the onset of the observed peaks. <sup>b)</sup> I = isotropic liquid, N = nematic phase, SmA = smectic A phase, Cr = crystal; monotropic transitions are given in parentheses. <sup>c)</sup> Glass-transition temperature. <sup>d)</sup> Data taken from [2c].

By DSC, an endotherm was detected for **2** at 151° during the first heating run. This transition was found to be reversible in subsequent heating–cooling cycles. The formation of a liquid-crystalline phase between *ca.* 80 and 151° was observed by POM. Slow cooling of the sample from the isotropic fluid revealed the formation of a smectic A phase. Indeed, typical focal-conic and homeotropic textures were observed (*Fig. 1*). The fact that no melting point was detected by DSC is, most likely, a consequence of the amorphous character of **2** in the solid state.

The liquid-crystalline behavior of **2** emphasizes the role played by  $C_{60}$  in the case of hexa-adducts: assembling six malonate derivatives with two different mesogens in a 5:1 ratio around a focal point provides the required structural anisotropy and intermolecular interactions for mesomorphism to occur. In such a system, the mesogenic units form a cylinder-like structure, the self-assembly of which gives rise to lamellar organization (*Fig. 2*). Interestingly, whereas the malonate derivatives gave rise to monotropic mesophases, the hexa-adduct **2** showed enantiotropic mesomorphism.

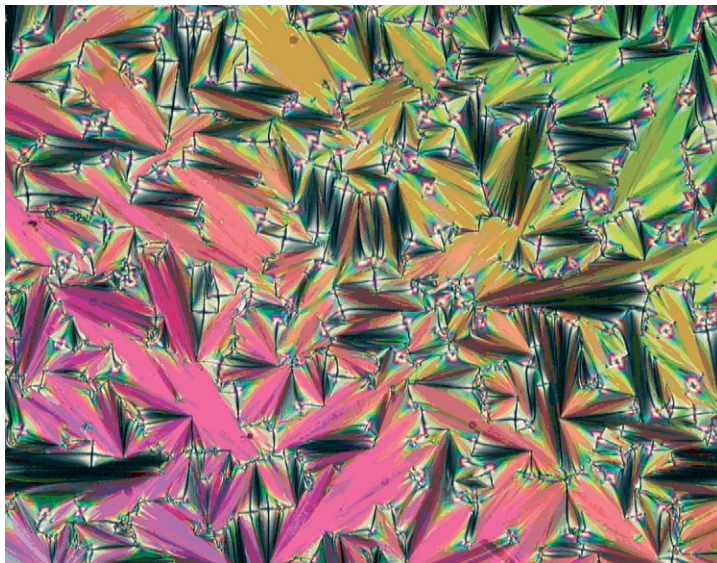


Fig. 1. Thermal-polarized optical micrograph of the focal-conic fan texture displayed by **2** in the smectic A phase upon cooling the sample from the isotropic liquid to a temperature of  $151^\circ$

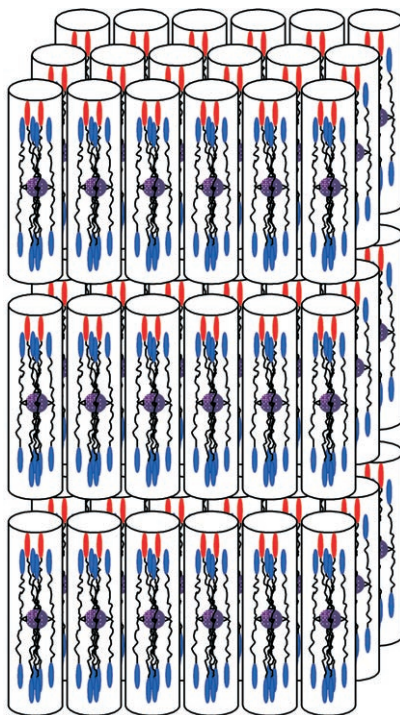


Fig. 2. Proposed model for the supramolecular organization of **2** within the smectic A phase

**Conclusions.** – We have demonstrated that liquid-crystalline mixed [5:1]hexa-adducts of  $C_{60}$  can be readily synthesized. Interestingly, poly-addition can be used for the preparation of fullerene-containing thermotropic liquid crystals from different mesogens. This result opens the door for the design of further polyfunctional fullerene materials.

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### Experimental Part

*General.* The synthesis and anal. data of **1** have been described before [2c]. UV/VIS Spectroscopic data are reported as  $\lambda_{\max}$  (in nm) and, in parentheses, as  $\epsilon$  (in  $\text{dm}^2 \text{mol}^{-1} \text{cm}^{-1}$ ). NMR chemical shifts  $\delta$  are reported in ppm rel. to the solvent. MS Data are reported in  $m/z$ .

*Compound Purification.* The intermediate compounds and the methanofullerene **3** were purified by column chromatography (CC) on silica gel, eluting with  $\text{CH}_2\text{Cl}_2$ /heptane 8:2 (for **5**),  $\text{CH}_2\text{Cl}_2$ /heptane 9:1 (for **4**), and toluene/heptane 1:1 and then toluene/AcOEt 7:3 (for **3**). The hexa-adduct **2** was first purified by CC ( $\text{SiO}_2$ ; toluene/heptane 1:1 and then toluene/AcOEt 96:4), and then by semi-prep. HPLC on  $\mu\text{Porasil Silica}$  (10  $\mu\text{m}$ ; column: 7.8 mm  $\times$  300 mm; toluene/heptane/AcOEt 88:10:2, 3 ml/min;  $t_R$  37 min).

*Data of 2.*  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ): 7.64 (*d*, 20 arom. H); 7.60 (*d*, 20 arom. H); 7.49 (*d*, 20 arom. H); 7.40 (*d*, 8 arom. H); 6.92 (*d*, 20 arom. H); 6.88 (*d*, 4 arom. H); 6.86 (*d*, 4 arom. H); 4.21 (*t*, 12  $\text{CO}_2\text{CH}_2$ ); 3.93 (*t*, 12  $\text{CH}_2\text{O}$ ); 3.91 (*t*, 2  $\text{CH}_2\text{O}$ ); 1.78–1.70 (*m*, 14  $\text{CH}_2\text{CH}_2\text{O}$ ); 1.65 (*quint.*, 12  $\text{CO}_2\text{CH}_2\text{CH}_2$ ); 1.41–1.24 (*m*, 164 aliph. H); 0.86 (*t*, 2 Me).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ ): 164.03; 160.23; 158.72; 158.68; 146.06; 145.41; 141.58; 133.43; 133.36; 132.94; 131.46; 128.64; 127.81; 127.30; 119.37; 115.33; 115.06; 115.03; 110.42; 69.60; 68.55; 68.49; 68.46; 67.44; 46.23; 32.24; 30.10; 29.95; 29.91; 29.85; 29.79; 29.72; 29.68; 29.64; 28.85; 26.50; 26.43; 26.26; 23.06; 14.27. Anal. calc. for  $\text{C}_{368}\text{H}_{370}\text{N}_{10}\text{O}_{38}$  (5540.92): C 79.77, H 6.73, N 2.53, O 10.97; found: C 79.64, H 6.82, N 2.54, O 11.00.

*Data of 3.* UV/VIS ( $\text{CH}_2\text{Cl}_2$ ): 426 (2940), 487 (1820), 686 (240).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.46 (*d*, 4 arom. H); 7.44 (*d*, 4 arom. H); 6.95 (*d*, 4 arom. H); 6.92 (*d*, 4 arom. H); 4.50 (*t*, 2  $\text{CO}_2\text{CH}_2$ ); 4.00–3.96 (*m*, 4  $\text{CH}_2\text{O}$ ); 1.88–1.75 (*m*, 12 H,  $\text{CH}_2\text{CH}_2\text{O}$ ,  $\text{CO}_2\text{CH}_2\text{CH}_2$ ); 1.47–1.30 (*m*, 44 aliph. H); 0.89 (*t*, 2 Me).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 164.15; 158.64; 145.78; 145.66; 145.57; 145.27; 145.08; 145.04; 145.01; 144.27; 143.49; 143.41; 142.60; 142.31; 141.36; 139.39; 133.71; 128.08; 115.13; 68.50; 68.44; 67.88; 32.26; 29.98; 29.86; 29.81; 29.74; 29.69; 29.66; 29.02; 26.50; 26.43; 23.10; 14.55. MALDI-TOF-MS: 1695.67 ( $[M+H]^+$ ,  $\text{C}_{123}\text{H}_{91}\text{O}_8^+$ ; calc. 1695.67). Anal. calc. for  $\text{C}_{123}\text{H}_{90}\text{O}_8$  (1696.06): C 87.10, H 5.35, O 7.55; found: C 87.03, H 5.51, O 7.46.

*Data of 4.*  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.46 (*d*, 4 arom. H); 7.45 (*d*, 4 arom. H); 6.95 (*d*, 4 arom. H); 6.93 (*d*, 4 arom. H); 4.14 (*t*, 2  $\text{CO}_2\text{CH}_2$ ); 4.00–3.96 (*m*, 4  $\text{CH}_2\text{O}$ ); 3.37 (*s*,  $\text{O}_2\text{CCH}_2\text{CO}_2$ ); 1.80–1.76 (*m*, 4  $\text{CH}_2\text{CH}_2\text{O}$ ); 1.65 (*quint.*, 2  $\text{CO}_2\text{CH}_2\text{CH}_2$ ); 1.50–1.30 (*m*, 44 aliph. H); 0.89 (*t*, 2 Me).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 167.15; 158.63; 158.61; 133.74; 133.70; 128.06; 115.12; 68.50; 68.45; 66.10; 42.12; 32.24; 29.91; 29.86; 29.80; 29.73; 29.68; 29.62; 28.88; 26.48; 26.21; 23.09; 14.54. Anal. calc. for  $\text{C}_{63}\text{H}_{92}\text{O}_8$  (977.40): C 77.42, H 9.49, O 13.09; found: C 77.27, H 9.49, O 13.24.

*Data of 5.*  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.47 (*d*, 2 arom. H); 7.45 (*d*, 2 arom. H); 6.95 (*d*, 2 arom. H); 6.93 (*d*, 2 arom. H); 3.99 (*t*, 2  $\text{CH}_2\text{O}$ ); 3.65 (*t*,  $\text{CH}_2\text{OH}$ ); 1.80 (*quint.*, 2  $\text{CH}_2\text{CH}_2\text{O}$ ); 1.59–1.30 (*m*, 24 aliph. H); 0.89 (*t*, Me).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 158.61; 133.74; 133.71; 128.07; 115.13; 68.50; 68.47; 63.51; 33.21; 32.24; 29.94; 29.91; 29.80; 29.72; 29.67; 26.47; 26.14; 23.08; 14.54.

*Optical and Thermal Studies.* Polarized optical microscopy was performed on a *Zeiss-Axioskop* polarizing microscope equipped with a *Linkam THMS-600* variable-temperature stage, under  $\text{N}_2$ . Transition temperatures and enthalpies were determined on a *Mettler-Toledo-822e* differential-scanning calorimeter at a rate of  $10^\circ/\text{min}$  under  $\text{He}/\text{N}_2$ .

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