A nematic [60]fullerene supermolecule: when polyaddition leads to supramolecular self-organization at room temperature[†]

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Received 11th January 2007, Accepted 12th February 2007 First published as an Advance Article on the web 1st March 2007 DOI: 10.1039/b700460e

The synthesis, liquid-crystalline properties and supramolecular organization of a [60]fullerenebased supermolecule are described, and the great potential of the spherical carbonated polyhedron to produce new materials through its multiple and addressable regioselective functionalization is emphasized. Indeed, hexaaddition on the carbon sphere has allowed the preparation, in 50% yield, of the first room-temperature enantiotropic nematic C_{60} -based material, even though the promoter was not mesomorphic. Despite the high molecular weight of such a supermolecule, the resulting material was revealed to be easily oriented in its mesophase by a magnetic field; this has allowed, by small angle X-ray diffraction investigations, a fine description of the molecular organization and of the corresponding relevant interactions involved. These results open the way to multifuntional materials that can take advantage of such an easy orientation of the grafted active chromophores (donor and acceptor) to be particularly efficient (for example in the design of photovoltaic materials).

Introduction

Over the last decade, [60]fullerene has attracted considerable attention in materials science.¹ Notably, several efforts have been aimed at producing liquid-crystalline C60-based materials of added value in the form of increased processability, film formation, and control over self-assembly. This requires that some shape anisotropy should be imparted to C_{60} , which is perfectly isotropic. Indeed, for such systems, the tendency of the anisotropic moieties to enforce an ordered self-assembly must be sufficiently strong and properly designed to accommodate spheres. There are two main approaches to design fullerene-containing liquid crystals: covalent and noncovalent modifications. Two examples of the non-covalent approach are based on the formation of inclusion complexes in which C₆₀ either resides within cavities of host molecules, such as dendritic porphyrins,² cyclotriveratrylene,³ or is linked to hexaphenyltriphenylene forming a 1 : 1 mixture with hexakis(4-nonylphenyl)dipyr $azino[2,3-f:2',3'-h]quinoxalene.^4$ Within the covalent approach, a number of different mesogenic units have been introduced to obtain a variety of fullerene-containing thermotropic liquid-crystalline materials.^{5,6} For such systems, the main criterion for LC phase induction is the adequacy of the fullerene and mesogenic side-groups cross-sections. In addition, small anisotropic units are often insufficient

as interactions are too weak to generate mesomorphism.⁷ Examples of C₆₀ derivatives possessing a high LC character (bearing more than two anisotropic moieties per C₆₀ via a polyaddition⁸ or dendritic approach⁹) showed either a transient nematic,^{8b} a chiral nematic,¹⁰ or a smectic A phase.^{8a,8c,10} In these cases, the properties of the materials were mostly dominated by the anisotropic moieties, due to dilution of the C₆₀ unit. In another approach, C₆₀ is placed at the apex of cone-shaped molecules, forming a new type of mesomorphic compound, which self-assembles into thermo- and lyotropic columnar liquid-crystal-line mesostructures.¹¹

The design and selection of molecular building blocks to reach such orientational orderings and particularly the nematic phase close to or just above room temperature is therefore challenging, as shown in reports on systems containing multivalent cores ranging from soft and flexible such as carbosilazane,¹² siloxane,¹³ and silsesquioxane,¹⁴ to hard such as gold nanoparticles.¹⁵ Such systems are technologically relevant too, as the nematic phase often allows the control of the macroscopic alignment in thin films, important for potential technological applications.

As C_{60} can be considered as a versatile hard building block for dendritic systems due to its tunable core valency (1 to 6) and regioselective polyaddition, we were interested in further investigating its use as a template to build multicomponent supermolecules. Applying the "orthogonal transposition" described by Krautler and Maynollo¹⁶ and Diederich's method of "tether-directed remote functionalization"¹⁷ for specific multifunctionalized [60]fullerene, it may be possible to regioselectively prepare new three-dimensionally structured molecules and thus new structural motives that can not be obtained by starting from other cores such as silsesquioxanes¹⁴ or gold nanoparticles.¹⁵

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[†] Electronic supplementary information (ESI) available: NMR [¹H (300 MHz) and ¹³C (75 MHz), CDCl₃] and UV-visible spectra of **2** and **1**, DSC curves of **5**, **2** and **1**, X-Ray diffraction pattern obtained for **2** at 80 °C, evolution of the X-ray pattern of **2** and **1** with temperature, variation of the lamellar periodicity *d* with temperature for **2** and **1**. See DOI: 10.1039/b700460e

Here, we report on the synthesis, liquid-crystalline properties and supramolecular organization of the first room-temperature nematic [60]fullerene hexaadduct 1 (Scheme 1), obtained in 50% yield, the highest yield so far reported for hexaaddition on C_{60} .^{8,10,22b} Hexaadduct 1 can be easily oriented under a magnetic field. As it will be shown, the selected design, *i.e.* polyaddition of side-on connected malonates on the carbon hard core, is a suitable method for obtaining stable anisotropic materials, even starting from non-mesomorphic promoters. Therefore, assembling 12 amorphous units around the 3-D focal template allows mesomorphism through induced collective structural anisotropy and hierarchical intermolecular interactions.

Experimental

General

All reagents were used as purchased from commercial sources without further purification. Solvents were dried using standard techniques prior to use. All reactions were performed in standard glassware under an inert argon atmosphere. Drying *in vacuo* was done at 10^{-2} Torr. Products were isolated by column chromatography (silica gel 60, particle size 40–63 µm, 230–400 mesh, Merck). TLC was performed using precoated glass sheets with silica gel 60 F₂₅₄, Merck. UV/Vis spectra (λ_{max} in nm (ε)) were measured on a Hitachi U-3000 spectrophotometer. NMR spectra were recorded on a Bruker

AM 300 (300 MHz) with solvent signal as reference (δ in ppm). MALDI-TOF mass spectra were measured on a Brucker BIFLEXTM matrix-assisted laser desorption time-of-flight mass spectrometer (MALDI-TOF).

POM, DSC and XRD measurements of the mesomorphic materials

The optical textures of the mesophases were studied with a Leitz polarizing microscope equipped with a Mettler FP80 hot-stage and a FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 10 °C min⁻¹ on heating. The apparatus was calibrated with indium (156.6 °C, 28.4 J g⁻¹) and gallium (29.8 °C) as the standards. The TGA measurements were carried out on a SDTQ 600 apparatus at scanning rate of 10 °C min⁻¹. The oriented XRD patterns were recorded using a sealed-tube generator (900 W) equipped with a pinhole CuK α (λ = 1.542 Å) parallel beamline based on a homemounted Kirkpatrick-Baez optics coupled with a HiStar detector (Bruker AXS). The crude sample was placed in Lindemann capillary of 1 mm diameter and 10 µm wall thickness and aligned in a home-made permanent magnetic field oven (1.0 T). The sample temperature was controlled to within ± 0.03 °C. Two different detector-sample distances were used: 111.5 and 328.0 mm. The patterns were analyzed using home-made ImageJ plug-ins (φ and 2θ profiles).



Scheme 1 Synthesis of mesomorphic hexaadduct 1: (a) 10-bromodecanol,¹⁹ K₂CO₃, KI, DMF, 80 °C, 96%; (b) NaOH–H₂O, MeOH, reflux, 97%; (c) 4-octyloxyphenol,²⁰ DCC, 4-(*N*-pyrrolidino)pyridine, CH₂Cl₂, Ar, rt, 78%; (d) 10% Pd/C, H₂, 1,4-dioxane, 93%; (e) 4-octyloxybenzoic acid,²¹ DCC, 4-(*N*-pyrrolidino)pyridine, THF, Ar, rt, 71%; (f) malonyl dichloride, Et₃N, CH₂Cl₂, Ar, rt, 80%; (g) *i*) C₆₀, DMA, toluene, Ar, rt, 2 h, *ii*) **8**, CBr₄, DBU, 3 weeks, 50%.

Computational modeling

The molecular mechanics studies have been performed on SGI Origin 2800 and Octane² calculators using Insight II and Discover 3 software from Accelrys (www.accelrys.com) with the cvff forcefield.

Synthetic procedures and analytical data

4-Octyloxyphenol,²⁰ methyl 4-octyloxybenzoate and 4-octyloxybenzoic acid,²¹ methyl 2-hydroxy-4-benzyloxybenzoate **2**¹⁸ and 10-bromodecanol¹⁹ were synthesized according to literature procedures.

Synthesis of methyl 2-[(10-hydroxy)decyloxy]-4benzyloxybenzoate 3

10-Bromodecanol¹⁹ (5.95 g, 25.09 mmol) was added to a mixture of methyl 2-hydroxy-4-benzyloxybenzoate 2^{18} (5.40 g, 20.91 mmol), anhydrous potassium carbonate (14.45 g, 104.55 mmol) and potassium iodide (7 mg, 0.04 mmol) in DMF (100 mL) and the reaction mixture was heated at 80 °C for 20 h. The resulting mixture was cooled to room temperature, filtered through celite and the filter pad was washed with CH₂Cl₂. The solvent was evaporated and the residue taken up in diethyl ether. The organic layer was washed with aqueous NaCl (2 \times 200 mL) and water, then dried (MgSO₄), filtered and evaporated to dryness. Column chromatography (SiO₂, CH₂Cl₂) vielded 8.31 g (96%) of **3** as white crystals. Mp 57.5 °C. Elemental analysis: calc. (found) for C₂₅H₃₄O₅, C 72.44 (72.85), H 8.27 (8.38). ¹H NMR (CDCl₃, 300 MHz): δ 1.32 (m, 14H), 1.83 (m, 2H), 3.64 (t, J = 5 Hz, 2H), 3.85 (s, 3H), 3.98 (t, J = 7 Hz, 2H), 5.09 (s, 2H), 6.55 (m, 2H), 7.40 (m, 5H), 7.84 (d, J = 9 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 25.68, 25.87, 29.01, 29.23, 29.34, 29.43, 29.46, 32.75, 51.56, 63.00, 68.87, 70.14, 100.73, 105.33, 112.81, 127.51, 128.19, 128.64, 133.73, 136.23, 160.74, 163.18, 166.34.

Synthesis of 2-[(10-hydroxy)decyloxy]-4-benzyloxybenzoic acid 4

NaOH (9.61 g, 240 mmol) was added to a solution of **3** (8.3 g, 20.02 mmol) in methanol–water (400 : 42 mL) and heated at reflux for 2 h. The mixture was cooled to room temperature, diluted in water (200 mL) and concentrated. Hydrochloric acid was added (to reach pH 2) leading to a white precipitate, which was filtered off and washed with water (until pH 7 was reached). No further purification was necessary to yield 7.77 g (97%) of **4** as white crystals, Mp 82 °C. Elemental analysis: calc. (found) for $C_{24}H_{32}O_5$, C 71.97 (71.73), H 8.05 (8.16). ¹H NMR (CDCl₃, 300 MHz): δ 1.32 (m, 14H), 1.89 (m, 2H), 3.65 (t, *J* = 8 Hz, 2H), 4.18 (t, *J* = 6 Hz, 2H), 5.12 (s, 2H), 6.60 (d, *J* = 2 Hz, 1H), 6.72 (dd, *J* = 9 Hz and 2 Hz, 1H), 7.74 (m, 5H), 8.14 (d, *J* = 9 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 25.65, 25.77, 28.75, 29.05, 29.23, 29.26, 29.33, 32.70, 62.98, 70.17, 70.46, 100.25, 107.34, 110.71, 127.54, 128.42, 128.74, 135.48, 135.75, 158.91, 164.06, 165.22.

Synthesis of 4'-octyloxyphenyl 2-[(10-hydroxy)decyloxy]-4benzyloxybenzoate 5

A solution of **4** (7.5 g, 18.73 mmol), 4-octyloxyphenol²⁰ (4.16 g, 18.73 mmol), N,N'-dicyclohexylcarbodiimide (4.75 g,

GI in dry CH₂Cl₂ (375 mL) was stirred overnight at room temperature under argon. The solvent was removed and the residue purified by column chromatography (SiO₂, CH₂Cl₂) and then washed with hexane to yield 8.86 g (78%) of **5** as a white solid, Mp 53.8 °C. Elemental analysis: calc. (found) for C₃₈H₅₂O₆, C 75.46 (75.15), H 8.67 (8.78). ¹H NMR (CDCl₃, 300 MHz): δ 0.89 (t, J = 7 Hz, 3H), 1.23 (m, 24H), 1.80 (m, 4H), 3.63 (t, J = 6 Hz, 2H), 3.95 (t, J = 6 Hz, 2H), 4.01 (t, J = 6 Hz, 2H), 5.13 (s, 2H), 6.60 (m, 2H), 6.89 (d, J = 9 Hz, 2H), 7.08 (d, J = 9 Hz, 2H), 7.39 (m, 5H), 8.02 (d, J = 9 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.08, 22.65, 25.68, 25.94, 26.04, 29.10, 29.23, 29.28, 29.36, 29.40, 29.46, 31.80, 32.78, 63.06, 68.44, 68.94, 70.23, 100.71, 105.49, 112.05, 115.02, 115.95, 122.57, 127.54, 128.27, 128.71, 134.32, 144.50, 156.61, 161.42, 163.73, 164.50.

23.04 mmol) and 4-(N-pyrrolidino)pyridine (7.1 g, 47.95 mmol)

Synthesis of 4'-octyloxyphenyl 2-[(10-hydroxy)decyloxy]-4hydroxybenzoate 6

A solution of 5 (8 g, 13.23 mmol) and 10% palladiumon-carbon catalyst (533 mg) in 1,4-dioxane (200 mL) was stirred under a hydrogen atmosphere for 3 days. The crude mixture was then filtered through celite and the filter pad washed with CH₂Cl₂. The solvent was removed and the crude product re-crystallized in toluene to yield 6.33 g (93%) of 6 as a white solid, Mp 110.4 °C. Elemental analysis: calc. (found) for C₃₁H₄₆O₆, C 72.34 (72.10), H 9.01 (9.10). ¹H NMR (CDCl₃, 300 MHz): δ 0.89 (t, J = 7 Hz, 3H), 1.27 (m, 24H), 1.80 (m, 4H), 3.65 (t, J = 4 Hz, 2H), 3.95 (t, J = 6 Hz, 2H), 4.00 (t, J = 6 Hz, 2H), 5.95 (s, 1H), 6.46 (m, 2H), 6.90 (d, J = 9 Hz, 2H), 7.08 (d, J = 9 Hz, 2H), 7.96 (d, J = 9 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.08, 22.64, 25.57, 25.78, 26.02, 28.94, 29.08, 29.18, 29.20, 29.23, 29.26, 29.34, 31.80, 32.59, 63.12, 68.46, 68.88, 100.51, 107.35, 111.09, 115.03, 122.56, 134.50, 144.43, 156.62, 161.66, 161.86, 164.79.

Synthesis of 4'-octyloxyphenyl 2-[(10-hydroxy)decyloxy]-4-[(octyloxyphenyl)- 4 benzoyloxy]benzoate 7

A solution of 6 (6.3 g, 12.24 mmol), 4-octyloxybenzoic acid²¹ (3.06 g, 12.24 mmol), N,N'-dicyclohexylcarbodiimide (3.03 g, 14.68 mmol) and 4-(N-pyrrolidino)pyridine (453 mg, 3.06 mmol) in dry THF (150 mL) was stirred overnight at room temperature under argon. The reaction mixture was evaporated to dryness and the crude product purified by column chromatography (SiO2, CH2Cl2). Re-crystallization in petroleum ether-toluene yields 6.53 g (71%) of 7 as white crystals, Mp 89.6 °C. Elemental analysis: calc. (found) for C₄₆H₆₆O₈, C 73.96 (73.58), H 8.91 (9.01). ¹H NMR (CDCl₃, 300 MHz): δ 0.90 (t, J = 6 Hz, 6H), 1.25 (m, 34H), 1.79 (m, 6H), 3.62 (t, J = 6 Hz, 2H), 3.96 (t, J = 6 Hz, 2H), 4.00 (t, J = 6 Hz, 4H), 6.90 (m, 6H), 7.12 (d, J = 9 Hz, 2H), 8.06 (d, J =9 Hz, 2H), 8.14 (d, J = 9 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.09, 22.64, 25.67, 25.90, 25.97, 26.03, 29.04, 29.07, 29.20, 29.23, 29.28, 29.31, 29.34, 29.39, 29.44, 31.79, 31.81, 32.78, 63.06, 68.38, 68.45, 69.18, 107.11, 113.40, 114.39, 115.06, 116.73, 121.01, 122.48, 132.38, 133.36, 144.36, 155.67, 156.75, 160.55, 163.79, 164.32, 164.47.

Synthesis of malonate 8

Et₃N (1.22 mL, 8.66 mmol) was added to a mixture of 7 (6.5 g, 8.7 mmol) and malonyl dichloride (0.42 mL, 4.33 mmol) in dry CH₂Cl₂ (230 mL). The mixture was stirred overnight at room temperature and evaporated to dryness. The residue purified by column chromatography (SiO₂, CH₂Cl₂) to yield 5.41 g (80%) of 8 as white crystals, Mp 75 °C. Elemental analysis: calc. (found) for $C_{95}H_{132}O_{18}$, C 73.05 (72.98), H 8.52 (8.53). ¹H NMR (CDCl₃, 300 MHz): δ 0.90 (t, J = 7 Hz, 12H), 1.30 (m, 68H), 1.80 (m, 12H), 3.36 (s, 2H), 3.95 (t, J = 6 Hz, 4H), 4.05 (t, J = 6 Hz, 8H), 4.12 (t, J = 6 Hz, 4H), 6.87 (m, 12H), 7.11 (d, 100)J = 9 Hz, 4H), 8.06 (d, J = 9 Hz, 4H), 8.14 (d, J = 9 Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.08, 22.64, 25.74, 25.89, 25.97, 26.03, 28.43, 29.07, 29.16, 29.20, 29.23, 29.27, 29.31, 29.34, 29.40, 31.78, 31.80, 41.63, 65.63, 68.37, 68.41, 69.17, 107.11, 113.39, 114.38, 115.03, 116.71, 121.01, 122.47, 132.36, 133.35, 144.34, 155.67, 156.75, 160.56, 163.78, 164.29, 164.39, 166.68.

Synthesis of [60]fullerene hexaadduct 1

A solution of 9,10-dimethylanthracene (DMA) (173 mg, 0.84 mmol) and C₆₀ (50 mg, 0.07 mmol) in dry toluene (50 mL) was stirred for 2 h under argon at room temperature. Malonate 8 (1.31 g, 0.84 mmol), CBr₄ (278 mg, 0.84 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.21 mL, 1.4 mmol) were then added and the resulting solution was stirred at room temperature for 3 weeks before solvent evaporation. The crude mixture was separated by flash chromatography (SiO₂, hexane to remove DMA then toluene-AcOEt 96: 4 to elute 1) and the fraction corresponding to expected hexaadduct was later purified by gel permeation chromatography (SX-1 biobeads, CH₂Cl₂) to yield 350 mg (50%) of 1 as a pale orange glassy solid. MALDI-TOF MS: (C630H780O108) 9858.95 $[M-C_{14}H_{21}O_2]$. ¹H NMR (CDCl₃, 300 MHz): δ 0.88 (t, J = 7 Hz, 72H), 1.30 (m, 408H), 1.79 (m, 72H), 3.92 (br s (t), 24H), 4.02 (br s (t), 48H), 4.20 (br s (t), 24H), 6.87 (m, 72H), 7.07 (d, J = 7 Hz, 24H), 8.03 (d, J = 9 Hz, 24H), 8.10 (d, J = 9 Hz, 12H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.08, 22.63, 25.81, 25.96, 26.03, 28.41, 29.07, 29.19, 29.21, 29.26, 29.31, 29.34, 29.53, 31.78, 45.35, 66.94 (C_{sp}³ of C₆₀), 68.35, 69.07, 69.16, 107.09, 113.35, 114.35, 114.99, 116.63, 120.99, 122.44, 132.32, 133.29, 141.06 (Csp2 of C60), 144.33, 145.74 (Csp2 of C60), 155.67, 156.72, 160.56, 163.73, 163.79, 164.23.

Results and discussion

The synthesis of the hexaadduct 1 is depicted in Scheme 1. Reaction of methyl 2-hydroxy-4-benzyloxybenzoate 2^{18} with 10-bromodecanol¹⁹ under etherification conditions (K₂CO₃, KI, DMF, 80 °C) followed by hydrolysis of the corresponding methyl ester 3 afforded benzoic acid 4, which was then esterified with 4-octyloxyphenol²⁰ using standard DCC/4-PP coupling conditions. Hydrogenation of benzyl-protected compound 5 followed by esterification with 4-octyloxybenzoic acid²¹ led to the primary alcohol 7. Treatment of 7 with malonyl dichloride in the presence of triethylamine afforded compound 8, which was subjected to the Hirsch methodology²² for the preparation of "all-e" [60]fullerene hexaadduct based on DMA-templating. Hexaadduct 1 was obtained in 50% yield (0.35 g) as a pale orange glassy solid.

All of the spectroscopic measurements were consistent with the proposed molecular structure. The ¹³C-NMR spectrum of **1** shows the diagnostic three signals of $T_{\rm h}$ -symmetrical [60]fullerene hexaadduct at 66.94 ppm (C_{sp3}), 141.06 ppm (C_{sp2}) and 145.74 ppm (C_{sp2}). The structure and purity of compound **1** was also confirmed by ¹H-NMR and MALDI-TOF spectra. The GPC analysis showed a monomodal molecular weight distribution, with a polydispersity of 1.03.

The thermal behaviour of the hexaadduct 1 was studied by differential scanning calorimetry (DSC), polarized optical microscopy with a heating stage (POM) and temperature dependent wide- and small-angle X-ray diffraction (WAXS, SAXS). POM observations on the first heating showed that the compound is birefringent and very fluid above 38 $^{\circ}$ C, suggesting the occurrence of a mesophase. On slow cooling from the isotropic liquid (Fig. 1), point singularities with 2- and 4-Schlieren brushes slowly developed in the natural texture, indicative of a nematic phase.

Two phase transitions were detected by DSC during the first heating run (Fig. 2); a broad exothermic transition at 38 °C followed by a sharp transition at 60 °C could be measured, corresponding to the crystal/solid-to-mesophase and to the mesophase-to-isotropic liquid transformations, respectively.

On cooling, the same sharp peak at 60 °C was detected, but the mesophase was strongly supercooled down to room temperature and froze into a glassy solid ($T_g = 13$ °C). On subsequent heating–cooling cycles, a stable and reproducible behaviour took place with the reversible sequence Glass (G) 13 Nematic (N) 60 Isotropic (I).

In order to identify the mesophase and elucidate the supramolecular organization, wide- and small-angle XRD on aligned samples with a magnetic field was used (1.0 T). The diffractogram registered at 50 °C revealing three reflections (Fig. 3): *i*) a rather diffuse reflection in the small angle part, centred on the field direction ($\varphi = 0^{\circ}$), with a spacing $d_A = 33.35$ Å (A, Fig. 3). The correlation length of this reflection (radial extension) was estimated to be *ca.* $L \sim 190$ Å (from $\Delta 2\theta$ using the Scherrer formula), with an azimuthal distribution $\Delta \varphi = 40^{\circ}$ (FWHM); *ii*) a diffuse reflection in the medium-angle part, tilted with respect to the field direction with a maximum intensity at $\varphi = 45^{\circ}$, with a spacing of $d_B = 18.1$ Å and a much shorter correlation length, L' (B, Fig. 3, $L' \sim 22$ Å, $\Delta \varphi = 50^{\circ}$); *iii*) a diffuse wide-angle reflection, perpendicular to



Fig. 1 POM image obtained for hexaadduct 1 at 55 $^{\circ}$ C on slow cooling from the isotropic liquid.



Fig. 2 DSC curves obtained for hexaadduct 1: top, first heating; bottom, second heating–cooling cycle. G = glass, N = nematic phase and I = isotropic phase.

the field direction ($\varphi = 90^{\circ}$), with a spacing of $d_{\rm C} = 4.4$ Å (C, Fig. 3). The correlation length is of the same magnitude as that of the medium reflection B ($L'' \sim 21$ Å, $\Delta \varphi = 50^{\circ}$).

Both the reflections A and C reflect the nematic ordering of the system; C is assigned to the molten chains, and to the mesogenic side-groups, which are aligned in the same direction as the magnetic field, whilst A corresponds to a short range lamellar ordering with a mean molecular area of about 500 Å² (cybotactic groups, *vide infra*).²³ Since the maximum intensities of A and C are located along the meridian and the equator, respectively, the mesogenic subunits are not tilted within the layers embryos.

In addition, the FWHM associated to the distribution around both the maximum intensity centres extend up to $40-50^{\circ}$ ($\Delta \varphi$), which correspond to the nematic director fluctuations. As for the radial distribution width (2θ), the FWHM associated to the A reflection is unusually small for a nematic phase, corresponding to a large correlation length of about 6–7 molecular layers. Finally, there is a diffuse reflection (B), which is not present in any X-ray pattern of oriented classical nematics. This additional reflection is in a direction tilted with respect to the field direction and should correspond to some additional periodicity within the cybotactic clusters.



Fig. 3 X-Ray pattern recorded at 50 °C for the hexaadduct 1: (a) oriented pattern in the magnetic field (right) and sketch representing the three reflections (right); (b) top, 2θ profile of oriented pattern by integration over full azimuthal φ range; bottom, 2θ profile obtained from pattern with larger film–sample distance (328.0 mm) and peak deconvolution.

The periodicity of B and the abnormal width of A are specific to the structure of the hexaadduct molecule **1** with respect to classical nematogens, in that the supermolecule has a hierarchical structure, made of 12 lateral side-mesogenic groups that are covalently connected to C_{60} . Thus, this periodicity of B is necessarily associated to the position of the C_{60} moieties, which should be slightly correlated between two adjacent neighbouring layers. This additional ordering within the nematic phase is consistent with the abnormal large correlation length of the reflection A. The absence of any visible signal corresponding to some correlations between the Published on 01 March 2007. Downloaded by Temple University on 24/10/2014 08:34:17.

 C_{60} moieties within these layers embryos can be attributed to the continuity of the electronic density between the C_{60} embedded by the polarizable parts of the mesogens, as proposed by the model in Fig. 4 resulting from a Molecular Dynamics simulation. Such a periodic molecular model for 1 was built by retracting the parameters of a cell containing 8 molecules down to the estimated molecular volume, $V_{\rm M} \sim$ 16500 Å³. Indeed, the cell parameters were set from the experimental X-ray data, assuming a hexagonal 2-D closepacking of the supermolecules and considering two molecular layers ($a = b = 2^{1/2} \cdot 3^{-1/4} (V_{\rm M}/d_{\rm A})^{1/2} = 25$ Å, $c = 2d_{\rm A} = 66.7$ Å, $\gamma = 120^\circ$, $\alpha = \beta = 90^\circ$, $V_{\rm cell} = abc = ca^2/3$, Z = 4); the resulting density was close to 1. The simulation consisted of a 100 ps

C₆₀ self-organization (Fig. 4). , as ular **Conclusions** or 1 This work is the first step towards our attempt to reach and to

control ordered arrays containing [60]fullerenes. Hexaaddition on the carbonated polyhedron has allowed the preparation, high vield, of an enantiotropic, room-temperature in nematic material, despite the absence of mesomorphism of the malonate side-group promoter. Here, we showed that the specific architecture of the hexaadduct induces a nematic phase with unusual features. The highly symmetric [60]fullerene accordingly represents a particularly versatile scaffold for the regioselective covalent assembly of a variety of regular threedimensionally structured molecules, some of which may enlarge the existing repertoire of programmed molecular components for the construction of useful ordered materials. Thus, combining the two classes of materials *i.e.* mesomorphic [60]fullerene-based compounds (spontaneous organization) and donor-acceptor dyads, will allow exploration of one of the most promising ways towards efficient exciton dissociation, in order to reach high charge mobility and therefore high conversion yields. As such, derivatization of compound 1 by appropriate electron donors and acceptors using regioselective hexaaddition on the carbon sphere (multicomponent systems^{8*a*}), following the methods of Krautler¹⁶ and Diederich¹⁷. is currently in progress in our laboratory. These investigations should permit the understanding of new relationships between photo-induced inter- and/or intramolecular energy and/or electron transfer versus molecular architecture and supramolecular order. We anticipate that this versatile strategy for producing covalent donor-acceptor [60]fullerene-based nematic hexaadducts will lead to a new class of potentially interesting photovoltaic materials.

isotherm at 323 K, and confirmed the proposed molecular

This work was supported by the CNRS and University Louis Pasteur, Strasbourg. We would like to thank the Région Alsace for a fellowship to Mrs Hind Mamlouk. We also warmly thank Ms Laurence Oswald and Emilie Couzigné for technical assistance and Mr Nicolas Beyer for the design and construction of the XRD punctual beam experiment.

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