A Liquid Crystalline Supramolecular Complex of C_{60} with a Cyclotriveratrylene Derivative

Delphine Felder, Benoît Heinrich, Daniel Guillon, Jean-François Nicoud, and Jean-François Nierengarten*[a]

Dedicated to Professor Andreas Hirsch on the occasion of his 40th birthday

Abstract: Cyclotriveratrylene (CTV) derivatives substituted with 9 (**1**) or 18 (**2**) long alkyl chains have been prepared. Whereas no liquid crystalline behavior has been observed for **1**, the CTV derivative **2** has mesomorphic properties. Indeed, at room temperature compound **2** exhibits a nematic phase characterized by cybotactic groups with a local lamello-columnar order. Both CTV derivatives **1** and **2** are able to form supramolecular complexes with C_{60} in the solid state. In both cases, the 2:1 host–guest species have been obtained as brown compounds. No liquid crystalline behavior was observed for the supramolecular complex $[C_{60} \subset (\mathbf{1})_2]$. In contrast, observation of the brown product obtained from C_{60} and the CTV derivative **2** directly after preparation by polarized optical microscopy revealed a fluid birefringent phase at room temperature. When the sample is heated above 70 °C, the birefringence of the texture under the microscope disappears and the X-ray diffraction pattern is transformed into a pattern characteristic of a cubic phase. For the first time in thermotropic liquid crystals, the space group of this cubic phase can be assigned as $I4_132$.

Keywords: fullerenes · host–guest chemistry · liquid crystals · supramolecular chemistry

Introduction

The self-assembly of nanoscale architectures on the basis of instructions stored in the building components and the self-organization of the resulting discrete assemblies into more ordered systems such as liquid crystals, micelles, and colloids is a field of growing interest with unlimited possibilities for fundamental discoveries and practical applications.[1, 2] Fullerenes and their derivatives have shown a wide range of chemical and physical properties that make them attractive candidates for a variety of interesting features in supramolecular chemistry and materials science.[3] An important issue for applications of this new carbon allotrope appears to be the incorporation of C_{60} into well-ordered structures.[3, 4] Although the incorporation of fullerenes in thin, ordered films has been achieved with success during the past few years,[4, 5] liquid crystal ordering of fullerenes has been investigated to a much lesser extent.[6] In fact, the C_{60} subunit does not behave as a mesogenic unit, and therefore the preparation of fullerene-containing liquid crystals would appear to be difficult.[6, 7] The only examples of fullerene derivatives with liquid crystalline behavior have been reported by R. Deschenaux and co-workers, and are mainly based on the functionalization of the C_{60} sphere with mesogenic cholesterol subunits.[8]

As a part of this research, we became interested in a supramolecular approach for fullerene-containing liquid crystals based on the formation of an inclusion complex of C_{60} with a macrocyclic derivative. In fact, several recent studies have shown that the cyclotriveratrylene (CTV) macrocycle is a good candidate for the formation of inclusion complexes with C_{60}.[9, 10] Furthermore, the CTV core appears to be appropriate to produce mesophases when functionalized; indeed, several liquid crystalline CTV derivatives have already been described.[11] Therefore, a CTV substituted with long alkyl chains is virtually programmed for self-assembly in a discrete inclusion complex with the fullerene sphere and for self-organization of the resulting aggregates into an extended lattice with liquid crystalline properties. Here we report the synthesis of the CTV derivatives **1** and **2** for the complexation of C_{60}. Whereas no liquid crystalline behavior has been observed for the 2:1 host–guest complex obtained from **1** and C_{60}, the corresponding supramolecular species obtained from **2** and C_{60} shows mesomorphic properties.

[a] Dr. J.-F. Nierengarten, D. Felder, Dr. B. Heinrich, Dr. D. Guillon, Prof. J.-F. Nicoud
Groupe des Matériaux Organiques
Institut de Physique et Chimie des, Matériaux de Strasbourg
Université Louis Pasteur and CNRS
23, rue du Loess, 67037 Strasbourg (France)
Fax: (+33) 388-10-72-46
E-mail: niereng@michelangelo.u-strasbg.fr

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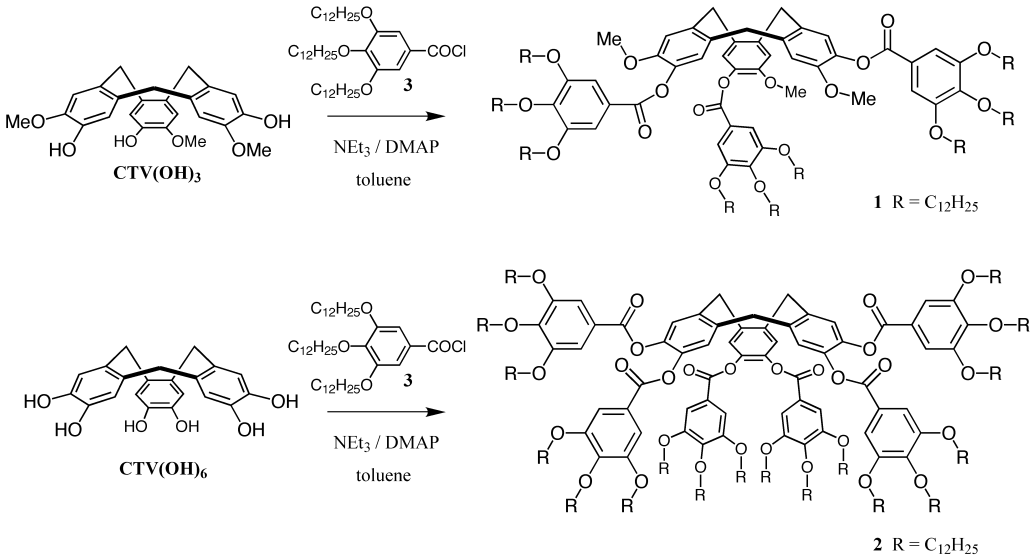

Scheme 1. Synthesis of CTV derivatives **1** and **2**.

Results and Discussion

Synthesis and solution studies: The synthetic route leading to the CTV derivatives **1** and **2** is shown in Scheme 1. **CTV(OH)$_3$** was prepared in three steps from vanillyl alcohol according to the procedure described by A. Collet and co-workers.[12] Treatment of **CTV(OH)$_3$** with 3,4,5-tridodecyloxybenzoyl chloride[13] (**3**) in the presence of 4-dimethylaminopyridine (DMAP) and NEt_3 in dry toluene afforded compound **1** in 76% yield. CTV derivative **2** was prepared under similar conditions by reaction of commercially available **CTV(OH)$_6$** with acid chloride **3**. In spite of the presence of an excess of **3**, the esterification of **CTV(OH)$_6$** was difficult to complete, probably due to steric crowding, and compound **3** was obtained in a low yield (15%). When the reaction mixture was heated at 80°C for a prolonged period of time, degradation took place and no further effort was made to optimize the conditions.

The formation of host–guest complexes in C_6H_6 solutions between C_{60} and **1** or **2** was followed by the continuous changes observed in the UV-visible spectra upon successive additions of the host to the fullerene solutions (Figure 1).

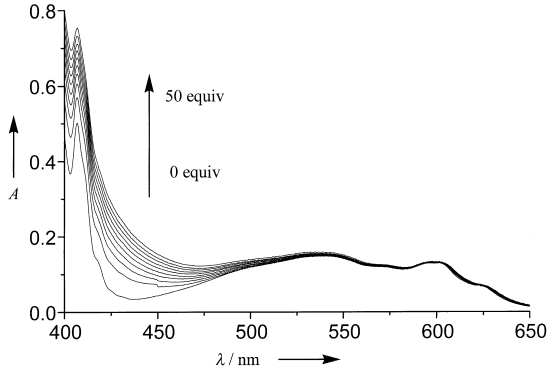

Figure 1. Absorption spectra of C_{60} in the presence of **2** in C_6H_6 at 298 K.

Abstract in French: *Des dérivés du cyclotrivératrylène (CTV) substitués par 9 (**1**) ou 18 (**2**) longues chaînes alkyles ont été synthétisés. Alors qu'aucune propriété cristal liquide n'a pu être observée pour le composé **1**, le CTV **2** présente des propriétés mésomorphes. De fait une phase nématique, caractérisée par des groupes cybotactiques de type lamello-colonnaire, a été mise en évidence à température ambiante pour le composé **2**. Les CTV **1** et **2** forment des complexes supramoléculaires avec le C_{60}. Aucune propriété mésomorphe n'a été observée pour le complexe $[C_{60} \subset (\mathbf{1})_2]$. Par contre, l'observation du complexe $[C_{60} \subset (\mathbf{2})_2]$ au microscope polarisant révèle une phase fluide biréfringente à température ambiante. Lorsque l'échantillon est chauffé, la biréfringence disparaît à 70°C et le diagramme de diffraction des rayons X montre les caractéristiques d'une phase cubique de groupe de symétrie $I4_132$. C'est la première fois qu'un tel groupe de symétrie est mis en évidence pour une phase mésomorphe thermotrope de type cubique.*

Specifically, each new addition of **1** or **2** to the C_{60} solution in C_6H_6 led to an increase in the absorption in the whole visible region, with the most pronounced effect at approximately 430 nm. These observed spectral changes are similar to those previously described in the literature for the addition of other CTV derivatives to fullerene solutions[10] and are characteristic of complexation.[10, 14]

During the UV-visible titrations of C_{60} solutions ($0.5-2\times10^{-4}$ M, fixed concentration) with **1** or **2** in C_6H_6, no isobestic points were observed. Furthermore, the Job plots[15] were poorly reproducible and the low variations in absorbance made their interpretation particularly difficult. Treatment of the titration data with the Benesi–Hildebrand equation[16, 17] gave the association constant values ($230\pm30\,M^{-1}$ for **1** and $330\pm30\,M^{-1}$ for **2** at 298 K), which are in good agreement with the formation of solvated 1:1 complexes. The binding isotherms also provide a good fit for a 1:1 stoichiometry.[17] The stoichiometry of the host–guest complexes obtained by

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crystallisation between **1** or **2** and C_{60}, however, is 2:1. This apparent contradictory host–guest ratio has also been observed in several recent examples of fullerene-based supramolecular assemblies, and it is quite reasonable to have a different (lower) complexation ratio in dilute solution to that in the solid state. Furthermore, the binding behaviour observed in solution for both **1** and **2** is in good agreement with those of other examples of substituted CTV derivatives already reported in the literature. Effectively, solvated 1:1 complexes have usually been observed.[10]

as smectic or columnar, but not developed on a large scale.[18] However, in the present work, the number and position of the diffuse reflections (Table 1) could not be interpretated by assuming only a smectic or a columnar order within the

Table 1. Description of the X-ray pattern of the nematic phase of CTV derivative **2** at 25 °C and proposition of indexation for a lamello-columnar lattice.

Signal	$2\theta_{mes}$[°]	d_{mes} [Å]	$\Delta 2\theta$ [°]	L [Å]	N	I[a]	hkl	$2\theta_{calcd}$ [°]	d_{calcd} [Å]
I	2.25	39.3 ± 1	0.45	170	4.5	VS	001		
II	4.5	19.6 ± 1	0.7		(6)	W	002		
III	6.7	13.2 ± 0.5	1.9	40	3	M	$110/1\bar{1}0$	6.7	13.2
IV	10.4	8.5 ± 0.3	1.9	40	5	M	200	10.4	8.5
V	14	6.3 ± 0.5	2	40	6	VW	$220/2\bar{2}0$?, h_x?	13.4	6.6
VI	21.0	4.2 ± 0.1	4.5	18	4.3	S	D_0		

[a] VS: very strong, S: strong, M: medium, W: weak, VW: very weak.

Liquid crystalline properties of CTV derivative 2: Whereas CTV derivative **1** does not exhibit any liquid crystalline behavior, compound **2** shows mesomorphic properties. These have been deduced from optical and X-ray diffraction properties. Polarized optical microscopy revealed a fluid birefringent phase at room temperature for **2** (Figure 2) and

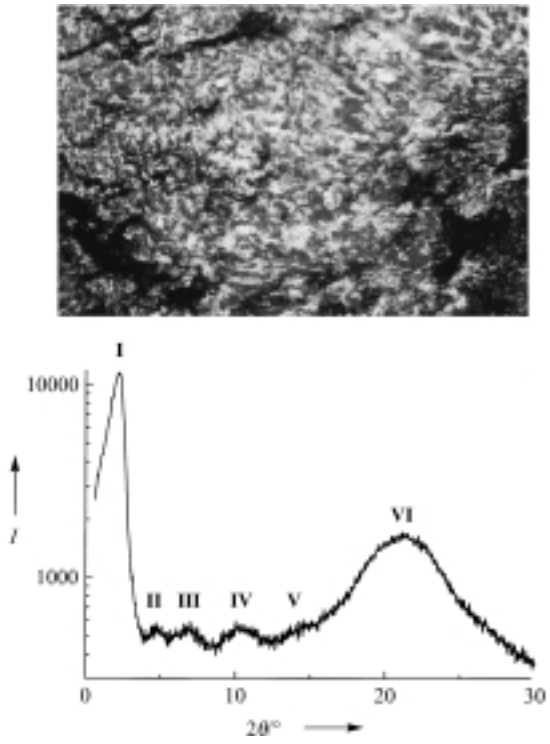

Figure 2. Top: Optical texture observed with a polarizing microscope at 25 °C for the CTV derivative **2**. Bottom: X-ray diffraction pattern of the nematic mesophase recorded at 25 °C for compound **2**.

the clearing temperature was determined to be 75 °C. The X-ray diffraction patterns in the liquid crystalline phase contain only diffuse reflections both in small- and wide-angle regions; this suggests that this phase is nematic in nature (Figure 2). These diffuse reflections indicate the presence of cybotactic groups. These generally correspond to groups of molecules locally arranged in a more ordered structure such cybotactic groups. Indeed, they correspond to a lamello-columnar order,[19] that is, smectic layers with the existence of columns oriented parallel to the smectic planes. Thus, the reflections **I** and **II** in the small-angle region would result from the local lamellar stacking, corresponding to a layer spacing, d, of about 39 Å. From the width of the (001) reflection, one can estimate a correlation distance, L, of about 170 Å, in a direction parallel to the layer normal; this corresponds to about four to five molecular layers. The reflections **III** and **IV** were considered to correspond to the (110)/($1\bar{1}0$) and (200) reflections, respectively, of a centered rectangular columnar lattice ($a = 17.1 \pm 0.6$ Å; $b = 20.9 \pm 2.5$ Å). The resulting columnar area ($s_{m1} = s/2 = 180 \pm 25$ Å^2) is consistent with the one calculated from the ratio of the molecular volume (V_m) to d, by assuming a density of 1.0 ± 0.1 g cm^{-3} ($s_{m2} \approx 180 \pm 20$ Å^2). This value is larger than the molecular area found in the smectic A phase for other CTV derivatives that contain only six aliphatic tails (84 ± 8 Å^2),[11] but is close to the minimum value imposed by the bulkiness of nine stretched alkyl chains oriented parallel to the normal of the layer, when half of the 18 chains are rejected on each side of the CTV core ($9 \times 21.3 = 192$ Å^2). This index is therefore much more likely than the alternative index (**III** ≡ 200; **IV** ≡ $110/1\bar{1}0$), which would imply a much too small columnar area ($s_{m1} = s/2 = 120 \pm 20$ Å^2) with respect to the bulkiness of the chains. The correlation distances, L,[20] associated to the columnar ordering within the cybotactic groups are about four times smaller than that associated with the smectic ordering, but they also correspond also to about four molecular layers. The very weak diffuse signal, **V**, may correspond to the reflection [(220)/($2\bar{2}0$)] of the bidimensional lattice, that is, to the second order of the reflection **III**. However, it cannot be excluded that it occurs from a repetition distance associated to the piling of the molecular cores, although an intracolumnar spacing of 4.7 Å can be deduced from the columnar area variation for an homologous series of other CTV derivatives that have the hexagonal columnar phase.[11] The reflection **VI** is attributed as usual in mesophases to the lateral interactions between the alkyl tails; its position and width being typical for molten aliphatic moieties. There is no significant change in the shape of these reflections as a function of temperature. Only small shifts in the position of the wide-angle reflections could be

observed. When cooling down from 25 to $-100\,^{\circ}C$, the repetition distance associated to the reflection **VI** decreases by 0.2 Å, which is in agreement with the value determined from the volume contraction for liquid paraffins (0.20 Å).[21] The spacing for **III** decreases by about 0.15 Å, but the spacing for **IV** increases by about 0.3 Å; this corresponds to a decrease in b of 1.3 Å and to an increase in a of 0.5 Å, respectively.

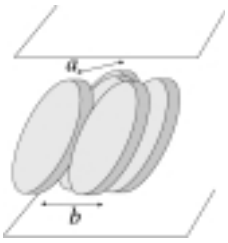

Figure 3. Schematic view of the local molecular packing within the smectic layers of the cybotactic groups of the nematic mesophase for compound **2**.

It should be noted that the geometry of the local columnar lattice deviates considerably from the hexagonal symmetry condition ($a/b = 3^{0.5}$). This indicates an important tilt of the molecular cores with respect to the lattice normal, the main in-plane component of the tilt lying along a (Figure 3).[22]

The supramolecular complexes of C_{60} with the CTV derivatives: Slow evaporation of C_6H_6 solutions of mixtures of C_{60} and CTV derivative **1** or **2** in various proportions afforded the corresponding supramolecular host–guest complex. For both **1** and **2**, the 2:1 host–guest species have been obtained as brown compounds. It should be noted that in the presence of an excess of C_{60}, the host–guest complexes were obtained together with crystalline C_{60}. On the other hand, with an excess of the CTV derivative **1** or **2**, non-homogeneous mixtures were obtained. In fact, two phases were present, a colorless one corresponding to pure **1** or **2** and a brown one corresponding to the 2:1 host–guest complexes. The formation of the 2:1 complexes is in apparent contradiction with the X-ray crystallographic analysis of the inclusion complex obtained from a CTV derivative bearing six unsubstituted benzoyl arms [CTV(OBz)$_6$] and C_{60} described by H. Matsubara and co-workers,[10c] where effectively a 1:1 complex was obtained in the solid state. However, close analysis of the crystal packing shows that two kinds of C_{60} molecules are present, one is encapsulated within a cavity of two host molecules, the other is located without hosts between two inclusion complexes. In other words, this structure could be considered as a 2:1 host–guest inclusion complex "solvated" with a fullerene sphere. In our case, it is reasonable to assume that such a structure can not be obtained due to the presence of the 18 or 36 long aliphatic chains around the 2:1 inclusion complexes, the fullerenes and the alkyl chains being amphipathic.

No liquid crystalline behavior could be observed for the supramolecular complex [$C_{60} \subset$ (**1**)$_2$], and furthermore, this complex was not thermally stable. At about 60 °C, precipitation of small C_{60} crystals from a colorless liquid, presumably pure **1**, was observed; this phase separation was irreversible. In contrast, such behavior was not observed with the supramolecular complex [$C_{60} \subset$ (**2**)$_2$] even on repeated heating–cooling cycles. Observation of the product obtained from C_{60} and CTV derivative **2** directly after solvent evaporation by polarized optical microscopy revealed a fluid, birefringent phase at room temperature.

The X-ray diffraction patterns are similar to those of the lamello-columnar ordering registered with the pure CTV, with the same reflections **I** to **VI**. The reflections **I** and **II** correspond to smaller distances, indicating a reduction of the layer spacing (of about 10 %). On the other hand, the two-dimensional lattice area deduced for the complex is somewhat larger than that measured for the pure CTV. This would be consistent with the incorporation of some C_{60} in the sublayer formed by the molecular cores, thereby increasing the area reported for one CTV molecule and the area of the rectangular lattice.

When the sample was heated above 70 °C, the birefringence of the texture under the microscope disappears and the X-ray diffraction pattern transformed into a pattern characteristic of a cubic phase (Figure 4). This phase transition was irreversible. This was confirmed by differential scanning calorimetry (DSC). During the first heating run, DSC analysis of the supramolecular complex [$C_{60} \subset$ (**2**)$_2$] gave one endotherm at 70 °C. The enthalpy value associated with this phase transition was found to be 13.6 J g^{-1}. During the cooling run, no exotherm could be seen, which indicates the irreversibility of the phase transition, and the endotherm observed during the first heating run could not be observed anymore during the second run. Finally, no additional endotherm could be detected at higher temperature.

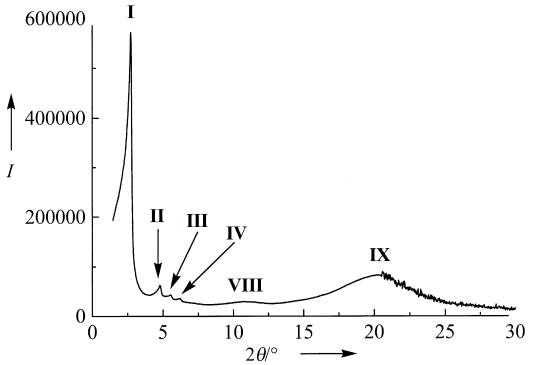

Figure 4. X-ray diffraction pattern of the cubic mesophase recorded at 25 °C for [$C_{60} \subset$ (**2**)$_2$] (the reflections **V**, **VI**, and **VII** could not be extracted from background on the counter patterns or on the scans of film patterns, although they are clearly distinguished on the original long-exposure photographic film patterns).

In the X-ray pattern of the cubic phase obtained upon heating, the small-angle region contains seven sharp reflections, which correspond to the following integer square spacing ratios: 1:3:4:5:6:7:8, labelled **I** to **VII**, (the reflections **V**, **VI** and **VII** could not be extracted from background on the counter patterns or on the scans of film patterns, although they are clearly distinguished on the original long-exposure photographic film patterns). The wide-angle region contains two diffuse reflections **VIII** and **IX** at about 8.2 ± 0.1 Å and 4.4 ± 0.05 Å, respectively. The 4.4 Å reflection corresponds to the lateral distance between alkyl tails, while the 8.2 Å reflection is probably related to a repetition distance between the complexes formed by the CTV molecular cores and the fullerene molecules. Table 2 lists the indexation of reflections **I** to **VII** for the smallest possible primitive, body-centered and

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Table 2. Indexation of the sharp small-angle reflections in the X-ray pattern of the cubic mesophase obtained at 20 °C for the CTV derivative **2**/C_{60} mixture 2:1, within the smallest primitive, body-centered and face-centered lattices possible.

			Primitive[b]		Body-centered[c]		Face-centered[d]	
Signal	$[d_1/d_i]^2$	I[a]	hkl	$h^2+k^2+l^2$	hkl	$h^2+k^2+l^2$	hkl	$h^2+k^2+l^2$
–	–	–	–	–	–	–	111	3
–	–	–	100	1	–	–	200	4
I	1	VS	110	2	110	2	220	8
–	–	–	–	–	–	–	311	11
–	–	–	111	3	–	–	222	12
–	–	–	200	4	200	4	400	16
–	–	–	–	–	–	–	331	19
–	–	–	210	5	–	–	420	20
II	3	M	211	6	211	6	422	24
–	–	–	–	–	–	–	511/333	27
III	4	M	220	8	220	8	440	32
–	–	–	–	–	–	–	531	35
–	–	–	221/300	9	–	–	600/442	36
IV	5	M	310	10	310	10	620	40
–	–	–	–	–	–	–	533	43
–	–	–	311	11	–	–	622	44
V	6	VW	222	12	222	12	444	48
–	–	–	–	–	–	–	711/551	51
–	–	–	320	13	–	–	640	52
VI	7	VW	321	14	321	14	642	56
–	–	–	–	–	–	–	553/731	59
VII	8	VW	400	16	400	16	800	64

[a] 1 VS: very strong, S: strong, M: medium, W: weak, VW: very weak. [b] At 20 °C: $d_{110} = 31.9$ Å, $a = 45.1$ Å, $V = 91.8 \times 10^3$ Å^3. [c] At 20 °C: $d_{110} = 31.9$ Å, $a = 45.1$ Å, $V = 91.8 \times 10^3$ Å^3. [d] At 20 °C: $d_{220} = 31.9$ Å, $a = 90.2$ Å, $V = 734.5 \times 10^3$ Å^3.

face-centered cubic lattices. However, the body-centered lattice is probably the relevant one, as no particular extinction rules could explain the number of missing low-angle reflections for both alternate types of cubic lattices. In this case, it should be emphasized that the reflection (200) is missing. Since a rather high intensity would have been expected from its location between reflections **I** and **II**, the absence of this reflection probably results from a particular extinction rule. This exists only for two body-centered cubic space groups: $I4_132$ (no. 214) and $I\bar{4}3d$ (no. 220), whereby the presence of the (222) reflection excludes the $I\bar{4}3d$ space group. Although specific features of the structure factor may also lead to the same extinctions of the symmetry-allowed reflections, the space group $I4_132$ is the only one that fits the observed reflection series, based on the extinction rules which results from the space group symmetry, and is, therefore, the most probable one. To our knowledge, this is the first time that the space group $I4_132$ has been assigned for a cubic mesophase. It should be pointed out that such behavior has already been theoretically predicted.[23]

No evolution of the X-ray patterns was observed over several days at temperatures below 80 °C. Above this temperature, the X-ray patterns changed irreversibly, with additional sharp reflections appearing continuously in the small-angle region, while optical microcope observations gave evidence of the presence of small birefringent crystallites appearing in the overall isotropic texture. This irreversible evolution may occur from a macroscopic segregation of the C_{60} molecules within the CTV matrix, the resulting variation of local concentration leading to the coexistence of different phases. Such phases were not studied further. Due to this slow and irreversible evolution, it was not possible to determine the clearing temperature. This is also consistent with the DSC analysis, effectively, no transition corresponding to the clearing point could be detected for $[C_{60} \subset (\mathbf{2})_2]$. It should be pointed out that the covalent fullerene derivatives with liquid crystalline properties reported by R. Deschenaux are thermally stable.[8] However, in contrast to the supramolecular complex $[C_{60} \subset (\mathbf{2})_2]$, which is stable from room temperature up to 80 °C, these C_{60} derivatives do not show mesomorphic properties at room temperature.

Conclusions

Our findings provide further insight into the construction of supramolecular assemblies of C_{60}. Initially, host–guest chemistry with fullerenes was used for the efficient separation of fullerenes.[9, 10, 14] In the preparation of the first example of a liquid crystalline host–guest complex of C_{60}, we have shown that the supramolecular chemistry of fullerenes can also be used in the formation of ordered fullerene assemblies that are easy to process for future applications in material science.

Experimental Section

General: Reagents and solvents were purchased as reagent grade and used without further purification. Toluene was distilled over sodium and benzophenone. Compounds 3,4,5-tridodecyloxybenzoyl chloride (**3**)[13] and **CTV(OH)$_3$**[12] were prepared as previously reported. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were achieved at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from Merck. Thin-layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from Merck, visualization by UV light. Melting points were measured on an electrothermal digital melting point apparatus and are uncorrected. UV/Vis spectra were measured on a Hitachi U-3000 spectrophotometer. IR spectra were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC200 with solvent peaks as reference. DSC analyses were performed on a DSC 7 Perkin–Elmer apparatus at a scan rate of 10 °C min^{-1}. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg. X-ray patterns were recorded on samples filled in Lindemann glass capillaries with two setups based on focalised, linear $CuK_{\alpha 1}$ beams produced with sealed tubes and bent quartz monochromators. Patterns were systematically recorded as a function of temperature by using a home-made oven controlled by an INSTEC unit (residual temperature fluctuations of ±0.02 °C) and an INEL CPS120 counter. For a better signal to background ratio of the higher order reflections of the cubic lattice, long-exposure patterns were registered at a few temperatures on KODAK scientific imaging films, with a second setup equipped with a home made

vacuum stand alone oven (residual temperature fluctuations of $\pm 1\,^{\circ}C$). The films were scanned with an EPSON GT-7000 scanner and the image background corrected and integrated in order to get intensity versus 2θ files. A θ-θ diffractometer was also used. This third setup based on a parallel CuK_{α} beam produced by a sealed tube, a secondary beam monochromator and a Xe counter (Philips X-PERT system) was used to verify the diffuse signals found with the INEL counter and to follow the shifts in their location (Lorentzian fits) in subambient conditions, whereby the sample was introduced as a few hundred μm thick film in a TK450 vacuum oven (Anton Paar).

2,7,12-Tri(3,4,5-tridocyloxybenzoyloxy)-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (1): A solution of **3** (3.31 g, 4.77 mmol) in toluene (10 mL) was added dropwise over 1 h to a stirred solution of **CTV(OH)$_3$** (0.5 g, 1.22 mmol), DMAP (0.673 mg, 5.5 mmol), and NEt_3 (0.665 mL, 4.77 mmol) in toluene (40 mL) under Ar at 0 °C. The reaction mixture was warmed slowly to room temperature (over 1 h) and stirred for 24 h at room temperature, then 2 h at 80 °C. The resulting mixture was poured into water. The organic layer was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), filtered, and evaporated. Column chromatography (SiO_2, $CHCl_3$) followed by recrystallisation from acetone yielded 2.23 g (0.937 mmol, 76 %) of **1**. Colorless solid; m.p. 60 °C; ^{1}H NMR ($CHCl_3$, 200 MHz): $\delta = 0.89$ (t, $J = 6$ Hz, 27 H), 1.35 (m, 162 H), 1.80 (m, 18 H), 3.67 (d, $J = 14$ Hz, 3 H), 3.80 (s, 9 H), 4.03 (t, $J = 6$ Hz, 18 H), 4.82 (d, $J = 14$ Hz, 3 H), 6.94 (s, 3 H), 7.13 (s, 3 H), 7.40 (s, 6 H); ^{13}C NMR ($CHCl_3$, 50 MHz): $\delta = 14.08$, 22.66, 26.06, 29.29, 29.37, 29.61, 29.65, 30.31, 31.90, 36.52, 56.22, 69.14, 73.51, 108.56, 114.18, 123.79, 124.07, 131.48, 137.86, 138.66, 142.74, 149.92, 152.86, 164.48; IR (CH_2Cl_2): $\tilde{\nu} = 1732\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{153}H_{252}O_{18}$ (2379.7): C 77.22, H 10.67; found C 77.03, H 10.78.

2,3,7,8,12,13-Hexakis(3,4,5-tridocyloxybenzoyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (2): A solution of **3** (7.38 g, 10.64 mmol) in toluene (20 mL) was added dropwise over 1 h to a stirred solution of **CTV(OH)$_6$** (0.50 g, 1.36 mmol), DMAP (1.5 g, 12.28 mmol), and NEt_3 (1.48 mL, 10.64 mmol) in toluene (60 mL) under Ar at 0 °C. The resulting mixture was warmed slowly to room temperature (over 1 h) and stirred at this temperature for 24 h, then 2 h at 80 °C before being poured into water. The toluene solution was washed twice with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), filtered, and evaporated. Two successive column chromatographic separations (SiO_2, $CHCl_3$/hexane 6:2) yielded 0.9 g (0.21 mmol, 15 %) of **2**. Colorless liquid crystalline product (see text); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.88$ (t, $J = 6$ Hz, 54 H), 1.26 (m, 324 H), 1.72 (m, 36 H), 3.79 (t, $J = 6$ Hz, 12 H), 3.80 (d, $J = 12$ Hz, 3 H), 3.95 (t, $J = 6$ Hz, 24 H), 4.90 (d, $J = 12$ Hz, 3 H), 7.20 (s, 12 H), 7.41 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta =$ 14.08, 22.67, 26.06, 26.15, 29.37, 29.51, 29.69, 29.75, 30.37, 31.93, 69.00, 73.42, 108.28, 123.18, 124.84, 137.17, 141.15, 142.84, 152.79, 163.97; IR (CH_2Cl_2): $\tilde{\nu} = 1731\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{279}H_{474}O_{30}$ (4308.81): C 77.77, H 11.09; found C 77.50, H 11.21.

[$C_{60} \subset$ (2)$_2$]: A solution of **2** (100 mg, 0.0185 mmol) and C_{60} (0.5 equiv) in C_6H_6 (100 mL) was allowed to stand at room temperature until complete evaporation of the solvent. The resulting mixture was further dried under high vacuum for 12 h. A homogeneous dark brown product was thus obtained. Elemental analysis calcd (%) for $(C_{279}H_{474}O_{30})_2 \cdot (C_{60})_1 \cdot (C_6H_6)_6$ (9799.4): C 80.10, H 10.11; found: C 80.23, H 10.34.

Determination of the association constants: Binding studies were performed in C_6H_6 solution at 298 ± 1 K. In a typical experiment, a 1 mL volume of a 1.39×10^{-4} M C_{60} solution was placed in the sample cell. An aliquot of a 6.93×10^{-3} M stock solution of compound **1** (or **2**) was added to the sample cell, and, after homogenization, the absorption spectrum was recorded. Additional aliquots of **1** (or **2**) were added to the sample cell, and the spectrum was recorded after each addition. The association constant was calculated from the absorption intensities changes observed at 430 nm compared to pure C_{60} using the Benesi–Hildebrand equation.[16] All experiments were performed at least in triplicate.

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