An optically-active liquid-crystalline hexa-adduct of [60]fullerene which displays supramolecular helical organization†

Stéphane Campidelli,∗a Torsten Brandmüller,b Andreas Hirsch,*b Isabel M. Saez,c John W. Goodby∗∗c and Robert Deschenaux∗∗a

Polyaddition of mesogenic moieties to C60 were found to yield chiral supermolecular nanoparticles which exhibit iridescent helical chiral nematic phases.

Self-organization has opened up new and exciting perspectives in the design and engineering of novel, controlled architectures on the nano- and mesoscopic length scales. Liquid crystals are one type of material that self-organizes into complex, hierarchical structures. Functional liquid crystal assemblies offer the possibility of fabricating dynamic, addressable structures where the functional moieties are organized in a pre-determined and controllable fashion.2b

Chiral nematic liquid crystals form helical superstructures where the local director of the nematic phase is rotated in either a right- or left-handed direction perpendicular to the molecular long axes. When the helical pitch is of the order of the wavelength of visible light, chiral nematic phases (N*) display iridescent coloured textures, associated with Grandjean plane textures. The origin of the interference colour of this mesophase is the helical structure itself; the pitch length, along with the mean refractive index, determines the wavelength of the reflected light. The pitch depends on local environment such as the temperature or applied electric fields, so the colour of the material can be controlled by external stimulation. Temperature sensors based on the N* phase have been available for many years and, more recently, the photonic properties of such mesophases have been applied to yield light-emitting materials.3

[60]Fullerene (C60) was successfully incorporated into liquid crystal systems4–9 to give nematic, chiral nematic, smectic A, smectic B, columnar and cubic phases. Recently, it was shown that hexa-addition of a malonate derivative, which possessed a monotropic nematic phase, yielded a fullerene derivative which exhibited an enantiotropic smectic A phase.4c This result indicated that C60 can be used as a platform for the synthesis of liquid-crystalline materials from a non-mesomorphic addend. A bischolesterol derivative was used to prepare a hexa-adduct of C60.8

As expected (due to the cholesterol units) a smectic A phase was obtained.4c,b,d

In the case of polyadducts, C60 plays the role of a focal point. Polyaddition is therefore an elegant means to incorporate C60 into a specific liquid-crystalline environment. The sixfold addition of malonates to C60 also gives rise to beautiful structural motifs. If mixed hexa-adducts are used (i.e. different addends forming the hexa-adduct) interesting properties for the resulting compounds are observed. For example, the use of polar dendrimers as one type of addend, with the other five being non-polar alkyl chains, led to amphiphilic hexa-adducts that form well-defined supra-structures such as micelles and vesicles.10,11 Such precisely defined structures are of great importance in material and pharmaceutical sciences, e.g. in drug delivery.

In order to explore the influence of polyaddition on the formation of chiral liquid-crystalline phases, we synthesized mono- (1) and hexa- (2) adducts of C60 (Fig. 1). The latter structure is interesting for the exploration of the material properties of the chiral mesogens when assembled around a focal point. It is also interesting to examine how the selection of the directionality of the mesogenic units is made in a spherical environment. This model system could thus inspire the design of future chiral liquid-crystalline dendrimers.12 The optically-active mesogenic unit 13 (Scheme 1) was used to functionalize C60 with dendritic malonates containing either 4 or 8 units.4c,12 In both cases, the methanofullerenes exhibited the chiral nematic phase.

The syntheses of 1 and 2 are presented in Scheme 1. Esterification of alcohol derivative 13 with malonyl chloride led to malonate 3. Addition of 3 with C60 in the presence of I2 and DBU furnished the mono-adduct 1. Reaction of 9,10-dimethylanthracene14 with C60 followed by addition of 3 in the presence of 9

Fig. 1 Structure of mono-adduct 1 and hexa-adduct 2 of fullerene.
Scheme 1 Reagents and conditions: (i) malonyl chloride, Et₃N, CH₂Cl₂, rt, 63%; (ii) C₆₀, I₂, DBU, toluene, rt, 64%; (iii) C₆₀, 9,10-dimethylanthracene, toluene, rt, and then 3, CBr₄, DBU, rt, 1.4%.

CBr₄ and DBU yielded hexa-adduct 2. The structure and purity of 1–3 were confirmed by ¹H and ¹³C NMR spectroscopy, UV-vis spectroscopy and elemental analysis (see ESI†).

The thermal and liquid-crystalline properties of 1–3 were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The transition temperatures and enthalpies are reported in Table 1.

Malonate 3 exhibited a chiral nematic phase identified by the formation of small focal-conic domains which transformed into the Grandjean plane and fingerprint textures with pitch bands upon cooling.

Mono-adduct 1 was found to be non-mesomorphic. A glass transition was observed upon cooling. The non-mesomorphic character of 1 is due to the spherical structure of C₆₀ which dominates and prevents the formation of anisotropic molecular objects.

On slow cooling from the isotropic liquid, hexa-adduct 2 displayed a highly birefringent texture but no characteristic defects were observed. However, after about 2 hours, areas of schlieren and pseudo-focal conic textures were identifiable. Therefore, the sample was annealed just below the clearing point. After 24 hours, large areas of the preparation evolved to show the Grandjean plane texture and fingerprint defects (Fig. 2, left); where the sample was not in contact with the coverslip, the texture evolved more easily, displaying pseudo-focal conics (Fig. 2, right). In the Grandjean plane texture the sample was clearly helical, showing a left-handed helix (as also observed for precursor 4), from which we concluded that 2 exhibited a chiral nematic phase. An insight into the supramolecular organization of this system in the mesophase can be obtained from the value of the pitch length of the chiral nematic phase. The pitch was determined via POM by measuring the number of pitch bands per unit length from the fingerprints and pseudo-focal conic defects.

For 2, a value of 2.0 μm for the pitch length was obtained at room temperature. The pitch values obtained by the same method yielded 1.9 μm for the malonate precursor 3 at room temperature and 1.7 μm for the chiral monomer 4 at 100 °C. Although a strict comparison of the pitch values is precluded since they were determined at different temperatures, it is not unreasonable to assume that the helical organization of 2 and 3, present at higher temperatures, is locked in the glassy state at room temperature, and so provides a valuable and consistent picture of the supramolecular organization of the chiral nematic phase. As observed, the pitch of 2 is similar to that of 3, and only marginally longer than that of 4 (perhaps reflecting the fact that it was determined at higher temperature), which leads to the conclusion that although the thermal stability of the mesophase for 2 is slightly lower than for 3, the fullerene moiety in 2 is shielded very effectively among the laterally attached mesogens, without disturbing the helical supramolecular organization of the mesophase (Fig. 3). Furthermore, comparison of the thermal stability and pitch values of 2 and those of the dendritic mono-adduct tetramer (ρ = 5 μm; N* → I = 69 °C)⁵⁶ reveals that C₆₀ is better

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tg°C</th>
<th>N* → I°C</th>
<th>ΔH/kJ mol⁻¹</th>
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<tr>
<td>3</td>
<td>−1</td>
<td>133</td>
<td>1.8</td>
</tr>
<tr>
<td>1</td>
<td>49</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>47</td>
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</tr>
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</table>

a Tg = glass transition temperature, N* = chiral nematic phase, I = isotropic liquid; temperatures are given as the onset of the peak obtained during the second heating run. b Determined during the first cooling run.

Fig. 2 Textures displayed by 2: Grandjean-plane texture on the contact area (left) and pseudo-focal conic texture with pitch bands on the non-contact area (right).

Fig. 3 Supramolecular organization of 2 within the chiral nematic phase.
embedded within the self-organizing system in the hexa-adduct than in the dendritic mono-adduct, undoubtedly because in 2 the addends are symmetrically distributed all over the fullerene sphere effectively isolating it, whereas in the mono-adduct C_{60} is left comparatively more exposed, increasing the possibility of aggregation interactions between the C_{60} units, which are detrimental to mesophase formation. Qualitative observation of the viscosity of the samples (2 is markedly less viscous than the monoadduct) points to a similar conclusion.

It is also interesting to consider how the selection process for the helical organization of 2 is generated upon cooling from the isotropic liquid. As the C_{60} core of the material is spherical, and the mesogenic units are attached by relatively short methylene spacers relative to the particle core size and spherical nature, it is not unreasonable to assume that, in the liquid phase, the mesogenic units are symmetrically disposed about the central core. Cooling into the chiral nematic phase, however, the helical organization would be expected to be a result of the organized packing of the dendritic supermolecules, i.e. they are no longer spherical. However, when the diameter of the C_{60} core is compared to the length of the mesogenic units, it is clear that flexible, random packing of the mesogenic units about the core in the liquid crystal state is not possible, and that the mesogens are required to be organized in their packing arrangements relative to one another, both on the surface of the dendrimer and between individual dendrimers. One possibility is shown in Fig. 3 where the mesogenic units are oriented parallel to one another, thus when the material cools into the liquid-crystalline phase directional order of the mesogens is selected by the external environment, such as the surface. In doing so, this information is transmitted to the other mesogens associated with the spherical dendrimer and further to the neighbouring dendritic supermolecular compounds. Alternatively, for an individual dendrimer it is possible for the local director of the mesogens to spiral around the C_{60} core to give poles at the top and bottom of the structure (Fig. 4), i.e. a molecular boojum. Thus, the spherical dendrimer will have a well-defined chiral surface, thereby resulting in a chiral nanoparticle. When the chiral nanoparticles pack together they will do so through chiral surface recognition processes, resulting in the formation of a helical supramolecular structure. Consequently, the chiral supramolecular nanoparticles transmit their local organization through amplification to adjacent supermolecules resulting in values of the helical twisting power that are lower than might be expected for such large molecular entities.

Thus, the development of well-controlled synthetic methods to produce polyadducts of C_{60} opens the door towards new chiral supermolecular nanoparticles. In case of liquid crystals, C_{60} is hidden in the mesogenic cloud, and does not alter the supramolecular organization encoded in the mesogens, but instead aids in its amplification.

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Notes and references