Functional polypedes—chiral nematic fullerenes†

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Self-organising, functional materials created by bottom-up synthesis represent important steps forward in the development of novel materials, here we report on the preparation and properties of a chiral nematic tetrapedal liquid crystal that has been functionalised with C_{60}.

The successful creation of fullerene-containing liquid crystals opens avenues to the design of new and unique mesomorphic functional materials.[1,2] Such materials combine the exceptional electrochemical and photophysical properties of fullerenes with those of self-organising and self-assembling media. The association of such properties could be used in the evolution of solar cell technologies,[3] and in the development of supramolecular redox and optical molecular switches[4] based on photoinduced electron transfer, for example, between ferrocene and fullerene units.[5] Three strategies have been developed for the preparation of fullerene-containing liquid crystals: (i) fullerene (C_{60}) was functionalised with liquid-crystalline malonate derivatives, via use of the Bingel-reaction,[6] leading to mesomorphic methanofullerenes or, alternatively, derivatisation of C_{60} was achieved using the 1,3-dipolar cycloaddition reaction[7] with liquid-crystalline aldehyde derivatives, giving rise to mesomorphic fulleropyrrolidines; with both these sets of materials displaying nematic and/or smectic A phases;[1] (ii) complexation of C_{60} with a liquid-crystalline cyclotriveratrylene (CTV) derivative gave a non-covalent molecular assembly which showed a nematic phase characterized by cybotactic groups and a cubic phase of $I4_132$ symmetry;[8] and (iii) C_{60} was derivatised with five rod-like aromatic units leading to materials with conical molecular structures that exhibited thermotropic and lyotropic columnar phases.[2] However, studies of chiral systems, with their attendant physical properties of thermochromism, ferroelectricity and/or pyroelectricity, have not yet been entered into. Such investigations are expected to yield fascinating results with respect to the super- and supra-molecular chemistry associated with fullerene.

To induce form chirality into C_{60} systems, we introduced, within the malonate addend, laterally branched chiral mesogenic groups. Such entities have been previously demonstrated to generate chiral nematic (N*) phases in polypedal liquid crystal systems.[9] Compound 1[10] (Fig. 1), which has four aromatic rings, was found to be a very good promoter of liquid-crystalline properties and a useful material for attaching to dendritic cores. Indeed, grafting of 1 onto octasilsesquioxanes gave rise to materials exhibiting N* and columnar phases.[9] We anticipated that the three-dimensional structural analogy between fullerene and the octasilsesquioxane core could lead to chiral phases also in the case of C_{60}. The synthesis of the methanofullerene 2 (Fig. 2), which represents the first liquid-crystalline fullerene derivative that possesses a chiral mesophase, is shown in Scheme 1.

Esterification of 5-benzyloxyisophthalic acid 3[11] with 1 yielded the protected intermediate 4, the deprotection of which gave the phenol derivative 5. Condensation of 5 with 4-(10-hydroxydecyloxy)benzoic acid, 6,[12] (structure not shown) produced 7, which was treated with malonyl chloride to give the malonate derivative 8. Finally, addition of 8 to C_{60} led to the target compound 2. The structures and purities of all of the compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy, UV-vis spectroscopy, and elemental analysis. The analytical data will be reported in detail in the forthcoming full paper.

The thermal and liquid-crystalline properties of 2, 4, 5, 7 and 8 were investigated by differential scanning calorimetry (DSC) and polarized transmitted light microscopy (POM). Their transition temperatures and those of the liquid-crystalline substrate 1 are collected in Table 1. All the mesomorphic compounds gave rise to N* phases which were identified by POM from the formation of typical plane and fingerprint textures and pitch bands. In some cases, when the sample was cooled slowly from the isotropic liquid, small focal-conics were observed.

Only 1 exhibited a crystalline state, whereas 2, 4, 5, 7 and 8 all showed glass transitions. This is due to the fact that 2, 4, 5, 7 and 8 were isolated as non-crystalline materials: they were analysed after purification by column chromatography. The fullerene derivative 2 showed a higher viscosity than the other compounds, including the malonate 8. This behaviour is in agreement with previous observations,[1] and is attributed, at least in part, to C_{60}–C_{60} interactions. Furthermore, 2 showed a much lower isotropization temperature than 8. This result
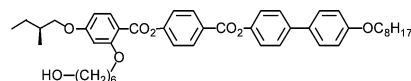
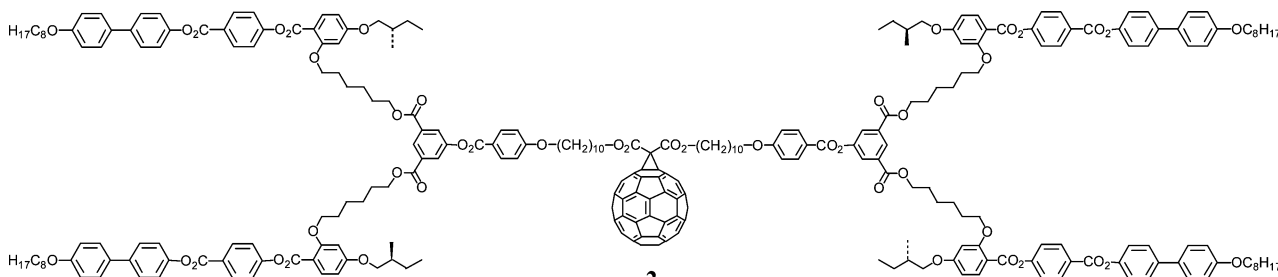Fig. 1 Structure of the chiral liquid-crystalline promoter 1 (S-absolute configuration).

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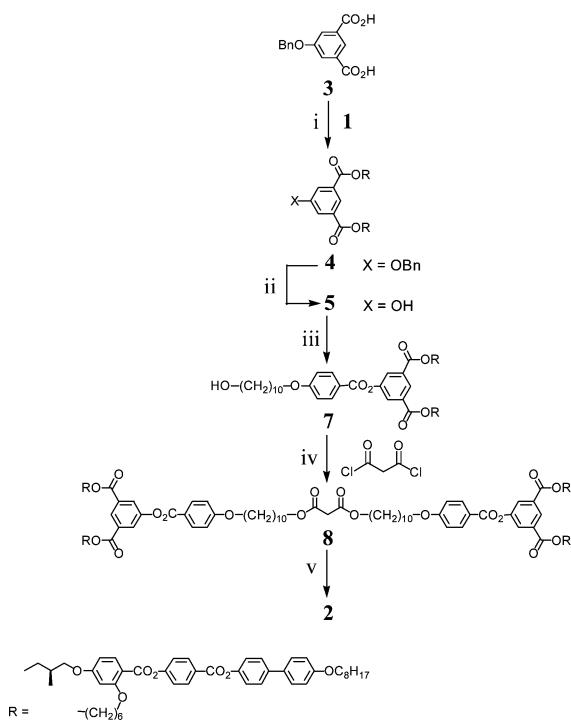Fig. 2

Scheme 1 *Reagents and conditions:* i, 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS), *N,N*′-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine (4-ppy), CH$_2$Cl$_2$, 0 °C and then room temperature (rt), 85%; ii, H$_2$ (4 bar), Pd/C, CH$_2$Cl$_2$–EtOH, rt, 89%; iii, 4-(10-hydroxydecyloxy)benzoic acid (**6**),[12] DCC, DPTS, 4-ppy, CH$_2$Cl$_2$, 0 °C and then rt, 80%; iv, Et$_3$N, CH$_2$Cl$_2$, rt, 79%; v, C$_{60}$, I$_2$, DBU, toluene, rt, 57%.

Table 1 Phase-transition temperatures^a of compounds **1,2,4,5,7** and **8** (between parentheses, the enthalpy changes ΔH in kJ mol^{-1})

Compound	Cr → N*/°C	T_g/°C	N* → I/ °C
1[10]	100.2		137.8
4		6	102^b (1.4)
5		23	129 (1.8)
7		12	103 (1.9)
8		20	113 (3.7)
2		26	69^b (1.9)

^{a} T_g = 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; the T_g's were determined during the first cooling run. ^{b} Determined as the maximum of the peak during the second heating run.

Fig. 3 Supermolecular organization of the chiral nematic phase displayed by **2**.

indicates that the C$_{60}$ unit tends to lower the stabilization of the liquid-crystalline phase, probably because of steric effects arising from its bulky spherical shape. Thus, the spherical shape of C$_{60}$ is not conducive towards the formation of calamitic liquid crystal phases, and in this case, it acts almost as a non-mesogenic dopant.

Comparison of the helical pitch length in the N* phases of the liquid-crystalline substrate **8** and the fullerene derivative **2** allowed us to examine the effect that C$_{60}$ has on the self-organising process. The pitch was determined in each case by measuring the number of pitch bands per unit length in the N* phase. For **8**, the pitch had a value of 2.5 ± 0.5 μm at 95.3 °C, and for **2** the value was 5 ± 0.5 μm near to the clearing point. It should be noted that the transition from the isotropic liquid to the mesophase was relatively broad, existing over a few degrees, which is typical for the behaviour of polypedal systems. For both **2** and **8**, the pitch appeared to be invariant with respect to temperature. Although these values should be
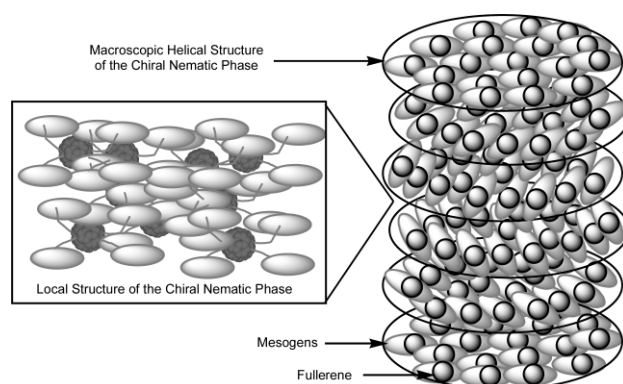
treated with caution (the method carries considerable error because comparisons were made at different reduced temperatures), they provide a valuable insight in the properties of the N* phase. For example, if we consider that the C$_{60}$ and dendritic units act as diluents to the self-organising system provided by the unsubstituted mesogenic addends (1.5 μm), then we can determine the effective helical twisting power β_M (μm^{-1} mol^{-1}). For **8**, this value is approximately 0.52 whereas for **2** it is 0.31. Consequently, the two materials have similar values for their helical pitches and helical twisting powers. Thus, the question becomes "does the fullerene polypede interact in the form of discrete molecular entities, or do the mesogenic units act relatively independently of the fullerene unit and of the polypede as a whole"? These studies cannot differentiate between the two; however, it is clear that because the pitch lengths are similar that C$_{60}$ fits within the helical structure formed by the mesogens themselves without causing any significant perturbation to the pitch. This gives us the surprising result that, although C$_{60}$ lowers the clearing point, we can effectively camouflage large structures like C$_{60}$ within the self-organising system as shown in Fig. 3. Similarly, it is also interesting that we can incorporate such non-mesogenic units into polypedes without markedly suppressing the liquid-crystalline properties. This means that we can build functionality into polypedal systems to create materials that are conceptually like proteins.

Notes and references

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