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Optically active liquid-crystalline fullerodendrimers from enantiomerically pure fulleropyrrolidines

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A synthetic methodology based on the 1,3-dipolar cycloaddition reaction was developed to design enantiomerically pure liquid-crystalline fullerodendrimers.

Chiral nanotechnology[1] has recently attracted growing interest in the scientific community for optically active building blocks, self-assembling and self-organizing nanomaterials,[2] and as unique components in materials science for the development of innovative devices such as molecular switches[3] and molecular motors.[4] However, despite their unique photophysical and electrochemical properties, only a few optically active fullerene derivatives have been reported to be prepared *via* regio- and stereo-selective 1,3-dipolar cycloaddition reactions.[5–8]

Recently, we described the synthesis, characterization and liquid-crystalline properties of four diastereoisomerically pure fulleropyrrolidines, all of which exhibited chiral nematic (N*) phases.[9] Based on this approach, we have now developed a synthetic methodology for the design of optically active liquid-crystalline fullerodendrimers from enantiomerically pure fulleropyrrolidines, which have allowed us to explore the relationship between molecular structure, intermolecular interactions and mesoscopic organization in relation to chirality transfer. Our conceptual design is based on a 1,3-dipolar cycloaddition reaction which generates a rotationally fixed stereogenic center in a pyrrolidine ring adjacent to a [60]fullerene (C_{60}) moiety.[10]

Esterification of bromoacetic acid with commercially available (*R*)-(+)-α-methyl-2-naphthalenemethanol (*R*)-**1** led to ester derivative (*R*)-**2** (Scheme 1). The latter compound was converted to the amine (*R*)-**3**. Subsequent condensation of (*R*)-**3** with formaldehyde and C_{60} under standard 1,3-dipolar cycloaddition conditions[10] gave diastereoisomers (*R*,*S*)-**4** and (*R*,*R*)-**4** which were easily and efficiently separated by HPLC using a non-chiral μPorasil stationary phase and CH_2Cl_2/heptane mixture as eluent (Fig. S1), with diastereoisomer (*R*,*S*)-**4** eluting first. Deprotection of (*R*,*S*)-**4** and (*R*,*R*)-**4** with trifluoroacetic acid led to the corresponding carboxylic acid derivatives which were condensed with phenol-based second generation dendron **5**[9] to give enantiomerically pure fullerodendrimers (*S*)-**6** and (*R*)-**6**.

Slow diffusion of heptane in a CH_2Cl_2 solution containing the compound that eluted first on HPLC for the synthesis of (*R*,*S*)-**4**/(*R*,*R*)-**4** gave dark red crystals which were analyzed by X-ray diffraction (Fig. 1). The (*R*,*S*)-**4** derivative crystallized in the chiral orthorhombic space group $P2_12_12_1$ as a CH_2Cl_2 solvate.

The circular dichroism spectra of diastereoisomers **4** (Fig. S2) and enantiomers **6** (Fig. 2) are in agreement with their absolute spatial configuration. Indeed, from literature data,[5,8] a negative Cotton effect at 430 nm corresponds to the *S*-configuration of the stereogenic center in the pyrrolidine ring, as found for (*R*,*S*)-**4** and (*S*)-**6**, whereas a positive Cotton effect at 430 nm corresponds to the *R*-configuration, as found for (*R*,*R*)-**4** and (*R*)-**6**. Compound (*R*,*S*)-**4** for which the stereochemistry was established by means of X-ray diffraction fully supports the CD data.

Both fullerodendrimers display an enantiotropic mesophase between the glass transition at 70 °C and the isotropization at 110 °C (Table 1, Fig S3). The enthalpy of isotropization is identical for both enantiomers. Comparison of isotropization temperatures and enthalpy of the transitions between dendron **5** and fulleropyrrolidines (*R*)-**6** and (*S*)-**6** indicates that C_{60} destabilizes the mesophase.

The defect textures of the compounds were examined by polarized optical microscopy. The samples were heated to the isotropic state and cooled (0.1 °C min^{-1}) to 105 °C. Upon annealing at this temperature, samples of (*R*)-**6** and (*S*)-**6** displayed the Grandjean-plane texture with oily streak defects (floating edge dislocations; Fig. 3, Fig. S4). The presence of this texture unequivocally identifies the phase as the N* phase. Rotation of the analyzer showed that the enantiomers have opposite twist directions, the helical macrostructure of the mesophase being right-handed for (*R*)-**6** and left-handed for (*S*)-**6**.

On prolonged annealing, the Grandjean texture gradually became populated by fingerprint defects arising from homeotropic boundary conditions (Fig. S5). (*R*)-**6** developed the characteristic textures with more ease than (*S*)-**6**. The pitch (ρ) of the chiral nematic phase was determined from the fingerprint texture, since the distance between adjacent, equidistant dark (or bright) lines corresponds to half of the pitch length.[12] The pitch values at room temperature are $\rho = 3.4 \pm 0.1$ μm for (*R*)-**6** and $\rho = 4.4 \pm 0.1$ μm for (*S*)-**6**.

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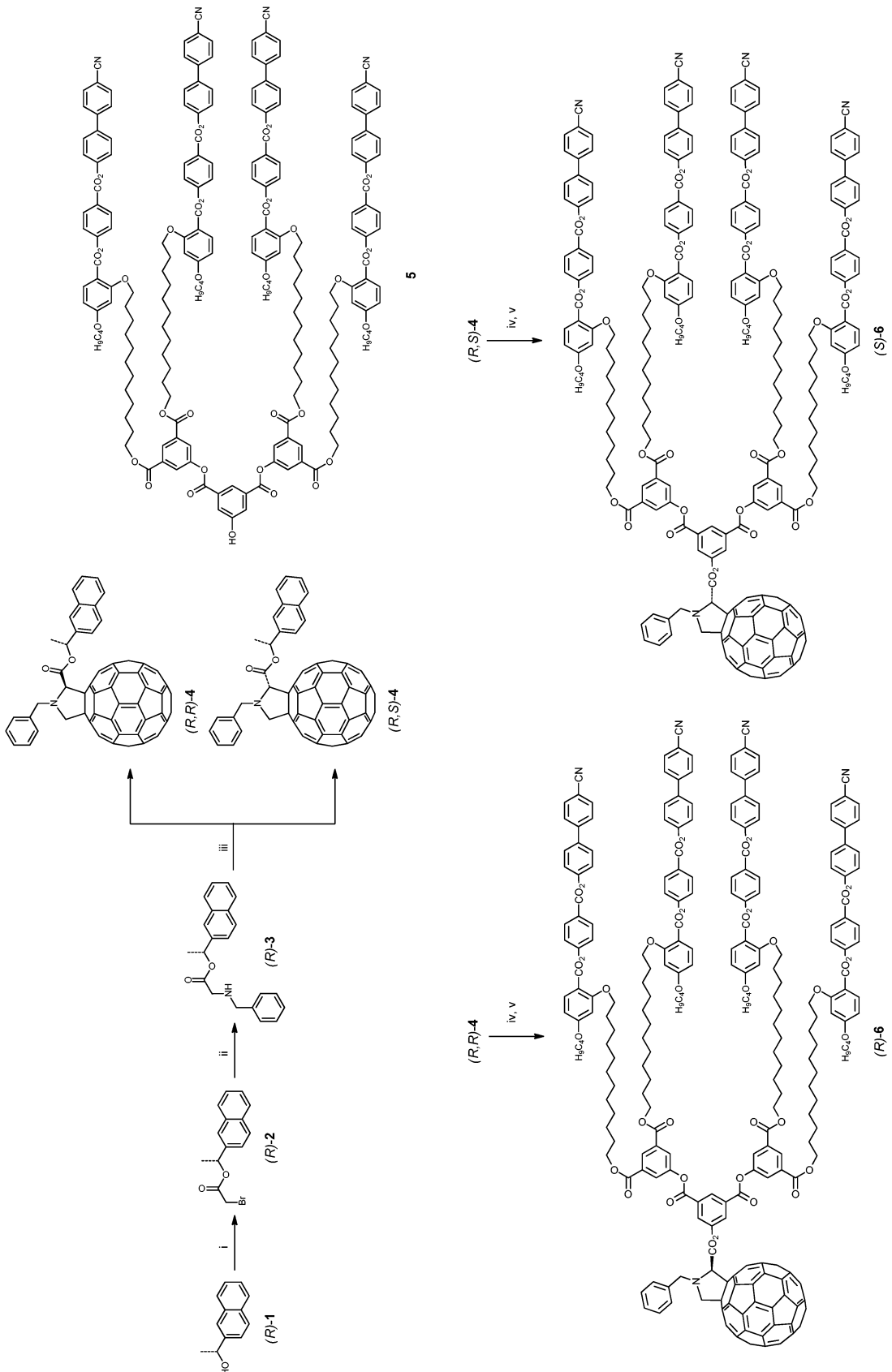

Scheme 1 *Reagents and conditions*: (i) bromoacetic acid, DCC, DMAP, CH_2Cl_2, 0 °C to r.t., 97%; (ii) benzylamine, Et_3N, THF, 0 °C to r.t., 88%; (iii) C_{60}, formaldehyde, toluene, reflux, 20 h, 25% for (*R*,*S*)-**4** and 31% for (*R*,*R*)-**4**; (iv) TFA, CH_2Cl_2, r.t.; (v) **5**, DCC, DPTS, CH_2Cl_2, 0 °C to r.t., 63% for (*R*)-**6** and 63% for (*S*)-**6**. For abbreviations, see ref. 11.

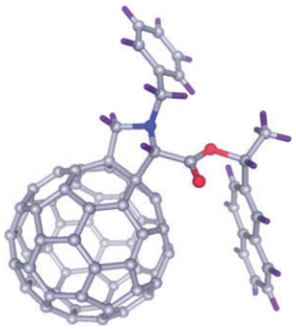

Fig. 1 View of the molecular structure of the compound (*R*,*S*)-**4** (the solvent molecule has been omitted for clarity).

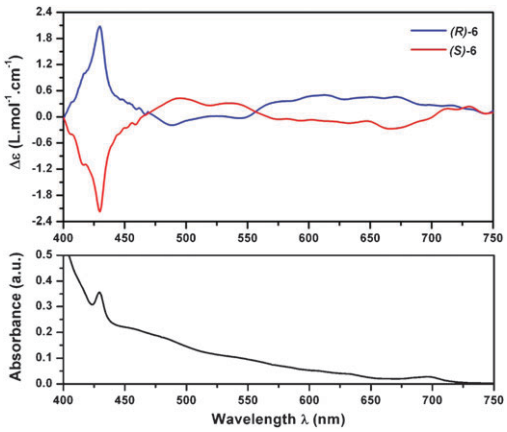

Fig. 2 CD (top) and UV-vis (bottom) spectra of (*S*)-**6** and (*R*)-**6** in CH_2Cl_2.

Table 1 Phase-transition temperatures and enthalpy changes of dendron **5** and fullerodendrimers (*S*)-**6** and (*R*)-**6**[a]

Compound	T_g/°C	Transition	T/°C	ΔH/kJ mol^{-1}
5[9]	51	N → I	164	2.2
(*S*)-**6**	70	N* → I	110	0.3
(*R*)-**6**	70	N* → I	110	0.3

[a] T_g, glass transition temperature; N, nematic phase; N*, chiral nematic phase; I, isotropic liquid. Temperatures are given as the onset of the peaks obtained during the second heating run; the T_g values were determined during the first cooling run.

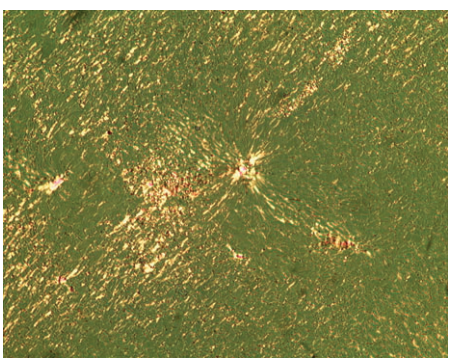

Fig. 3 Grandjean-plane texture displayed by (*R*)-**6** at 105 °C (×100).

This response of the cholesteric phase, *i.e.* similar magnitude of the pitch (and hence of helical twisting power) and opposite helical sense, mirrors the observation of their identical magnitude but opposite sign Cotton effects in solution, as expected for enantiomers.

The results described here regarding the relationship between the molecular chirality, the handedness of the resulting macroscopic helix and the induced helical twisting power of the chiral nematic phase demonstrate unambiguously that the mesophase chirality is controlled at the molecular level by the stereogenic center of the fulleropyrrolidine ring.

In conclusion, we have reported an elegant concept for the synthesis of enantiomerically pure fulleropyrrolidines. The latter materials were used as chiral platforms for the design of optically active liquid crystals. In these materials, the nature of the mesomorphic dendron controls the type of mesophase exhibited, whereas the stereochemical structure of the fulleropyrrolidine dictates the handedness of the helical supramolecular structure of the mesophase, and ultimately the transmission of molecular chirality to the bulk self-organizing mesophase.

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