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The first examples of monodispersive liquid crystalline tetramers possessing four non-identical anisometric segments

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The molecular design, synthesis and thermal behaviour of the first liquid crystalline tetramers composed of four non-identical mesogenic entities connected covalently through paraffinic spacers are presented. These new molecular structures consisting of a tolan (half disc-shaped), azobenzene (photoactive), biphenyl and cholesteryl ester (thermochromic) cores, connected through either an even–even–odd or an odd–even–odd paraffinic spacer, exhibit features of a columnar mesophase.

1. Introduction

It is well known that architecture and functionalization are essential aspects in the molecular engineering of liquid crystals (LCs) for the control of important physical properties such as optical anisotropy, dielectric anisotropy, supramolecular order, thermal stability, etc. of mesophases [1]. In addition, it is advantageous if phenomena such as high electrical conductivity [2], photochromism [3] and thermochromism [4] are associated with the synthesized LCs. Thus the preparation of new multifunctional LCs that exhibit these properties requires an appropriate design and high yield synthetic strategies. The linear oligomeric liquid crystals (LOLCs) that are formed by joining mesogenic segments in an end–end (axial) fashion by means of polymethylene, or an oligo (oxyethylene) or oligosiloxyl group, seem to offer a unique and practical route to the design of multifunctional systems. Currently LOLCs are attracting special attention, not only because they are considered as model compounds for polymeric liquid crystals but also due to their unique thermal behaviour [5–7]. Most importantly, these non-conventional LCs can exhibit properties usually associated with polymers, while still retaining the fluidity and viscosity of a low molar mass LC. Further, if the LOLC is monodisperse it will lead to rather well defined properties, unlike the situation with polymers.

Thus different anisometric sub-units (mesogens) associated with a particular function/phenomenon can be grafted into a single molecule through flexible covalent linkages. This results in systems able not only to form thermotropic mesophases, due to their anisotropic molecular shape, but also of forming supramolecular structures owing to non-covalent intermolecular interactions. Of all the linear oligomeric molecular architectures known to support liquid crystalline behaviour, the first member, namely the dimer (also referred to as a dimesogen) composed of either identical (symmetrical) or non-identical (unsymmetrical) mesogenic segments connected by a central spacer has been extensively studied [5]. The addition of one–six mesogenic moieties to a dimer via a flexible spacer result in the next higher oligomers which have been referred to in general as a trimer, tetramer, pentamer, hexamer, heptamer and octamer respectively. Based on the molecular structure of the individual mesogenic segments, there can be three combinations: (i) symmetrical LOLCs where all the segments are structurally similar, (ii) semi-symmetrical LOLCs in which some of the segments are identical, and (iii) unsymmetrical LOLCs where no two segments are identical. Trimers of types (i) and (ii) were reported for the first time in 1986 and since then a few other examples have been reported [6*a–f*]. Recently, there have been two reports [6*g*, *i*], including one from our laboratory [6*i*] of the first examples of trimers of type (iii).

A type (i) tetramer was first reported by Keller in 1985 but this material was not mesogenic [7*a*]. Later in 1989 Griffin *et al.* reported a series of tetrameric monodisperse model compounds chemically related to known main chain liquid crystalline polymers; interestingly all of them were found to be mesogenic [7*c*]. It was only recently in 1999 that Imrie *et al.* extended this approach to furnish the first examples of the type (ii) tetramers

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[7d]. To the best of our knowledge type (iii) unsymmetrical tetramers consisting of four non-identical mesogenic segments connected linearly have not previously been reported. Therefore we aimed to design and synthesize unsymmetrical tetramers that (1) have chiral, thermochromic and photochromic segments, and (2) can possibly bridge the low molar mass LCs and polymers and thus furnish the first liquid crystalline unsymmetric tetramer composed of four structurally different mesogenic entities.

2. Molecular design

To meet the first criterion, the cholesterol moiety in the form of its ester derivative (cholesteryl ester) was chosen to be the chiral segment. Recently it has been shown that the combination of the cholesteryl ester unit with either a tolan (diarylacetylene) [5a] or biphenyl unit [5b] via a polymethylene spacer furnishes dimers exhibiting a chiral nematic (N*) mesophase known for thermochromic properties (temperature dependent wavelength of selective reflection) [4]. The linking of the cholesteryl ester entity with a biphenyl unit through a paraffinic spacer accounts for two mesogenic segments of the tetramer, and is anticipated to impart the thermochromic functionality to it. To incorporate a molecular segment with photochromic functionality that is a promising phenomenon in many practical applications [3], we included an azobenzene moiety which links to other mesogenic segments through the spacer.

On the other hand, among the polycatenars, tetracatenar-type mesogens (especially biforked) exhibit a rich mesomorphism showing lamellar, columnar (Col), cubic (Cub) and nematic (N) phases [8]. To have such an attractive feature in the proposed tetramer, we planned to incorporate a tetracatenar-type structure. New, linear addition of several mesogenic moieties through spacers leads to a macromolecule that may generally have a high clearing temperature and reduced solubility in most common organic solvents. It is known that these problems may be solved by a lateral substitution. Therefore the fourth mesogenic entity needs to resemble a semi-biforked entity having a lateral alkoxy substitution, giving the segment a half-disc-like structure. During our design we kept all these points in view, leading us to the synthesis of a new 2,3,4-trialkoxy-substituted diphenylacetylene (tolan) segment that is used as the fourth mesogenic unit.

3. Synthesis

In our present studies the molecular design and synthesis incorporates the cholesteryl ester (as a chiral entity), biphenyl (as a supportive entity for thermochromism), azobenzene (as a photoactive mesogen), and tolan (as a half-disc) as segments interconnected through either even–even–odd (EEO) or odd–even–odd (OEO) paraffinic spacers to obtain liquid crystalline tetramers **1** and **2**, respectively. We envisaged that the target liquid crystalline tetramers **1** and **2** could be obtained by condensing two important unsymmetrical dimers **3** and **4a**,**b** as shown in a retrosynthetic manner in figure 1. Accordingly the unsymmetrical dimer **3** was prepared from the monomeric molecules **5** and **6**. The other dimers **4a**,**b** were realized by employing dimeric phenols **7a**,**b** which in turn were prepared by coupling compounds **8a**,**b** and **9** (figure 1). The spectral data of all the intermediates and tetramers were found to be consistent with their molecular structure.

The detailed synthetic procedures will be published elsewhere. Selected data are now presented for the tetramer **2**. $R_f = 0.57$ (4:1 CH_2Cl_2–hexanes). A yellow solid, m.p. 202°C, yield 177 mg (42%). IR (KBr pellet): ν_{max} 2923, 2852, 1730, 1603, 1581 and 1513 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.87 (d, $J = 8.88$ Hz, 4H, Ar), 7.46 (m, 6H, Ar), 7.13 (d, $J = 8.6$, 1H, Ar), 7.01 (d, $J = 2.76$, 2H, Ar), 6.98 (d, $J = 2.76$, 2H, Ar), 6.95 (d, $J = 7.32$, 2H, Ar), 6.93 (d, $J = 7.36$, 2H, Ar), 6.85 (d, $J = 8.88$, 2H, Ar), 6.60 (d, $J = 8.76$, 1H, Ar), 5.37 (brd, $J = 4.52$, 1H, olefinic), 4.62 (m, 1H, $-CH-O-CO-$), 4.02 (m, 16H, $8\times -OCH_2-$), 2.32 (brt, $J = 7.38$, 4H, 2× allylic methylene), 2.03–0.86 (m, 117H, $5\times -CH_3$, $48\times -CH_2-$, $6\times -CH-$), 1.01 (s, 3H, $-CH_3$), 0.86 (d, $J = 4.8$, 3H, $-CH_3$) and 0.68 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, spin echo FT): 172.99 (CO), 161.06 (C), 161.01 (C), 158.82 (C), 158.18, 158.06 (C), 154.36 (C), 153.99 (C), 147.07 (C), 141.98 (C), 139.7 (C), 133.56 (C), 133.37 (C), 132.78 (CH), 127.67 (CH), 127.47 (CH), 124.33 (CH), 122.53 (CH), 116.05 (C), 114.78 (CH), 114.68 (CH), 114.46 (CH), 111.03 (C), 108.20 (CH), 91.59 (C), 84.7 (C), 74.22 (CH_2), 73.82 (CH), 73.76 (CH_2), 68.84 (CH_2), 68.05 (CH_2), 67.77 (CH_2), 67.54 (CH_2), 56.71 (CH), 56.18 (CH), 50.01 (CH), 42.33 (CH_2), 39.76 (CH_2), 39.53 (CH_2), 38.12 (CH_2), 37.01 (CH_2), 36.61 (CH_2), 36.21 (CH_2), 35.79 (CH), 34.59 (CH_2), 31.92 (CH_2), 30.52 (CH_2), 30.34 (CH_2), 29.69 (CH_2), 29.36 (CH_2), 29.00 (CH_2), 28.22 (CH_2), 28.00 (CH), 27.84 (CH_2), 26.25 (CH_2), 26.12 (CH_2), 26.04 (CH_2), 25.64 (CH_2), 24.81 (CH_2), 24.28 (CH_2), 23.85 (CH_2), 22.79 (CH_3), 22.68 (CH_2), 22.55 (CH_3), 21.04 (CH_2), 19.23 (CH_3), 18.72 (CH_3), 14.08 (CH_3), and 11.86 (CH_3). FAB Mass: 1751.0 $[MH]^+$. Elemental analysis: calcd for $C_{116}H_{170}N_2O_{10}$, C 79.5, H 9.78, N 1.59; found, C 79.25, H 9.86, N 1.21%.

4. Characterization

The LC properties of these tetramers were investigated using (i) optical polarizing microscopy (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler

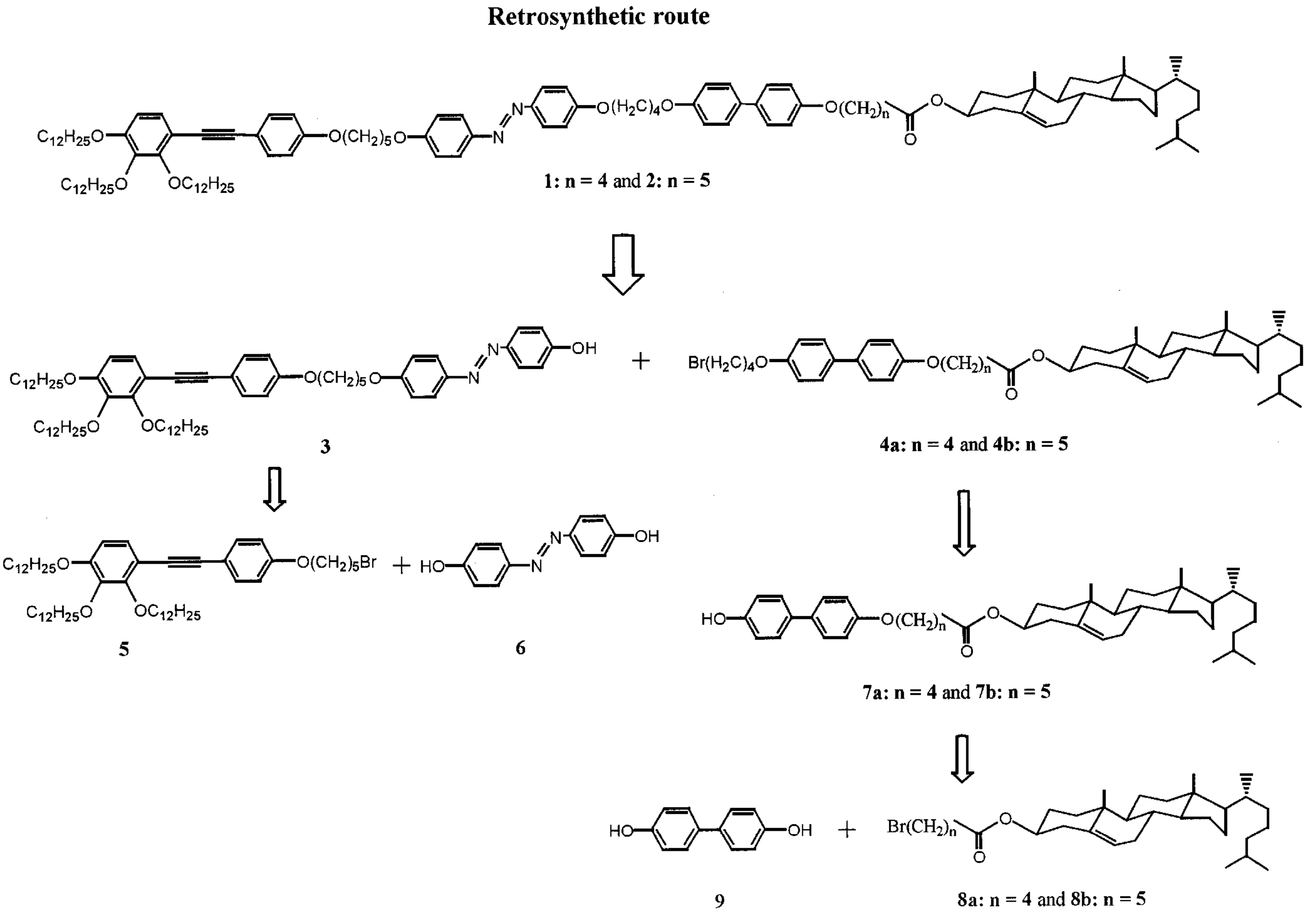

Figure 1. Retrosynthetic route for the preparation of liquid crystalline tetramers (**1**, **2**) and their intermediates (**3**, **4a**,**b**, **5**, **6**, **7a**,**b**, **8a**,**b**, **9**).

FP90), (ii) differential scanning calorimetry (Perkin Elmer DSC7) and (iii) X-ray diffraction (XRD). On melting at a temperature of 134.8°C for compound **1** and at 98.8°C for **2**, both showed a pseudoisotropic texture. This was true whether the substrate was just a clean glass plate or a glass plate treated with either a polyimide solution for planar orientation or a silane solution for homeotropic alignment. On shearing, the pseudoisotropic pattern changed to a birefringent texture, which almost immediately relaxed back into the pseudoisotropic texture in the case of **1**. The birefringent pattern resembled the sandy texture usually observed in polymeric samples. Even at high magnification we could obtain no more details about the texture. This birefringent texture remained until the samples transformed to the isotropic phase at 191.2 and 202.5°C for **1** and **2**, respectively. On cooling from the isotropic phase, a slight supercooling was observed and the transition to the mesophase with the sandy texture was observed at 188.6°C ($\Delta H = 13.1\ \mathrm{J\,g^{-1}}$) and 201.2°C ($\Delta H = 15.1\ \mathrm{J\,g^{-1}}$) for **1** and **2**, respectively. In case of the tetramer **1**, no other textural change was seen before crystallization, at 93°C. These transitions were highly reproducible, indicating the stability of this tetramer.

In compound **2**, while cooling, neither a textural change nor crystallization was seen until room temperature was reached. The DSC traces (figure 2) show a transition to a glassy state at 77.4°C; this remains until −65°C, the lowest temperature that could be achieved with the instrument. On subsequent heating from −65°C, the glassy phase transforms to the mesophase at 97.2°C, which remains unaltered until the isotropic phase is reached. It is known that upon keeping a sample at room temperature for a certain period of time, the glassy state usually slowly transforms into the crystalline state. But this does not seem to occur with **2** even after several months. These transitions were also highly reproducible during repeated heating and cooling cycles. As a representative case the chemical stability of **2** was investigated by taking DSC scans after keeping the sample at 110°C for 15 h; it was found that the transition temperatures agreed well with those of previous runs.

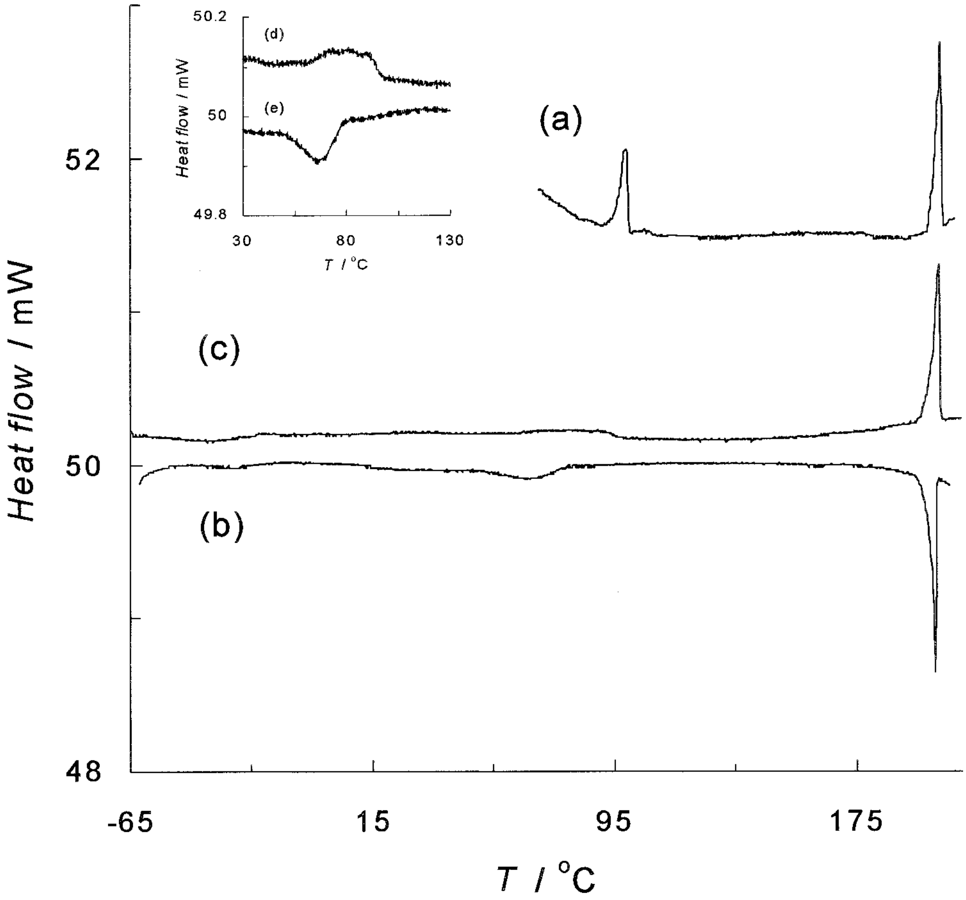

Figure 2. DSC thermograms obtained for tetramer **2** at a rate of 5°C $\min^{-1}$: (*a*) first heating, (*b*) subsequent cooling from isotropic liquid state to −65°C, (*c*) subsequent heating from −65°C. As can be seen for the curves (*b*) and (*c*) [shown on an enlarged scale in the inset as (*d*) and (*e*), respectively] neither crystallization nor melting peaks are observed; instead peaks at 77.4 and 97.2°C corresponding to the transition between the glassy state and the mesophase appear during the cooling and the heating cycles.

XRD studies were carried out using an image plate detector (MAC Science, Japan) equipped with double mirror focusing optics, with the sample contained in a Lindemann capillary tube. The diffraction patterns obtained in the mesophase of both compounds were quite similar. The pattern, along with the derived one-dimensional intensity vs. 2θ profile obtained at 170°C with the tetramer **1**, is shown in figure 3. In the low angle region four sharp peaks are observed: one very strong and three weak reflections. Identifying the first peak with the Miller index (2 0 0), the four reflections conform to the expected values from a two-dimensional rectangular lattice. In the wide angle region there is a diffuse reflection corresponding to spacing of 4.7° A. Based on these features it is tempting to propose that the mesophase could be a rectangular columnar ($\mathrm{Col_r}$) mesophase. This proposal is partially supported by the following observations. For some polar calamitic molecules and pure polycatenar compounds with non-polar chains no lamellar mesophase has been observed [8]. This kind of a behaviour, especially in polycatenars, is expected because the small differences in space filling between the rigid cores and the pendant terminal chains can be compensated by tilting of the aromatic cores with respect to the layer normal. If, however, the difference is substantial, tilting of the molecules alone cannot sufficiently reduce this steric frustration. In such cases the layers may break up into ribbon-like aggregates which can organize to a columnar phase. Assuming such a structure, the lattice parameters are calculated to be $a = 128$ Å and $b = 37.2$ Å. However in the absence of a clear optical texture it is not possible to identify the mesophase uniquely. The appearance of a pseudo-isotropic texture suggests that a uniaxial phase, and hence the presence of a two-dimensional lattice, seems to be contradictory. In the light of two recent observations [9] a lamellocolumnar phase cannot be ruled out. In such a phase the flat aromatic cores are stacked to form

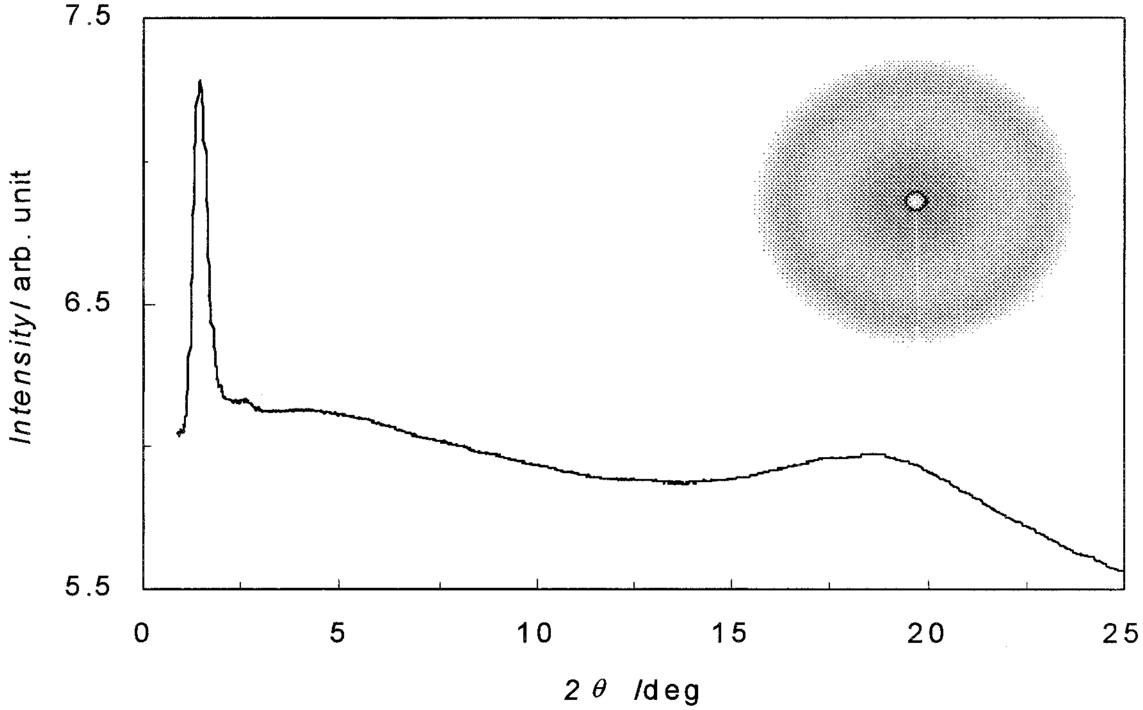

Figure 3. One-dimensional intensity vs 2θ profile derived from the XRD pattern (inset) obtained at 170°C for the tetramer **1**.

columns and these in turn are arranged in smectic-like layers. Further studies are required to establish the nature of the phase.

5. Conclusion

We have achieved the synthesis of the first thermotropic monodispersive liquid crystalline tetramers possessing four non-identical anisometric entities connected by flexible spacers. Molecular design of these novel tetramers incorporates the cholesteryl ester (as a chiral entity), biphenyl (as a supportive entity for thermochromism), azobenzene (as a photoactive mesogen), and tolan (as a half-disc) as segments interconnected through even–even–odd (EEO) and odd–even–odd (OEO) paraffinic spacers. These compounds are thus multifunctional and can exhibit properties usually associated with polymers, whilst still retaining the fluidity and viscosity of low molar mass LCs, and thereby bridging the gap between low molar mass LCs and high molar mass polymeric LCs. The concept of such molecular design originates from the novel approach that, by grafting different anisometric sub-units (mesogens) associated with a particular function/phenomenon in a single component system through covalent flexible linkages, one can obtain supramolecular systems able not only to form thermotropic mesophases due to their anisotropic molecular shape, but also capable of structure formation resulting from non-covalent intermolecular interactions. An exhaustive investigation focusing on molecular design and synthesis leading to multifunctional LOLCs is essential in order to provide potential materials required for many practical applications.

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