Tailor-designed polyphilic promotors for stabilizing dispersions of carbon nanotubes in liquid crystals†

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We present a potent multifunctional molecular design concept for promoting the dispersion of carbon nanotubes (CNTs) in thermotropic liquid crystals (LCs), making CNT-in-LC dispersions of unprecedented stability possible and broadening the scope of potential applications.

Extraordinary electrical, thermal and mechanical performance renders carbon nanotubes (CNTs) highly attractive for a broad range of new materials and devices.[1–3] Due to their extreme anisotropy, in shape as well as properties, the ability to align the tubes is key to many proposed CNT applications. This is particularly difficult—but all the more important—for the randomly aligned and entangled CNTs resulting from substrate-free growth, to date the only synthesis approach that is commercially viable and allows purification and fractionation of the nanotubes.[4] Liquid crystals (LCs) represent a unique platform for addressing this problem since their inherent long-range order can provide macroscopic-scale control of the orientation of nanotubes dispersed in them.[5–10] Further promoted by a number of remarkable phenomena observed in CNT-doped LCs, such as electroactive super-elongation of CNT-clusters,[11] improvement in electro-optic response of LCs,[8,12,13] CNT self-assembly into platelets,[14] or polarization of light and nanotube-induced filament formation,[15] the study of LC–CNT composites has during the last few years grown into an important and vibrant area of research. A major obstacle limiting the speed of progress, both in terms of research and applications, is however the lack of a reliable and versatile method for dispersing CNTs stably at sufficient concentration in LCs. Most liquid crystals are inadequate hosts for CNTs[16] since they have been optimized for other purposes, *e.g.* to meet specific demands on optical and elastic properties required for the proper performance of an LC-based device. A key factor in advancing the field would therefore be the development of a general means of stabilizing CNT-in-LC dispersions that works with any host LC and preferably with any CNT type.

In this Communication we present the first thrust to provide such an instrument, by introducing a new type of polyphilic molecule that stabilizes the interface between CNT guest and LC host, thereby functioning as a dispersion promotor. The molecules are tailored for the purpose by following a general design concept where a mesogenic unit and a CNT anchor group are combined *via* a flexible spacer (Fig. 1). With the right combination of these components we achieve a dramatic stabilization of CNT suspensions in standard commercial nematic LC mixtures, even for the case that the LC on its own is a poor CNT solvent.

For realizing stable suspensions of CNTs one is typically faced with the choice between covalent functionalization of the nanotube wall[17] and the addition of a multifunctional dispersion promotor molecule. We pursue the latter route since covalent functionalization affects the physical properties of CNTs negatively.[18] For the case of thermotropic LC hosts this is a much more challenging task than for the commonly encountered case of aqueous CNT dispersion, where coating of the nanotubes by surfactants provides efficient stabilization. Since CNTs as well as LCs are nonpolar, classical surfactants are of no use, calling for a new design paradigm for molecules that can stabilize CNT–LC suspensions.

Inspired by encouraging results from studies of aqueous nanotube dispersion using surfactants based on pyrene or similar polycyclic aromatic moieties[19–22] we have used pyrene, anthracene and terphenyl for providing the CNT anchoring function. These moieties are expected to have high affinity for CNTs due to aromatic π–π stacking with the graphene surfaces of the nanotubes. Pyrene was also used recently as the CNT anchor group in a rare case of promotor molecules developed for non-polar solvents[23] as well as in a multifunctional assembly promotor for CNT-based hybrid photovoltaics.[24]

Since our purpose is to use standard commercial nematic LCs as host we use a derivative of the commonly employed cyanobiphenyl motif as our mesogenic group. As spacer group an undecyl or a tetra(ethylene oxide) chain was used. The resulting molecules **1a–c** and **2a,b** (Fig. 2) represent polyphiles composed of three intrinsically incompatible units: the
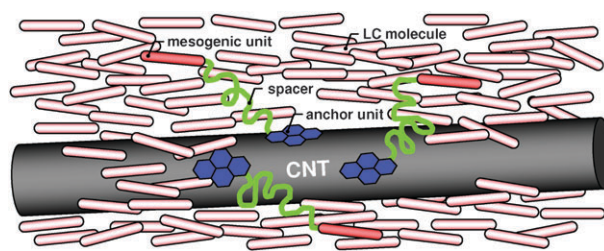
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Fig. 1 Tailor-designed polyphiles, exhibiting a CNT-anchoring group (blue) and a mesogenic unit (red) connected *via* a flexible spacer (green), promote the dispersion of CNTs in LCs.
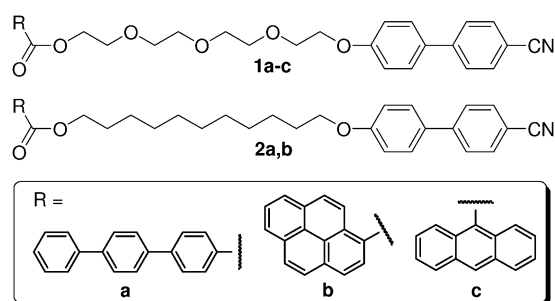
Fig. 2 Structures of the new dispersion promotor molecules.

rod-like mesogenic units, which should be compatible with the LC host but incompatible with the flexible spacers and the anchor groups; the rigid aromatic anchoring unit which should interact with CNTs but ideally not with the LC host; and the flexible spacer units which should be incompatible with the aromatic cores of the LC units as well as with the anchor groups.

The synthesis of the polyphiles was carried out in a modular approach as outlined in the supporting information. Compounds **2a** and **2b** are liquid crystalline themselves whereas the series with the tetra(ethylene oxide) spacer melt directly from the crystal into an isotropic phase, *cf.* supporting information. For investigation of the performance in promoting CNT dispersion the polyphiles were first added at a concentration on the order of 10 mg mL^{-1} to the target LC, here the commercial multicomponent nematic mixture RO-TN-403/015S (Hoffmann-Laroche), mainly composed of cyanobiphenyl, cyanoterphenyl and phenylpyrimidine mesogens. Single-wall CNTs (Unidym Hipco) were then added at a concentration of 0.1 mg mL^{-1} and dispersed by means of sonication (Dr Hielscher UIS 250V sonotrode, 250 W@24 kHz) for 20 min, the sample kept in a water bath for cooling. To assess the quality of the different dispersions we subjected all samples, including a reference sample where the CNTs had been dispersed in the pristine LC without any added promotors, to long-term centrifugation at 12 800 *g*, studying the quantity of nanotubes remaining in the supernatant as reflected by its darkness. On its own, RO-TN-403/015S is a rather poor CNT host, as revealed in the centrifugation test after which essentially all nanotubes dispersed in the pure LC were in a sediment. The supernatant had the same visual appearance as the pristine LC, *cf.* Fig. 3 (sample labelled 'ref').

Among the samples with added dispersion promotor the result depended strongly both on the CNT anchor

group and the linker chain. With the undecyl spacer (compounds **2a** and **2b**) only marginal improvement was observed. This was somewhat greater with the pyrene anchor group than when terphenyl was used, as seen by the supernatant of the pyrene sample being slightly darker than that of the reference sample, whereas the supernatant of the sample to which **2a** had been added was nearly indistinguishable from the reference supernatant. In contrast, promotor molecules with tetra(ethylene oxide) spacers dramatically improved the dispersion stability when the CNT anchor group was either pyrene (**1b**) or anthracene (**1c**). As seen in Fig. 3 the supernatant of the dispersions prepared with these additives remained very dark even after four hours of centrifugation.

The reason for the much better performance of the additives with tetra(ethylene oxide) spacer is most likely the stronger incompatibility of these flexible and polar spacers with the liquid crystal as well as with the anchor group. Almost all previous work on CNT dispersion with the aid of pyrene-based surfactants has been carried out with water as host liquid, giving the hydrophobic effect an important role in stabilizing the dispersion. This contribution disappears when the host is a thermotropic LC because of the nonpolarity of guest particles as well as host liquid. By incorporating a polar and flexible oligo(ethylene oxide) spacer a nanoscale incompatibility was introduced that separates the CNT anchor groups from the mesogenic moieties. Spacers and mesogenic units are thus excluded from CNTs and anchor groups, resulting in a reinforcement of the interaction between the latter components, similar to the action of the hydrophobic effect in aqueous systems in promoting surfactant adsorption onto nonpolar species. The incompatibility, which we believe is a major factor in improving the efficiency of the CNT dispersion promotor, is less pronounced in series **2** with alkyl spacers, as these are non-polar and more rigid. This explains why the series **2** molecules are much inferior promotors of CNT solubilization in LCs.

Interestingly, the tetra(ethylene oxide)-based additive with a terphenyl anchor group (**1a**) did not perform well, one reason most likely being that terphenyl is a common core in liquid crystal molecules, *i.e.* it is in itself mesogenic to some extent giving it a strong tendency to mix with the LC host. Moreover, the non-coplanar arrangement of the three phenyl rings prevents close contact with the CNT surface. These considerations as well as the experimental results indicate that terphenyl is in fact not a good CNT anchor group, despite its linearly extended aromatic π system. More detailed characterization of the mixtures by complementary methods is on-going and the results will be published in a follow-up paper.

Although compounds **1b** and **1c** yield greatly improved stability of the CNT-in-LC suspension, nanotube flocculation was seen also in these suspensions after about a week, at least with the host LC used here. Further refinements of the details of the molecular structures of the promotor molecules are thus called for but the present results serve as proof of the basic concept. Depending on exactly which host LC is intended it may be advantageous to use other mesogenic groups, a modification which can easily be employed within our modular approach.
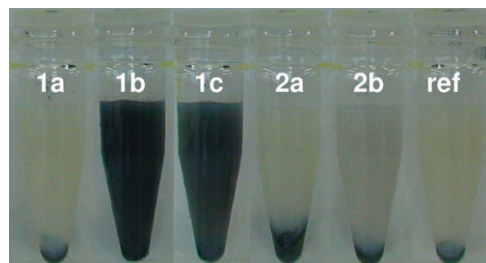

Fig. 3 Dispersions of Hipco SWCNTs (0.1 mg mL^{-1}) in the pristine nematic LC (ref) and in the same LC with polyphilic additives (**1a**–**2b**) after 20 min tip sonication followed by 4 h centrifugation.

In summary, we have developed a new design strategy for molecules promoting dispersion of non-functionalized carbon nanotubes in thermotropic liquid crystals, substantially increasing the stability of such dispersions. The generic character makes the design concept versatile enough to be compatible with essentially any desired combination of carbon nanotube and liquid crystal, thereby greatly broadening the scope of potential applications of CNT–LC composites and facilitating research on these systems. The employment of this type of tailored polyphilic molecule may thus open a door to removing the current main obstacle in the exploitation of liquid crystal–nanotube suspensions, of considerable interest for developing functional composites enhanced through the unique properties of high concentrations of uniformly aligned CNTs as well as for improving nematic-based electrooptic devices.

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