ZnO/Liquid Crystalline Nanohybrids: From Properties in Solution to Anisotropic Growth

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Abstract: Branched thermotropic liquid crystals (LCs) were successfully used as stabilizers for the synthesis of isotropic photoluminescent ZnO nanoparticles (NPs) in solution. ¹H NMR spectroscopy and differential scanning calorimetry experiments demonstrate the existence of specific interactions between the LC and both the ZnO precursor and ZnO NPs. This offers the possibility for some branched molecules to act as structurally ordered hosts for the anisotropic growth of ZnO NPs.

Keywords: anisotropic growth • liquid crystals • morphology control • nanoparticles • photoluminescence • zinc oxide

Over the past decade, composites based on the dispersion of nanoparticles (NPs) in liquid crystals have been of growing interest.^[1] The driving force of research in this field is the possible development of new materials or devices with multiple or improved properties. Indeed, NPs may influence the state^[2] or the surface anchoring of doped LCs.^[3] The electro-optical behavior of LC/NP systems may then be adjusted by changing the NP content.^[4,5] Conversely, the properties of the nanomaterial may be modified and even controlled by the LC matrix.^[6,7]

Achieving such a goal often requires functionalization of NPs with LC moieties to improve compatibility between NPs and LC or to obtain new LC nanohybrids. Indeed, LC hybrids involving gold,^[8-10] cobalt,^[11] cadmium selenide or cadmium telluride,^[12] and iron oxide NPs^[13,14] have been described. In a previous article we reported the first successful hybridization of small-sized ZnO NPs with a mesogenic molecule.^[15] Due to the presence of fluxional ligands, the hybridized material presented mesomorphic behavior even with a high content of inorganic material. However, the fluxionality of these ligands at the surface of the NP may hinder their application due to the presence of excess free ligands present in solution. In addition, in most cases these

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hybrids were obtained in a two-step process. Recently, branched capping agents have attracted special interest in the field of nanohybrids due to their effective stabilization properties for ZnO nanoparticles in polar and non-polar solvents.^[16–18] These stabilizers are characterized by their threedimensional molecular shapes; they also have low mobility at the NP surface and present a large number of functional end groups, which makes them easy to tailor for end-user purposes.

Here, we report the elaboration of ZnO NP hybrids, synthesized by using an organometallic method and using macromolecules (i.e., Tren-LCs) as the sole stabilizing agents (see Scheme 1). This approach involves the hydrolysis of dicyclohexylzinc, [Zn(Cy₂)] in air to give ZnO NPs with volatile cyclohexane as the unique side product.^[19] This process may avoid disruption of the liquid crystalline mesophase during NP formation, and the use of branched LC molecules with amino groups may favor the interactions with both the NP precursor and the resultant NP, which thus allows for a one-step synthesis of ZnO NPs.^[18,20] Moreover, the use of highly viscous LCs should prevent fast disruption of the LC structural organization during the NP formation. Depending on the functionality, two liquid crystals designated as Tren-OMeLC and Tren-CNLC (see below) were chosen. To assess the key interactions involved in the formation of ZnO NPs, we investigated three different systems. First, the preparation of ZnO with simple LC acrylates (OMeLC and CNLC) in THF was studied. The second system involved the synthesis of ZnO NPs in THF containing a Tren-LC. The scope of the latter was the formation of LC colloidal solutions of ZnO NPs and the investigation (in solution) of the interactions between 1) the LC and the zinc precursor and 2) the LC and the synthesized ZnO NPs. Lastly, we have used this information to control the growth of ZnO NPs by using the bulk state of thermotropic LC.

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Scheme 1. General synthesis for Tren-based liquid crystals: Tren-OMeLC and Tren-CNLC. Tren=tris(2-aminoethyl)amine, OMeLC=4-(acryloyloxybutyloxy)phenyl-4'-(methoxy)benzoate, CNLC=4-(acryloyloxybutyloxy)phenyl-4'-(cyano)benzoate.

Results and Discussion

Synthesis of liquid crystals: Two branched thermotropic liquid crystals were synthesized by a Michael addition reaction between Tren and OMeLC or CNLC, as depicted in Scheme 1.^[21] Briefly, a solution of Tren in chloroform was added dropwise at 0°C to a reaction flask containing an excess of mesogenic acrylate in the same solvent. The mixture was then stirred at room temperature. The reaction was monitored by ¹H NMR through the decrease of alkene signals of the acrylate reagent at $\delta = 6$ ppm upon completion. The excess acrylate was then removed by washing the resulting product in hot ethanol to give the final products as Tren-OMeLC and Tren-CNLC in the form of viscous gums.

Although both OMeLC and CNLC precursors exhibit a monotropic mesophase, differential scanning calorimetry (DSC) demonstrates that both branched polymers present a similar behavior with a stable liquid crystalline state (see Table 1). Figure 1a shows the thermogram for Tren-OMeLC. It presents a glass temperature at -22 °C. This behavior is normally observed for larger polymers, but has already been reported for low-molar-mass compounds supercooled to a glassy state.^[22,23] An isotropic/LC phase transition was also recorded at around 15 °C. The texture observed between crossed polarizers by polarized optical microscopy (POM; Figure 1b and c) together with the X-ray

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Table 1.	DSC data	for	LCs and	LC/ZnO	hybrids
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Sample	$T_{\rm g}^{[{\rm a}]}\left[{}^{\bullet}\!\mathrm{C}\right]$	$T_{\mathrm{LC-I}}^{[b]} [^{\circ}\mathrm{C}]$	$\Delta H \left[\mathrm{J}\mathrm{g}^{-1} ight]$	Mesophase type ^[c]
OMeLC	_	40	1.0	N ^[d]
Tren-OMeLC	-22	10	0.9	N
Tren-OMeLC/ZnO	-5.3	29	< 0.2 ^[g]	N
(synthesized in solvent)				
Tren-OMeLC/ZnO ^[e]	-1	37	0.4	Ν
(synthesized in bulk)				
CNLC	_	35	0.5	$N^{[d]}$
Tren-CNLC	8	58	0.8	Ν
Tren-CNLC/ZnO	-4.7	29	$< 0.2^{[g]}$	Ν
(synthesized in solvent)				
Tren-CNLC/ZnO ^[f]	4	49	0.6	Ν
(synthesized in bulk)				

[a] The glass transition temperatures, $T_{\rm g}$, were recorded in heating cycles at 5 °C min⁻¹. [b] The transition temperatures, $T_{\rm LC-1}$, were taken to be the average of the onset and endset values of peaks recorded during cooling cycles at -5 °C min⁻¹. [c] N: nematic phase. [d] Nematic monotropic. [e] Containing ZnO nanowires synthesized in the nematic bulk state of Tren-OMeLC with a molar ratio of 0.4:1.0 Tren-OMeLC/[Zn(Cy)₂]. [f] Containing isotropic ZnO nanoparticles synthesized in the nematic bulk state of Tren-CNLC with a molar of 0.45:1.0 Tren-CNLC/[Zn(Cy)₂]. [g] Approximate value due to low peak intensity.

scattering pattern that only displays a diffuse ring at high angles (d=4.5 Å) (Figure 1d and e) confirm the nematic (N) organization of the LC below the clearing temperature. Tren-CNLC presents a nematic phase below 58 °C and a T_g at 8.1 °C (see S1 in the Supporting Information).

Synthesis of hybrid zinc oxide nanoparticles in solution: Formation of ZnO NPs decorated with hyperbranched thermotropic LC polymers was performed in THF by using a onestep hydrolysis of the organometallic precursor, dicyclohexyl zinc $[Zn(C_6H_{11})_2]$ ($[Zn(Cy)_2]$). This method generally involves the use of amine ligands with long alkyl chains as stabilizers and takes advantage of the exothermic reaction commonly displayed by organometallic complexes in air.^[19] Using $[Zn(Cy)_2]$ as a precursor provides a safer synthetic method than other organometallic complexes, such as diethyl zinc, which was used by Richter and co-workers^[17] and is a precursor with more easily controlled hydrolysis.^[24] In a typical experiment, a given quantity of either Tren-OMeLC or TREN-CNLC was dissolved in a volume of dry THF. One equivalent of $[Zn(Cy)_2]$ was then added and the mixture was allowed to stand for 1 h under an argon atmosphere. For both Tren-OMeLC and Tren-CNLC, three different mixtures with molar ratios of 0.2, 0.5, and 1.0 Tren-LC/ $[Zn(Cy)_2]$ were prepared. The vial containing the mixture was then removed from the inert conditions and opened to the atmosphere. At this point the organozinc precursor was exposed to moisture and formed zinc oxide.

A turbid yellow luminescent suspension was formed when the Tren-LC/[Zn(Cy)₂] ratio was equal to 0.2, whereas the higher ratios (0.5 and 1.0) led to the formation of stable luminescent solutions of ZnO NPs (Figure 2b). In the first case, the amount of LC was not enough to stabilize the ZnO NPs, which thus leads to the formation of both aggregates

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Figure 1. a) Thermogram for Tren-OMeLC during a heating/cooling cycle at a rate of 5 °Cmin⁻¹. Blue and red arrows correspond to cooling and heating processes, respectively. b,c) Thread-like texture of Tren-OMeLC and Tren-CNLC, respectively, observed between crossed polarizers on cooling from the isotropic state. d) X-ray scattering pattern and e) the corresponding diffraction intensity profile for TREN-OMeLC. The diffusion at small angles close to the center of the 2D X-ray image is related to reflections from the sample holder. The increased intensity (orange color) shows that the mesogens were partially aligned.



Figure 2. a) TEM micrograph and histogram from a Tren-OMeLC/ZnO solution showing ZnO NPs of 3.4(0.3) nm (ca. 300 nanoparticles analyzed) obtained from a synthetic ratio of Tren-OMeLC/[Zn(Cy)₂] 0.5:1. b) The colloidal solution in THF and c) the same solution showing luminescence under a UV lamp at $\lambda = 365$ nm.

and dispersed NPs as observed in TEM micrographs (see S2 in the Supporting Information). In the latter two cases, transparent colloidal solutions were obtained with no precipitation over several weeks. The formation of isotropic regular ZnO NPs by using Tren-based LC solutions has been further confirmed by TEM. Thus, in a system in which the synthetic molar ratio of Tren-OMeLC/[Zn(Cy)₂] is set to 0.5:1, NPs of 3.4(0.3) nm were obtained (see Figure 2a). This is in agreement with DLS measurements of a colloidal solution of Tren-OMeLC/ZnO hybrid in THF (5.5 mm) in which Tren-OMeLC alone presents a Stokes radius of less than 2 nm and the Tren-OMeLC/ZnO hybrid has a radius of around 4.3(0.7) nm. Similar results were obtained with Tren-CNLC/ZnO presenting an average diameter of 6.0(0.7) nm (see S3 in the Supporting Information). The difference in size may come from the difference in the kinetics of the reaction. In addition, the systems also conserved their yellow luminescent properties, which originate from the ZnO NPs (Figure 2c). However, when the ratio $\text{Tren-LC}/[\text{Zn}(\text{Cy})_2]$ was equal to 1.0, the yellow luminescence was masked due to the high quantity of organic material (see S4 in the Supporting Information). These results prove that an interaction takes place between the LC and ZnO NPs and is an efficient one as confirmed by the stabilization of NPs in solution. To better understand the precise nature of these interactions and the role of the stabilizer's architecture, further ¹H NMR spectroscopy experiments were performed in solution, first with LC moieties only (OMeLC and CNLC) and then with the branched LCs (Tren-OMeLC and Tren-CNLC).

Interactions between Tren-LC and [Zn(Cy)₂] or ZnO NPs, an NMR spectroscopic study: The ability of LC acrylate moieties alone to induce the stabilization of ZnO NPs was first evaluated by forming ZnO NPs in a solution of LC acrylate (OMeLC or CNLC) in THF. Similar results were obtained for both types of LCs. In a typical experiment, $[Zn(Cy)_2]$ was added to a solution of LC acrylate with an $LC/[Zn(Cy)_2]$ ratio of 3:1. This ratio was chosen to correspond to the amount of LC present in the Tren-LC/ $[Zn(Cy)_2]$ mixture (0.5:1.0). To understand any possible interactions occurring between the organozinc precursor and the LC, NMR spectroscopy of these mixtures was carried out in [D₈]THF. No clear modifications of the NMR signal of the LC molecules upon introduction of $[Zn(Cy)_2]$ were observed (see Figure S5A and S5B in the Supporting Information). When the NMR tube containing the $LC/[Zn(Cy)_2]$ mixture was then opened to the air (hydrolysis of the precursor to form zinc oxide), the LC NMR signals stay unmodified but a second set of NMR signals slowly start to appear. These new peaks are much broader than the original LC NMR signal (see Figure S5A and S5B in the Supporting Information). Furthermore, DOSY experiments showed a reduced self-diffusion coefficient for these new species $(2.0 \times$ $10^{-10} \text{ and } 2.6 \times 10^{-10} \text{ } \text{m}^2 \text{s}^{-1}$ for OMeLC and CNLC solutions, respectively) compared with that of the LC molecule alone $(9.2 \times 10^{-10} \text{ and } 9.9 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \text{ for OMeLC and CNLC, re$ spectively). The slow-diffusing species can be clearly identified by a diffusion-filtered ¹H NMR experiment that shows no presence of alkene protons from the acrylate (see Figure S5C and S5D in the Supporting Information). An integration of ¹H NMR signals in the diffusion-filtered spectrum resulted in an unexpected increase in the alkane proton number. Two possible explanations for this observation can be suggested. The first possibility is that the conjugate addition of dicyclohexyl zinc to the acrylate forms the 1,4-addition product, a reaction previously reported in the literature.^[25,26] The second possibility involves an acrylate polymerization, which would form larger, slower-diffusing species. Whatever the nature of this reaction may be, the NMR spectroscopy study does not allow us to precisely identify the nature of the interaction with the NPs. The observed results may come from either interactions of the modified LC with the NP surface or the formation of polymeric species (interacting or not with the NPs). The type of interaction, if any, did not occur with specific atoms because all the proton signals experienced a change in electronic environment. This may lead us to conclude that the type of interaction was of a steric nature due to the vicinity of ZnO NPs. In any case, this was not sufficient to stabilize most of the formed NPs, as confirmed by the observed precipitation in the reaction vial and the formation of ZnO aggregates clearly observed in TEM micrographs (see Figure S6 in the Supporting Information). Moreover, the remaining solution presents no additional luminescent properties.

Although LC moieties alone were not able to lead to the formation of stable ZnO NPs, the previously mentioned results showed that stabilization of ZnO NPs by Tren-based LCs was possible. Interactions between the zinc precursor and the branched polymer host were assessed by using ¹H NMR spectroscopy. NMR experiments were carried out in [D₈]THF for Tren-LC alone, Tren-LC/[Zn(Cy)₂] (pre-hydrolysis), and Tren-LC/ZnO (post-hydrolysis). Similar results were obtained for both Tren-OMeLC and Tren-CNLC. The ¹H NMR spectra show a broadening of the LC NMR signals in the presence of $[Zn(Cy)_2]$ (Figure 3 and Figure S7A and B in the Supporting Information). For Tren-CNLC, the broadening was only observed for protons in the α -position with respect to amine functionalities in the polymeric core (δ (¹H)=2.81, 2.57, and 2.47 ppm). This suggests that in the pre-hydrolysis state the zinc precursor interacts with the nitrogen atoms present in the LC. This phenomenon has been previously reported for nitrogen-containing molecules, such as polyamidoamine-based dendritic macromolecules^[18] or amines with long alkyl chains.^[27] For Tren-OMeLC, the broadening was more uniformly observed for all the Tren-LC resonance signals and it is possible that carbonyl functions are also involved in the interaction between Tren-OMeLC and $[Zn(Cy)_2]$. In general, the Tren-LC NMR signals have a complex line shape that indicates a certain degree of spatial inhomogeneity in the sample, which is unaffected by thermal agitation, even in the case of LC only (see Figure S7C and D in the Supporting Information). Addition of [Zn(Cy)₂] to Tren-LC (pre-hydrolysis state) induced only slight changes in this inhomogeneity. On the

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Figure 3. ¹H NMR spectra at 291 K for Tren-CNLC only in [D₈]THF (2.2 mM; bottom), after addition of 8 equiv of $[Zn(Cy)_2]$ before exposure to air (middle) and after exposure to air for 4 h (top). Proton signal assignment: a) NCH₂CH₂COO-, b) -NCH₂CH₂N-, and c) -NCH₂CH₂COO-. #: [Zn(Cy)₂] signals, \odot : THF).

other hand, after hydrolysis of $[Zn(Cy)_2]$, a global sharpening of peaks was observed, which indicates the generation of a more homogeneous environment. Thus, the presence of the NPs induces structural rearrangements within the macromolecules. However, interaction between the Tren-LC molecules and the ZnO NPs was not clearly observed. DOSY experiments were then performed on these systems and analyzed by using the CONTIN method (see Figure S7E and F in the Supporting Information). The average Tren-LC diffusion coefficients are only slightly affected by the presence of ZnO NPs. The major change can be observed in the diffusion coefficient distribution profiles, which show an increasing population of slower diffusing species in the presence of ZnO NPs. This can be clearly observed for the decay of the Tren-LC signals during the diffusion measurements, in which some Tren-LC molecules show slightly slower diffusion in the presence of ZnO NPs. We also confirmed that, in the absence of ZnO NPs, the Tren-LC molecules have a more uniform signal decay profile (see Figure S7G and H in the Supporting Information). No transferred NOE could be detected in a NOESY experiment on the post-hydrolysis state (see Figure S7I in the Supporting Information), which excludes a fast exchange of Tren-LC molecules between the NP surfaces and the solution.

In conclusion, the NMR studies demonstrate the existence of specific interactions between $[Zn(Cy)_2]$ precursor and Tren-LC through nitrogen atoms. The extent of this interaction depends strongly on the nature of the LC moiety. After hydrolysis and NP formation, there is probably no specific chemical interaction between Tren-LC molecules and the ZnO NPs. However, the nanoparticles do affect the structural arrangement of the Tren-LC molecules in solution to a certain extent, which indicates steric interactions between the NPs and the macromolecules.

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Figure 4. Emission spectra for a solution of Tren-OMeLC/ZnO nanocomposite in THF (0.011 M with respect to LC) when excited at wavelengths of 340 (\blacktriangle), 360 (\bullet), and 380 nm (\odot). A)–C) Images of the solution when irradiated at wavelengths of 380, 360, and 340 nm, respectively.

Photoluminescent properties of Tren-LC/ZnO nanohybrids: As commonly found in the literature, zinc oxide presents interesting luminescent properties in the visible region of the spectrum. Absorption spectroscopy on a given NP colloidal solution of Tren-OMeLC/ZnO (Tren-OMeLC/[Zn(Cy)₂] 0.5:1), shows an absorption up to $\lambda = 355 \text{ nm}$ ($\approx 3.49 \text{ eV}$). This is typical physical behavior for nanometric zinc oxide NPs with a bandgap at approximately $\lambda = 365$ nm (3.4 eV). The photoluminescent properties of this solution are presented in Figure 4. Three emissions were observed depending on the excitation wavelength. A yellow emission centered at $\lambda = 565$ nm was observed when the Tren-OMeLC/ ZnO solution was irradiated at a wavelength of $\lambda = 340$ nm, which is known for ZnO NPs. The origin of this emission is attributed to surface defects, such as oxygen vacancies in the structure.^[28] Interestingly, when the sample was subject to an excitation wavelength of $\lambda = 380$ nm, an emission band centered at $\lambda = 460$ nm was recorded. This blue emission has been previously reported by our group for ZnO NPs prepared following this organometallic synthesis.^[29] When the system was irradiated at $\lambda = 360$ nm, a broad white-colored emission band was observed. This is due to the fact that at this excitation wavelength a competition exists between the two previously discussed photoemissions.

Liquid crystal behavior in bulk: We study here the mesomorphic behavior of the synthesized bulk Tren-LC/ZnO hybrids by using DSC, POM, and X-ray scattering. Between crossed polarizers the Tren-OMeLC/ZnO hybrid displays a birefringent texture at room temperature, owing to the anisotropic nature of the liquid crystal. This texture was observed up to around 29°C, after which the material starts losing its birefringence. Thermograms for Tren-OMeLC/ ZnO confirm these observations. In fact, a transition peak occurs at 29 °C and a change in heat capacity linked to a T_{s} could be observed at -5 °C (see Table 1). Between these two extremes (-5 and 29°C), SAXS measurements showed diffused rings (d=4.5 Å) characteristic of the nematic LC phase. Because pure Tren-OMeLC exhibits the LC state between -22.0 and 10°C, we can clearly conclude that the presence of ZnO NPs shifted the mesophase temperature window towards higher temperatures. Interestingly, the opposite phenomenon was observed for Tren-CNLC/ZnO NPs (see Table 1). In that case, the introduction of ZnO NPs was accompanied by a decrease in the glass transition temperature (destabilization) of LC phases, as generally reported in the literature.^[30] This might suggest that Tren-OMeLC interacts with ZnO NPs in a very specific way that favors the existence of stable mesophases, as we observed previously with more fluxional systems.[15]

Synthesis of Tren-LC/ZnO nanocomposites in the absence of a solvent: To take advantage of the interactions between LC moieties and ZnO NPs, we decided to perform the formation of ZnO NPs directly inside the bulk LC mesophase. Tren-CNLC and Tren-OMeLC exhibit a nematic LC phase at temperatures close to ambient. This avoids any organozinc precursor thermal breakdown before NPs are produced. In a typical LC/ZnO nanocomposite synthesis, a given amount of Tren-LC was dissolved in a minimum amount of dry THF under an argon atmosphere. To this solution one equivalent of [Zn(Cy)₂] was then added (Tren-LC/[Zn(Cy)₂] ratio 0.4:1). The prerequisite for the chosen quantities of products is that the expected ZnO NP content in the final product does not exceed 10% of the total weight of the system. This is done as a precaution so as not to disrupt any LC order in the material. Still under inert conditions, the vial was left open and THF was allowed to evaporate from the mixture. Some solvent was mixed in at the pre-hydrolysis state to ensure good material homogeneity. Once the mixture was dried it was placed in an oil bath at 20°C and opened to the atmosphere. Moisture in the air breaks down the precursor and nucleation and growth of ZnO NPs follows. The material was then investigated by TEM. Interestingly, by using Tren-OMeLC in a nematic state, it was found that the ZnO NPs grew in a certain preferred direction. The NPs seem to adopt a worm-like morphology and present a dense population. This anisotropy can be clearly seen in Figure 5. The nanoworms have an average width of 2.5-

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Figure 5. a, b) TEM micrographs obtained for Tren-OMeLC/ZnO nanocomposite synthesized in the liquid crystalline state (Tren-LC/[Zn(Cy)₂] ratio 0.4:1) at 0°C, showing anisotropic wire-like nanoparticles with lengths that range from 5 to 100 nm and a width of 2.5(0.2) nm; scale bars are 100 nm. c, d) The two HRTEM micrographs represent perpendicular and parallel orientations to the *z* plane, respectively. Insets: The corresponding numerical FT-diffractograms for the given crystalline region.

(0.2) nm and various lengths up to around 100 nm. The crystalline nature of the ZnO nanoworms was then demonstrated by using high-resolution transmission electron microscopy (HRTEM). HRTEM micrographs and a typical numerical diffractogram (Fourier transform) are shown in Figure 5. The measurement of the radial distances of the different spots corresponds to the hexagonal wurtzite structure of ZnO crystals (a=b=3.2 Å and c=5.2 Å, space group)P6mc). This experiment also demonstrates that the anisotropic growth proceeds along the c axis. To prove that the anisotropic growth of ZnO nanoparticles comes about due to the order existing in the LC state, we have performed exactly the same synthesis but at a temperature of 25°C. At this temperature, the LC alone is in the isotropic state according to its DSC thermogram (see Figure 1). Results from TEM showed ZnO NPs with no sort of organization or anisotropy (see Figure S8 in the Supporting Information).

The in situ synthesis of ZnO NPs within Tren-CNLC in the absence of solvent was then performed. The same synthetic procedure as for Tren-OMeLC was adopted; however, the reaction temperature was set at 20 °C (mesophase temperature for Tren-CNLC; see Table 1). TEM micrographs for the resultant product showed the formation of isotropic NPs of an average diameter of 3.2(0.3) nm (see Figure S9 in the Supporting Information). In this case, the LC state did not have an important effect on the growth of ZnO NPs unlike the case for Tren-OMeLC, this may be mainly due to a difference in the interactions with $[Zn(Cy)_2]$ or ZnO NPs, as demonstrated previously. The effect of hydrolysis temperature could not be excluded. However because the branched LCs are not liquid crystalline in the same temperature range, no experiment can confirm this effect. Nevertheless, we have shown that the cooling of the reaction temperature does not affect the shape of the NPs for amine ligands with long alkyl chains.

We studied the mesomorphic behavior of the synthesized bulk Tren-LC/ZnO hybrids by using DSC (see Figure S10 in the Supporting Information), POM (see Figure 6) and X-ray



Figure 6. POM images for a) Tren-OMeLC/ZnO and b) Tren-CNLC/ZnO at RT after cooling from the isotropic state.

scattering. A nematic mesophase was still observed by SAXS between -1 and 37 °C (see Figure S11 in the Supporting Information). Interestingly, as observed for ZnO NPs generated in solution, the presence of ZnO NPs shifts the mesophase temperature window towards higher temperatures. When ZnO NPs were synthesized in the isotropic phase of the LC, DSC results showed a near-complete disappearance of the N-I transition peak and poor birefringence under a POM. This confirmed that the LC state was somehow perturbed by the inorganic content introduced. In this regard, we suggest that the growth of ZnO NPs outside the mesophase leads to a lack of morphological control and the formation of large ZnO aggregates (observed in TEM). Consequently this leads to a disruption of the LC's intrinsic N phase. These results demonstrate that preparation of ZnO NPs inside the LC phase is crucial to control the properties of the LC/NP composite.

Conclusion

Herein we reported the use of thermotropic liquid crystal macromolecules as efficient stabilizing agents for the direct synthesis of isotropic ZnO NPs in solution. Moreover, we demonstrated that the structural order present in these branched LCs can be exploited for anisotropic growth of ZnO nanostructures. Tren-OMeLC allowed the formation of ZnO nanoworms, thus proving the direct effect of the organized nematic phase on the morphology of the nanoparticles. The control of shape and size at the nanoscale level is desirable due to its influence on potential applications. Therefore, we suggest that LCs in which the mesophase only depends on temperature can be ideal candidates as organization agents at the nanoscale level.

Experimental Section

Materials: Unless otherwise stated, all chemicals were used as provided by suppliers (Acros, Fluka, or Aldrich) without any further modifications. Oxygen- and moisture-sensitive substances and reactions were handled either in an MBraun Inert Gas System or under an argon atmosphere in carefully dried glassware, by using standard Schlenk techniques. THF used for sensitive compounds was obtained from an MBraun Purificator followed by degassing. The residual water content was systematically measured by Karl Fischer coulometric titration using a Metrohm instrument. Dicyclohexyl zinc precursor was purchased from NANOMEPS.

4'-(4-Acryloyloxybutyloxy)phenyl-4-(methoxy)benzoate (OMeLC): The synthesis of OMeLC was adapted from a literature procedure.^[31] Diethylazodicarboxylate (5.6 g, 32.0 mmol) was added dropwise to a solution of 4-(methoxy)phenyl-4'-(hydroxy)benzoate (6.4 g, 34.2 mmol), 4-hydroxybutyl acrylate (7.8 g, 32 mmol), and triphenylphosphine (TPP, 8.4 g, 32.0 mmol) in THF (150 mL). The reaction mixture was stirred for 24 h at RT, after which the volatile components were removed under vacuo. To precipitate phosphine the residue was dissolved in cyclohexane/ethyl acetate (25 mL, 20:5 v/v). It was then recrystallized from ethanol to give a white crystalline product (yield: 60 %). ¹H NMR (500 MHz, [D₈]THF): $\delta = 1.82 - 1.90$ (m, 4H; -CH₂-CH₂-CH₂-CH₂-), 3.86 (s, 3H; -OCH₃), 4.00 (t, J=6.5 Hz, 2H; -COO-CH₂-), 4.21 (t, J=6.5 Hz, 2H; -CH₂-O-Ar), 5.81 (m, 1H; -OCO-CH=CH₂), 6.05 (m, 1H; -OCO-CH=CH₂), 6.32 (m, 1H; -OCO-CH=CH₂), 6.93 (d, J=9.0 Hz, 2H; Ar-H-1), 7.02 (d, J=9.0 Hz, 2H; Ar-H-4), 7.10 (d, J = 9.0 Hz, 2H; Ar-H-2), 8.10 ppm (d, J = 9.0 Hz, 2H; Ar-H-3)

4-Cyano-4'-(4-acryloyloxybutyloxy)biphenyl (CNLC): Diethylazodicarboxylate (4.4 g, 25.5 mmol) was added dropwise to a solution of 4-hydroxy-4'-cyano biphenyl (3.6 g, 18.6 mmol), 4-hydroxybutyl acrylate (3.7 g, 25.5 mmol), and TPP (6.7 g, 25.5 mmol) in THF (50 mL). The reaction mixture was stirred for 24 h at RT, after which the volatile components were removed under vacuo. To precipitate phosphine, the residue was dissolved in cyclohexane/ethyl acetate (25 mL, 20:5 v/v). It was then recrystallized from ethanol to give a white crystalline product (yield: 60%). ¹H NMR (500 MHz, [D₈]THF): δ =1.84–1.90 (m, 4H; -CH₂-CH₂-CH₂-CH₂-Q-Ar), 5.75 (m, 1H; -OCO-CH=CH₂), 6.12 (m, 1H; -OCO-CH=CH₂), 6.33 (m, 1H; -OCO-CH=CH₂), 7.01 (d, *J*=9 Hz, 2H; Ar-H-1), 7.62 (d, *J*=9 Hz, 2H; Ar-H-2), 7.61–7.77 ppm (m, 4H; Ar-H-3,4).

Tren-OMeLC: Tren-OMeLC was synthesized as previously described.^[20] Briefly, 4-(acryloyloxybutyloxy)phenyl-4'-(methoxy)benzoate (882 mg, 2.38 mmol) was transferred to a round-bottomed flask and dissolved in chloroform (8 mL) with stirring. Tris(2-aminoethyl)amine (50 mg, 0.34 mmol) was then dissolved in chloroform (1 mL) and added dropwise to the reaction flask over an ice bath. The flask was then left to stir at RT under an argon atmosphere for 4 d, during which the initially colorless reaction mixture turned pale pink. Any volatile solvents were then removed under vacuo and the residue was stirred in hot ethanol for 10 min. This latter solvent was removed while hot by using a syringe. This was repeated three consecutive times. Residual solvent was removed under reduced pressure to give a pink viscous product (yield: 21%). ¹H NMR (500 MHz, [D₈]THF): $\delta = 1.73 - 1.85$ (m, 24H; -CH₂-CH₂-), 2.45 (m, 12H; -N-CH₂-CH₂-COO-), 2.55 (m, 12H; -NCH₂CH₂N-), 2.79 (m, 12H; -N-CH2-CH2-COO-), 3.85 (m, 18H; -OCH3), 3.98 (m, 12H; -COO-CH₂-), 4.11 (m, 12H; -CH₂-O-Ar), 6.91 (m, 12H; Ar-H-1), 7.01 (m, 12H; Ar-H-4), 7.08 (m, 12H; Ar-H-2), 8.07 ppm (m, 12H; Ar-H-3); MS (MALDI-TOF): m/z calcd for C₁₃₂H₁₅₀N₄O₃₆: 2368.0; found: 2368.4.

Tren-CNLC: 4-Cyano-4'-(4-acryloyloxybutyloxy)biphenyl (300 mg, 0.93 mmol) was transferred to a round-bottomed flask and dissolved in chloroform (8 mL) with stirring. Tris(2-aminoethyl)amine (20 mg, 0.13 mmol) was then dissolved in chloroform (1 mL) and added dropwise to the reaction flask over an ice bath. The rest of procedure is as described for Tren-OMeLC. The final product was obtained as a pale yellow gum (yield: 13%). ¹H NMR data is available in the Supporting Information section. ¹H NMR (500 MHz, $[D_8]$ THF): δ =1.80–1.90 (brs, 24H; -CH₂-CH₂-), 2.44 (t, *J*=7.5 Hz, 12H; -N-CH₂-CH₂-COO-), 2.54 (brs, 12H; -NCH₂CH₂N-), 2.77 (t, *J*=7.5 Hz, 12H; -N-CH₂-CH₂-COO-)

),4.02 (m, 12H; -COO-CH₂-), 4.11 (m, 12H; -CH₂-O-Ar), 7.00 (d, J = 9 Hz, 12H; Ar-H-1), 7.61 (d, J = 9 Hz, 12H; Ar-H-2), 7.73 ppm (m, 24H; Ar-H-3,4); MS (MALDI-TOF): m/z calcd for $C_{126}H_{132}N_{10}O_{18}$: 2074.0; found: 2074.0.

Synthesis of OMeLC/ZnO and CNLC/ZnO (in solvent): In a screw-top vial, the LC (24 mg, 6.6×10^{-2} mmol) was dissolved in dried and <degassed THF (6 mL) under an inert atmosphere inside a glovebox. Dicyclohexyl zinc precursor (5 mg, 2.2×10^{-2} mmol) was then added to the solution. The reaction vial was closed and left to stand for 30 min. The solution was then taken out of the glovebox and opened to the atmosphere to decompose the precursor and form ZnO nanoparticles.

Synthesis of Tren-OMeLC/ZnO or Tren-CNLC/ZnO (in solvent): In a screw-top vial, Tren-LC $(1.1 \times 10^{-2} \text{ mmol})$ was dissolved in dried and degassed THF (6 mL) under an inert atmosphere inside a glovebox. Dicyclohexyl zinc precursor (5 mg, $2.2 \times 10^{-2} \text{ mmol})$ was then added to the solution. The reaction vial was closed and left to stand for 30 min. The solution was then taken out of the glove box and opened to the atmosphere in order to decompose the precursor and form ZnO nanoparticles.

Synthesis of Tren-OMeLC/ZnO (no solvent): Tren-OMeLC (16 mg, 6.7×10^{-3} mmol) or Tren-CNLC (16 mg, 7.7×10^{-3} mmol) was transferred to a Schlenk tube and dissolved in dry THF (300 µL) under inert conditions inside a glovebox. Dicyclohexyl zinc precursor (4 mg, 1.7×10^{-2} mmol) was then added to the solution containing the LC. THF in the reaction tube was then evaporated under vacuo (still inside the glovebox). When the mixture was dry, it was placed in an ice bath at the desired temperature. After which the Schlenk tube was opened to the atmosphere.

Characterization: To determine the structural characteristics of obtained products, NMR spectra were recorded by using a Bruker Avance 500 spectrometer equipped with a 5 mm triple-resonance inverse Z-gradient probe. Unless otherwise mentioned, measurements were performed in deuterated THF or chloroform at RT. The chemical shifts, δ , are given in ppm. The 2D NOESY measurements were performed with a mixing time of 100 ms. All diffusion measurements were made by using the stimulated echo pulse sequence with bipolar gradient pulses and were processed with the Laplace inversion routine CONTIN (Topspin software). The temperatures at which glass transitions (T_g) and crystallizations (T_c) occur were determined by using DSC by using a Mettler Toledo DSC 1 STARe System thermal analysis calorimeter equipped with a gas controller GC200. Temperatures at which phase transitions occurred were taken to be the temperature at the top of the DSC peaks as the temperature decreased at different rates: 20, 10, 5, and 1°Cmin⁻¹, and finally extrapolated to 0° Cmin⁻¹. T_{g} was measured as the temperature increased at a rate of 10°Cmin⁻¹. Characterization of liquid crystalline phases was performed by using a hot-stage FP 82HT (Mettler Toledo) under a polarized light optical microscope BX50 from Olympus. For X-ray scattering measurements, a microfocus rotating anode X-ray source (Rigaku Micro Max-007 HF) combined with high-performance multi-layer optics and three-pinholes collimation provided intense X-ray radiation on the sample. The sample holder was mounted on an X-Y stage. A two-dimensional detector (image plate from Mar Research) collected the scattered radiation. The sample-detector distances were varied to obtain wide and small angles and calibration of this distance was performed by using silver behenate as a reference. DLS measurements were carried out by using a Malvern Instruments Nano-ZS equipped with a He–Ne laser ($\lambda =$ 633 nm). The correlation function was analyzed by using the general purpose method (NNLS) to obtain the distribution of diffusion coefficients (D) of the solutes. The apparent diameter was then determined by using the Stokes-Einstein equation. Mean diameter values were obtained from three different runs. Standard deviations were evaluated from diameter distribution. Besides scattering measurements, the morphology of the obtained nanohybrids was studied by using TEM. Samples for TEM were prepared by slow evaporation of droplets of colloidal solution deposited on a carbon-coated 200 mesh copper TEM grid (Ted Pella). The samples were then carefully dried overnight under a pressure of 5×10^{-5} mbar by using a BOC Edward turbomolecular pump. The TEM experiments were performed at the microscopy service of University Paul Sabatier (TEMS-CAN) by using a JEOL JEM1011 electron microscope operating at 100 kV with a resolution point of 0.45 nm. The nanoparticle size-distribu-

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tion histograms were determined by using magnified TEM images. The size distribution of the particles was determined by measuring a minimum of 200 particles of each sample. The observed size distributions were analyzed in terms of Gaussian statistics. For photoluminescent analysis emission, spectra were recorded by using a Horiba–Jobin–Yvon Fluoromax-4 spectrofluorometer equipped with a xenon lamp.

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