Supporting Information

For

Liquid Crystal Based on Hybrid Zinc Oxide Nanoparticles

Sarmenio Saliba,^{a,b,c} Yannick Coppel,^{a,b} Patrick Davidson,^d Christophe Mingotaud,^{a,c} Bruno Chaudret,^{a,b} Myrtil L. Kahn^{a,b} * and Jean-Daniel Marty^{a,c} *

^a University of Toulouse, 118 route de Narbonne, 31062, Toulouse, France
 ^b Laboratoire de Chimie de Coordination, UPR 8241, 31077, Toulouse, France
 ^c Laboratoire IMRCP, CNRS UMR 5623, 31062, Toulouse, France
 ^d Laboratoire de Physique des Solides, UMR 8502, 91405, Orsay, France

1. Experimental

1.1. Explanation of techniques and solvents

PFG-NMR spectra were obtained using a Bruker Avance500 spectrometer equipped with a 5 mm triple-resonance inverse Z-gradient probe. All diffusion measurements were made using the stimulated echo pulse sequence. The recycle delay was adjusted to 3s. The strength of the gradient was calibrated by measuring the self diffusion of the residual HDO signal in a 100% D₂O sample at 298K (1.90 x 10^{-9} m².s⁻¹). The shape of the gradients was rectangular and the strength was varied in 16 increments (2-95%) of the gradient ramp created by the Bruker software DOSY. For 2D diffusion ordered spectroscopy (DOSY), after Fourier transformation and baseline correction, the diffusion dimension was processed with the Bruker Topspin software package DOSY. Unless otherwise mentioned, measurements were performed in deuterated THF, at room temperature. The chemical shifts δ are given in ppm, using tetramethylsilane (TMS) as an internal standard.

Differential scanning calorimetry data has been measured on a NETZCH DSC204 from *Erich NETZSCH GmbH & Co. Holding KG*. The heat rate varied from 1 to 40 °C/min. Substances were well sealed in a metal crucible. The phase transition temperature was taken as the average between the Onset and End temperatures. Data was calculated using software by Netzsch.

X-ray scattering experiments were performed with a setup already described (1). The X-ray beam delivered by a rotating anode generator was monochromatized ($\lambda_{CuK\alpha} = 0.1541 \text{ nm}$) and focused by an osmic X-ray optics. The sample was held in a sealed Lindemann glass capillary of 1 mm diameter placed in an oven between the poles of a permanent magnet (B = 0.7 T). The scattered X-rays were detected with a Princeton CCD camera; the sample-to-detector distance was 60 mm and typical exposure times were around 10 minutes.

TEM samples were prepared by slow evaporation of droplets of colloidal solution deposited on carbon-supported copper grids. Micrographs were taken using a JEOL 120kV electronic microscope. The nanoparticle size-distribution histograms were determined by using magnified TEM images. The size distribution of the particles was determined by measuring a minimum of 300 particles. The size distributions observed were generally analyzed in terms of Gaussian statistics.

Characterization of liquid crystalline phases was performed on a hot stage FP 82HT from Mettler Toledo under a polarized light optical microscope BX50 from Olympus. Emission spectra were recorded using a PTI spectrometer equipped with a Xenon Lamp. An HP 8452A Diode Array Spectrometer was used for absorption spectra recording.

Unless otherwise stated, the chemicals have been used as provided from the suppliers and water content was systematically measured by Karl Fischer coulometric titration on a Metrohm instrument. Sensitive substances and reactions were handled in an MBraun Inert Gas System or under an argon atmosphere in carefully heated glassware, using the standard Schlenk techniques. Zinc precursor was purchased from NANOMEPS. Removal of water from organic layers was carried out using Magnesium Sulfate, dried, min. 99.5 %. MW=120.36 supplied by Sigma-Aldrich[®]. Column chromatography was performed using silica gel Geduran[®] 0.040-0.063 mm from *Merck KGaA*. For the thin layer chromatography, TLC plates silica gel 60 F₂₅₄ on aluminum foil from *Merck KGaA*, have been used. The eluent is given in relation with the corresponding $R_{\rm f}$ value. The detection was performed with UV light of 254 nm wavelength.

1.2. Synthetic Procedures

4'-(hexyloxyphthalimide)biphenyl-4-carbonitrile



 $M_w = 424.49 \text{ gmol}^{-1}$

4'-hydroxybiphenyl-4-carbonitrile (1.79 g, 9.15 mmol), K_2CO_3 (2.34 g, 16.9 mmol) and DMF (50 mL) were transferred to a pre-dried round bottomed flask under an argon atmosphere. N-(6-Bromohexyl) phthalimide (2.63 g, 8.5 mmol) was then added to the reaction flask. The mixture was stirred overnight under reflux at 120 °C. The resulting suspension was placed in a separating funnel and portions of ethyl acetate (50 mL), chloroform (50 mL) and water (100 mL) were added. The organic phase was separated and the aqueous remainder was extracted with ethyl acetate (3 x 100 mL). The organic phases were collected and washed with sat. NaHCO₃ solution. The resulting solution was dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to give a white solid (3.25 g, 84 % yield).

¹**H-NMR (500 MHz, CDCl₃):** $\delta = 1.38-1.59$ (m, 4H, 7, 8-H); 1.68-1.77 (q, 2H, 9-H); 1.78-1.85 (q, 2H, 6-H); 3.70 (t, 2H, 10-H); 3.99 (t, 2H, 5-H); 6.97 (d, 2H, 4-H); 7.51 (m, 2H, Ar-H); 7.61-7.72 (m, 6H, 11, Ar-H); 7.82-7.85 (m, 2H, 1-H) ppm.

MS (DCI): m/z (%) = 442.2 [MNH4⁺] (100), 425.2 [MH⁺] (5).

4'-(6-aminohexyloxy)biphenyl-4-carbonitrile (60CBNH₂)



 $M_w = 294.39 \text{ gmol}^{-1}$

An ethanolic suspension (30 mL) of 4'-(hexyloxyphthalimide) biphenyl-4-carbonitrile (3.25 g, 7.66 mmol, 1.0 equiv) was prepared in a pre-dried, two-necked round-bottomed flask. The mixture was heated to 90 °C at which point hydrazine monohydrate (740 µL; 15.32 mmol; 2.0 equiv) was added drop wise over a period of 10 minutes. The mixture turned colorless followed by the formation of a white precipitate. The system was left to stir overnight at the stated temperature, under reflux. Volatile components were removed under vacuum and residue was dissolved in a mixture of water (200 mL), CHCl₃ (200 mL) and methanol (5 mL) in a separating funnel. Some precipitate was observed to be insoluble in the organic phase therefore a 2M NaOH solution was added drop wise until indicator resulted in a highly basic pH. This was done in order to make sure all ammonium forms of the product were reversed to amines. The organic phase was separated and the aqueous phase extracted three times with CHCl₃ (3x100 mL). Organic extracts were combined and washed with sat. NaHCO₃ solution. Organic extract was then dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The powder was purified via column chromatography on silica gel [eluents: CHCl₃:MeOH (95:5) until impurities were out followed by CHCl₃:MeOH:NH₄OH (83:15.5:1.55) to run down the pure amino-product] to give a pale yellow product [1.172 g, 52] % yield, $R_f = 0.43$ (83:15.5:1.55)].

¹H-NMR: Spectra and other info available in:

- Zhang, C; Zhang, Y.; Hang, D.; Shen, J.; Dong, Q., *Jingxi Huagong*, 2005, 22(11), 806-808.
- (2) Chien, L. C.; Cada, L. G ; Xie, L., Liq. Cryst., 1992, 12, 853.

MS (DCI): m/z (%) = 295.2 [MH⁺] (100), 323.2 [MC₂H₅⁺] (25), 294.2 [M⁺] (10).

2. Characterization

2.1. NMR Spectroscopy

2.1.1. ¹H-NMR Spectroscopy

Here below is a summary of α -proton chemical shifts (δ) for octylamine (OA) (-CH₂NH₂) and 6OCBNH₂ (-CH₂NH₂).

Table S1. Octylamine δ for molecules free in solution and in the presence of ZnO nanoparticles.

	OA (free)	OA/ZnO
Proton type	OA α -protons -C H₂- NH ₂	
Chemical Shift (δ / ppm)	2.623	2.66
Multiplicity	triplet	triplet

Table S2. 6OCBNH₂ δ for molecules free in solution and in the presence of ZnO nanoparticles.

	6OCBNH ₂ (free)	60CBNH₂/ZnO/OA
Proton type	$6OCBNH_2 \alpha$ -protons $-CH_2NH_2$	
Chemical Shift (δ / ppm)	2.66	2.68
Multiplicity	triplet	triplet

Table S3. Stepwise addition of $6OCBNH_2$ to OA results in a gradual chemical shift as evidence for a ligand exchange process.

	OA/ZnO/60CBNH ₂			
	OA α -protons –CH ₂ NH ₂			
Equivalence of	0.6	1.0	1.6	2.7
60CBNH ₂				
Chemical Shift (2.644	2.638	2.634	2.629
δ / ppm)				
Multiplicity	triplet	triplet	triplet	triplet

2.1.2. DOSY

The changes in diffusion coefficient for a system were octylamine previously stabilizing ZnO nanoparticles is now being replaced by the thermotropic LC molecule $6OCBNH_2$.



Figure S1. A) Self-diffusion coefficient trends for $60CBNH_2$ molecules for different equivalents of $60CBNH_2$ to ZnO/OA; a) 0.5, b) 1.0, c) 1.1, d) 1.6, e) 2.7, f) $60CBNH_2$ free in solution. B) Self-diffusion coefficient trends for OA molecules for different equivalents of $60CBNH_2$ to ZnO/OA; a) 0.0 (ZnO/OA alone) b) 0.5, c) 1.0, d) 1.1, e) 1.6, f) 2.7, g) OA free in solution.

Sample	$D_{\rm OA}$ / m ² s ⁻¹	$D_{60CBNH_2}/\mathrm{m}^2\mathrm{s}^{-1}$
OA	1.55 x 10 ⁻⁰⁹	
6OCBNH ₂		9.23 x 10 ⁻¹⁰
ZnO/OA	7.50 x 10 ⁻¹⁰	
ZnO/OA/0.5 eq 6OCBNH ₂	8.38 x 10 ⁻¹⁰	7.48 x 10 ⁻¹⁰
ZnO/OA/1.0 eq 6OCBNH ₂	9.31 x 10 ⁻¹⁰	7.96 x 10 ⁻¹⁰
ZnO/OA /1.1 eq 6OCBNH2	9.91 x 10 ⁻¹⁰	8.28 x 10 ⁻¹⁰
ZnO/OA/1.6 eq 6OCBNH ₂	1.05 x 10 ⁻⁰⁹	8.39 x 10 ⁻¹⁰
ZnO/OA/2.7 eq 6OCBNH ₂	1.08 x 10 ⁻⁰⁹	8.89 x 10 ⁻¹⁰

Table S4. Self-diffusion coefficient values for the given samples



Figure S2. Filtered Diffusion NMR Spectra for a) octylamine at the surface of the nanoparticles; b) $6OCBNH_2$ at the surface of the nanoparticles.

Table S5. The table below shows a comparison of ligand exchange experiments carried out using two liquid crystals; a) 5CB and b) $6OCBNH_2$. These compounds are very similar however the former does not have amine functionalities. These following results show the importance of the $-NH_2$ group for ligand-nanoparticle interaction.

	5CB NC - ZnO/OA	60CBNH2 NC - C - O + ZnO/OA
¹H NMR	No signal shifts Chemical shift for OA protons No interaction (ArCN-NP)	No Ar signal shifts (complement) Chemical shift of α -Hs to NH ₂ Evidence for interaction (-NH2-NP)
DOSY	No change whatsoever in diffusion rates Imp: diffusion of OA stays the same	Change in diffusion coefficient LC alone is faster than LC+ZnO+OA (23%) Increase conc ⁿ 6OCBNH2 = OA diffuses faster
Filtered Diffusion		The appearance of OA protons The appearance of 6OCBNH2 protons Both strongly bonded to NP

2.2. Differential Scanning Calorimetry

6OCBNH₂ exhibits a crystalline (*Cr*) to nematic (*N*) transition at 68 °C and a *N* to *I* transition at $T_c = 92$ °C.



Figure S3a. DSC thermogram for 6OCBNH₂ recorded at a rate of 5°C/min.



Figure S3b. DSC thermogram recorded for a ZnO/LC (50 wt % ZnO-OA) hybrid.

The presence of ZnO nanoparticles affects the original mesophase of $6OCBNH_2$. The temperature range of the nematic phase increases with the amount of incorporated ZnO NPs (Figure S4). Also, both Cr/N and N/I transitions became broader.



Figure S4. Phase diagram for 6OCBNH₂/ZnO/OA hybrid containing different ratios of components.

2.3. Polarized Light Optical Microscopy



Figure S5. POM images showing changes from Schlieren to marble nematic textures upon increasing LC to nanoparticle ratio; (a) 6OCBNH₂, (b) 6OCBNH₂:ZnO/OA 7.4:1, (c) 6OCBNH₂:ZnO/OA 3.7:1, (d) 6OCBNH₂:ZnO/OA 0.7:1.

2.4. SAXS measurements



Figure S6. Typical X-ray scattering pattern of the nematic phase of $60CBNH_2$ aligned in a 0.7 T magnetic field at 75 °C.

The X-ray scattering pattern of the $60CBNH_2$ compound, in its liquid-crystalline phase at 75 °C, only displays diffuse scattering rings (The weak sharp diffraction lines arise from a small proportion of crystalline phase due to a temperature gradient in the heating cell.) Moreover, the nematic phase could be aligned by applying a 0.7 T magnetic field, resulting in an anisotropic scattering pattern. Such a pattern is quite typical of an aligned nematic phase of rod-like mesogens as the diffuse ring corresponds to lateral interferences among rods aligned along the field.



Figure S7. Typical two-dimensional image obtained by X-ray measurements for the nematic phase of 6OCBNH₂:ZnO/OA 7.4:1 aligned in a 0.7 T magnetic field at 80 °C. The dark areas in the pattern are only an artefact due to the shade of the sample holder that blocks air scattering. The inner and outer diffuse rings correspond to the distances 7.7 and 4.5 Å respectively (the latter one being characteristic to lateral interferences among LC, the precise

nature of the second one may correspond to LC separated by OA molecules but its precise nature as yet to be fully elucidated).

2.5. UV-Spectroscopy



Figure S8. Absorption spectrum for 6OCBNH₂-ZnO/OA hybrid (1:1 molar eq)