SUPPORTING INFORMATION

Doping of Nematic Cyanobiphenyl Liquid Crystals with Mesogen-Hybridized Magnetic Nanoparticles

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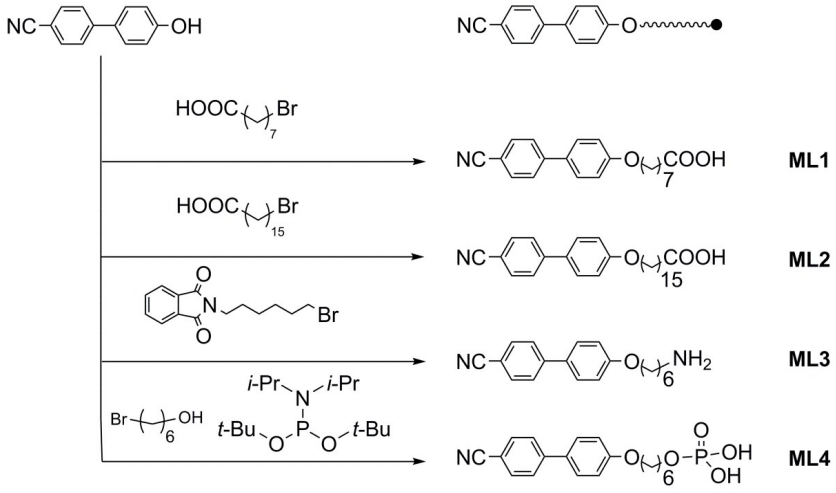
The supporting information gives further details on the synthesis of the materials, the (pro)mesogenic ligands, Fe_3O_4@oleic acid nanoparticles and the characterization of the materials.

Materials

The following chemicals were commercially purchased and used as received: 6-bromohexanol (97%), N-(6-bromohexyl)phthalimide (97%), 8-bromooctanoic acid (97%), 4-cyano-4'-pentylbiphenyl (99%), 4-hydroxy-4-biphenylcarbonitrile (99%), and tetrabutylammonium hydrogen sulphate (97%) from Alfa Aeser; 16-bromohexadecanoic acid (≥ 99%), di-tert-butyl diisopropylphosphoramidite (95%), hydrazine hydrate (reagent grade; 50 - 60%), iron(II)chloride (98%), iron(III)chloride (reagent grade), meta-chloroperoxybenzoic acid (≤ 77%), 1H-tetrazole (0.45 M in acetonitrile), and trifluoroacetic acid (99%) from Sigma Aldrich; dimethylformamide (reagent grade) from Amresco; cobalt(II)chloride (≥ 99%) from Carl Roth; perchloric acid solution (1.0 M in water) from Fluka; sodium hydride (suspension 60% in paraffin oil) from Merck; ethanol (absolute; ≥ 99.8%) and sodium hydrogen sulphite (reagent grade) from VWR Chemicals. Deionized water (18.2 MΩ·cm at 25°C) was freshly prepared using a Milli-Q® system (Merck).

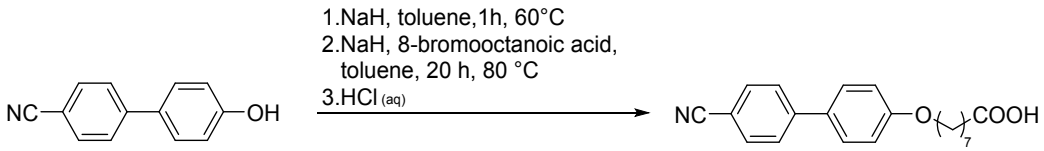
Synthesis of the (pro)mesogenic ligands



Scheme S1. Schematic representation for the synthesis of the (pro)mesogenic ligands ML1, ML2, ML3, and ML4 from 4'-hydroxy-4-biphenylcarbonitrile.

The synthesis and the properties of (pro)mesogenic ligands (i.e., 8-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)octanoic acid (ML1), 4'-((6-aminohexyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (ML3), and 6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl dihydrogen phosphate (ML4)) have been previously reported elsewhere and are described briefly.[60-62] The ligand 16-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexadecanoic acid (ML2) was prepared corresponding to ML1.

Synthesis of 8-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)octanoic acid (ML1)[S1]



Scheme S2. Synthesis of the mesogenic ligand ML1.

4'-hydroxy-4-biphenylcarbonitrile (1.95 g, 10 mmol) and sodium hydride suspension (420 mg sodium hydride suspension in paraffin oil (i.e., NaH 252 mg, 10.5 mmol;)) were dissolved under inert conditions in a mixture of toluene (100 mL) and dimethyl sulfoxide (20 mL) and stirred for 4 h at room temperature. The mixture (solution I) was heated to 60°C (1 h). 8-bromooctanoic acid (2.23 g, 10 mmol) and sodium hydride suspension (420 mg sodium hydride suspension in paraffin oil (i.e., NaH 252 mg, 10.5 mmol;)) were dissolved in a mixture of toluene (100 mL) and dimethyl sulfoxide (20 mL) and stirred for 4 h at room temperature. To this solution (solution II) tetrabutylammonium hydrogen sulphate (170 mg, 0.5 mmol) was added and solution II was stirred for 30 min at 60°C. Solution II was then added dropwise to solution I. The mixture of solution I and II was heated to 80°C and stirred for 20 h. After cooling to room temperature, the product was precipitated by pouring the reaction mixture into hydrochloric acid (40 mL, 1 M in water). It was filtered and successively washed (three times each) with water and ethanol/water (1:4 v/v). The final product was obtained from recrystallization in methanol in a yield of 76% (2.25 g, 7.6 mmol) as white powder.

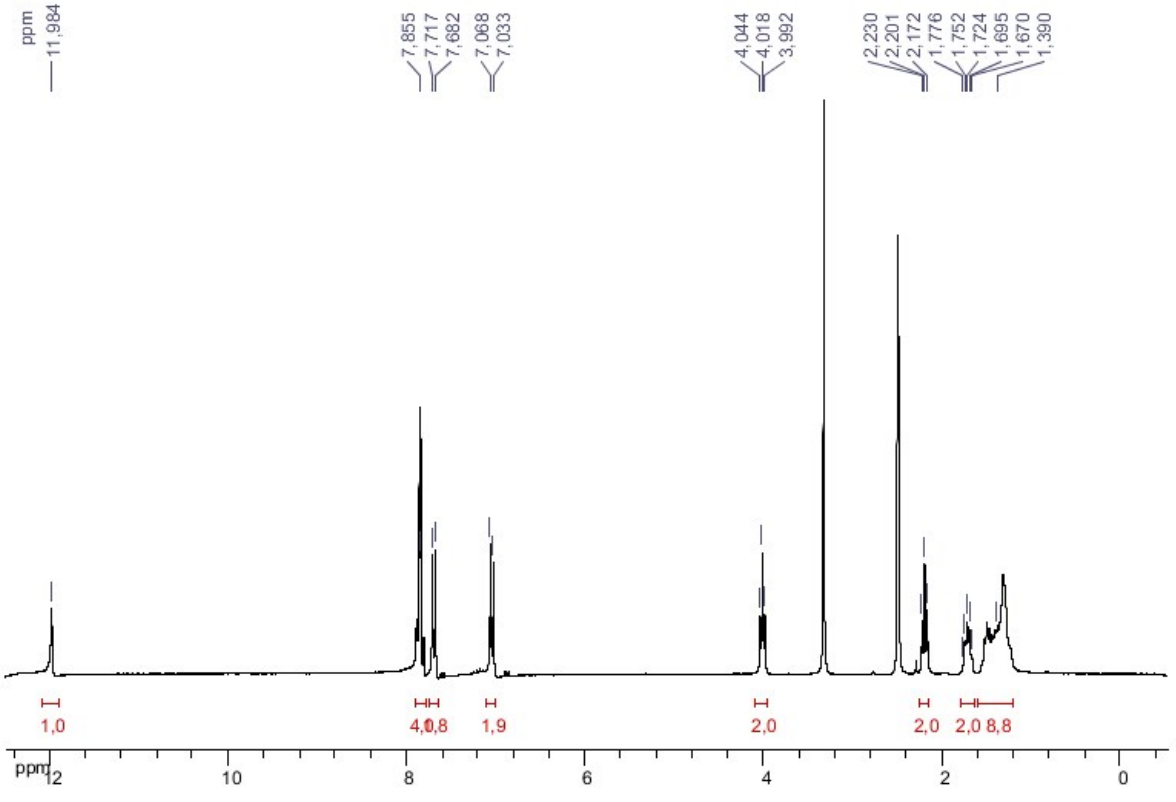
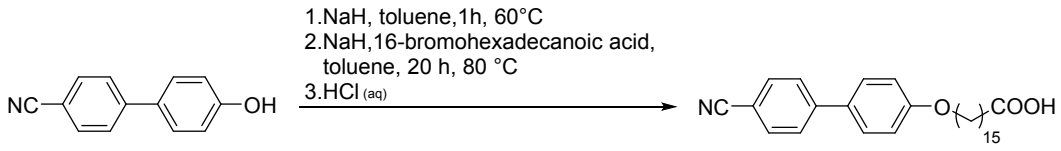


Figure S1. ^{1}H NMR (200 MHz, [D_6] DMSO / [D_4] methanol, 25°C): δ = 11.98 (s, 1 H; COOH), 7.80 - 7.91 (m, 4 H; CH), 7.70 (d, ^{3}J(H-H) = 8.7 Hz, 2 H; CH), 7.05 (d, ^{3}J(H-H) = 8.7 Hz, 2 H; CH), 4.02 (t, ^{3}J(H-H) = 6.4 Hz, 2 H; CH_2O), 2.20 (t, ^{3}J(H-H) = 7.3 Hz, 2 H; CH_2), 1.72 (qi, ^{3}J(H-H) = 6.4 Hz, 2 H; CH_2), 1.20 - 1.58 ppm (m, 8 H; CH_2).

Synthesis of 16-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexadecanoic acid (ML2)



Scheme S3. Synthesis of the (pro-)mesogenic ligand ML2.

4'-hydroxy-4-biphenylcarbonitrile (1.95 g, 10 mmol) and sodium hydride suspension (420 mg sodium hydride suspension in paraffin oil (i.e., NaH 252 mg, 10.5 mmol;)) were dissolved under inert conditions in a mixture of toluene (120 mL) and dimethyl sulfoxide (24 mL) and stirred for 4 h at room temperature. The mixture (solution I) was heated to 60°C (1 h). 16-bromohexadecanoic acid (3.35 g, 10 mmol) and sodium hydride suspension (420 mg sodium hydride suspension in paraffin oil (i.e., NaH 252 mg, 10.5 mmol;)) were separately dissolved in a mixture of toluene (120 mL) and dimethyl sulfoxide (24 mL) and stirred for 4 h at room temperature. To this solution (solution II) tetrabutylammonium hydrogen sulphate (170 mg, 0.5 mmol) was added and solution II was stirred for 30 min at 60°C. Solution II was then added dropwise to solution I. The mixture of solution I and II was heated to 80°C and stirred for 20 h. After cooling to room temperature, the product was precipitated by pouring the reaction mixture into hydrochloric acid (40 mL, 1 M in water). It was filtered and successively washed (three times each) with water and ethanol/water (1:4 v/v). The final product was obtained from recrystallization in methanol in a yield of 79% (3.56 g, 7.92 mmol) as white powder.

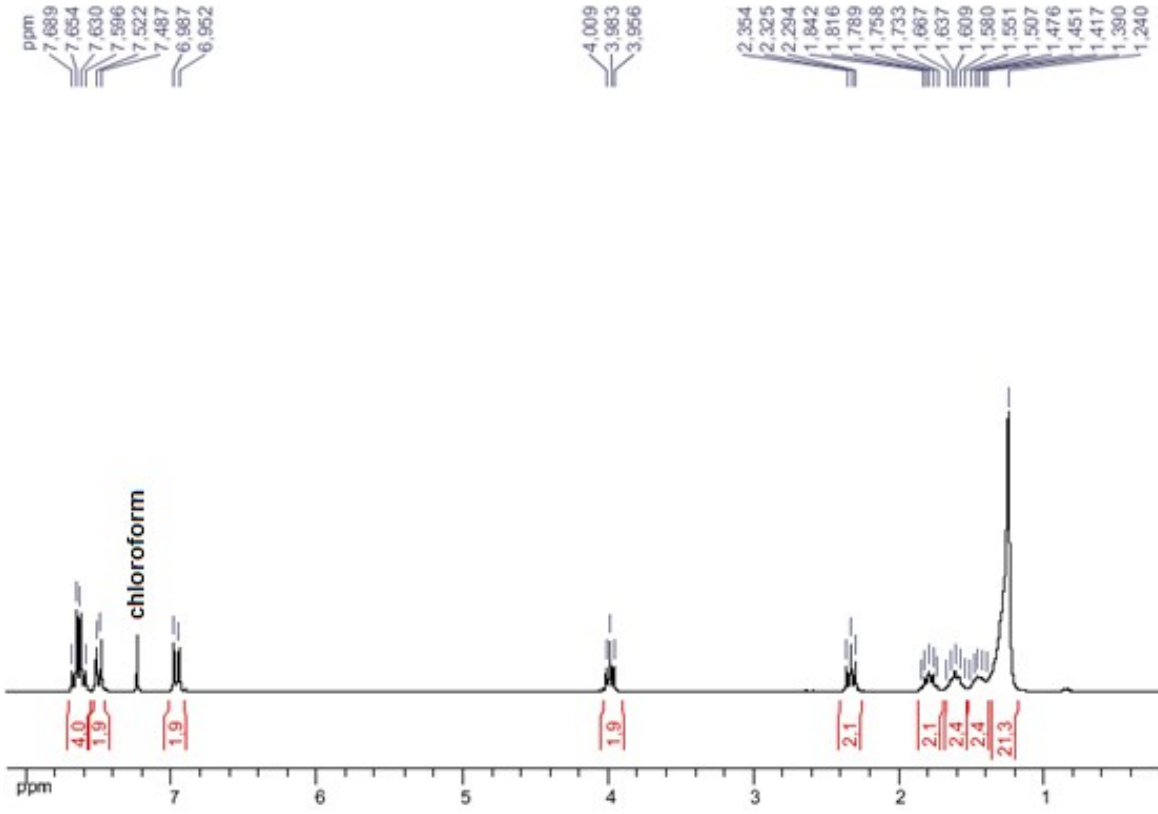


Figure S2. ^{1}H NMR (200 MHz, [D_1] chloroform, 25°C): δ = 7.64 (dd, ^{3}J(H-H) = 14.7, 8.4 Hz, 4 H; CH), 7.50 (d, ^{3}J(H-H) = 8.8 Hz, 2 H; CH), 6.97 (d, ^{3}J(H-H) = 8.8 Hz, 2 H; CH), 3.98 (t, ^{3}J(H-H) = 6.5 Hz, 2 H; CH_2O), 2.33 (t, ^{3}J(H-H) = 7.5 Hz, 2 H; CH_2), 1.79 (qi, ^{3}J(H-H) = 6.5 Hz, 2 H; CH_2), 1.61 (qi, ^{3}J(H-H) = 7.5 Hz, 2H; CH_2), 1.14 - 1.53 ppm (m, 22 H; CH_2).

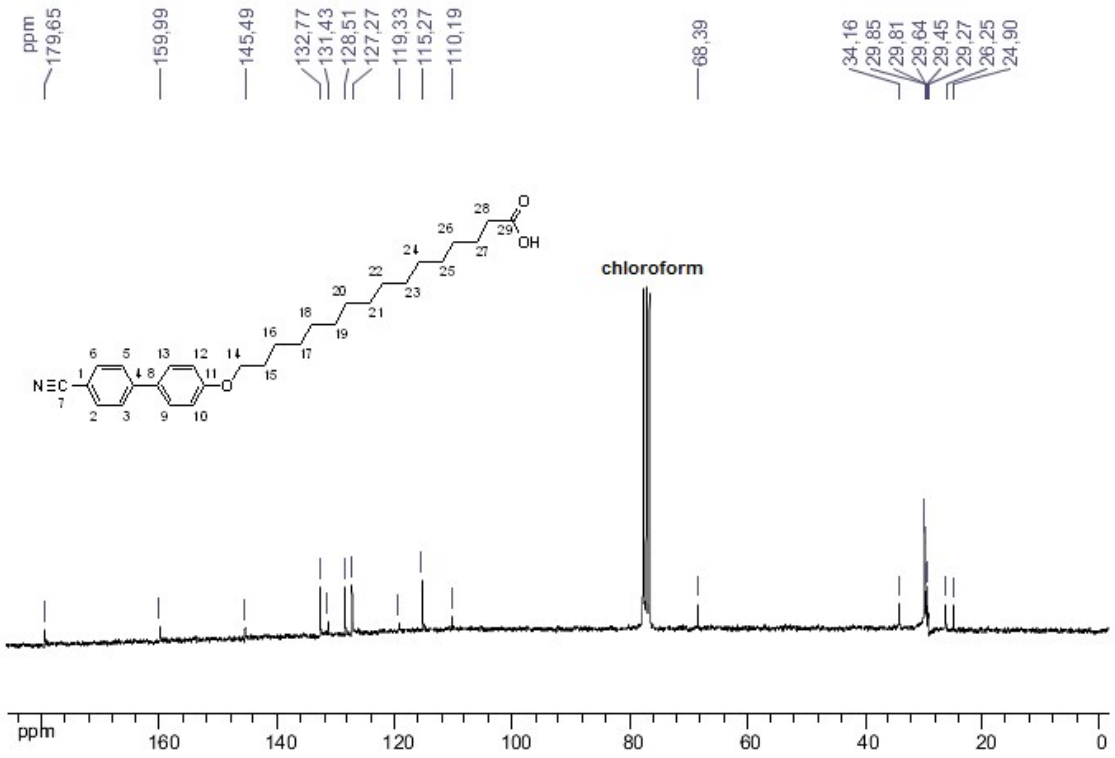
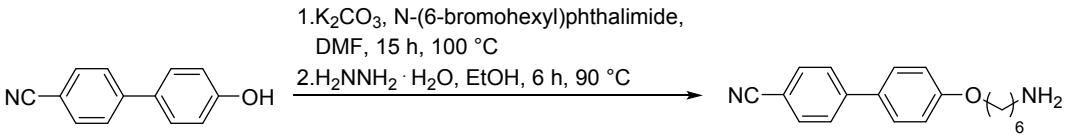


Figure S3. ^{13}C NMR (60 MHz, [D_1] chloroform, 25°C): δ = 179.65 (s, 1 C; C-29), 159.99 (s, 1 C; C-11), 145.49 (s, 1 C; C-4), 132.77 (s, 2 C; C-2, C-6), 131.43 (s, 1 C; C-8), 128.51 (s, 2 C; C9, C-13), 127.27 (s, 2 C; C-3, C-5), 119.33 (s, 1 C; C-7), 115.27 (s, 2 C; C-10,C-12), 110.19 (s, 1 C; C-1), 68.39 (s, 1 C; C-14), 34.16 (s, 1 C; C-28), 29.27-29.85 (s, 11 C; C-15,C-17 - C-26), 26.25 (s, 1 C; C-16), 24.90 ppm (s, 1 C; C-27).

Synthesis of 4'-((6-aminohexyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (ML3)[S2]



Scheme S4. Synthesis of the mesogenic ligand ML3.

Under inert conditions 2.3 g (11.78 mmol) 4'hydroxybiphenyl-4-carbonitrile, 2.8 g (9.03 mmol) N-(6-bromohexyl)phthalimide and 3.0 g (21.76 mmol) potassium carbonate were dispersed in 65 mL dimethylformamide and refluxed for 15 h at 100°C. The suspension was extracted with 260 mL ethyl acetate, chloroform and deionized water (1:1:2 v/v). The aqueous phase was extracted three times with 130 mL ethyl acetate. The organic phase and the extracts were washed with saturated sodium hydrogen carbonate solution, dried over magnesium sulphate, filtrated and the solvent removed under reduced pressure. The intermediate 4'-(hexyloxyphthalimide)biphenyl-4-carbonitrile (ML3_1) was obtained as pale yellow powder (2.9 g, 6.87 mmol, 70% yield).

ML3_1 (2.9 g, 6.87 mmol) was dispersed in 27 mL ethanol and heated to 90°C. Within 10 minutes 0.66 mL (13.73 mmol) hydrazine hydrate was added dropwise and stirred at 90°C for 6 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue dissolved in 405 mL deionized water, chloroform, methanol and 1 M aqueous sodium hydroxide solution (40:40:1 v/v; pH 12). The organic phase was separated and the aqueous phase was extracted three times with 100 mL chloroform. The combined organic extracts were washed with saturated sodium hydrogen carbonate solution, dried over magnesium sulphate, filtrated and concentrated. The raw product was purified by column chromatography on silica gel (chloroform/methanol = 95:9 to 5:1 and finally chloroform/methanol/ammonium hydroxide = 83:15:1.5). The product was obtained as pale yellow powder in a yield of 1.7 g (related to ML3_1 62%; 5.77 mmol).

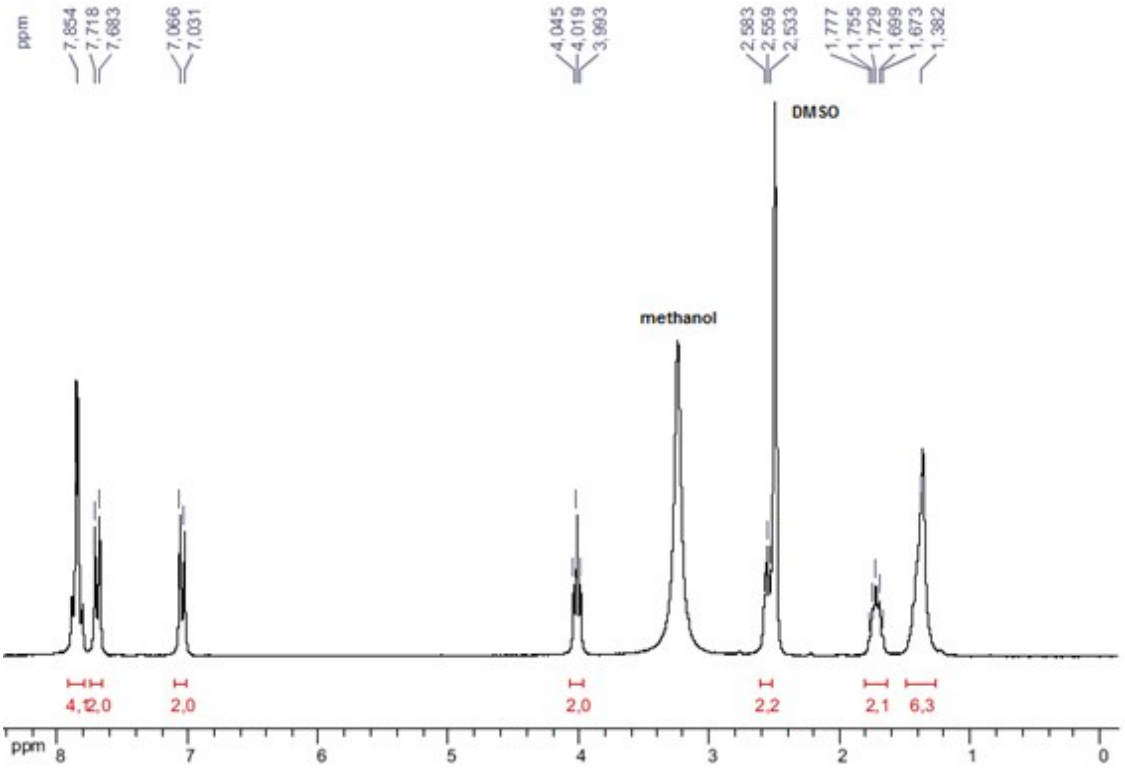
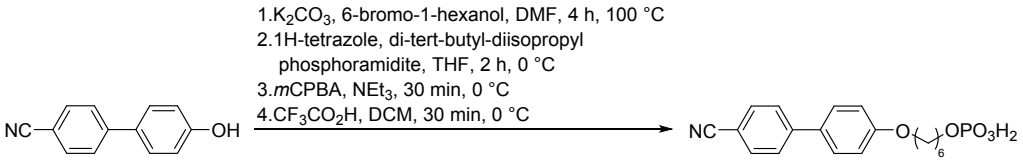


Figure S4. ^{1}H NMR (200 MHz, [D_6] DMSO / [D_4] methanol, 25°C): δ = 7.79 - 7.92 (m, 4 H; CH) , 7.70 (d, ^{3}J(H-H) = 8.7 Hz, 2 H; CH), 7.05 (d, ^{3}J(H-H) = 8.7 Hz, 2 H; CH), 4.02 (t, ^{3}J(H-H) = 6.4 Hz, 2 H; CH_2O), 2.56 (t, ^{3}J(H-H) = 6.8 Hz, 2 H, CH_2), 1.73 (qi, ^{3}J(H-H) = 6.4 Hz, 2 H; CH_2), 1.27 - 1.49 ppm (m, 6 H; CH_2).

Synthesis of 6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl dihydrogen phosphate (ML4)[S3]



Scheme S5. Synthesis of the mesogenic ligand ML4.

4'-hydroxybiphenyl-4-carbonitril (2.45 g, 12.55 mmol) was dissolved in a suspension of 3.5 g (25.33 mmol) potassium carbonate in 100 mL dimethylformamide. The suspension was heated to 100°C and 2.5 g (13.8 mmol) 6-bromohexanol in 20 mL dimethylformamide were added dropwise. The mixture was refluxed at 100°C for 4 h. After cooling to room temperature, 1 M HCL solution was added (pH 6). The product was extracted with 250 mL dichloromethane, cyclohexane and deionized water (1:5:5 v/v). The organic phase was separated and the aqueous phase was washed three times with 50 mL cyclohexane. The combined organic extracts were dried under reduced pressure. The intermediate 4'-((6-hydroxyhexyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (ML4_1) was obtained as an oily compound (93%, 3.5 g, 11.8 mmol).
ML4_1 (3.4 g, 11.7 mmol) was dissolved in 40 mL tetrahydrofuran and 66.6 mL (30 mmol) 1*H*-tetrazole in acetonitrile (0.45 M). After cooling to 0°C, 4.4 mL (14 mmol) di-tert-butyl diisopropylphosphoramidite was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. A solution of 5.3 g (30.7 mmol) *meta*-chloroperoxybenzoic acid in 40 mL dichloromethane was then added dropwise at 0°C, and the mixture was stirred for 10 min at room temperature. The product was mixed with 440 mL aqueous sodium hydrogen sulphite solution (10 wt.-%), diethyl ether and deionized water (1:5:5 v/v). The organic phase was separated and the aqueous phase three times extracted with 100 mL diethyl ether. The combined organic extracts were washed with an aqueous sodium hydrogen sulphite solution (10 wt.-%), a saturated aqueous ammonium chloride solution, an aqueous sodium hydroxide / sodium hydrogen carbonate solution (pH 10), and a saturated aqueous sodium chloride solution, successively. The organic phase was dried over magnesium sulphate, filtrated and concentrated under reduced pressure. The raw product was purified by column chromatography on silica gel (hexane / ethyl acetate = 3:1 to 1:1). The intermediate di-tert-butyl (6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl) phosphate (ML4_2) was obtained in a yield of 3.4 g (related to ML4_1 60%; 6.97 mmol) as a colourless oil.

In the final step 3 g (6.15 mmol) ML4_2 was dissolved in 20 mL dichloromethane, cooled to 0°C and 10 mL (129 mmol) trifluoroacetic acid added dropwise. The reaction mixture was stirred (30 min, 0°C) and allowed to warm up to room temperature. The raw product was dried under reduced pressure and recrystallized from dichloromethane. The product was obtained as a pale brown to white powder in a yield of 1.96 g (related to ML4_2 85%; 5.23 mmol).

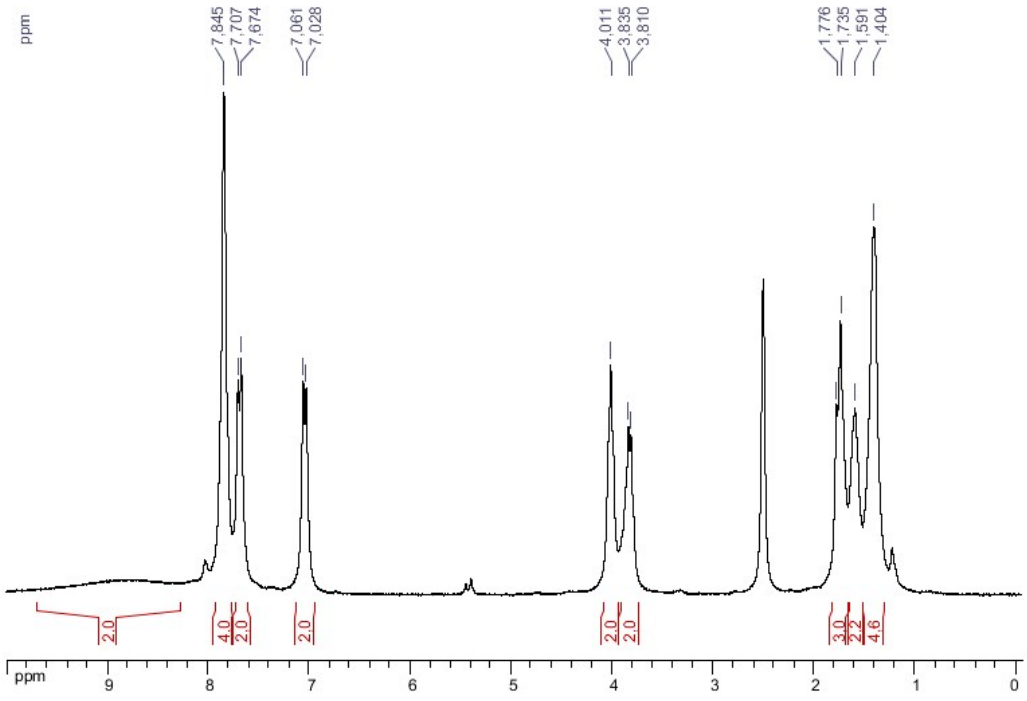


Figure S6. ^{1}H NMR (200 MHz, [D_6] DMSO, 25°C): δ = 8.28 - 9.72 (s, broad, 2 H; P-OH), 7.77 - 7.93 (m, ^{3}J(H-H) = 9 Hz, 2 H; CH), 7.69 (d, ^{3}J(H-H) = 7.7 Hz; 2 H; CH), 7.04 (d, ^{3}J(H-H) = 7.7 Hz, 2 H; CH), 4.01 (t, ^{3}J(H-H) = 5.6 Hz, 2 H; CH_2O), 3.82 (dt, ^{3}J(H-H) = 6.3, 6.3 Hz, 2 H; CH_2O), 1.66 - 1.82 (m, 2 H, CH_2), 1.59 (t, ^{3}J(H-H) = 6.3 Hz, 2 H; CH_2), 1.26 - 1.51 ppm (m, 4 H; CH_2).

Synthesis of oleic acid coated MNPs[S4]

Fe_3O_4 nanoparticles which were coated with oleic acid were synthesized using a procedure reported in reference [S5]. The particles were spherical in shape with a mean particle diameter of 10.7 (± 0.9) nm.

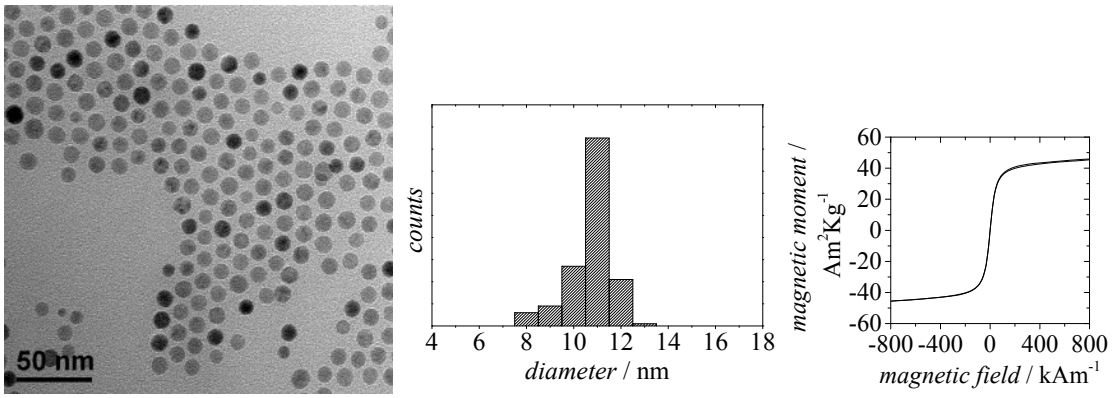


Figure S7. TEM image, particle size distribution and room temperature magnetization curve (M_s = 45 Am^2kg^{-1}) of 10.7 ± 0.9 nm Fe_3O_4 nanoparticles.

Characterization

MNP@ML nanoparticles and MNP@ML-5CB hybrids

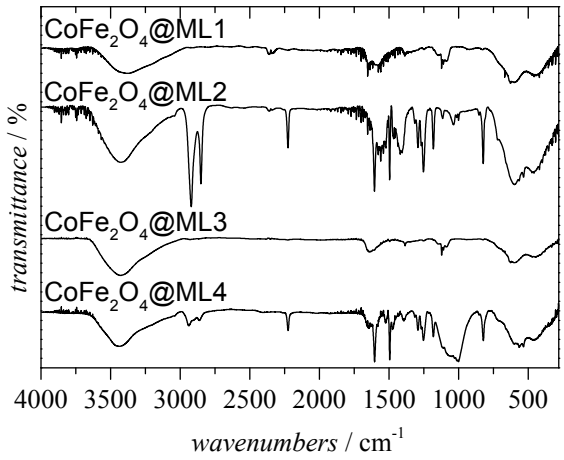


Figure S8. IR spectra of MNP@MLx.

Dynamic scanning calorimetry

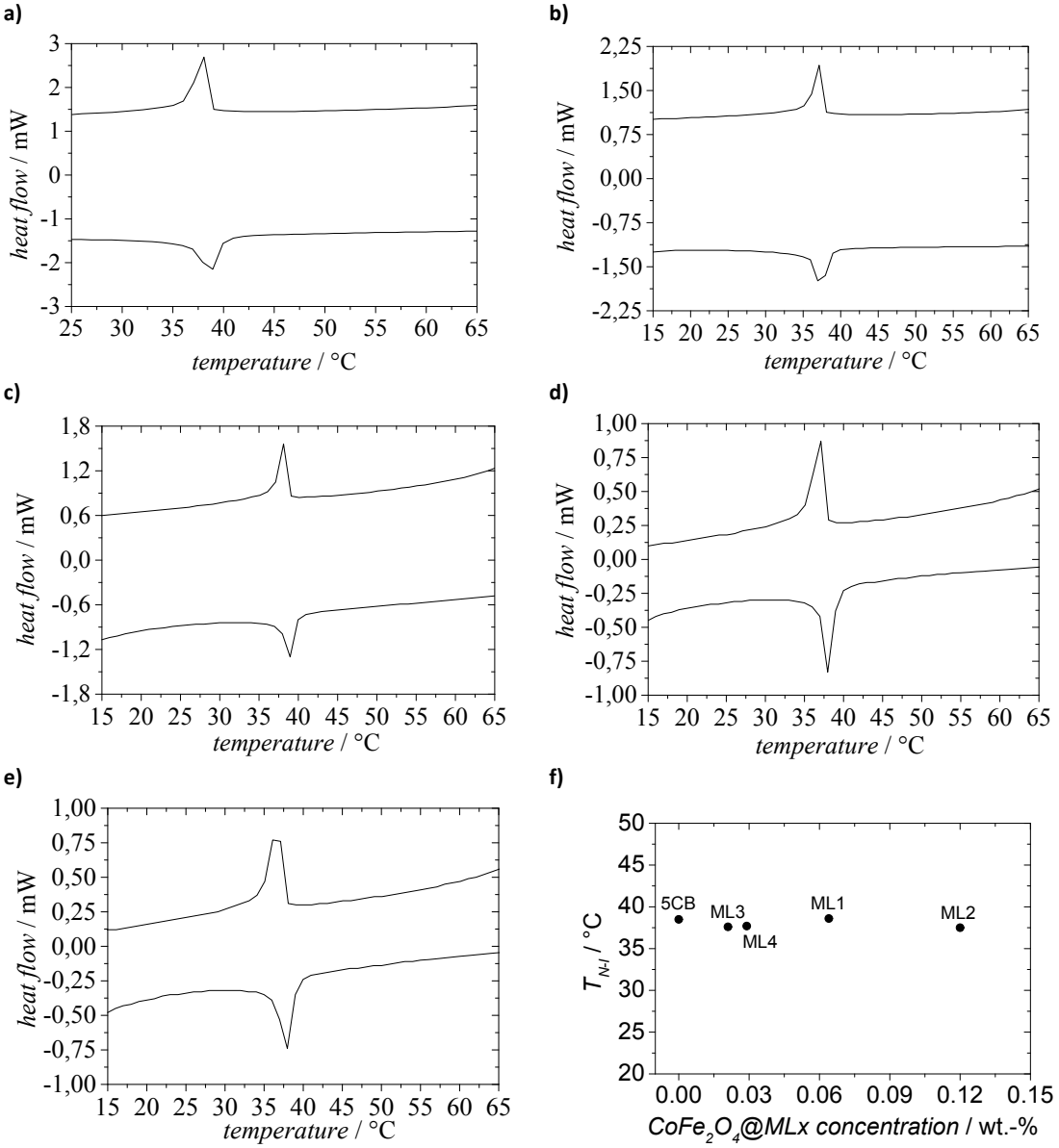


Figure S9. DSC thermogram of pure LC (i.e., 5CB) (a). DSC thermograms of LC (i.e., 5CB) doped with different types of MNPs ($CoFe_2O_4$@MLx with MLx: ML1 (b), ML2 (c), ML3 (d), and ML4 (e)). (f) Clearing temperatures T_{N-I} of $CoFe_2O_4$@MLx-5CB hybrids. No significant influence on the T_{N-I} was observed, neither by increasing the amount of MNPs in the hybrids nor by changing the type of the (pro)mesogenic ligand.

Magneto-optical properties

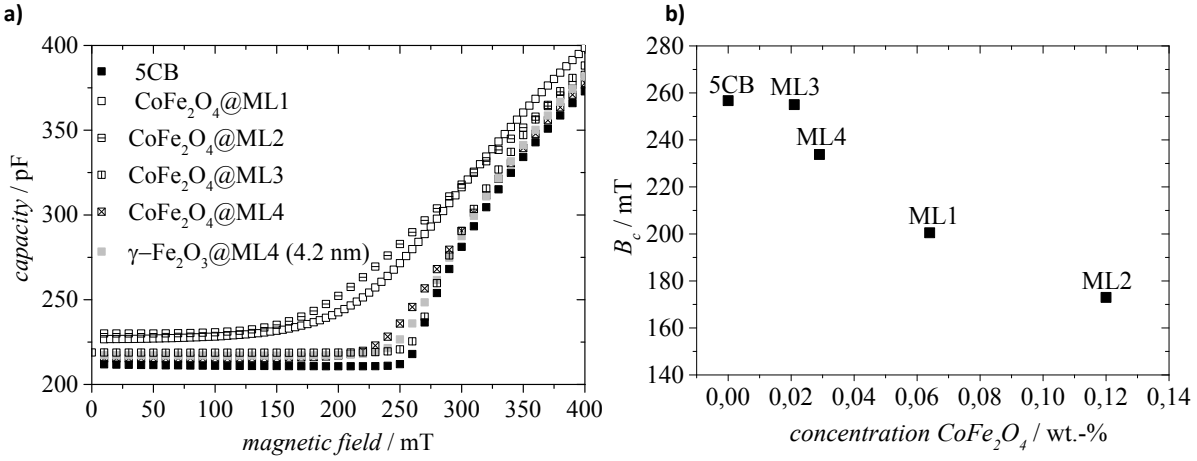


Figure S10. a) Magnetic Fréedericksz transition (B_c) curves for non-doped 5CB and 5CB doped with γ-Fe_2O_3@ML4 (4.2 nm) and $CoFe_2O_4$@MLx (2.5 nm), respectively. b) B_c for $CoFe_2O_4$@MLx-5CB hybrids containing an increasing amount of MNPs.

References

S1 W. Huang, C. D. Han, *Macromolecules* **2006**, *39*, 4735.

S2 K. Kanie, T. Sugimoto, *J. Am. Chem. Soc.* **2003**, *125*, 10518.

S3 K. Kanie, A. Muramatsu, *J. Am. Chem. Soc.* **2005**, *127*, 11578.

S4 J. Park, K. An, Y. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang, T. Hyeon, *Nat. Mater.* **2004**, *3*, 891.