Supporting information

Towards efficient dispersion of carbon nanotubes in thermotropic liquid crystals

Stefan Schymura[1], *Martin Kühnast*[1,2], *Vanessa Lutz*[3], *Stefan Jagiella*[3], *Ursula Dettlaff-Weglikowska*[4], *Siegmar Roth*[4], *Frank Giesselmann*[3], *Carsten Tschierske*[2], *Giusy Scalia*[5]* and *Jan Lagerwall*[1]*

[1]Martin Luther University Halle-Wittenberg, Institute of Chemistry – Physical Chemistry, Von-Danckelmann-Platz 4, 06120 Halle (Germany)

[2]Martin Luther University Halle-Wittenberg, Institute of Chemistry – Organic Chemistry, Kurt-Mothes Straße 2, 06120 Halle (Germany)

[3]University of Stuttgart, Institute for Physical Chemistry, Pfaffenwaldring 55, 70569 Stuttgart (Germany)

[4]Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart (Germany) *and* Korea University, School of Electrical Engineering, Anam-Dong,136-713, Seoul (Korea)

[5]ENEA C.R. Portici, 80055 Portici (NA) (Italy)

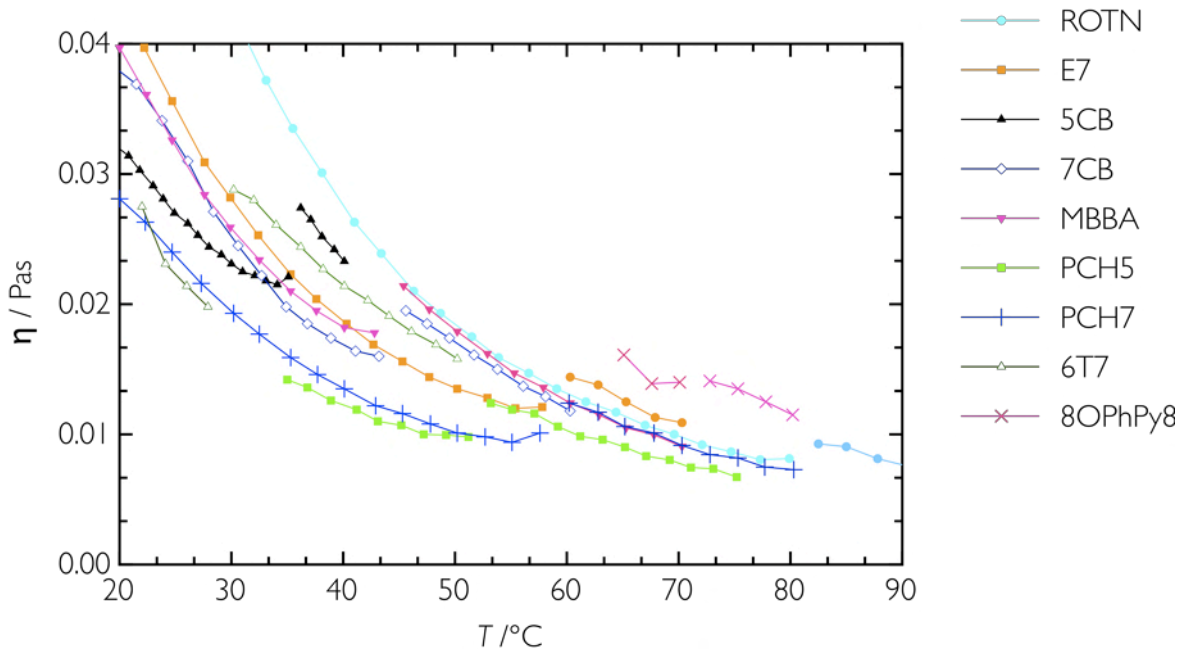


Figure SI1. Effective viscosity η (as measured by a standard rheometer) of all LCs as a function of temperature *T*.

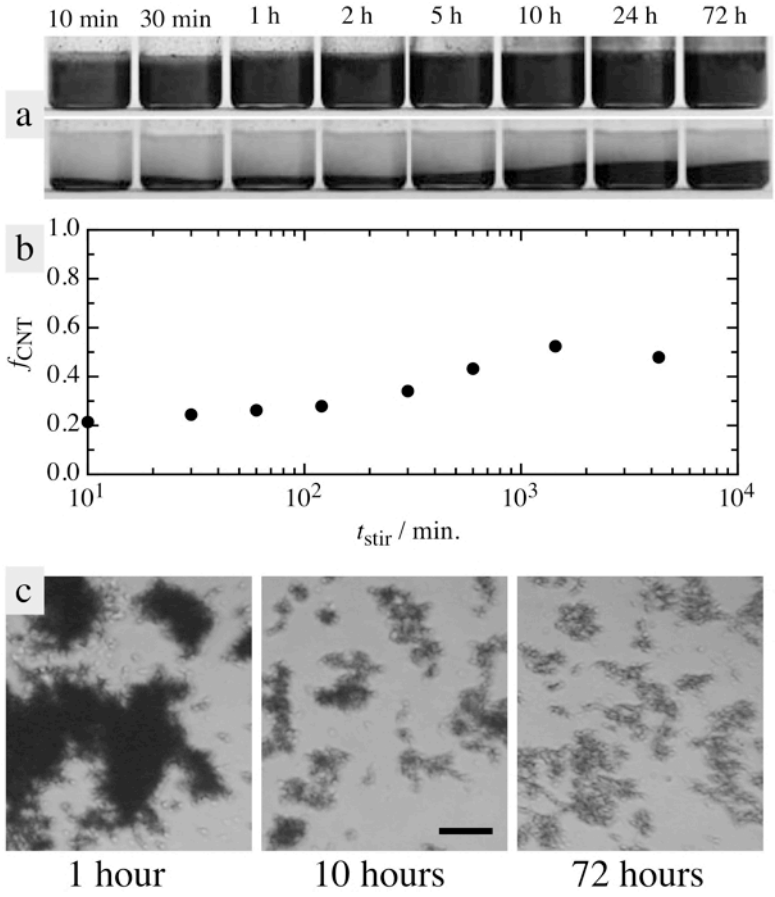


Figure SI2. (*a*) Samples of ROTN with 1 mg mL^{-1} SWCNTs stirred between 10 minutes and 72 hours, before (top) and after (bottom) centrifugation. (*b*) Fraction f_{CNT} with CNTs after centrifugation versus stirring time t_{stir}. (*c*) Microscopic photos (sample between microscope slide and cover glass) taken directly after terminating stirring. Scalebar = 40µm.

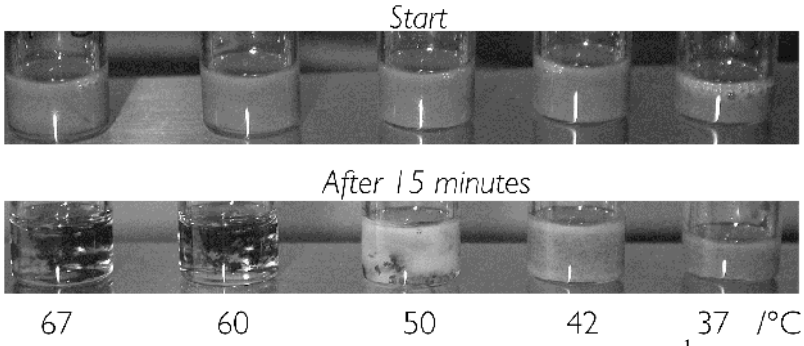


Figure SI3. Initially identical dispersions of CNTs in E7 (0.1 mg ml^{-1}) directly after stirring (top) and after fifteen minutes standing (bottom) at temperatures below, around and above the clearing point of the host (58°C).

Movie SI4: High-speed video of SWCNT dispersion by sonotrode treatment in different liquid hosts. One second in the movie corresponds to 12.5 ms in reality. The samples and their respective temperatures (all LC samples were heated to just above the clearing point) are, from left to right, ROTN (85°C), E7 (64°C), 5CB (37°C), 7CB (43°C), MBBA (51°C), PCH5 (56°C), PCH7 (59°C), 6T7 (30°C), 8OPhPy8 (74°C), NMP (20°C), SDBS + water (20°C) and pure water (20°C).

Details on high-speed video recording experiment:

The increasing opacity of each sample was measured using the image analysis features of the high-speed video camera software (Motion ProX Studio). The total brightness of a ~25 mm^2 area just below the sonotrode was measured in each frame of video since turning on the sonication power, normalizing the value to the initial video frame. For the experiment a water bath was kept on a heating plate and in it were immersed a sample vial with weighed-out dry CNTs (1 mg) as well as a second vial containing 1 mL of the host liquid. The sonotrode was positioned from the start for acting on a liquid filled into the first of these vials. Once the desired bath temperature had been attained a Pasteur pipette preheated with an air gun was used to transfer the liquid to the vial containing the CNTs and immediately afterwards the video recording and sonotrode treatment were started. Because the LCs have some solvation power on CNTs, the addition of LC to the vial immediately led to a swelling of the CNT powder, making the CNT component look substantially larger in these vials than in the vials with aqueous solvent or NMP, in which no or only negligible swelling took place. Moreover, the mass of swelled CNTs stayed at the vial bottom after addition of the LC, whereas the non-

swelled grains in case of the isotropic solvents were distributed throughout the sample as a result of the solvent addition, even before turning on the sonication. In the movie SI4 and the corresponding still images in Figure 2b these two effects gives the false impression that less CNTs would be present in the reference experiments with isotropic solvents but this is not the case. The initial cavitation often produced a brief artifact dip in transmission, particularly dramatic for the case of water as solvent in Fig. 2a.

As one might suspect that the required variation in temperature of the liquid host within the experiment would have an impact on the result we performed the experiment with NMP as host at room temperature as well as at 90°C, the latter being above the highest temperature used for the LCs. As shown below, the results were similar, confirming that the effect of the temperature variations in the experiment is small. This is in fact to be expected since all liquids are far below their boiling points and it is the distance to this temperature that is thermodynamically relevant.

Movie SI5: High-speed video of SWCNT dispersion by sonotrode treatment in NMP at room temperature (left) and at 90°C (right). Note that the sonotrode was positioned slightly lower in the 90° experiment, most likely leading to a somewhat different effective power to the sample.

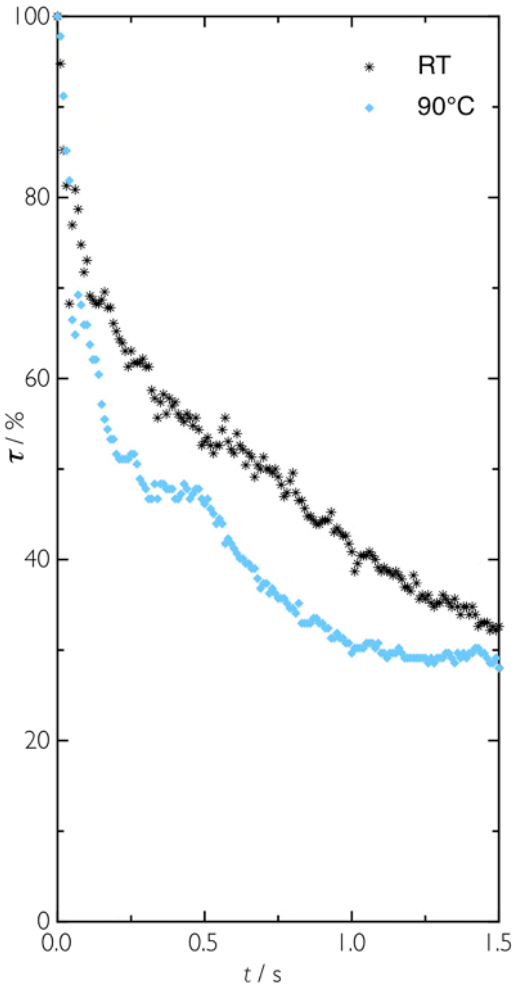


Figure SI6: The first 1.5 s of the sonotrode-mediated SWCNT dispersion process in NMP at room temperature and at 90°C, as expressed by the transparency τ of the sample as a function of sonication time *t*, the data being extracted from high-speed video images (movie SI5).

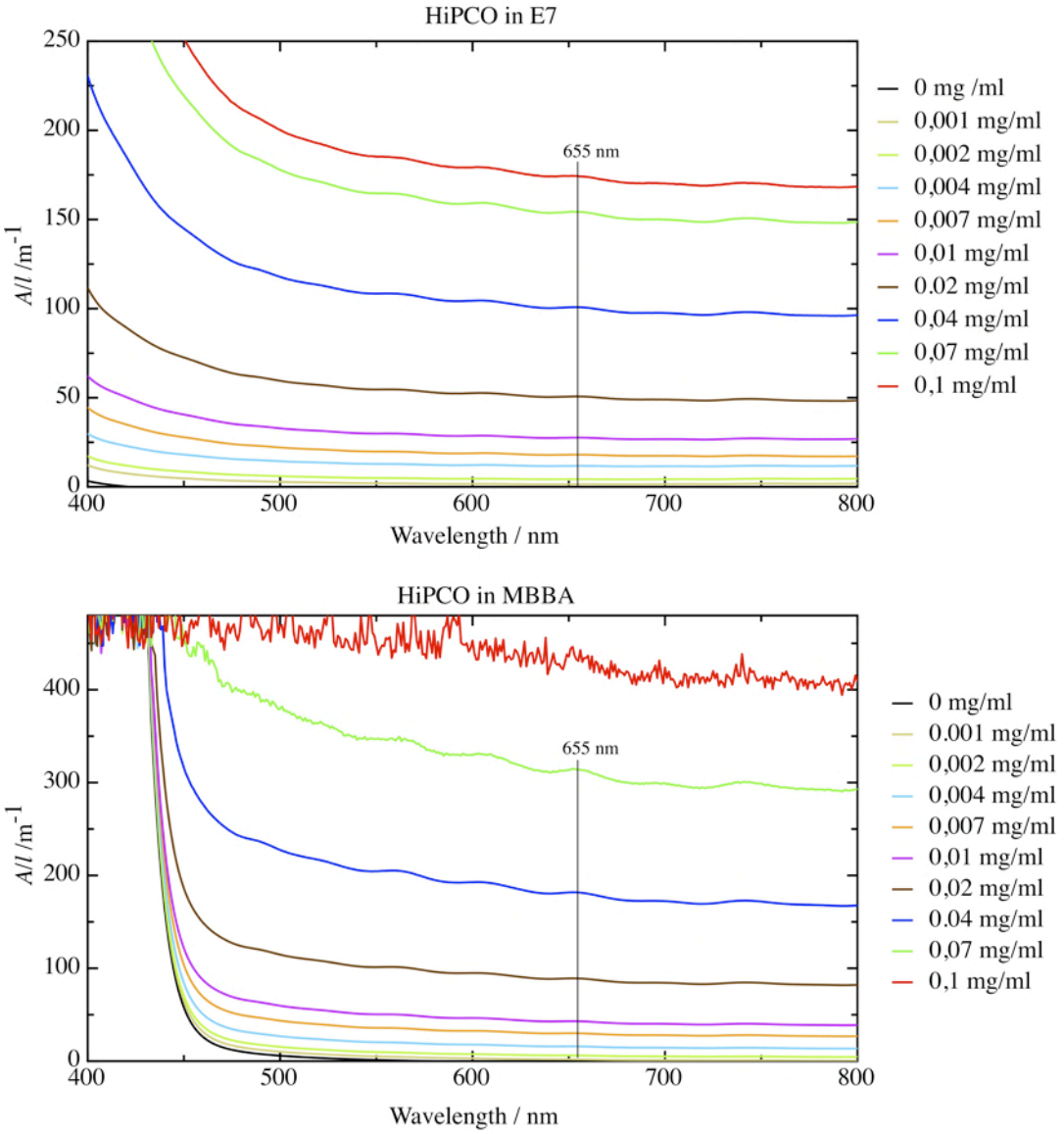


Figure SI7: Sample thickness-normalized absorption A/l as a function of wavelength for dispersions of HiPCO in E7 and MBBA, respectively, heated to the isotropic phase just prior to measuring.

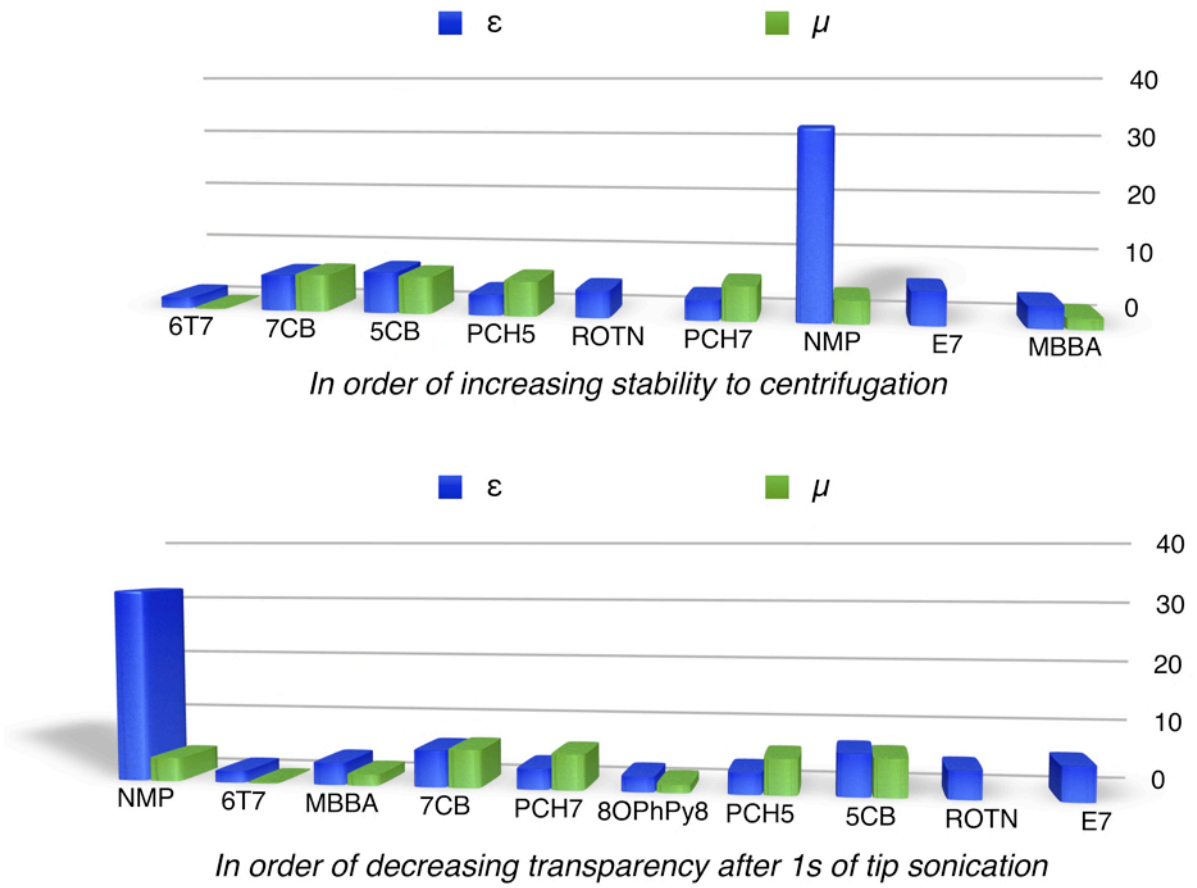


Figure SI8: Magnitude μ of the molecular dipole moment and dielectric permittivity ε_r in the isotropic phase for all organic solvents, listed in order of better performance in the experiment testing dispersion stability after centrifugation (Figure 3) and 1 s of sonotrode treatment (Figure 2).

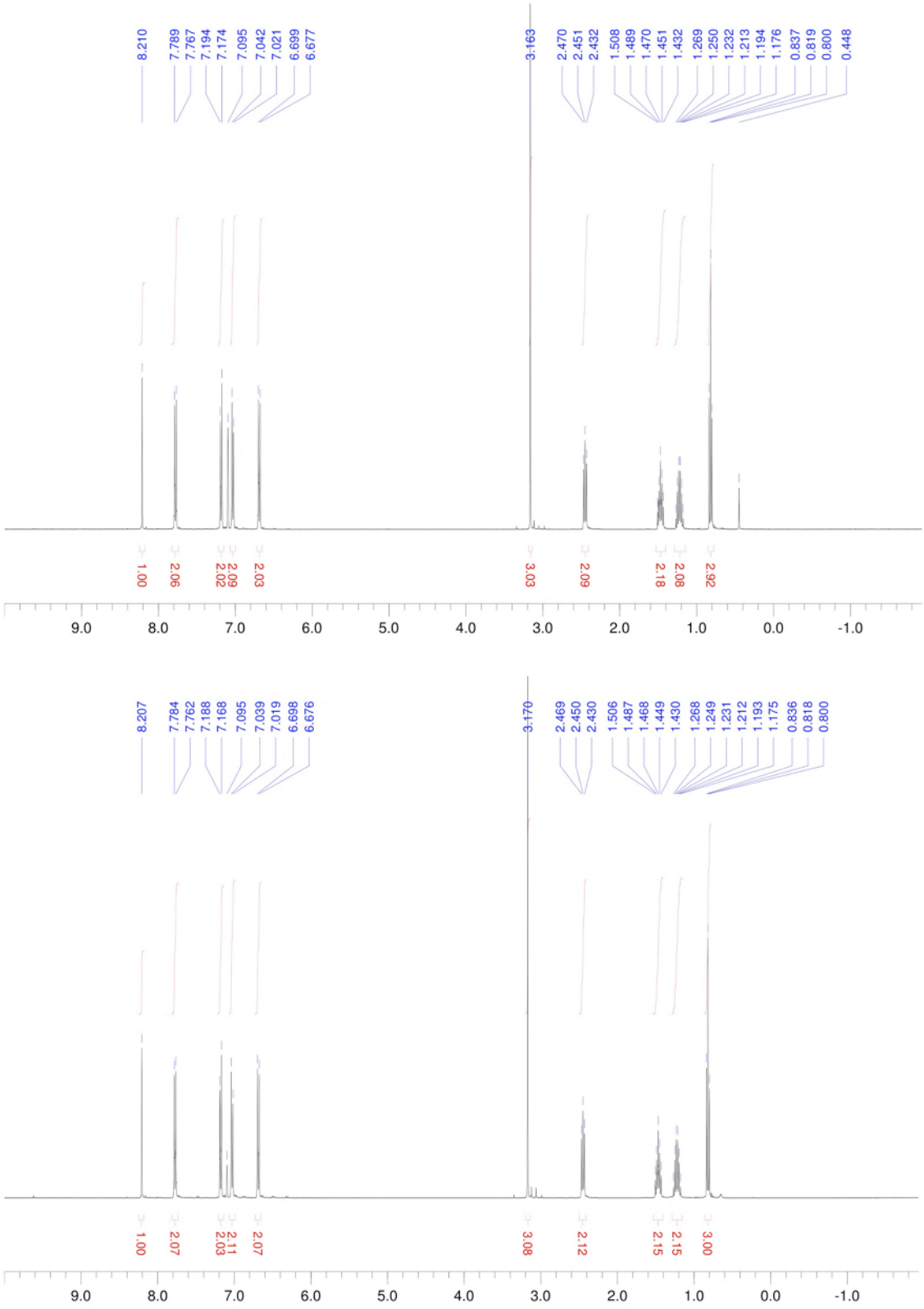


Figure SI9: ^{1}H-NMR (C_6H_6, 400 MHz) spectra of MBBA, the pristine sample (top) and the supernatant after used for CNT suspension (bottom): δ 8.21 (s, 1H, HC=N), 7.77 (d, 2H, *J* 8.8, Ar-H), 7.18 (d, 2H, *J* 8.2, Ar-H), 7.03 (d, 2H, *J* 8.2, Ar-H), 6.69 (d, 2H, *J* 8.8, Ar-H), 3.17 (s, 3H, OCH_3), 2.45 (t, 2H, Ar-CH_2), 1.47 (m, 2H, CH_2), 1.22 (m, 2H, CH_2), 0.82 (t, 3H, *J* 7.3, CH_3). Peak at 0.45 refers to H_2O. Solvent residual peak 7.16.

Sources of commercial substances

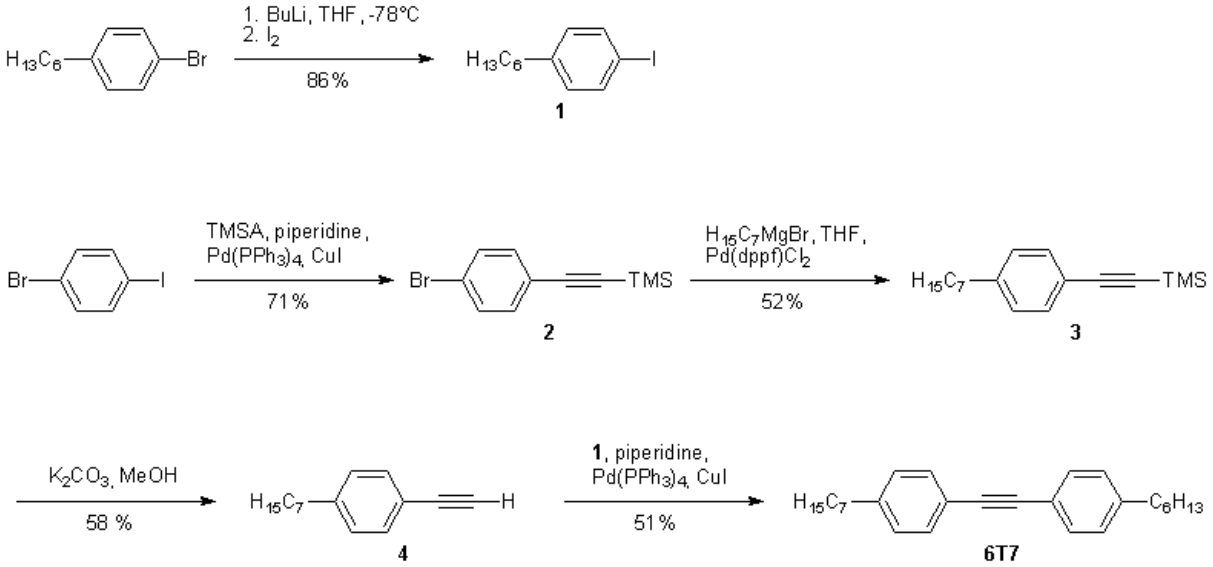
The sources of the commercial LCs were: 5CB, 7CB, MBBA and 8OPhPy8: Synthon (Germany); PCH-5 and E7: Merck (Germany); PCH-7 Merck/Nematel (Germany); ROTN: Hoffmann-LaRoche (Switzerland). NMP and SDBS were acquired from Roth (Germany).

Synthesis of 6T7

General notes

All reactions were carried out under argon atmosphere using standard schlenk technique, unless otherwise noted. 1-bromo-4-iodobenzene (ABCR), trimethylsilylacetylene (ABCR), were obtained commercially and used without further purification. $Pd(PPh_3)_4$ was synthesised according to literature. THF and diethylether were freshly destilled from sodium/benzophenone under argon before use. Piperidine was dried over molecular sieve 3Å. Column chromatographic purifications were performed with Merck silica gel (particle size 0.040-0.063 mm). Analytical thin layer chromatography was performed with Merck TLC aluminium sheets silica gel 60 F_{254}. NMR spectra were obtained on Varian Gemini 2000. Elemental composition was determined by Erba CHNO-Analyser 1120. Melting points are determined on Boëtius hot stage microscope and are not corrected. Differential calorimetric investigations were carried out with a Perkin Elmer DSC-7.

Synthetic details and spectroscopic data



Scheme SI9

1-n-hexyl-4-iodobenzene (**1**)[S1],[S2]

n-BuLi (7.8 mL, 1.6M in hexane, 12.5 mmol, 1.1 eq) was added dropwise to a solution of 1-bromo-4-iodobenzene (2.75 g, 11.4 mmol, 1.0 eq) in dry THF (30 mL) at -78°C. After 30 minutes, a solution of iodine (3.18 g, 12.5 mmol, 1,1 eq) in dry THF (20 mL) was added slowly. After 20 minutes the reaction was heated to RT. After concentration under reduced pressure, the remaining liquid was dissolved in diethyl ether (50 mL) and washed with $Na_2S_2O_3$ solution. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. Purification by column chromatography (petroleum ether) provides **1** as a colorless oil (2.83 g, 86 %).

^{1}H-NMR ($CHCl_3$, 400 MHz): δ 7.56 (d, 2H, *J* 8.2, Ar-H), 6.91 (d, 2H, *J* 8.2, Ar-H), 2.52 (t, 2H, *J* 7.6, Ar-CH_2), 1.55 (m, 2H, CH_2), 1.27 (t, 6H, CH_2) 0.86 (t, 3H, CH_3).

(2-(4-Bromophenyl)ethynyl)trimethylsilane (**2**)[S3]

A solution of 1-iodo-4-bromobenzene (30.00 g, 0.106 mol, 1.0 eq), $Pd(PPh_3)_4$ (0.61 g, 0.53 mmol, 0.5 mol-%) and CuI (0.20 g, 1.06 mmol, 1 mol-%) in piperidine (80 mL) is degassed by bubbling argon through the mixture for 20 minutes. Then trimethylsilylacetylene (16.2 mL, 0.117 mol, 1.1 eq) is added slowly to the water cooled reaktion flask, which leads to

immediate temperature rise and precipitation of solid. After stirring for 30 minutes solvent is removed under reduced pressure. Water (50 mL) is added to the residue, folllowed by extraction with diethyl ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent is evaporated. The crude product is purified by column chromatography (petroleum ether) and then recrystalised twice from methanol to afford **2** (19.08 g, 71 %) as colorless needles.

mp 60 °C (Lit. 61 °C[S4], 62 °C[S3]), ^{1}H-NMR ($CHCl_3$, 400 MHz): δ 7.41 (d, 2H, *J* 8.3, Ar-H), 7.29 (d, 2H, *J* 8.3, Ar-H), 0.23 (s, 9H, Si-CH_3).

(2-(4-Heptylphenyl)ethynyl)trimethylsilane (**3**)

Preparation of Grignard solution (~ 1.8 mol/kg): Magnesium turnings (3.26 g, 0.134 mol, 1.2 eq) were activated by stirring under argon atmosphere over night. Then a solution of n-heptylbromide (20.00 g, 0.111 mol, 1.0 eq) in diethyl ether (55 mL) is added dropwise at such a rate as to maintain gentle reflux. After the addition is complete, the mixture is refluxed for another 30 minutes and then cooled to RT. To remove residual magnesium the solution is filtrated through a fritted glas filter plate (Por 4).

Kumada cross-coupling:[S5] To a solution of **2** (13.66 g, 53.9 mmol, 1.0 eq) and Pd(dppf)Cl_2 (60 mg, 74 μmol, 0.1 mol-%) in THF (100 mL) the Grignard solution (60 g, 0.107 mol, 2.0 eq) is added via syringe. After refluxing for 4 hours water (100 mL) is carefully added, followed by concentration of the reaction mixture in vacuo. The residue is extracted with diethyl ether (2 x 50 mL). The combined organic layers are dried over $MgSO_4$ and concentrated in vacuo. Column chromatography (hexane) followed by vacuum distillation affords **3** (7.63 g, 52 %) as a colorless oil.

^{1}H-NMR ($CHCl_3$, 400 MHz): δ 7.35 (d, 2H, *J* 8.1, Ar-H), 7.07 (d, 2H, *J* 7.9, Ar-H), 2.56 (t, 2H, *J* 7.7, Ar-CH_2), 1.56 (m, 2H, CH_2), 1.30-1.20 (m, 8H, CH_2), 0.86 (t, 3H, *J* 6.7, CH_3), 0.22 (s, 9H, Si-CH_3).

1-Ethynyl-4-heptylbenzene (**4**)[S6]

A solution of **3** (5.50 g, 20.2 mmol, 1.0 eq) in THF (50 mL) is added to a suspension of K_2CO_3 (6.85 g, 49.5 mmol, 2.5 eq) in methanol (50 ml) and stirred over night. No care was taken to exclude air or moisture. After concentration of the mixture in vacuo, water (20 mL) is added followed by extraction with diethyl ether (2 x 30 mL). The combined organic layers were dried over $MgSO_4$ and solvent is removed by rotary evaporation. The resulting residue is purified by vacuum distillation to give **4** (2.35 g, 58 %) as a colorless oil.

bp 73 °C (1.5E-2 mbar) ^{1}H-NMR ($CHCl_3$, 400 MHz): δ 7.38 (d, 2H, *J* 8.1, Ar-H), 7.11 (d, 2H, *J* 8.1, Ar-H), 3.01 (s, 1H, C≡C-H), 2.58 (t, 2H, *J* 7.7, Ar-CH_2), 1.58 (m, 2H, CH_2), 1.28 (m, 8H, CH_2), 0.86 (t, 3H, *J* 6.8, CH_3).

1-(2-(4-Heptylphenyl)ethynyl)-4-hexylbenzene (**6T7**)

A solution of CuI (70 mg, 0.4 mmol, 4 mol-%), $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol, 2 mol-%) and **1** (2.83 g, 9.8 mmol, 1.0 eq) in piperidine (10 mL) is degassed by bubbling argon through the mixture for 20 minutes. Then **4** (1.96 g, 9.8 mmol, 1.0 eq) dissolved in piperidine (10 mL) is added, resulting in an immediate precipitation of solid accompanied by heating. After stirring for 30 minutes the mixture is concentrated in vacuo. A solution of HCl (10 %, 30 mL) is then added to the residue followed by extraction with petroleum ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, the solvent removed an the residue subjected to column chromatography (petroleum ether) leading to a colorless, isotropic liquid. For further purification the crude product is dissolved in hot ethanol and slowly droped into an ice cooled beaker, wich leads to precipitation of a white solid. After centrifugation at low temperature the supernatant is dicarded, the solid suspended in cold ethanol and again centrifugated. Drying in vacuo yields the product (1.82 g, 51 %) as liquid crystaline liquid.

phase sequence: Cr 20.5 (SmX 18.8) N 29.4 Iso (Lit. Cr 19.3 Sm 20 N 30 Iso[S7]) ^{1}H-NMR ($CHCl_3$, 400 MHz): δ 7.41 (d, 4H, *J* 8.1, Ar-H), 7.13 (d, 4H, *J* 8.1, Ar-H), 2.59 (t, 4H, *J* 7.7,

Ar-CH_2), 1.59 (m, 4H, CH_2), 1.29 (m, 14H, CH_2) 0.87 (t, 6H, *J* 6.8, CH_3). ^{13}C-NMR ($CHCl_3$, 100 MHz): δ 143.2, 131.4, 128.4, 120.6, 88.9, 35.9, 31.8, 31.7, 31.3, 31.2, 29.3, 29.2, 29.0, 22.7, 22.6, 14.1.

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