Supporting Information

Tailor-designed polyphilic promotors for stabilizing dispersions of carbon nanotubes in liquid crystals
Martin Kühnast,a,b Carsten Tschierske,*,a Jan P. F. Lagerwall * ,b

a Organic Chemistry, Institute of Chemistry, Martin Luther University Halle-Wittenberg, Kurt Mothes Str. 2, D-06120 Halle (Saale), Germany; Fax: +49 345 552 7346; Tel: +49 345 552 5664; E-mail: carsten.tschierske@chemie.uni-halle.de

b Physical Chemistry, Institute of Chemistry, Martin Luther University Halle-Wittenberg, von-Danckelmann Platz 4, D-06120 Halle (Saale), Germany; E-mail: jan.lagerwall@lcsoftmatter.com

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1. Synthesis and analytical data

Scheme S 1: Synthesis of compounds 1a,b and 2a-c, respectively. Reagents and conditions.
i: TsCl, aq. NaOH, THF, 5 °C ii: K2CO3, 4-hydroxy-4'-cyanobiphenyl, TBAF, butanone, reflux; iii: 1. SOCl2, reflux, 2. piperidine, R-COOH, DMAP, CH2Cl2, reflux.
General remarks:
4-Hydroxy-4'-cyanobiphenyl, 11-bromo-1-undecanol, tetraethylene glycol, 4-toluenesulfonyl chloride, N,N-dimethylaminopyridine (DMAP), p-terphenyl-4-carboxylic acid, pyrene-1-carboxylic acid, anthracene-9-carboxylic acid were obtained from Sigma Aldrich and used as obtained.

4'-(11-Hydroxyundecyloxy)biphenyl-4-carbonitrile 3[S1]
A mixture of 4-hydroxy-4'-cyanobiphenyl (2.00 g, 10.2 mmol), K₂CO₃ (2.83 g, 20.5 mmol), 11-bromo-1-undecanol (2.57 g, 10.2 mmol) and tetrabutylammonium iodide (10 mg) in 2-butanone (150 mL) was refluxed for 48 h under an argon atmosphere. After evaporation of the solvent under reduced pressure the residue was dissolved in chloroform (100 mL) and washed with water (100 mL). The organic layer was dried over MgSO₄ and evaporated in vacuo. The obtained product was crystallized twice from methanol yielding 3 (2.9 g, 7.9 mmol, 77 %) as colorless leaflets (phase sequence see below).

\[ \text{H-NMR (400 MHz, CDCl}_3\text{)} \delta = 7.66 (d, 2H, J = 8.5 Hz, Ar-H), 7.61 (d, 2H, J = 8.5 Hz, Ar-H), 7.50 (d, 2H, J = 8.8 Hz, Ar-H), 6.97 (d, 2H, J = 8.8 Hz, Ar-H), 3.98 (t, 2H, J = 6.5 Hz, Ar-OC\text{H}_2), 3.62 (t, 2H, J = 6.6 Hz, CH\text{H}_2-\text{OH}), 1.79 (m, 2H, CH\text{H}_2), 1.55 (m, 2H, CH\text{H}_2), 1.45 (m, 2H, CH\text{H}_2), 1.39-1.21 (m, 17H, CH\text{H}_2).

2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate 6[S2]
To a chilled mixture of tetraethylene glycol (175.6 g, 0.90 mol), NaOH (5.47 g, 0.14 mol), THF (25 mL) and water (30 mL) a solution of 4-toluenesulfonyl chloride (16.70 g, 87.5 mmol) in THF (100 mL) was added over a period of 1 h. After addition was completed the mixture was stirred at 5°C for 2 h, poured into ice water (500 mL) and extracted with dichloromethane (3 x 150 mL). The combined organic layers were washed with water (5 x 200 mL), and dried over MgSO₄. Evaporation of the solvent yields 6 (27.4 g, 78.5 mmol, 90 %) as a colorless oil which was used without further purification.

\[ \text{H-NMR (400 MHz, CDCl}_3\text{)} \delta = 7.77 (d, 2H, J = 8.3 Hz, Ar-H), 7.31 (d, 2H, J = 8.0 Hz, Ar-H), 4.14 (m, 2H, Ar-OC\text{H}_2), 3.71-3.55 (m, 16H, OC\text{H}_2), 2.42 (s, 3H, Ar-C\text{H}_3), 2.23 (s, br, 2H, CH\text{H}_3-\text{OH}).

4'-(2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethoxy)biphenyl-4-carbonitrile 5[S1]
A mixture of 4-hydroxy-4'-cyanobiphenyl (4.00 g, 20.5 mmol), K₂CO₃ (5.66 g, 41.0 mmol), tosylate 6 (7.14 g, 20.5 mmol) and tetrabutylammonium iodide (20 mg) in 2-butanolone (200 mL) was refluxed for 24 h under an argon atmosphere. After evaporation of the solvent under reduced pressure, the residue was dissolved in diethyl ether (100 mL) and carefully washed with water (3 x 100 mL). The organic layer was dried over MgSO₄ and evaporated in vacuo. Purification of the obtained product by column chromatography (eluent: ethyl acetate) yields 5 (4.7 g, 12.7 mmol, 62 %) as a slightly yellowish oil.

\[ \text{H-NMR (400 MHz, CDCl}_3\text{)} \delta = 7.67 (d, 2H, J = 8.5 Hz, Ar-H), 7.61 (d, 2H, J = 8.5 Hz, Ar-H), 7.50 (d, 2H, J = 8.8 Hz, Ar-H), 7.00 (d, 2H, J = 8.8 Hz, Ar-H), 4.17 (m, 2H, Ar-OC\text{H}_2-\text{CH}_2), 3.87 (m, 2H, Ar-OC\text{H}_2-\text{CH}_2), 3.74-3.66 (m, 10H, OC\text{H}_2), 3.59 (m, 2H, CH\text{H}_2-\text{OH}).

General procedure for esterification:
All reactions were carried out in an argon atmosphere. A mixture of the corresponding carboxylic acid (1.0 eq.) and thionyl chloride (5 mL per mmol carboxylic acid) was refluxed until all solid was dissolved followed by additional
heating for 24 h. After evaporation of excess thionyl chloride at reduced pressure the obtained acid chloride was carefully dried in vacuo and finally flushed with argon. The acid chloride was then treated with a solution of the corresponding alcohol (1.0 eq.), dry pyridine (10 eq.) and DMAP (5 mol-%) in dry dichloromethane (5 mL per mmol alcohol). After refluxing for 24 h the mixture was washed with water, 10 % HCl, conc. NaHCO₃-solution and dried over MgSO₄ (1a was worked up in a different way). The product obtained by evaporation of the solvent was purified as described below.

11-(4′Cyanobiphenyl-4-yloxy)undecyl p-terphenyl-4-carboxylate 1a
Prepared from p-terphenyl-4-carboxylic acid (0.20 g, 0.73 mmol), thionylchloride (3.6 mL), 3 (0.27 g, 0.73 mmol), pyridine (0.6 mL, 0.58 g, 7.29 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (3.6 mL). The precipitated raw product was filtrated and washed with methanol and pentane. Crystallization (first from chloroform, then from ethyl acetate) yields 1a (0.28 g, 0.45 mmol, 62%) as colorless needles (phase sequence, see Table S1, for copies of NMR spectra, see Figures S1 and S2).

\[ \begin{align*} \text{1H-NMR (400 MHz, CDCl}_3 & \text{)} \delta = 8.11 (d, 2H, J = 8.3 Hz, Ar-H), 7.72-7.58 (m, 12H, Ar-H), 7.52-7.41 (m, 4H, Ar-H), 7.36 (m, 1H, Ar-H), 6.96 (d, 2H, J = 8.8 Hz, Ar-H), 4.33 (t, 2H, J = 6.6 Hz, COO-CH}_2, 3.98 (t, 2H, J = 6.6 Hz, Ar-OC-CH}_2, 1.38-1.73 (m, 4H, CH}_2), 1.53-1.28 (m, 14H, CH}_2); \text{13C-NMR (200 MHz, CDCl}_3) \delta = 166.5, 159.8, 145.2, 145.0, 141.0, 140.4, 138.8, 132.5, 131.2, 130.1, 129.3, 128.9, 128.3, 127.6, 127.0, 126.8, 119.1, 115.1, 110.0, 68.1, 65.1, 29.5, 29.3, 29.2, 28.7, 26.0. \end{align*} \]

11-(4′Cyanobiphenyl-4-yloxy)undecyl pyrene-1-carboxylate 1b
Prepared from pyrene-1-carboxylic acid (0.20 g, 0.81 mmol), thionylchloride (4.1 mL), 3 (0.30 g, 0.81 mmol), pyridine (0.7 mL, 0.64 g, 8.12 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (4.1 mL). Column chromatography (eluent: chloroform) followed by crystallization (acetonitrile) yields 1b (0.19 g, 0.32 mmol, 76 %) as colorless needles (phase sequence see Table S1; for copies of NMR spectra, see Figures S3 and S4).

\[ \begin{align*} \text{1H-NMR (400 MHz, CDCl}_3 & \text{)} \delta = 9.25 (d, 1H, J = 9.4 Hz, Ar-H), 8.61 (d, 1H, J = 8.1 Hz, Ar-H), 8.27-8.20 (m, 3H, Ar-H), 8.18-8.14 (m, 2H, Ar-H), 8.09-8.02 (m, 2H, Ar-H), 7.65 (d, 2H, J = 8.5 Hz, Ar-H), 7.60 (d, 2H, J = 8.6 Hz, Ar-H), 7.48 (d, 2H, J = 8.8 Hz, Ar-H), 6.95 (d, 2H, J = 8.8 Hz, Ar-H), 4.49 (t, 2H, J = 6.7 Hz, COO-CH}_2, 3.97 (t, 2H, J = 6.5 Hz, Ar-OCH}_2, 1.89 (m, 2H, CH}_2), 1.78 (m, 2H, CH}_2), 1.61-1.23 (m, 14H, CH}_2); \text{13C-NMR (200 MHz, CDCl}_3) \delta = 168.1, 159.8, 145.2, 134.2, 132.5, 131.2, 131.0, 131.0, 129.5, 129.3, 128.3, 127.1, 127.0, 126.3, 126.2, 126.1, 124.9, 124.8, 124.2, 124.1, 123.9, 119.1, 115.1, 110.0, 68.1, 65.1, 29.5, 29.4, 29.3, 29.2, 28.8, 26.2. \end{align*} \]

2-(2-(2-(4′-Cyanobiphenyl-4-yloxy)ethoxy)ethoxy)ethoxy)ethoxyethoxyethyl p-terphenyl-4-carboxylate 2a
Prepared from p-terphenyl-4-carboxylic acid (0.20 g, 0.73 mmol), thionylchloride (3.6 mL), 5 (0.27 g, 0.73 mmol), pyridine (0.6 mL, 0.58 g, 7.29 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (3.6 mL). The product was crystallized twice from methanol, yielding 2a (0.16 g, 0.26 mmol, 35 %) as colorless needles (melting point see Table S1; for copies of NMR spectra, see Figures S5 and S6).

\[ \begin{align*} \text{1H-NMR (400 MHz, CDCl}_3 & \text{)} \delta = 8.11 (d, 2H, J = 8.3 Hz, Ar-H), 7.69-7.55 (m, 12H, Ar-H), 7.48-7.43 (m, 4H, Ar-H), 7.36 (m, 1H, Ar-H), 6.96 (d, 2H, J = 8.5 Hz, Ar-H), 4.49 (m, 2H, COO-CH}_2), 4.13 (dd, 2H, J = 4.3 Hz, J = 5.0 Hz, Ar-OCH}_2), 3.85 (m, 4H, OCH}_2CH}_2), 3.70 (m, 8H, OCH}_2CH}_2O); \text{13C-NMR (200 MHz, CDCl}_3) \delta = 166.4, 159.4, \end{align*} \]
2-(2-(2-(2-(4'-Cyanobiphenyl-4-yloxy)ethoxy)ethoxy)ethoxy)ethyl pyrene-1-carboxylate 2b
Prepared from pyrene-1-carboxylic acid (0.20 g, 0.81 mmol), thionylchloride (4.0 mL), alcohol 5 (0.30 g, 0.81 mmol), pyridine (0.7 mL, 0.64 g, 8.12 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (4.0 mL). The product was first subjected to column chromatography (eluent: chloroform) followed by an additional column chromatography (eluent: diethylether). 2b (0.29 g, 0.48 mmol, 59 %) was obtained as a greenish highly viscous fluid, which crystallizes after a few days (melting point see Table S1; for copies of NMR spectra, see Figure S7 and S8).

$^1$H-NMR (400 MHz, CDCl$_3$) δ = 9.23 (d, 1H, J = 9.4 Hz, Ar-H), 8.63 (d, 1H, J = 8.1 Hz, Ar-H), 8.25-8.18 (m, 3H, Ar-H), 8.15-8.12 (m, 2H, Ar-H), 7.60 (d, 2H, J = 8.3 Hz, Ar-H), 7.51 (d, 2H, J = 8.3 Hz, Ar-H), 7.38 (d, 2H, J = 8.7 Hz, Ar-H), 6.88 (d, 2H, J = 8.7 Hz, Ar-H), 6.68 (d, 2H, J = 8.3 Hz, Ar-H), 4.64 (m, 2H, COO-CH$_2$), 4.06 (m, 2H, Ar-OCH$_2$), 3.95 (m, 2H, OCH$_2$), 3.82-3.69 (m, 10H, OCH$_2$CH$_2$O); $^{13}$C-NMR (200 MHz, CDCl$_3$) δ = 167.9, 159.3, 145.1, 134.3, 132.4, 131.5, 131.2, 131.0, 129.6, 129.4, 128.5, 128.2, 127.1, 127.0, 126.3, 126.2, 124.9, 124.8, 124.2, 124.1, 123.5, 119.1, 115.1, 110.0, 70.8, 69.6, 69.3, 67.5, 64.3.

2-(2-(2-(2-(4'-Cyanobiphenyl-4-yloxy)ethoxy)ethoxy)ethoxy)ethyl anthracene-9-carboxylate 2c
Prepared from anthracene-9-carboxylic acid (0.20 g, 0.90 mmol), thionylchloride (4.5 mL), alcohol 5 (0.33 g, 0.90 mmol), pyridine (0.73 mL, 0.71 g, 9.00 mmol), DMAP (6 mg, 0.05 mmol) in dichloromethane (4.5 mL). Purification of the product by column chromatography (eluent: diethylether) yields 2c (0.34 g, 0.59 mmol, 65 %) as a yellowish highly viscous fluid which crystallizes after a few days (melting point see Table S1; for copies of NMR spectra, see Figures S9 and S10).

$^1$H-NMR (400 MHz, CDCl$_3$) δ = 8.49 (s, 1H, Ar-H), 8.11 (d, 2H, J = 8.6 Hz, Ar-H), 7.98 (d, 2H, J = 8.2 Hz, Ar-H), 7.64 (d, 2H, J = 8.3 Hz, Ar-H), 7.57 (d, 2H, J = 8.3 Hz, Ar-H), 7.54-7.43 (m, 6H, Ar-H), 6.92 (d, 2H, J = 8.6 Hz, Ar-H), 4.75 (m, 2H, COO-CH$_2$), 4.07 (m, 2H, Ar-OCH$_2$), 3.92 (m, 2H, OCH$_2$), 3.79 (m, 2H, OCH$_2$), 3.70 (m, 8H, OCH$_2$); $^{13}$C-NMR (200 MHz, CDCl$_3$) δ = 174.2, 169.4, 159.4, 145.1, 142.5, 141.8, 132.5, 131.6, 131.5, 130.9, 129.4, 128.5, 128.3, 128.2, 128.1, 127.7, 127.1, 127.0, 126.9, 126.5, 126.1, 125.6, 125.4, 125.2, 119.0, 115.2, 115.1, 110.1, 110.0, 70.8, 70.7, 70.6, 70.5, 69.6, 69.1, 68.6, 67.5, 66.1, 64.6, 64.5, 55.0.
Figure S1. $^1$H-NMR spectrum of 1a.
Figure S2. $^{13}$C-NMR spectrum of 1a.
Figure S3. $^1$H-NMR spectrum of 1b.
Figure S4. $^{13}$C-NMR spectrum of 1b.
Figure S5. $^1$H-NMR spectrum of 2a.
Figure S6. $^{13}$C-NMR spectrum of 2a.
Figure S7. $^1$H-NMR spectrum of 2b.
Figure S8. $^{13}$C-NMR spectrum of 2b.
Figure S9. $^1$H-NMR spectrum of 2c.
Figure S10. $^{13}$C-NMR spectrum of 2c.
2. Transition temperatures

*Table S1:* Transition temperatures determined by DSC (10 K/min, peak temperatures in the first heating/cooling scan) and POM (marked with *)

<table>
<thead>
<tr>
<th>compound</th>
<th>transition temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Cr ←165 Sm →161 N ←182 Iso</td>
</tr>
<tr>
<td></td>
<td>134 Sm ←161 N ←181 Iso</td>
</tr>
<tr>
<td>1b</td>
<td>Cr ←124 N →110* Iso</td>
</tr>
<tr>
<td></td>
<td>113 N ←110* Iso</td>
</tr>
<tr>
<td>2a</td>
<td>mp: 133*</td>
</tr>
<tr>
<td>2b</td>
<td>mp: 80*</td>
</tr>
<tr>
<td>2c</td>
<td>mp: 125*</td>
</tr>
<tr>
<td>3</td>
<td>Cr ←76* Sm →85* N ←94 Iso</td>
</tr>
</tbody>
</table>

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3. Differential scanning calorimetry (DSC) curves

**Figure S11.** Second heating scan of 1a at 10 K/min.

**Figure S12.** First cooling scan of 1a at 10 K/min.
**Figure S13.** Second heating scan of 1b at 10 K/min.

**Figure S14.** First cooling scan of 1b at 10 K/min.
4. Textures of liquid crystalline compounds (POM)

*Figure S15.* Micrograph of 1a at 159 °C (a) and 187 °C (b) (crossed polarizers, on cooling).

*Figure S16.* Micrograph of 1b at 101 °C (crossed polarizers, on cooling).

*Figure S17.* Micrograph of 3 at 85 °C (a) and 90 °C (b) (without cover slip, crossed polarizers, on cooling).

5. References