

## Electronic Supplementary Information

### At the boundary to banana-shaped liquid crystals: Polar properties of phases formed by new asymmetric achiral four-ring bent-core mesogens

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#### Content:

1. Experimental procedure to prepare compound **4-O**
2. Analytical data of compounds **4-O**, **14-O**, and **12-O-Cl**

1. Experimental procedure: 1-(4-n-butyloxybenzoyl)-4-[4-(4-n-butyloxybenzoyloxy)phenyl]-piperazine (**4-O**)

A mixture of 1.94 g (0.01 mol) 4-n-butyloxybenzoic acid, 0.89 g (0.005 mol) 4-hydroxyphenyl piperazine, 2.3 g (0.011 mol) dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine in 60 ml dichloromethane was stirred at room temperature for about 24 hours. A precipitation of dicyclohexylurea was separated, the solvent evaporated and the crude material purified by recrystallization from ethanol - DMF (10:1) several times. Yield: 1.8 g, 68.1 %, white crystals, mp.114 °C.

2. Analytical data:

Compound **4-O**: <sup>1</sup>NMR (200 MHz, CDCl<sub>3</sub>): δ 0.97 (m, 6H, 2xCH<sub>3</sub>), 1.44-1.82 (m, 8H, 4xCH<sub>2</sub>), 3.16 (broad, 4H, piperazine), 3.77 (broad, 4H, piperazine), 3.98 (t, <sup>3</sup>J= 6.6 Hz, 2H, OCH<sub>2</sub>), 4.03 (t, <sup>3</sup>J= 6.4 Hz, 2H, OCH<sub>2</sub>), 6.88-6.96 (m, 6H, Ar-H), 7.08 (d, <sup>3</sup>J=8.9 Hz, 2H, Ar-H), 7.39 (d, <sup>3</sup>J= 8.7 Hz, 2H, Ar-H), 8.09 (d, <sup>3</sup>J= 8.9 Hz, 2H, Ar-H).

Elemental analysis: calculated for Mm 530.28, (C<sub>32</sub>H<sub>38</sub>N<sub>2</sub>O<sub>5</sub>): C 72.43, H 7.22, N 5.28; found C 72.41, H 7.27, N 5.15

Compound **14-O**: <sup>1</sup>NMR (400 MHz, CDCl<sub>3</sub>): δ 0.86 (t, <sup>3</sup>J= 6.9, 6H, 2xCH<sub>3</sub>), 1.24-1.53 (m, 44H, 21xCH<sub>2</sub>), 1.75-1.81 (m, 4H, 2xCH<sub>2</sub>), 3.15 (s, broad, 4H, piperazine), 3.77 (s, broad, 4H, piperazine), 3.96 (t, <sup>3</sup>J=6.5 Hz, 2H, CH<sub>2</sub>O), 4.02 (t, <sup>3</sup>J=6.5 Hz, 2H, CH<sub>2</sub>O), 6.88-6.95 (m, 6H, Ar-H), 7.10 (d, <sup>3</sup>J=8.9 Hz, 2H, Ar-H), 7.39 (d, <sup>3</sup>J=8.7 Hz, 2H, Ar-H), 8.09 (d, <sup>3</sup>J=8.9 Hz, 2H, Ar-H)

Elemental analysis: calculated for Mm 823.98, (C<sub>52</sub>H<sub>78</sub>N<sub>2</sub>O<sub>5</sub>): C 76.99, H 9.69, N 3.45; found C 76.96, H 9.77, N 3.29

Compound **12-O-Cl**: <sup>1</sup>NMR (400 MHz, CDCl<sub>3</sub>): δ 0.86 (t, <sup>3</sup>J= 6.6, 6H, 2xCH<sub>3</sub>), 1.25-1.54 (m, 36H, 18xCH<sub>2</sub>), 1.80-1.88 (m, 4H, 2xCH<sub>2</sub>), 3.16 (s, broad, 4H, piperazine), 3.76 (s, broad, 4H, piperazine), 4.04 (t, <sup>3</sup>J=6.5 Hz, 2H, CH<sub>2</sub>O), 4.09 (t, <sup>3</sup>J=6.4 Hz, 2H, CH<sub>2</sub>O), 6.91-6.97 (m, 4H,

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Ar-H), 7.09 (d,  $^3J=8.9$  Hz, 2H, Ar-H), 7.31 (dd,  $^3J=8.4$  Hz,  $^4J=1.7$  Hz, 1H, Ar-H), 7.47 (d,  $^3J=8.6$  Hz, 1H, Ar-H), 8.03 (dd,  $^3J=8.6$  Hz,  $^4J=1.9$  Hz, 1H, Ar-H), 8.17 (d,  $^4J=1.9$  Hz, 1H, Ar-H)

Elemental analysis: calculated for Mm 811.20 (C<sub>48</sub>H<sub>68</sub>N<sub>2</sub>O<sub>5</sub>Cl<sub>2</sub>): C 69.97, H 8.32, N 3.40, Cl 8.61; found C 70.06, H 7.79, N 3.42, Cl 8.76