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# Supplementary Information. The influence of phenyl and phenoxy modification in the hydrophobic tails of di-*n*-alkyl phosphate amphiphiles on aggregate morphology

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## Experimental

The NMR spectra were recorded on a Varian Gemini-200 (<sup>1</sup>H-NMR at 200 MHz, <sup>13</sup>C-NMR at 50.3 MHz) or on a Varian VXR-300 (<sup>1</sup>H-NMR at 300 MHz, <sup>13</sup>C-NMR at 75.5 MHz). Chemical shifts (δ) are in ppm and relative to the residual proton resonance in CDCl<sub>3</sub> (<sup>1</sup>H: δ 7.26 ppm, <sup>13</sup>C: δ 77.0 ppm). Melting points were determined on a Kofler hot stage or a Mettler FP2 melting point apparatus equipped with a Mettler FP 21 microscope and are uncorrected. Solvents were dried and purified by distillation. Water used in the experiments was bidistilled in an all quartz apparatus or purified by a Millipore system. Elemental analyses were carried out in the analytical department of our laboratory.

## Synthesis

### 11-Bromo-1-phenylundecan-1-one<sup>1</sup>

A mixture of 11-bromoundecanoic acid (3.343 g, 0.0126 mol) and thionyl chloride (2 mL, 0.03 mol) was stirred overnight. After cooling to 0 °C, benzene was added. Then AlCl<sub>3</sub> (1.91 g, 0.0142 mol) was added in small portions. The resulting mixture was stirred for an hour at room temperature, for an hour at 60 °C and subsequently poured into ice water. The aqueous layer was extracted with ether (3x30 mL) and the ether layer was dried (MgSO<sub>4</sub>) and evaporated to yield an oil (2.954 g, 9.1 mmol, 72 %); <sup>1</sup>H-NMR (200MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.3Hz, 2H), 7.61–7.42 (m, 3H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.92–1.66 (m, 4H), 1.30 (bs, 12H); <sup>13</sup>C-NMR (50MHz, CDCl<sub>3</sub>) δ 200.63, 137.05, 132.88, 128.54, 128.04, 38.60, 34.07, 32.80, 29.40, 29.34, 28.72, 28.13, 24.32.

### 11-Oxo-11-phenyl undecyl acetate

A solution of 11-bromo-1-phenylundecan-1-one (2.954 g, 9.1 mmol) and silver acetate (1.515 g, 9.1 mmol) in acetic acid was refluxed overnight, poured into 20% Na<sub>2</sub>CO<sub>3</sub> and the product was extracted with ether. Evaporation yielded a yellow oil. Yield 99%; <sup>1</sup>H-NMR (200MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.55–7.27 (m, 3H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.04 (s, 3H), 1.73–1.61 (m, 4H), 1.29 (m, 12 H); <sup>13</sup>C-NMR (50MHz, CDCl<sub>3</sub>) δ 200.63, 200.69, 137.05, 132.88, 128.54, 128.04, 64.68, 38.60, 29.42, 29.33, 29.20, 28.56, 25.87, 24.34, 21.02, 20.57.

### 11-Phenylundecan-1-ol

11-Oxo-11-phenyl undecyl acetate was added to a mixture of 60 mL diethylene glycol, KOH (2 g, 0.04 mol) and 3 mL of hydrazine hydrate 90 % (0.05 mol). The mixture was refluxed for an hour and then the excess of hydrazine and water was distilled off. The mixture was refluxed for 30 min. and allowed to cool. Water and a 10% HCl solution were added. The aqueous layers were extracted with ether and the ether layers were washed with water, sodium bicarbonate and brine. Evaporation gave a white solid, which was crystallised from petroleum ether 40–60. Yield 28%; mp. 27.5–29 °C<sup>2</sup>(bp. 180°C/0.1 mm); <sup>1</sup>H-NMR (200MHz, CDCl<sub>3</sub>) δ 7.31–7.16 (m, 5 H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.60 (t, *J* = 7.1 Hz, 2H), 1.60–1.57 (m, 4H), 1.28 (bs, 12H); <sup>13</sup>C-NMR (50MHz, CDCl<sub>3</sub>) δ 142.92, 128.37, 128.18, 125.51, 63.09, 35.97, 35.79, 31.51, 29.55, 29.40, 29.31, 25.71.

### Methyl 6-oxo-6-(4-pentylphenyl)hexanoate

Monomethyl adipoyl chloride (5.320 g, 0.0297 mol) and *n*-pentylbenzene (4.415 g, 0.0297 mol) were dissolved in dichloromethane and AlCl<sub>3</sub> (12 g, 0.09 mol) was added in small portions at 0°C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and was stirred for an hour. Then ice water and 5% HCl (aq) were added. The mixture was extracted with dichloromethane, the organic layer was washed with saturated NaHCO<sub>3</sub> and dried on calcium chloride. Evaporation of the solvent yielded a yellow oil, which was used without further purification. Yield 7.921 g (0.0273 mol, 92%); <sup>1</sup>H-NMR (200 MHz) δ 7.86 (d, *J* = 8.06 Hz, 2H), 7.25 (d, *J* = 8.06 Hz, 2H), 3.66 (s, 3H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.1 Hz, 2H), 2.37 (t, *J* = 6.7 Hz, 2H), 1.75–1.72 (m, 6H), 1.34–1.31 (m, 2H), 0.88 (t, *J* = 6.3 Hz, 3H).

### 6-(4-Pentylphenyl)hexanoic acid

A mixture of methyl 6-oxo-6-(4-pentylphenyl)hexanoate (7.921 g, 0.0273 mol), potassium hydroxide (5.611 g, 0.100 mol) and 4.5 mL hydrazine hydrate (0.09 mol) in 70 ml diethylene glycol was heated to reflux for an hour. The water and excess hydrazine hydrate were distilled off and the mixture was heated at 190 °C for three hours. The reaction mixture was subsequently cooled, diluted with water and acidified. The precipitate was dissolved in ethanol and water was added. The resulting precipitate was dissolved in ether and treated with activated carbon. Filtration and evaporation yielded a white wax (2.888 g, 0.011 mol, 40%). <sup>1</sup>H-NMR(200 MHz, CDCl<sub>3</sub>) δ 7.08 s, 4H), 2.61–2.52 (m, 4H), 2.35 (t, *J* = 7.4, 2H), 1.74–1.52 (m, 4H), 1.45–1.21(m, 8H), 0.88(t, *J* = 6.6Hz, 3H); <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>) δ 178.57, 140.24, 139.55, 128.27, 128.19, 35.50, 35.25, 33.72, 31.55, 31.26, 31.13, 28.69, 24.53,22.54, 14.03.

### 6-(4-Pentylphenyl)-1-hexanol

6-(4-Pentylphenyl)hexanoic acid (2.888 g, 0.011 mol) was added to a suspension of sodium borohydride (1.040 g, 0.0275 mol) in dry THF. After the evolution of hydrogen had ceased, a solution of iodine (3.046 g, 0.012 mol) was added dropwise at 0 °C. After the

addition was complete, the mixture was heated to reflux overnight. After cooling to room temperature, the reaction was quenched by slow addition of methanol. The mixture was stirred for half an hour and then the solvents were evaporated. The residue was stirred in 20% KOH (aq) for two hours. Then the suspension was extracted with ether (3x 50 ml), the combined ether layers were washed with a saturated ammonium chloride solution and dried on magnesium sulfate. Evaporation of the ether yielded a colourless oil (2.280 g, 0.00917 mol, 83%);  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.08 (bs, 4H), 3.63 (t,  $J = 6.5$  Hz, 2H), 2.57 (t,  $J = 7.6$  Hz, 2H), 2.56 (t,  $J = 7.7$  Hz, 2H), 1.60–1.27 (m, 16H), 0.89 (t,  $J = 6.7$  Hz, 3H);  $^{13}\text{C-NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  140.16 (s), 139.83 (s), 128.24 (2d), 63.02 (t), 35.51 (t), 35.43 (t), 32.69 (t), 31.56 (t), 31.49 (t), 31.27 (t), 29.08 (t), 25.59 (t), 22.54 (t), 14.03 (t).

### 11-Phenoxy-1-undecanol

A mixture of phenol (3.746g 0.0398 mol), 11-bromo-undecanol (10.000 g, 39.8 mmol),  $\text{K}_2\text{CO}_3$  (15 g, 0.011 mol) and a catalytic amount of KI was refluxed in acetone for 4 days. The reaction mixture was poured into water, and the acetone was distilled off. The precipitate was filtered off and crystallised from pet-ether 40- 60. Yield of 11-phenoxy-1-undecanol: 9.531 g. (90%); mp 50-54 °C (57-58 °C  $l^3$ );  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.3-7.25 (m, 2H), 6.95-6.88 (m, 3H), 3.95 (t, 6.6 Hz, 2H), 3.64 (t, 6.6Hz, 2H), 3.41 (s, 1H), 1.82-1.75 (m, 2H), 1.62-1.30 (m, 16H);  $^{13}\text{C-NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  159.19, 129.48, 120.53, 114.58, 67.96, 63.12, 32.88, 29.64, 29.60, 29.39, 26.14, 25.83.

### 6-(4-Pentylphenoxy)-1-hexanol

4-*n*-Pentylphenol (5.04 g, 0.03068 mol), 6-bromohexanol (5.512 g, 0.03044 mol), 4.2 g potassium carbonate and a catalytic amount of potassium iodide (ca. 0.1 g) were dissolved in acetone and heated at reflux for 4 days. Then the mixture was poured into 200 mL of water and extracted with diethyl ether. Evaporation of the ether gave an oil. Yield: 7.716 g (0.02918 mol, 95%);  $^1\text{H-NMR}$  (200MHz,  $\text{CDCl}_3$ )  $\delta$  7.08 (d,  $J = 8.5$  Hz, 2H), 6.81 (d,  $J = 8.5$  Hz, 2H), 3.94 (t,  $J = 6.4$  Hz, 2H), 3.66 (t,  $J = 6.4$  Hz, 2H), 2.54 (t,  $J = 7.7$  Hz, 2H), 1.79–1.18 (m, 14H), 0.89 (broad s, 3H);  $^{13}\text{C-NMR}$  (50MHz)  $\delta$  157.02, 134.90, 129.17, 114.20, 67.78, 62.85, 34.98, 32.63, 31.42, 29.27, 25.88, 25.5, 22.53, 14.03.

### Phosphates

A general procedure for the synthesis of the phosphates is given. To  $\text{PCl}_3$  (1 eq.) and pyridine (1.86 eq.) in dry THF and under a nitrogen atmosphere the corresponding alcohol was added (1.86 eq.) at 0° C. The reaction was allowed to warm up to room temperature and stirred for three days. The solvent was evaporated and the residue was dissolved in 5 ml of pyridine/water (20:1) and iodine (1.11 eq.) was added. The mixture was stirred at room temperature for three days.

### bis(11-Phenylundecyl) hydrogen phosphate ( $\text{C}_{11}\text{Phen}$ )

After stirring of the phosphite diester in pyridine/ $\text{H}_2\text{O}$  and iodine, first the pyridine was evaporated then saturated sodium thiosulfate was added. The precipitate was filtered off and crystallised from ether/dichloromethane (1:1) Yield 0.389 g, 0.7 mmol, 34%; mp. 64–65 °C;  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.10 (m, 10H), 3.76(m, 4H), 2.54 (t,  $J = 7.7$ Hz, 4H), 1.55–1.52 (m, 4H), 1.21 (bs, 32H);  $^{13}\text{C-NMR}$ (50 MHz, $\text{CDCl}_3$ )  $\delta$  142.83, 128.28, 128.12, 125.45, 65.64 (d,  $J_{\text{CP}} = 5.1$  Hz), 35.90, 1.47, 30.74, 30.58, 29.57, 29.30, 25.73;  $^{31}\text{P-NMR}$ (200 MHz, $\text{CDCl}_3$ )  $\delta$  0.90; Anal. Calcd for  $\text{C}_{34}\text{H}_{55}\text{O}_4\text{P}$ : C, 73.08; H, 9.92. Found C, 72.4; H, 10.40.

### bis[6-(4-Pentylphenyl)hexyl] hydrogen phosphate ( $\text{C}_6\text{phenC}_5$ )

Upon adding a sodium thiosulfate solution, an oil separated and was taken up by ether. The aqueous layer was extracted three times with ether, the combined ether layers were dried on magnesium sulfate and the solvent was evaporated. The resulting waxy solid was recrystallised from ether / hexane. Yield 0.478 g, 0.85 mmol, 43%; mp. 52–57 °C;  $^1\text{H-NMR}$  (200 MHz, $\text{CDCl}_3$ )  $\delta$  7.07 (s, 8H), 4.26 (bs, 8H), 4.05–3.95 (m, 4H), 2.56 (2xt, 8H), 1.67–1.28 (m, 28H), 0.89 (t,  $J = 6.5$ Hz);  $^{13}\text{C-NMR}$  (50 MHz, $\text{CDCl}_3$ )  $\delta$  140.14, 139.70, 128.22, 128.16, 67.61 (d,  $J = 5.9$  Hz), 35.49, 35.38, 31.55, 31.37, 31.24, 30.14, 30.00, 28.80, 25.27, 22.52, 14.01;  $^{31}\text{P-NMR}$  (81 MHz,  $\text{CDCl}_3$ )  $\delta$  1.04; Anal. Calcd for  $\text{C}_{34}\text{H}_{55}\text{O}_4\text{P} \cdot \text{H}_2\text{O}$ : C, 70.80; H, 9.96. Found C, 71.1; H, 9.86.

### bis(11-Phenoxyundecyl) hydrogen phosphate ( $\text{C}_{11}\text{Ophen}$ )

To  $\text{PCl}_3$  (165  $\mu\text{L}$ , 1.89 mmol) dissolved in dry THF was added dropwise 530  $\mu\text{L}$  (3.78 mmol) of diisopropylamine in dry THF at –5 °C and under a nitrogen atmosphere. After addition, stirring was continued at room temperature for one hour. Then a solution of 11-phenoxyundecanol (1.000 g, 3.78 mmol) and ethyldiisopropylamine (658  $\mu\text{L}$ , 3.78 mmol) in dry THF was added slowly at –5 °C. After stirring at room temperature for 3 days, water was added. The layers were separated, the organic layer was dried and evaporated. The resulting solid was dissolved in 5 mL pyridine/water (20:1). Iodine (0.533 g, 2.10 mmol) was added and the mixture was stirred for 2 h. A saturated solution of sodium thiosulfate was added to destroy the excess of iodine and the white precipitate was filtered off and crystallised from dichloromethane / diethyl ether to yield, 0.3658 g, 0.62 mmol, 33%; mp. 92–92.5 °C;  $^1\text{H-NMR}$  (200 MHz, $\text{CDCl}_3$ )  $\delta$  7.32–7.25 (m, 4H), 6.97–6.88 (m, 6H), 4.08–3.92 (m, 8H), 1.82–1.66 (m, 8H), 1.31(m, 28 H);  $^{13}\text{C-NMR}$  (50 MHz, $\text{CDCl}_3$ )  $\delta$  159.10, 129.38, 120.42, 114.46, 67.83, 67.08(d,  $J(\text{C-OP}) = 6$  Hz), 29.51, 9.39, 29.29, 26.06, 25.43;  $^{31}\text{P-NMR}$  (81 MHz,  $\text{CDCl}_3$ )  $\delta$  0.93 ; Anal. Calcd for  $\text{C}_{34}\text{H}_{55}\text{O}_6\text{P} \cdot \text{H}_2\text{O}$ : C, 67.08; H, 9.44. Found C, 67.1; H, 9.37.

### bis[6-(4-Pentylphenoxy)hexyl] hydrogen phosphate ( $\text{C}_6\text{OphenC}_5$ )

The white solid was crystallised from dichloromethane / ether. Yield: 0.380 g, 0.64 mmol, 36%; mp. 67 °C (lc), 83 °C (l);  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10–6.70 (m, 8H), 3.97–3.77 (m, 8H), 2.48(t,  $J = 7.7$ Hz, 4H), 1.85–1.20 (m, 28H), 0.87 (t,  $J = 6.6$ Hz, 6H);  $^{13}\text{C-NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  157.01, 134.79, 129.13, 114.14, 67.73, 65.96 (d,  $J_{(\text{C-OP})} = 7.0$  Hz), 34.99, 31.43, 29.40, 25.95, 25.69, 22.53, 14.04;  $^{31}\text{P-NMR}$  (81 MHz, $\text{CDCl}_3$ )  $\delta$  1.00; Anal. Calcd for  $\text{C}_{34}\text{H}_{55}\text{O}_6\text{P} \cdot 2\text{H}_2\text{O}$ : C, 65.15; H, 9.49. Found C, 65.6; H, 9.18.

#### References

- 1 Rabjohn, N.; Cohen, M. S. *J. Am. Chem. Soc.* **1954**, *76*, 1280-1282.
- 2 Hubert, A. J. *J. Chem. Soc. C* **1967**, 235-238.
- 3 Hands, A. R.; Mercer, A. J. H. *J. Chem. Soc. C* **1968**, 1331-1337.