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# A Flexible, Bolaamphiphilic Template for Mesoporous Silicas

## Electronic Supporting Information

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## Experimental Methods

### Instrumentation and Reagents

<sup>1</sup>H NMR (200 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz); <sup>1</sup>H (300 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz); <sup>1</sup>H NMR (400MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (100MHz) spectra were recorded using Bruker DPX200; Bruker DPX300; and Bruker DRX400 NMR spectrometers respectively. Spectra were referenced internally to residual solvent: CDCl<sub>3</sub> δ 7.26 (<sup>1</sup>H NMR) and δ 77.0 (<sup>13</sup>C{<sup>1</sup>H} NMR); CD<sub>3</sub>OD δ 3.31 (<sup>1</sup>H NMR) and δ 49.0 (<sup>13</sup>C{<sup>1</sup>H} NMR). Mass spectra (ESI) were recorded on a Finnigan LCQ Ion Trap Mass Spectrometer. Elemental analyses were performed by the Microanalytical Unit at the Australian National University, Canberra. Melting points were recorded on a Gallenkamp melting point apparatus in air and are uncorrected. Conductimetry was performed at 25 °C using solutions of surfactants dissolved in MilliQ water at various concentrations. Specific conductivities were measured using an EDT Instruments FE280 conductivity meter, calibrated with 0.01 M potassium chloride. Flooding experiments were performed with a small amount of surfactant sandwiched between a glass slide and a cover slip; observation by optical microscopy was performed using a Leica DMLB microscope equipped with crossed polarizers, quarter-wave plate and DC 300 digital camera. A Linkam heating plate (T<sub>max</sub> 62.5 °C) was placed underneath the sample on the microscope stage when heating was required. Small Angle X-Ray Scattering (SAXS) were measured by using an Anton Paar SAXSess line collimation instrument with a sealed tube source and 1-D elliptical focusing graded multilayer mirror optics (*d* spacing = 4±0.07 nm) with a Max Flux Osmic block collimator. Data were recorded using 2-D position-sensitive image plates (42.3 × 42.3 μm<sup>2</sup> pixel size; sample-to-image plate distance, 264.5 mm). Image plates were read using a Perkin Elmer Cyclone phosphor storage system driven with OptiQuant software. Anton Parr

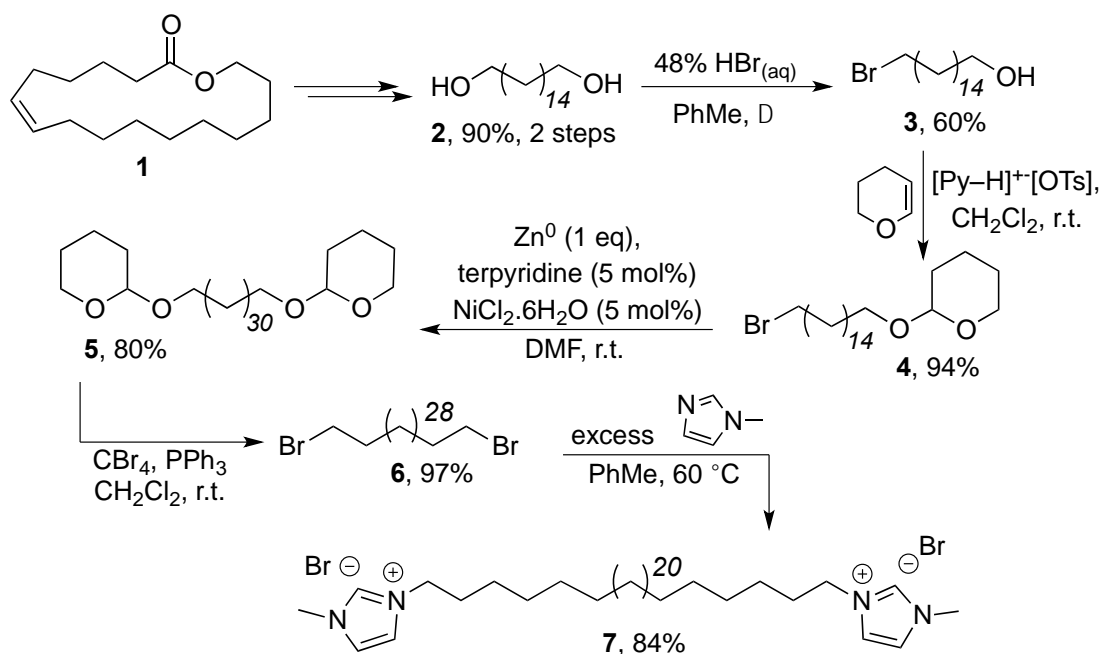
SAXSquant2D software was used to average the 2-D images. Transmission electron micrographs were recorded digitally with a Gatan slow-scan charge-coupled device (CCD) camera on a Phillips CM120 Biofilter electron microscope operating at 120 kV. The samples were prepared by dispersing the materials in ethanol and depositing the mixture on a holey carbon film on a 200 mesh copper grid which was then dried. Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP2020 Surface Area and Porosity Analyzer. Samples were degassed for at least 4 h at 473 K before analysis. The specific surface area *S*<sub>BET</sub> was obtained from the adsorption data by applying the BET equation in the relative pressure range from 0.04 to 0.2. The total pore volume *V*<sub>p</sub> was determined from the nitrogen adsorbed at a relative pressure of 0.96. The pore size-distribution was derived from the analysis of the adsorption branch of the isotherm using the BJH (Barrett-Joyner-Halenda) method. Alternatively, the non-local density functional theory (NLDFIT) embedded in the software (ASAP 2020 ver. 4.01) was applied to estimate pore size-distributions using the Tarazona model for cylindrical pore geometry.<sup>1-3</sup>

The following chemicals were used as received: tetraethyl orthosilicate (TEOS), 1-methylimidazole (99% redistilled), 3,4-dihydro-2H-pyran, 2,2':6',2''-terpyridine (Sigma Aldrich), zinc powder, tetrabromomethane, methanol, AR acetone (Merck), *para*-toluenesulfonic acid, 48% w/v aqueous hydrobromic acid, sodium hydroxide, 28% w/v aqueous ammonia, pyridine, nickel(II) chloride hexahydrate (Ajax), 1,12-dibromododecane (Fluka), absolute ethanol (CSR), and ω-6-hexadecenelactone (SAFC). Triphenylphosphine (Aldrich) was recrystallised from hexanes prior to use. Anhydrous *N,N*-dimethylformamide (Merck) was stored over 4 Å molecular sieves, under nitrogen. Solvents (dichloromethane, diethyl ether, hexane) were deoxygenated and dried over activated alumina using an apparatus derived from that described in the literature.<sup>4</sup>

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Scheme 1. Template synthesis.

### Template synthesis

1,16-Hexadecane diol (**2**) was prepared from  $\omega$ -6-hexadecanediol (1) according to previously described procedures.<sup>5</sup>

16-Bromohexadecanol (**3**) was prepared according to a published procedure.<sup>6,7</sup> A mixture of diol **3** (3.34 g, 12.9 mmol), 48% w/v aqueous hydrobromic acid (2 mL, ca 18 mmol) and toluene (70 mL) was purged with nitrogen, then heated to reflux in a closed, but expandable system (flask capped with an empty balloon) for 18 h. The reaction mixture was allowed to cool to room temperature and diluted with hexanes (70 mL). The precipitate was removed by filtration, affording starting material **2** (0.82 g, 24%) that was retained for recycling. The filtrate was washed with saturated, aqueous sodium hydrogencarbonate solution (70 mL), dried over sodium sulfate, filtered and concentrated to give a brown oil. Purification by flash chromatography, eluting with 2:3 diethyl ether/hexanes, afforded the desired product as a white solid (2.48 g, 60%), m.p. 55–57 °C.  $\lambda_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3291, 2918, 2849, 1473, 1462, 1062. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  ppm 3.64 (2H, t, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, CH<sub>2</sub>OH), 3.41 (2H, t, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, CH<sub>2</sub>Br), 1.85 (2H, app quint, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>2</sub>CH<sub>2</sub>OH), 1.56 (2H, m, CH<sub>2</sub>CH<sub>2</sub>Br), 1.45–1.19 (24H, m, CH<sub>2</sub>S). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  ppm 63.1, 34.0, 32.8(4), 32.8(2), 29.6(4), 29.6(0), 29.5, 29.4, 28.8, 28.2, 25.7, 5 resonances unresolved. *m/z* (EI, positive ion): 274, (2%, [M–C<sub>2</sub>H<sub>5</sub>OH]<sup>+</sup>), 253 (1%), 246 (1%), 234 (1%), 217 (1%), 203 (1%), 190–192 (2%), 176–178 (2%), 162–164 (5%), 148–150 (11%), 135–137 (6%), 123–125 (7%), 111–113 (16%), 97–99

(49%), 83–85 (65%), 69–71 (74%), 55–57 (100%).

2-(16-Bromohexadecyloxy)tetrahydro-2H-pyran (**4**) was prepared in 94% yield according to the procedure of Laville and coworkers.<sup>7</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  ppm 4.57 (1H, br t, <sup>3</sup>J<sub>HH</sub> = 3.3 Hz, pyranC2-H), 3.86 (1H, m, pyranC6-H), 3.73 (1H, app dt, <sup>3</sup>J<sub>HH</sub> = 9.6, 6.9 Hz, CHH'O), 3.50 (1H, m, pyranC6-H'), 3.40 (2H, t, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH<sub>2</sub>Br), 3.34 (1H, m, CHH'O), 1.84 (2H, app pent, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>2</sub>CHH'Br), 1.70 (1H, m, pyranC3-H), 1.60–1.53 (6H, m, CH<sub>2</sub>S & pyranylHs), 1.52–1.26 (25H, m, pyranyl & CH<sub>2</sub>S). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  ppm 98.8, 67.7, 62.3, 34.0, 32.8, 30.8, 29.8, 29.7, 29.6(3), 29.5(9), 29.5(2), 26.4(8), 29.4(2), 28.8, 28.2, 26.2, 25.5, 19.7, 4 resonances unresolved. The spectrum was found to be consistent with reported spectroscopic data.<sup>7</sup>

1,32-bis((tetrahydro-2H-pyran-2-yl)oxy)dotriacontane (**5**). To a green, homogeneous solution of bromopyran (**4**) (2.38 g, 5.87 mmol), nickel(II) chloride hexahydrate (86 mg, 363  $\mu$ mol) and 2,2':6',2''-terpyridine (85 mg, 363  $\mu$ mol) in *N,N*-dimethylformamide (40 mL), under nitrogen, was added zinc powder (475 mg, 7.25 mmol). The reaction became purple/brown within minutes and was further stirred under nitrogen, at room temperature, overnight (after 6.5 h, the reaction solution had become grey). The solution was concentrated, the residue resuspended in toluene (60 mL) at 60 °C and filtered through glass wool. The residue was further extracted with toluene (2  $\times$  40 mL). The combined extracts were concentrated and purified by flash chromatography, eluting with dichloromethane, affording a white solid (1.54 g, 80%), m.p. 71–72 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  ppm 4.58 (2H, br t, <sup>3</sup>J<sub>HH</sub> = 3.4 Hz,

2×pyranC2-H), 3.87 (2H, m, 2×pyranC6-H), 3.73 (2H, dt,  $^3J_{\text{HH}} = 9.3, 6.9$  Hz, 2×OCHH'), 3.48 (2H, m, 2×pyranC6-H'), 3.39 (2H, dt,  $^3J_{\text{HH}} = 9.3, 6.9$  Hz, 2×OCHH'), 1.83 (2H, m, 2×pyranC3-H), 1.71 (2H, m, 2×pyranC4-H), 1.62–1.49 (12H, 5 2×pyranC3&4H's; C5-Hs & 2×CH<sub>2</sub>S), 1.37–1.25 (56H, m, 28×CH<sub>2</sub>). The spectrum was found to be consistent with reported spectroscopic data.<sup>8</sup> *m/z* (ESI, positive ion): 652 ([M+H]<sup>+</sup>, 27%), 484 ([M–C<sub>10</sub>H<sub>15</sub>O<sub>2</sub>]<sup>+</sup>, 100%).

**1,32-Dibromodotriacontane (6).** To a solution of bis-THP ether **5** (1.54 g, 2.37 mmol) and tetrabromomethane (2.20 g, 6.62 mmol) in dichloromethane (100 mL), under nitrogen, was added triphenylphosphine (3.47 g, 13.25 mmol). The resulting yellow solution was stirred at room temperature overnight, concentrated, then adsorbed onto flash silica (9 g). Purification by flash 15 chromatography, eluting with 25% to 50% dichloromethane in hexanes (gradient), afforded the desired compound as a lustrous, white solid (1.40 g, 97%), m.p. 86.5–87 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ ppm 3.41 (4H, t,  $^3J_{\text{HH}} = 6.8$  Hz, 2×CH<sub>2</sub>Br), 1.85 (4H, app pent,  $^3J_{\text{HH}} = 7.1$  Hz, 2×CH<sub>2</sub>CH<sub>2</sub>Br), 1.42 (4H, br m, 20 2×CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Br), 1.30–1.25 (52H, m, 26×CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ ppm 33.9, 32.9, 29.7 (9 resonances), 29.6, 29.5, 29.4, 28.8, 28.2. The spectra were found to be consistent with reported spectroscopic data.<sup>8</sup>

**1,1'-(dotriacontane-1,32-diyl)bis(3-methyl-1H-imidazol-3-ium) bromide (7).** To a solution of dibromoalkane **6** (500 mg, 0.82 mmol) in toluene (5 mL), under nitrogen, was added 1-methylimidazole (2.0 mL, 25.1 mmol). The resulting homogeneous solution was stirred and heated at 60 °C for 24 h. The resulting slurry was allowed to cool to room temperature, 30 transferred to a centrifuge tube with ethyl acetate (10 mL final volume) and spun down. The supernatant was discarded, the pellet resuspended in methanol (3 mL), reprecipitated with ethyl acetate (11 mL) and spun down. The pellet was recrystallized from 10% v/v methanol in AR acetone, affording the desired 35 compound as white, lustrous, flakes (531 mg, 84%), m.p. 118–120 °C.  $\lambda_{\text{max}}$  (KBr)/cm<sup>–1</sup>: 3479, 3437, 3387, 3227, 3147, 3080, 3050, 2917, 2850, 2081, 1673, 1615, 1576, 1473, 1330, 1176, 1109, 847, 790, 761, 716. <sup>1</sup>H NMR (CDCl<sub>3</sub> + 3 drops MeOD, 400MHz): δ ppm 9.48 (2H, s, 2×Im2H), 7.46 (2H, s, 2×Im4H or 40 Im5H), 7.39 (2H, s, 2×Im5H or Im4H), 4.25 (4H, t,  $^3J_{\text{HH}} = 7.4$  Hz, 2×NCH<sub>2</sub>), 4.02 (6H, s, 2×NCH<sub>3</sub>), 1.89 (4H, m, 2×NCH<sub>2</sub>CH<sub>2</sub>), 1.34 (12H, m, 6×CH<sub>2</sub>), 1.29–1.20 (44H, m, 22×CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub> + 3 drops MeOD, 100 MHz): δ ppm 136.6, 123.4, 121.8, 49.9, 36.2, 30.0, 29.4(3) (9 resonances), 29.3(6), 29.3, 45 29.1, 28.8, 26.0 ppm. *m/z* (ESI, positive ion): 693 ([M–Br]<sup>+</sup>, 42%), 611 ([M–H]<sup>+</sup>, 12%), 307 (M<sup>2+</sup>, 100%). HRMS (ESI, positive ion): Found 693.5230, [C<sub>40</sub>H<sub>76</sub>N<sub>4</sub>(<sup>81</sup>Br)]<sup>+</sup> requires 693.5215. Anal. Calcd. for C<sub>40</sub>H<sub>76</sub>N<sub>4</sub>Br<sub>2</sub>: %C 62.2; %H 9.9; %N 7.3. Found: %C 62.3; %H 10.1; %N 7.2.

## 50 General Procedures for silica syntheses

Hydrolyses of tetraethyl orthosilicate under basic conditions were carried out in a solution of bolaamphiphile **7** in 15 mM aqueous sodium hydroxide solution (or 2% aqueous ammonia), under ambient atmosphere, for either 2 h or 72 h at 1 atm, or 72 h in an 55 autoclave under autogenous pressure.

### Variation in concentration of surfactant

2 h, 80 °C; 4 times cmc: A solution of 15 mM aqueous sodium

hydroxide (120 mL) and surfactant **7** (20 mg, 25.9 μmol) was 60 heated to an internal reaction temperature of 80 °C (reaction fitted with a reflux condenser), with stirring, under ambient atmosphere. Tetraethyl orthosilicate (1.25 mL, 5.61 mmol) was added dropwise and the reaction was stirred at 700 rpm for 2 h. The reaction was allowed to cool to room temperature and the pH 65 adjusted to 6–7 with 3 M aqueous hydrobromic acid. The suspension was centrifuged, the silica isolated and resuspended in water (30 mL) then similarly washed with ethanol (2 × 30 mL). The isolated silica was dried at 60 °C, then calcined at 550 °C for 4 h (ramp rate 5 °C/ min), affording silica, denoted S-1:200.

2 h, 80 °C; 20 times cmc: The reaction and workup were performed as described above using 15 mM aqueous sodium hydroxide (100 mL), surfactant **7** (80 mg, 104 μmol) and tetraethyl orthosilicate (1.05 mL, 4.69 mmol), affording silica 70 denoted S-1:45.

2 h, 80 °C; 40 times cmc: The reaction and workup were performed as described above using 15 mM aqueous sodium hydroxide (100 mL), surfactant **7** (155 mg, 201 μmol) and tetraethyl orthosilicate (1.05 mL, 4.69 mmol), affording silica 75 denoted S-1:23.

2 h, 80 °C; 54 times cmc: The reaction and workup were performed as described above using 15 mM aqueous sodium hydroxide (50 mL), surfactant **7** (108 mg, 134 μmol) and tetraethyl orthosilicate (523 μL, 2.35 mmol), affording silica 80 denoted S-1:17.

2 h, 80 °C; 120 times cmc: The reaction and workup were performed as described above using 15 mM aqueous sodium hydroxide (50 mL), surfactant **7** (227 mg, 294 μmol) and tetraethyl orthosilicate (525 μL, 2.36 mmol), affording silica 85 denoted S-1:8.

### 90 Variation in synthesis conditions

72 h, 100 °C and hydrothermal treatment: the reaction was performed as described above using 15 mM aqueous sodium hydroxide (120 mL), surfactant **7** (96 mg, 124 μmol) and 95 tetraethyl orthosilicate (1.25 mL, 5.61 mmol). After 2 h at 80 °C, the reaction was split into 2 portions and one portion stirred at 100 rpm for 72 h at 100 °C (external temperature). The other portion was transferred (45 mL) to a 50 mL PTFE-lined steel autoclave and heated to 100 °C for 72 h without stirring. Work-up 100 and isolation were performed as described above affording silicas denoted S-1:45-72h and S-1:45-HT.

NH<sub>3</sub>, 24 h, 60 °C, without stirring: The reaction was performed as described above using 2% w/v aqueous ammonia (12 mL), surfactant **7** (55 mg, 71 μmol) and tetraethyl orthosilicate (150 105 μL, 673 μmol) without stirring, affording silica denoted S-1:10-NS.

### Variation in synthesis conditions: TEOS:surfactant ratio 20:1

2 h, 80 °C; 72 h, 100 °C; and 2 h without stirring: in all cases the 110 reactions were performed at 20 times cmc, using 15 mM aqueous sodium hydroxide (100 mL), surfactant **7** (80 mg, 104 μmol) and tetraethyl orthosilicate (460 μL, 2.06 mmol), affording silicas denoted S-1:20, S-1:20-72h, S-1:20-NS.

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