Supplementary data

Soft Ordered Mesoporous Materials from Nonionic Isoprenoid-Type Monoethanolamide Amphiphiles Self-Assembled in Water

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Detailed Synthesis Methodology and Compound Characterization

General procedure for oxidation of fatty alcohols.

Example: 3,7,11,15-tetramethyl-hexadecanoic acid

(Phytanoic acid)

30 g of Phytanol was mixed into 600 ml of acetic acid. The mixture was somewhat hazy solution. This was cooled in an ice/water bath to about 16°C (close to the freezing point of glacial acetic acid, 16.7°C), and a solution of chromic oxide (Aldrich 99.9% CrO_3, 24 g) in water (30 ml) was added dropwise over 4 hours. After addition the temperature was allowed

to rise, and the mixture stirred at room temperature for a further 1.5 hours. Stirring was continued until an aliquot, extracted with petroleum spirit 60/80 no longer showed the alcohol as present by NMR. The reaction mixture was transferred to a separation funnel, where most of the formed acid separated as an oily upper layer. It was isolated from CH_3COOH phase and treated with a pinch of sodium metabisulphite ($Na_2S_2O_5$) dissolved in 50 ml of water. This completely decolourized the oil collected. The acetic acid phase was extracted twice with 200 ml portions of petroleum spirit 60/80 and the extracts were combined with the above oil/aqueous metabisulfite mixture.. The combined pet. spirit solution was washed with 100 ml brine, resulting in a colourless organic upper layer and light blue aqueous layer. The organic layer was filtered through a phase separating filter and evaporated, resulting in 28.9 g of a clear, almost colourless mobile oil. The crude product contained phytanoic acid as well as some ester (phytanyl phytanoate). These were separated by vacuum distillation using a Buchi Kugelrohr. The first distillation gave 17.69 g of acid and 9.65 g of the ester. More acid was recovered by hydrolysis of phytanyl phytanoate (refluxing its ethanol solution with 3 eq. of NaOH) and re-oxidation of the obtained alcohol/acid mixture in the same manner as above. In total 19.29 g of phytanoic acid was collected; yield 61.7%.

^{1}H NMR ($CDCl_3$) sl br d, δ0.84, 6H, splitting 6.3 Hz, CH_3; d, δ0.87, 6H, splitting 6.6 Hz, CH_3; d, δ0.97, 3H, splitting 6.5Hz, CH_3; m, δ0.95–1.45, 20H, CH_2 + CH; m, δ1.42–1.63, 1H CH; m δ1.85-2.05, 1H, C(3)H; ddd δ2.14, 1H, J -14.7 Hz, 8.5 Hz, 1.0

3,7-dimethyloctanoic acid

^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.2, bs, 1H, OH; 2.35, dd, *J* 14.9, 5.9 Hz, 1H, CH_2CO; 2.14, dd, *J* 14.9, 8.2 Hz, 1H, CH_2CO; 2.01-1.91, m, 1H, CH; 1.57-1.48, m, 1H, CH; 1.36-1.12, m, 6H, CH_2; 0.97, d, *J* 6.6 Hz, 3H, CH_3; 0.86, d, *J* 6.6 Hz, 6H, CH_3.

3,7,11-trimethyl-dodecanoic acid (HFarnesoic acid)

^{1}H NMR ($CDCl_3$): sl br d, δ0.84, 3H, splitting 6.2 Hz, CH_3; d, δ0.86, 6H, splitting 6.6 Hz, CH_3; sl br d, δ0.96, 3H, splitting 6.5 Hz, CH_3; m, δ0.97–1.40, 13H, CH_2 + CH; m, δ1.40–1.62, 1H, CH; m, δ1.85–2.05, 1H, CH; ddd, δ2.14, 1H, J –15.0 Hz 8.2 Hz 1.2 Hz, CH_2CO_2; sl br dd, δ2.35, 1H, J –15.0 Hz 5.9 Hz, CH_2CO_2.

General procedure for fatty acid chloride preparation.

Example: 7,11,15-tetramethyl-hexadecanoyl chloride (Phytanoyl chloride).

11.6 g of Phytanoic acid (37.11 mmol) was dissolved in 55 ml of dry dichloromethane in a RB flask equipped with a pressure equalizing funnel and maintained in Ar atmosphere. The solution was rapidly stirred at 20°C while oxalyl chloride (Aldrich 98%) (44.53 mmol, 1.2 mole equivalent) diluted with 20 ml of dry DCM to make ~2M solution was added dropwise. The mixture was allowed to stir at room temperature until NMR showed the complete conversion of acid into chloride, and then the excess oxalyl chloride and DCM was evaporated off. The product was distilled in a Buchi Kugelrohr to give 12.28 g of a colourless oil; yield 96.4%.

^{1}H NMR ($CDCl_3$) sl br d, δ0.85, 6H, splitting 6.2 Hz, CH_3; d, δ0.87, 6H, splitting 6.5 Hz, CH_3; d, δ0.99, 3H, splitting 6.7 Hz, CH_3; m, δ0.95–1.45, 20H, CH_2 + CH; m, δ1.42–1.63, 1H CH; m δ1.95-2.17, 1H, C(3)H; sl br dd δ2.68, 1H, J -16.1 Hz, 7.9 Hz, CH_2COCl; sl br dd, δ2.88, 1H, J -16.1 Hz, 5.6 Hz, CH_2COCl.

3,7-dimethyloctanoyl chloride

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.88, dd, *J* 16.0, 5.8 Hz, 1H, CH_2CO; 2.67, dd, *J* 16.0, 8.0 Hz, 1H, CH_2CO; 2.13-2.01, m, 1H, CH; 1.58-1.48, m, 1H, CH; 1.37-1.15, m, 6H, CH_2; 0.99, d, *J* 6.7 Hz, 3H, CH_3; 0.87, d, *J* 6.6 Hz, 6H, CH_3.

3,7,11-trimethyl-dodecanoyl chloride (*H-farnesoyl chloride)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.87, dd, *J* 16.0, 4.3 Hz, 1H, CH_2CO; 2.67, dd, *J* 16.0, 8.0 Hz, 1H, CH_2CO; 2.13-2.01, m, 1H, CH; 1.57-1.47, m, 1H, CH; 1.39-1.06, m, 13H, CH, CH_2; 0.99, d, *J* 6.6 Hz, 3H, CH_3; 0.86, d, *J* 6.6 Hz, 6H, CH_3; 0.85, d, *J* 6.7 Hz, 3H, CH_3.

General procedure for amide preparation.

Example: 3,7,11,15-Tetramethyl-hexadecanoic acid amide (Phytanoyl amide).

40 ml of commercial ammonia solution (sp gr 0.88) was cooled to 0°C and 15 g (45.32 mmol) of phytanoyl chloride diluted with 70 ml of chloroform (ethanol free) was added dropwise keeping the temp below 0°C. The reaction mixture, still kept in the cooling bath, was allowed to come slowly to room temperature and transferred to a separation funnel. The aqueous phase was washed with an additional 50 ml of chloroform and the combined chloroform solution was washed twice with 70 ml portions of water then filtered through a phase separating paper filter. After evaporation of the solvent a yellow semi-solid was obtained. It was redissolved in methanol and treated with activated carbon, filtered and evaporated again. The resulting white waxy solid was further dried on a freeze dryer.

Yield 88.3%.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.78, bs, 2H, NH; 2.28-2.24, m, 1H, CH_2CO; 2.03-1.90, m, 2H, CH_2CO, CH; 1.57-1.47, m, 1H, CH; 1.40-1.02, m, 20H, CH, CH_2; 0.96, d, *J* 6.3 Hz, 3H, CH_3; 0.86, d, *J* 6.6 Hz, 6H, CH_3; 0.84, d, *J* 6.6 Hz, 6H, CH_3.

3,7-dimethyloctanoic acid amide

^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.4, bs, 2H, NH; 2.24-2.16, m, 1H, CH_2CO; 2.03-1.86, m, 2H, CH_2CO, CH; 1.61-1.42, m, 1H, CH; 1.39-1.07, m, 6H, CH_2; 0.94, d, *J* 6.3 Hz, 3H, CH_3; 0.86, d, *J* 6.5 Hz, 6H, CH_3.

3,7,11-Trimethyl-dodecanoic acid amide (H-farnesoyl amide)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.45, bs, 2H, NH; 2.27-2.20, m, 1H, CH_2CO; 2.02-1.91, m, 2H, CH_2CO, CH; 1.8, bs, OH; 1.57-1.47, m, 1H, CH; 1.41-1.07, m, 13H, CH, CH_2; 0.96, d, *J* 6.2 Hz, 3H, CH_3; 0.86, d, *J* 6.6 Hz, 6H, CH_3; 0.84, d, *J* 6.8 Hz, 3H, CH_3.

General procedure for monoethanolamide preparation.

Example: 3,7,11,15-Tetramethyl-hexadecanoic acid (2-hydroxy-ethyl)-amide (Phytanoyl monoethanolamide.)

Ethanolamine (Aldrich, 99+% pure), 107.31 mmole (6.554 g; 3 eq.) was diluted with 65 ml of dry dichloromethane and placed in a 250 ml 2-neck flask equipped with a magnetic stirrer, a thermometer and a pressure equalizing dropping funnel and cooled under Ar atmosphere to -20°C. 1 eq. of phytanoyl chloride (11.84 g; 35.77 mmol) diluted with 35 ml of dry DCM was added dropwise, over 2.5 hours, at a temperature not higher than -15°C. The reaction mixture was colourless and heterogeneous. It was allowed to come to RT and left until the next day. DCM was removed on a rotary evaporator (as DCM/ aqueous phase did not separate

easily) and the residue was partitioned between 100 ml of diethyl ether and 50 ml of 10% brine. The ethereal layer was washed a second time with 50 ml of 10% brine and finally with 60 ml of water. After evaporation and drying under high vacuum, 12 g of a viscous pale yellowish oil was obtained; yield 94.4%.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.37, bs, 1H, NH; 3.73, t, *J* 5.0 Hz, 2H, OCH_2; 3.45-3.40, m, 2H, NCH_2; 2.93, bs, 1H, OH; 2.28-2.21, m, 1H, CH_2CO; 2.02-1.90, m, 2H, CH_2CO, CH; 1.57-1.47, m, 1H, CH; 1.39-0.99, m, 20H, CH, CH_2; 0.92, d, *J* 6.8 Hz, 3H, CH_3; 0.86, d, *J* 6.7 Hz, 6H, CH_3; 0.84, d, *J* 6.6 Hz, 6H, CH_3.

3,7-Dimethyl-octanoic acid (2-hydroxy-ethyl)-amide (3,7-dimethyloctanoyl monoethanolamide)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.94, bs, 1H, NH; 3.72, t, *J* 5.0 Hz, 2H, OCH_2; 3.45-3.41, m, 2H, NCH_2; 2.74, bs, 1H, OH; 2.26-2.18, m, 1H, CH_2CO; 1.99-1.92, m, 2H, CH_2CO, CH; 1.57-1.47, m, 1H, CH; 1.36-1.08, m, 6H, CH_2; 0.93, d, *J* 6.3 Hz, 3H, CH_3; 0.85, d, *J* 6.6 Hz, 3H, CH_3; 0.85, d, *J* 6.6 Hz, 3H, CH_3.

3,7,11-Trimethyl-dodecanoic acid (2-hydroxy-ethyl)-amide (H-farnesoyl monoethanolamide)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.36, bs, 1H, NH; 3.75-3.67, m, 2H, OCH_2; 3.43-3.29, m, 2H, NCH_2; 3.17, bs, 1H, OH; 2.26-2.18, m, 1H, CH_2CO; 1.99-1.89, m, 2H, CH_2CO, CH; 1.55-1.45, m, 1H, CH; 1.38-0.99, m, 13H, CH, CH_2; 0.91, d, *J* 6.1 Hz, 3H, CH_3; 0.85, d, *J* 6.6 Hz, 6H, CH_3; 0.82, d, *J* 6.7 Hz, 3H, CH_3.