Supporting Information

Self-Reproducing Micelles Coupled to a Secondary Catalyst

Elias A. J. Post, Andrew J. Bissette, and Stephen P. Fletcher*

Department of Chemistry, Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, U.K.
Corresponding Author: stephen.fletcher@chem.ox.ac.uk

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General Information

Procedures using oxygen- and/or moisture-sensitive materials were performed with anhydrous solvents under an atmosphere of anhydrous argon in flame-dried flasks, using standard Schlenk techniques. Analytical TLC was performed on precoated aluminum-backed plates (Silica Gel 60 F254; Merck), and visualised using aqueous ceric ammonium molybdate (CAM), aqueous basic potassium permanganate, or ninhydrin stains. Flash column chromatography was carried out using Merck Geduran® Si 60 (40-63 µm) silica gel. Compound was loaded on to the columns with Chemtube Hydromatrix from Agilent Technologies. Pressure was applied at the column head via a flow of nitrogen with the solvent system used in parentheses.

Cooling of reaction mixtures to 0 °C was achieved using an ice-water bath. Cooling to –10 °C was achieved using a salt-ice bath. Cooling to –78 °C was achieved using a dry ice-acetone bath.

Chemicals

All chemicals were purchased from Sigma Aldrich or Fluorochem Scientific and used without further purification. Dry CHCl3, THF, CH2Cl2, Et2O, toluene, benzene, hexane, pentane, DMF, and acetonitrile were collected fresh from an mBraun SPS-5 solvent purification system having been passed through anhydrous alumina columns. All other solvents were used as purchased from Sigma-Aldrich, Honeywell, or Fisher Scientific.

Equipment

All NMR spectra were recorded at room temperature. 1H NMR and 13C NMR spectra were recorded using Bruker AVIII HD 400 (400/101 MHz) and AVIII HD 500 (500/126 MHz) spectrometers. Chemical shifts are reported in p.p.m. from the residual solvent peak. Chemical shifts (δ) are given in p.p.m. and coupling constants (J) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Assignments were made with the assistance of 2D NMR experiments.

DOSY NMR measurements were performed using a Bruker AVIII HD 500 equipped with a TFI probehead at 298 K using the 2D sequence for diffusion measurement using double stimulated echo for convection compensation and longitudinal eddy current delay, using bipolar gradient pulses for diffusion, and using three spoil gradients (Bruker terminology: dstebpgp35) pulse sequence. The samples were thoroughly mixed using a Vortex Genie 2 mixer (Scientific Industries), and then measured. Samples containing saturated alkyne consequently had a small layer of neat alkyne above the D2O layer; sufficient D2O was used to ensure that the alkyne layer was not detectible by the NMR probe. Experiments were performed in two stages: initially 1D-edited DOSY experiments were used to optimize the diffusion period to Δ=100 ms. The 2D dstebpgp35 sequence was then used, based on the optimized Δ from the previous procedure and with δ=4 ms, with gradient amplitude ranging from 2 to 85% with 16 points in between. Data were analysed using the T1T2 module in TOPSPIN 3.2 and plots were generated using the eddosy module.

Infrared measurements (thin film) were carried out using a Bruker Tensor 27 FTIR with internal calibration in the range 4000-600 cm⁻¹.

Fluorimetry was performed using Edinburgh Instruments Spectrofluorometer FS5 model with Fluoracle software. The slit width for both excitation and emission was set at 1 nm.

DLS measurements were recorded using a Malvern Zetasizer Nano ZS DLS instrument and analysed with Zetasizer software. All samples were prepared in ultrapure Milli-Q water and filtered through 0.2 µm PTFE filters before measuring.
Experimental Procedures and Characterisation of Compounds

General procedure 1: Synthesis of protected surfactant products via CuAAC reaction
Conditions adapted from Shao et al. To a stirred suspension of Cul (0.02 eq) in degassed CH₂Cl₂ (160 mM) was added protected maltose azide 1a (1 eq), DIPEA (0.04 eq), AcOH (0.04 eq) and alkyne (1.4 eq). The resultant solution was stirred for 18 h. The reaction mixture was concentrated in vacuo, and the crude was purified with flash column chromatography. The column was eluted with EtOAc:hexane (1:1) to yield the product.

General procedure 2: Acetyl deprotection
Synthesis according to Mahon et al. To a stirred suspension of protected sugar (150 mM) in MeOH was added sodium methoxide (0.1 eq). Upon dissolution of the solid and concurrent disappearance of protected sugar (TLC control) the solution was neutralised using Amberlyst 15 resin (H⁺ form). The resin was filtered off and washed with MeOH and the filtrate was concentrated in vacuo. The residue was dried under high vacuum to give a deprotected sugar as a tacky, hygroscopic white foam.

General procedure 3: Setup of kinetic experiments
Maltose azide 1b (150 mg, 0.408 mmol, 1 eq, 1.5 mL of 100 mg/mL standard solution in D₂O), CuSO₄·5H₂O (6 mg, 0.024 mmol, 0.06 eq, 1 mL of 6 mg/mL standard solution in D₂O) (and deprotected surfactant in the reported concentrations for the seeded reactions) were added to D₂O (2.0 mL) to give a total volume of 4.5 mL in a round bottom flask (25 mL) with a stirrer bar of a similar size for each experiment. The flask was capped with a septum and the solution was degassed by bubbling argon through it for 30 minutes. O-phenylenediamine (6.6 mg, 0.061 mmol, 0.15 eq), alkyne (2 eq) and sodium ascorbate (16.2 mg, 0.082 mmol, 0.2 eq) were added. The reaction mixture was stirred at 200 rpm under a continuous flow of argon. Samples for analysis during the kinetic experiments were prepared at regular intervals by diluting 0.1 mL of the reaction mixture in 0.4 mL of D₂O and immediately taking a ¹H NMR measurement.

α/β-D-maltose octaacetate

![Chemical Structure of α/β-D-maltose octaacetate](image)

Synthesised according to Harvey et al. NaOAc (5.00 g, 61.0 mmol, 1.1 eq) was added to a stirred suspension of D-maltose (10.0 g, 29.2 mmol, 1 eq) in AcO (50 mL) at 140 °C. The reaction was stirred until deemed complete by disappearance of maltose (TLC control, 2:1 petroleum ether/EtOAc) (approx. 1 h). The reaction mixture was diluted with CH₂Cl₂ (50 mL). The organic mixture was washed with saturated aqueous NaHCO₃ (3 × 100 mL), dried (Na₂SO₄) and concentrated in vacuo to yield the peracetylated D-maltose (23.0 g, quantitative yield, α:β = 1:4.55) as an amorphous white solid.

¹H NMR (400 MHz, CDCl₃) δ 6.24 (d, J = 3.7 Hz, 1H, CH-6), 5.51 (dd, J = 10.2, 8.6 Hz, 1H, CH-4), 5.43 (d, J = 4.0 Hz, 1H, CH-12), 5.38 (dd, J = 10.6, 9.5 Hz, 1H, CH-3), 5.06 (t, J = 9.9 Hz, 1H, CH-10), 4.96 (dd, J = 10.1, 3.7 Hz, 1H, CH-5), 4.87 (dd, J = 10.5, 4.0 Hz, 1H, CH-11), 4.45 (dd, J = 12.4, 2.5 Hz, 1H, CH₃H₆₂), 4.22 (td, J = 12.4, 3.5 Hz, 2H, CH₃H₇ and CH₃H₈), 4.10 (dt, J = 10.0, 2.9 Hz, 1H, CH₃H₇), 4.04 – 4.02 (m, 1H, CH-9), 4.02 – 3.99 (m, 1H, CH-2), 3.94 (dt, J = 10.1, 3.1 Hz, 1H, CH₃H₈), 2.22 (s, 3H, CH₃CO), 2.14 (s, 3H, CH₃CO), 2.10 (s, 3H, CH₃CO), 2.07 (s, 3H, CH₃CO), 2.03 (s, 3H, CH₃CO), 2.02 (s, 3H, CH₃CO), 2.01 (s, 3H, CH₃CO), 1.99 (s, 3H, CH₃CO).

¹³C NMR (101 MHz, CDCl₃) δ 170.69, 170.62, 170.55, 170.09, 170.06, 169.95, 169.51, 169.04, 95.87, 88.93, 72.37, 72.29, 70.20, 70.15, 69.80, 69.34, 68.70, 67.96, 62.48, 61.42, 21.13, 21.04, 20.91, 20.80, 20.73 (2C), 20.71, 20.55.


Data reported here is for the β-anomer and is consistent with data in the literature.
Synthesised according to Mahon et al.² The crude maltose octaacetate (40.8 g, 60.1 mmol, 1.0 eq) was dissolved in CH₂Cl₂ (80 mL). HBr (80 mL, 33% solution in AcOH, 7.7 eq) was added slowly at 0 °C and the reaction stirred at rt until complete (TLC control, 3:1 petroleum ether/EtOAc, approx. 3 h). The reaction mixture was diluted with CH₂Cl₂ (100 mL) and H₂O (100 mL). The layers were separated, and the organic layer was washed with saturated aqueous NaHCO₃ (3 x 200 mL) and then brine (1 x 200 mL). The organic layer was dried (Na₂SO₄) and concentrated in vacuo to give a syrupy yellow oil (43.7 g). The crude bromide was dissolved in CHCl₃ (90 mL) and saturated aqueous NaHCO₃ (90 mL) was added. Tetraethylammonium iodide (20 g, 54.1 mmol, 0.9 eq) was added, followed by NaCN (slow addition, 5 min, 18.00 g, 213.8 mmol, 4.6 eq) and the reaction was stirred at rt for 18 h. The layers were partitioned and the organic layer washed with H₂O (100 mL), saturated aqueous NaHCO₃ (100 mL) and brine (100 mL). The organic layer was dried (MgSO₄) and concentrated in vacuo to give a brown solid. The crude product was recrystallised from a minimum of hot MeOH to give hepta-O-acetyl-1-deoxy-1-azido-β-d-maltopyranose 2a (26.0 g, 39.3 mmol, 65% over two steps) as a white crystalline solid.

³¹H NMR (400 MHz, CDCl₃) δ 5.40 (d, J = 4.0 Hz, 1H, CH-6), 5.34 (dd, J = 10.6, 9.5 Hz, 1H, CH-4), 5.25 (t, J = 8.9 Hz, 1H, CH-10), 5.04 (dd, J = 10.3, 9.5 Hz, 1H, CH-3), 4.84 (dd, J = 10.6, 4.0 Hz, 1H, CH-5), 4.77 (t, J = 8.9 Hz, 1H, CH-11), 4.19 (d, J = 8.7 Hz, 1H, CH-12), 4.50 (dd, J = 12.2, 2.6 Hz, 1H, CH₃-H₃-7), 4.23 (dd, J = 12.3, 4.2, 2.0 Hz, 2H, CH₂-H₅-7 and CH₂-H₅-11), 4.04 (dd, J = 12.5, 2.3 Hz, 1H, CH₂-H₅-1), 4.01 (dd, J = 9.8, 8.7 Hz, 1H, CH-9), 3.98 – 3.89 (m, 1H, CH-2), 3.77 (dd, J = 9.8, 4.5, 2.6 Hz, 1H, CH-8), 2.15 (s, 3H, CH₃-CO), 2.09 (s, 3H, CH₃-CO), 2.04 (s, 3H, CH₃-CO), 2.03 (s, 3H, CH₃-CO), 2.02 (s, 3H), 1.99 (s, 3H, CH₃-CO).

³¹C NMR (101 MHz, CDCl₃) δ 170.67, 170.57, 170.24, 170.09, 169.64, 169.56, 95.81, 87.58, 75.20, 74.36, 72.47, 71.61, 70.11, 69.38, 68.75, 68.07, 62.66, 61.59, 50.96, 50.96, 20.97, 20.90, 20.81, 20.72, 20.69 (3C).


Consistent with data in the literature.²

I-(Hepta-O-acetyl-1-deoxy-β-d-maltopyranosyl)-4-butyl triazole (4a)

Synthesised according to general procedure 1 using maltose azide 1a (1.00 g, 1.51 mmol), CuI (6 mg, 0.032 mmol), DIPEA (10 µL, 0.06 mmol), AcOH (3.5 µL, 0.06 mmol) and 1-hexyne (173 µL, 1.51 mmol). Flash column chromatography (50% EtOAc in hexane) provided I-(hepta-O-acetyl-1-deoxy-β-d-maltopyranosyl)-4-butyl triazole 4a (986 mg, 1.33 mmol, 88%) as a white foam.

³¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 0.8 Hz, 1H, CH-13), 5.86 (d, J = 9.3 Hz, 1H, CH-12), 5.50 – 5.40 (m, 2H, CH-6 and CH-10), 5.43 – 5.28 (m, 2H, CH-4 and CH-11), 5.08 (t, J = 9.9 Hz, 1H, CH-3), 4.88 (dd, J = 10.6, 4.0 Hz, 1H, CH-5), 4.48 (dd, J = 12.4, 2.4 Hz, 1H, CH₂H₅-7), 4.27 (dd, J = 4.3, 3.0 Hz, 1H, CH₂H₅-1), 4.24 (t, J = 3.7 Hz, 1H, CH₂H₅-7), 4.17 – 4.11 (m, 1H, CH-9), 4.07 (dd, J = 12.6, 2.4 Hz, 1H, CH₂H₅-1), 4.00 – 3.94 (m, 2H, CH-2 and CH-8), 2.74 – 2.68 (m, 2H, CH₂-15), 2.13 (s, 3H, CH₃-CO), 2.11 (s, 3H, CH₃-CO), 2.07 (s, 3H, CH₃-CO), 2.04 (s, 3H, CH₃-CO), 2.03 (s, 3H, CH₃-CO), 2.01 (s, 3H, CH₃-CO), 1.64 (p, J = 7.6 Hz, 2H, CH₂-16), 1.39 – 1.32 (m, 2H, CH₂-17), 0.92 (t, J = 7.3 Hz, 3H, CH₃-18).

³¹C NMR (101 MHz, CDCl₃) δ 170.68, 170.59, 170.44, 170.00 (2C), 169.52, 169.36, 149.18, 118.83, 95.97, 85.21, 75.35 (2C), 72.56, 70.94, 70.09, 69.29, 68.83, 67.99, 62.64, 61.52, 31.28, 25.35, 22.27, 20.92, 20.88, 20.79, 20.70 (3C), 20.25, 13.87.

IR (ATR) ν (cm⁻¹) thin film, CH₂Cl₂: 2959 (w), 1748 (s), 1434 (w), 1369 (m), 1225 (s), 1036 (s), 899 (w). 
[a]D²⁵ = +72.8 (c = 0.63, CH₂Cl₂).

1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hexyl triazole (4b)

Synthesised according to general procedure 1 using maltose azide 1a (1.00 g, 1.51 mmol), Cul (6 mg, 0.032 mmol), DIPEA (10 μL, 0.06 mmol), AcOH (3.5 μL, 0.06 mmol) and 1-octyne (230 μL, 1.6 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hexyl triazole 4b (782 mg, 1.05 mmol, 67%) as a white foam.

¹H NMR (400 MHz, CDCl₃) δ 7.42 (s, 1H, CH-13), 5.85 (d, J = 9.3 Hz, 1H, CH-12), 5.48 – 5.42 (m, 2H, CH-6 and CH-10), 5.42 – 5.30 (m, 2H, CH-4 and CH-11), 5.07 (t, J = 9.9 Hz, 1H, CH-3), 4.88 (dd, J = 10.6, 4.0 Hz, 1H, CH-5), 4.48 (dd, J = 12.4, 2.4 Hz, 1H, CH₂₆-7), 4.27 (t, J = 4.0 Hz, 1H, CH₆-8), 1.40 (d, J = 12.4, 2.3 Hz, 1H, CH₆-7), 1.01 – 0.93 (m, 2H, CH₂-2 and CH-8), 2.70 (dd, J = 8.6, 6.7 Hz, 2H, CHβ-15), 2.13 (s, 3H, CH₃CO), 2.11 (s, 3H, CH₃CO), 2.07 (s, 3H, CH₃CO), 2.03 (s, 3H, CH₃CO), 2.01 (s, 3H, CH₃CO), 1.65 (p, J = 7.4 Hz, 2H, CH₂-16), 1.29 (m, 6H, (CH₂)₅-17,18,19,20), 0.90 – 0.85 (m, 3H, CH₃CO), 1.15, 1.09, 0.79, 20.70, 20.92, 20.87, 20.70 (2C), 20.25, 14.18.

Consistent with data in the literature.⁴

1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-octyl triazole (4c)

Synthesised according to general procedure 1 using maltose azide 1a (1.00 g, 1.51 mmol), Cul (6 mg, 0.032 mmol), DIPEA (10 μL, 0.06 mmol), AcOH (3.5 μL, 0.06 mmol) and 1-decyne (290 μL, 1.6 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-octyl triazole 4c (1.20 g, 1.50 mmol, quantitative yield) as a white foam.

¹H NMR (400 MHz, CDCl₃) δ 7.42 (s, 1H, CH-13), 5.86 (d, J = 9.3 Hz, 1H, CH-12), 5.48 – 5.42 (m, 2H, CH-6 and CH-10), 5.35 (m, 2H, CH-4 and CH-11), 5.08 (t, J = 9.8 Hz, 1H, CH-3), 4.88 (dd, J = 10.5, 4.0 Hz, 1H, CH-5), 4.48 (dd, J = 12.4, 2.4 Hz, 1H, CH₂₆-7), 4.27 (t, J = 3.9 Hz, 1H, CH₂₆-1), 4.24 (t, J = 4.0 Hz, 1H, CH₂₆-7), 4.12 (dd, J = 9.8, 8.7 Hz, 1H, CH-9), 4.05 (dd, J = 12.5, 2.3 Hz, 1H, CH₂₆-1), 3.97 (m, 2H, CH₂-2 and CH-8), 2.74 – 2.67 (m, 2H, CH₂-15), 2.13 (s, 3H, CH₃CO), 2.11 (s, 3H, CH₃CO), 2.07 (s, 3H, CH₃CO), 2.03 (s, 3H, CH₃CO), 2.03 (s, 3H, CH₃CO), 1.84 (s, 3H, CH₃CO), 1.65 (m, 2H, CH₂-16), 1.36 – 1.21 (m, 10H, (CH₂)₅-17,18,19,20,21), 0.91 – 0.85 (m, 3H, CH₂-17).

¹C NMR (101 MHz, CDCl₃) δ 170.66, 170.58, 170.41, 169.99 (2C), 169.50, 169.32, 149.22, 118.81, 95.99, 85.23, 75.38, 75.35, 72.62, 70.96, 70.11, 69.32, 68.85, 68.04, 62.66, 61.56, 31.93, 29.38, 29.29, 29.22 (2C), 25.69, 22.74, 20.92, 20.86, 20.78, 20.69, 20.25, 14.18.

HRMS (ESI) m/z calcd for C₃₆H₄₉N₅O₁₇ [M+H]⁺: 800.3448, found: 800.3441.
Consistent with data in the literature.⁴
1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-decyl triazole (4d)

Synthesised according to general procedure 1 using maltose azide 1a (1.00 g, 1.51 mmol), Cul (6 mg, 0.032 mmol), DIPEA (10 µL, 0.06 mmol), AcOH (3.5 µL, 0.06 mmol) and 1-dodecyn (340 µL, 1.6 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-decyl triazole 4d (1.01 g, 1.22 mmol, 81%) as a white foam.

1H NMR (400 MHz, CDCl₃) δ 7.39 (s, 1H, CH-13), 5.83 (d, J = 9.3 Hz, 1H, CH-12), 5.45 – 5.40 (m, 2H, CH-6 and CH-10), 5.39 – 5.26 (m, 2H, CH-4 and CH-11), 5.04 (t, J = 9.9 Hz, 1H, CH-3), 4.85 (dd, J = 10.5, 4.0 Hz, 1H, CH-5), 4.45 (dd, J = 12.4, 2.4 Hz, 1H, CH₂-H₂-7), 4.24 (t, J = 4.1 Hz, 1H, CH₂-H₃-1), 4.21 (t, J = 4.1 Hz, 1H, CH₂-H₇-7), 4.11 (dd, J = 9.8, 8.6 Hz, 1H, CH-9), 4.05 (dd, J = 12.5, 2.4 Hz, 1H, CH₂-H₈-7), 3.95 (ddd, J = 10.0, 4.6, 2.5 Hz, 2H, CH-2 and CH-8), 2.66 (dd, J = 8.6, 6.7 Hz, 2H, CH₂-15), 2.10 (s, 3H, CH₃-CO), 2.08 (s, 3H, CH₃-CO), 2.04 (s, 3H, CH₃-CO), 2.00 (s, 3H, CH₃-CO), 1.98 (s, 3H, CH₃-CO), 1.81 (s, 3H, CH₃-CO), 1.62 (p, J = 7.7 Hz, 2H, CH₂-16), 1.25 (m, 14H, (CH₂)₇-17-23), 0.84 (t, J = 6.7 Hz, 3H, CH₂-24).

13C NMR (101 MHz, CDCl₃) δ 170.65, 170.55, 170.40, 169.98, 169.95, 169.48, 169.30, 149.21, 118.80, 95.98, 85.21, 75.37, 72.61, 70.95, 70.10, 69.30, 68.84, 68.03, 62.65, 61.55, 31.97, 29.66, 29.62, 29.42, 29.38, 29.22 (2C), 25.67, 22.75, 20.90, 20.85, 20.76, 20.67 (2C), 20.23, 14.19.

Consistent with data in the literature.⁴

1-(Hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole (4e)

Synthesised according to general procedure 1 using maltose azide 1a (1.00 g, 1.51 mmol), Cul (6 mg, 0.032 mmol), DIPEA (10 µL, 0.06 mmol), AcOH (3.5 µL, 0.06 mmol) and propargyl alcohol (96 µL, 1.7 mmol). Flash column chromatography (50% EtOAc in hexane) provided 1-(hepta-O-acetyl-1-deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole 4e (755 mg, 1.05 mmol, 70%) as a white solid.

1H NMR (400 MHz, CDCl₃) δ 7.70 (s, 1H, CH-13), 5.89 (d, J = 9.3 Hz, 1H, CH-12), 5.50 – 5.44 (m, 2H, CH-6 and CH-10), 5.41 – 5.31 (m, 2H, CH-4 and CH-11), 5.07 (t, J = 9.9 Hz, 1H, CH-3), 4.88 (dd, J = 10.5, 4.0 Hz, 1H, CH-5), 4.80 (d, J = 5.7 Hz, 2H, CH₂-OH-15), 4.49 (dd, J = 12.5, 2.4 Hz, 1H, CH₂-H₂-7), 4.28 – 4.22 (m, 2H, CH₂-15 and CH₂-H₇-7), 4.14 (m, 1H, CH-9), 4.07 (dd, J = 12.4, 2.3 Hz, 1H, CH₂-H₈-7), 3.98 (m, 2H, CH₂-2 and CH-8), 2.19 (t, J = 6.1 Hz, 1H, CH₂-OH-15), 2.10 (s, 3H, CH₃-CO), 2.11 (s, 3H, CH₃-CO), 2.06 (s, 3H, CH₃-CO), 2.03 (s, 6H, CH₂-CO and CH₂-CO), 2.01 (s, 3H, CH₃-CO), 1.86 (s, 3H, CH₃-CO).

13C NMR (101 MHz, CDCl₃) δ 170.72, 170.64, 170.46, 170.06 (2C), 169.56, 169.43, 120.16, 96.03, 85.41, 75.51, 75.27, 72.48, 71.06, 70.15, 69.35, 68.91, 68.06, 62.59, 61.58, 56.79, 29.73, 20.92, 20.84, 20.74 (3C), 20.37.

1-Deoxy-1-azido-β-D-maltopyranose (1b)

![Chemical structure of 1-Deoxy-1-azido-β-D-maltopyranose (1b)]

Chemical Formula: C_{12}H_{21}N_{3}O_{10}
Molecular Weight: 367.31

1H NMR (400 MHz, D_{2}O) δ 5.37 (d, J = 3.9 Hz, 1H, CH-6), 4.71 (d, J = 8.8 Hz, 1H, CH-12), 3.92 – 3.87 (m, 1H, CH-11), 3.78 (m, J = 12.1, 2.1 Hz, 1H, CH_{2}H_{4}-7), 3.75 (ddd, J = 12.9, 4.3, 2.3 Hz, 2H, CH_{2}H_{5}-1 and CH_{2}H_{5}-7), 3.71 – 3.61 (m, 6H, CH_{2}H_{5}-1 and CH-2 and CH-4 and CH-8 and CH-9 and CH-10), 3.53 (dd, J = 9.9, 3.9 Hz, 1H, CH-5), 3.37 (t, J = 9.4 Hz, 1H, CH-3), 3.25 (t, J = 9.1 Hz, 1H, CH-11).

13C NMR (101 MHz, D_{2}O) δ 99.47, 89.86, 76.39, 76.12, 76.00, 72.73, 72.62 (2C), 71.56, 69.21, 60.42, 60.37.

HRMS (ESI) m/z calcd for C_{12}H_{20}O_{10}N_{3} [M-H]: 366.1154, found: 366.1153.

Consistent with data in the literature.

1-(1-Deoxy-β-D-maltopyranosyl)-4-butyl triazole (3a)

![Chemical structure of 1-(1-Deoxy-β-D-maltopyranosyl)-4-butyl triazole (3a)]

Chemical Formula: C_{18}H_{31}N_{3}O_{10}
Molecular Weight: 449.46

Synthesised according to general procedure 2 using protected surfactant 4a (986 mg, 1.33 mmol) and NaOMe (40 mg, 0.74 mmol). After concentration in vacuo surfactant 1-(1-deoxy-β-D-maltopyranosyl)-4-butyl triazole 3a (422 mg, 0.939 mmol, 71%) was obtained as a hygroscopic, off white foam.

1H NMR (400 MHz, D_{2}O) δ 7.89 (s, 1H, CH-13), 5.62 – 5.58 (m, 1H, CH-12), 5.36 (d, J = 3.9 Hz, 1H, CH-6), 3.90 – 3.85 (m, 2H, CH-11 and CH-4), 3.79 (d, J = 11.6 Hz, 1H, CH_{2}H_{4}-7), 3.78 – 3.70 (m, 5H, CH_{2}H_{5}-7 and CH_{2}H_{5}-1 and CH_{2}H_{5}-1 and CH-2 and CH-10), 3.69 – 3.56 (m, 3H, CH_{4} and CH-8 and CH-9), 3.48 (dd, J = 9.9, 3.9 Hz, 1H, CH-5), 3.31 (t, J = 9.4 Hz, 1H, CH-3), 2.62 (t, J = 7.4 Hz, 2H, CH-15), 1.51 (p, J = 7.5 Hz, 2H, CH_{2}-16), 1.25 – 1.13 (m, 2H, CH_{2}-17), 0.77 (t, J = 7.4 Hz, 3H, CH_{3}-18).

13C NMR (101 MHz, D_{2}O) δ 148.93, 122.17, 99.53, 87.12, 77.36, 76.34, 75.62, 72.74, 72.68, 72.04, 71.60, 69.22, 60.37, 60.30, 30.53, 23.98, 21.27, 12.92.

HRMS (ESI) m/z calcd for C_{18}H_{30}O_{10}N_{3} [M+Na]$: 472.1902, found: 472.1900.

IR (ATR) ν (cm⁻¹) thin film, MeOH: 3350 (s), 2931 (m), 2360 (w), 1653 (w), 1457 (m), 1041 (s).

[a]_{D}^{25} = +73.6 (c = 1.00, MeOH).

1-(1-Deoxy-β-D-maltopyranosyl)-4-hexyl triazole (3b)

![Chemical structure of 1-(1-Deoxy-β-D-maltopyranosyl)-4-hexyl triazole (3b)]

Chemical Formula: C_{20}H_{35}N_{3}O_{10}
Molecular Weight: 477.51

Synthesised according to general procedure 2 using protected surfactant 4b (782 mg, 1.01 mmol) and NaOMe (20 mg, 0.37 mmol). After concentration in vacuo 1-(1-deoxy-β-D-maltopyranosyl)-4-hexyl triazole 3b (405 mg, 0.848 mmol, 84%) was obtained as a hygroscopic, off white foam.
1H NMR (400 MHz, D2O) δ 7.85 (s, 1H, CH-13), 5.60 – 5.55 (m, 1H, CH-12), 5.34 (d, J = 3.9 Hz, 1H, CH-6), 3.92 – 3.54 (m, 10H, CH-11, CH-10, CH2-1, CH2-7, CH2-3, CH4-4, CH-8, CH-9), 3.47 (dd, J = 9.9, 3.8 Hz, 1H, CH-5), 3.31 (t, J = 9.3 Hz, 1H, CH-2), 2.55 (t, J = 7.5 Hz, 2H, CH2-15), 1.49 (t, J = 7.2 Hz, 2H, CH2-16), 1.46 – 1.25 (m, 6H, (CH2)3-17,18,19), 0.71 (d, J = 6.5 Hz, 3H, CH3-20).

13C NMR (101 MHz, D2O) δ 122.14, 99.63, 87.19, 77.37, 76.36, 75.77, 72.78, 72.68, 72.05, 71.64, 69.22, 60.38, 60.31, 30.86, 28.37, 27.98, 24.45, 21.98, 13.40.

HRMS (ESI) m/z calc for C23H19O10N3Na [M+Na]+: 528.2528, found: 528.2525.

Consistent with data in the literature.4

1-(1-Deoxy-β-d-maltopyranosyl)-4-decyl triazole (3d)

Synthesised according to general procedure 2 using protected surfactant 4d (1.09 g, 1.32 mmol) and NaOMe (40 mg, 0.74 mmol). After concentration in vacuo 1-(1-deoxy-β-d-maltopyranosyl)-4-decyl triazole 3d (643 mg, 1.20 mmol, 92%) was obtained as a hygroscopic, off white foam.

1H NMR (400 MHz, MeOD) δ 7.94 (s, 1H, CH-13), 5.64 (d, J = 9.1 Hz, 1H, CH-12), 5.20 (d, J = 3.8 Hz, 1H, CH-6), 3.91 (t, J = 9.1 Hz, 1H, CH-11), 3.83 – 3.77 (m, 4H, CH2-1 and CH2-7 and CH2-11), 3.75 – 3.68 (m, 1H, CH2-1), 3.68 – 3.62 (m, 3H, CH-3 and CH-4 and CH-8), 3.62 – 3.57 (m, 1H, CH-9), 3.44 (dd, J = 9.7, 3.7 Hz, 1H, CH-5), 3.27 (t, J = 9.3 Hz, 1H, CH-2), 2.67 (t, J = 7.6 Hz, 2H, CH2-15), 1.68 – 1.58 (m, 2H, CH2-16), 1.36 – 1.19 (m, 14H, (CH2)3-17-23), 0.88 – 0.83 (m, 3H, CH3-24).

13C NMR (101 MHz, MeOD) δ 122.52, 102.90, 89.34, 80.25, 79.54, 78.23, 75.04, 74.85, 74.15, 73.54, 71.45, 62.70, 61.81, 33.05, 30.73, 30.68, 30.49 (2C), 30.45, 30.26, 26.26, 23.72, 14.44.


Consistent with data in the literature.4
1-(1-Deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole (3e)

Synthesised according to general procedure 2 using protected surfactant 4e (755 mg, 1.05 mmol) and NaOMe (20 mg, 0.37 mmol). After concentration in vacuo 1-(1-deoxy-β-D-maltopyranosyl)-4-hydroxymethyl triazole 3e (338 mg, 0.798 mmol, 76%) was obtained as a hygroscopic, off white foam.

$^1$H NMR (400 MHz, MeOD) δ 8.13 (s, 1H, CH-13), 5.61 (d, $J = 9.1$ Hz, 1H, CH-12), 5.22 (d, $J = 3.8$ Hz, 1H, CH-6), 4.68 (bs, 2H, CH$_2$OH-15), 3.92 (t, $J = 9.1$ Hz, 1H, CH-11), 3.89 – 3.78 (m, 4H, CH$_2$H$_5$-1 and CH$_2$-7 and CH-11), 3.74 (t, $J = 9.0$ Hz, 1H, CH$_2$H$_5$-1), 3.70 – 3.65 (m, 2H, CH-3 and CH-8), 3.65 – 3.57 (m, 2H, CH$_2$ and CH$_2$-9), 3.45 (dd, $J = 9.7$, 3.8 Hz, 1H, CH-5), 3.26 – 3.23 (m, 1H, CH$_2$OH-15).

$^{13}$C NMR (101 MHz, MeOD) δ 147.58, 122.05, 101.55, 88.10, 78.87, 78.23, 76.81, 73.67, 73.49, 72.78, 72.23, 70.08, 61.33, 60.43, 54.95.

HRMS (ESI) m/z calcd for C$_{15}$H$_{25}$N$_3$O$_{11}$Na [M+Na]$^+$: 446.1381, found: 446.1379.
**NMR Spectra of Synthesized Compounds**

Figure S1: $^1$H NMR spectrum of 4a in CDCl$_3$.

Figure S2: $^{13}$C NMR spectrum of 4a in CDCl$_3$. 
Figure S3: $^1$H NMR spectrum of 3a in MeOD.

Figure S4: $^{13}$C NMR spectrum of 3a in MeOD.
Figure S5: $^1$H NMR spectrum of 3b in D$_2$O.

Figure S6: $^{13}$C NMR spectrum of 3b in MeOD.
Figure S7: $^1$H NMR spectrum of 3c in MeOD.

Figure S8: $^{13}$C NMR spectrum of 3c in MeOD.
Figure S9: $^1$H NMR spectrum of 3d in MeOD.

Figure S10: $^{13}$C NMR spectrum of 3d in MeOD.
Figure S11: $^1$H NMR spectrum of 3e in MeOD.

Figure S12: $^{13}$C NMR spectrum of 3e in MeOD.
## DOSY Data

<table>
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<th>Entry</th>
<th>Species present</th>
<th>$D$ (surfactant 3c)</th>
<th>$D$ (1-decyne)</th>
<th>$D$ (ligand)</th>
<th>$D$ (azide 2b)</th>
<th>$D$ (TMS)</th>
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<td>Surfactant 3c (2 mM)</td>
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<td>-</td>
<td>-</td>
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<td>B</td>
<td>Surfactant 3c (24 mM)</td>
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<td>-</td>
<td>-</td>
<td>1.2</td>
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<td>ND</td>
<td>-</td>
<td>-</td>
<td>4.1</td>
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<tr>
<td>D</td>
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<td>E</td>
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<td>F</td>
<td>[Cu(Lig A)$_2$]$^+$ (6.8 mM)</td>
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<td>-</td>
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<td>-</td>
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<td>G</td>
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<td>8.0</td>
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Table S1: Diffusion coefficients extracted from DOSY experiments. The diffusion coefficients were recorded for all reaction components present in the system during the synthesis of 3c in water. $D$ values reported in $10^{-10}$ m$^2$s$^{-1}$. A decrease in the diffusion coefficient in the presence of surfactant 3c above the CMC indicates a strong association with the micelle. ND indicates that the diffusion coefficient could not be extracted because of the limited solubility of the compound in water. The Morris’ correlation$^5$ for small molecules predicts a MW of 516 g/mol for entry A and a MW of 339.5 g/mol for entry I. These predicted values are in close agreement with the actual molecular weights considering the model used for the predictions.
Fluorimetry Data

The critical micelle concentrations of the surfactants was determined with a fluorimetric procedure reported by London et al.\textsuperscript{5} The fluorescent molecule 1,6-diphenyl-1,3,5-hexatriene (DPH) emits a large increase in fluorescence when present in an apolar environment such as the micellar interior when a surfactant exceeds the critical micelle concentration. This property was used to determine the unknown CMC of various surfactant compounds. Fluorescence measurements were made with an Edinburgh Instruments Spectrofluorometer FS5 model. Instrument control and data processing were performed using Fluoracle software. The excitation wavelength was 358 nm and the emission wavelength was 430 nm. The excitation and emission slits were set at bandwidths of 1 nm. In all experiments, 1 cm path length quartz cuvettes were used. The protocol for CMC determination was as follows: 3 µL of 5 mM DPH dissolved in THF was added to various amounts of surfactant dissolved in a total volume of 3 ml of aqueous solution. The intercept of two trendlines, through the data points before and after the spike in fluorescence, was taken as the CMC.

Note: No increase in fluorescence was observed for surfactant 3a indicating that a 4-carbon aliphatic tail is likely too short to induce aggregation.

\begin{align*}
y &= 594.51x + 877.5 \quad R^2 = 0.99387 \\
y &= 8397x - 457120 \quad R^2 = 0.98411 \\
x &= 58.7 \text{ mM}
\end{align*}

\textbf{Figure S13}: a CMC of 58.7 mM was extracted from a plot of fluorescence measurements at various concentrations for surfactant 3b.
**Figure S14:** a CMC of 2.86 mM was extracted from a plot of fluorescence measurements at various concentrations for surfactant 3c.

**Figure S15:** a CMC of 0.37 mM was extracted from a plot of fluorescence measurements at various concentrations for surfactant 3d.
**DLS data**

Samples were prepared by dissolving an amount of surfactant in 1 mL of ultrapure Milli-Q water at a concentration above the CMC. This solution was filtered through a 0.2 µm PTFE filter right before performing a DLS measurement. Note: DLS results for surfactant 3a showed no aggregation around 10 nm only around 100 nm which can likely be attributed to noise. This is in agreement with the fluorimetry data and indicates that a 4-carbon aliphatic tail is likely too short to induce aggregation.

<table>
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<td>Dispersant Name: Water</td>
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<tr>
<td>Record Number: 11</td>
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<td>Material Rt: 1.45</td>
<td>Viscosity (CP): 0.8872</td>
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<tr>
<td>Material Absorption: 0.001</td>
<td>Measurement Date and Time: 08 February 2017 10:39 am</td>
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</table>

| Temperature (°C): 25.0 | Duration Used (s): 70 |
| Count Rate (Kcps): 246.0 | Measurement Position (mm): 3.00 |
| Cell Description: Disposable micro cuvette (40µl) | Attenuator: 9 |

| Z-Average (d.nm): 6.744 | Size (d.nm): Peak 1: 7.168 93.4 2.824 |
| PDI: 0.238 | % Intensity: Peak 2: 3533 6.6 1226 |
| Intercept: 0.758 | St Dev (d.nm): Peak 3: 0.000 0.0 0.000 |
| Result quality: Good |

**Figure S16:** The size distribution by intensity of a DLS measurement of surfactant 3b at 52 mM indicates micelle aggregates with a size of around 7 nm.
Figure S17: The size distribution by intensity of a DLS measurement of surfactant 3c at 24 mM indicates micelle aggregates with a size of around 7.5 nm.
Figure S18: The size distribution by intensity of a DLS measurement of surfactant 3d at 5 mM indicates micelle aggregates with a size range distributed around 15 nm.
Kinetic Data

$^1$H NMR spectra of key water soluble reaction components in D$_2$O

Figure S19: $^1$H NMR spectrum of 1-deoxy-1-azido-$\beta$-D-maltopyranose 1b in D$_2$O.

Figure S20: $^1$H NMR spectrum of 1-(1-deoxy-$\beta$-D-maltopyranosyl)-4-octyl triazole 3c in D$_2$O.
Figure S21: $^1$H NMR spectrum of $O$-phenylenediamine in D$_2$O.
**Stacked Spectra of Kinetic $^1$H NMR Experiments**

**Figure S22:** Stacked $^1$H NMR spectra of the unseeded reaction of 1b with 2c and ligand OPD. Data plotted in Figure 3, triangles.

**Figure S23:** Stacked $^1$H NMR spectra of the seeded reaction of 1b with 2c and ligand OPD seeded with 3c. Data plotted in Figure 3, squares.
Control experiments

**Figure S24:** Reaction kinetics for CuAAC of O-phenylenediamine (OPD) in tBuOH/D$_2$O (1:1). Complete conversion in 1.5 hours and no lag period is observed. The unseeded reaction still appears to have a sigmoidal rate profile. Seeding the reaction with 22 mM of product removes the sigmoidal shape but the total reaction time remains the same.

**Figure S25:** Kinetic profile for seeded reactions using 1 and 2c. Profile with black circles are under normal conditions when seeding with 22 mM of 3c. Purple crosses are when seeding with 22 mM of 3c but the concentration of starting materials is lowered by 22 mM by adding 1b (113 mg, 0.309 mmol) and 2c (129 mg, 0.717 mmol) instead of the standard conditions.
Figure S26: Kinetic profiles for reactions between 1 and 2a to form 3a showing inhibition when seeding with higher concentrations. Green circles represent the unseeded reaction. Red squares are when seeded with 50 mM of 3a. Blue triangles are when seeded with 80 mM of 3e. Orange squares are when seeded with 80 mM of 3a. Seeding with a non-surfactant such as 3e still appears to lead to inhibition indicating that the maltose-triazole moiety might be inhibitive binding to the copper catalyst at higher concentrations.

Figure S27: Kinetic profiles for reactions between 1 and 2b to form 3b showing a rate acceleration when seeded below the CMC. Red squares are the unseeded conditions while blue diamonds are when seeded with 36 mM of 3b.
References