**Electronic Supplementary Information**

# Sequential dynamic structuralisation by *in situ* production of supramolecular building blocks

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## Electronic Supplementary Information Index

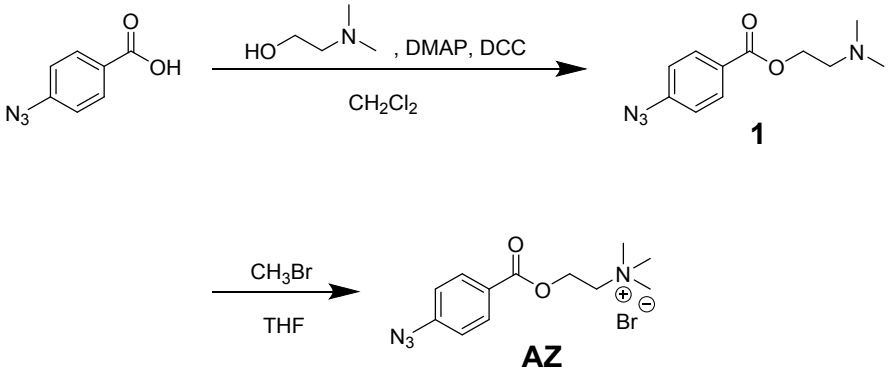
## Experimental procedures

### General

All commercially-available reagents and solvents were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), Wako Pure Chemical Industries, Ltd. (Osaka, Japan), or Kanto Chemical Co., Inc. (Tokyo, Japan), and were used as received without further purification. $^1$H NMR spectra were recorded on ECA-500 and ESC-400 Fourier Transform Spectrometers (JEOL Ltd., Tokyo, Japan) at 500 and 400 MHz, respectively. Chemical shifts were calculated in parts per million (ppm) using tetramethylsilane as a standard (0 ppm). High resolution electrospray ionization mass spectrometry (HR-ESI-MS) spectrum was measured by were recorded on a LCT-Premier (Waters Corp., Milford, Massachusetts, USA).

### Synthesis of the hydrophilic azide (AZ)

The hydrophilic azide **AZ** was synthesised according to Scheme S1. Full experimental details are provided in the following subsections.




**Scheme S1.** Synthesis of the hydrophilic azide (**AZ**).

*Synthesis of 4-azidebenzoyloxyethylene-N,N-dimethylamine (**1**)*

To a mixture of 4-azidobenzoic acid (3.26 g, 20.0 mmol), 4-dimethylaminopyridine (489 mg, 4.00 mmol), and 2-(dimethylamino) ethanol (2.40 mL, 24.0 mmol) in dichloromethane (30 mL), a solution of *N,N*′-dicyclohexylcarbodiimide (4.95 g, 24.0 mmol) in dichloromethane (10 mL) was added. The reaction mixture was stirred for 24 h at room temperature (24–26 °C). After this time, the solvent was removed *in vacuo*, and the residue was purified by silica gel column chromatography (chloroform/methanol, 4:1 (v/v), $R_f$ = 0.76) to give **1** as a yellow liquid (3.98 g, 85%).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 8.10–7.98 (2H, m), 7.12–7.00 (2H, m), 4.41 (2H, t, $J$ = 5.8 Hz), 2.70 (2H, t, $J$ = 5.8 Hz), 2.33 (6H, s). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 165.84, 144.81, 131.56, 126.83, 118.87, 63.17, 57.93, 45.94. HRMS (*m/z*): calcd for $C_{11}H_{15}N_4O_2$ 235.1195 $[M - Br]^+$; found 235.1206 $[M - Br]^+$.

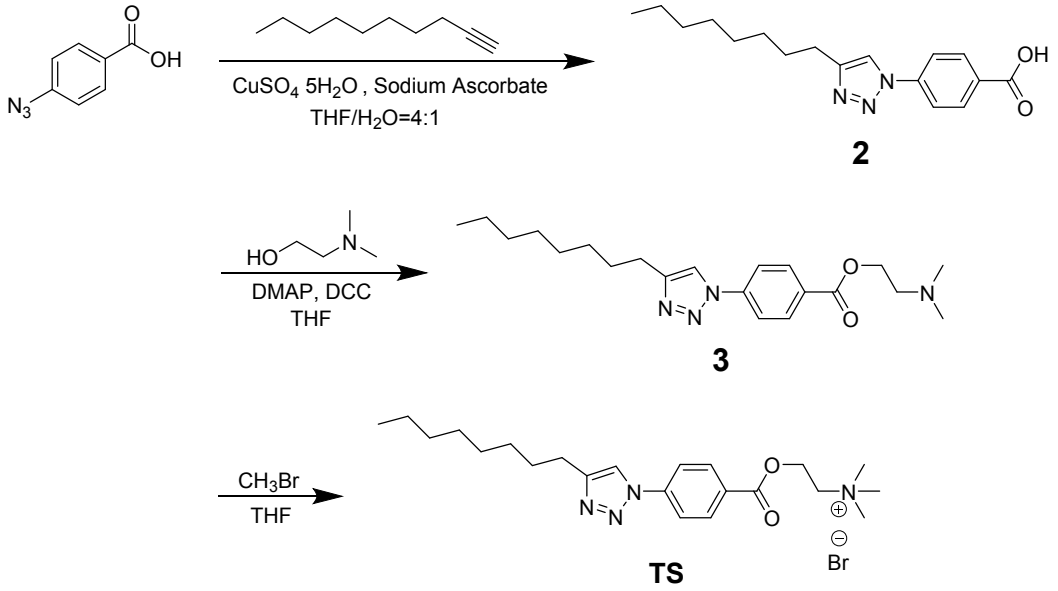
*Synthesis of 4-azidebenzoyloxyethylene-N,N,N-trimethylammonium bromide (**AZ**)*

To a solution of **1** (3.98 g, 17.0 mmol) in tetrahydrofuran (THF, 40 mL), 2 mol/L bromomethane in THF (10.2 mL, 20.4 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and then for 4 h at room temperature (24–26 °C). Following evaporation of the solvent, the residue was purified by precipitation using methanol (10 mL) and ethyl acetate (50 mL) to give **AZ** as a pale yellow solid (4.48 g, 80 %).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm): 8.09–7.96 (2H, m), 7.35–7.21 (2H, m), 4.70

(2H, s), 3.93–3.74 (2H, m), 3.20 (9H, s). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ (ppm): 164.42, 144.76, 131.31, 125.59, 119.43, 63.87, 58.68, 52.88. HRMS (*m/z*): calcd for $C_{12}H_{17}N_4O_2$ 249.1352 $[M - Br]^+$; found 249.1343 $[M - Br]^+$. M.p.: 178–182 $^oC$.

**Synthesis of the surface-active compound containing a 1,2,3-triazole moiety (TS)**




**Scheme S2.** Synthesis of the surface-active compound containing a 1,2,3-triazole moiety (**TS**).

*Synthesis of 4-(octyl triazole)benzoic acid (**2**)*

To a mixture of 4-azidobenzoic acid (3.26 g, 20.0 mmol) and 1-decyne (4.34 mL, 24.0 mmol) in THF (80 mL), an aqueous solution (9.96 mL) of $CuSO_4$•$5H_2O$ (99.8 mg, 0.400 mmol) and an aqueous solution (10 mL) of sodium ascorbate (792 mg, 4.00

mmol) were added. The reaction mixture was then stirred for 24 h at room temperature (24–26 °C). After removal of the volatile components *in vacuo*, the residue was extracted with ethyl acetate (100 mL) and washed three times with brine (100 mL), then dried using $MgSO_4$. The obtained filtrate was evaporated to give the crude product, which was purified by recrystallisation in THF (150 mL) to give **2** as a white solid (5.06 g, 84 %).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm): 8.71 (1H, s), 8.20–8.07 (2H, m), 8.10–7.96 (2H, m), 2.71 (2H, t, $J$ = 7.6 Hz), 1.74–1.58 (2H, m), 1.50–1.17 (m, 10H), 0.86 (3H, t, $J$ = 6.9 Hz). HRMS (*m/z*): calcd for $C_{17}H_{24}N_3O_2$ 302.1869 $[M + H]^+$; found 302.1864 $[M + H]^+$. M.p.: 244–248 °C.

*Synthesis of 4-(octyl triazole)benzoyloxyethelene-N,N,N-trimethylammonium bromide (**TS**)*

To a mixture of **2** (6.00 g, 19.9 mmol), 4-dimethylaminopyridine (486 mg, 3.98 mmol), and 2-dimethylaminoethanol (2.39 mL, 23.9 mmol) in THF (60 mL), a solution of *N,N'*-dicyclohexylcarbodiimide (4.93 g, 23.9 mmol) in dichloromethane (35 mL) was added. The reaction mixture was then stirred for 24 h at room temperature (24–26 °C) and filtered to remove the precipitate. Following evaporation of the filtrate, the residue was purified by silica gel column chromatography (chloroform/methanol, 10:1 (v/v)) to provide the crude 4-(octyl triazole)benzoyloxyethylene-*N,N*-dimethylamine (**3**) as a pale yellow solid (3.33 g). The molecular structure of **3** was confirmed by $^1$H NMR analysis in DMSO-$d_6$.

To a solution of **3** (crude product containing other trace compounds) (3.33 g) in

THF (50 mL), 2 mol/L bromomethane in THF (5.35 mL, 10.7 mmol) was added dropwise at 0 °C. The reaction mixture was then stirred for 15 min at 0 °C and subsequently for 4 h at room temperature (24–26 °C). Following evaporation of the solvent, the residue was purified by recrystallisation in chloroform (10 mL) to obtain **TS** as a white solid (3.35 g, 36% over the two-step reaction).

$^{1}$H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm): 8.75 (1H, s), 8.27–8.12 (2H, m), 8.16–8.03 (2H, m), 4.75 (2H, s), 3.96–3.78 (2H, m), 3.23 (9H, s), 2.72 (2H, t, $J$ = 7.6 Hz), 1.78–1.60 (2H, m), 1.50–1.12 (10H, m), 0.86 (3H, t, $J$ = 7.0 Hz). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ (ppm): 164.85, 149.18, 140.72, 131.75, 129.11, 120.83, 120.09, 64.43, 59.51, 53.48, 31.81, 29.28, 29.24, 29.15, 29.11, 25.49, 22.63, 14.48. HRMS (*m/z*): calcd for $C_{22}H_{35}N_4O_2$ 387.2760 $[M - Br]^+$; found 387.2726 $[M - Br]^+$. M.p.: 186–191 °C.

**Observation of sequential structuralisation**

The hydrophobic alkyne, 1-decyne (174 μmol) was dispersed in an aqueous solution (1.2 mL) of **AZ** (174 μmol) containing $CuSO_4$•$5H_2O$ (34.8 μmol) and sodium ascorbate (87.0 μmol) over 5min using a vortex mixer. The resulting mixture was then stirred for 3 h at room temperature (23–25 °C) prior to the addition of $PdCl_2$ (20.1 mg, 11.3 μmol) to the dispersion. Following sonication for 5 min, the mixture was visually observed with stirring over 24 h at room temperature (23–25 °C).

**Microscopic observations**

1-Decyne (174 μmol) was added to an aqueous solution (1.2 mL) containing **AZ** (174

μmol), $CuSO_4$•$5H_2O$ (34.8 μmol), and sodium ascorbate (87.0 μmol). After shaking for 5 min using a test tube mixer, the resulting dispersion was stirred for 0–180 min at room temperature (24–26 °C). The obtained sample dispersion was then encased in a thin glass-chamber (15×15×0.28 mm; Frame Seal Chamber, MJ Research Inc., Waltham) and the micrometre-sized oil droplets were observed at room temperature (24–26 °C) using a phase-contrast microscope (BX51, Olympus, Tokyo, Japan) equipped with a CCD camera (DP22, Olympus, Tokyo, Japan).

**Solubilisation tests for determination of the CMC**

The critical micelle concentration (CMC) of **TS** was measured by the solubilisation method using 1-(*o*-tolylazo)-2-naphthol as a hydrophobic dye. 1-(*o*-Tolylazo)-2-naphthol (5 mg) was added to an aqueous solution of **TS** (1–10 mM), and after sonicating for 5 min, the dispersions were stirred for 1 h at room temperature (24–26 °C). The resulting precipitate was then removed by filtration and the UV-Vis absorbance of the transparent filtrate was measured three times at 500 nm for each **TS** concentration (UV-1800, Shimadzu, Tokyo, Japan).

**UV-Vis measurements**

Palladium(II) chloride (0–60 mol% relative to **TS**) was added to a $D_2O$ solution of **TS** (40 mM, 1.2 mL). After sonicating for 5 min, the mixture was stirred for 24 h at room temperature (24–26 °C). All samples were diluted 5-fold using $D_2O$, and the absorbances of the solutions were measured at room temperature by UV-Vis

spectrometer (UV-1800, Shimadzu, Tokyo, Japan).

## Figures

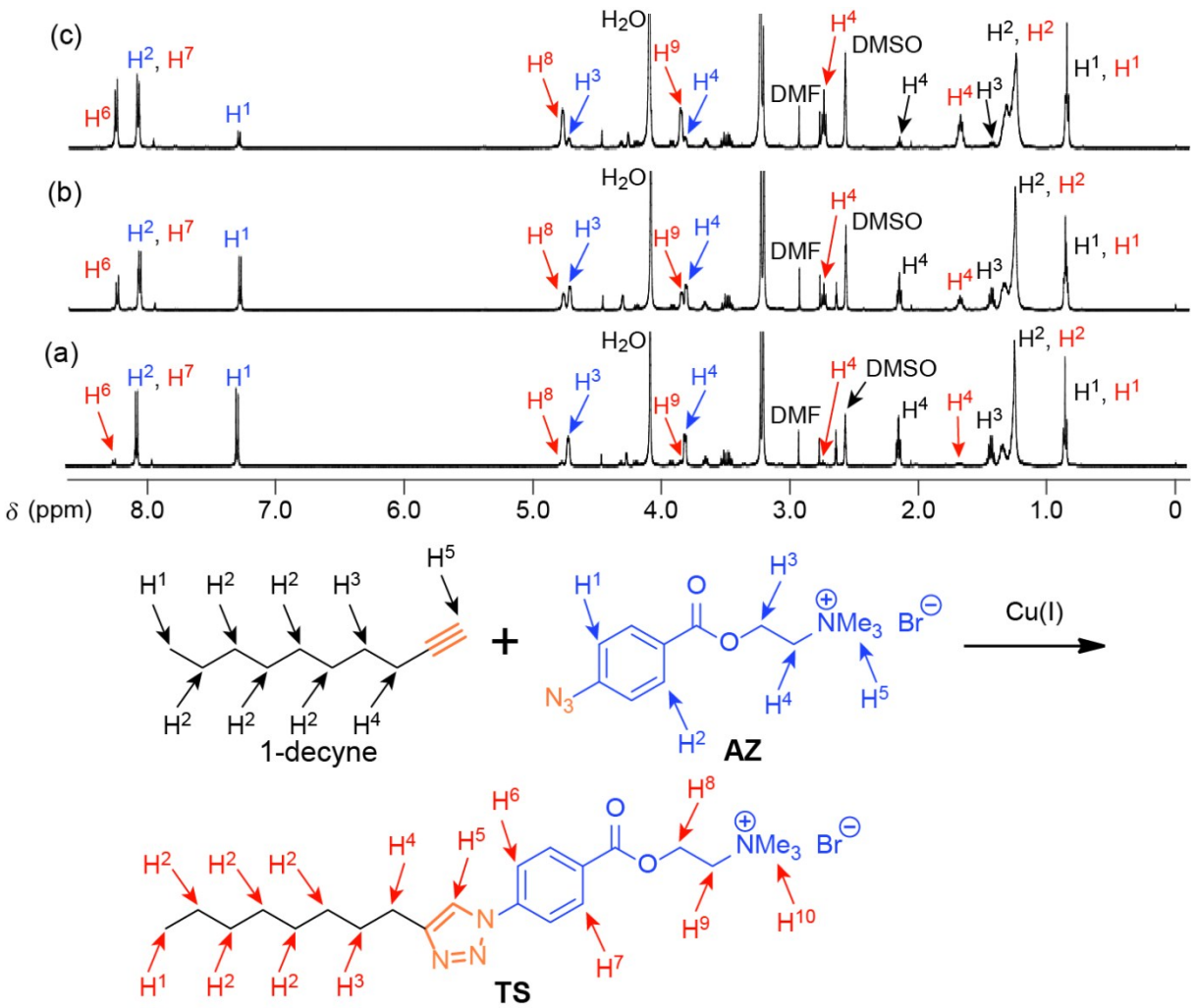



**Fig. S1** $^{1}$H NMR spectra ($D_2O$ and DMSO-mixed solutions with 2/7 (vol/vol)) containing 1-decyne (174 μmol), **AZ** (174 μmol), copper(II) sulfate (34.8 μmol) and sodium ascorbate (87 μmol) after (a) 5 min, (b) 35 min, and (c) 65 min at room temperature (24–26 °C). The quantity of **TS** generated in the sample solution was calculated from the ratio of the integration of the benzene methine proton ($H^6$) of **TS** ($\delta$ 8.22 ppm) and the methyl protons of DMF ($\delta$ 2.92 ppm).

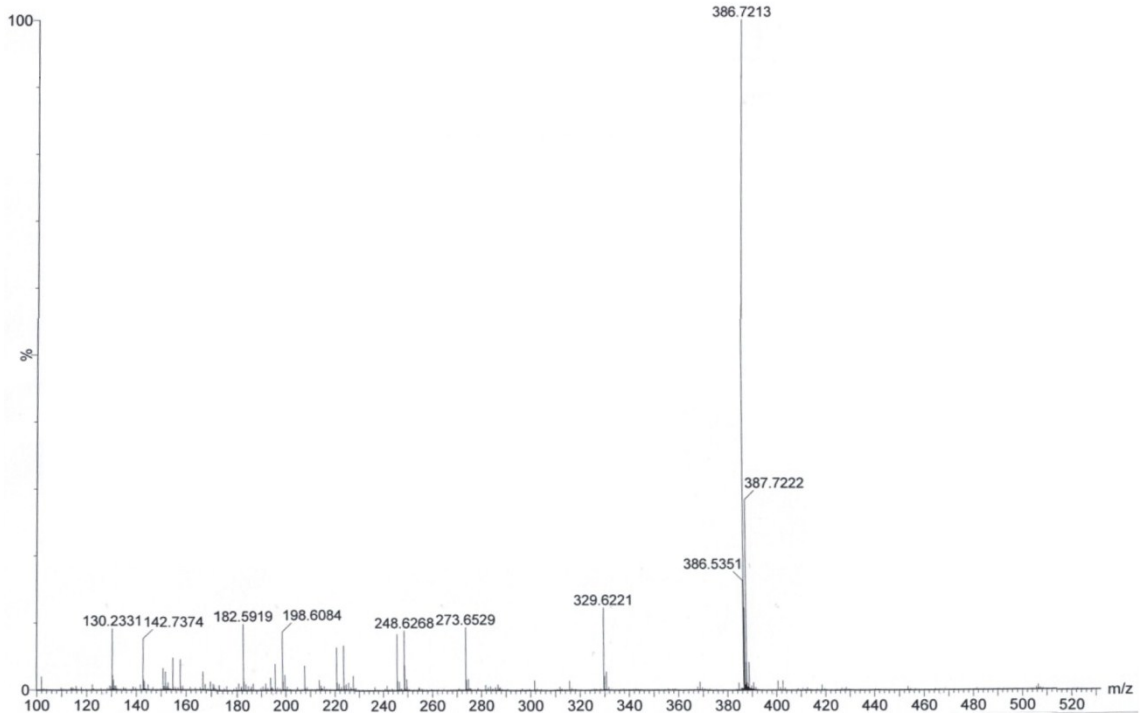



**Fig. S2** Electrospray ionisation-mass spectrum (in acetonitrile) of the reaction mixture containing 1-decyne and **AZ** in the presence of copper(I) at room temperature (24–26 $^{o}$C) after 24 h. While the surface-active **TS** was identified as a product, complex formation between **TS** and copper(I) was not confirmed. HRMS (*m/z*): calcd for $C_{22}H_{35}N_4O_2$ 387.2760 $[M - Br]^+$; found 386.7213 $[M - Br]^+$.

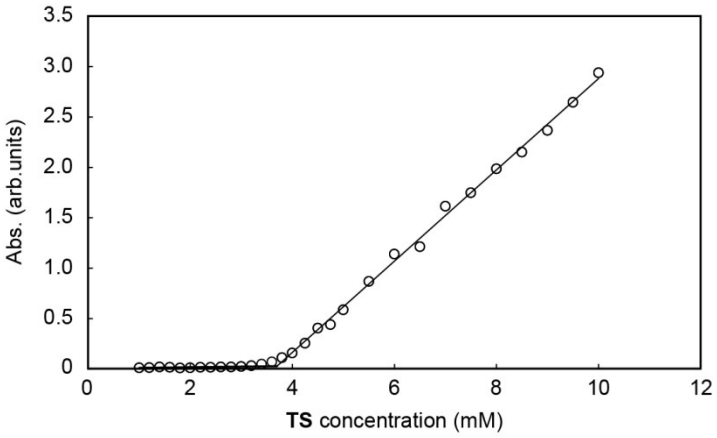



**Fig. S3** Absorbance at 500 nm of the transparent solutions containing various concentrations of **TS** after filtration of the precipitated hydrophobic dye, 1-(*o*-tolylazo)-2-naphthol, at room temperature (24–26 °C). Based on these measurements, the CMC value of **TS** was determined to be 3.7 mM.

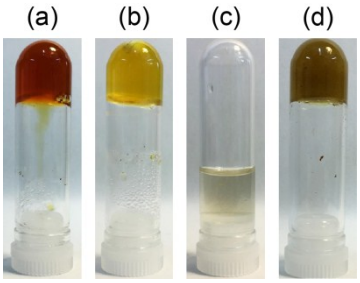



**Fig. S4** Transition from a gel to a sol. Photographic images of (a) the hydrogel in the absence of **EDA**, (b) the hydrogel in the presence of 60 mM **EDA**, (c) the sol in the presence of 120 mM **EDA**, and (d) the regenerated hydrogel after the addition of further $PdCl_2$.

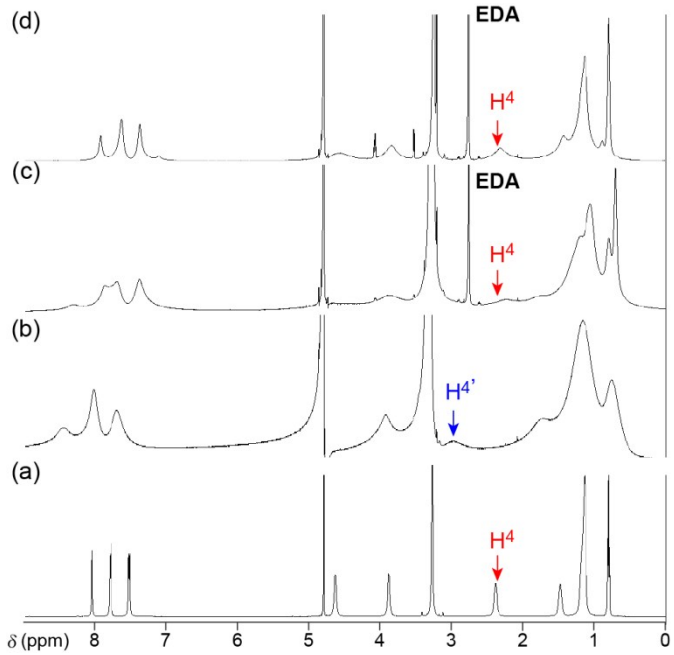



**Fig. S5** $^{1}$H NMR spectra of the $D_2O$ solutions containing $PdCl_2$, **TS**, and **EDA** in the following molar ratios: (a) 0/100/0, (b) 50/100/0, (c) 50/100/50, and (d) 50/100/100. $PdCl_2$ (10.6 mg, $PdCl_2$/**TS** = 50/100) was added to a $D_2O$ solution of **TS** (100 mM, 1.2 mL). After sonicating for 5 min, the mixture was stirred for 24 h at room temperature (24–26 °C). The sample changed from colourless to orange due to the coordination of **TS** to palladium(II). To the solution of the **TS**-palladium(II) complex, **EDA** (4.01 μL or 8.02 μL, $PdCl_2$/**TS**/**EDA** molar ratio = 50/100/50 or 50/100/100) was added and the mixture was stirred for 24 h at room temperature (24–26 °C). In the presence of 100 mM **EDA**, 19% of the **TS** was hydrolysed to produce the corresponding carboxylic acid and alcohol bearing a quaternary ammonium group. However, no $H^{4'}$ signal corresponding to the complex was observed, suggesting that gelation was caused by the formation of complexes between **TS** and palladium(II).

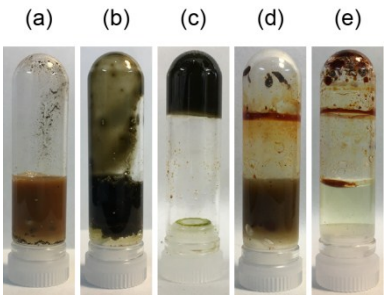



**Fig. S6** Photographic images of the dynamic structuralisation in the presence of both copper(I) and palladium(II). The dispersion composed of 1-decyne, **AZ**, $CuSO_4$, sodium ascorbate, and $PdCl_2$ was stirred at room temperature (24–26 $^oC$) for (a) 0 h, (b) 16 h, and (c) 24 h. Also shown are the dispersions (d) in the absence of $CuSO_4$ and (e) in the absence of sodium ascorbate after 24 h.