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Supplementary information

Formations of reactive aerogels and their Reactivity in aqueous media. Wettability induces hydrophobic vs. hydrophilic selectivity.

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Materials.

The gel forming compounds **1**, **2** and **3** have been synthesized according published procedures.[1] Pure samples of products **4** and **6** have been prepared as standards by Huisgen addition in solution as previously reported. The synthesis of **5** has been done by reacting solid **2** with $Me(OCH_2CH_2)_3N_3$ in water and is described below.

Reactions with solid 2 and 3.

A heterogeneous mixture of alkyne **2** (55 mg, 79 μmol) and $MeO(EO)_3N_3$ (32.3 mg, 170 μmol, 2.1 equiv.) and water (5 ml) is degassed and stirred under Ar at 25 °C. Sodium ascorbate (3.1 mg, 16 μmol, 0.2 equiv.) and $CuSO_4$•$5H_2O$ (2 mg, 8 μmol, 0.1 équiv.) are sequentially added to the mixture. The suspension is stirred for 72 h and filtered. The obtained solid is dissolved in CH_2Cl_2, dried ($MgSO_4$,) and concentrated under vacuum. The solid residue is chromatographed (MeOH/ CH_2Cl_2: 4/96 eluent) to yield afford pure 4 as a white solid (70 mg, yield 80 %) : ^{1}H RMN (400 MHz, $CDCl_3$): δ [ppm] 7.58 (s broad, 1 H, $NH_{triazole}$), 7.13 (d, 2H, *J* = 6.48 Hz, C2-H, C6-H), 6.59 (s, 1H, H_4), 5.54 (s broad, 2 H, NH amide), 4.54 (s broad, 2H, $N_{triazole}CH_2$), 4.28 (t, 2H, *J* = 6.48 Hz, $COOCH_2$), 3.96 (t, 4H, *J* = 6.16 Hz, $ArOCH_2$), 3.89 (t, 2H, *J* = 4.6 Hz, $N_{triazole}CH_2CH_2$), 3.60 (m, 8H, $O(CH_2)_2O(CH_2)_2O$), 3.53 (s broad, 2H, $CH_2C_{triazole}$), 3.37 (s, 3H, OCH_3), 3.23 (m, 4H, $CONHCH_2$), 2.70 (s broad, 2H, $C_{triazole}CH_2CH_2$), 2.18 (t, 4H, *J* = 7.32 Hz, $NHCOCH_2$), 1.79-1.71 (m, 10 H, $ArOCH_2CH_2$, $COOCH_2CH_2$, $NHCOCH_2CH_2$), 1.49-1.25 (32 H, CH_2), 0.87 (t, 6 H, *J* = 7.00 Hz, CH_2CH_3).^{13}C NMR (100 MHz, CDCl3) : δ [ppm] 173.08

(CONH), 166.82 (COO), 160.35 (C3, C5), 132.61 (C1), 131.4 ($CH_{triazole}$), 108.03 (C2, C6), 106.58 (C4), 72.28 (CH_2OMe), 70.85 ($O(CH_2)_2O(CH_2)_2O$), 69.00 ($N_{triazole}CH_2CH_2O$), 68.32 (ArOCH2), 65.61 (ArCOOCH2), 59.36 (OCH_3), 39.86 ($N_{triazole}CH_2$), 37.06 (CONHCH2), 31.79 (NHCOCH2), 29.96 ($CH_3CH_2CH_2$), 29.65, 29.24, 26.92, 26.09, 25.80, 22.86 (CH_2CH_3), 14.32 (CH_2CH_3) ; IR (ATR-diamond) ν_{max} : 3301 (br, ν NH), 3072 (ν CH_{ar}), 2952 (ν_{as}, CH_3), 2925 (ν_{as}, CH_2), 2870 (ν_s, CH_3), 2855 (ν_s, CH_2), 1725 (s, ArCOO, νCO), 1715 (s), 1638 (s, amide I), 1612 (ν -N=N-), 1599 (ν C=C), 1545 (s, δ NH, amide II band), 1465 (s, CH_2 scissor), 1452 (s), 1383, 1346 (s), 1299 (ν C-N, amide III and triazole),1249, 1239, 1227, 1202 (w),1175 (s, ν N-N), 1158, 1109 (s), 1068, 1051, 960, 893, 875, 846, 834, 793, 763, 724, 676 cm^{-1}; HRMS (ESI+) m/z 894.6476 (MLi^+, calcd pour $C_{49}H_{85}N_5O_9Li$: 894.65073). (Anal. C, 66.45 ; H 9.73 ; N, 7.80. Calcd for $C_{49}H_{85}N_5O_9$: C, 66.26 ; H 9.65 ; N, 7.88).

Similar procedure was used with **2** and $C_{10}H_{21}N_3$ to yield pure **5** (54 % yield) and identical to the previously described material,[1] and with **3** and propargylic acid to yield **6** (quantitative yield), identical to previously described material.[2]

Formation of aerogels.

An organogel prepared from **1**, **2** or **3** (ca 1 cc, 2 % in C_6H_{12}) is inserted in a steel mesh basket and the basket is placed in the critical point drying chamber. The chamber is filled with liquid CO_2 at -10°C at a pressure higher than 73 atm. After 10 min part of the liquid CO_2 is removed and replaced by fresh one and this step is repeated a second time. The chamber is heated at 45 °C for 15 min, which transform all the liquid CO_2 into supercritical fluid. CO_2 is then let leaked slowly out of the chamber until the pressure reaches room pressure.

Reaction with aerogels.

An aerogel of **2** (about 1 cc, 20 mg) was put in a mesh basket and immersed in water ; the water was degassed and put under Ar. The azide, ascorbic acid and $CuSO_4$•$5H_20$ were added sequentially and let under Ar for 48 hrs. The macroscopic aspect of the aerogel was unchanged. A small piece of of the aerogel is analyzed by SEM and the rest is dissolved in CH_2Cl_2, died ($MgSO_4$) and analyzed by TLC and NMR, and compared with pure sample of **4** or **5**. Weighted amounts of the crudes (about 5 mg) were dissolved in 3 mL THF and volumes of 200 μL of the solution were injected on a chromatography set-up composed of a pump (Shimadzu DGU-20A) operating at a flow of 1 ml/min, a column PL (granulometry 10 μ), a differential refractometer from Shimadzu (RID6A) and a UV detector from Shimadzu (5SPD 10 Avp). The pure starting materials and final products (**4** or **5**) were injected separately in order to identify the elution times and to calculate the molar extinction (ε) and refraction increment (dn/dc). The concentrations in the crude were measured from the areas from both the RI and UV traces. The results were in good agreement for both detections. The ratio of final compound/reactants was also in good agreement with NMR.

SEM.

The aerogels were coated with gold and observed with a JEOL JSM-6700F field emission microscope.

References.

1. Nguyen, T.-T.-T.; Simon, F.-X.; Schmutz, M.; Mésini, P. J., *Chem. Commun.* **2009**, 3457-3459.
2. Nguyen, T.-T.-T.; Simon, F.-X.; Combet, J.; Schmutz, M.; Mésini, P. J., *Soft Matter* **2011,** 7, 1121-1128.