Supplementary Material (ESI) for Soft Matter

pH and Cation-Responsive Supramolecular Gels Formed by Cyclodextrin Amines in DMSO

Wei Deng, David H. Thompson*

Supporting information

Measurements

^{1}H NMR spectra were recorded on a 300 MHz VARIAN INOVA 300 NMR spectrometer at 30 ^{o}C. Chemical shifts were referenced to the residual protonated solvent peak. FT-IR measurements were performed on a JASCO FT/IR-410 spectrometer using KBr as the dispersant. Elemental analyses were recorded on an Elementar Vario EL-III instrument. Gels were prepared by sonicating with a Heat Systems-Ultrasonic W350 unit fitted with a 1/8" microtip.

Materials

All solvents were of reagent grade, purchased from commercial sources, and used without further purification, except DMF and toluene, which were dried over CaH_2 under N_2, filtered and distilled under reduced pressure. α-CD, β-CD, NaOH, I_2, Ph_3P and *p*-toluenesulfonyl chloride were obtained from Aldrich-Sigma, Inc.

Syntheses

Hepta-6-amino-β-CD (1) and hepta-6-iodo-β-CD (5),

These compounds were prepared as previously reported.[1]

Sythesis of Hepta-6-hydrazyl-β-CD (2). Hepta-6-Iodo-β-CD (**5**) (1.0 g, 0.5 mmol) was dissolved in 50 mL anhydrous hydrazine, then stirred at 60 °C under an atmosphere of N_2 for 24 h. The solution was then concentrated under reduced pressure to a few milliliters before pouring into acetone (300 ml). A fine white precipitate was formed and gathered by filtration. The precipitate was washed with acetone and dried under vacuum to yield a stable white powder. Yield = 0.52g (54%). ^{1}H NMR (270 MHz, D_2O, δ): 5.13-5.09 (s, 7H, C1H of CD), 4.28-4.02 (b, 7H, NH), 4.02-3.22 (m, 42H, C2H, C3H, C4H, C5H and C6H of CD), 2.00-1.80 (b, 14H, NH_2). ^{13}C NMR (75 MHz, D_2O, δ): 101.9 (C(1) of β-CD), 81.6 (C(4) of β-CD), 73.0 (C(3) of β-CD), 72.4 (C(2) of β-CD), 72.0 (C(5) of β-CD), 45.9 (C(6) of β-CD).

Sythesis of Hepta-6-(2'-hydroxyethyl)amino-β-CD (3) This was prepared as described for Compound **2**, except that ethanolamine was used as nucleophile instead of hydrazine. Yield = 0.51g (70%). ^{1}H NMR (270 MHz, D_2O, δ): 5.10-5.05 (s, 7H, C1H of CD), 4.00-3.85 (m, 14H, C3H and C5H of CD) 3.75-3.42 (m, 28H, C2H, C4H and C6H of CD), 3.01-2.82 (m, 2H, ethanolamine CH_2O), 2.78-2.72 (t, 2H, ethanolamine CH_2N). ^{13}C NMR (75 MHz, D_2O, δ): 104.1 (C(1) of β-CD), 84.6 (C(4) of β-CD), 74.0 (C(3) of β-CD), 73.2 (C(2) of β-CD), 72.5 (C(5) of β-CD), 67.5(CH_2-OH), 58.7 (C(6) of β-CD), 57.5 (CH_2-N).

Sythesis of Hepta-6-(2'-aminoethyl)amino-β-CD (4) This was prepared as described for Compound **2**, except that ethylenediamine was used as nucleophile instead of hydrazine. Yield = 0.47g (66%). ^{1}H NMR (270 MHz, D_2O, δ): 5.21-5.15 (s, 7H, C1H of CD), 4.10-3.82 (m, 21H, C3H and C5H of CD and NH) 3.77-3.54 (m, 28H, C2H, C4H and C6H of CD), 3.21-2.97 (m, 2H, N1-CH_2), 2.97-2.88 (t, 2H, N2-CH_2), 2.68-2.56 (b, 14H, NH_2). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 102.0 (C(1) of β-CD), 82.3 (C(4) of β-CD), 73.2 (C(3) of β-CD), 72.5 (C(2) of β-CD), 72.1 (C(5) of β-CD), 55.2 (C(6) of β-CD), 53.9 (NH-CH_2), 45.2(CH_2-NH_2).

Gelation procedure. Two methods were used to prepare gels – bulk heating and ultrasonic dispersion.

Heating method: The desired amount of gelator in the corresponding solvent was heated in a screw-capped tube for 1 hour. It then was cooled to 20°C and stored for several days to allow gelation to ensue.

Ultrasonic method: A 1/8" microtip probe sonicator was used. The desired amount of gelator was

suspended in the corresponding solvent and the sample sonicated in pulsed mode (50% duty cycle) at 50 Watts for 10 minutes to disperse the sample, followed by continuous sonication for 5 minutes. The sample then cooled to 20°C, leading to the formation of a gel state.

Figure S1. Photograph of gel-sol transition upon addition of urea (concentration of **1** was 2 wt%).

References

(1) (a) B. B. Ghera, F. Perret, A. Baudouin, A. W. Coleman and H. Parrot-Lopez *New J. Chem.*, 2007, **31**, 1899–1906. (b) P. R. Ashton, R. Koniger, and J. F. Stoddart *J. Org. Chem.,* 1996, **61**, 903-908