Chirality Transfer based on Dynamic Covalent Chemistry: from Small chiral Molecule to Supramolecule

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Experimental section.

Materials.

3-Pyridinecarboxaldehyde (97%), 1-bromododecane(98%), dimethyl L-(+)-tartrate (98%), dimethyl D-(-)-tartrate (98%), hydrazine hydrate (98%), CDCl3 (99.96%), DMSO (99.96%) and D2O (99.96%) were purchased from J&K Scientific Ltd. Diethyl ether, cyclohexane and CH3OH were obtained from Shanghai Chemical Co. All the materials were used as received without any purification. Deionized water was used throughout all the experiments.

Synthesis of 3-formyl-N-dodecylpyridinium bromide (C12BAD).1

3-Pyridinecarboxaldehyde (1.5 g, 14.0 mmol) was dissolved in 1-bromododecane (15 mL) and then the mixture refluxed with stirring for 48
h under a nitrogen atmosphere. After the reaction, the reaction mixture was cooled to room temperature. An excess of 1-bromododecane was washed with cyclohexane (3×15 mL) and the crude product was purified by diethyl ether (2×15 mL) and dried to give blue-gray solid product (C$_{12}$BAD). $^1$H NMR (300 MHz, D$_2$O): δH/ppm: 0.72 (t, 3H), 1.13-1.22 (m, 20H), 1.91 (t, 2H), 4.52 (t, 2H), 7.99 (t, 1H), 8.54 (d, 1H), 8.74 (d, 1H), 8.87 (s, 1H).

**Synthesis of 2, 3-dihydroxysuccinohydrazide (TDH).**
Dimethyl L-(+)-tartrate (98%)/dimethyl D-(-)-tartrate (98%) (2.0 g, 5.6 mmol) was dissolved in MeOH (30 mL). Hydrazine hydrate (1.405 g, 28 mmol, 2.5 equiv) was added and the reaction stirred at room temperature for 2 h. Then, the reaction was refluxed with stirring for 12 h under a nitrogen atmosphere. After the reaction, some solid separated out and the resulting white solid washed with cold MeOH (2×10 mL) and diethyl ether (2×10 mL). $^1$H NMR (300 MHz, DMSO): δH/ppm: 8.78 (s, 2H), 5.36 (d, 2H), 4.26 (s, 2H), 4.23 (s, 2H).

**Characterization.**

$^1$H NMR measurements. $^1$H NMR spectra were run on a Bruker Advance 300 spectrometer equipped with a pulse field gradient module (Z-axis) using a 5 mm BBO probe. The instrument was operated at a frequency of 300.13 MHz at 25 ± 0.1 °C.

**UV-Vis Spectroscopy.** The UV-Vis spectroscopy measurements of a series of samples were carried out on a UV-4100 spectrophotometer using
10 mm path length quartz cell. The scan rate for each measurement was 120 nm·min$^{-1}$.

**FTIR spectra.** FTIR spectra were obtained using a PerkinElmer Spectrum Two FTIR Spectrometer in the range of 4000-450 cm$^{-1}$.

**Rheological measurements.** Rheological measurements were performed on a Haake RS6000 rheometer using a cone-plate system (C35/1°Ti L07116, diameter: 35 mm, cone angle: 1°). All measurements were carried out at 25.0 °C by using a Circulator HAAKE DC10 cyclic water bath (Karlsruhe, Germany).

**Field-emission scanning electron microscopy (FE-SEM).** A small volume of gel sample was placed on a silica wafer, and most of the colloid gel was removed using small forceps to form a thin film. The wafers were freeze-dried in a vacuum extractor for 1 day. Then the silica wafers were observed on a JEOL JSM-6700F FE-SEM.

**Atomic Force Microscopy (AFM).** AFM images were recorded under ambient conditions by using a Veeco Nanoscope Multimode III SPM operating in tapping mode.

**Small angle X-ray scattering (SAXS).** SAXS was performed using an Anton-Paar SAXSessmc2 system with Ni-filtered Cu Ka radiation (0.154 nm) operating at 50 kV and 40 mA. The distance between the sample and the detector was 264.5 mm. The measured exposure time was 600 s.

**Circular dichroism (CD).** Circular dichroism (CD) measurements were
performed on a JASCO J-810 spectropolarimeter, which was flushed with constant nitrogen flow during operation to purge the ozone generated by the light source of the instrument. The spectra were smoothed by using the noise-reducing option in the operating software of the instrument. Three scans were averaged per spectrum to improve the signal-to-noise ratio. Wavelength scans were recorded at 1 nm intervals from 700 to 200 nm. The samples were determined using a 0.1 mm path length quartz cuvette at 25 °C.

**Additional Results**

![ESI-MS profiles](example.png)

**Fig. S1** ESI-MS profiles of the mixing solutions of two building blocks C\textsubscript{12}BAD and TDH (a) C\textsubscript{12}BAD: TDH = 1: 1; (b) C\textsubscript{12}BAD: TDH = 2: 1.

![UV-Vis curves](example.png)

**Fig. S2** (a) UV-Vis curves of the aqueous solutions of TDH, C\textsubscript{12}BAD and A at pH=4 (the concentration of: $C_{TDH}=1\times10^{-4}$ M; $C_{C12BAD}$, $C_A$ and $C_B = 5\times10^{-5}$ M); (b, c)
Variation in absorbance of the A solution at pH <2 and \( \approx 4 \) with time increasing. It is noting that, the adsorption intensity of the peaks became lower (Fig. S2c) than that of the original A (1:1), which is probably caused by dilution and ionic strength effects.³

**Fig. S3** Thermal stimuli-responsive gel-sol-gel transition of chiral supramolecular hydrogels (a) C\(_{12}\)BAD: TDH = 1: 1; (b) C\(_{12}\)BAD: TDH = 2: 1.

**Fig. S4** AFM images of hydrogels fabricated by C\(_{12}\)BAD and TDH with different molar
ratios. (a, a') $C_{12}\text{BAD}/D\text{-TDH} = 1 : 1$; (b, b') $C_{12}\text{BAD}/L\text{-TDH} = 2 : 1$; (c, c') $C_{12}\text{BAD}/D\text{-TDH} = 2 : 1$

**Fig. S5** CD spectra of the hydrogels of after mixing building blocks of D 2:1-1 ($C_{12}\text{BAD}: D\text{-TDH} = 2:1$) and L 2:1-1 ($C_{12}\text{BAD}: L\text{-TDH} = 2:1$) 36 hours; D 2:1-2 ($C_{12}\text{BAD}: D\text{-TDH} = 2:1$) and L 2:1-2 ($C_{12}\text{BAD}: L\text{-TDH} = 2:1$) 60 hours.

**Fig. S6** Dynamic oscillatory stress sweep and frequency sweep of hydrogels with different configurations of dihydrazide (D/L-TDH) and different molar ratios (1 : 1 and 2 : 1; concentration fixed at 30 mM), respectively.
Fig. S7 SAXS patterns for samples formed by C12BAD/D-TDH (a) and C12BAD/L-TDH (b) with different molar ratios.

Reference

