Electronic Supplementary Information for

Ammonia-Modulated Reversible Gel-Solution Phase Transition and Fluorescence Switch for a Salicylhydrazide-Based Metal-Organic Gel

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1. EXPERIMENTAL SECTION

1.1 Synthesis of H$_6$L

**4,4’-oxydibenzoyl chloride**: 4,4’-oxybisbenzoic acid (2.58 g, 10 mmol) was refluxed with SOCl$_2$ (20 mL) and DMF (N,N-dimethylformamide, 40 μL) for 9 hours. After reaction, excess solvent and reactants were removed with rotary evaporation, leaving light yellow solid of 4,4’-oxydibenzoyl chloride.

**4,4’-oxybis(N’-(2-hydroxybenzoyl)benzohydrazide) (H$_6$L)**: 10 mL DMF solution of 4,4’-oxydibenzoyl chloride (2.95 g, 10 mmol) and 10 mL DMF solution of Et$_3$N (triethylamine, 1.4 mL) and salicylhydrazide (3.65 g, 24 mmol) were mixed with ice-bath. The mixture was warmed to room temperature and refluxed for 9 h. The solvent was removed with reduced pressure distillation to get the crude product as a brown solid. After washed with ethanol for several times, white product was obtained with ~80% yield. The product was characterized by $^1$H-NMR and mass spectrum. $^1$H NMR (400 MHz,DMSO-d$_6$, ppm, Fig. S1): δH 11.95 (s, 2 H, OH), 10.71 (s, 4 H, NH), 8.01 (d, J = 35.4 Hz, 4 H, Ar-H), 7.94 (d, J = 35.4 Hz, 2 H, Ar-H), 7.48 (t, J = 7.2 Hz, 2 H, Ar-H), 7.25 (d, J = 8.7 Hz, 4 H, Ar-H), 6.99 (q, 4 H, Ar-H). ESI-MS (Fig. S2): 525.1426(Exp.), 526.1488(Calc. for H$_6$L). Elemental analysis: N: 10.24% (Cald. 10.64%), C: 62.74% (Cald. 63.87%), H: 4.23% (Cald. 4.21%).

Scheme S1. The synthesis of H$_6$L.

1.2 Preparation of Gel2/1

**Fresh gel for Gel2/1**: Typical preparation is to mix two 0.5 mL DMF solution that contains Zn(CH$_3$COO)$_2$·9H$_2$O (0.0250 mmol, 0.0055g) and H$_6$L (0.0125 mmol, 0.0066g) separately together. Ultrasonic oscillate the mixture to make a uniform solution. The solution is allowed to stand for two days to obtain fresh gel of Gel2/1.

**Xerogel for Gel2/1**: The xerogel was prepared by leaving the fresh Gel2/1 in the air to
dry naturally for 1 week.

1.3 Dye adsorption tests

Four kinds of dye molecules were chosen to study the adsorption capacity of the xerogel for Gel2/1: methyl violet, methylene blue, phenyl red and methylene orange. The dyes were dissolved in water to make the aqueous dye solution in $1.67 \times 10^{-4}$ mol·L$^{-1}$. 2.5 mg xerogel was added into 1 mL dye solution, mixing for 1 hour by ultrasonic oscillation to run the adsorption test. The resultant was centrifuged to obtain upper clear liquid which is recorded by UV-Vis absorption spectra to evaluate the adsorption capacity.

1.4 Cycling experiments of the fluorescence sensing for NH$_3$

The fluorescence sensing for NH$_3$ along with phase transformation experiment detail is as follows. An open glass bottle that contains 1 mL fresh gel of Gel2/1 (labeled as Gel$^0$) was placed in a sealed vessel that contains ammonia aqueous for a few minutes. The ammonia vapor was allowed to diffuse into the glass bottle to react with the fresh gel inside. The transformation from gel to solution would be observed during the diffusion. The resultant was light yellow solution (labeled as Solution$^{C1}$). If the above procedure was conducted in dark room under UV light, the fluorescent gel could be observed to transform to dark solution along with the ammonia diffusion. After the phase transformation was completed, the light yellow solution was allowed to stand open for two days to evaporate the ammonia gas. Transparent gel phase would be obtained (labeled as Gel$^{C1}$). Cycling experiments for this phase transformation was conducted repeatedly for 7 times. The corresponding samples of Gel$^0$, Solution$^{C1-C7}$, Gel$^{C1-C7}$ were tested by fluorescence spectrometer to assess their fluorescence sensing behavior.

1.5 Measurement details.

Rheological measurements were performed on a stress controlled rheometer (AR2000ex, TA instruments) with a cone-plate sensor. The cone is made of standard ETC steel with a diameter of 20 mm and a cone angle of 2 degree. The gap between the center of the cone and the plate is 50 mm. Each sample was kept for 5 min on the plate to reach equilibrium before testing. The $^1$H NMR spectrum was recorded on BRUKER AVANCE III 400 MHz spectrometer. High Resolution Mass spectrum was carried out by using Thermo Fisher Scientific 1100 LC/MSD Trap XCT spectrometer. MALDI-MS (Matrix Assisted Laser
Desorption Ionization mass) spectrum was taken on MicroFlex MALDI-TOF-MS spectrometer with Micro SCOUT Plate (MSP) for 96 sample points, a cassette N₂ laser, laser wavelength at 337 nm and frequency at 60 Hz, and the matrix molecule is 2,5-dihydroxy benzoic acid (DHB). IR, UV-Vis absorption and fluorescence spectroscopy were recorded by FT-IR spectrum 2000 (4000–400 cm⁻¹), Perkin-Elemer Lambda 900 and Edinburgh FL-FS 920 TCSPC spectrometer, respectively. The photos of photoluminescence were taken under a WD-9403E hand-held ultraviolet lamp. The FESEM and TEM images were obtained on Nova NanoSEM 230 Microscopy and TECNAI G2F20 Field Emission Transmission Electron Microscopy, respectively. KQ-100E ultrasonic cleaner was used for ultrasonic oscillation. The elemental analysis was performed on Vario EL Cube. The thermal analysis was recorded on STA 448C TGA/DSC 3+ HT/1600 (25-1000 °C, Ar, 10 °C/min).
2. Spectral data of the H<sub>6</sub>L and Gel2/1

2.1 <sup>1</sup>H NMR and mass spectra of H<sub>6</sub>L

Fig. S1 the <sup>1</sup>H NMR of H<sub>6</sub>L (DMSO-d<sub>6</sub>).

Fig. S2 Mass spectrum for the solution of H<sub>6</sub>L in negative ion mode, with the range of 490.00-800.00. The m/z signals 525.1426, could be attributed to H<sub>5</sub>L<sup>−</sup> (Calc. 526.1488).
Fig. S3 Thermal analysis of H₆L.
2.2 IR spectrum of Gel2/1

Fig. S4 IR spectra of zinc acetate, H₆L and the xerogel of Gel2/1, left: 4000-400 cm⁻¹, right: 1800-1200 cm⁻¹.
2.3 Dynamic rheology of Gel2/1

Fig. S5 a) Strain sweep at a frequency of 1 rad·s⁻¹ of Gel2/1. b) Frequency sweep of G' and G'' for Gel2/1 at a strain of 0.01%.
2.4 UV-Vis adsorption spectra of Gel2/1 dealt with ammonia vapor

Fig. S6 The UV-Vis adsorption spectra for three different cases as follows: (1) Gel\(^0\): the original Gel2/1; (2) Solution\(^{c1}\): the gel to solution phase transition after ammonia treatment for 5 min; (3) the intermediate soft colloidal sol phase for the Gel2/1 treated with ammonia vapor for 1 min.
2.5 HRMS-ESI spectra

Fig. S7 The HRMS-ESI spectrum for the solution after complete ammonia treatment, negative mode, 600-3000.

Fig. S8 The HRMS-ESI spectrum for the gel solution (5 min after mixing reactants) in acetonitrile, positive mode, 700-3000.
Fig. S9 The HRMS-ESI spectrum for the gel solution (5 min after mixing reactants) in acetonitrile, negative mode, 700-3000.