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# **Electronic Supplementary Information**

for

# Stimutateous Enhancement of Mechanical Strength and Luminescence Performance in Double Network Supramolecular Hydrogels

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#### **Materials and Methods**

All chemicals were commercially available unless noted otherwise. Compound **3** was prepared according to the reported reference.<sup>1</sup> Rheological tests of hydrogels were carried out by using an Anton Paar model MCR-301 rheometer, with a 25 mm diameter parallel plate attached to a transducer. The steady-state luminescence spectra were measured on an Edinburgh Instruments FS920P near-infrared spectrometer, with a 450 W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines mm<sup>-1</sup>), an emission monochromator (600 lines mm<sup>-1</sup>), a semiconductor cooled Hamamatsu RMP928 photomultiplier tube. Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer in the range of 400–4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> (16 scans were collected). Light transmittance were recorded on a Varian Cary Model 50 UV/vis spectrophotometer. Tensile properties were determined according to CMT6104. The measurements were carried out at a crosshead speed of 100 mm/min.

#### **Preparation of Compound 2:**

Compound **3** (239 mg, 1 mmol), allyl bromide (240 mg, 2 mmol), and K<sub>2</sub>CO<sub>3</sub> (690 mg, 5 mmol) were added into 30 mL anhydrous acetone with stirring. The mixture was heated at 70 °C for 24 h under N<sub>2</sub> atmosphere. After cooled, the reaction mixture was filtered and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub>. Then the filtrate was concentrated under reduced pressure. The residue was dissolved by CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and then washed twice with saturated NaCl solution. Then the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by column chromatography over silica gel (eluent: 2:1 PE/EtOAc), compound **2** was obtained as white powder in 92% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (s, 2H), 6.05 (m, 1H), 5.43 (ddd, J = 13.9, 11.7, 1.2 Hz, 2H), 4.71 (d, J = 5.4 Hz, 2H).), 4.48 (q, J = 7.2 Hz, 4H), 1.46 (t, J = 7.1 Hz, 6H). HRMS [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>5</sub><sup>+</sup> 280.1185; found: 280.1183; Anal Cald for C<sub>14</sub>H<sub>17</sub>NO<sub>5</sub>: C, 60.21; H, 6.14; N, 5.02; Found: C, 60.18; H, 6.54; N, 4.97.

### **Preparation of Compound L:**

Compound **2** (280 mg, 1 mmol) was dissolved in THF 20 mL, then an aqueous solution of KOH (224 mg, 4 mmol) 2 mL was added. The reaction mixture was stirred at 50 °C for 2 h, acidified with concentrated HCl to pH 4. The obtained white precipitate was collected by centrifugalization and washed with cold water for 2 times to afford the desired product in 80% yield. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  7.74 (s, 2H), 6.02 (ddd, J = 22.7, 10.7, 5.5 Hz, 1H), 5.46 – 5.30 (m, 2H), 4.89 (d, J = 5.4 Hz, 2H). MS [M - H]<sup>-</sup> calcd for C<sub>10</sub>H<sub>8</sub>NO<sub>5</sub><sup>-</sup> 222.0; found: 221.7; Anal Cald for C<sub>10</sub>H<sub>9</sub>NO<sub>5</sub>: C, 53.82; H, 4.06; N, 6.28; Found: C, 53.18; H, 4.54; N, 6.07.

#### **Preparation of Ln**·L<sub>3</sub>:

L (200 mg, 0.09 mmol) was dissolved in 10 mL ethanol and ethanol solution of TbCl<sub>3</sub> (0.1 mol/L, 0.3 mL) was added with stirring. The mixture was then heated at 80 °C overnight. After cooled, the reaction mixture was poured into 100 mL diethyl ether, the obtained pale yellow precipitate was collected by centrifugalization to afford the desired product in 90% yield. **Eu**·L<sub>3</sub> was prepared according to the similar procedure.

#### **Preparation of DN Supramolecular Hydrogel:**

Acrylamide (712 mg, 10 mmol, 0.54 mL) was dissolved in water (1.46 ml) to prepare acrylamide stock solution. Then, **Eu·L**<sub>3</sub> (116mg, 0.125mmol) was added. Next, the photoinitiator, lithium acylphosphinate<sup>2</sup> (LAP) (26.8 mg, 0.086 mmol) was added to 1 mL borate buffer (0.1M, PH = 10.2). The two solutions were bubbled with nitrogen for 10 min to eliminate the dissolved oxygen, then mixed and added to PVA solution (89 mg in 2 mL H<sub>2</sub>O) and further bubbled with nitrogen for 10 min. The oxygen-free solution was irradiated with ultraviolet light (8 mW/cm<sup>2</sup>, wavelength 365 nm) for 1 h to ensure complete gelation. The obtained hydrogel was stored at -20°C for 24 h and then warmed up for testing. Tb<sup>3+</sup> containing supramolecular hydrogel was prepared according to similar method. Hydrogels with varying Ln·L<sub>3</sub> concentration were prepared by changing *C*[Ln·L<sub>3</sub>] and *C*[AAM] to keep *C*[mon] at 2.025 M (*C*[mon]= *C*[Ln·L<sub>3</sub>] + *C*[AAM]).

## **Estimation of Coordinated Water Number:**

The coordinated water number in the first coordination sphere of  $Tb^{3+}$  ion was estimated by using equation 1:<sup>3</sup>

$$q = 5.0(\tau_{H}^{-1} - \tau_{D}^{-1} - 0.06)$$
 1

The coordinated water number in the first coordination sphere of  $Eu^{3+}$  ion was estimated by using equation 2:<sup>4</sup>

$$q = 1.2(\tau_{H}^{-1} - \tau_{D}^{-1} - 0.25)$$

Where, q represents the coordinated water molecules,  $\tau_H$  and  $\tau_D$  is the luminescence lifetime measured in H<sub>2</sub>O and D<sub>2</sub>O, respectively.



Figure S1. Synthetic route of allyl modified PDA ligand L



Figure S2. <sup>1</sup>H NMR spectrum of compound 2 (CDCl<sub>3</sub>, 400 MHz, 25 °C).



Figure S3. The ESI-HRMS spectrum of compound 2.



Figure S4.  $^{1}$ H NMR spectrum of L (D<sub>2</sub>O, 400 MHz, 25 °C).



Figure S5. The MS spectrum of L.



Figure S6. FT-IR spectrum of L, Tb·L<sub>3</sub> and Eu·L<sub>3</sub>.

Compare to individual L, in the FT-IR spectrum of both  $\mathbf{Tb}\cdot\mathbf{L}_3$  and  $\mathbf{Eu}\cdot\mathbf{L}_3$ , the absorption bands at 1720 cm<sup>-1</sup> assigned to C=O stretching vibrations of PDA disappeared, indicating to the coordination of PDA with  $\mathrm{Ln}^{3+}$  ion (Figure S6)<sup>5</sup>



Figure S7. (A) Emission changes of L ( $1.0 \times 10^{-5}$  M) upon addition of 0-0.5 equiv of EuCl<sub>3</sub> in H<sub>2</sub>O at 25 °C.(B) The emission intensity change at 615 nm versus Eu<sup>3+</sup>/L molar ratio. ( $\lambda$  ex= 280 nm)

The coordination stoichiometry between **L** and lanthanide ions was further identified by luminescence titration in H<sub>2</sub>O. As shown in Figure S7, upon stepwise addition of Eu<sup>3+</sup> the characteristic emission bands of Eu<sup>3+</sup> corresponding to  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J = 0–4) transitions with sharp peaks at 582, 594, 615, 650, and 694 nm, appeared and increased gradually, the curve of emission intensity of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  at 615 nm shows an inflection point at a molar ratio of 0.33 (Figure S7B), corresponding to a 3:1 L/Eu<sup>3+</sup> coordination complex<sup>6</sup>.<sup>8</sup> Tb·L<sub>3</sub> was prepared and characterized according to the same method.



**Figure S8**. UV–Vis transmittance spectrum of Eu<sup>3+</sup> containing DN supramolecular hydrogel (A) and the corresponding thin film (B).



Figure S9. The tensile stress-strain curves of the luminescent DN supramolecular hydrogels with varying  $Eu^{3+}/Tb^{3+}$  molar ratio and the self-healed hydrogel (C[VA] = 0.4 M,  $C_{[AAM]} = 2.0$  M,  $C[Ln \cdot L_3] = 25$  mM).



**Figure S10**. The normalized excitation (left) and emission (right) luminescence spectra of Tb based (A) and Eu based (B) supramolecular hydrogel.

We subsequently investigated the photoluminescent properties of our supramolecular hydrogels in detail. The excitation spectrum of  $Tb^{3+}$  containing hydrogel was obtained by monitoring the  ${}^{5}D_{4} \rightarrow {}^{7}F_{2}$  transition at 543 nm. A broad band in the range of 250-350 nm ascribed to the absorption of PDA ligand was observed, suggesting occurrence of the PDA to  $Tb^{3+}$  energy transfer (Figure S10A). The corresponding emission spectrum consists of four sharp emission lines at 490, 543, 582, and 621 nm, assigned to the transitions from the  ${}^{5}D_{4}$ level to the  ${}^{7}F_{J}$  levels (J =6, 5, 4, 3), of which, the  ${}^{5}D_{4} \rightarrow {}^{7}F_{2}$  line as the prominent one and responsible for the green emission. From the excitation spectrum of Eu<sup>3+</sup> containing hydrogel, we can also observe the ligand broad absorption ranged from 250 nm to 350 nm. The emission spectrum of Eu<sup>3+</sup> containing supramolecular hydrogel displayed five sharp peaks at 582, 594, 615, 650, and 694 nm, which could be assigned to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J = 0–4) transitions. Among the peaks, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  band at 615 nm is predominantly responsible for the luminescence emission in red (Figure S10B).



**Figure S11.** The DN supramolecular hydrogels pictures under 254 nm UV lamp illumination corresponding to Figure 3A and 3B.



**Figure S12.**The decay curves of  $\mathbf{Tb} \cdot \mathbf{L}_3$  dissolved in D<sub>2</sub>O (A) and H<sub>2</sub>O (B),  $\mathbf{Tb}^{3+}$  containing DN supramolecular hydrogel prepared in D<sub>2</sub>O (C) and H<sub>2</sub>O (D),  $\mathbf{Tb}^{3+}$  containing thin film prepared in D<sub>2</sub>O (E) and H<sub>2</sub>O (F). (excited at 280 nm and monitored at 543 nm)



**Figure S13.**The decay curves of  $Eu \cdot L_3$  dissolved in D<sub>2</sub>O (A) and H<sub>2</sub>O (B),  $Eu^{3+}$  containing DN supramolecular hydrogel prepared in D<sub>2</sub>O (C) and H<sub>2</sub>O (D),  $Eu^{3+}$  containing thin film prepared in D<sub>2</sub>O (E) and H<sub>2</sub>O (F). (excited at 280 nm and monitored at 615 nm)

#### **Supporting Videos.**

#### **Supporting Video S1**

This movie shows the stretching of a ribbon-shape supramolecular hydrogel (50 mm  $\times$  20 mm  $\times$  3 mm) till 50 times its original length without rupture. (Note: this movie was speeded up by 32  $\times$  its original speed.)

## **Supporting Video S2**

This movie shows the cycle stretch/retract of Eu based supramolecular hydrogel for several times with no obvious elongation, to illustrate the reliable fatigue resistance of our hydrogel. (Note: this movie was speeded up by  $4 \times$  its original speed.)

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