Using metal-ligand interactions to access biomimetic supramolecular polymers with adaptive and superb mechanical properties

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Materials, Methods and Characterization

Materials. All reagents were used as received from commercial suppliers without further purification unless otherwise stated. Toluene, dichloromethane (CH_2Cl_2), dimethyl formamide (DMF), diisopropylanmine (DIPA) and acetonitrile were distilled under N₂ over CaH₂, tetrahydrofuran (THF) over Na, prior to use.

Safety Comments. Sodium azide is very toxic, personal protection precautions should be taken. As low-molecular-weight organic azides are potential explosives, care must be taken during their handling. Generally, when the total number of carbon $(n_{\rm C})$ plus oxygen $(n_{\rm O})$ atoms is less than the total numbers of nitrogen atoms $(n_{\rm N})$ by a ratio of three, that is, $(n_{\rm C}+n_{\rm O})/n_{\rm N} < 3$, the compound is considered as an explosive hazard. In these instances, the organic azido compound was prepared prior to use and used immediately.

General Methods. ¹H NMR spectra were recorded on a Bruker spectrometer (400 MHz), chemical shifts were referenced to CDCl₃ internal standard (7.26 ppm for ¹H). Molecular weight and PDI were measured by GPC (Waters 1515 Binary HPLC Pump, Waters 2414 Refractive Index Detector). THF or DMF/chloroform was used as an eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene (PS) standards were used for calibration.

Dynamic Mechanical Analysis (DMA). Films were cut into rectangular shape (5.0 \times 15 mm) and loaded onto the instrument (NETZSCH DMA 242C). The storage modulus and loss modulus were monitored under a frequency of 1.0 Hz as a function of temperature from -150 to 80 °C with a heating speed of 10 °C min⁻¹.

Thermogravimetric Analysis (TGA). TGA measurements were performed on a TA STD Q600 instrument. Samples of about 8 mg were loaded under nitrogen atmosphere. The weight loss was recorded from room temperature to 700 °C with a heating rate of 10 °C min⁻¹.

Modulated differential scanning calorimetry (**MDSC**). MDSC was carried out on a TA Q2000 instrument using the modulated method. The sample was cooled down to -90 °C and heated to 180 °C with a rate of 10 °C/min. A sinusoidal temperature oscillation was overlaid on the linear ramp with a modulation amplitude of 3 °C every 60 s. The reversing heat flow which contains the information of glass transition was recorded.

Transition Electron Microscopy (TEM). TEM was carried out on a JEM-1400 microscope operated at a voltage of 120 KV. Samples were made by drop dilute solutions of the metallo-supramolecular polymers on carbon coated copper grid followed by drying in vaccuo.

Florescence Measurement. Films were directly stuck onto the glass slides and tested on Hitachi F7000 fluorescence spectrometer. The excitation wavelength was 365 nm, and the emission wavelength between 200 and 900 nm were monitored.

Wide Angle X-ray Diffraction (WAXD). Films were adhered on clean glass substrates. Experiments were done on a Rigaku Ultima IV X-ray diffractometer with a wavelength of 0.154 nm and an acquisition time of 30 minutes.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR). ATR-FTIR spectra were collected using a Nicolet Avatar 360 with an

Omni-Sampler ATR accessory (Ge crystal, single-bounce beam path, 45° incident angle, 32 scans, 4 cm⁻¹ resolution). An advanced ATR correction was applied to all spectra.



Figure S1. Synthesis of the ligand macromolecular **5** via chain extension reaction of PTHF prepolymer using a bis-hydroxyl functionalized BTP ligand **3** which was obtained through CuACC of 2,6-diethynyl pyridine **2** and 3-azidopropan-1-ol **3**.



Figure S2. Stress-strain curves of cast films with different stoichiometric ratios of metal ion to 5: (a) Zn^{2+} only, (b) Eu^{3+} only.



Figure S3. SAXS spectra of films with different stoichiometric ratios of metal ion to BTP ligand: (a) Zn^{2+} only and (b) Eu^{3+} only.

When 25% of BTPs are complexed with Zn^{2+} ions, i.e., **25:0**, the q_1 peak is flattened at low q and its position shifts to lower q value (Figure S3a), indicating less volume fraction of the hard domains and further average spacing between them, respectively. Sharper q_1 peaks can be seen when more than 50% of BTPs are complexed with Zn^{2+} ions and their positions are almost constant around 0.5 nm⁻¹. Similar behavior can be observed in **0:25** films (Figure S3b, red dashed line). Thus the phase separation of metal-ligand complex is significantly influenced by the stoichiometric ratios of the metal ions.



Figure S4. SAXS spectra of films with different stoichiometric ratios of Zn^{2+} : Eu³⁺ at stoichiometric ratio of metal to BTP.



Figure S5. XRD spectra of films with different stoichiometric ratios of Zn^{2+} : Eu^{3+} at stoichiometric ratio of metal to BTP. Lines are vertically shifted for clarity. The q_2 peak at $2\theta = 7.5^{\circ}$ becomes sharper as ratio of Eu^{3+} increases, which infers more ordered packing inside the hard domains in Eu^{3+} containing films.



Figure S6. TGA measurements of films with different stoichiometric ratios of Zn^{2+} : Eu³⁺ at stoichiometric ratio of metal to BTP.



Figure S7. TGA measurements of films with different stoichiometric ratios of metal ion to BTP ligand: (a) Zn^{2+} only and (b) Eu^{3+} only.



Figure S8. Dynamic mechanical thermal analysis of films with different stoichiometric ratios of Zn^{2+} : Eu³⁺ at stoichiometric ratio of metal to BTP: (a) *E*' and (b) tan δ as a function of temperature.



Figure S9. Dynamic mechanical thermal analysis of films with different stoichiometric ratios of metal ion to BTP ligand: (a), (b) E' and tan δ of films with Zn^{2+} only; and (c), (d) E' and tan δ of films with Eu³⁺ only.

Samples were cooled directly to -150 °C and tested. The increase of modulus at about -75 °C is due to the cold crystallization of PTHF chain segments. The introduction of metal ions exacerbates the cold crystallization, especially Eu^{3+} ions. The control sample is greatly softened after 50 °C.



Figure S10. SAXS of 100:0 film at different temperatures as indicated in the legend. The position of the q_1 peak is unaltered by varying temperature thus the metal-ligand hard phase is very thermally stable.



Figure S11. MDSC of the three metallo-supramolecular samples and the control sample. More obvious transitions starting at around 160 °C are observed for the Eu³⁺ containing samples than the **100:0** sample. The endothermal peaks at around 0-30 °C are the melting of PTHF crystallites.



Figure S12. SAXS of films **100:0** and **50:50** under stretching. (a) Scattering intensities of **100:0** films under different macroscopic strains indicated in the legend. The dashed line indicates the positions of the q_1 peaks. (b) Scattering intensities of **50:50** films under different macroscopic strain indicated in the legend. The solid color arrows indicate the shifting of the q_1 peaks whereas dashed color arrows indicate the appearance of q_1^N peaks



Figure S13. SAXS spectra of films 100:0 (a) and 0:100 (b) at large strains plotted in linear scale.



Figure S14. TEM of **100:0** (a) and **0:100** (b). Methanol was used to prepare solution of **100:0** for drop casting. As **0:100** cannot be dissolved in methanol, a mixture of chloroform and methanol (50:50, vol:vol) were used to prepare solution of **0:100**.



Figure S15. FTIR spectra of 100:0, 0:100 and 0:0 films. Hydrogen bonding was found in both the metal ion containing and the control samples.



Figure S16. (a) Images of cast films with different stoichiometric ratios of Zn^{2+} : Eu³⁺ at stoichiometric ratio of metal to BTP under UV radiation of 365 nm; (b) Photoluminescence spectra of the films within 380 to 650 nm (excited at 365 nm).



Figure S17. UV (365 nm) induced temperature variation of 100:0 and 0:100 films probed by infrared camera.



Figure S18. TGA curves of **100:0**, **0:100** and **0:0** films treated with methanol vapor for 15 min right before TGA measurement. The concentration of Zn^{2+} in **100:0** is 1.5 times that of Eu³⁺ in **0:100**.

Reference

(1) Yuan J.; Fang X.; Zhang L.; Hong G.; Lin Y.; Zheng Q.; Xu Y.; Ruan Y.; Weng W.; Xia H.; Chen G.; J.

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