Self-healing metallo-supramolecular polymers from ligand macromolecule synthesized via copper-catalyzed azide-alkyne cycloaddition and thiol-ene double "click" reactions

Bo Yang,[ab] Huan Zhang,[a] Huiying Peng,[a] Yuanze Xu,[a] Bowei Wu,[a] Wengui Weng,*[a] and Lei Li[ab]

[a] *Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China.*

E-mail: wgweng@xmu.edu.cn

[b] *Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, P. R. China.*

Synthesis of BTP ligand

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 N_2 over CaH_2, 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_C) plus oxygen (n_O) atoms is less than the total numbers of nitrogen atoms (n_N) by a ratio of three, that is, $(n_C+n_O)/n_N < 3$, 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. All reactions requiring inert gas were performed under N2 atmosphere. Column chromatography was carried out with 200-400 mesh silica gels using specified eluents. ^{1}H NMR spectra were recorded on a Bruker spectrometer (400 MHz), chemical shifts were referenced to $CDCl_3$ internal standard (7.26 ppm for 1H). ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 MHz), chemical shifts were referenced to $CDCl_3$ internal standard (77.16 ppm for ^{13}C). Molecular weight and PDI were measured by GPC (Waters 1515 Binary HPLC Pump, Waters 2414 Refractive Index Detector). THF was used as an eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene (PS) standards were used for calibration.

High-Resolution Mass Spectroscopy. HR-MS spectra were recorded on a Bruker En Apex ultra 7.0T FT-MS apparatus.

MALDI Spectroscopy. The MALDI-MS measurements were carried out with a Bruker MicroFlex MALDI-TOF-MS. A 4 $mg \cdot mL^{-1}$ solution of compound **6** in tetrahydrofuran, 30 μL of a 20 $mg \cdot mL^{-1}$ solution of sodium trifluoroacetate (NaTFA, in tetrahydrofuran) was added to aid cationization. A 20 $mg \cdot mL^{-1}$ solution of 1,8,9-anthracenetriol (dithranol) matrix was prepared in tetrahydrofuran solvent, and equal volumes of matrix and sample were mixed together.

The sample:matrix solution was spotted on a stainless steel MALDI plate. MALDI experiments were conducted in reflection mode. Spectra were obtained with delayed extraction at laser powers slightly above the threshold power for detection of sample ions. Spectra from 100 to 500 laser shots were accumulated to obtain a composite spectrum.

Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Nicolet 380 FT-IR spectrometer as KBr disks.

Wide angle X-ray diffraction (WAXD). Films containing different types of metal ions (0.2 g) were dissolved in CHCl3 (1 mL) and then spin-coated on clean glass substrate with a speed of 2000 rpm for 25 sec. Measurements were done on a Rigaku Ultima IV X-ray diffractometer with a wavelength of 0.154 nm and an acquisition time of 30 min.

Florescence spectroscopy. Solutions were prepared with a concentration of 29 mg·mL^{-1} in $CHCl_3$ and tested on Hitachi F7000 fluorescence spectrometer. Samples were excited with a wavelength of 365 nm and 254 nm. The emission between 200 and 800 nm were recorded.

Synthesis 1. 1 was prepared according to literatures[1-5] with modifications. To a 50 mL flask was added 2,6-dibromopyridine (2.0 g, 8.4 mmol, 1 equiv.), CuI (0.032 g, 0.17 mmol, 0.02 equiv.) and $Pd(PPh_3)_4$ (0.195 g, 0.17 mmol, 0.02 equiv.), then evacuated at room temperature for 10 min and flushed with N_2, and 15 mL THF and 15 mL DIPA were added via a syringe under N_2. After freeze degassing (3x), TMS-acetylene (2.92 mL, 21.1 mmol, 2.5 equiv.) was added via a syringe in a counterflow of N_2. The reaction mixture was stirred at 50 °C for 6 h and after consumption of 2,6-dibromopyridine indicated by TLC monitoring (CH_2Cl_2/hexane 1/1) the mixture was cooled down to room temperature and the solvent was removed. Purification using column chromatography (CH_2Cl_2/hexane 1/1) gave 2,6-bis(trimethylsilylethynyl)pyridine **1** (1.98 g, 8.13 mmol, 98% yield) as white powder. ^{1}H NMR (400 MHz , $CDCl_3$): δ = 7.58 (1H, t, J = 8.0 Hz, C_{Ar}-H), 7.37 (2H, d, J = 8.0 Hz, C_{Ar}-H), 0.25 (18H, s, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 143.4 (2C), 136.2, 126.7 (2C), 103.3 (2C), 95.4 (2C), -0.34 (6C).

Synthesis 2. 2 was prepared according to literatures[1-5] with modifications. To a flask was added **1** (1.98 g, 8.13 mmol, 1 equiv.), K_2CO_3 (3.36 g, 24.4 mmol, 3 equiv.), methanol (15 mL) and diethyl ether (15 mL). The reaction was stirred at room temperature for 4 h and then additional diethyl ether (20 mL) and deionized water (30 mL) were added. After extracting with diethyl ether and deionized water for 3 more, the organic phase was collected and the solvent was removed. Purification using column chromatography (CH_2Cl_2/hexane 2/3) gave 2,6-bis(ethynyl)pyridine **2** (0.68 g, 5.37 mmol, 66% yield). ^{1}H NMR (400 MHz , $CDCl_3$): δ = 7.65 (1H, t, J = 7.8 Hz, C_{Ar}-H), 7.37 (2H, d, J = 7.8 Hz, C_{Ar}-H), 3.16 (2H, s, C≡CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 142.7 (2C), 136.6, 127.1 (2C), 82.1 (2C), 77.8 (2C).

Synthesise 3. **3** was prepared according to literatures[1-5] with modifications. To a mixture of 3-bromo-1-propene (5.0 g, 41.33 mmol, 1 equiv.), sodium azide (8.06 g, 123.99 mmo, 1.3 equiv.) and DMF (30 mL) was added. After stirring at room temperature for 1 day, the product was extracted with CH_2Cl_2/H_2O (3x). The combined organic phases were dried by rotary evaporator at the temperature below 10 ^oC gave 3-azido-1-propene **3** (2.81 g, 33.82mmol, 81% yield). ^1H NMR (400 MHz , $CDCl_3$), $\delta = 5.90$ (1H, ddt, $J = 16.8, 9.2, 7.2$ Hz, $CH{=}CH_2$), 5.35 (1H, d, $J = 16.8$ Hz, $CH{=}CH_2$), 5.18 (1H, d, $J = 9.2$ Hz, $CH{=}CH_2$), 3.97 (2H, d, $J = 7.2$ Hz, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 131.3, 119.1, 53.3$.

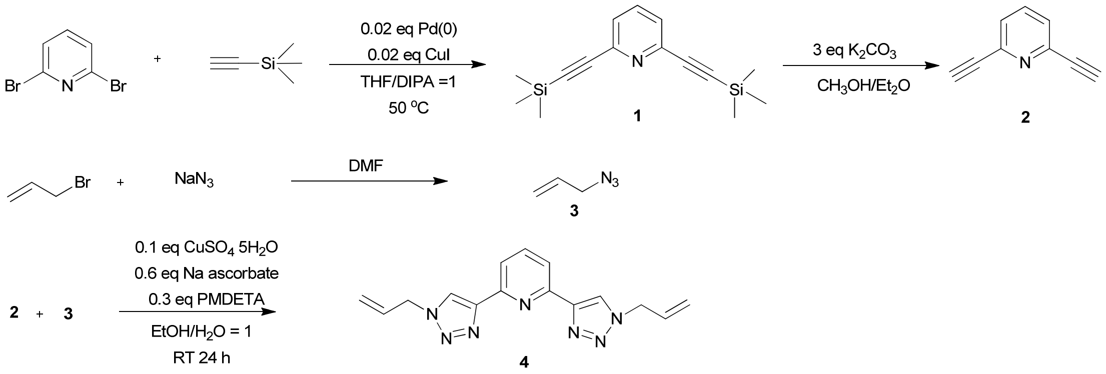
Synthesis 4. 4 was prepared according to literatures[1-5] with modifications. A solution of **2** (1.0 g, 7.86 mmol, 1 equiv.), **3** (1.632 g, 19.66 mmol, 2.5 equiv.), $CuSO_4{\cdot}5H_2O$ (0.39 g, 1.57 mmol, 0.2 equiv.), sodium ascorbate (0.93 g, 4.72 mmol, 0.6 equiv.) and pentamethyldiethylenetriamine (PMDTA) (0.409 mL, 3.94 mmol, 0.5 equiv.) in a 1:1 mixture of $EtOH:H_2O$ was stirred at room temperature for 1 day. After removal of the solvents in vacuo, the crude product was purified by column chromatography (CH_2Cl_2:acetone, 3:1) to afford **4** (1.9 g, 6.49 mmol, 80% yield). ^1H NMR (400 MHz , $CDCl_3$): $\delta = 8.19$ (2H, s, C_{Ar}-H), 8.12 (2H, d, $J = 7.84$ Hz, C_{Ar}-H), 7.89 (1H, t, $J = 7.84$ Hz, C_{Ar}-H), 6.12 (2H, ddt, $J = 16.4, 10.3, 6.2$ Hz, $CH{=}CH_2$), 5.38-5.45 (4H, m, $CH{=}CH_2$), 5.08 (4H, d, $J = 6.2$ Hz, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 150.0$ (2C), 148.5 (2C), 137.8, 131.0 (2C), 122.0 (2C), 120.4 (2C), 119.4 (2C), 52.8 (2C). HRMS(ESI):m/z[M]:calced for $[C_{15}H_{15}N_7]^+$ 293.1389, found for 293.1389.

Synthesis diacryloyl PTHF 5. A mixture of PTHF (Mn = 2000, 6.0 g, 3.0 mmol, 1.0 equiv.) and triethylamine (2.54 mL, 30 mmol, 10 equiv.) in dichloromethane (30 mL) were sealed in a flask (100 mL) and acryloyl chloride (4.21 mL, 30 mmol, 10 equiv.) was added. The mixture was stirred at room temperature for 1 day followed by precipitation in diethyl ether. After the removal of solvents in vacuo, the raw product was purified by chromatography to obtain diacryloyl PTHF **5** (3.0 g, 1.5 mmol, 50% yield). ^1H NMR (400 MHz , $CDCl_3$, Me_4Si): δ (ppm) = 6.42 (2H, d, $J = 16.5$ Hz, $CH{=}CH_2$), 6.14 (2H, dd, $J = 16.5, 10.8$ Hz $CH{=}CH_2$), 5.84 (2H, d, $J = 10.8$ Hz, $CH{=}CH_2$), 4.21 (4H, t, $J = 6.5$ Hz, $COOCH_2$), 3.40-3.50 ((4n+4)H, m, OCH_2), 1.60-1.70 ((4n+8)H, m, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 166.3$ (2C), 130.5 (2C), 128.6 (2C), 70.6 (2n+2), 64.4 (2C), 26.5 (2n+4).

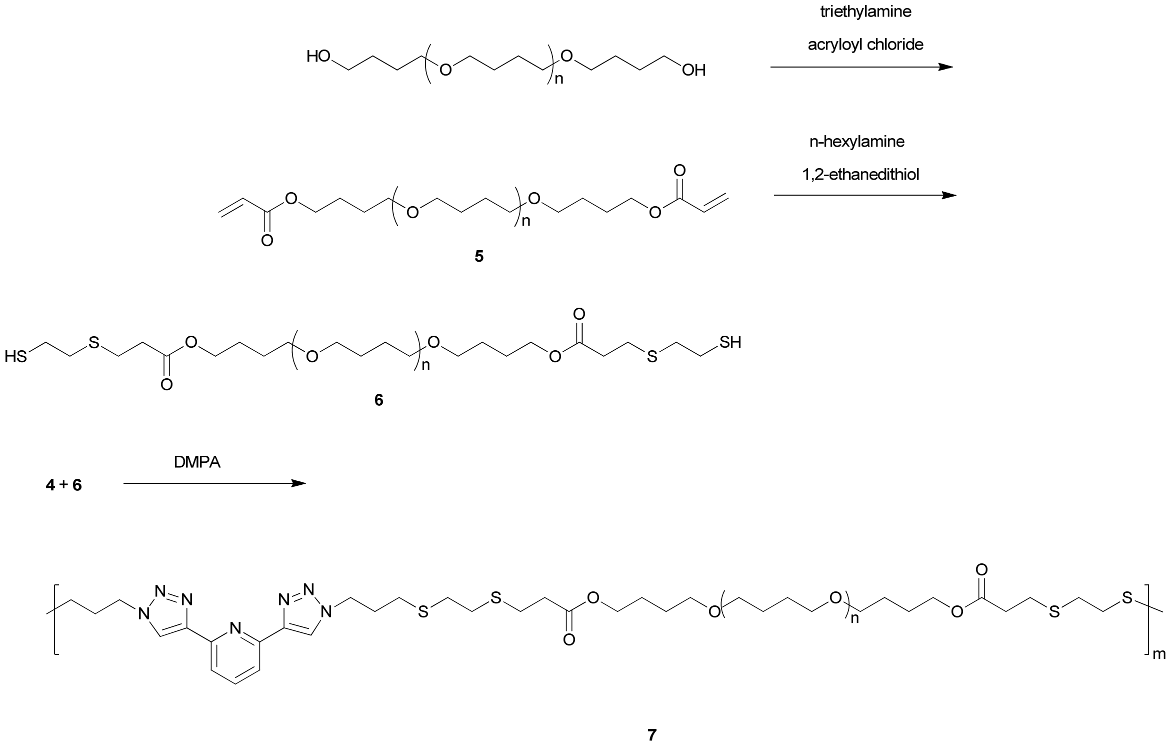
Synthesis bis-thiol functionalized PTHF 6. 1,2-ethanedithiol (840 μL, 10 mmol, 10.0 equiv.)

and 10 μL *n*-hexylamine as catalyst were charged into a flask and the mixture was evacuated at RT and flushed with N_2 three times. Then 2.0 g (1.0 mmol, 1.0 equiv.) diacryloyl PTHF dissolved in 20 mL dichloromethane was added dropwise via a syringe under N_2.The reaction mixture was stirred at RT for 1.5 h. The crude product was then purified by dialysis under to afford the bis-thiol functionalized PTHF **6** (1.6 g, 0.8 mmol, 80% yield). ^{11}H NMR (CDCl3, 400 MHz): δ (ppm) = 4.15 (4H, t, J = 6.5 Hz), 3.35-3.50 ((4n+4)H, m, OCH_2), 3.0-3.05 (4H, m, CH_2SH), 2.75-2.95(8H, m, SCH_2), 2.60-2.65 (4H, m, $COCH_2$), 1.55-1.70 ((4n+8)H, m, CH_2), 1.49 (2H, t, J = 7.8 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 171.8 (2C), 70.6 ((2n+2)C), 64.7 (2C), 40.1, 38.5, 34.9, 31.6, 31.1,27.6, 27.1((2n+4)C), 26.5, 22.4.

Scheme S1 Synthesis of bis-ene functionalized BTP ligand **4** using CuAAC click chemistry.



Scheme S2 Synthesis of ligand macromolecule via thiol-ene click chemistry.



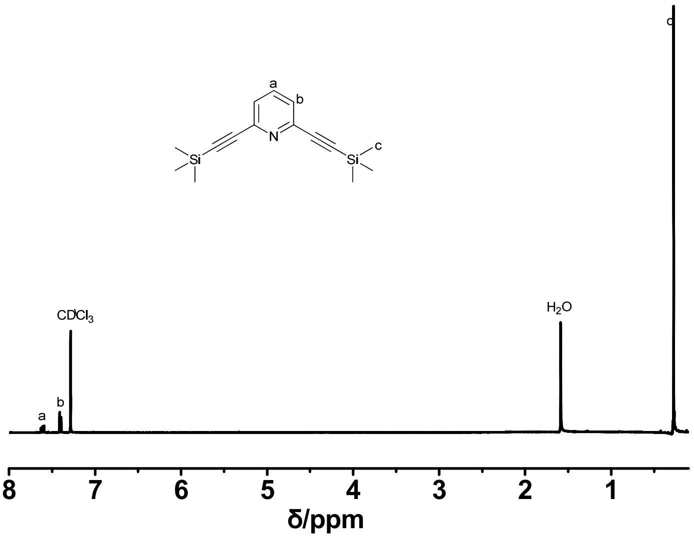


Fig. S1 ^{1}H NMR of **1** in $CDCl_3$.

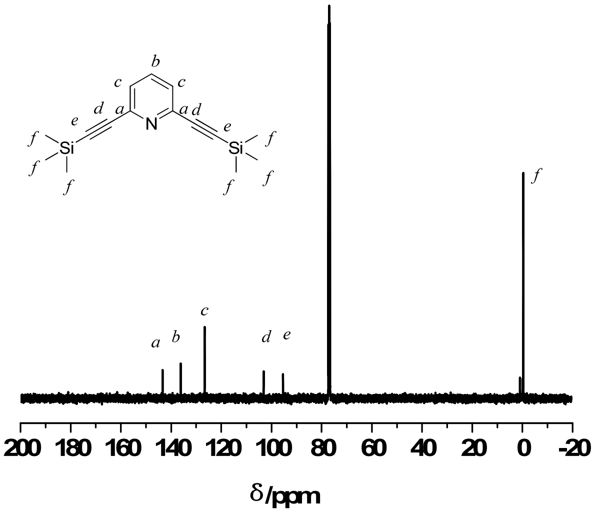


Fig. S2 ^{13}C NMR of **1** in $CDCl_3$.

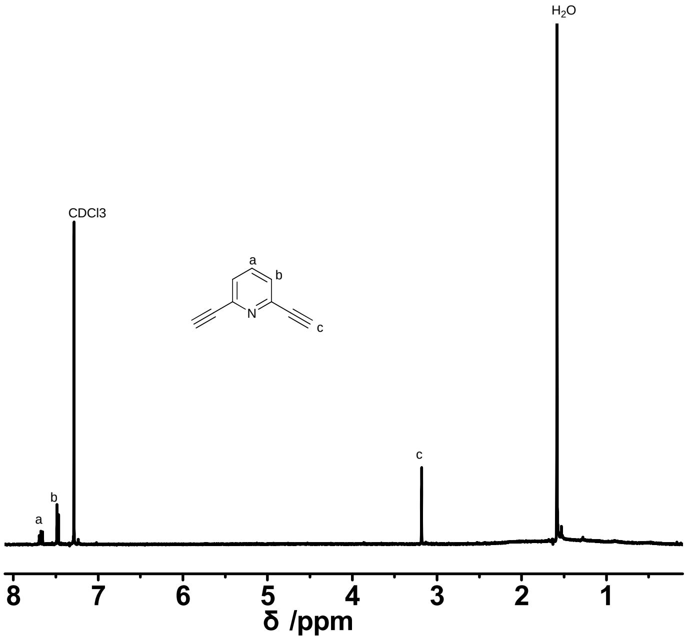


Fig. S3 ^{1}H NMR of **2** in CDCl$_3$.

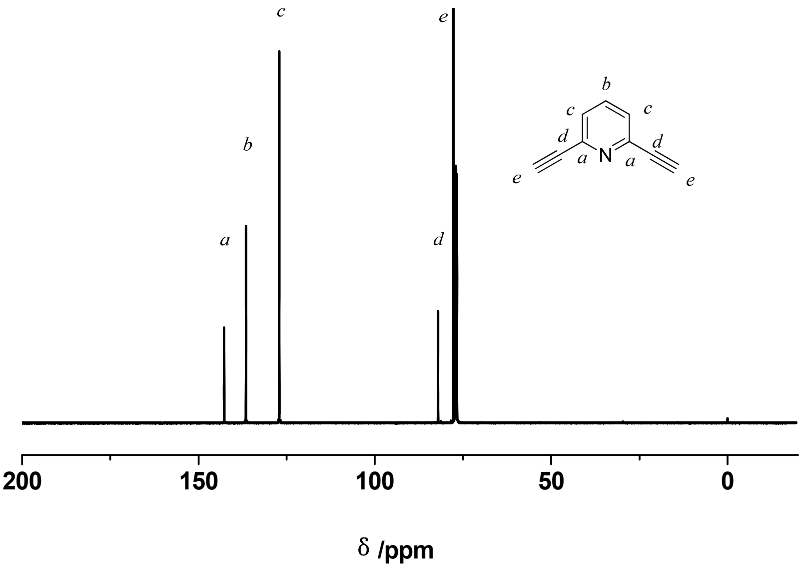


Fig. S4 ^{13}C NMR of **2** in CDCl$_3$.

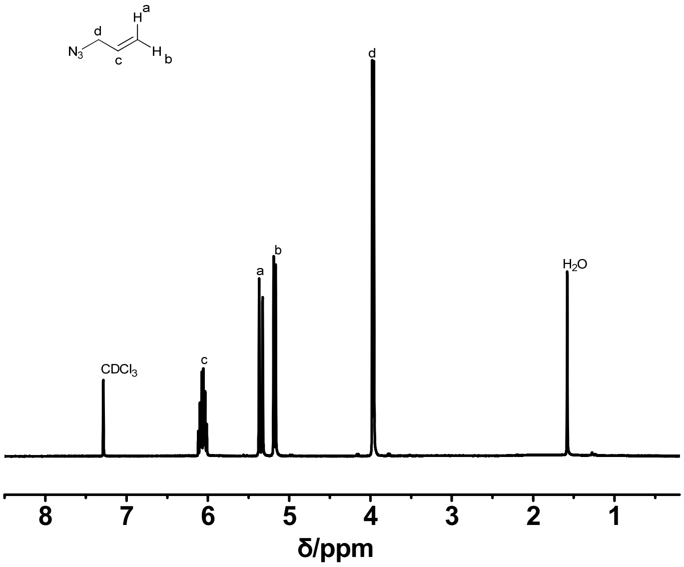


Fig. S5 ^{1}H NMR of **3** in $CDCl_3$.

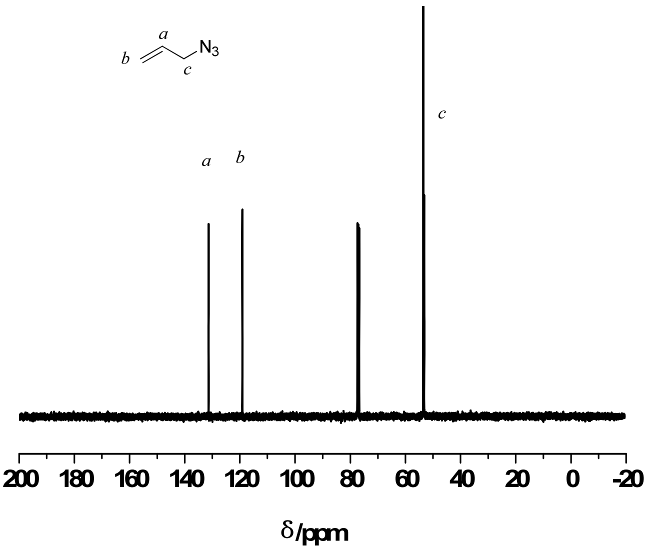


Fig. S6 ^{13}C NMR of **3** in $CDCl_3$.

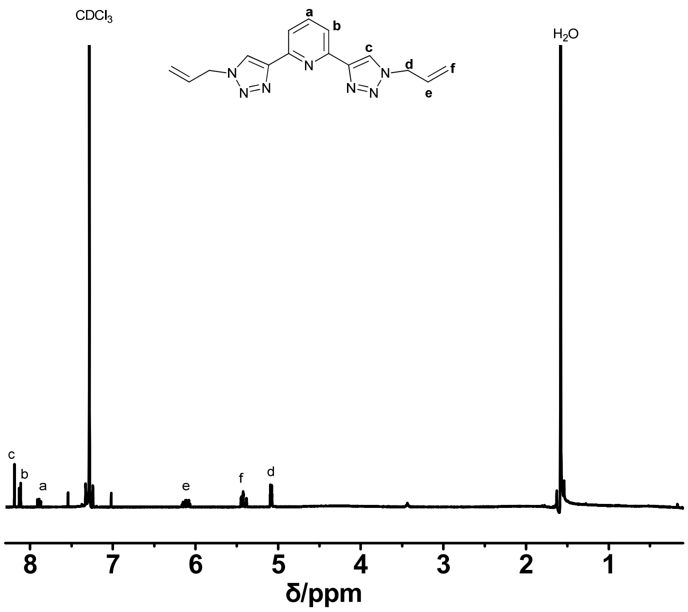


Fig. S7 ^{1}H NMR of **4** in CDCl$_3$.

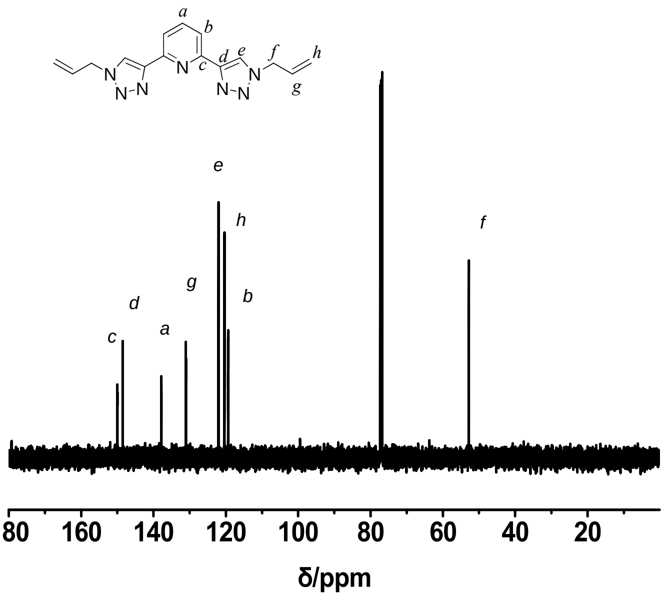


Fig. S8 ^{13}C NMR of **4** in CDCl$_3$.

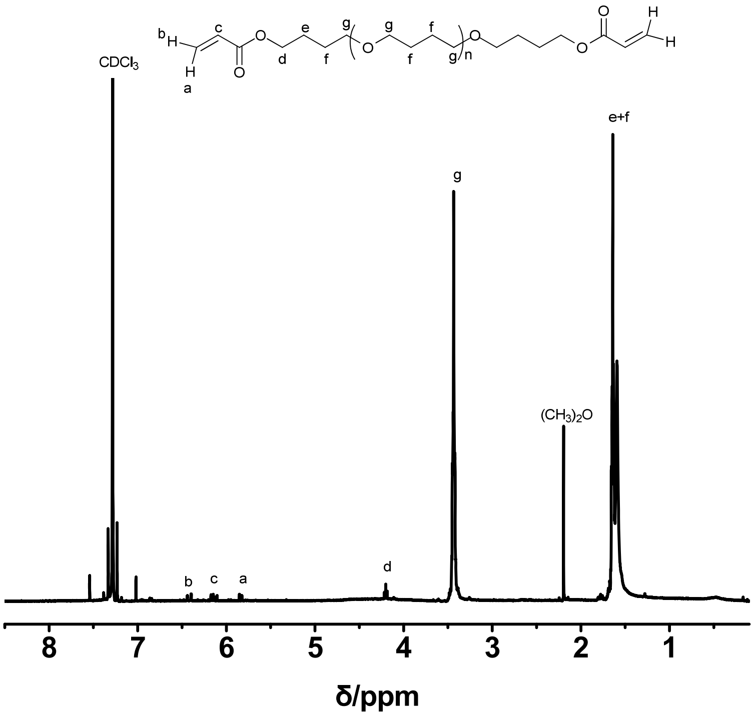


Fig. S9 ^{1}H NMR of **5** in $CDCl_3$.

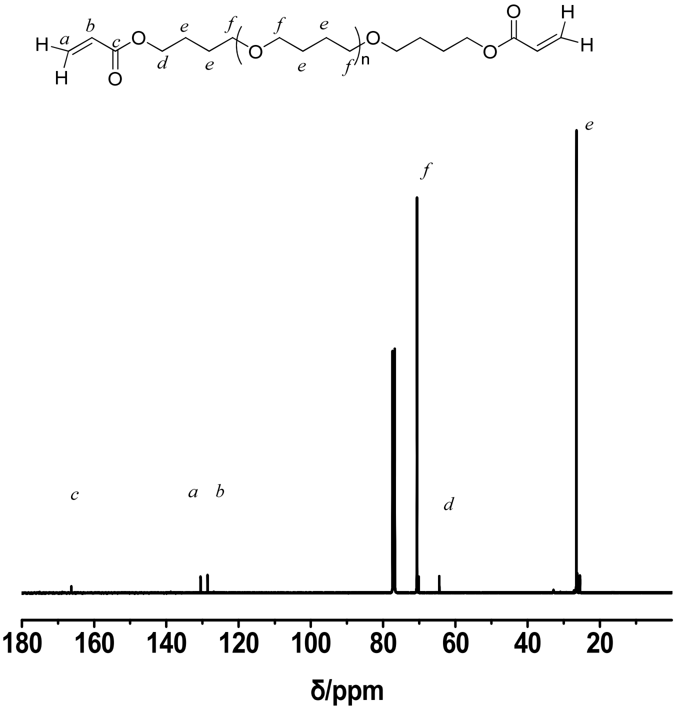


Fig. S10 ^{13}C NMR of **5** in $CDCl_3$.

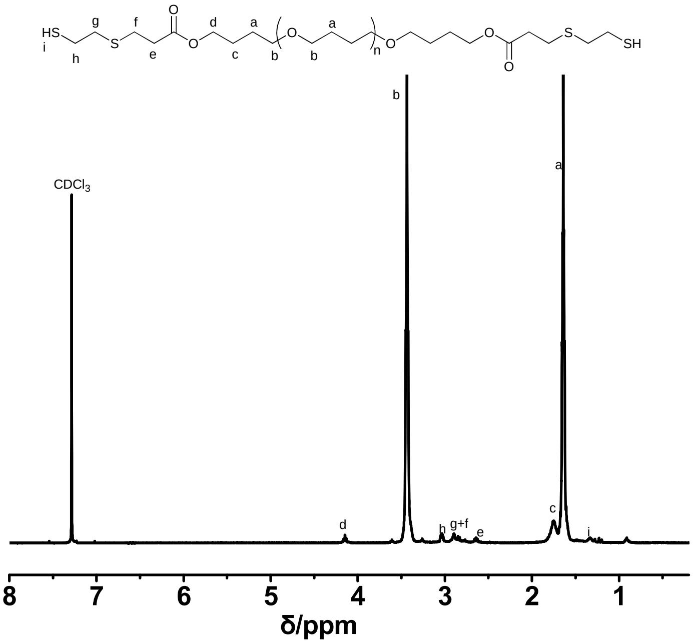


Fig. S11 ^{1}H NMR of **6** in $CDCl_3$.

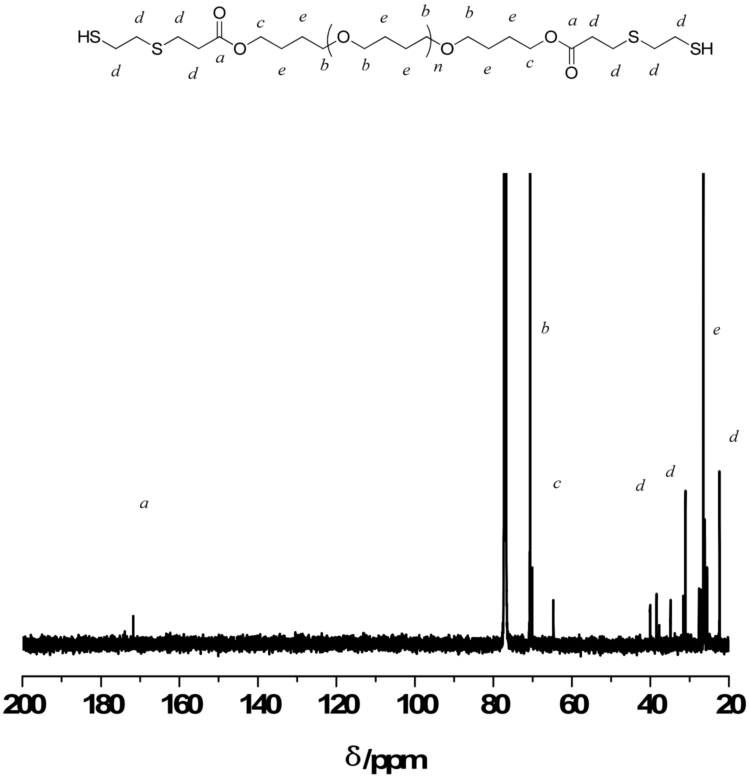


Fig. S12 ^{13}C NMR of **6** in $CDCl_3$.

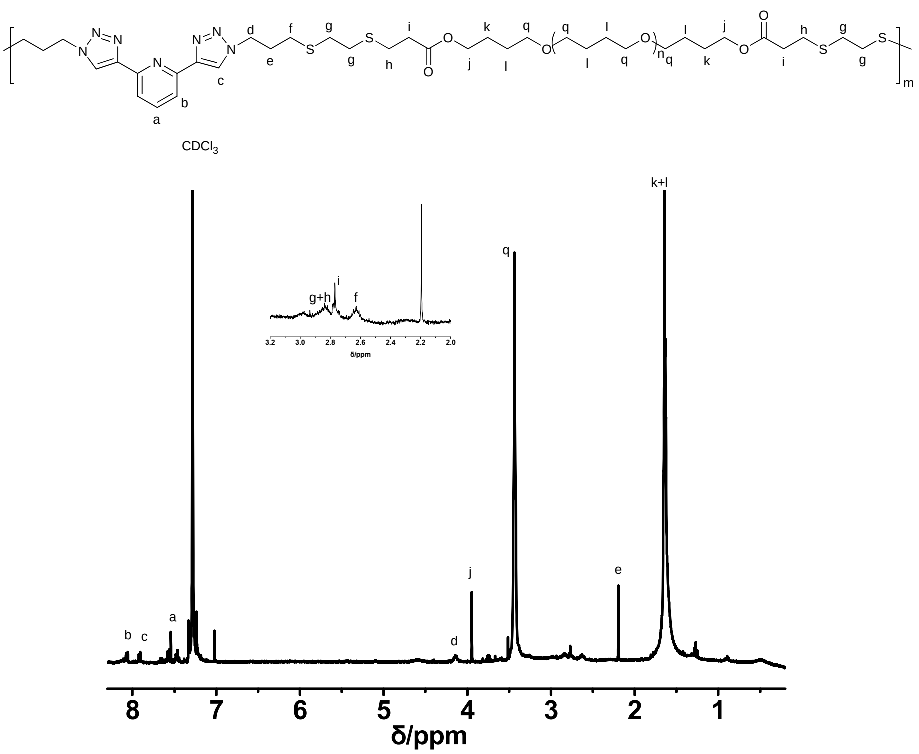


Fig. S13 ^{1}H NMR of **7** in $CDCl_3$.

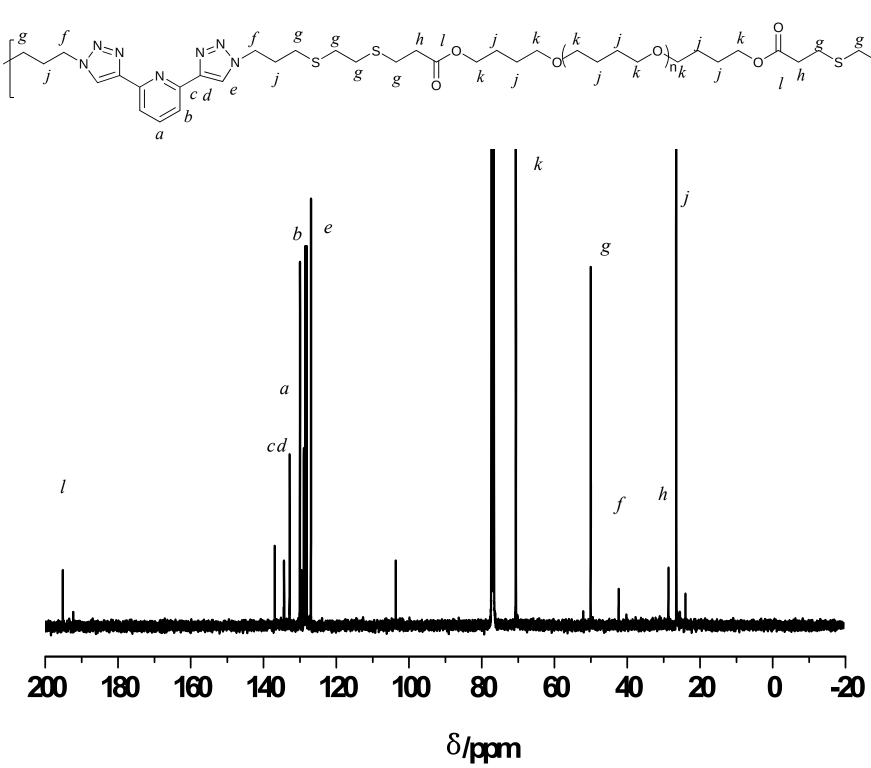


Fig. S14 ^{13}C NMR of **7** in $CDCl_3$.

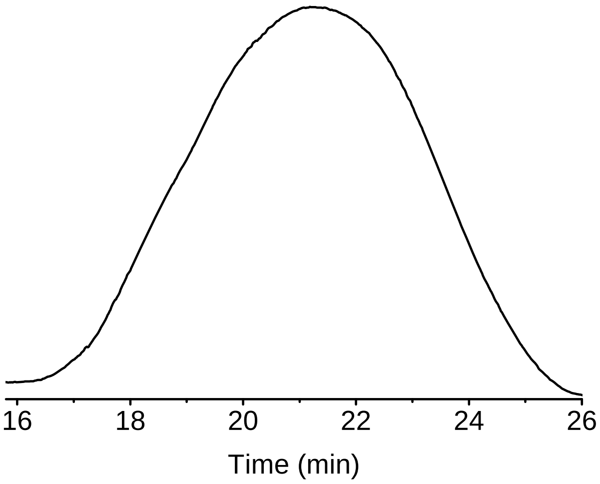


Fig. S15 GPC trace of the ligand macromolecule **7**.

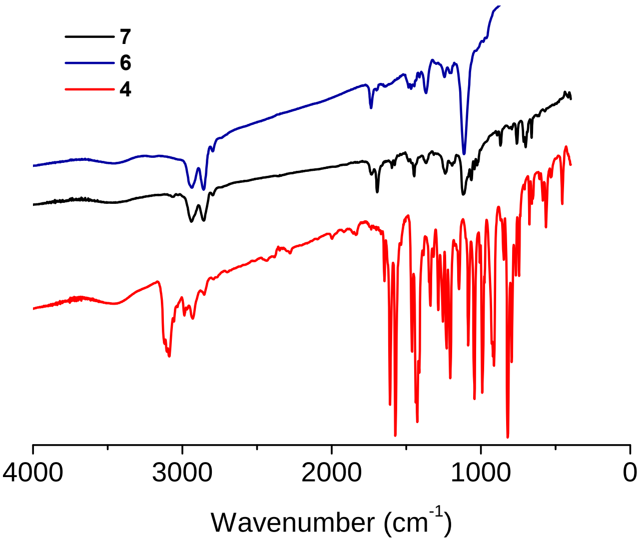


Fig. S16 FTIR spectra of **4**, **6** and the ligand macromolecule **7**.

The disappearance of ene absorption peak at 3087 cm^{-1} is a good indication of the successful thiol-ene reaction.

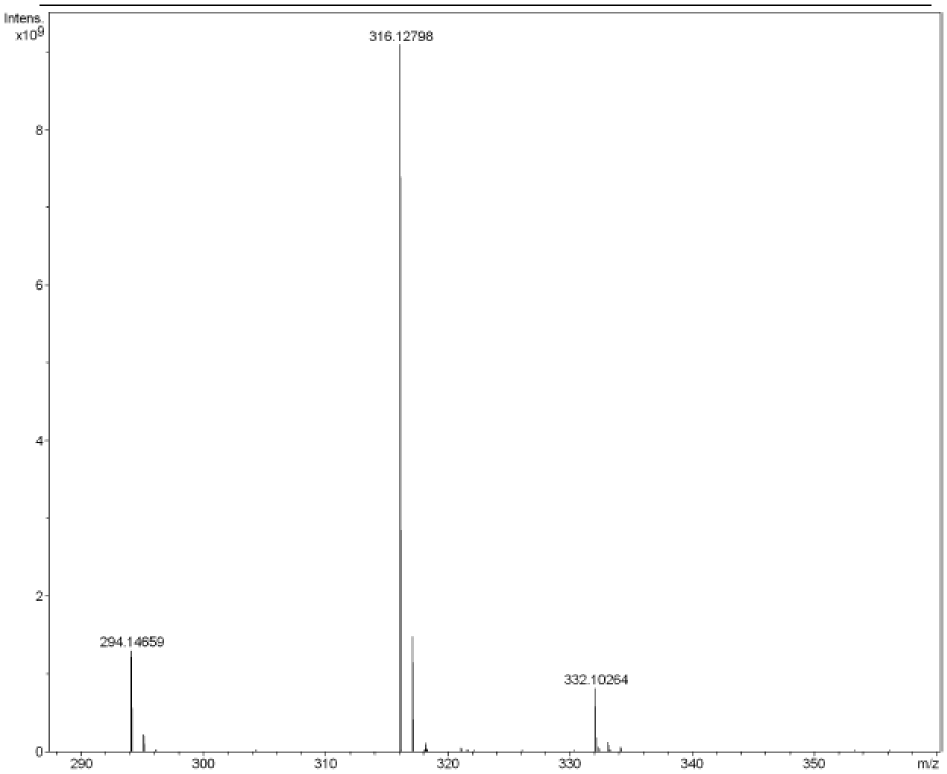


Fig. S17 High resolution mass spectroscopy of **4**.

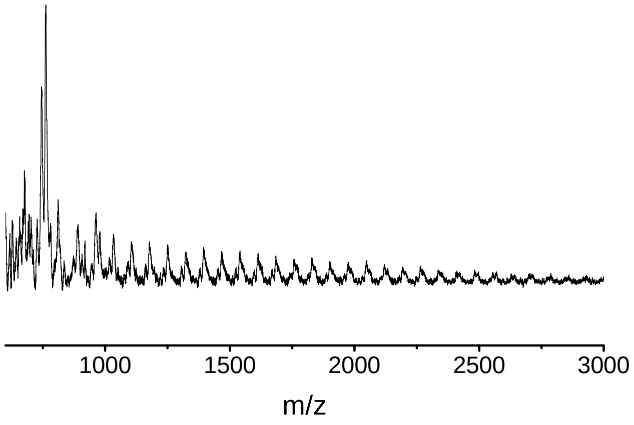


Fig. S18 MALDI mass spectroscopy of **6**.

A spectrum of intense peaks at lower masses and a 'tailing off' of intensities at higher masses is typical MALDI behavior for a polymer of high polydispersity.[6]

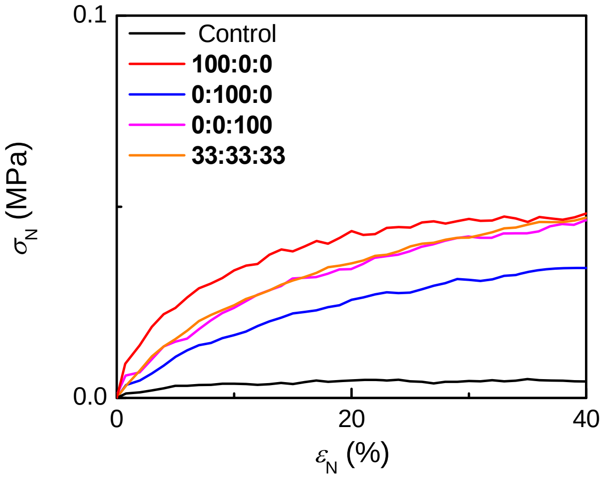


Fig. S19 stress strain curves of **Fig. 2** at small strain. The control sample denotes films made from the ligand macromolecule **7** only.

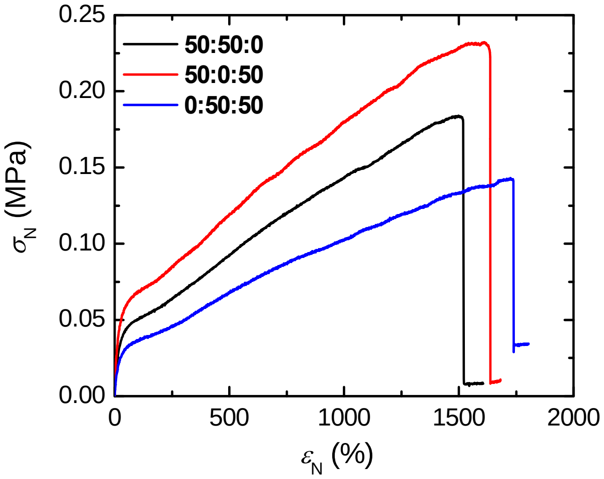


Fig. S20 Stress-strain relationships of films containing different stoichiometric ratios of Zn^{2+}: Eu^{3+}: Tb^{3+} indicated in the legend.

Table S1 Tensile modulus, tensile strength, fracture strain and toughness of films containing different stoichiometric ratios of Zn^{2+}: Eu^{3+}: Tb^{3+}

Sample	Tensile modulus (KPa)	Tensile strength (KPa)	Fracture strain (%)	Toughness (KPa)
50:50:0	203 ± 16	178 ± 31	1800 ± 270	2010 ± 670
50:0:50	243 ± 51	231 ± 2	1700 ± 180	2740 ± 320
0:50:50	154 ± 16	136 ± 11	1700 ± 350	1560 ± 410

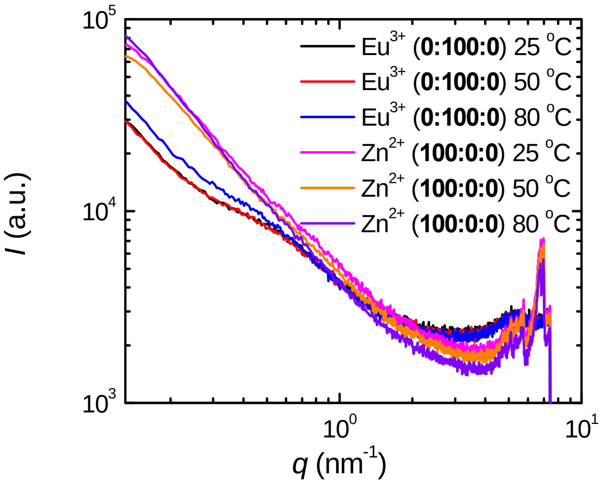


Fig. S21 SAXS of Eu^{3+} (**0:100:0**) and Zn^{2+} (**100:0:0**) containing films at varied temperatures (25 °C, 50 °C and 80 °C)

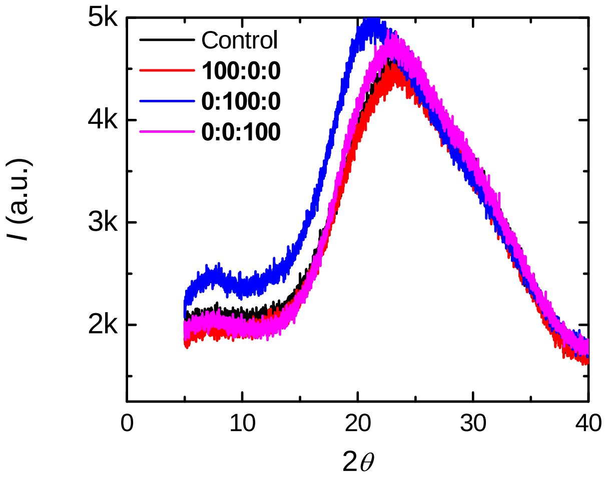


Fig. S22 WXRD of films containing different metal ions as well as the control sample. The control sample denotes films made from the ligand macromolecule **5** only.

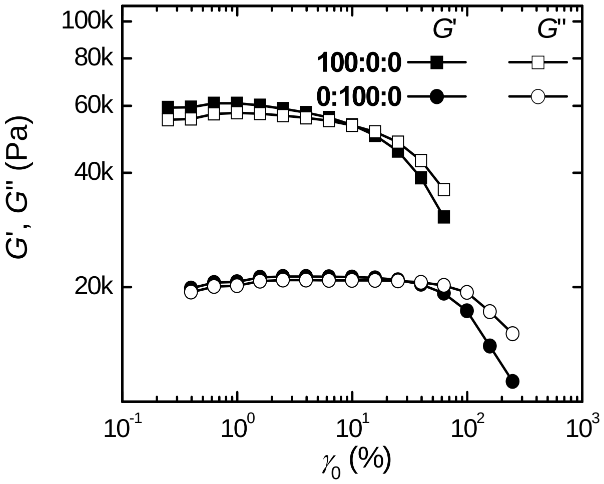


Fig. S23 Strain sweep tests at 60 ^{o}C to break up the network formation of the metal-supramolecular complex for Zn^{2+} (**100:0:0**) and Eu^{3+} (**0:100:0**) films.

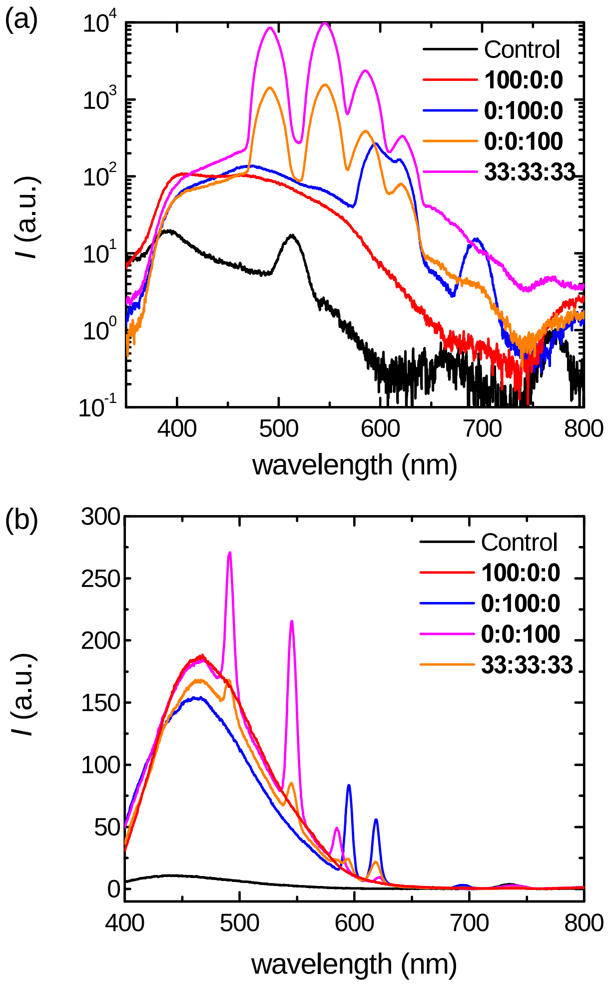


Fig. S24 Fluorescent spectroscopy of films containing different metal ions as shown in the legend under different UV excitations (a) 254 nm and (b) 365 nm. The control sample denotes films made from the ligand macromolecule **7** only.

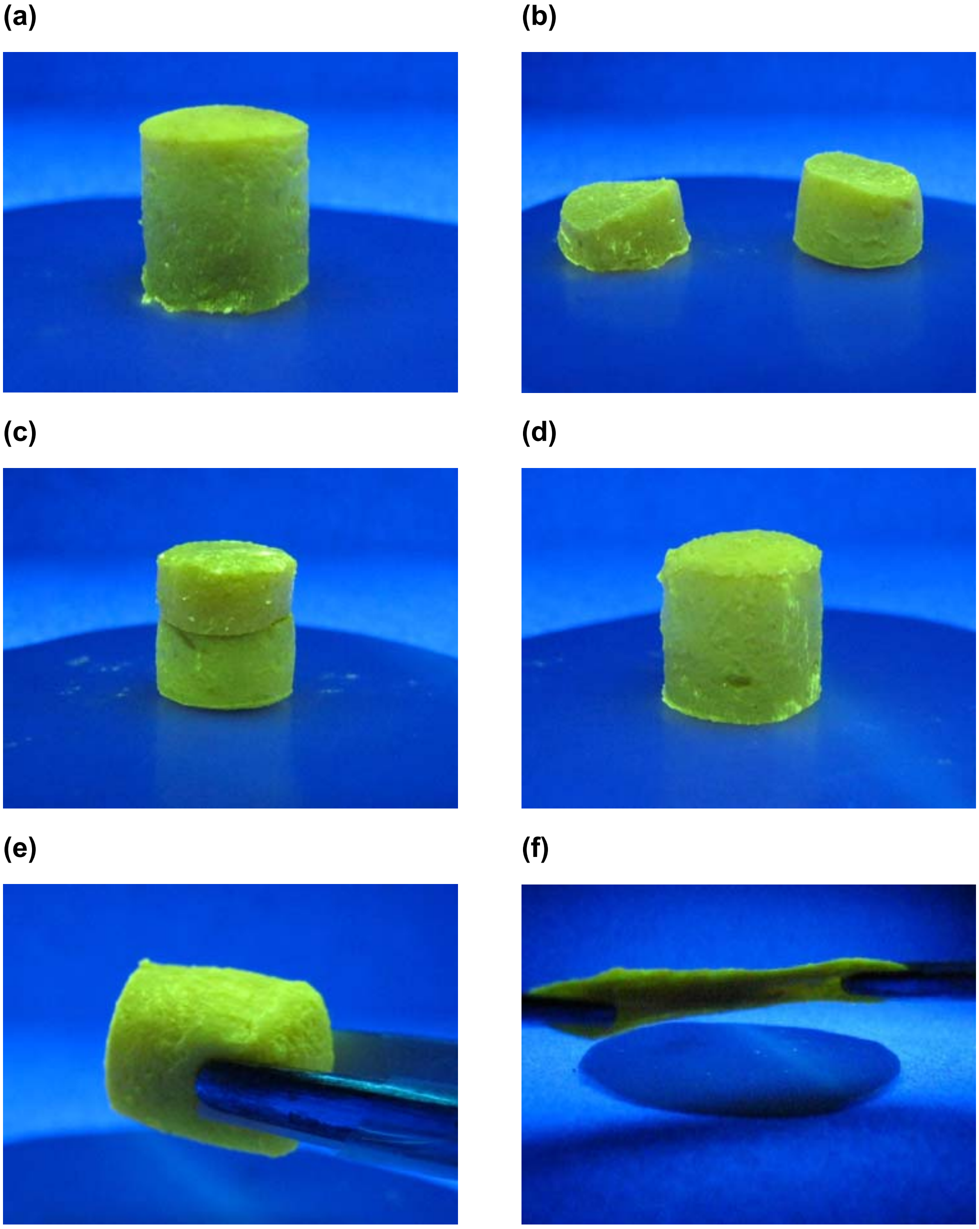


Fig. S25 Self-healing of metallo-supramolecular gel with only Tb^{3+} (**0:0:100**). (a) Fresh gel swollen in toluene (250 mg·mol^{-1}); (b) Gel was cut into two pieces; (c) Cut gel pieces were stacked up before self-healing; (d) and (e) Stacked gels subjected to self-healing under saturated toluene atmosphere for 20 h; (f) The healed gel was then subjected to stretching. Images were taken under UV light (254 nm).

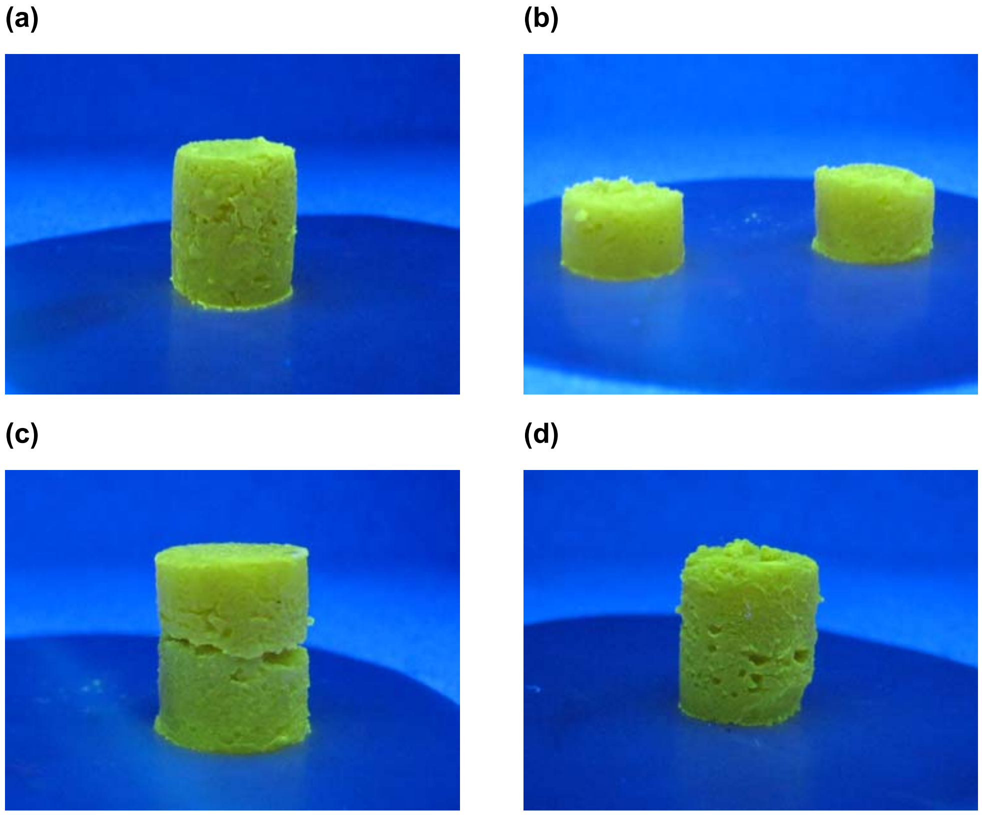


Fig. S26 Self-healing of metallo-supramolecular gel with only Tb^{3+} (**0:0:75**, off-stoichiometry metal ion concentration). (a) Fresh gel swollen in toluene (400 $mg \cdot mol^{-1}$); (b) Gel was cut into two pieces; (c) Cut gel pieces were stacked up before self-healing; (d) Stacked gels subjected to self-healing under saturated toluene atmosphere for 20 h. Images were taken under UV light (254 nm). The gel was prepared with higher concentration than that of **0:0:100** due to the lower metal ion concentration. The original and the healed **0:0:75** were both more brittle than the healed **0:0:100**.

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