

## **Imine-functionalized polysiloxanes for supramolecular elastomers with tunable mechanical properties**

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### **Experimental Section**

#### **Materials**

Octamethylcyclotetrasiloxane (D<sub>4</sub>) and 3-aminopropyl-methyl-diethoxysilane were obtained as the commercial products and used directly. Tetramethylammonium hydroxide pentahydrate, Benzaldehyde, 4-chlorobenzaldehyde, methyl 4-formylbenzoate, 4-nitrobenzaldehyde, 1-naphthaldehyde, *N*-methyl benzaldimine, cupric chloride were purchased from Shanghai Saan Chemical Technology Co. Ltd (China). iron (III) chloride sodium and sulfate anhydrous were obtained from Tianjin Cociensi Biochemical Technology Co. Ltd (China) and Tianjin Kemeiou Chemical Reagent Co. Ltd (China). 2,4-dinitrotoluene (DNT) was provided by Shanghai Aladdin Biochemical Technology Co. Ltd (China). Dimethyl sulfoxide, dichloromethane, methanol, toluene, tetrahydrofuran were supplied by Tianjin Fuyu Fine Chemical Co. Ltd (China).

#### **Characterization and measurements**

Nuclear magnetic resonance (<sup>1</sup>H NMR) were measured with a Bruker Advance 400 spectrometer at room temperature. Deuterated chloroform (CDCl<sub>3</sub>) was used as a solvent without tetramethylsilane (TMS). Fourier transform infrared spectrum (FT-IR) was recorded on a Bruker TENSOR 27 infrared spectrophotometer by using the KBr pellet technique from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The gel permeation chromatography (GPC) measurements of polymers (P0-5%, P1-5%, P0-10% and P1-10%) were carried out with a Waters 1515 pump, a 2414 refractive index detector, and a HT3+HT2 liquid chromatography, the gel permeation chromatography (GPC) measurements of polymers (P2-5%, P3-5%, P4-5% and P5-5%) were performed with a Waters liquid chromatography equipped with a 2414 refractive index detector, all samples were measured with the column temperature was 40 °C and THF flow rate was stable at 1.0 mL/min. The ultraviolet absorption

spectras of polymers and elastomers in THF solution were measured with a Beijing TU-1901 double beam UV-Vis spectrophotometer in the wavelength range of 200-600 nm. The fluorescence (excitation and emission) spectras were measured with a Hitachi F-4500 fluorescence spectrophotometer using a monochromatic Xe lamp as an excitation source. Thermogravimetric analysis (TGA) was carried out by TA ADTQ600 apparatus from room temperature to 800 °C with a heating temperature ramping rate of 10 °C/min under a N<sub>2</sub> atmosphere. Differential scanning calorimetry (DSC) was measured with SDTQ 600 of TA Instrument from -140 °C to 100 °C with a heating and cooling temperature ramping rates of 10 °C /min under the N<sub>2</sub> flow. Scanning electronic microscopy images (SEM) and EDS (including elemental mapping) were obtained by using a Gemini-SEM-300 instrument (Carl Zeiss Microscopy GmbH), Samples were cut and coated with a thin layer of gold before investigation. Strain-stress curves were recorded by using universal material testing machine at room temperature with stretching rate of 200 mm/min. In all tensile tests, the samples were cut into dumbbell shape with a size of 50 × 4 × 0.45 mm<sup>3</sup>.

### **Synthesis of the poly[(aminopropyl)methylsiloxane-co-dimethylsiloxane] P0**

P0 was synthesized via hydrolysis and ring opening polymerization. The obtained polysiloxanes were named as P0-X (X represents the molar ratio of (aminopropyl)methylsiloxane units in all siloxane units).

For P0-5%, D<sub>4</sub> (100 g, 0.337 mol), 3-aminopropyl-methyl-diethoxysilane (13.6 g, 0.083 mol), H<sub>2</sub>O (2.6 g, 0.142 mol), Me<sub>4</sub>NOH·5H<sub>2</sub>O (0.08 g, 0.05 wt%), and DMSO (1.14 g, 1.0 wt%) were added to a three-neck flask with a stir bar. The mixture was refluxed and stirred for 4 h at 100 °C. Ethanol and water were removed under reduced pressure distillation at 50 °C. The obtained mixture was stirred slowly at 120 °C for 24 h. Finally, the catalyst was destroyed by increasing the temperature to 140 °C for half an hour. The low boiling components were removed by reduced pressure distillation at 180 °C. P0-5% was obtained as a colorless transparent viscous liquid. Yield: 93%. P0-10% was synthesized similarly. For P0-5%, the  $M_n$  is 29000 and the  $\overline{M}_w$  is 1.75. For P0-10%, the  $M_n$  is 16000 and the  $\overline{M}_w$  is 1.56.

### **Synthesis of the imine-functionalized polymers**

P0-5% (3.5 g) and corresponding aromatic aldehydes with a molar ratio of 1:1 (NH<sub>2</sub>:CHO=1:1) were

added into 20 mL dichloromethane and stirred by a magnetic stirrer at room temperature for 4 h. Then the mixture was dried with anhydrous sodium sulfate, and precipitated in methanol for three times to give imine-functionalized polymers as colorless transparent viscous liquid. The yields range from 70% to 80%. For polymers P1-5%, P1-10%, P2-5%, P3-5%, P4-5% and P5-5%, the  $M_n$  are 33000, 40000, 31000, 32000, 41000, 34000, respectively. The  $\overline{M}_w$  are 2.10, 1.50, 1.74, 1.56, 2.43, 1.47, respectively.

### **Preparation of the supramolecular coordination elastomers based on polymer P1- (5%, 10%)**

For example P1-5%-Cu-0.50: P1-5% (2.3 g),  $\text{CuCl}_2$  (0.099 g) were added into 3/1 toluene/methanol mixed solution with a molar ratio of 2:1 ( $\text{C}=\text{N}:\text{Cu}^{2+}=2:1$ ). After mixing well, the mixture was poured into a teflon mold and kept at room temperature for 12 h. Then, it was heated at 60 °C for 24 h in a vacuum drying oven to obtain the stretchable supramolecular coordination elastomer P1-5%-Cu-0.50. All samples were prepared using a same process with corresponding compositions (**Table S1**).

### **Preparation of the supramolecular coordination elastomers based on polymers from P2-5% to P5-5%**

All samples were prepared using the same procedure as P1-5%-Cu-0.50, except that the polymer  $\text{P}_n$ -5% was different (**Table S2**).

### **Polymer P1-5% for fluorescence detection of $\text{Fe}^{3+}$ and DNT**

To the solution of P1-5% in THF (1 mg/mL, 1800  $\mu\text{L}$ ) was added the solution of  $\text{FeCl}_3$  in  $\text{CH}_3\text{OH}$  (4 mg/mL, 0, 5, 10, 20, 30, or 40  $\mu\text{L}$ ) and DNT in  $\text{CH}_3\text{OH}$  (40 mg/mL, 0, 20, 40, 60, 80, or 100  $\mu\text{L}$ ). Subsequently, corresponding amounts of methanol were added to keep the volume to methanol to be 200  $\mu\text{L}$  for all solutions. All these samples were examined with fluorescence spectrophotometer excited at 376 nm.

**Table S1.** Feed components of the supramolecular elastomers based on polymer P1-(5%, 10%)

Samples	Molar ratio C=N:M <sup>n+</sup>	P1-5%/ P1-10% (g)	Metal salts (g)
P1-5%-Cu-0.50	0.50	2.30	0.099
P1-10%-Cu-0.50	0.50	2.30	0.188
P1-10%-Cu-0.33	0.33	2.10	0.114
P1-10%-Cu-0.25	0.25	2.10	0.086
P1-5%-Fe-0.33	0.33	2.10	0.061
P1-10%-Fe-0.33	0.33	2.10	0.138

**Table S2.** Feed components of the supramolecular elastomers based on polymers from P2-5% to P5-5%

Samples	Molar ratio C=N:Cu <sup>2+</sup>	Pn-5% (g)	CuCl <sub>2</sub> (g)
P2-5%-Cu-0.50	0.50	2.30	0.099
P3-5%-Cu-0.50	0.50	2.30	0.099
P4-5%-Cu-0.50	0.50	2.30	0.099
P5-5%-Cu-0.50	0.50	2.30	0.099

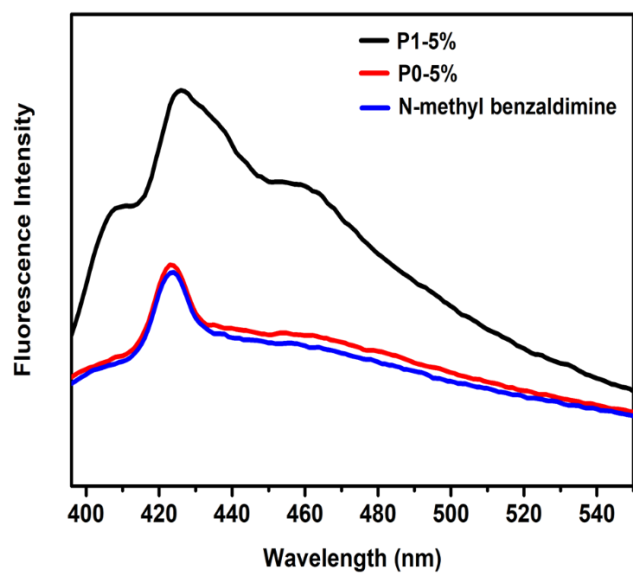


Fig. S1 Fluorescence excitation spectra of polymers P1-5%, P0-5% and *N*-methyl benzaldimine.

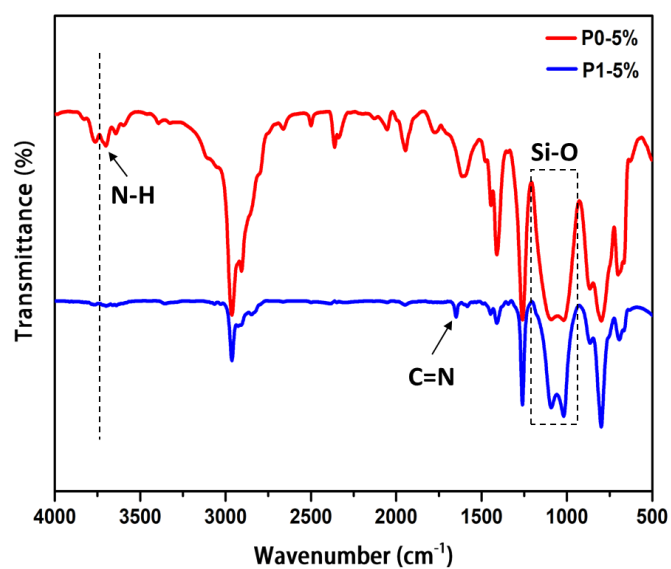


Fig. S2 FT-IR spectra of polymers P0-5% and P1-5%.

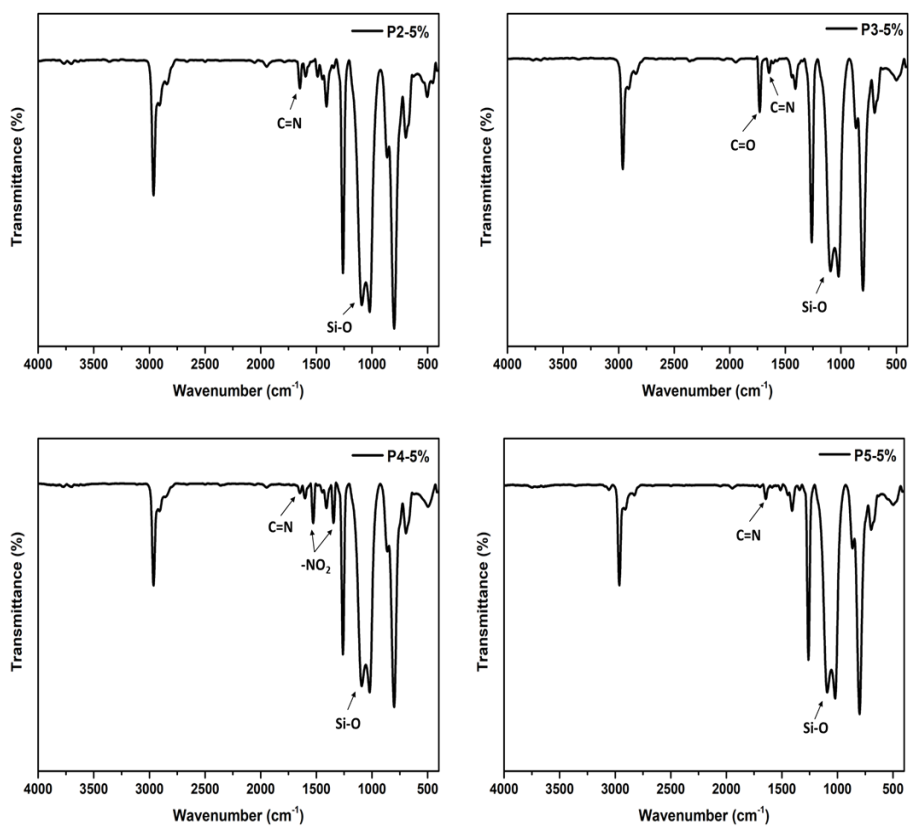


Fig. S3 FT-IR spectra of polymer P2-5%, P3-5%, P4-5% and P5-5%.

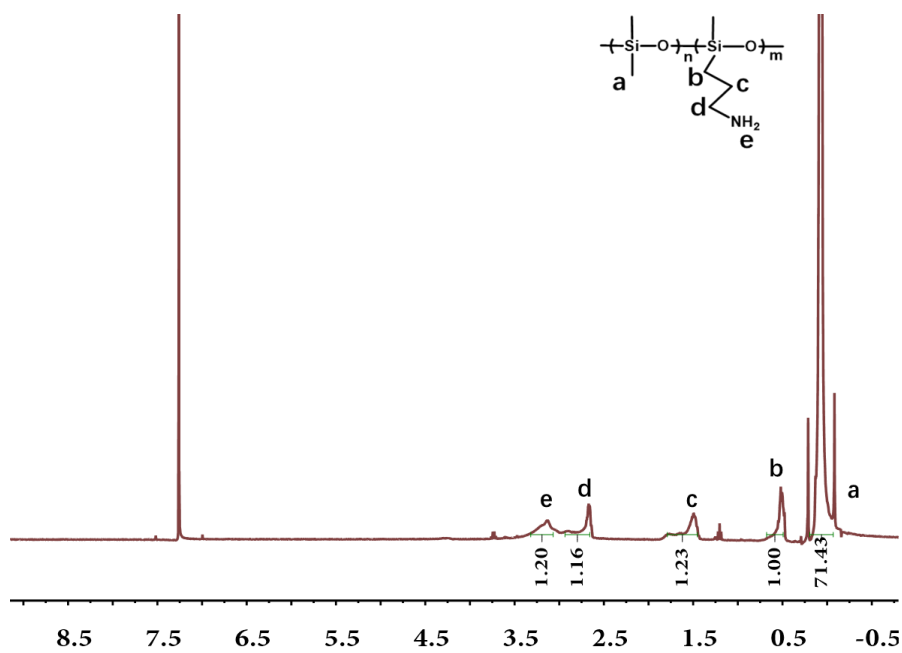


Fig. S4 <sup>1</sup>H NMR spectra of polymer P0-5%.

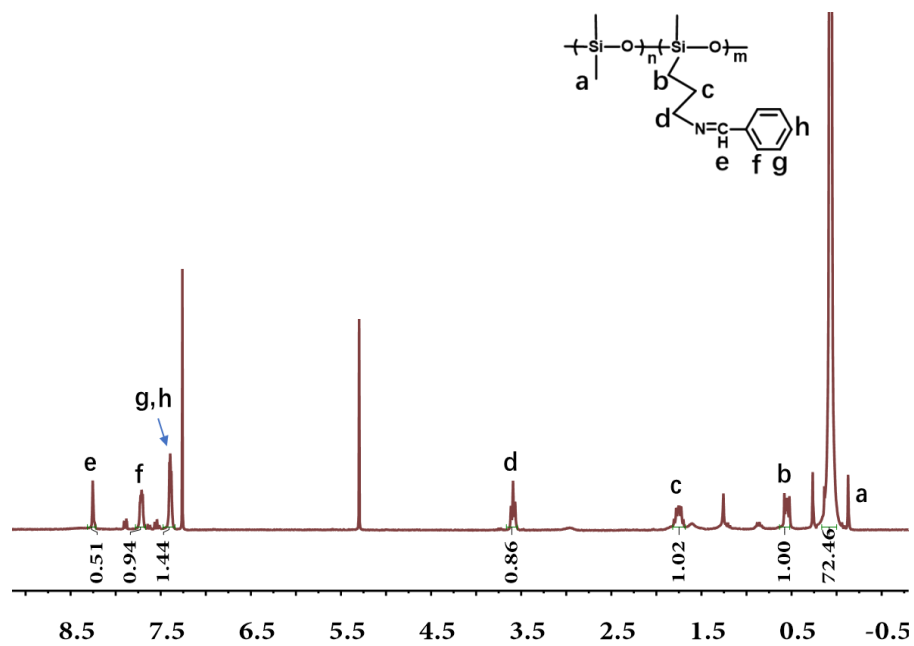


Fig. S5 <sup>1</sup>H NMR spectra of polymer P1-5%.

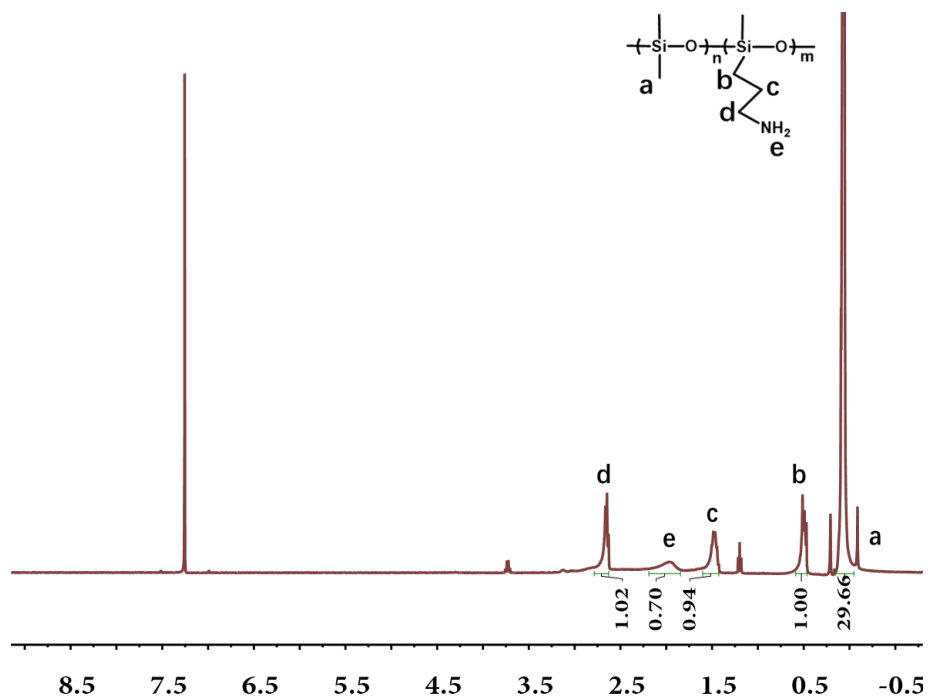


Fig. S6 <sup>1</sup>H NMR spectra of polymer P0-10%.

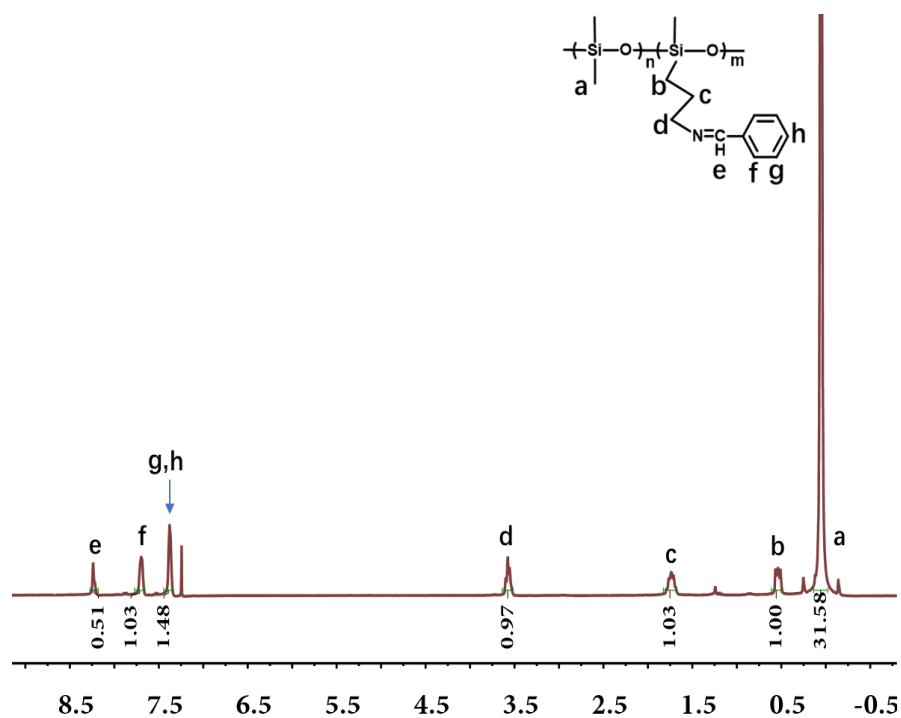


Fig. S7  $^1\text{H}$  NMR spectra of polymer P1-10%.

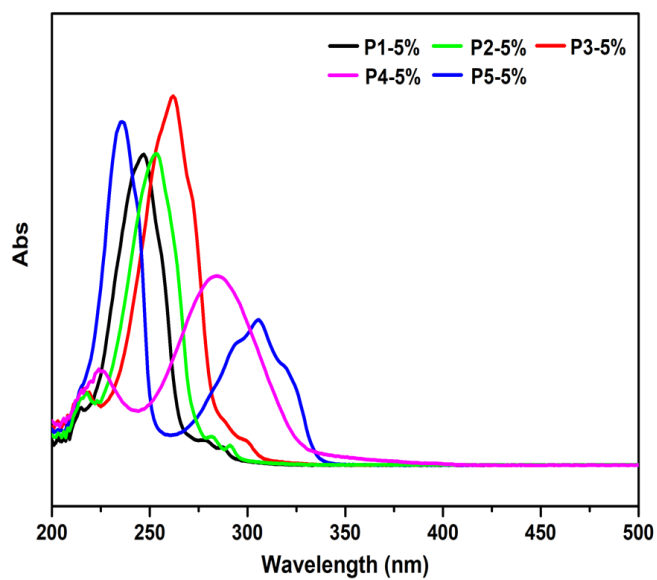
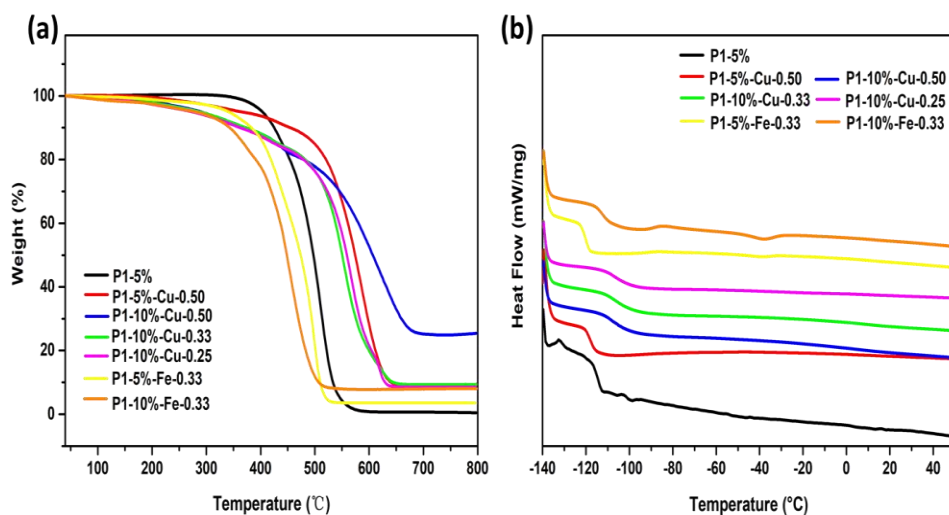
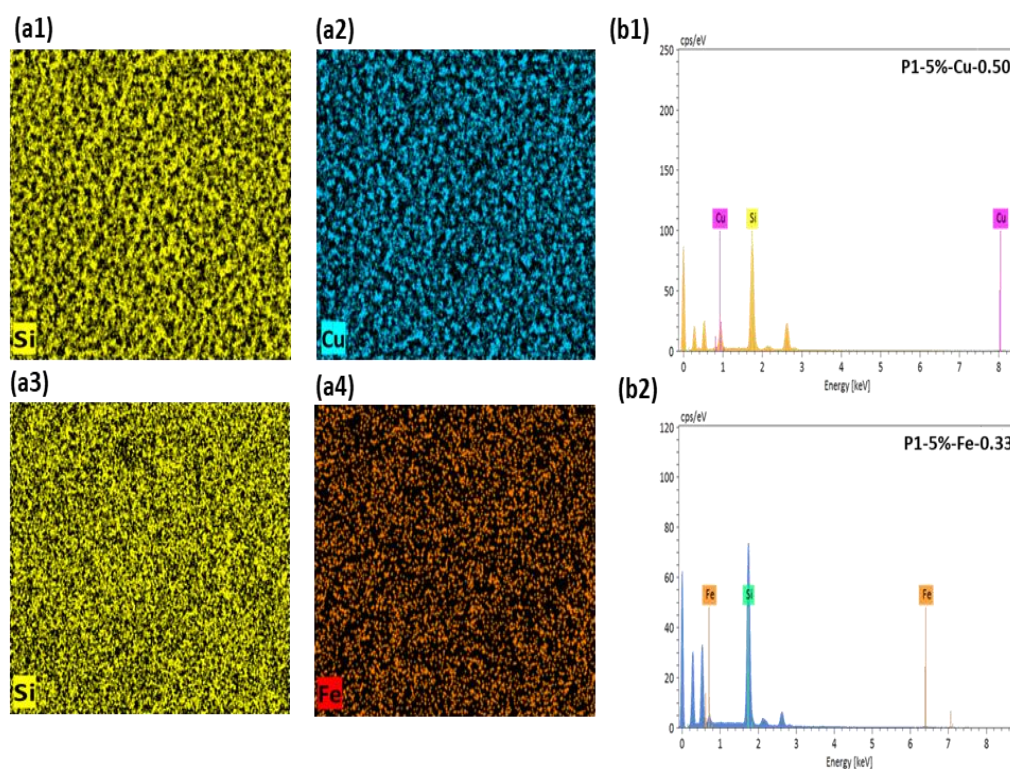


Fig. S8 UV-Vis spectra of polymers P1-5%, P2-5%, P3-5%, P4-5% and P5-5%.





**Fig. S9** TGA thermograms (a) and DSC curves (b) of coordination elastomers based on polymer P1-(5%, 10%).



**Fig. S10** Element distribution of supramolecular coordination elastomers P1-5%-Cu-0.50 (a1-2, b1), P1-5%-Fe-0.33 (a3-4, b2) by EDS.

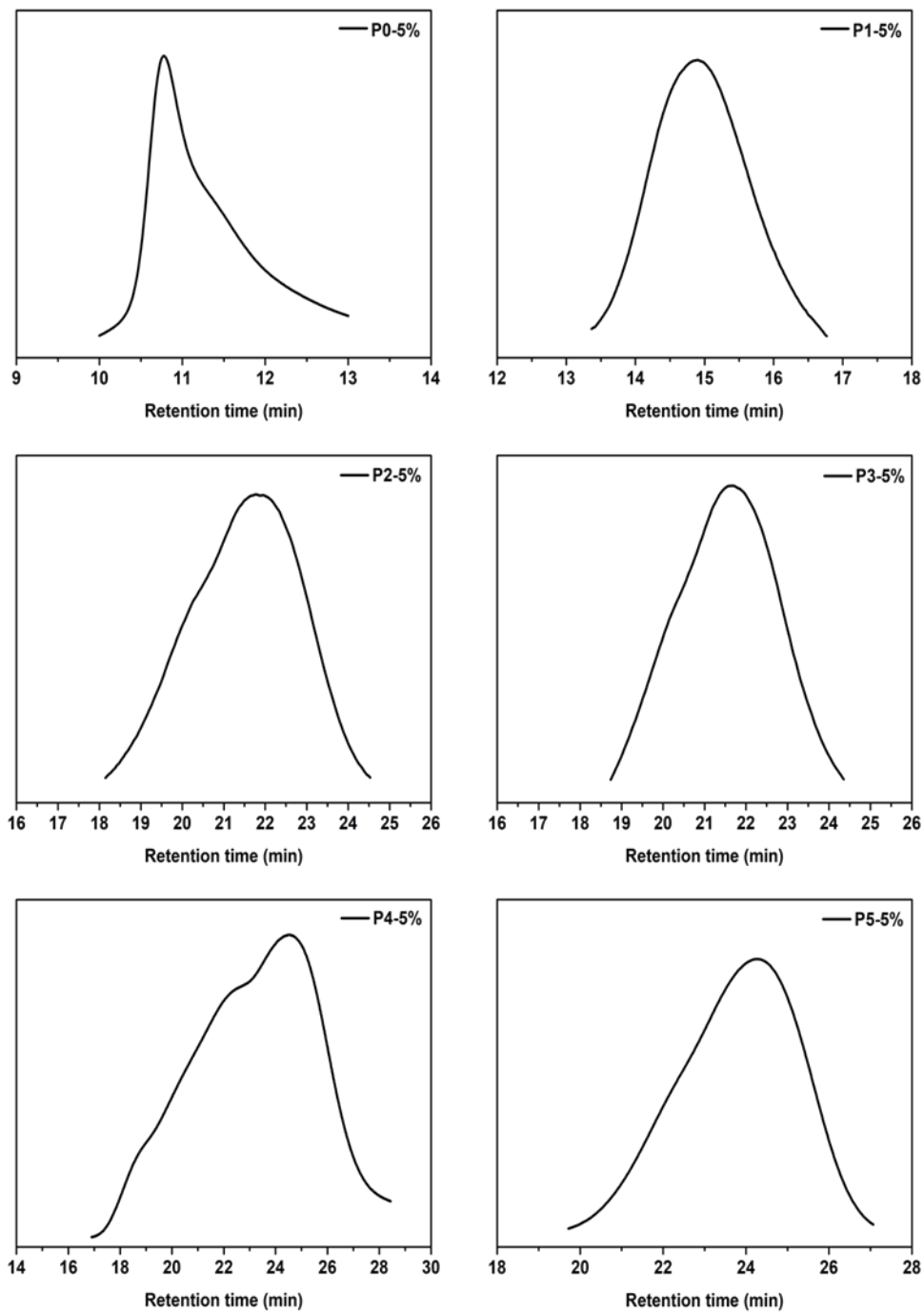
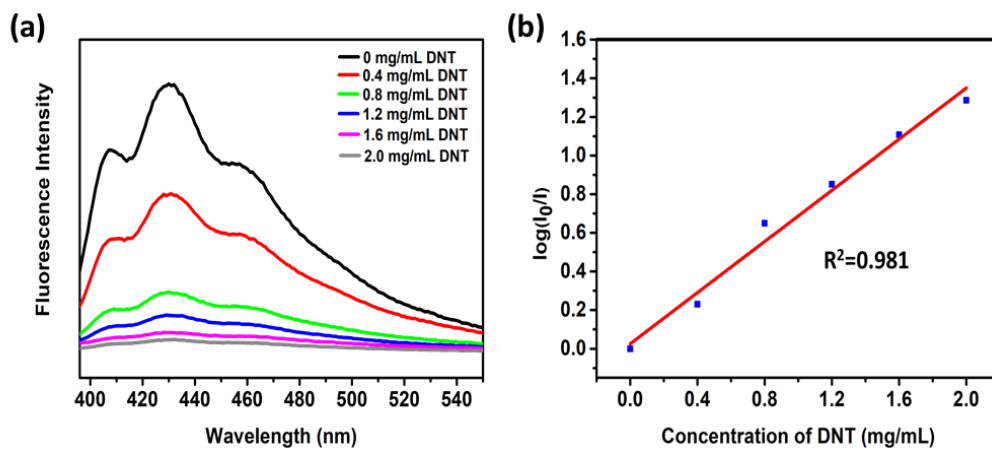


Fig. S11 GPC curves of polymers P0-5%, P1-5%, P2-5%, P3-5%, P4-5%, and P5-5%.



**Fig. S12** (a) Fluorescence spectra of **P1-5%** after adding different DNT concentrations. (b) the dependence of  $\log(I_0/I)$  on the concentration of DNT within the range of 0 - 2.0 mg/mL.