A Self-healing PDMS Polymer with Solvatochromic Property

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Experimental section

Chemicals

Poly(dimethylsiloxane)bis(3-aminopropyl) terminated (M_n = 5000-7000) were purchased from Gelest. The remaining chemical sand solvents were purchased from Sigma-Aldrich. 5-(4H-1,2,4-triazol-4-yl)isophthalic acid (TIA) was synthesized according to reference. [1] All of the chemicals were used as received without further purification.

Materials and general measurements

NMR (^{1}H) spectra were recorded on a Varian Mercury 500 NMR spectrometer in deuterated solvents at room temperature. Absorption spectra were recorded on an Agilent Cary 6000i UV/Vis/NIR Spectrophotometer. Analytical gel permeation chromatography (GPC) experiments were performed on an Agilent 1100 chromatographic instrument. Differential Scanning Calorimetry (DSC) experiments were performed using a Model Q2000 from TA Instruments (USA). The temperature range is −100 to 100 °C, at a heating and cooling speed of 10 °C/min. Thermogravimetric analyses (TG) were performed on a simultaneous SDT 2960 thermal analyzer from 35 to 800 °C with a heating rate of 10 °C/min under N_2 atmosphere.

Synthesis of Macromolecular Ligand

Synthesis of 5-(4H-1,2,4-triazol-4-yl)isophthaloyl dichloride (TIDC): 5-(4H-1,2,4-triazol-4-yl)isophthalic acid (0.234g,1mmol) was refluxed in $SOCl_2$ (10 mL) at 80°C for 24 h. The excess $SOCl_2$ was then removed under reduced pressure to afford the **TIDC** compound. This compound was used directly for the subsequent reaction without characterization.

Synthesis of TIA-PDMS: Et_3N (0.5 mL) was added to a solution of bis(3-aminopropyl) terminated Poly(dimethylsiloxane) (5 g, 1 mmol) in CH_2Cl_2(50 mL) at 0°C. After stirring for 2 hours, a solution of TIDC (1mmol) in CH_2Cl_2 (20 mL) was added dropwise. The temperature of the resulting solution was kept at 0°C with ice water at Nitrogen atmosphere and stirred for 30 mins. After reaction, the solution was concentrated to 1/4 of its volume and 60 mL MeOH was

poured into it. White precipitate-like viscous liquid appeared and mixture was settled for a while. The upper clear solution was then decanted. 20 mL CH_2Cl_2 was added to dissolve the product. The dissolution-precipitation-decantation process was repeated for three times and the final product was subjected to vacuum evaporation to remove the solvent and trace of Et_3N. Yield: 3.5 g (70%). ^{1}H-NMR (500 MHz, CD_2Cl_2-d_2): δ =11.27 (s, CONH), 8.26 (s, N=C-H), 8.05 (s, Ar C-H), 7.83 (s, Ar C-H), 1.51 (m, -CH_2-CH_2-), 0.61(m, Si-CH_2CH_2), 0.18 (m, Si-CH_3). Molecular weight according to GPC: M_w=159000 (PDI = 5.18).

Preparation of Metallopolymer Films

Typical procedure for the preparation of metal supra-molecular film: A certain amount of MeOH solution of metal chloride (100 mg/mL) was added to a solution of TIA-PDMS (1 g) in CH_2Cl_2 (10 mL). The mixed solution was stirred for 1 day at room temperature and then concentrated to about 2 mL. The concentrated solution was poured into polytetrafluoroethene (PTFE) mold and dried at room temperature for one day followed by drying at 100 °C for 12 h. The as prepared film has a size of 75 × 14 × 1.0 mm^3.The films were then peeled off from the PTFE mold for further testing.

Mechanical and Self-Healing tests

Mechanical tensile-stress experiments were performed using an Instron5848 Microtester. Three samples were tested for each volume fraction. Tensile experiments were performed at room temperature (25 °C) at different sample size and strain rate when evaluating the stretchability. For other controlling measurements and healing experiments, samples with the same size (25 × 5 × 1.0 mm^3) were tested at the same strain rate of 5 mm min^{-1}. For self-healing tests, the film was cut into two pieces and then put together. The two cut interfaces were brought back together for 1 min. The film was then healed at different temperature for different times and healed in solvents. The healed films were then stretched following the same procedure to obtain the stress−strain curves.

Reference

1. T. Panda,T. Kundu and R. Banerjee. *Chem. Commun.*, 2012, **48**, 5464–5466.

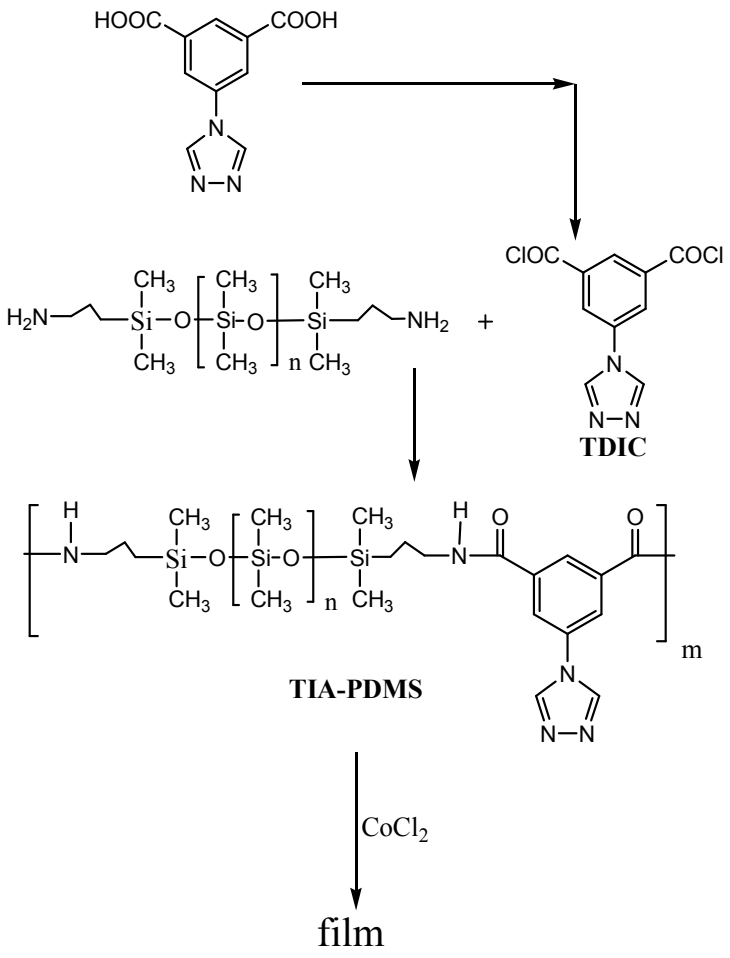

Figure S1.Process to synthesis of the polymer

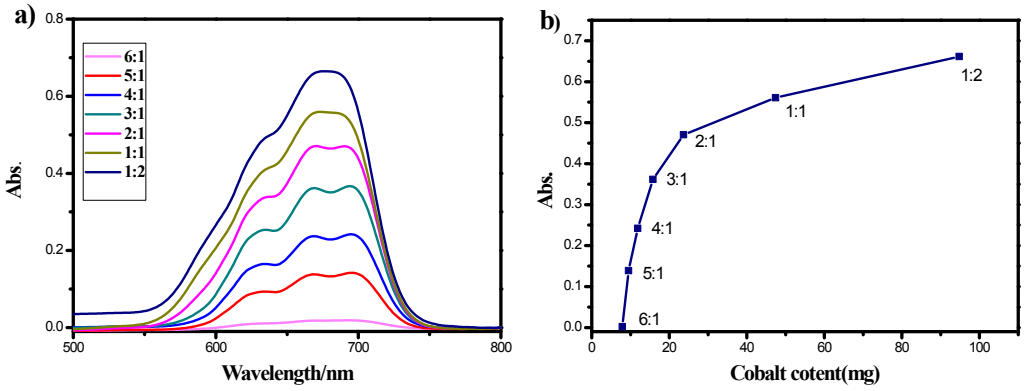

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Figure S2. a) The UV-Vis spectra of Co-TIA-PDMS in CH_2Cl_2 with different ligand to metal molar ratios (from 6:1 to 1:2); b) The dependence of absorbance at 669 nm on the different Cobalt content ($CoCl_2$ (mg) in 1 g TIA-PDMS).

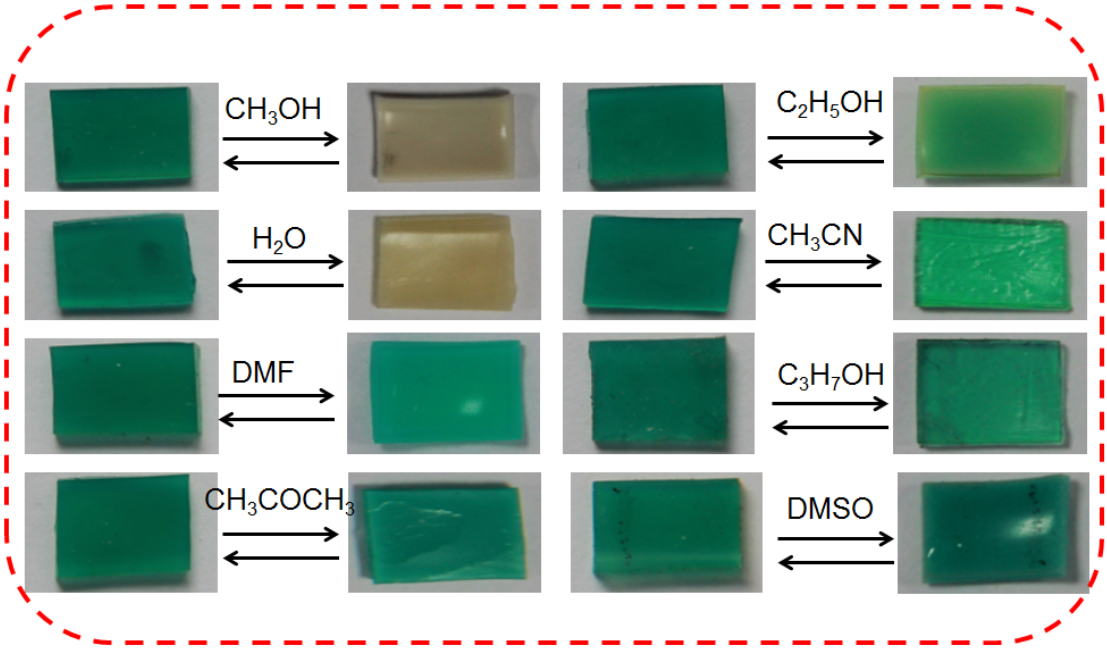

Figure S3. Chromic property in different solvents.

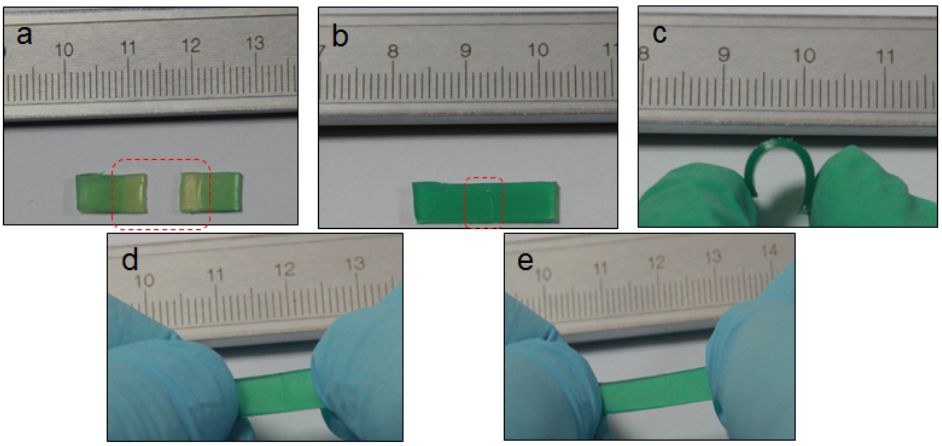

Figure S4.The methanol pretreatment assisted self-healing. The film after treating with methanol at the cut surface shows color change at one end (a). After healing at room temperature, the two cut films are reconnected while scars can be observed (b). The healed film can be bent or stretched (before stretch (d) and after stretch (e)).

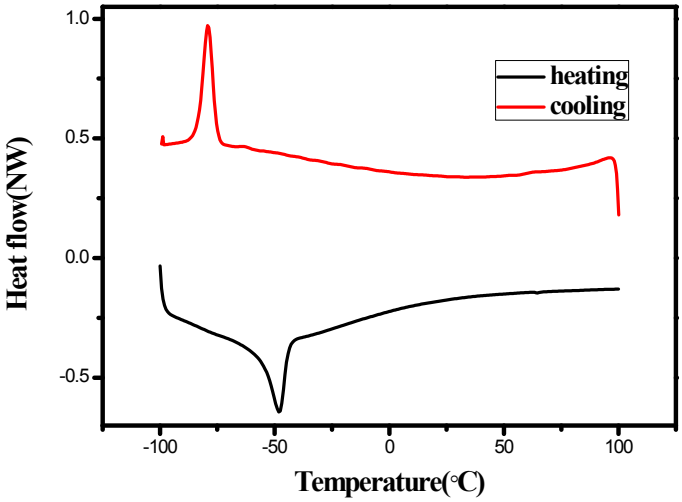

Figure S5. The DSC curves of Co-TIA-PDMS. The exothermal peak at -79.2 °C and endothermic peak at -48.2 °C corresponded to the crystallization and melting, respectively. The T_g must be below 100 °C as there is no other exothermal/endothermal signal between the crystallization point and the lowest measurable temperature of our instrument.

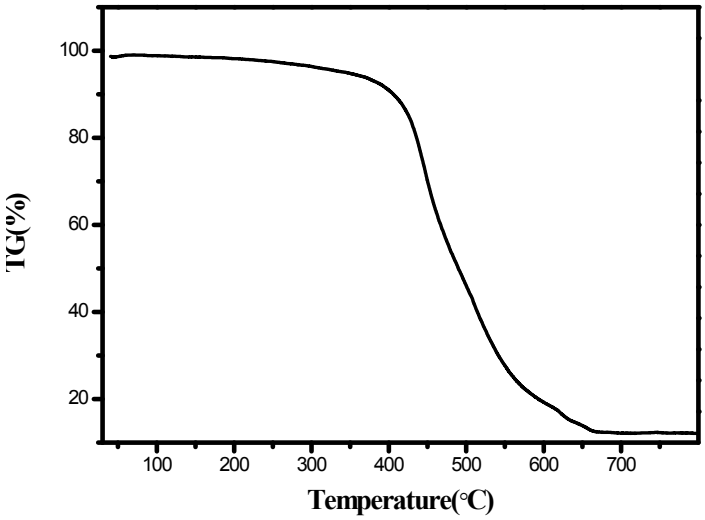

Figure S6. The TG curves of Co-TIA-PDMS.

Table S1. Self-healing efficiencies of Co-TIA-PDMS film at different conditions.

Heal at different temperature for 24h					
	140°C	120°C	100°C	80°C	25°C
Self-healing efficiency(%)[a]	52.2	47.3	33.5	20.7	1.25
Heal at different time (h)					
	24	12	6	1	
Self-healing efficiency(%)[a]	47.3	35.9	25.1	21.6	
Heal in methanol at different time (h)					
	48	24	12		
Self-healing efficiency(%)[a]	33.5	22.3	12.6		

[a] The self-healing efficiencies were calculated from the ratio of integrated area under the stress-strain curves of original and healed samples.