Supporting Information

Modulating the Thermomechanical Properties and Self-Healing Efficiency of Siloxane-Based Soft Polymers Through Metal-Ligand Coordination

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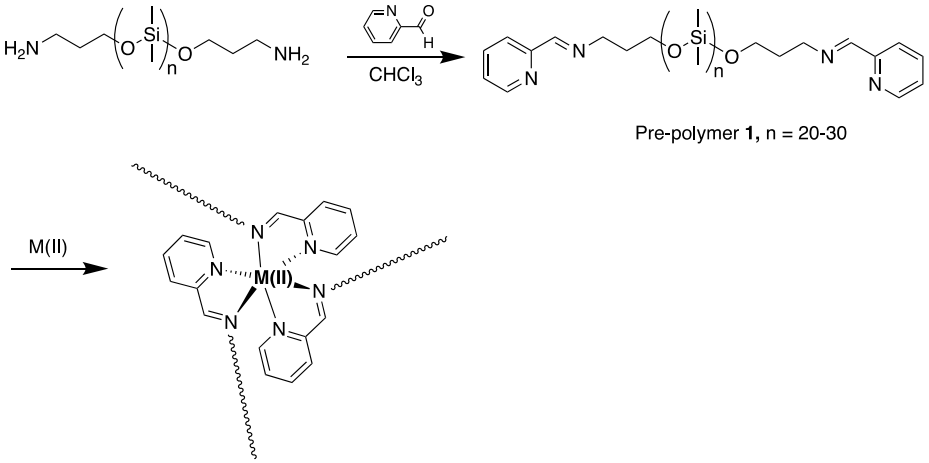
General Procedure and Materials

Materials: Commercial reactants were used without further purification unless stated otherwise. All the solvents used in these reactions were distilled prior to use. Pre-polymer **P1** was prepared from pyridine-2-carboxaldehyde and aminopropyl-terminated polydimethylsiloxane with molecular weight of 1000 Da, and dispersity of 1.33 (purchased from Gelest, Pennsylvania, USA) as previously reported.[1] Iron (II) tetrafluoroborate hexahydrate, Cobalt (II) tetrafluoroborate hexahydrate, Zinc tetrafluoroborate hydrate, Zinc trifluoromethanesulfonate and Zinc perchlorate hexahydrate were purchased from Sigma-Aldrich and used as received.

Measurements and Characterization: UV-Visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. Calorimetric studies were conducted on a TA instruments DSC2500 and thermal gravimetric analysis was performed on a TA instruments TGA5500. Nitrogen (99.999%) was used to purge the systems at a flow rate of 60 mL/min. All samples were run in aluminum crucibles. TGA samples were held at 25 °C for 30 min before heated to 500 °C at a rate of 10 °C/min.

Sample Preparation: Pre-polymer **P1** was solubilized in dichloromethane, filtered on 0.45 μm filter, crosslinked with either $Fe(BF_4)_2$, $Co(BF_4)_2$, $Zn(BF_4)_2$, $Zn(ClO_4)_2$ or $Zn(OTf)_2$. The resulting materials was casted into custom-made dog-bone shaped PTFE mold with dimensions in accordance to the ASTM standard for thermoplastic elastomers (ASTM D412). Once a gel was formed, the samples were placed in a vacuum oven at 50 °C and left to dry for 48 hours. Once dried, the sample was slowly peeled off and used directly for further characterizations.

Evaluation of self-healing properties: Self-healing was evaluated by using a flat molded sample which was cut in half with a blade, pressed back together and left to heal for 2 hours before being characterized. Tensile-strain analysis was performed on an Instron Tensile Strain instrument with a test rate of 5 mm/min.



Scheme S1. Synthesis of pre-polymer **1** followed by chemical crosslinking with M(II) salts.

Material Characterization

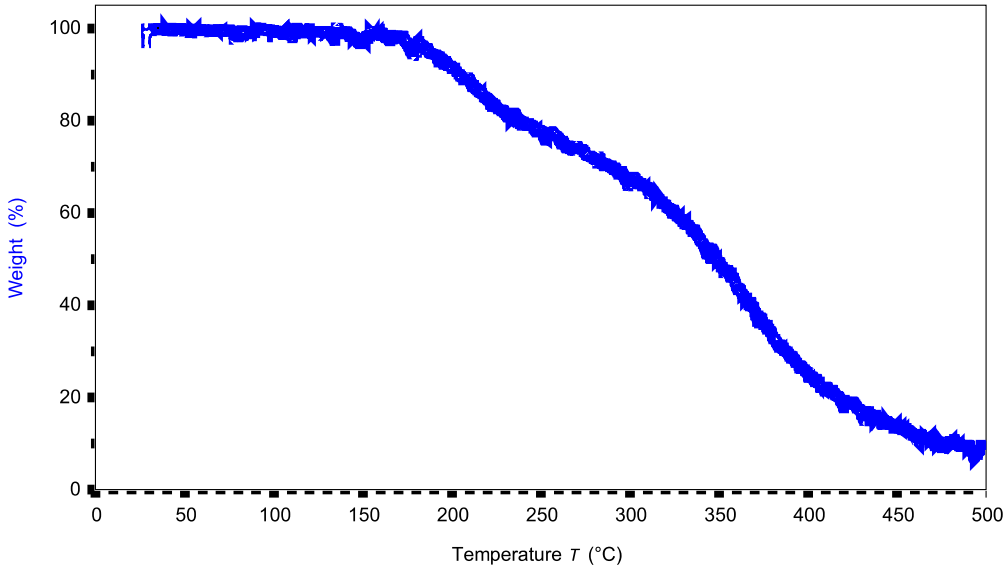


Figure S1. Thermogravimetric analysis of pre-polymer **P1** crosslinked with $Co(BF_4)_2$

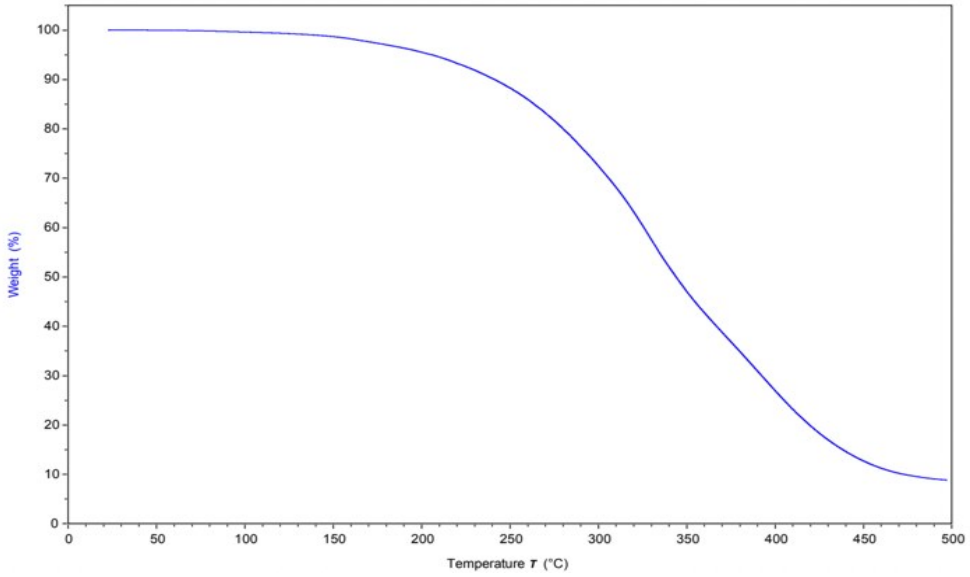


Figure S2. Thermogravimetric analysis of pre-polymer **P1** crosslinked with $Fe(BF_4)_2$

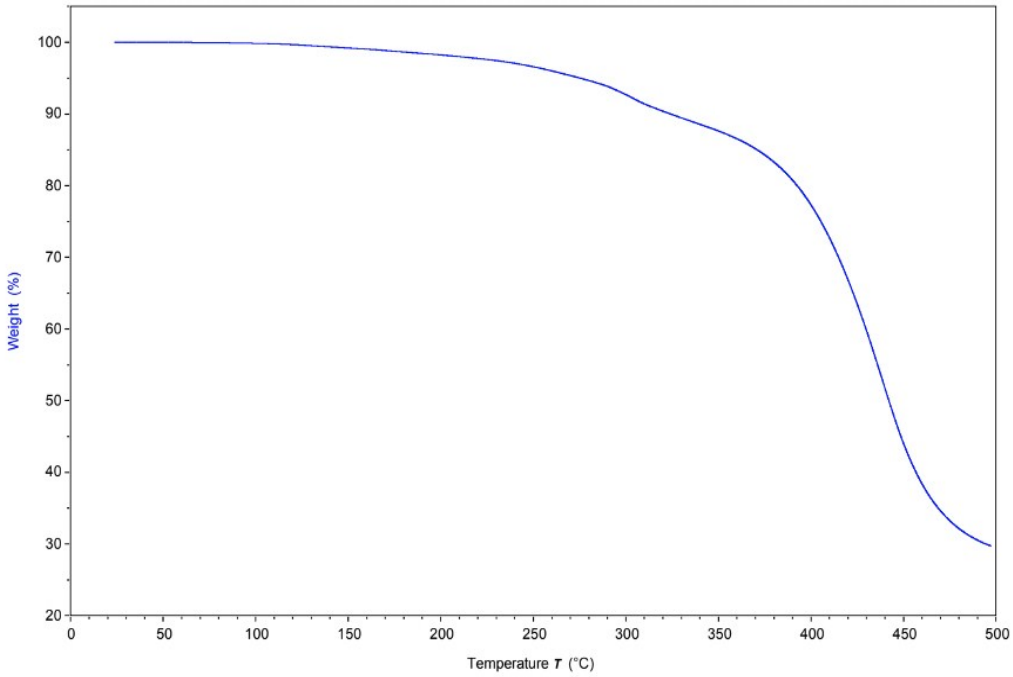


Figure S3. Thermogravimetric analysis of pre-polymer **P1** crosslinked with $Zn(OTf)_2$

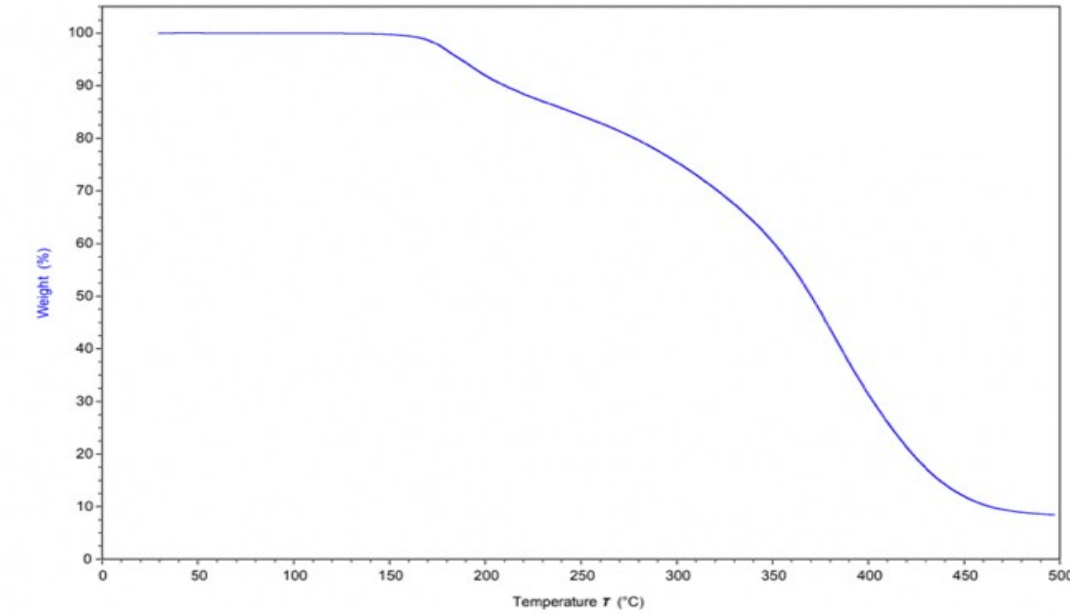


Figure S4. Thermogravimetric analysis of pre-polymer **P1** crosslinked with $Zn(BF_4)_2$

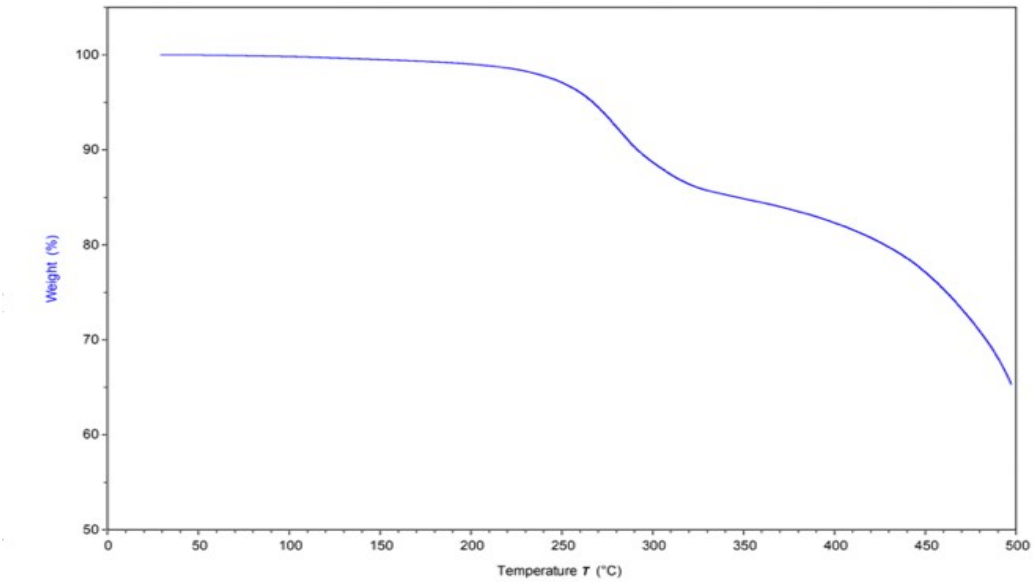


Figure S5. Thermogravimetric analysis of pre-polymer **P1** crosslinked with $Zn(ClO_4)_2$

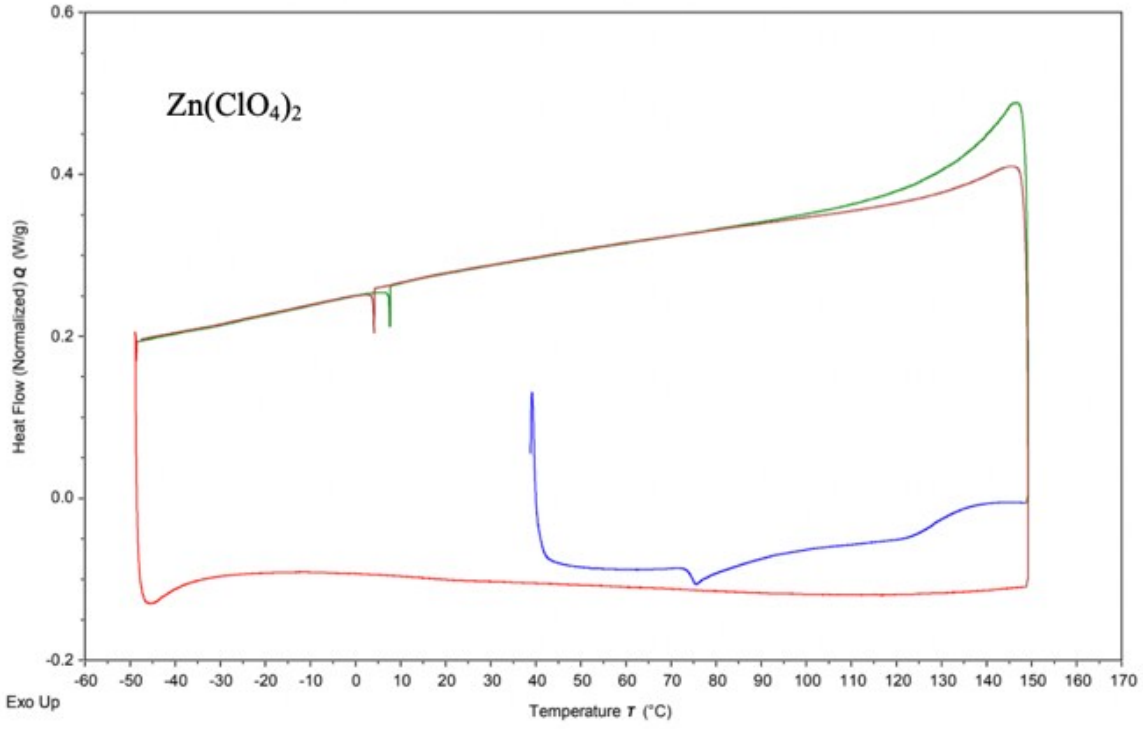


Figure S6. Differential scanning calorimetry curve for pre-polymer **P1** crosslinked with $Zn(ClO_4)_2$

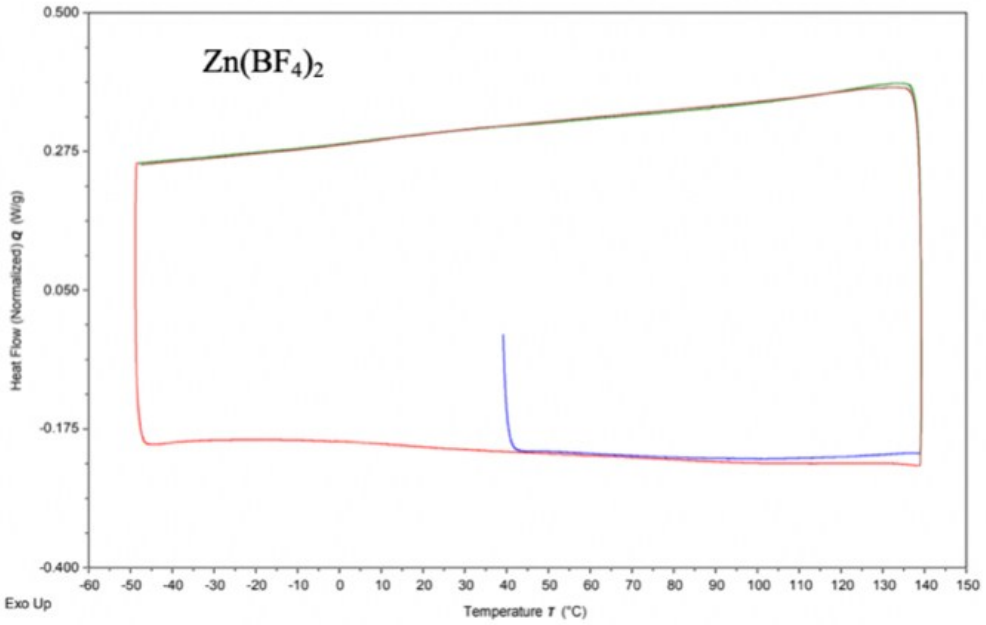


Figure S7. Differential scanning calorimetry curve for pre-polymer **P1** crosslinked with $Zn(BF_4)_2$

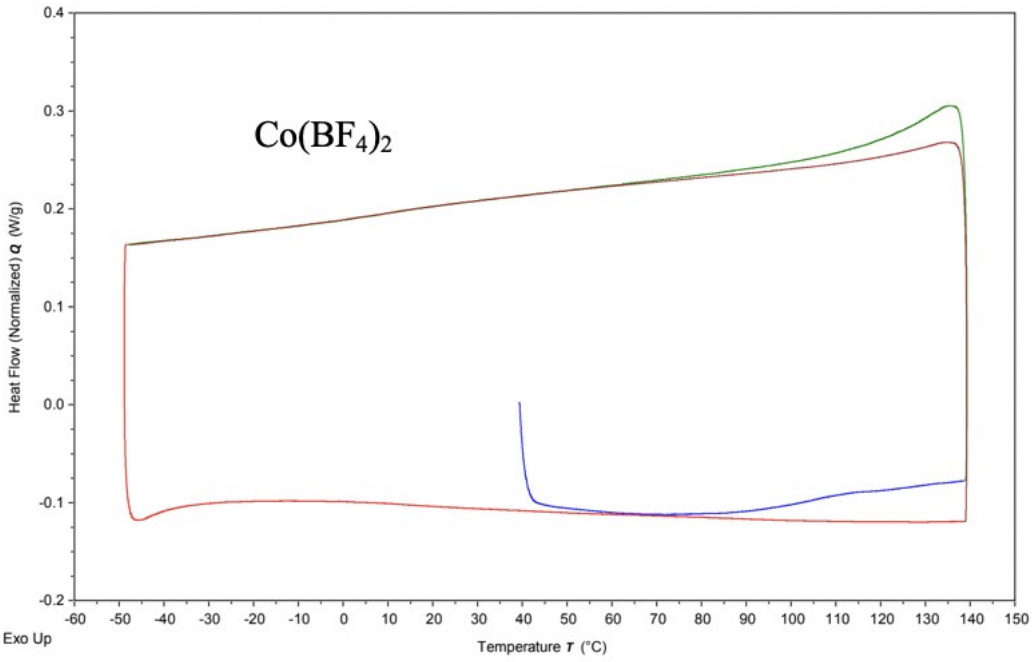


Figure S8. Differential scanning calorimetry curve for pre-polymer **P1** crosslinked with $Co(BF_4)_2$

Figure S9. Differential scanning calorimetry curve for pre-polymer **P1** crosslinked with $Fe(BF_4)_2$

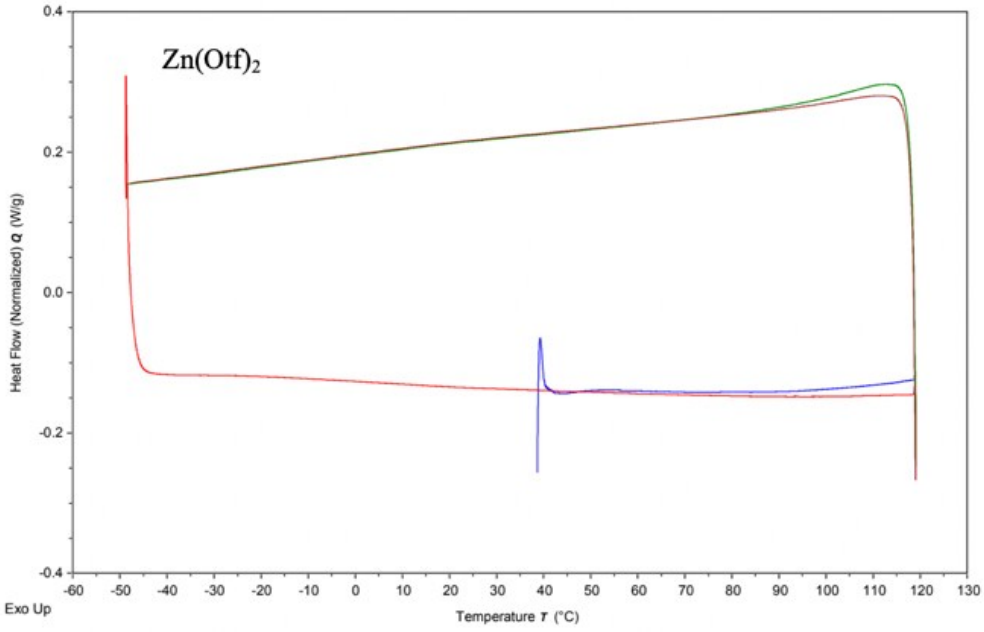


Figure S10. Differential scanning calorimetry curve for pre-polymer **P1** crosslinked with Zn(OTf)

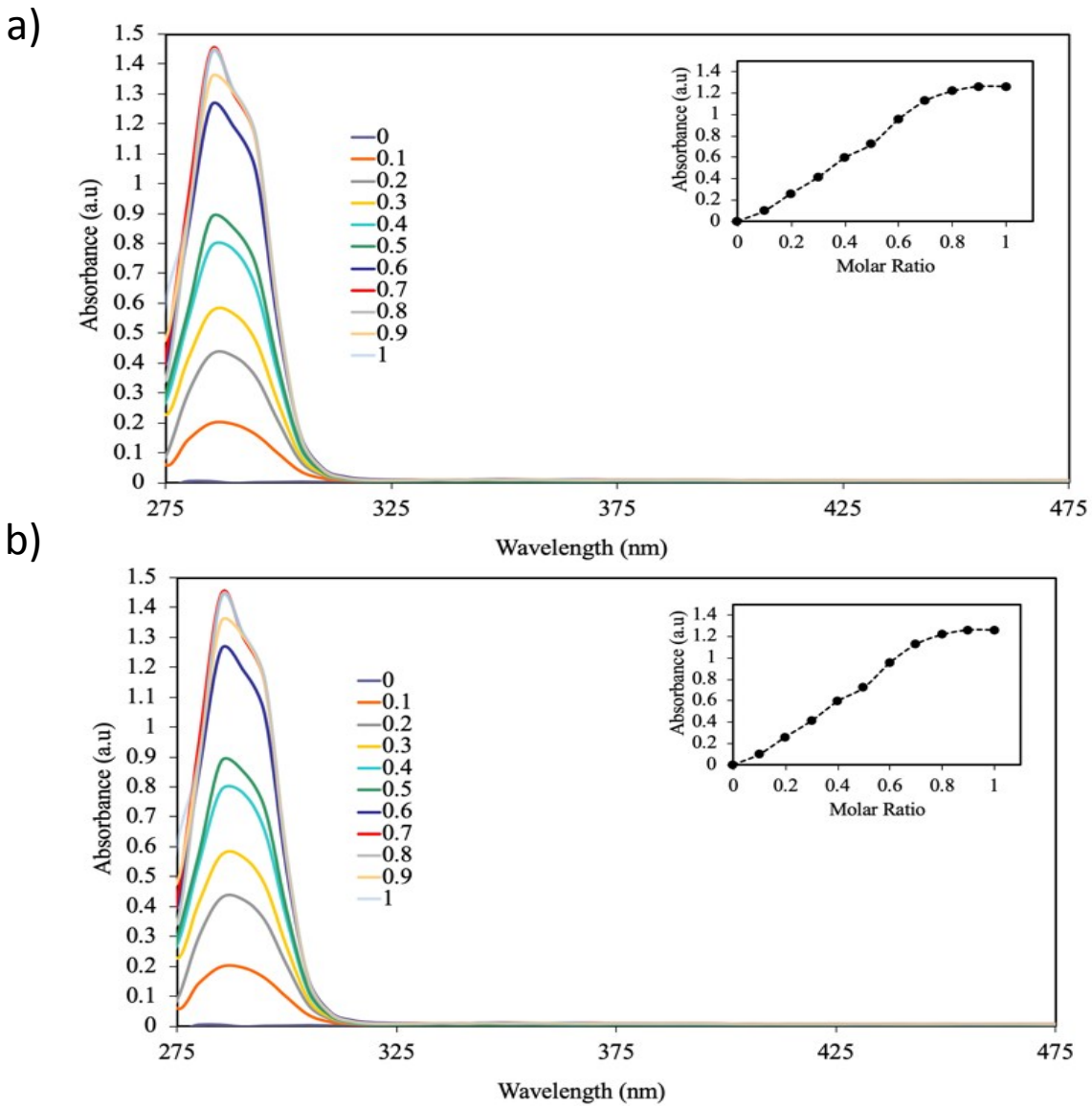


Figure S11. a) UV-vis absorption spectra of **P1** in CH_2Cl_2 with $Zn(OTf)_2$; b) UV-vis absorption spectra of **P1** in CH_2Cl_2 with $Zn(ClO_4)_2$; insets plot molar ratio of each Zn(II) salt versus absorbance at 290 nm. Each titration included 0.1 molar equivalents of the respective metal salt per N-ligand in **P1**.

References

1 J. Pignanelli, B. Billet, M. Straeten, M. Prado, K. Schlingman, M. J. Ahamed and S. Rondeau-Gagne. Imine and metal–ligand dynamic bonds in soft polymers for autonomous self-healing capacitive-based pressure sensors, *Soft Matter*, 2019, **15**, 7654–7662.