Supporting Information

Self-Healing and Shape Memory Capabilities of Copper-Coordination Polymer Network

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Experimental Section

N, N-Bis (2-hydroxyethyl) pyrazinamide (BIN) and isonicotinate-functionalized polyesters (PIE) were synthesized as our previous report. PIE Polymer was soaked into 4 g/L CuSO₄ solution for 1 h, then wiped the water of surface and further dried under vacuum at room temperature for 24 h. The resultant Cu-PIE films were prepared for Dynamic Mechanical Analysis (DMA), shape memory test, self-healing performance test.

To further confirm the successful synthesis of the coordination polymer, solid UV-vis spectrophotometer in the wavelength range of 250–800 nm.

The absorbance marked as was measured with UV-vis spectrophotometer (UV-2550, Shimadzu, Japan) at 490 nm. The increase with the ratio increasing. C shows the concentration of the curve’s turning point of copper-coordination polymer and its value is 10.3 mg/mL. N represents the number of copper ions coordinated with the pyridine containing in polymer matrix.

Thermal properties of polymers were determined by TG (TA TG-Q500). The heating range of 0~600℃ and the heating ratio was 10 ℃/min.

DMA was measured using a specimen with size of 10 × 3 × 1 mm (length × width × thickness) carried out with a DMA (TA DMA-Q 800) at heating ratio of 3 ℃/min.

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from 0 to 50 °C and at frequency of 1 Hz. The storage modulus $E'$ and tan datle were tested.

Thermal properties of polymers were determined by DSC (TA DSC-Q100). In order to eliminate any unknown thermal history of the samples, heating and cooling were repeated from −20 °C to 110 °C, the DSC curves of the second heating and cooling process were obtained. Both the heating and cooling ratio was 10 °C/min. All data were used from the second heating process.

The Cu-PIE samples were immersed in 20 mL 4 g/L CuSO4 solution for 1 h, and the CuSO4 solution at the designated time were analyzed with Atomic Absorption Spectrometry (AAS, Thermo Elemental S4).

The Cu ion release from the Cu-PIE was measured with Inductively Coupled Plasma Mass Spectrometry (ICP, NexION 300X). The Cu-PIE samples were immersed in 10 mL water in 25 ℃ and 37 ℃ for 24 h. And when the Cu-PIE samples were immersed in water for 2 h, 4, 8, 16, 24, 30 h, 2 mL water was pipetted at each time point. Then the water containing the released Cu ions at the designed time were measured by ICP.

Shape memory fixity ratio and recovery ratio were measured using strip shaped specimens measured by DMA with a controlled force mode according to our designed experiment. Firstly, straining the specimen at a constant stress rate at 37 ℃ obtained a temporary shape, marked as $\varepsilon_1$; and then cooled to -10 ℃ and released the stress, marked as $\varepsilon_2$; Secondly, the temporary shape was heated from -10 ℃ to 50 ℃, the strain marked as $\varepsilon_0$. The shape memory fixity ratio and recovery ratio were calculated according to the following equations:

$$R_f = \frac{\varepsilon_2}{\varepsilon_1} \times 100\%$$  
(2)

$$R_r = \left(1 - \frac{\varepsilon_0}{\varepsilon_1}\right) \times 100\%$$  
(3)
Self-healing property of Cu-PIE was characterized by tensile tests. The fractured parts of the Cu-PIE were put together, and placed in an oven at 45 °C for different times. Then the self-healing efficiency was calculated as the ratio of tensile strength of self-healed (\(\sigma_1\)) and original Cu-PIE (\(\sigma_0\)).

The healing efficiency was calculated according to the following equation:

\[
\text{Healing efficiency} = \frac{\sigma_1}{\sigma_0} \times 100\%
\]  

(4)

Notes and references


Figure S1. The FTIR spectrum of PIE and Cu-PIE.
Figure S2. TG curves of PIE and Cu-PIE.

Figure S3. DSC curves of PIE and Cu-PIE.
Figure S4. DMA curves of PIE and Cu-PIE.
**Figure S5.** The amount of Cu ions released from Cu-PIE in PBS at 37 °C and 25 °C respectively at different time points.

**Figure S6.** The investigation of rod-like Cu-PIE.

**Table S1** The self-healing efficiency upon different water content and healed time

<table>
<thead>
<tr>
<th>Water content</th>
<th>Self-healing efficiency</th>
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<tbody>
<tr>
<td></td>
<td>0.5 h</td>
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<tr>
<td>0</td>
<td>11.62%±1.11%</td>
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<tr>
<td>5%</td>
<td>43.48%±2.16%</td>
</tr>
<tr>
<td>10%</td>
<td>33.13%±1.29%</td>
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