## Electronic Supplementary Information (ESI)

# Cu<sup>2+</sup> Triggered Shrinkage of a Natural Betulin-Derived

## Supramolecular Gel to Fabricate Moldable Self-Supporting Gel

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#### 1. Synthesis and characterization of Ph-BL and Py-BL



**Scheme S1.** Synthetic route of **Ph-BL** and **Py-BL**. (a) 4-Nitrophenyl chloroformate, dry pyridine and THF, rt, 12 h; (b) 4-Pyridinemethaneamine, DCM,  $Et_3N$ , 40 °C, 48 h.



<sup>13</sup>C NMR spectrum of Ph-BL (100 MHz, CDCl<sub>3</sub>, ppm)



<sup>13</sup>C NMR spectrum of **Py-BL** (100 MHz, CDCl<sub>3</sub>, ppm)

2. CD spectra of Py-BL shrunken gel containing 0.6-1.0 eq. Cu<sup>2+</sup>



Figure S1. CD spectra of Py-BL (1.4 mM) shrunken gel containing 0.6-1.0 eq. Cu<sup>2+</sup>.



#### 3. TEM images of Py-BL shrunken gel at different Cu<sup>2+</sup>/Py-BL molar ratios

**Figure S2.** TEM images of **Py-BL** shrunken gel (1.4 mM) at different  $Cu^{2+}/Py-BL$  molar ratios: (a) 0.2, (b) 0.3, (c) enlarged area of (b), (d) 0.4, (e) 0.6, (f) enlarged area of (e), (g) 0.7 (h) 0.8 and (i) 0.9.

4. TEM images of Py-BL/Fe<sup>3+</sup> sol and Py-BL/Al<sup>3+</sup> sol



Figure S3. TEM images of (a) Py-BL/Fe<sup>3+</sup> and (b) Py-BL/Al<sup>3+</sup> sol at a molar ratio of 1:1



### 5. TEM images of Py-BL gel with other metal ions

Figure S4. TEM images of Py-BL gel with various metal ions at a molar ratio of 1:1

6. ANS binding fluorescence assay of shrunken gel



**Figure S5.** ANS binding fluorescence assay showed a blue shift of fluorescent emission, indicating an increased hydrophobicity of the shrunken gel

#### 7. FT-IR spectra of powder of Py-BL, xerogels of Py-BL and Py-BL/Cu<sup>2+</sup>



**Figure S6.** FT-IR spectra of **Py-BL** powder, **Py-BL** gel and **Py-BL**/Cu<sup>2+</sup> (0.5 eq.) shrunken gel

8. Insulation property of Py-BL gel



**Figure S7.** Photograph implying that LED bulb could not be lit when **Py-BL** gel was connected in the circuit