

## Supporting Information

### Novel two-component gels with multi-stimuli response: the gel–sol phase transition and color changes

Kaiqi Fan <sup>a</sup>, Xiaobo Wang <sup>b</sup>, Zhigang Yin <sup>a</sup>, Caijing Jia <sup>a</sup>, Baohao Zhang <sup>c</sup>, Liming Zhou<sup>\*a</sup>, Jian Song<sup>\*c</sup>

#### Table of contents:

<b>1. Materials</b>	<b>1</b>
<b>2. Instrumentation</b>	<b>1</b>
<b>3. Synthesis</b>	<b>2</b>
<b>4. Properties of two-component gel</b>	<b>3</b>
<b>Table S1</b>	<b>3</b>
<b>Figure S1</b>	<b>4</b>
<b>Figure S2</b>	<b>4</b>
<b>Figure S3</b>	<b>5</b>
<b>Figure S4</b>	<b>5</b>
<b>Figure S5</b>	<b>6</b>
<b>Figure S6</b>	<b>6</b>
<b>Figure S7</b>	<b>7</b>
<b>Figure S8</b>	<b>8</b>
<b>Figure S9</b>	<b>9</b>
<b>Figure S10</b>	<b>10</b>
<b>Figure S11</b>	<b>11</b>
<b>Scheme S1</b>	<b>12</b>

## 1. Materials

D-Gluconic acid, benzaldehyde, DMAP (4-dimethylaminopyridine), hydrazine hydrate (80%), 1,3-propanediamine, 1,6-hexanediamine, were purchased from Shanghai Jingchun Scientific Co., Ltd. Compounds CPTP were prepared according to literature procedures<sup>s1-s2</sup>. The chemical reagents were commercially available and directly utilized without further purification.

## 2. Instrumentation

**NMR experiments:** All 400 MHz NMR studies were carried out on a Bruker DPX 400 MHz spectrometer using cryo probe in DMSO-*d*<sub>6</sub>.

**Mass spectrometry:** Mass spectra were recorded on a TOF-QII high-resolution mass spectrometer.

**Scanning Electron Microscope (SEM):** The morphologies of the xerogels were obtained by a Hitachi S-4800 SEM instrument operating at 3-5 kV. Samples were prepared by dropping the diluted solution of gels on the thin aluminum sheets and then dried under vacuum for 24 h. We coated the samples with a thin layer of Au before the experiment.

**FT-IR spectroscopy:** IR spectra were collected by a FTS3000 spectrometer with KBr pellets. The xerogels were prepared by drying gels on glass slides under vacuum for 24 h.

**UV spectroscopy:** UV spectroscopy was performed on a Jasco V-570 UV/vis/NIR spectrophotometer. The path length of the quartz cell was 10 mm.

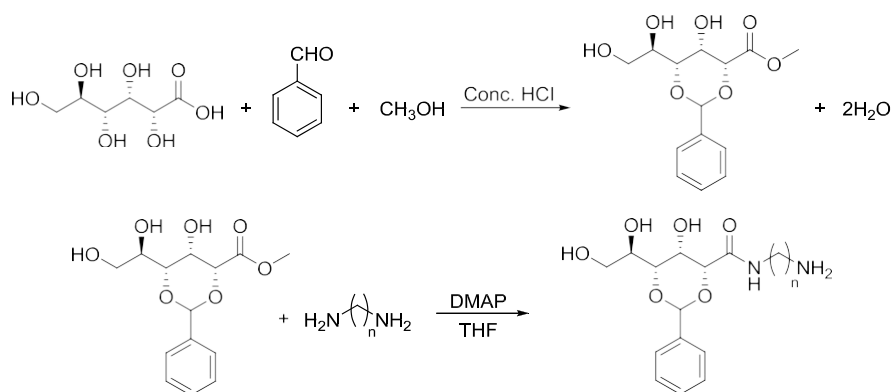
**Fluorescence emission spectroscopy:** Fluorescence emission spectra were recorded on a Hitachi F-2500 fluorimeter.

**Gelation test:** Gelation tests in organic solvents were investigated by a typical tube inversion method. These tests were performed by adding the weighed amount of gelators into the measured volume of solvent in the tube (10 mm diameter) and then heating the tube until the gelators were dissolved or could not be dissolved ever. A “stable to inversion test tube method” was adopted. Each experiment was done in duplicate.

**Gel-sol phase transition temperature measurements ( $T_{gel}$ ):** The gel-sol transition temperature was determined by a conventional “ball-drop method”. A small glass ball with a diameter of 5 mm (0.15 g) was placed on the top of the gel in a test tube (10 mm diameter) which was in a thermostated oil bath and was heated at ca. 1.5 °C/min. The temperature corresponding to submersion in the solution was regarded as the  $T_{gel}$  of the gel. The measured experiments were carried out in duplicate.

**Rheological Study:** Measurements were performed using a strain-controlled rheometer (Anton Paar Physica MCR 301) equipped with steel-coated parallel-plate geometry (15 mm diameter). The gap distance was fixed at 0.5 mm. A solvent trapping device was placed above the plate and measurement was set at 25°C in order to avoid solvent evaporation. The frequency sweep at a constant strain of 0.1% was obtained from 0.1 to 100 rad·s<sup>-1</sup>. Strain sweep was performed in the 0.01%-1000% range at a constant frequency (1 Hz).

### 3. Synthesis



**Scheme S1.** The synthetic route of Cn

The synthetic route for Cn was shown in Scheme S1, and the detailed synthetic methods are described below.

#### (1) Synthesis of the precursors 2,4-benzylidene Methyl-D-Gluconate:

The synthesis and characterization of the precursors 2,4-benzylidene Methyl-D-Gluconate was reported previously.<sup>S3</sup>

#### (2) Synthesis of Compounds Cn:

5 g (0.017 mol) 2,4-benzylidene Methyl-D-Gluconate was dissolved in 50 mL methanol, then 4.88 g (0.042 mol) 1,6-hexanediamine and 0.01 g DMAP (0.008 mmol) were added. The reaction mixture was stirred for 12 h and then 20 ml water was added. Subsequently, the white solid was collected by filtration. The filter cake was washed with water for twice and recrystallized with methanol to obtain compound C6 with a yield of 82%. Similarly, C0, C3 were obtained from 2,4-benzylidene Methyl-D-Gluconate with hydrazine hydrate and 1,3-propanediamine respectively and purified by the same method.

#### (3) Chemical

##### Identification C0

<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>, TMS): δ 8.57 (s, 1H, CONH), 7.61-7.59 (m, 2H, Ar-H), 7.40-7.37 (m, 3H, Ar-H), 5.64 (s, 1H, OCHO), 4.75 (d, J=7.12 Hz, 1H, OH), 4.62 (d, J=8.74 Hz, 1H, OH), 4.47 (d, J= 8.28 Hz, 1H, OH), 4.45 (s, 1H, CH), 4.31 (s, 2H, NH<sub>2</sub>), 3.99 (d, J=8.78, 1H, CH), 3.67-3.65 (m, 1H, CH), 3.56-3.55 (m, 1H, CH<sub>2</sub>), 3.41 (m, 1H, CH<sub>2</sub>), 3.35 (m, 1H, CH).

<sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 169.65, 167.68, 139.84, 139.54, 131.83, 130.53, 129.46, 127.50, 98.68, 79.33, 69.57, 62.54, 52.17. HRMS calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup>: 321.1063; Found: 321.1132.

##### C3

<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>, TMS, 25 °C): δ 7.57-7.56 (m, 3H, Ar-H), 7.39-7.38 (m, 2H, Ar-H), 7.37 (m, 1H, CONH), 5.67 (s, 1H, OCHO), 4.37 (s, 2H, OH), 4.01 (s, 1H, OH), 3.75 (m, 1H, CH), 3.59 (m, 1H, CH), 3.56 (m, 2H, CH<sub>2</sub>), 3.45-3.42 (m, 2H, CH<sub>2</sub>), 3.20 (m, 1H, CH), 2.51 (m, 2H, CH<sub>2</sub>), 1.53-1.50 (m, 1H, CH), 1.47(m, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 168.51, 139.49, 132.79, 131.57, 130.93, 129.45, 127.79, 98.75, 80.95, 79.96, 69.69, 63.15, 40.69, 38.90, 31.09, 27.46. HRMS calcd for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup>: 363.1532; Found: 363.1611

#### C6

<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>, TMS, 25 °C): δ 7.59-7.58 (m, 2H, Ar-H), 7.40-7.39 (m, 3H, Ar-H), 7.35-7.34 (m, 1H, CONH), 5.65 (s, 1H, OCHO), 4.36 (s, 1H, OH), 4.01 (s, 1H, OH), 3.74-3.69 (m, 2H, CH<sub>2</sub>), 3.61-3.56 (m, 2H, CH<sub>2</sub>), 3.44-3.40 (m, 6H, CH, CH<sub>2</sub>), 1.78-1.25 (m, 8H, CH<sub>2</sub>).

<sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 168.25, 139.59, 131.89, 131.59, 130.72, 129.25, 127.59, 98.59, 80.75, 79.75, 69.71, 62.94, 62.82, 40.94, 38.76, 33.94, 29.80, 26.77, 26.64. HRMS calcd for C<sub>19</sub>H<sub>30</sub>N<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup>: 405.2002; Found: 405.2044

#### 4. Properties of two-component gel:

**Table S1** Results of the gelation studies for different gelators in various solvents.<sup>a</sup>

Solvents	C <sub>0</sub>	C <sub>3</sub>	C <sub>6</sub>	C <sub>0</sub> /CPTP	C <sub>3</sub> /CPTP	C <sub>6</sub> /CPTP
CHCl <sub>3</sub>	I	I	I	I	I	I
o-xylene	I	I	OG	I	I	I
THF	I	OG	OG	I	I	I
n-octane	I	I	OG	I	I	I
H <sub>2</sub> O	P	S	S	P	PG	PG
DMF	S	S	S	S	S	S
DMSO	S	S	S	S	S	S
ethanol	S	S	S	I	I	P
methanol	S	S	S	I	I	S
n-butanol	I	I	I	I	I	I
n-octanol	I	I	OG	I	I	P
methanol/H <sub>2</sub> O (1:1)	P	P	S	I	OG(57.4)	OG(62.3)
ethanol/H <sub>2</sub> O (1:1)	P	S	S	P	OG(60.1)	OG(64.7)
DMF/H <sub>2</sub> O (1:1)	S	S	S	S	OG(65.8)	OG(70.1)
DMSO/H <sub>2</sub> O (1:1)	S	S	S	PG	OG(69.3)	OG(73.9)

<sup>a</sup> PG, partial gel; OG, opaque gel; P, precipitation; S, solution; I, insoluble. Numbers in parentheses present the gel-to-sol transition temperature (T<sub>gel</sub>) in °C. Total gelator concentration = 2% (w/v, g/mL) in each case.

### 1) Effect of the gelators concentration on the $T_{gel}$ .

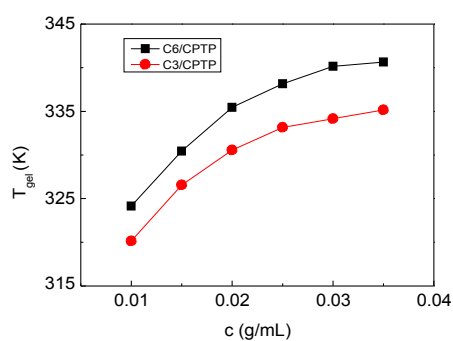


Fig. S1 Effect of the gelator C6/CPTP concentration on the  $T_{gel}$  of the gel in methanol/ $H_2O$

### 2) Variable-temperature UV/vis absorption spectra

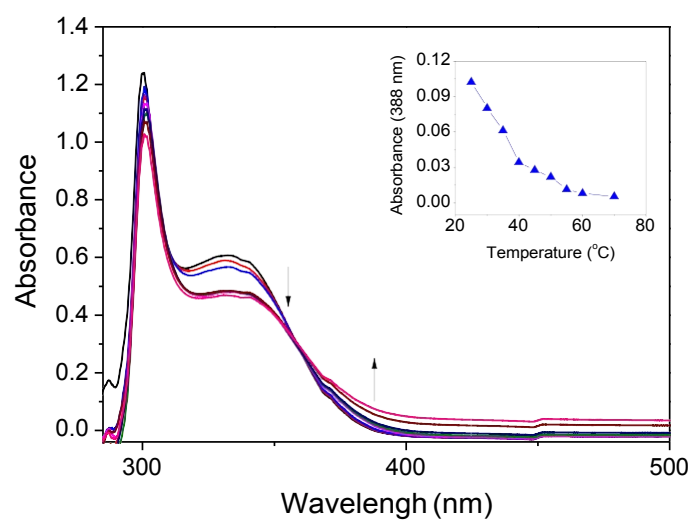


Fig. S2 Variable-temperature UV/vis absorption spectra of C6/CPTP (2.5 mM) in methanol/ $H_2O$  (v/v=1/1). The arrows indicate spectral changes with decreasing temperature. The inset shows a plot of absorption at 388 nm against the temperature.

### 3) IR spectroscopy

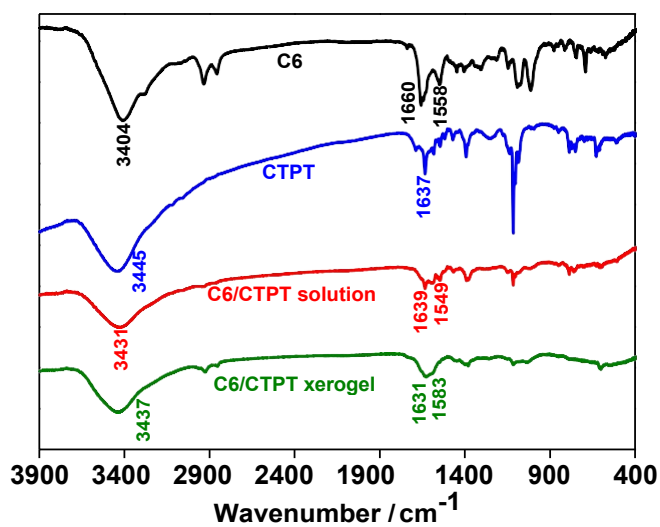


Fig. S3 FTIR spectra of C6, CPTP, C6/CPTP solution in DMF (0.2mmol) and C6/CPTP xerogel obtained from DMF/H<sub>2</sub>O gel.

### 4) Rheology

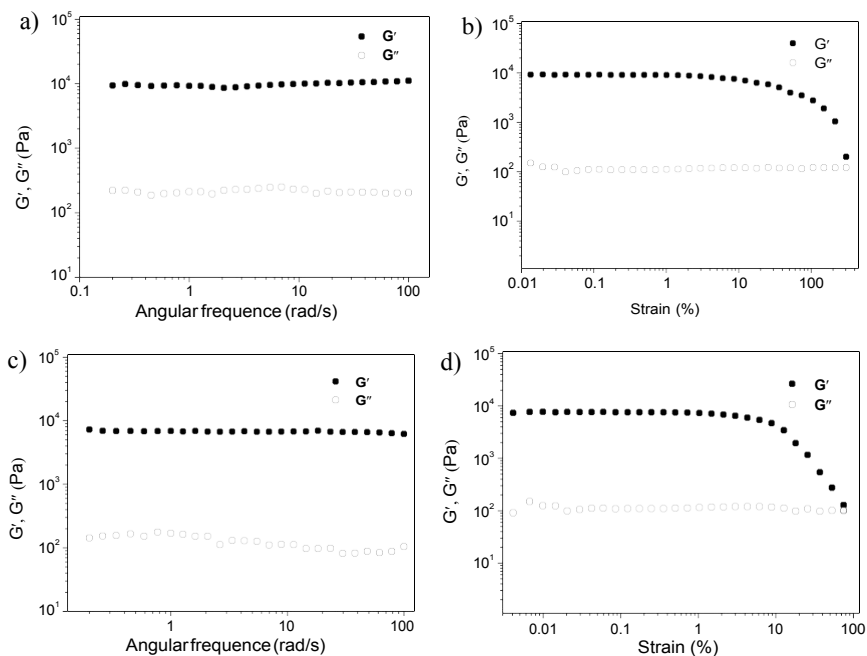


Fig. S4 Frequency sweep and stress sweep of DMF/H<sub>2</sub>O gel formed by C6/CPTP (a, b) and C3/CPTP (c, d); G', closed circles; G'', open circles.

## 5) NMR spectroscopy

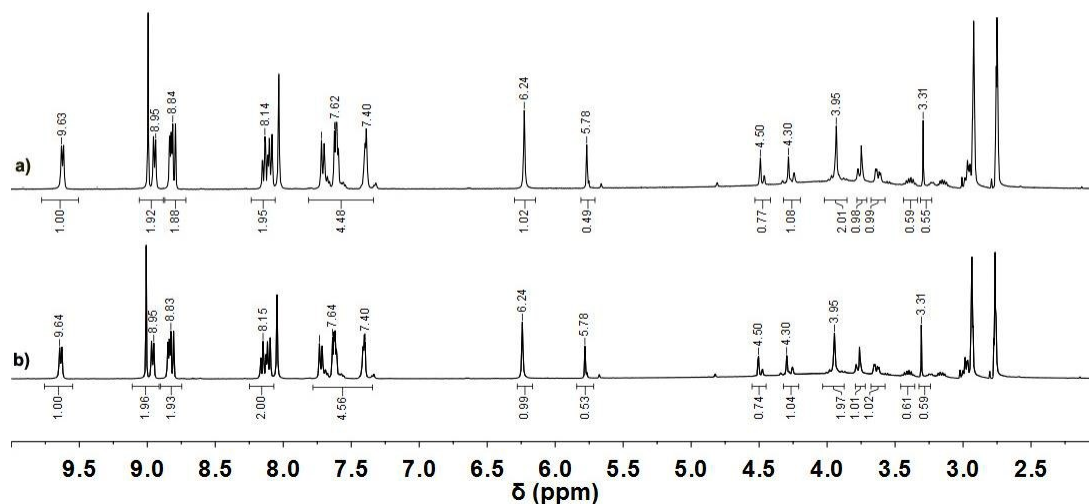


Fig. S5 Parts of the  $^1\text{H}$  NMR spectra of (a) newly prepared C6/CPTP solution in  $\text{DMF-d}_7$  and (b) the solution after irradiation for 30 min

## 6) UV/vis absorption spectra of C6/CPTP in the presence of different metal ions

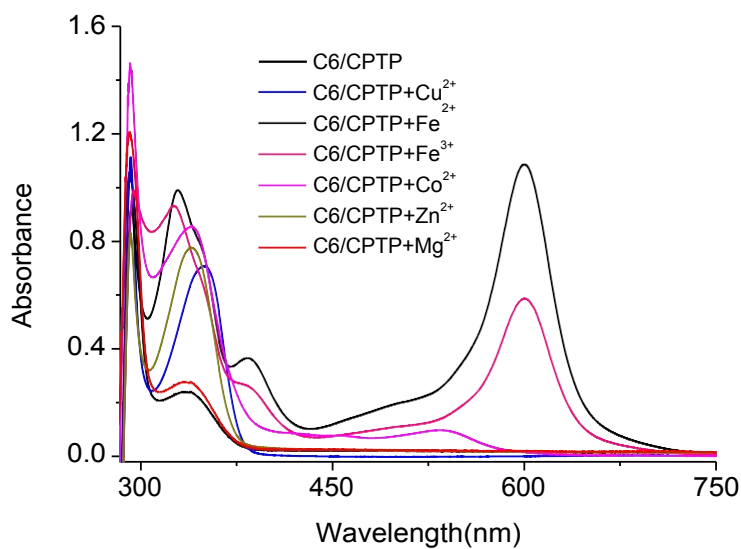


Fig. S6 UV/vis absorption spectra of C6/CPTP ( $2 \times 10^{-5} \text{ M}$ ) in the presence of different metal ions ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) in  $\text{DMF/H}_2\text{O}$  ( $v/v = 1/1$ ).

7) UV-Vis titration of C6/CPTP in the presence of Cu(II)

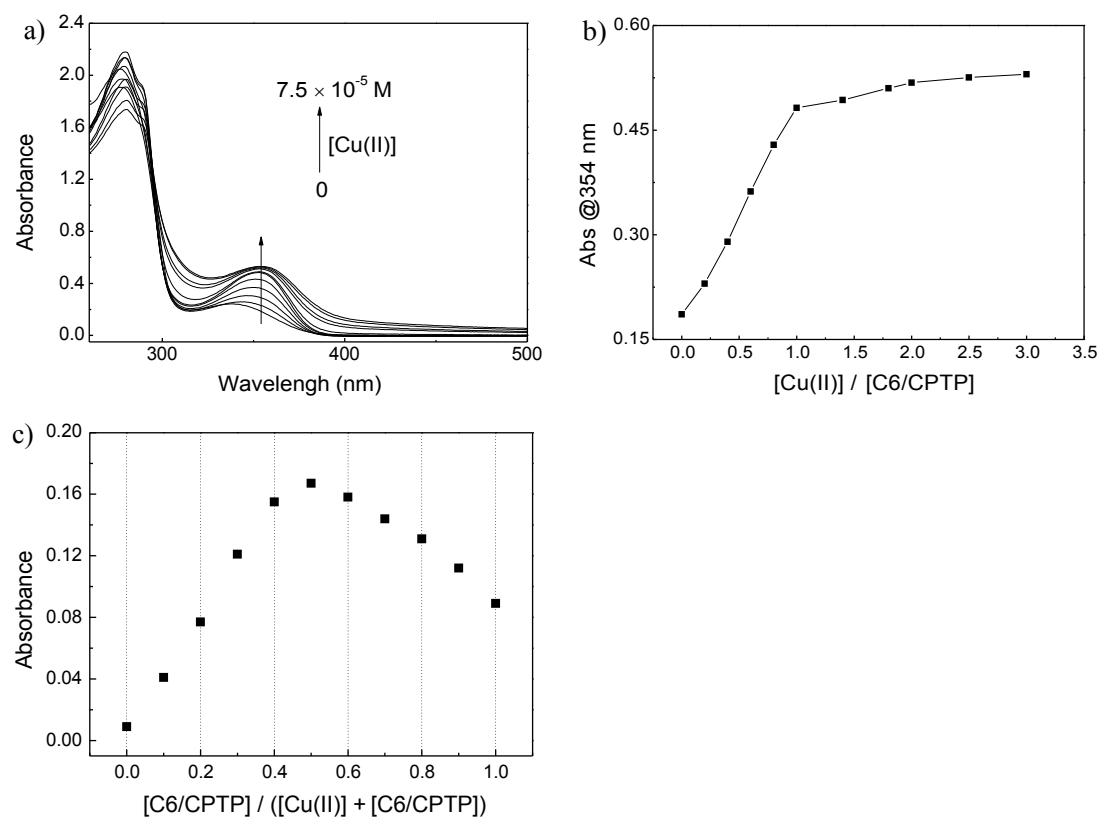


Fig. S7 (a) Absorption spectra of C6/CPTP in the presence of increasing concentration of Cu(II).  $[Cu(II)] = 0 - 7.5 \times 10^{-5}$  M and  $[C6/CPTP] = 2.5 \times 10^{-5}$  M. (b) Plots of absorbance at 354 nm versus  $[Cu(II)] / [C6/CPTP]$  derived from Fig. S7(a). (c) Job plot of C6/CPTP and the Cu(II) ion complex.



### 8) UV-Vis titration of C6/CPTP in the presence of Co(II)

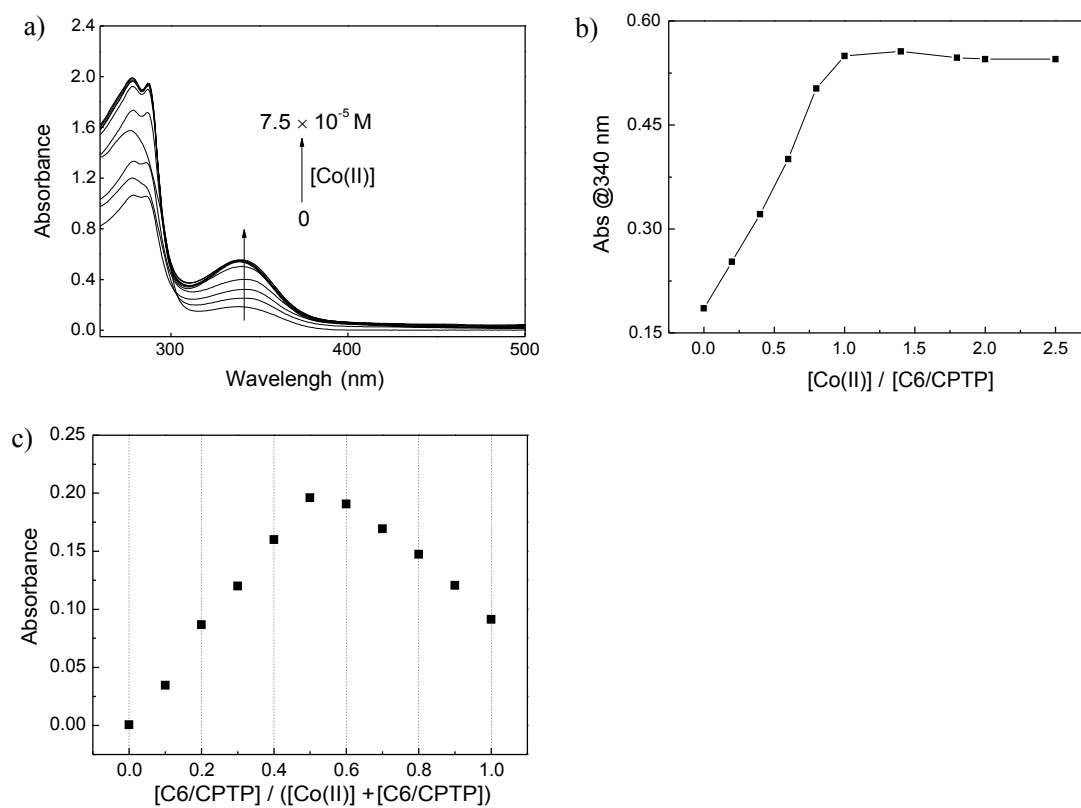


Fig. S8 (a) Absorption spectra of C6/CPTP in the presence of increasing concentration of Co(II).  $[Co(II)] = 0 - 7.5 \times 10^{-5}$  M and  $[C6/CPTP] = 2.5 \times 10^{-5}$  M. (b) Plots of absorbance at 345 nm versus  $[Co(II)] / [C6/CPTP]$  derived from Fig. S8(a). (c) Job plot of C6/CPTP and the Co(II) ion complex.

9) UV-Vis titration of C6/CPTP in the presence of Zn (II)

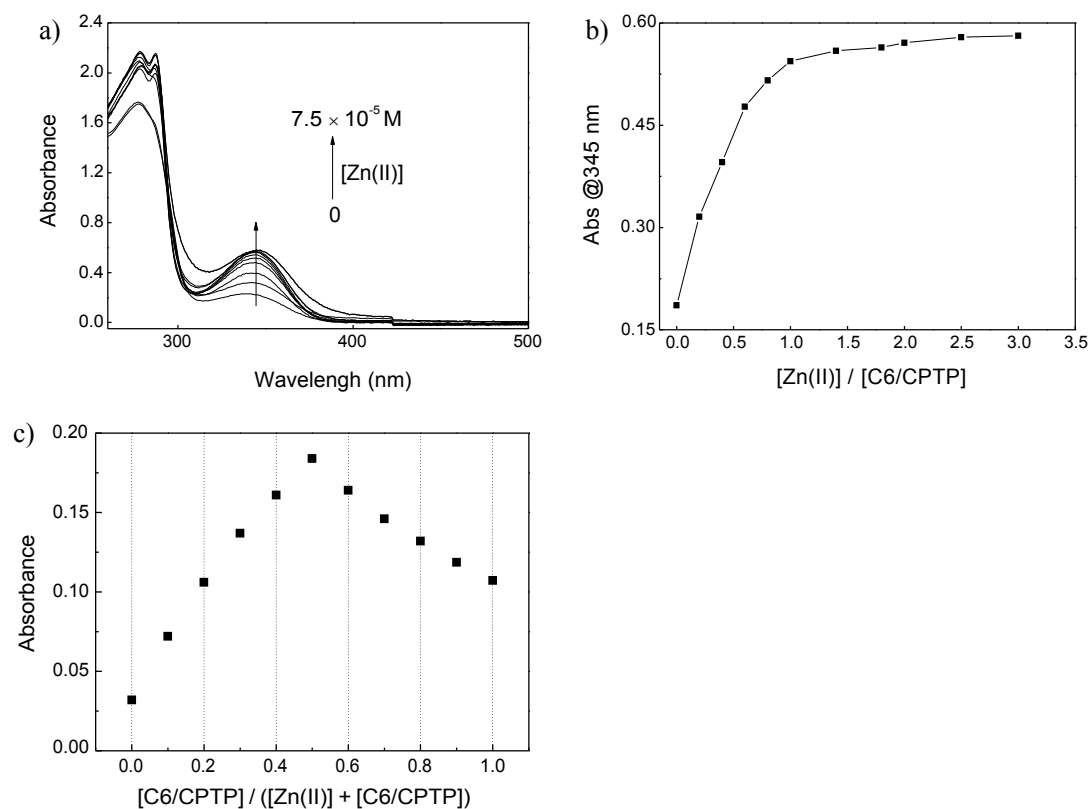


Fig. S9 (a) Absorption spectra of C6/CPTP in the presence of increasing concentration of Zn(II).  $[\text{Zn(II)}] = 0 - 7.5 \times 10^{-5} \text{ M}$  and  $[\text{C6/CPTP}] = 2.5 \times 10^{-5} \text{ M}$ . (b) Plots of absorbance at 345 nm versus  $[\text{Zn(II)}] / [\text{C6/CPTP}]$  derived from Fig. S9(a). (c) Job plot of C6/CPTP and the Zn(II) ion complex.

### 10) UV-Vis titration of C6/CPTP in the presence of Fe(II)

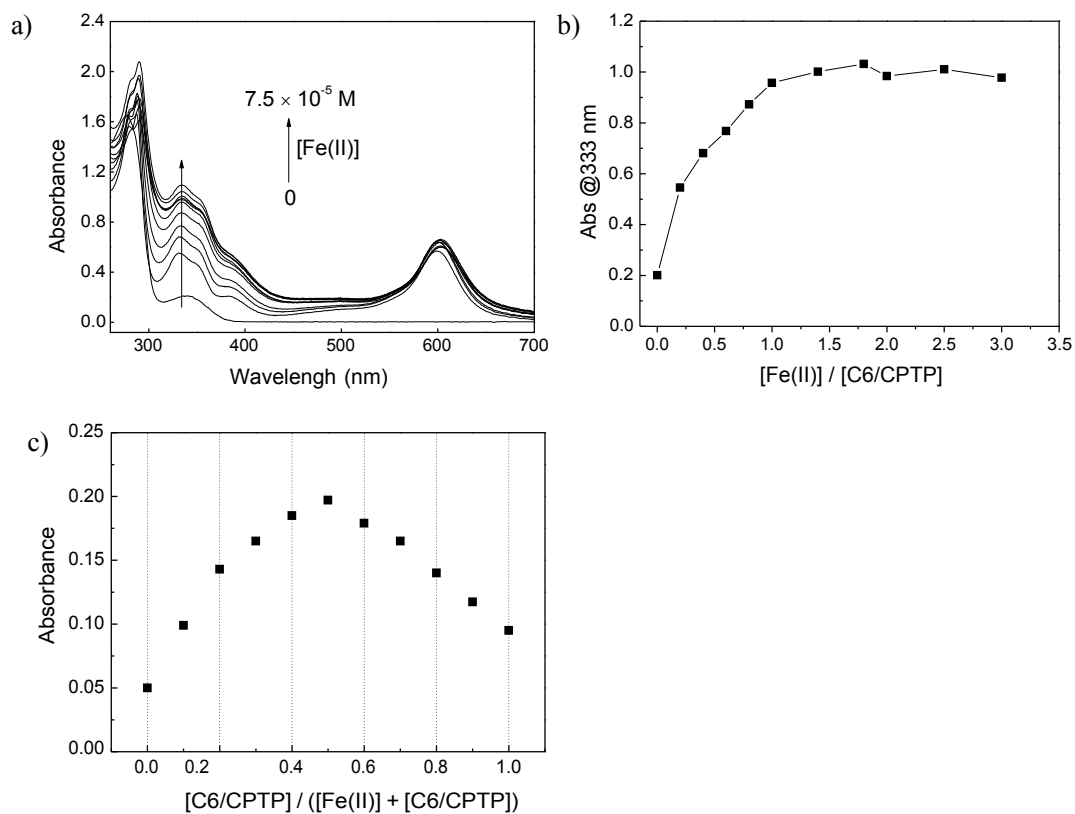


Fig. S10 (a) Absorption spectra of C6/CPTP in the presence of increasing concentration of Fe(II).  $[\text{Fe(II)}] = 0 - 7.5 \times 10^{-5} \text{ M}$  and  $[\text{C6/CPTP}] = 2.5 \times 10^{-5} \text{ M}$ . (b) Plots of absorbance at 333 nm versus  $[\text{Fe(II)}] / [\text{C6/CPTP}]$  derived from Fig. S10(a). (c) Job plot of C6/CPTP and the Fe(II) ion complex.

### 11) UV-Vis titration of C6/CPTP in the presence of Fe(III)

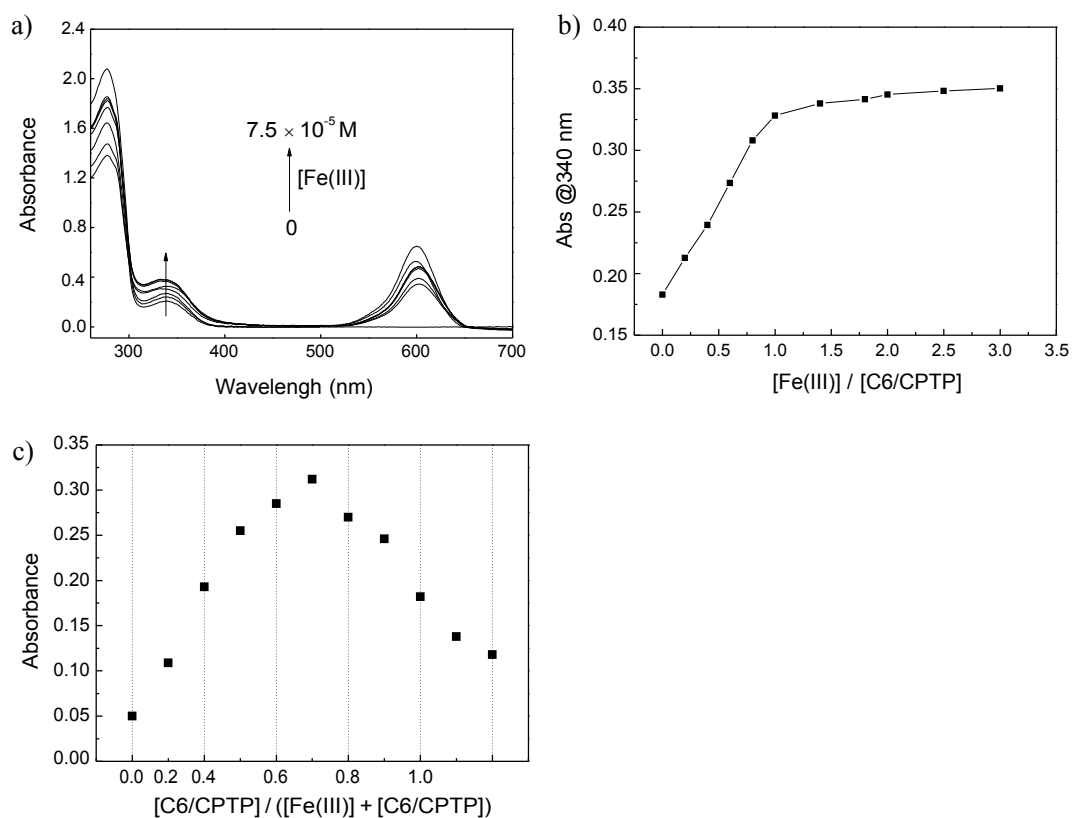
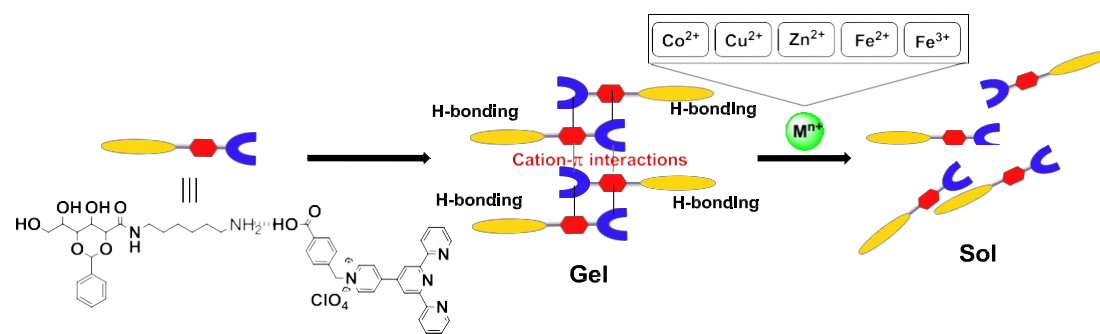


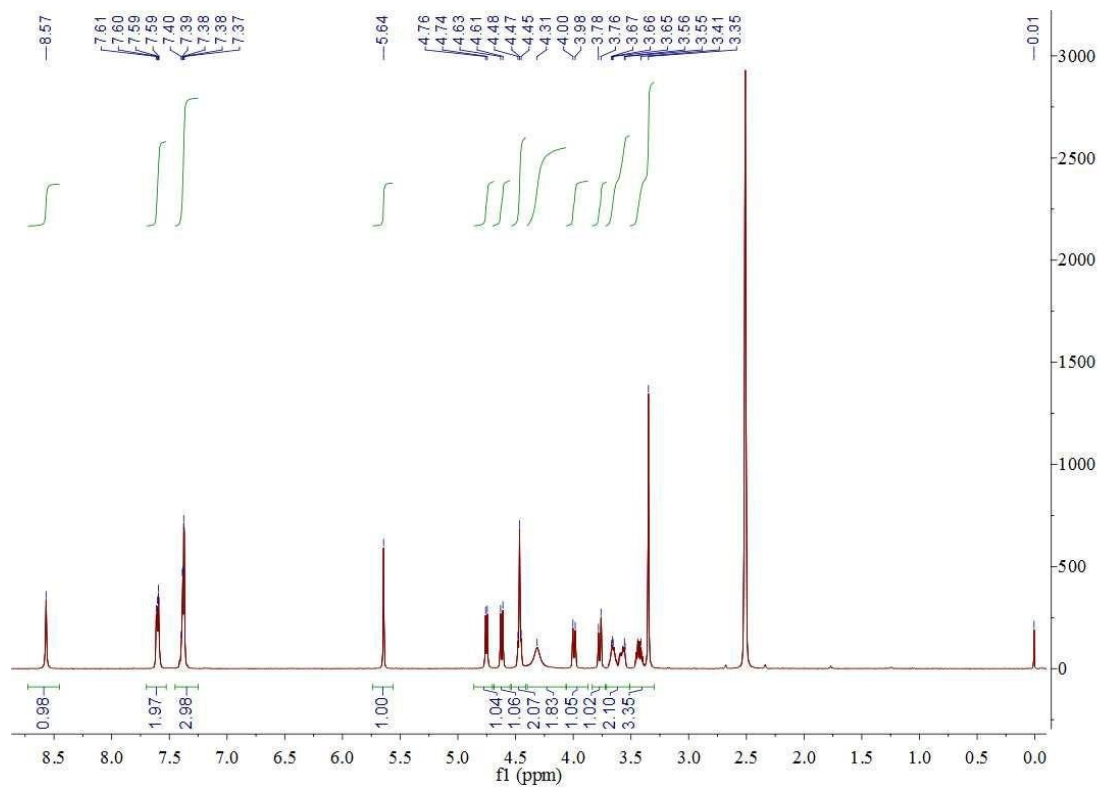
Fig. S11 (a) Absorption spectra of C6/CPTP in the presence of increasing concentration of Fe(II).  $[\text{Fe(II)}] = 0 - 7.5 \times 10^{-5} \text{ M}$  and  $[\text{C6/CPTP}] = 2.5 \times 10^{-5} \text{ M}$ . (b) Plots of absorbance at 340 nm versus  $[\text{Fe(III)}] / [\text{C6/CPTP}]$  derived from Fig. S11(a). (c) Job plot of C6/CPTP and the Fe(III) ion complex.

## 12) The presumed self-assembly and metal ions stimuli-response mechanism

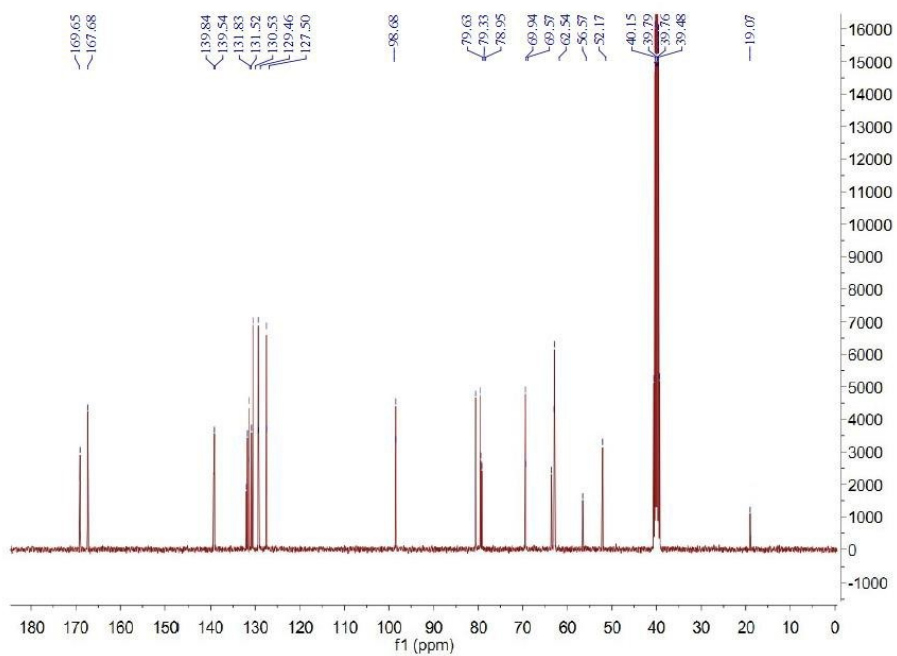


Scheme S1 The presumed self-assembly and metal ions stimuli-response mechanism.

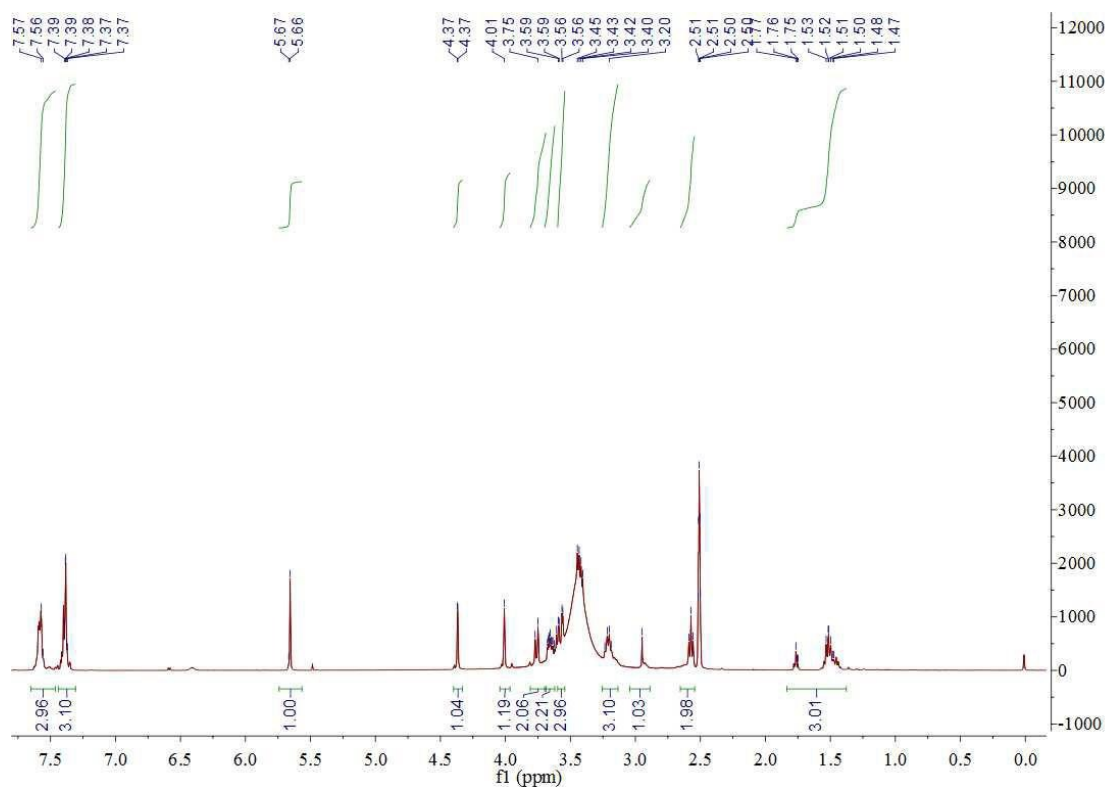
$^1\text{H}$  NMR (400MHz) Spectra of C0 in DMSO-d<sub>6</sub>:



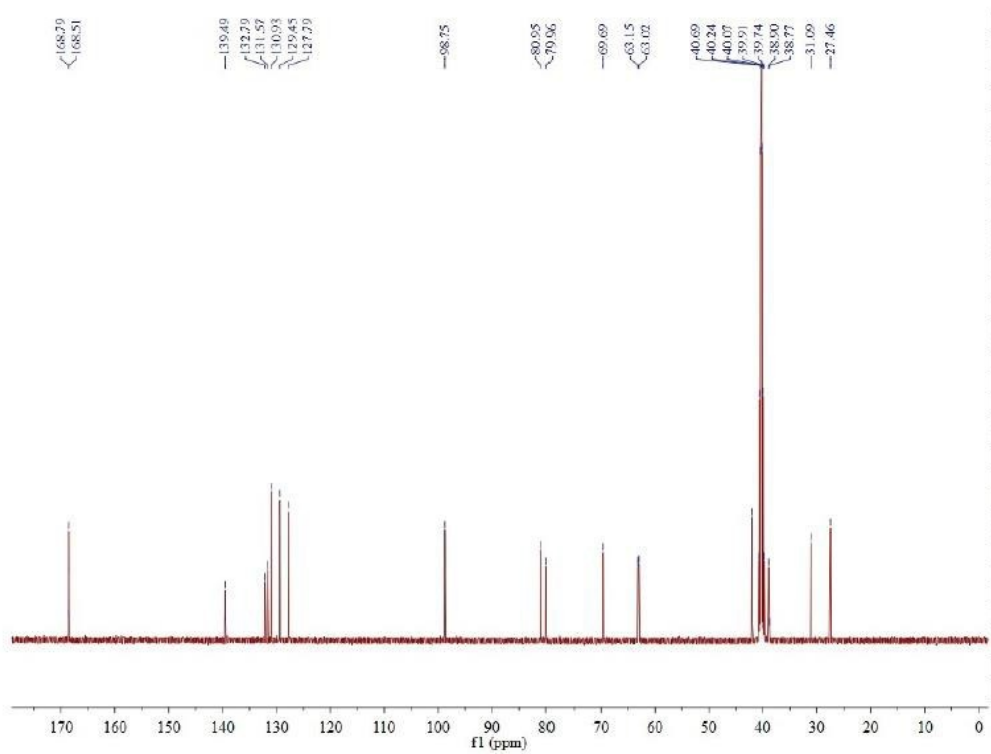
$^{13}\text{C}$  NMR (400MHz) Spectra of C0 in DMSO-d<sub>6</sub>:



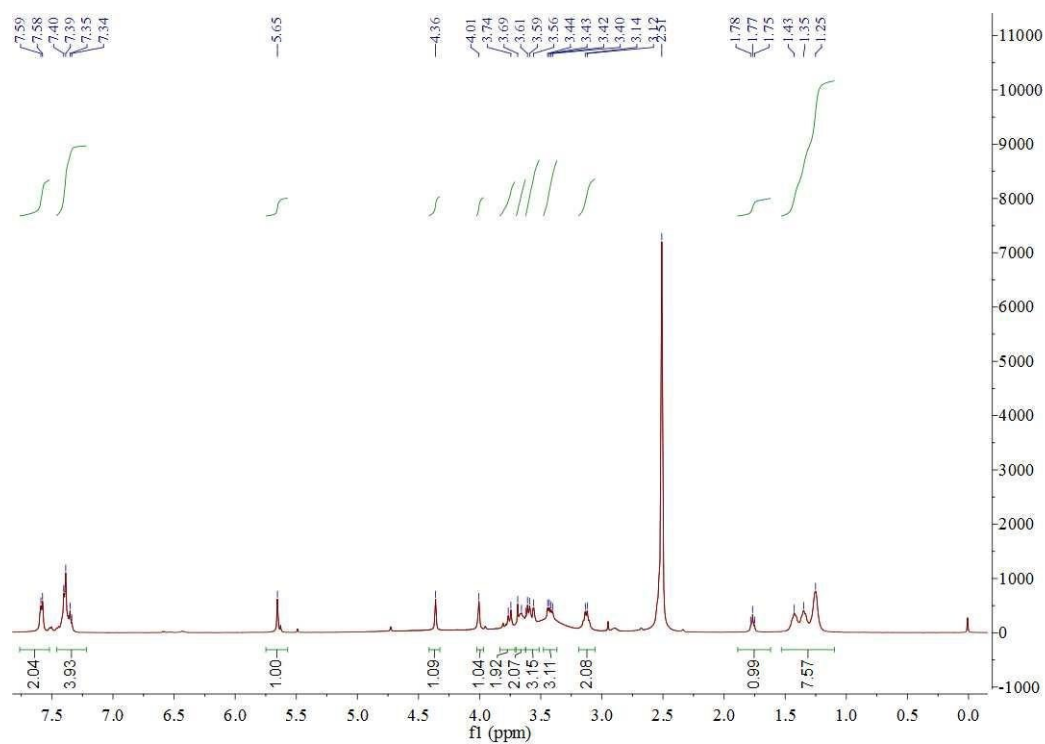
<sup>1</sup>H NMR (400MHz) Spectra of C3 in DMSO-d6:



<sup>13</sup>C NMR (400MHz) Spectra of C3 in DMSO-d6:



<sup>1</sup>H NMR (400MHz) Spectra of C6 in DMSO-d6:



<sup>13</sup>C NMR (400MHz) Spectra of C6 in DMSO-d6:

