

## Electronic Supplementary Information (ESI)

### Self-assembled Metalgels Formed From N, N', N''-tris(4-pyridyl)-trimesic amide in Aqueous Solution Induced by Fe(III)/Fe(II) Ions

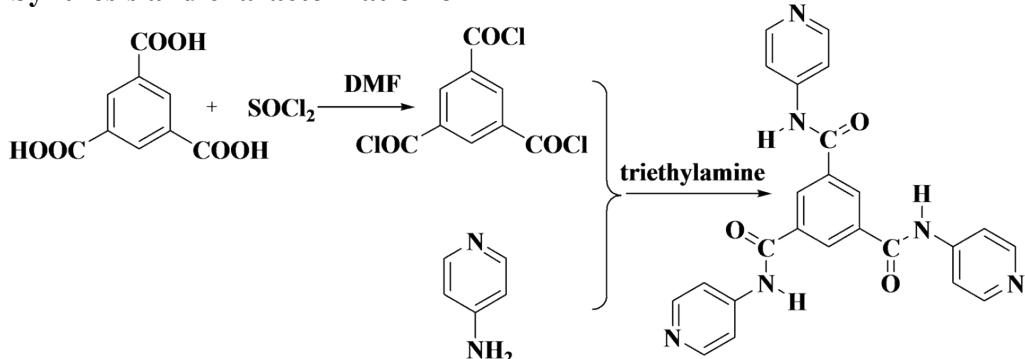
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#### 1) Synthesis and characterization of TPTA



Scheme S1 Synthetic routes of ligand TPTA.

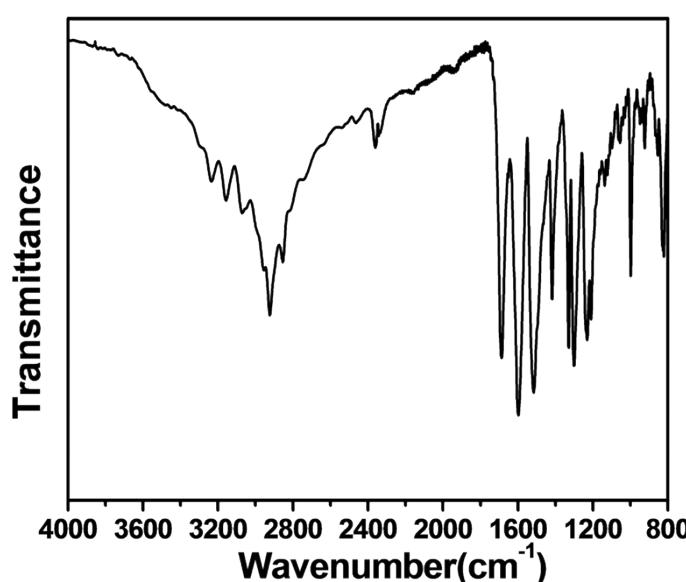
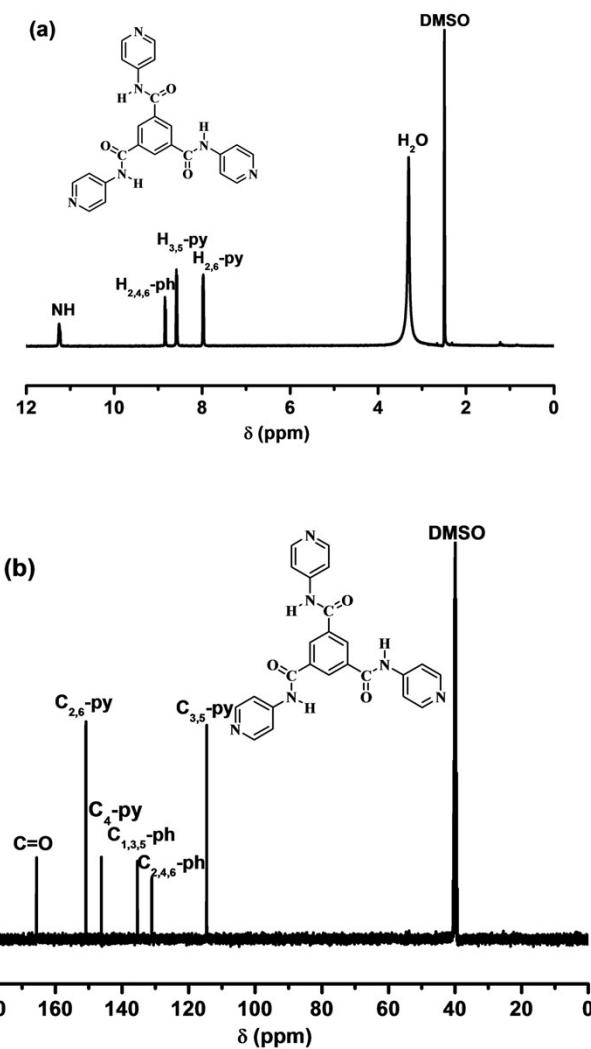
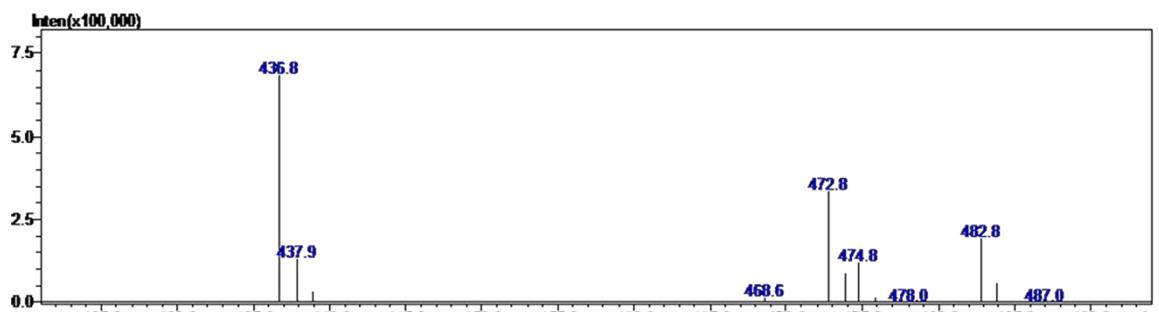


Fig. S1 FT-IR spectrum of the TPTA.



**Fig. S2** <sup>1</sup>H NMR (a) and <sup>13</sup>C NMR (b) spectrums of TPTA (DMSO-*d*<sub>6</sub>, 400MHz, 298K)



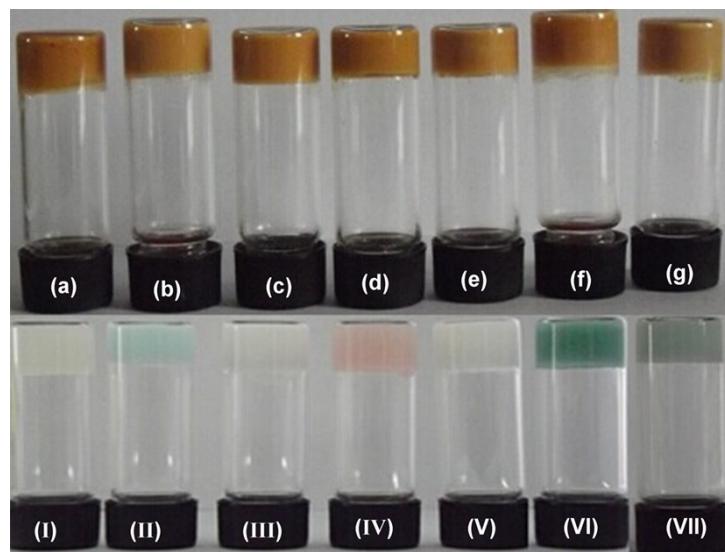
**Fig. S3** Mass spectra of TPTA (LCMS-2010A, Shimadzu, 298 K)

## 2) Gelation data

**Table S1** The gelation abilities of TPTA in the presence of different metal ions

Reagents		Behaviour
A	B	
TPTA	CuSO <sub>4</sub> ·5H <sub>2</sub> O	I
TPTA	CuCl <sub>2</sub> ·2H <sub>2</sub> O	I
TPTA	CoCl <sub>2</sub> ·6H <sub>2</sub> O	I
TPTA	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	I
TPTA	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	I
TPTA	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	I
TPTA	ZnCl <sub>2</sub>	I
TPTA	Pb(NO <sub>3</sub> ) <sub>2</sub>	I
TPTA	AgNO <sub>3</sub>	I
TPTA	RuCl <sub>3</sub> ·3H <sub>2</sub> O	I
TPTA	NaCl	I
TPTA	MgCl <sub>2</sub>	I
TPTA	KCl	I
TPTA	MnCl <sub>2</sub>	I
TPTA	CrCl <sub>2</sub>	I
TPTA	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	I
TPTA	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	I
TPTA	FeCl <sub>3</sub> ·6H <sub>2</sub> O	OG
TPTA	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	OG
TPTA	Fe <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>	OG
TPTA	FeCl <sub>2</sub> ·4H <sub>2</sub> O	OG
TPTA	Fe(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	OG
TPTA	FeSO <sub>4</sub> ·7H <sub>2</sub> O	OG

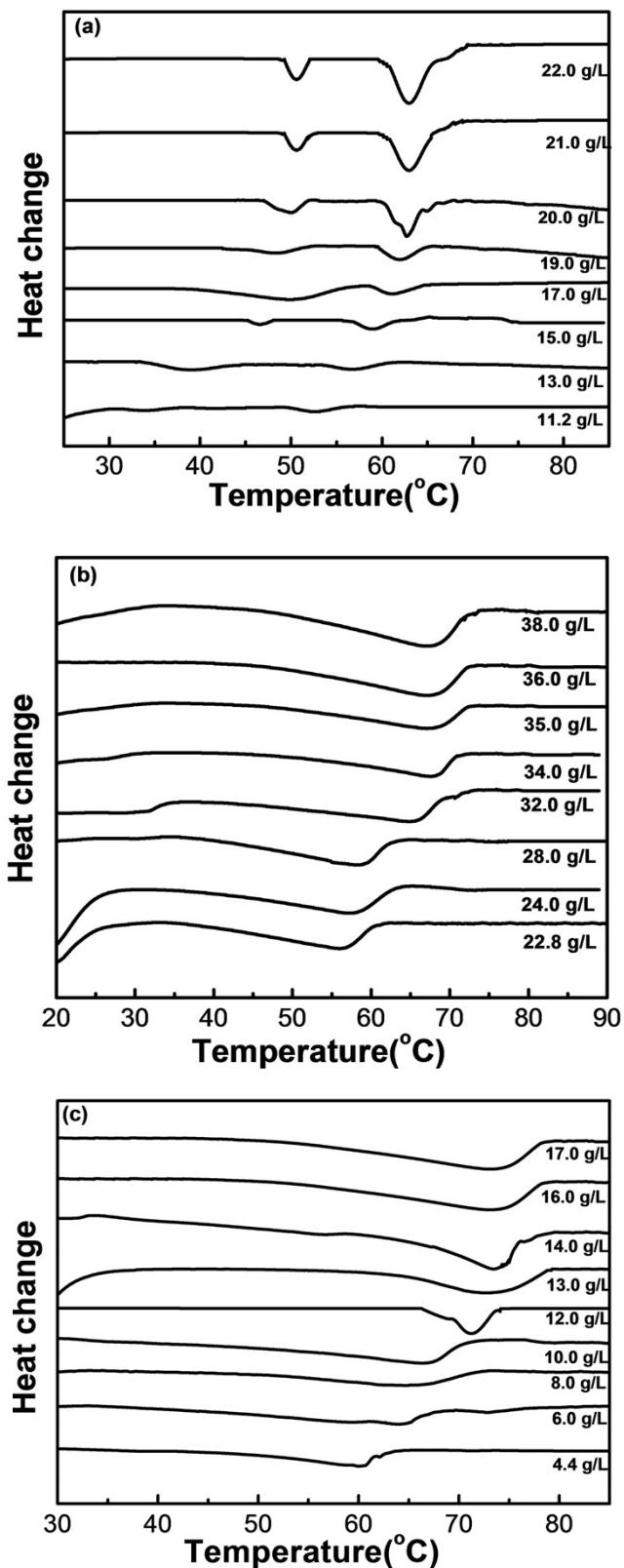
OG= opaque gel; I= insoluble



**Fig. S4** The photographs of metallogeles in mixed metal ion solution

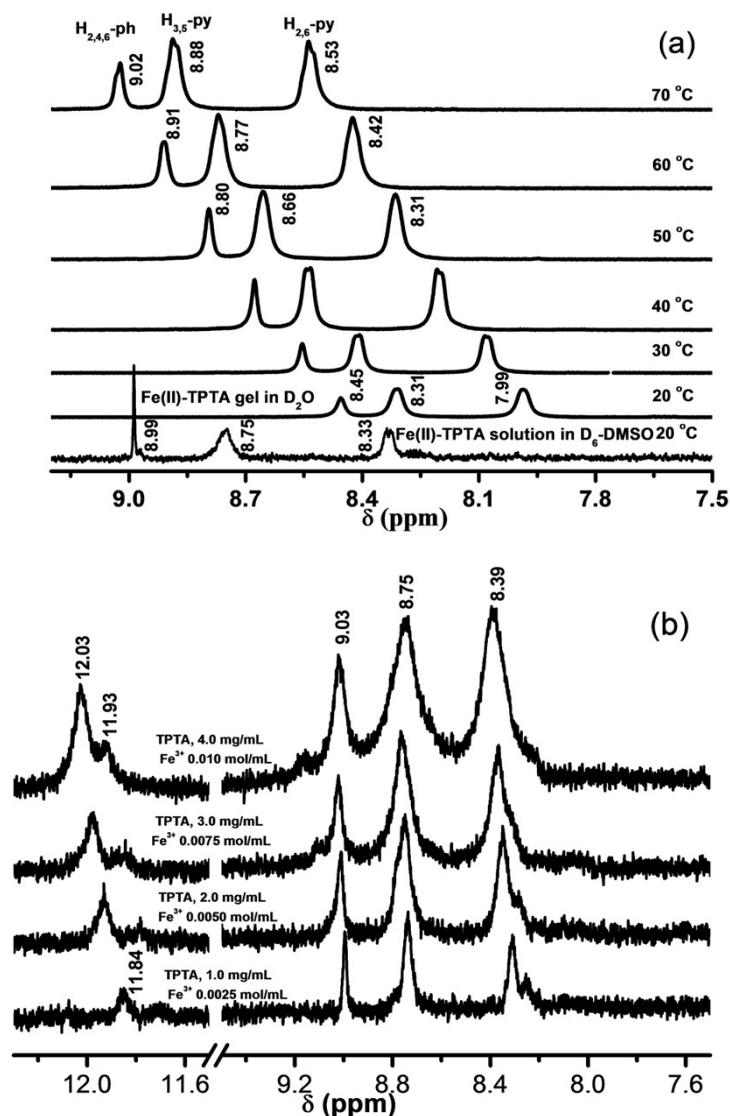
(a)-(g),  $\text{Fe}^{3+}(0.10 \text{ mol/L})+\text{M}(0.10 \text{ mol/L})$ : (a)  $\text{M} = \text{Na}^+$ ; (b)  $\text{M} = \text{Cu}^{2+}$ ; (c)  $\text{M} = \text{Mn}^{2+}$ ; (d)  $\text{M} = \text{Co}^{2+}$ ; (e)  $\text{M} = \text{K}^+$ ; (f)  $\text{M} = \text{Cr}^{2+}$ ; (g)  $\text{M} = \text{Na}^++\text{K}^++\text{Cu}^{2+}+\text{Co}^{2+}$   
(I)-(VII),  $\text{Fe}^{2+}(0.01 \text{ mol/L})+\text{M}(0.01 \text{ mol/L})$ : (I)  $\text{M} = \text{Na}^+$ ; (II)  $\text{M} = \text{Cu}^{2+}$ ; (III)  $\text{M} = \text{Mn}^{2+}$ ; (IV)  $\text{M} = \text{Co}^{2+}$ ; (V)  $\text{M} = \text{K}^+$ ; (VI)  $\text{M} = \text{Cr}^{2+}$ ; (VII)  $\text{M} = \text{Na}^++\text{Cu}^{2+}+\text{K}^+$

### 3) Date of differential scanning calorimetry (DSC)



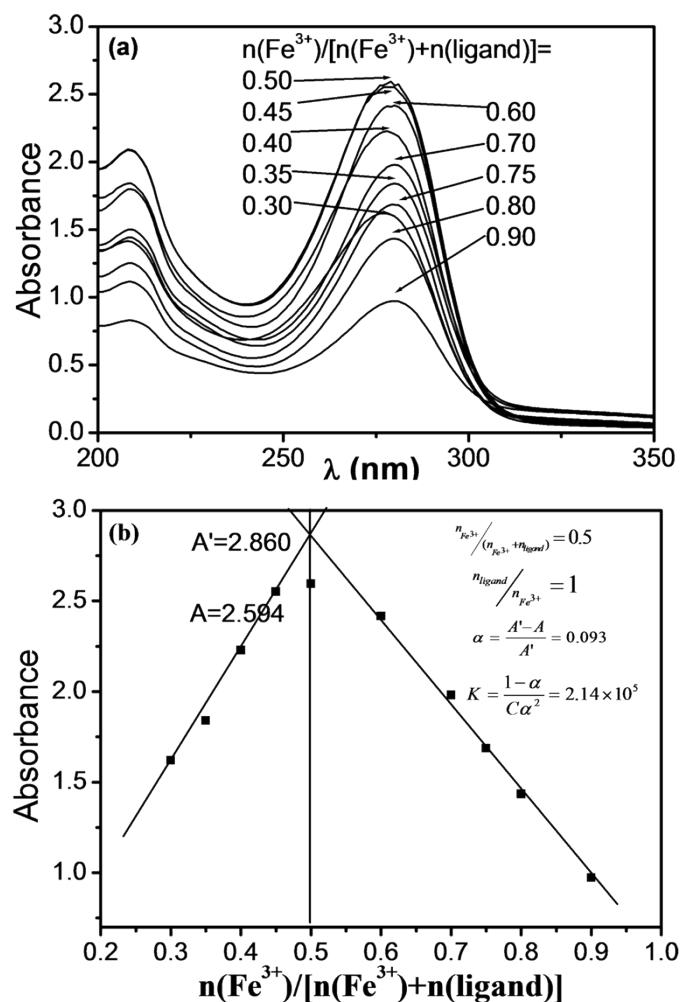
**Fig S5** DSC thermograms from first heating of metallogeles prepared by varying concentrations of TPTA in aqueous solution containing: (a) 0.050 mol/L  $\text{Fe}^{3+}$ ; (b) 0.10 mol/L  $\text{Fe}^{3+}$ ; (c) 0.010 mol/L  $\text{Fe}^{2+}$ .

**4) Date of  $^1\text{H}$  NMR spectroscopy**

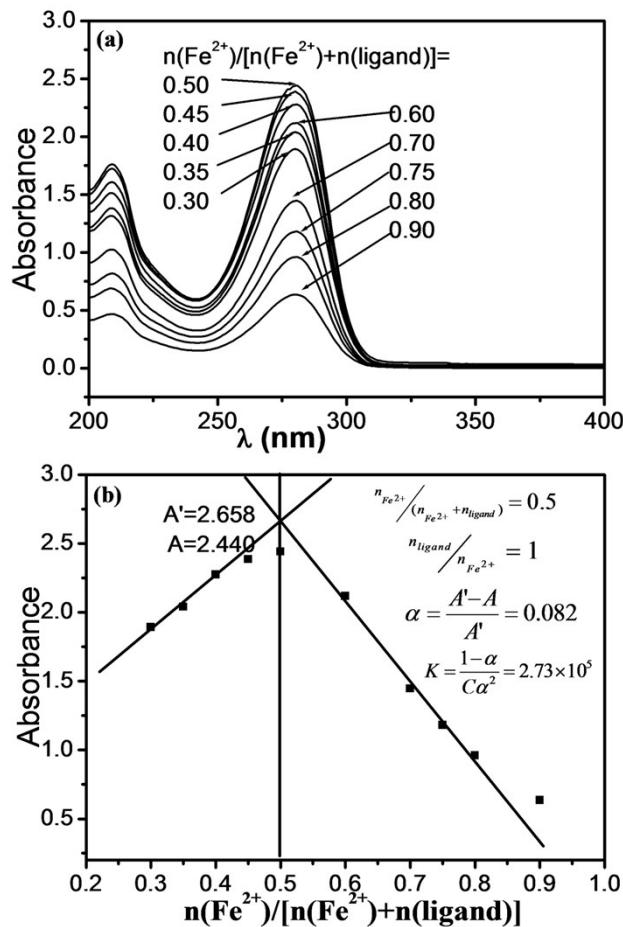


**Fig. S6** (a) Variable-temperature  $^1\text{H}$  NMR spectroscopy for Fe(II)-TPTA gel in  $\text{D}_2\text{O}$  (0.010 mol/L  $\text{Fe}^{2+}$ , 4.4 g/L TPTA); (b) Concentration-dependent  $^1\text{H}$  NMR spectra of Fe(II)-TPTA in  $\text{D}_6\text{-DMSO}$  at 20 °C.

## 5) Date of UV-Vis spectra

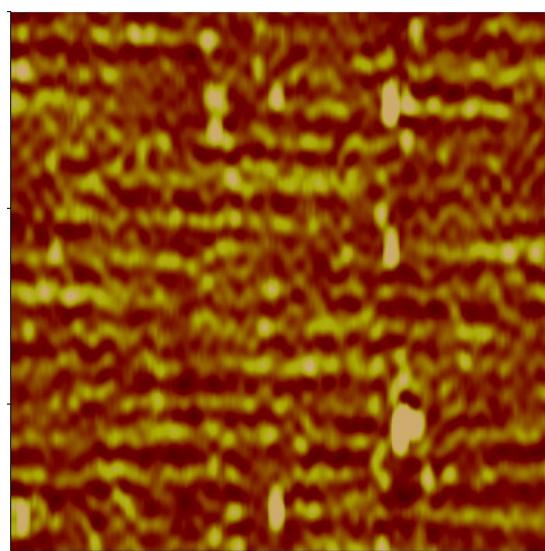


**Fig. S7** (a) UV-Vis spectra of TPTA solution at various coordination molar ratio of  $\text{Fe}^{3+}$  to TPTA in aqueous solution; (b) the absorbance of TPTA at the  $\lambda=281$  nm.



**Fig. S8** (a) UV-Vis spectra of TPTA solution at various coordination molar ratio of  $\text{Fe}^{2+}$  to TPTA in aqueous solution; (b) the absorbance of TPTA at the  $\lambda=281$  nm.

#### 6) STM images of Fe(II)-TPTA assembling structure



**Fig. S9** STM image of Fe(II)-TPTA self-assembled structure (27.49 nm × 27.49 nm, V= 749.8 mV, I = 347.9 pA).