Electronic Supplementary Information (ESI)

Non-conjudated polyurethane polymer dots based on crosslink enhanced emission (CEE) and application in Fe^{3+} sensing

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Material & Instrumentation

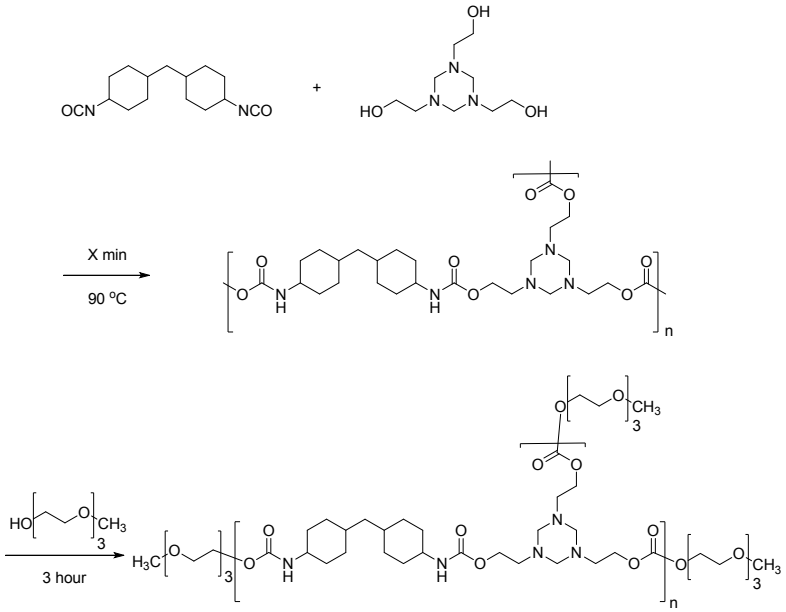
Paraformaldehyde was purchased from Sinopharm (China). 2-Aminoethanol and Triethylene glycol monomethyl ether (TGME) were purchased from Aladdin (China). Dibutyltin dilaurate was purchased from Energy-Chemical (China). Dicyclohexylmethane 4, 4`-Diisocyanate (HMDI) was purchased from TCI. All other common reagents and solvent were received from commercial sources and used without further purification. The pure water was measured with a DDSJ-308F conductometer (Shanghai INESA Instrument) at 25 °C.

NMR spectra were measured in DMSO-*d6* on Bruker-Avance (400 MHz for ^{1}H and 101 MHz for ^{13}C) with TMS as an internal reference. Fourier transform infrared (FTIR) Spectroscopy (Nicolet 6700, Thermoscientific, USA): The spectra were measured with a spectrometer. Absorbance spectra were collected using a spectral resolution of 4 cm^{-1} at room temperature over a frequency range of 4000-500 cm^{-1}. The background spectra were recorded on corresponding KBr. The microstructure was observed by Transmission electron microscope (TEM, JEOL2100 HR, Japan). Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO-TGA/DSC I instrument with a heating rate of $10^{o}C\ min^{-1}$ in flowing N_2 and a sample of 3-5 mg. Size distribution histogram was obtained using Malvern Nano ZS. UV-vis absorption spectra of the samples were recorded using a Lambda 950 spectrophotometer (Perkin-Elmer). All the fluorescence measurements were acquired on a Hitachi F4600 and Edinburgh Instrument FLS920.

Synthesis of Hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine (HTHT)

Hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine was synthesized according to the literature method.[1]
^{1}H NMR (400 MHz, DMSO) δ 4.56 (s, 3H), 3.50-3.10 (br, 6H), 3.43 (m, 12H), 3.37 (t, J = 4.8 Hz, 6H), 2.53 (t, J = 5.6 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 74.85, 72.60, 69.52, 60.70, 52.05.

Synthesis of Hyperbranched polyurethanes (HPUs-Tx)



Hyperbranched polyurethanes (HPUs) were prepared by a two-step procedure in a N_2 atmosphere at $90^{o}C$ with 0.5% w/w Dibutyltin dilaurate as a catalyzer. In the first step, 1 mmol HTHT and the catalyzer were dissolved in 15 mL ethylenedichloride. Next, the solution was mixed with 2 mmol HMDI, stirred by 400 rpm and heated slowly to $90^{o}C$ in order to form the cores of polymer dots. In the second stage, after continuing stirring for X min (X = 1, 5,

10, 15, 20), an excess of TGME (3 mL) was added into the reaction and stirred for 3 hours to block the polymer generally. In the end, the mixture was cooled at room temperature and precipitated from ether. The resulting precipitate was filtered, washed with water and dried in vacuo to give a yellow gel **HPUs-T_X (X** = 1, 5, 10, 15, 20**)**: **HPUs-T_1** 1.04 g; **HPUs-T_5** 1.25 g; **HPUs-T_{10}** 1.40 g; **HPUs-T_{15}** 1.39 g; **HPUs-T_{20}** 1.35 g.

Synthesis of Hyperbranched polyurethanes (HPUs-T0)

This **HPUs-T_0** was synthesized according to the **HPUs-T_X** method. In the second stage, after continuing stirring for 15 min, an excess of methanol (3 mL) was added into the reaction and stirred for 3 hours: **HPUs-T_0** 0.92 g.

(1) (a) J. M. Bakke, J. Buhaug and J. Riha, *Ind. Eng. Chem. Res.*, 2001, **40**, 6051; (b) G. O. Jones, J. M. Garcia, H. W. Horn and J. L. Hedrick, *Org. Lett.*, 2014, **16**, 5502.

Emission spectra of HPUs-T15 in DMSO / H_2O mixture

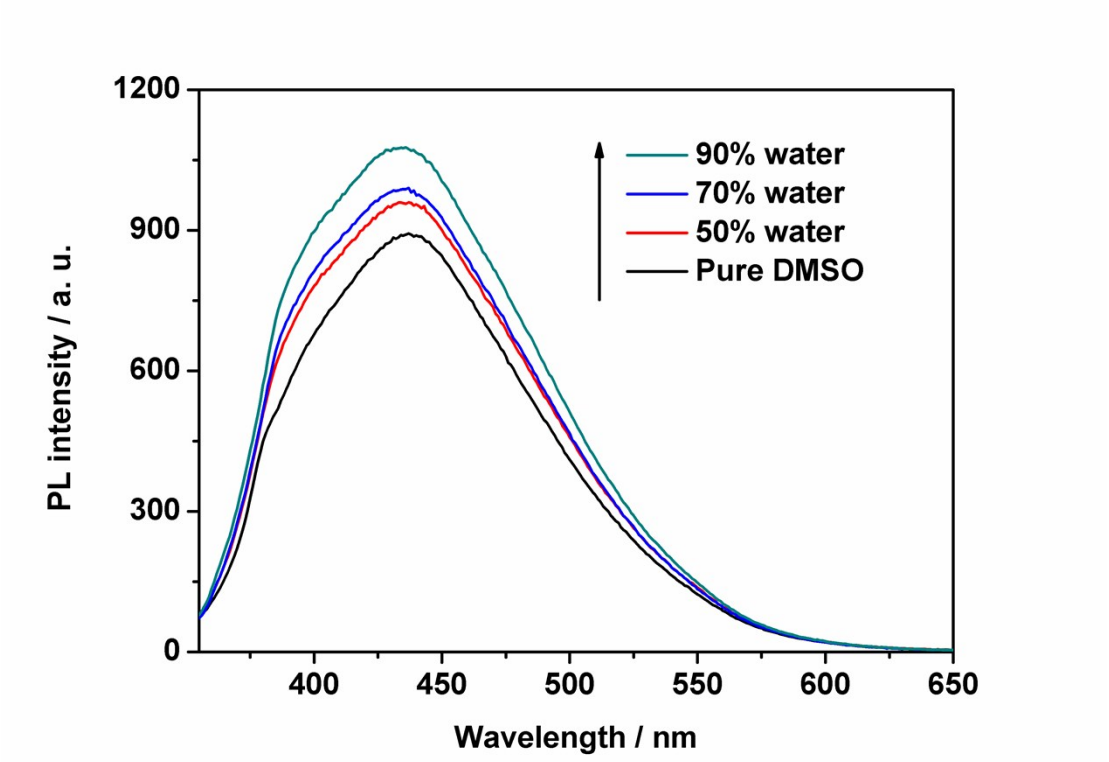


Fig. S1 Emission spectra of the **HPUs-T15** (0.5 mg/mL) in DMSO and 50~90 % water in DMSO.

Emission spectra and size distribution histogram of HPUs-Tx in 10%DMSO / 90%H_2O mixture

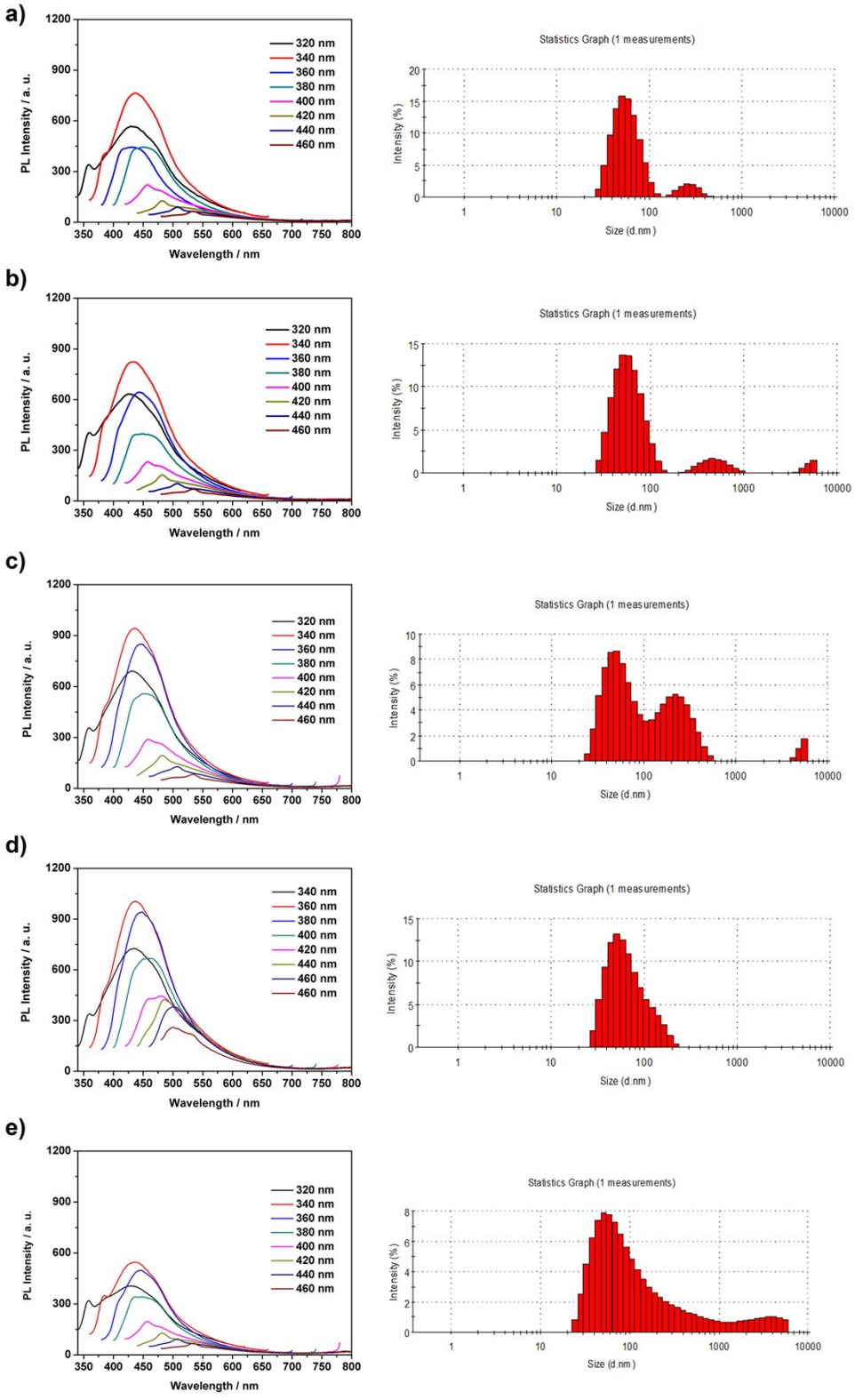


Fig. S2 Emission spectra (left) and size distribution histogram (right) of NCPDs by **HPUs-Tx** (0.5 mg/mL) in DMSO–H_2O (10 mM) (1:9, v/v): (a) **HPUs-T1**; (b) **HPUs-T5**; (c) **HPUs-T10**; (d) **HPUs-T15**; (e) **HPUs-T20**.

^{1}H NMR spectra of HTHT

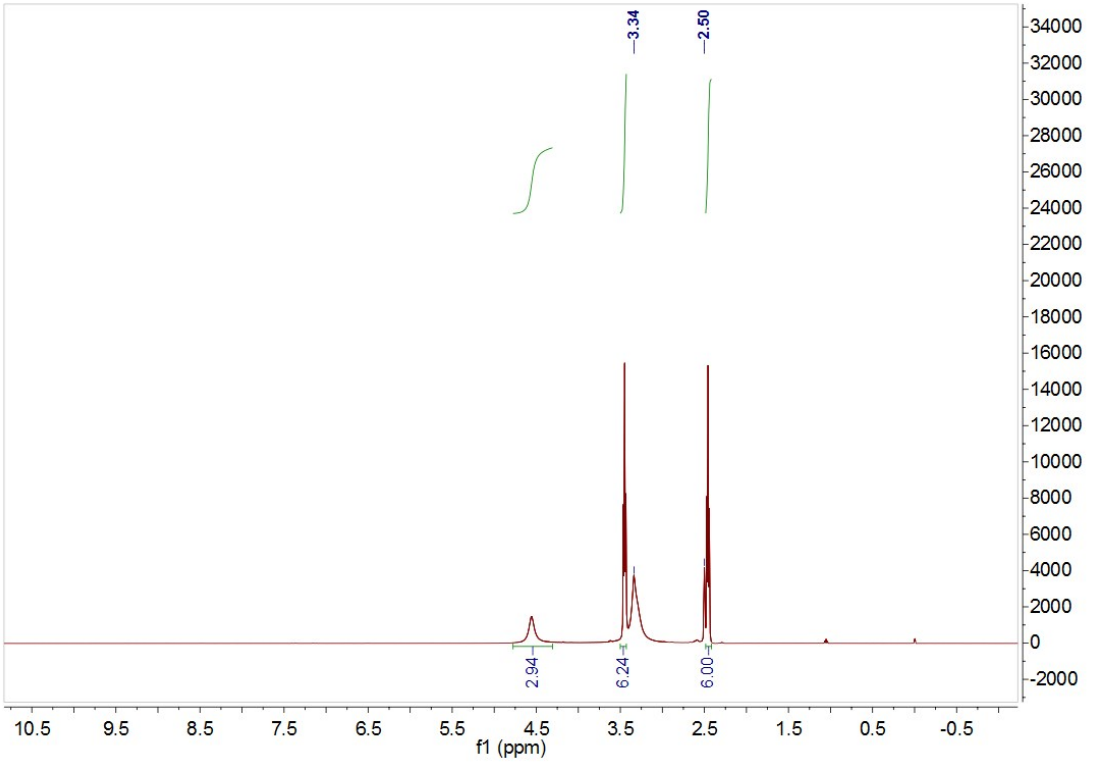


Fig. S3 ^{1}H NMR spectra of **HTHT**.

^{1}H NMR spectra of HPUs-T15

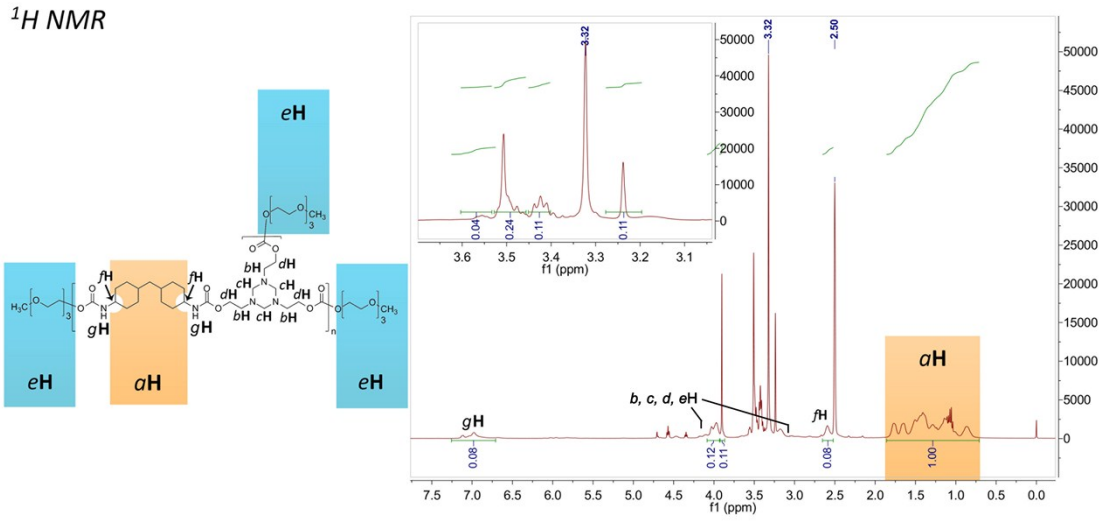


Fig. S4 ^{1}H NMR spectra of **HPUs-T15**.

Fluorescence quantum yield (Φ) of HTHT and HPUs-Tx

No.	Compound	Fluorescence quantum yield[a] Φ (%)	
		DMSO	DMSO:H_2O=1:9
0	**HTHT**	0.0	0.0
1	**HPUs-T1**	1.4	1.6
2	**HPUs-T5**	1.5	1.8
3	**HPUs-T10**	2.0	2.2
4	**HPUs-T15**	2.1	2.2
5	**HPUs-T20**	1.1	1.3

Table. S1 [a]Quinine sulphate was used as standard whose quantum yield is 0.63 in 0.1N H_2SO_4 at λ_{ex}= 340 nm

Photo of HPUs-Tx in pH = 1 and 2

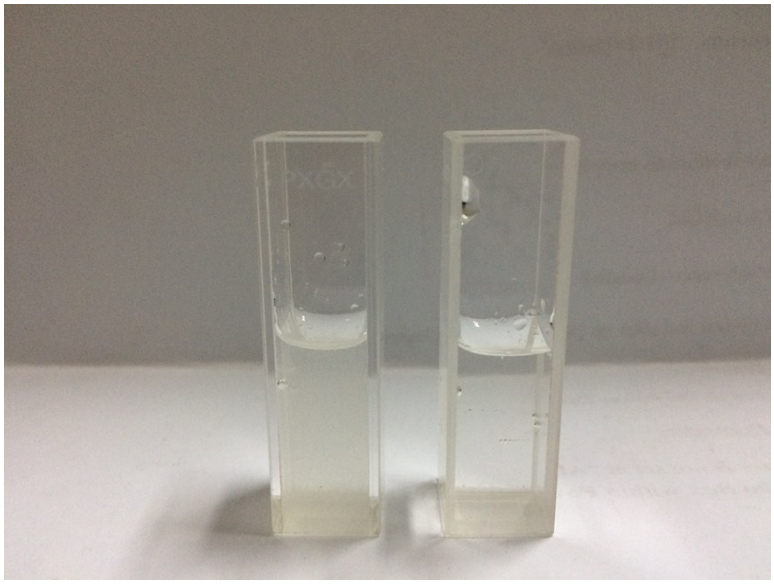
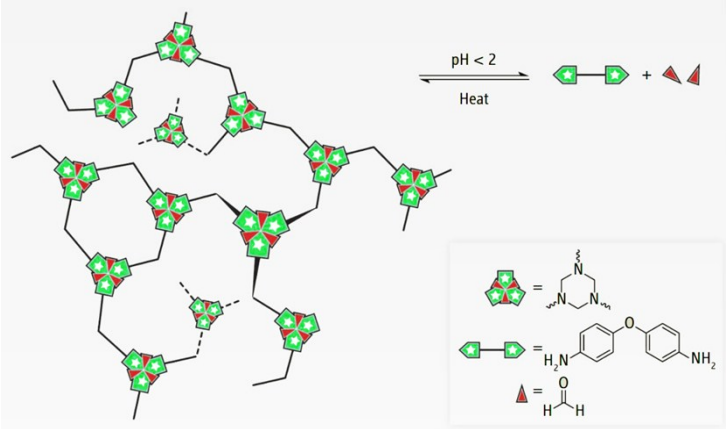


Fig. S5 Photo of the **HPUs-T15** (0.5 mg/mL) in DMSO–H_2O (10 mM) (1:9, v/v): (left) pH = 1; (right) pH = 2.

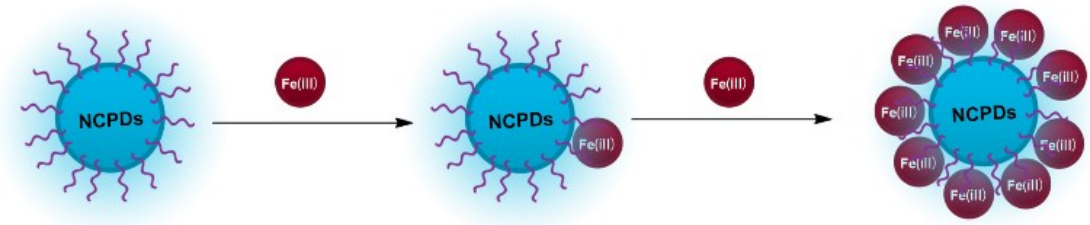
Mechanism of the polymer based on non-conjugated triazine ring in pH < 2



Scheme. S1 Mechanism[2] of the polymer based on non-conjugated triazine ring in pH < 2

(2) T. E. Long, *Science*, 2014, **344**, 706.

Mechanism of NCPDs vs Fe^{3+}



Scheme. S2 The mechanism of NCPDs *vs* Fe^{3+}.

MS spectra of NCPDs, NCPDs-Fe^{3+} and NCPDs in pH=1

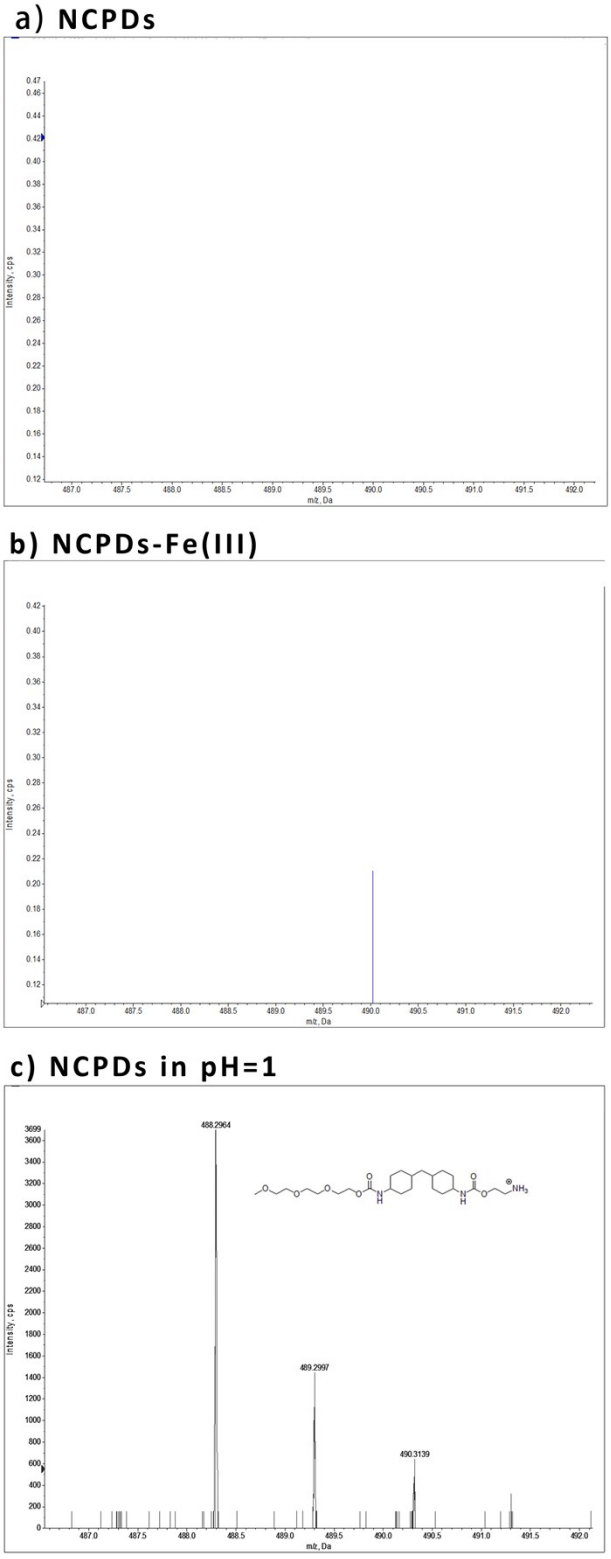


Fig. S6 MS spectra of (a) **HPUs-T15** (0.5 mg/mL) in DMSO–PBS buffer (10 mM) (pH=7.4, 1:9, v/v); (b) **HPUs-T15** (0.5 mg/mL) by alternating addition of 100 μM Fe^{3+} in DMSO–PBS buffer (10 mM) (pH=7.4, 1:9, v/v); (c) **HPUs-T15** (0.5 mg/mL) in DMSO–HCl(aq) (pH=1.0, 1:9, v/v)

UV absorption spectra of NCPDs, Fe^{3+} and NCPDs-Fe^{3+}

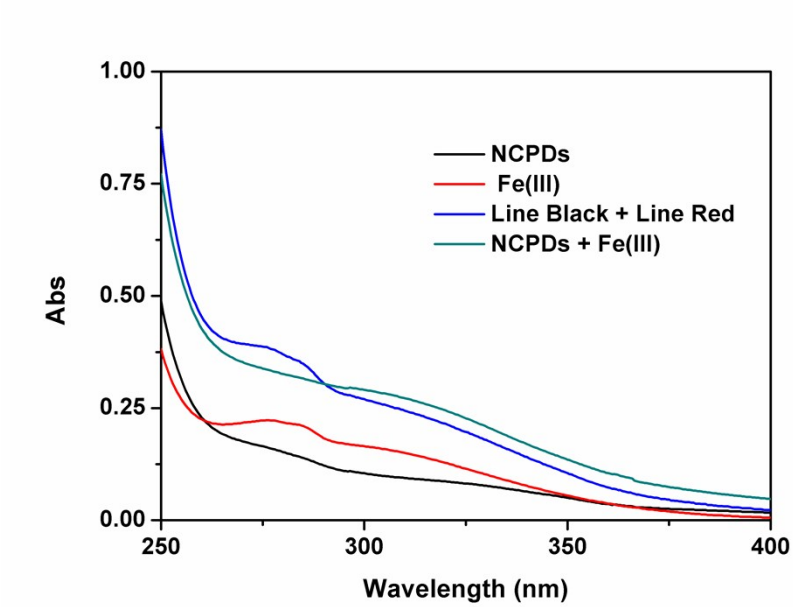
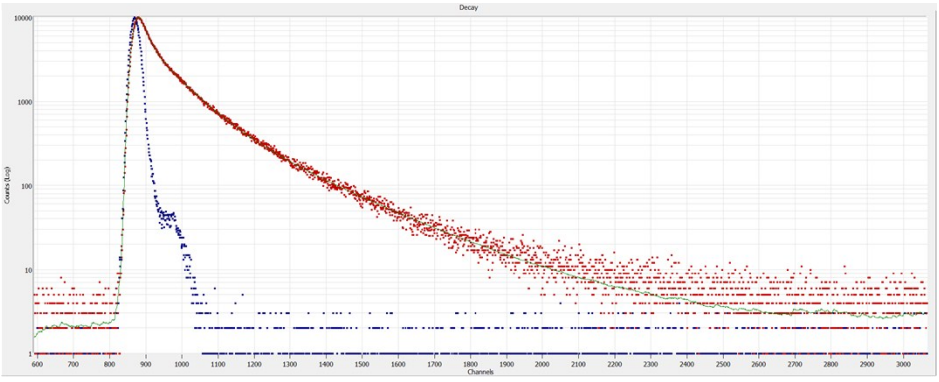
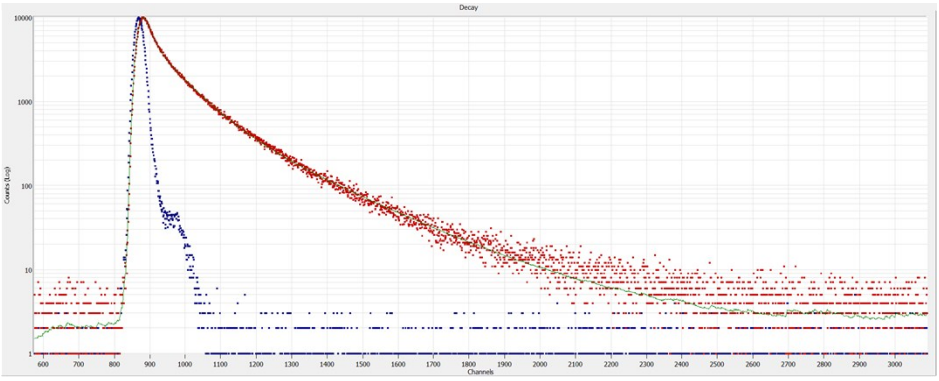


Fig. S7 UV absorption spectra of 0.5 mg/mL **NCPDs** , 100 μM Fe^{3+} and 0.5 mg/mL **NCPDs** + 100 μM Fe^{3+}, in DMSO-PBS buffer (pH=7.4, 1:9, v/v).

Fluorescence lifetime spectra of NCPDs and NCPDs-Fe^{3+}



τ(NCPDs) = 2.54239 ns



τ(NCPDs + Fe^{3+})= 2.51154 ns

Fig. S8 Fluorescence lifetime spectra of **NCPDs**, **NCPDs** + Fe^{3+}, in DMSO-PBS buffer (pH=7.4, 1:9, v/v).

Emission spectra of NCPDs, NCPDs-Fe^{3+} and NCPDs-Fe^{3+}-EDTA

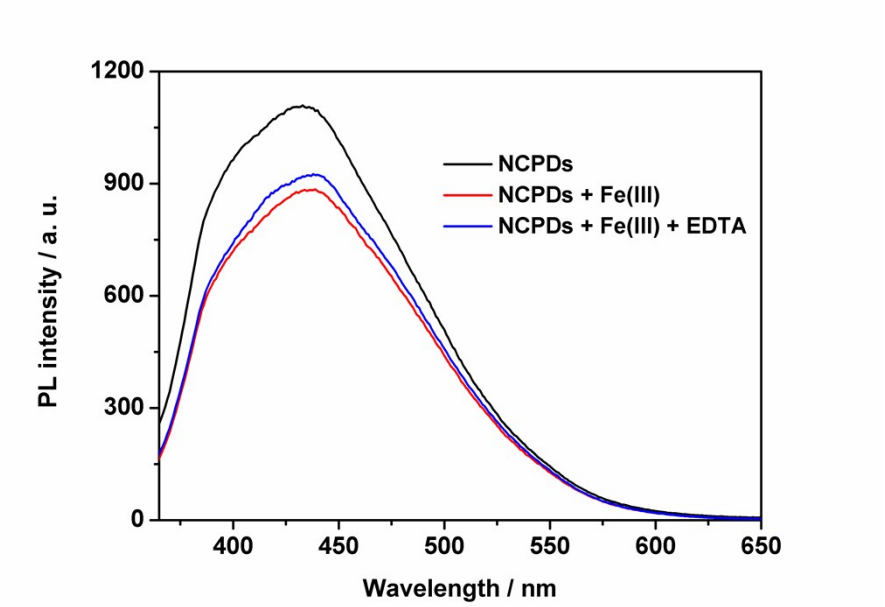


Fig. S9 Emission spectra of the **HPUs-T15** (0.5 mg/mL) in DMSO–PBS buffer (10 mM) (pH=7.4, 1:9, v/v) by addition of (black line) none; (b) 50 μM Fe^{3+}; (c) 50 μM Fe^{3+} and then 50 μM EDTA.

^{1}H NMR spectra of NCPDs and NCPDs-Fe^{3+}

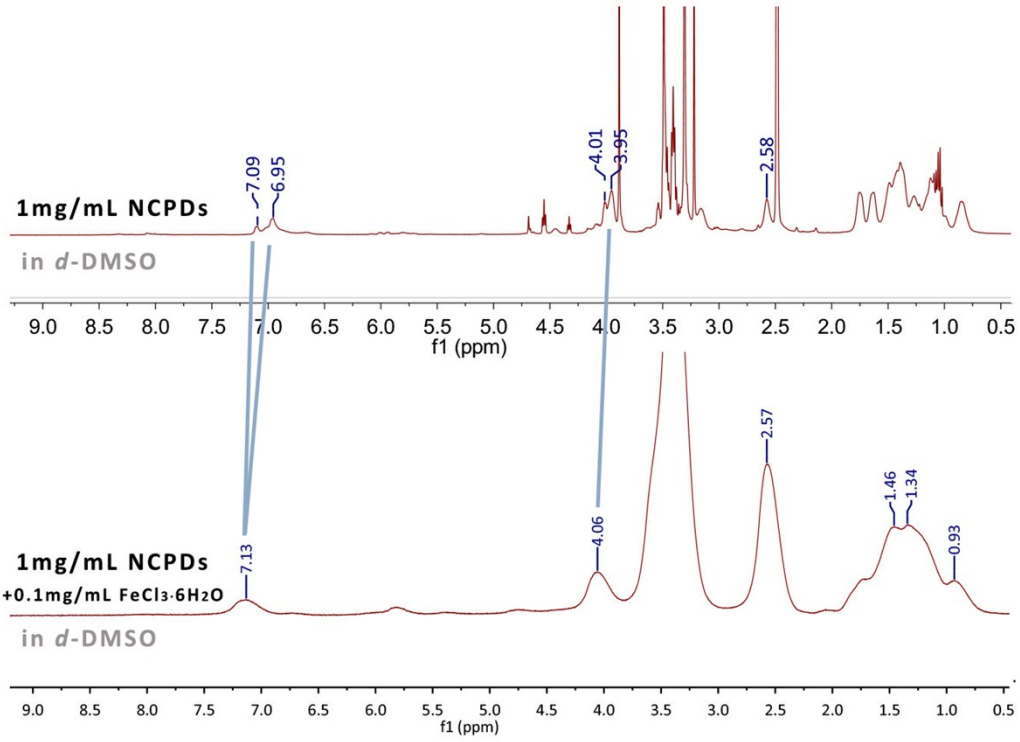


Fig. S10 ^{1}H NMR spectra of **NCPDs** and **NCPDs** + Fe^{3+} in *d*-DMSO.