Supporting information

A novel colorimetric and fluorescent chemosensor for acetate ion in aqueous media based on Rhodamine 6G-phenylurea conjugate in the presence of Fe(III) ion

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Contents

1 apparatus and reagents

A Techcomp UV-8500 spectrophotometer (Shanghai, China) was used for absorption measurement. The fluorescence spectra were recorded with a Hitachi F-2500 spectrofluorimeter. NMR spectra were measured on a Bruker DMX-500 spectrometer at 500 MHz in CD_3CN. All other chemicals used were local products of analytical grade. Distilled water was used throughout the experiment. The solutions of metal ions were prepared from their perchlorate salts. The solutions of anions were prepared from their sodium salts. All solvent used in spectroscopic analysis are spectrostropic grade.

2 Synthesis and structural characterization of RGPU

Rhodamine 6G hydrochloride (1.9g, 4mmol) was refluxing in CH_3OH with NH_3 continuously pumped into for about 4h. As cooling at room temperature, the resulting precipitates were filtered off, washed with 20ml methanol and dried under vaccum. Then the residue was dissolved in 20 ml dry DMF and NaH (0.24g, 10mmol) was slowly added. The mixture was stirred about 15 minutes. After the colorless changing to orange, PhNCO (0.71g, 6mmol) dissolved in about 15 ml dry DMF was dropwise added in 20 minutes. At the end of the addition, the mixture was stirred about 30 minutes. The solvent was removed and the obtained residue was purified by silica gel column chromatography with Petroleum ether/EtOAc (3:1, v/v) as eluent to afford 0.74g **RGPU** as a white solid,

Yield, 34.7%. m.p.: 268-269°C. ^{1}HNMR (CD$_3$OCD$_3$, 500MHz, TMS) : δ =10.94(s, 1H); 8.30 (d, J = 7.5 Hz, 1H); 7.72 (t, J=7.5Hz, 1H); 7.65 (t, J = 7.5 Hz, 1H); 7.46 (d, J = 8.5 Hz, 2H); 7.25 (t, J= 7.5 Hz, 2H) ; 7.13 (d, J = 7.5 Hz, 1H); 7.00 (t, J = 7.0 Hz, 1H); 6.33 (m, J = 11 Hz 4H); 4.43 (s, 2H); 3.25 (m, J = 6.5 Hz, 4H); 1.99 (s, 6H); 1.28 (t, J = 7 Hz, 6H). ^{13}C NMR(CD$_3$OCD$_3$, 250MHz, TMS) : δ 166.5, 151.7, 147.6, 138.4, 135.1, 128.8, 127.0, 124.4, 123.6, 123.1, 119.0, 117.3, 106.9, 96.2, 37.9, 16.0, 13.8. ESI-MS 533.4 [M+H]$^+$; Anal. Cacld for C$_{33}$H$_{32}$N$_4$O$_3$: C, 74.41; H, 6.06; N, 10.52; Found: C, 74.37; H, 6.35; N, 10.81.

3. General procedure for AcO$^-$ detection

A 1.0×10^{-4}M stock solution of **RGPU** was prepared in CH$_3$CN. To 10-mL glass tubes containing different amounts of Fe^{3+} and anions, proper amounts of the solution of **RGPU** was directly added with micropipette, then diluted with H$_2$O and CH$_3$CN to 10mL and mixed. The absorption and fluorescence sensing of metal ions were running immediately.
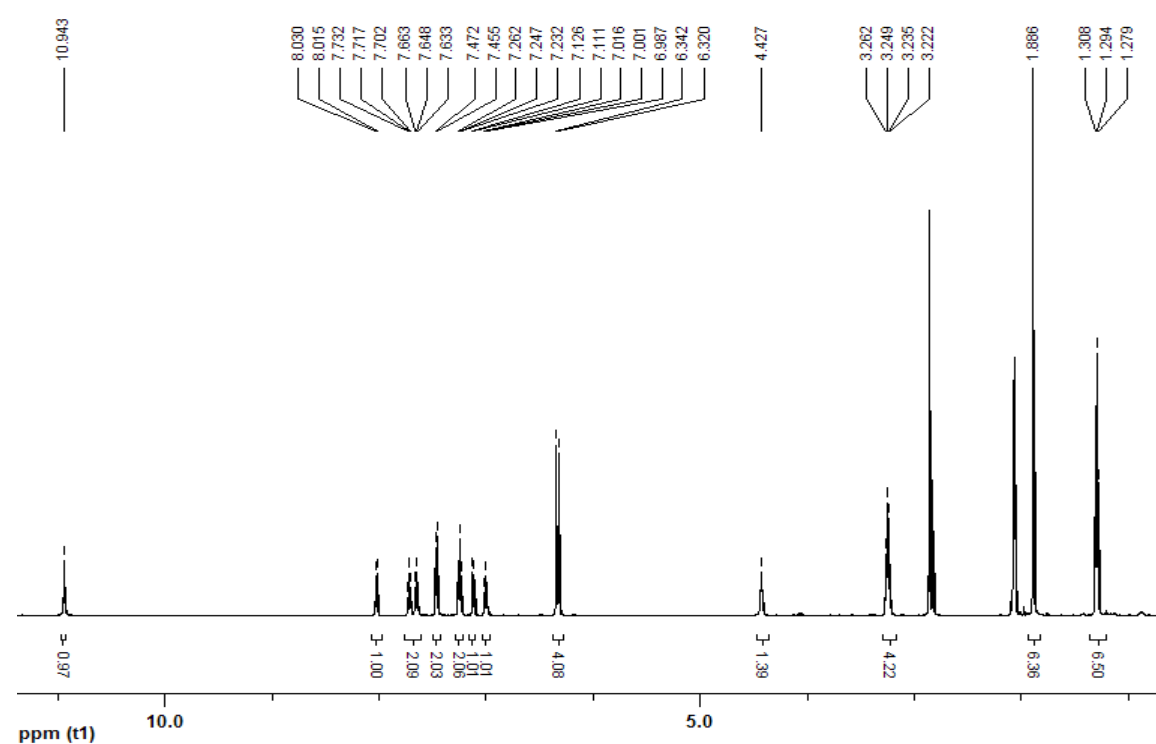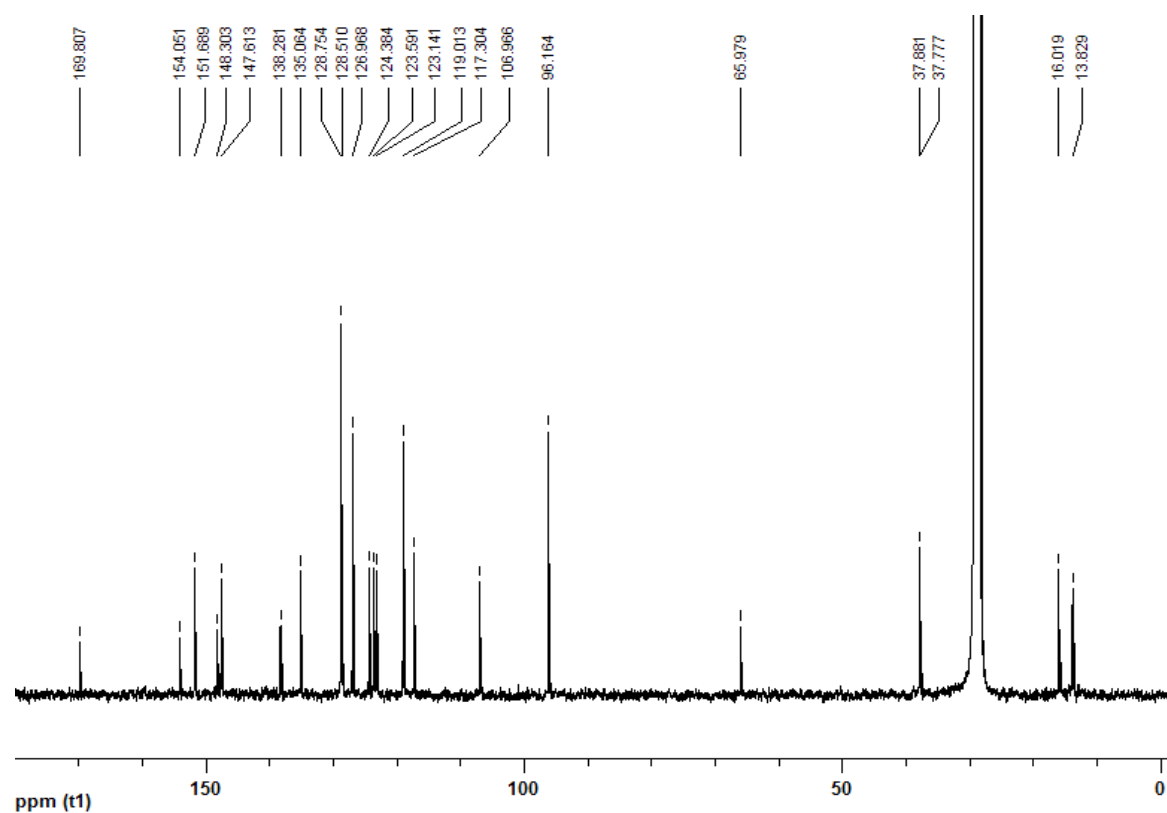

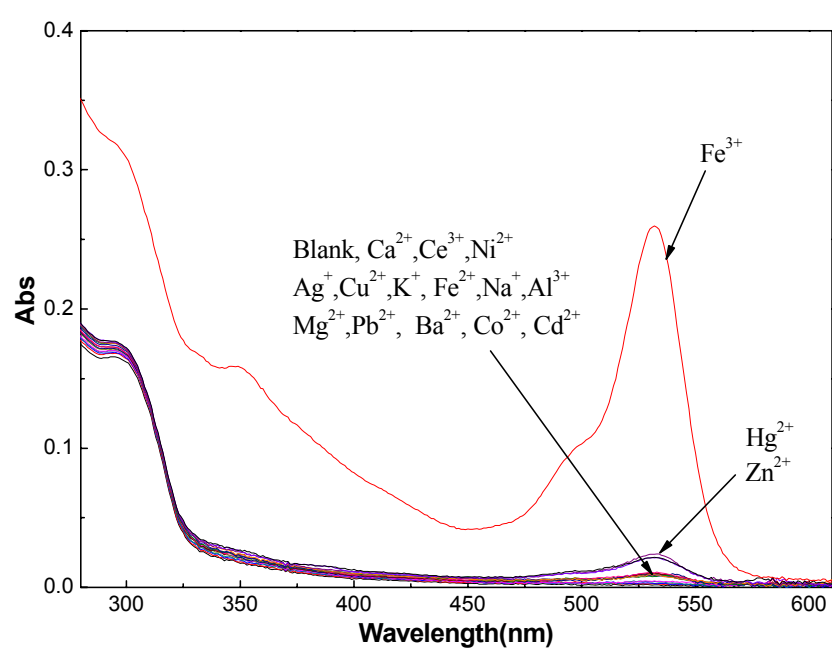Fig. S1 ^{1}H NMR of **RGPU**

S3

Fig. S2 ^{13}C NMR of **RGPU**

Fig. S3 Absorption spectra of **RGPU** (10 µM) upon addition of respective metal ions (as perchlorate salt, 50 equiv.) inCH$_3$CN-H$_2$O (1/1, v/v).
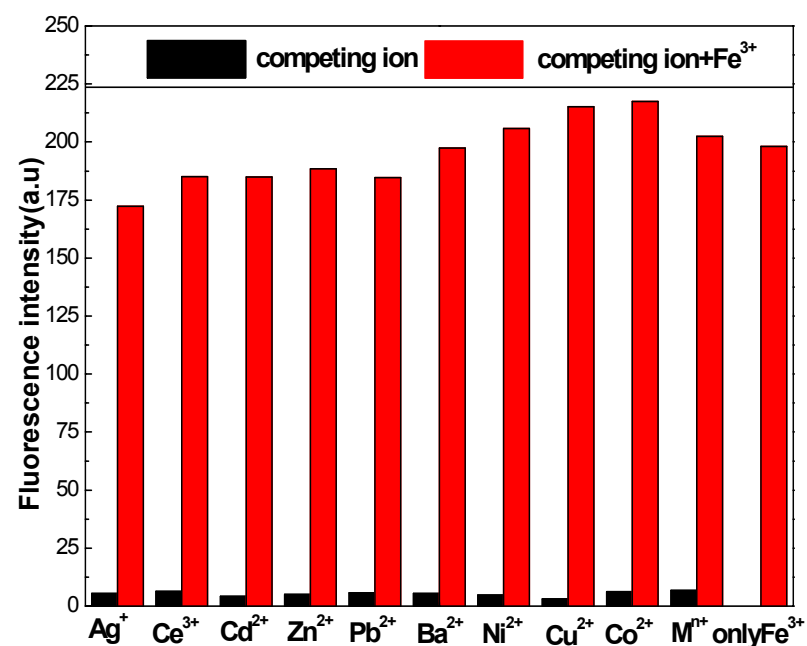
S4

Fig. S4 Fluorescene intensity of **RGPU** (1 µM) upon the addition of 20 µM Fe^{3+} in the presence of 100 µM background metal ions (M^{n+}: Hg^{2+}, K^+, Na^+, Al^{3+}, Mg^{2+}) in CH_3CN-H_2O (1:1, v/v), λex = 483nm.
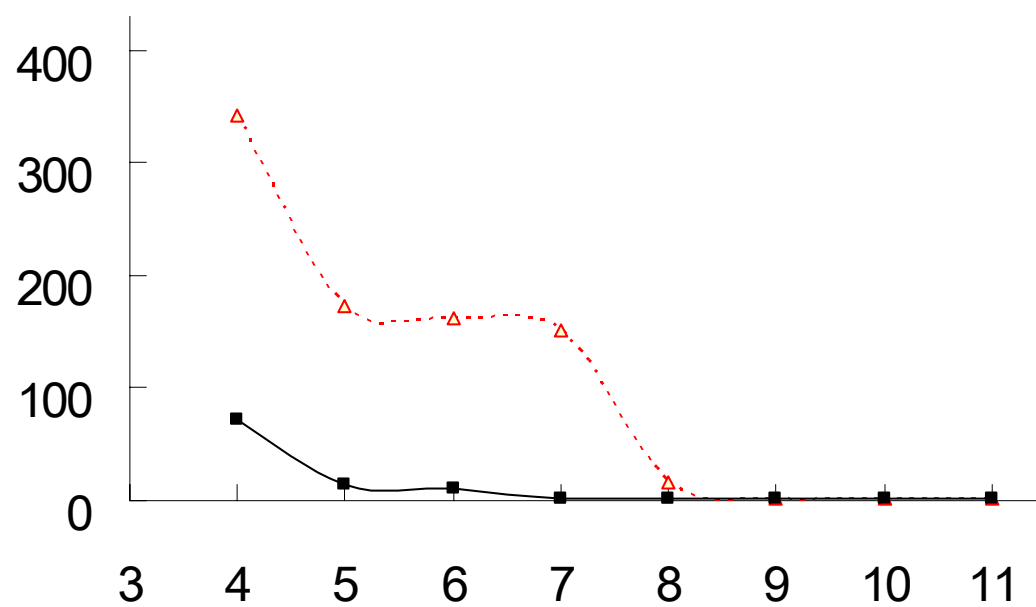

Fig. S5 Variation of fluorescence intensity of **RGPU** (1µM) in CH_3CN-H_2O (1:1, v/v) with (red) and without (black) Fe^{3+} (15µM) as a function of pH.

S5

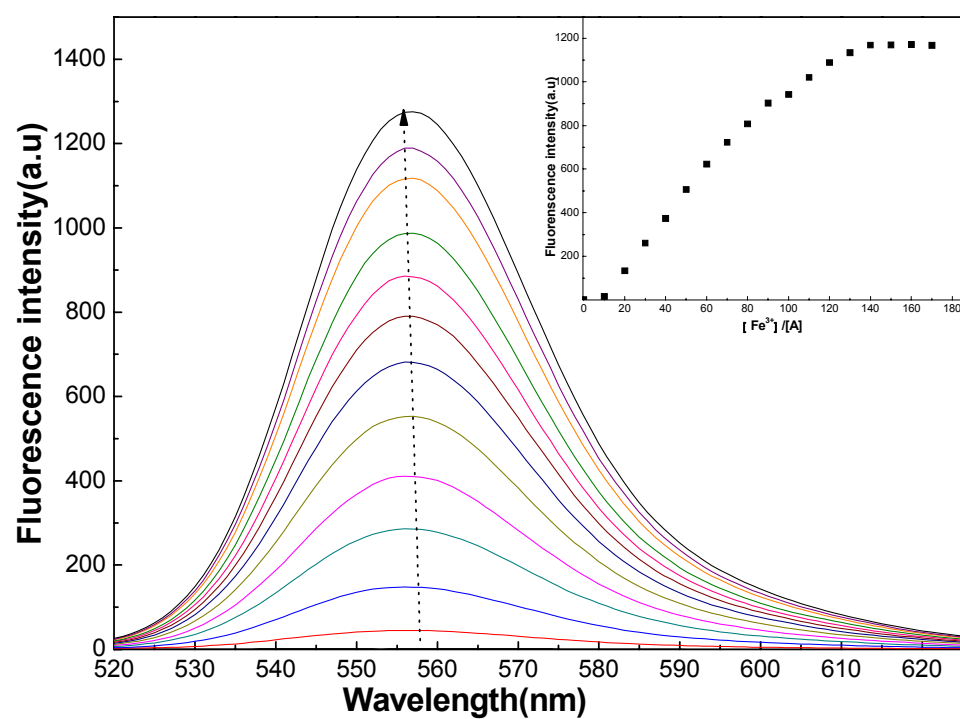**Fig. S6** Fluorescence (λex = 483 nm) titration spectra of **RGPU** (1 μM) with Fe^{3+} (0 ~ 11 0μM) in CH_3CN-H_2O (1/1, v/v)
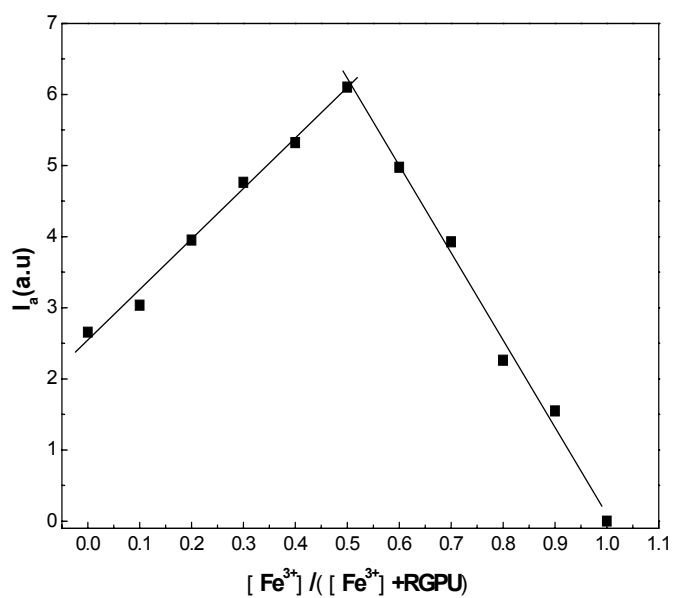
Fig. S7   Job's plot of the complex formed by **RGPU/Fe^{3+}**
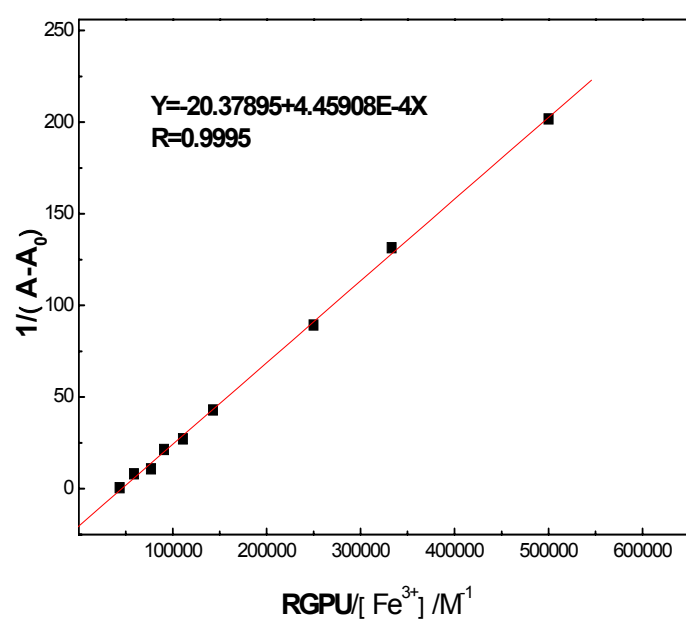
S6

Fig. S8   Benesi-Hildebrand plot of **RGPU** (1μM) in CH$_3$CN/H$_2$O (1:1 v/v) assuming
1:1 stoichiometry between **RGPU** and Fe^{3+}

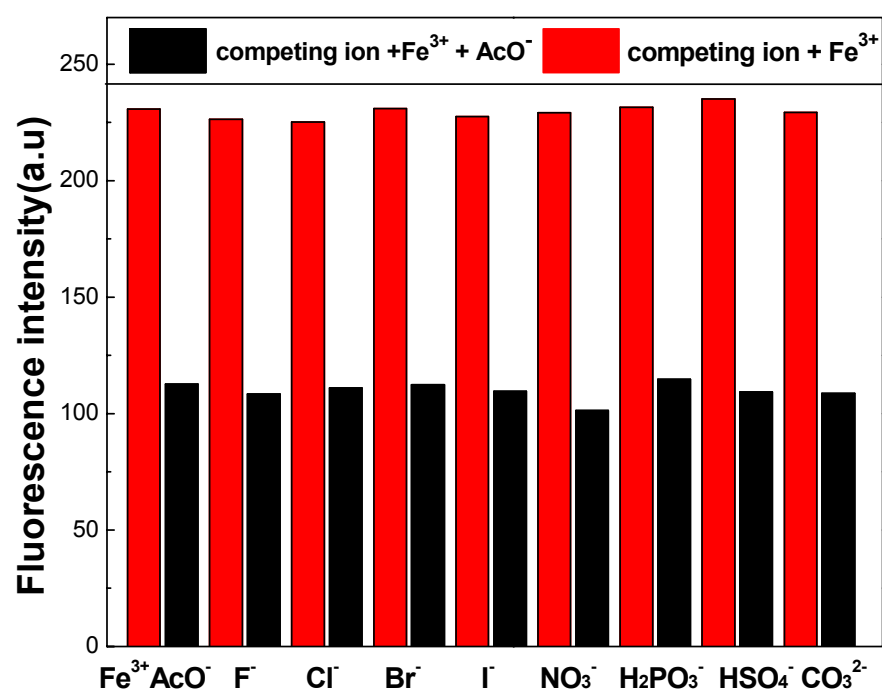
Fig. S9 Fluorescence intensity of **RGPU**(1 μM) upon addition of 10 equiv. AcO$^-$ in the
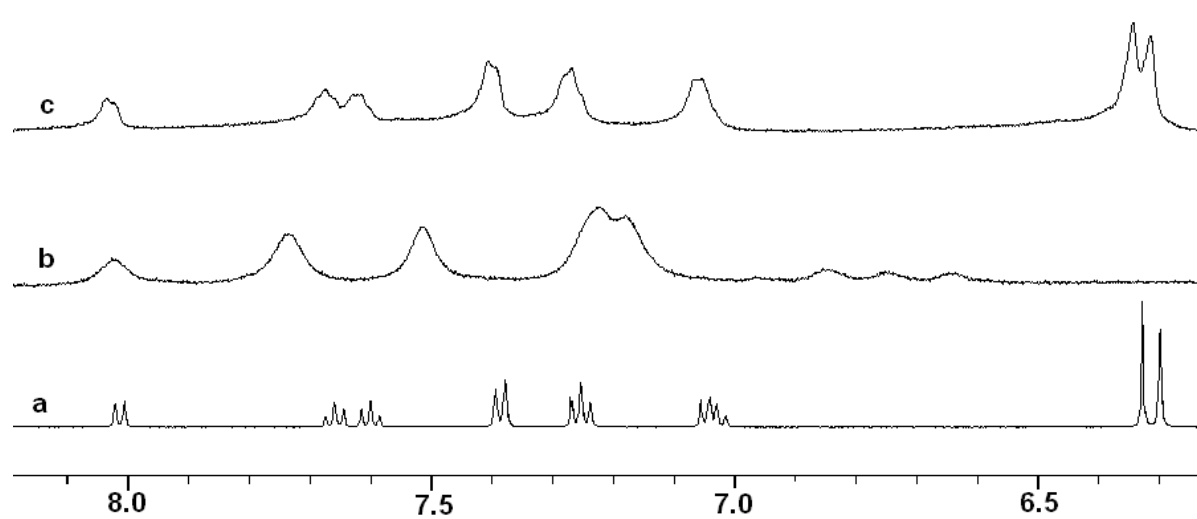presence of 20 μM Fe^{3+} and 20 μM other anion in CH$_3$CN-H$_2$O (1:1 v/v). λex = 485nm.

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Fig. S10   Partial ^{1}H NMR spectra of (a) **RGPU**(5mM) in CD$_3$CN; (b) **RGPU** in CD$_3$CN in the presence of Fe^{3+}(50mM); (c) **RGPU** in CD$_3$CN in the presence of Fe^{3+} ion(50mM) and AcO$^-$ (20mM).