Electronic Supplementary Information

for

Formation of blue fluorescent ribbons of 4',4''''-(1,4-phenylene)bis(2,2':6',2''-terpyridine) and highly selective visual detection of iron(II) cations

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Theoretical computation

Full geometry optimization and electronic structure calculation of PBTPy were first performed in vacuum using the B3LYP functional with 6-31G (d) basis set.[1] In order to obtain relatively accurate energy and structure, the geometry of the PBTPy in solvent DMSO was reoptimized by using the polarized continuum model (PCM) with the same basis set.[2] Frequency calculations at the same level were performed to confirm each stationary point to be a true energy minimum. All calculations presented in this work were carried out by the Gaussian03 program package.[3]

Additional figures

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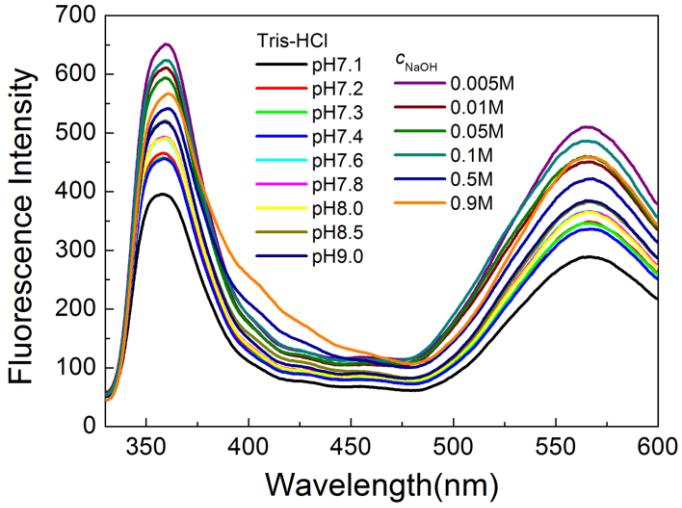

Fig. S1 Fluorescence emission spectra of PBTPy (5.0×10^{-5} mol/L) in different pH values of tris-HCl buffer and in different concentrations of NaOH with the excitation wavelength of 306 nm.

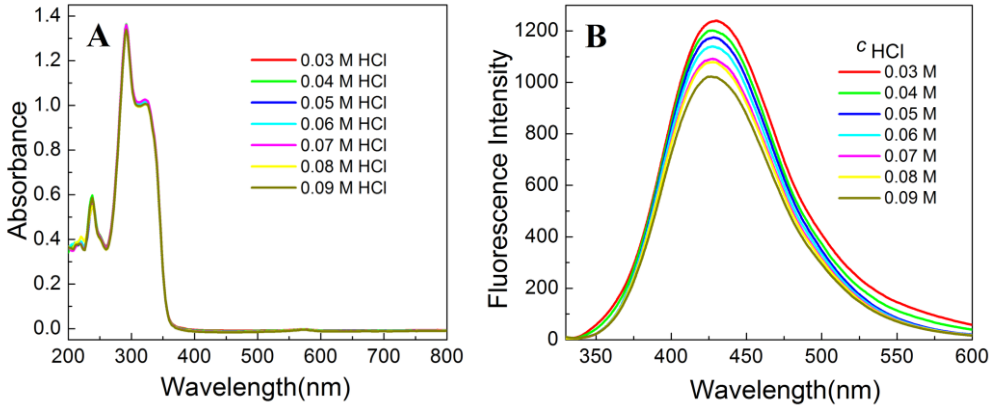

Fig. S2 The absorption (A) and fluorescence (B) spectra of PBTPy in acidic conditions with the excitation wavelength of 306 nm. c_{PBTPy}, 5.0×10^{-5} mol/L; c_{HCl} (mol/L), 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09.

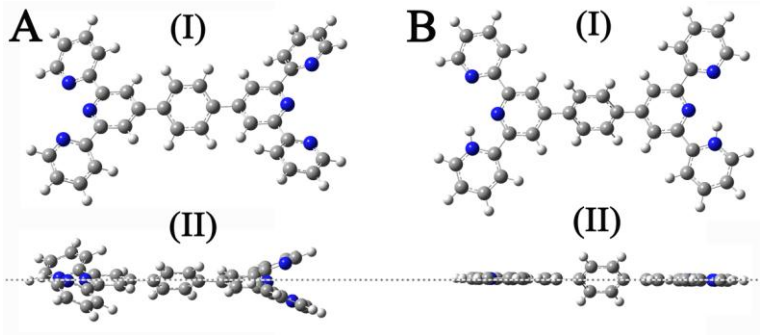

Fig. S3 The monomer of PBTPy computed in neutral conditions (A) and in acidic

conditions with two nitrogen atoms protonated (B). (I) and (II) represent the same structure viewed from different angles. Gray sphere, carbon atom; blue sphere, nitrogen atom; light gray sphere, hydrogen atom.

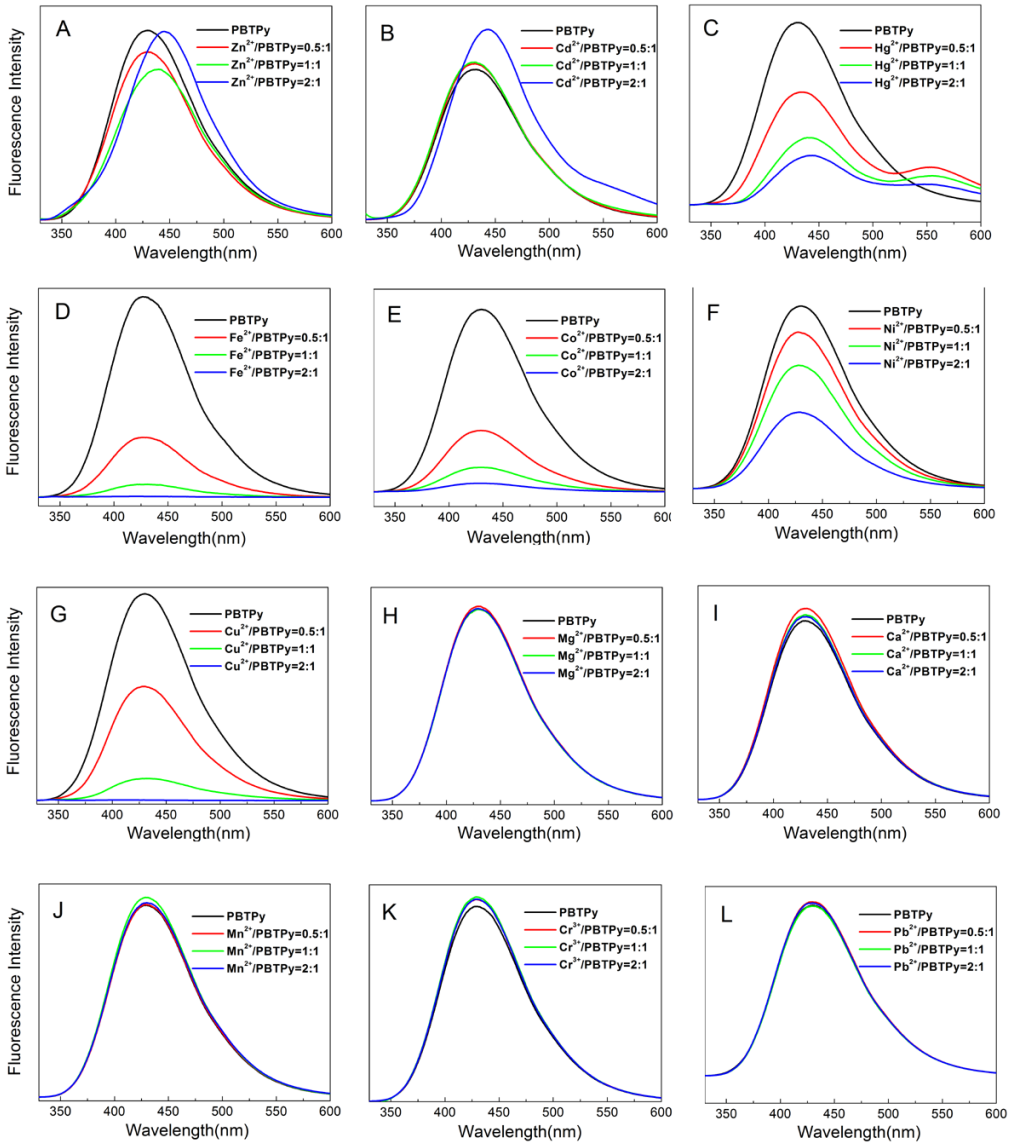

Fig. S4 Fluorescence spectra of PBTPy aggregations upon titration with metal ions including Zn^{2+}, Cd^{2+}, Hg^{2+} Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, and Pb^{2+} in the medium of 0.03 mol/L HCl when excited at 306 nm.

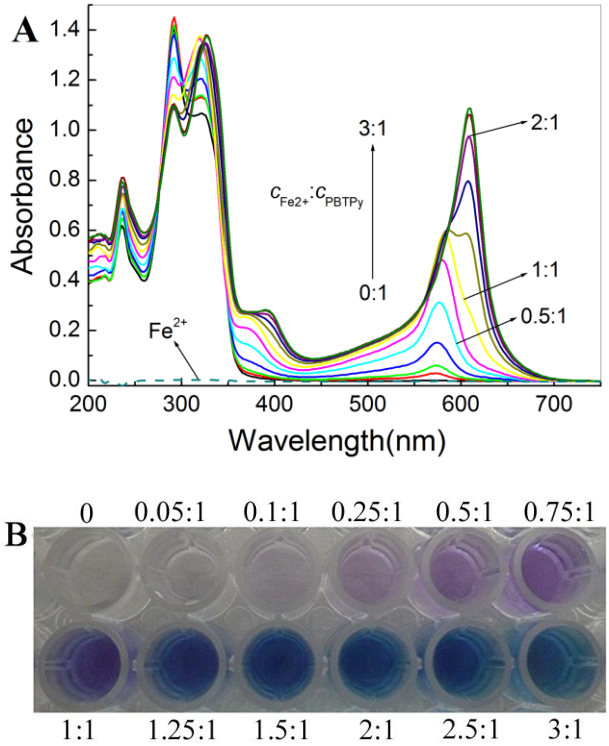

Fig. S5 UV-vis absorption spectra (A) and the observed color changes (B) of the aggregations of PBTPy (5.0×10^{-5} mol/L) upon the titration of Fe^{2+} in the medium of 0.03 mol/L. The dashed cyan line represents the absorption spectrum of Fe^{2+} (1.0×10^{-4} mol/L). The increased absorbance (ΔA) at 576 nm of the PBTPy aggregations was linearly correlated with the concentration of Fe^{2+} in the range of 2.5-37.5 μmol/L (ΔA = -0.0052 + 0.012 c (mol L^{-1}), r=0.9999, from three measurements).

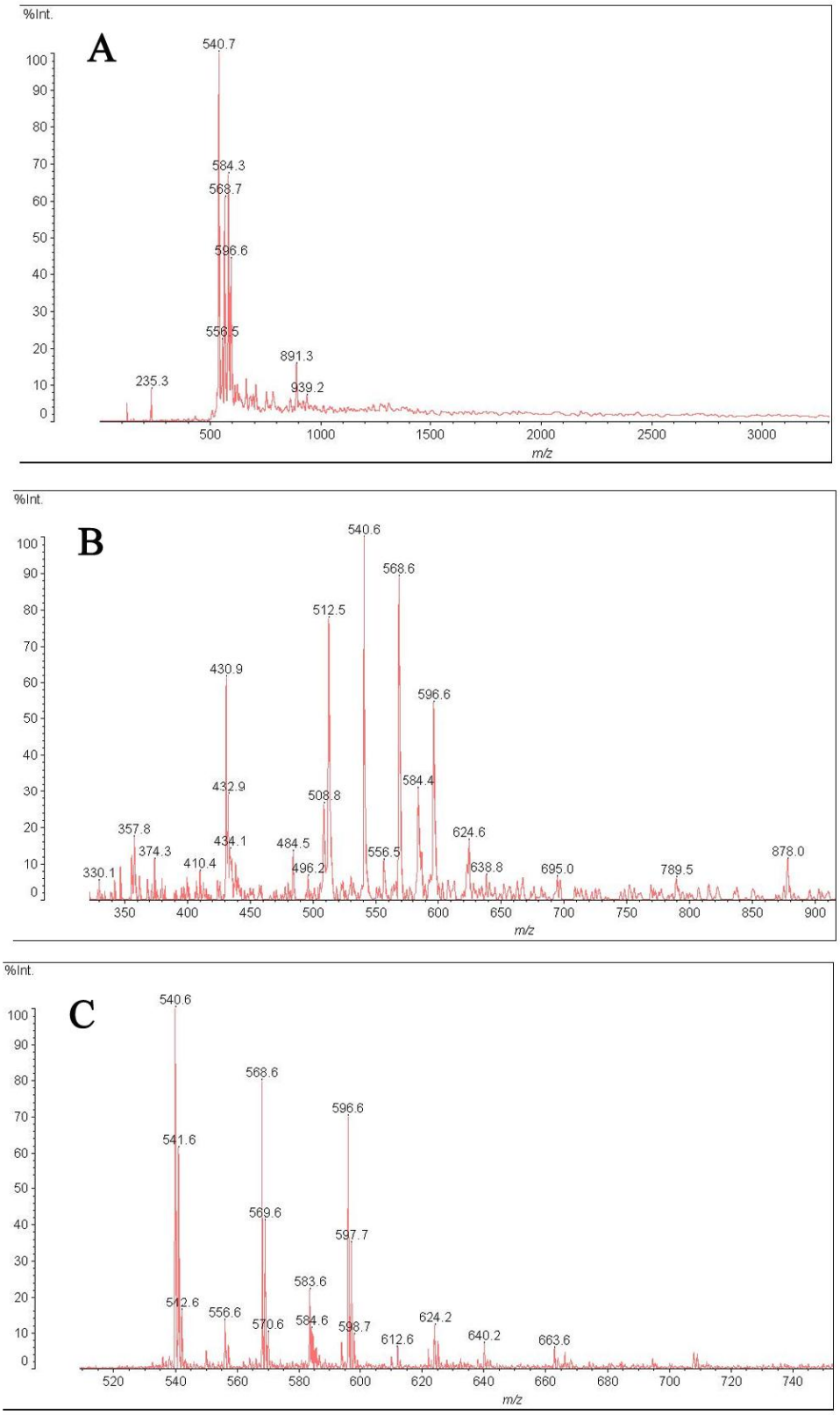

Fig. S6 The mass spectra of PBTPy aggregations upon titration with Fe^{2+} in 0.03 mol/L HCl by keeping the concentration ratio of PBTPy/Fe^{2+} as (A) 2:1, (B) 1:1, (C) 1:2.

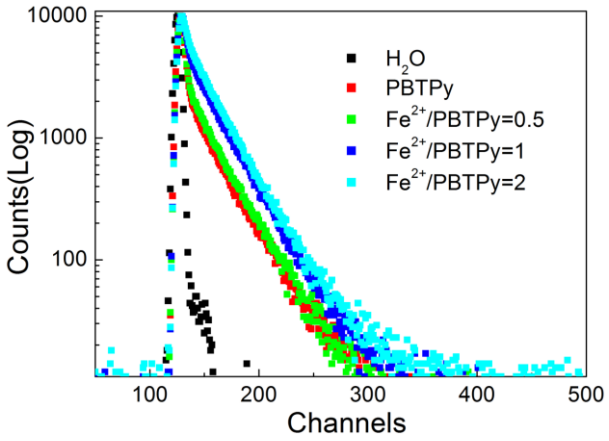

Fig. S7 The fluorescence decay curves of the PBTPy aggregations in the absence and presence of Fe^{2+} in the acidic condition. c_{PBTPy}, 5.0×10^{-5} mol/L; c_{Fe2+}/ c_{PBTPy} = 0.5, 1, 2.

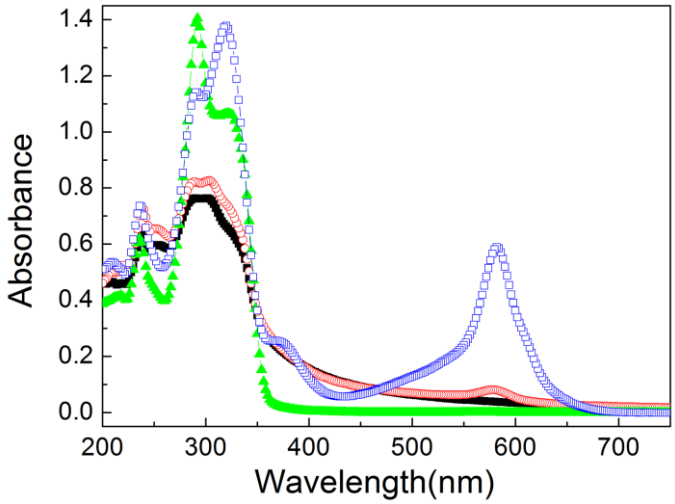

Fig. S8 The absorption spectra of the aggregations of PBTPy in the absence of Fe^{2+} in the neutral condition (■) and in the acidic condition (▲), and in the presence of Fe^{2+} in the neutral condition for three hours (○) and in the acidic condition for 40 minutes (□). c_{PBTPy}, 5.0×10^{-5} mol/L; c_{Fe2+}, 5.0×10^{-5} mol/L.

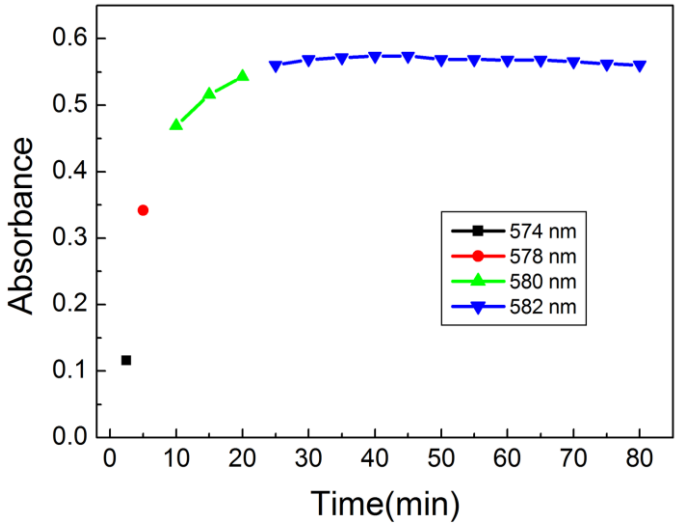

Fig. S9 The response time of the aggregations of PBTPy for sensing of Fe^{2+} by keeping the concentration ratio of PBTPy/Fe^{2+} as 1:1 in 0.03 mol/L HCl. c_{PBTPy}, 5.0×10^{-5} mol/L; c_{Fe2+}, 5.0×10^{-5} mol/L.

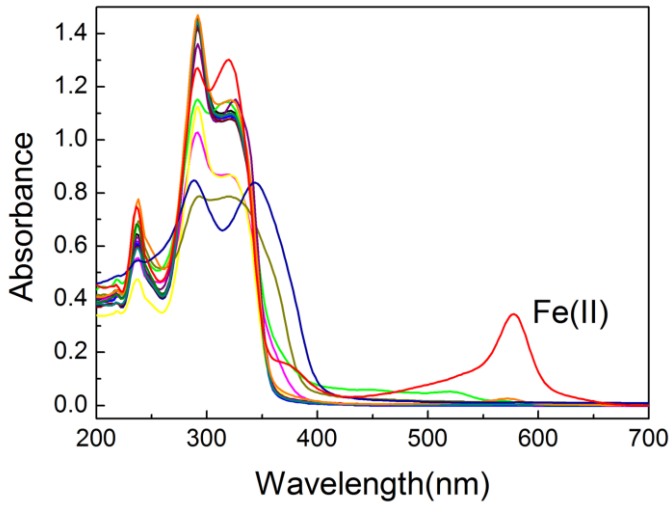

Fig. S10 Changes in the absorption spectra of aggregations of PBTPy (5.0×10^{-5} mol/L) upon the addition of Fe^{2+} (2.5×10^{-5} mol/L) and other metal ions (5.0×10^{-5} mol/L) including Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+} and Cu^{2+} in the medium of 0.03 mol/L HCl.

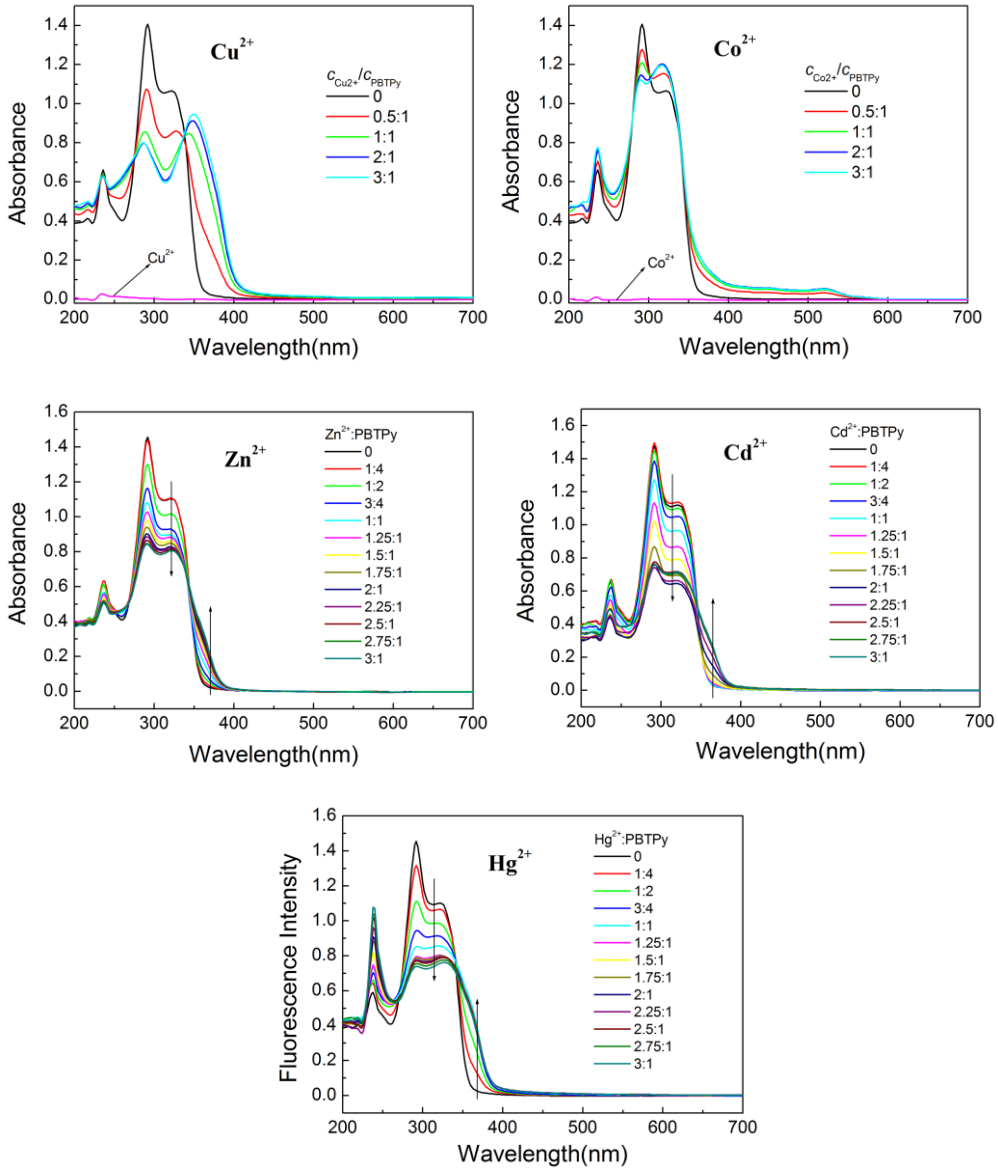

Fig. S11 UV-vis absorption spectra of the aggregations of PBTPy (5.0×10^{-5} mol/L) upon addition of Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, and Co^{2+} in the medium of 0.03 mol/L HCl.

Table S1 Fluorescence lifetimes of the PBTPy aggregations in the absence and presence of Fe^{2+} fitted by a three-exponential function

Sample	λ_{em} /nm	τ_1/ns (%)	τ_2/ns (%)	τ_3/ns (%)
0.03 M HCl+PBTPy	430.0	2.9 (16.4)	0.3 (55.3)	7.2 (28.3)
0.03 M HCl+PBTPy+0.5 equiv Fe^{2+}	430.0	2.1 (9.0)	0.2 (51.1)	6.2 (39.9)
0.03 M HCl+PBTPy+1 equiv Fe^{2+}	430.0	4.3 (30.7)	0.5 (27.8)	6.8 (41.5)
0.03 M HCl+PBTPy+2 equiv Fe^{2+}	430.0	4.7 (55.9)	0.4 (19.1)	7.8 (25.0)

References

1. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
2. S. Miertus and J. Tomasi, *Chem. Phys.*, 1982, **65**, 239-245.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al, *Gaussian, Revision D02*, Gaussian, Inc.: Wallingford CT, 2004.