Supporting Information

Improving Ion Selectivity of 1,4,7-Triazacyclononane-Based Receptors by Zinc Coordination: "Turn-On" Chemosensor for $Br^-$and Fe^{3+} Ions

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Number of tables	**2**

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Reference.

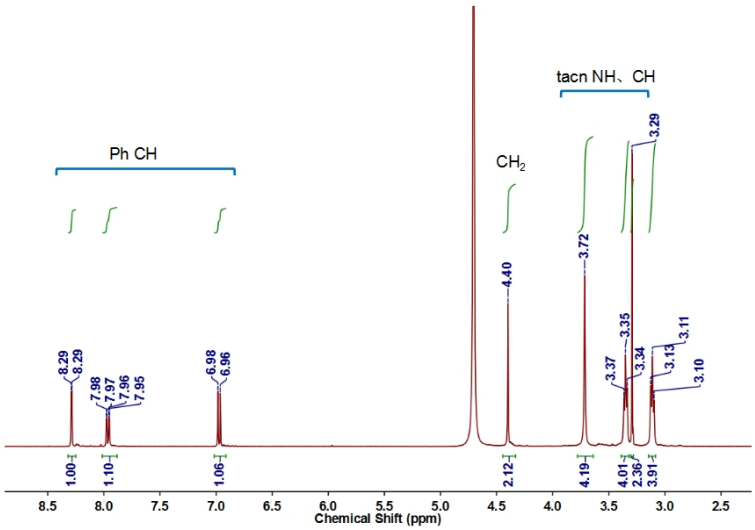


Figure S1. 400 MHz ^{1}H NMR spectroscopy of btacn (D_2O, 300 K, ppm).

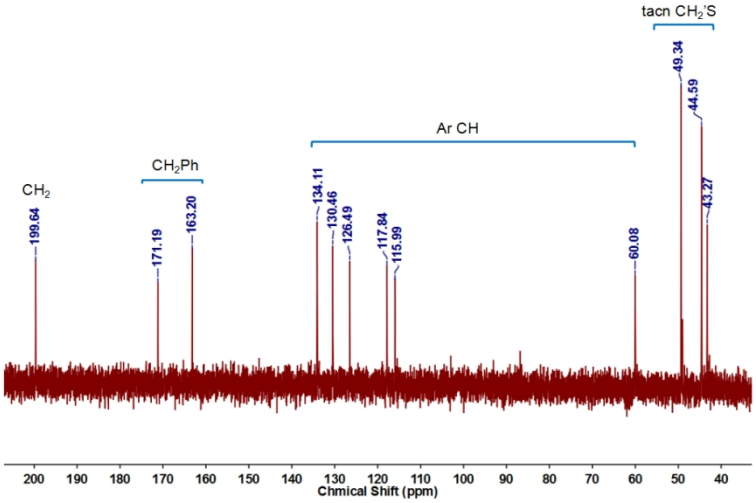


Figure S2. 100 MHz ^{13}C NMR spectroscopy of btacn (D_2O, 300 K, ppm).

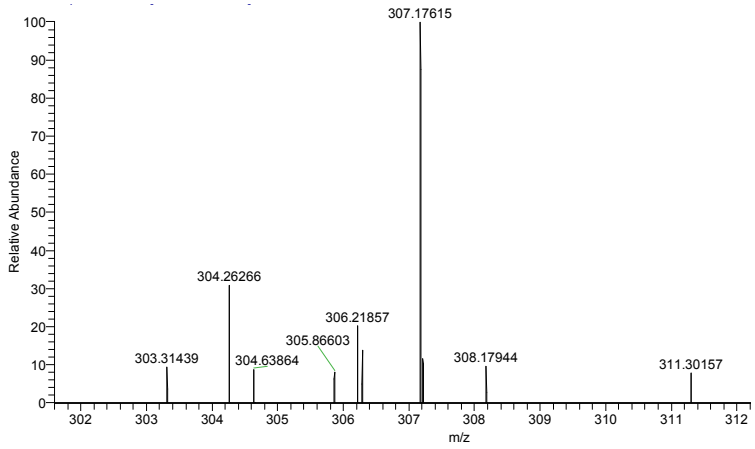


Figure S3. ESI-mass spectrum of btacn in D_2O; calcd for $C_{15}H_{23}O_3N_4^+$ ([btacn+H^+]$^+$) 307.37, found 307.17.

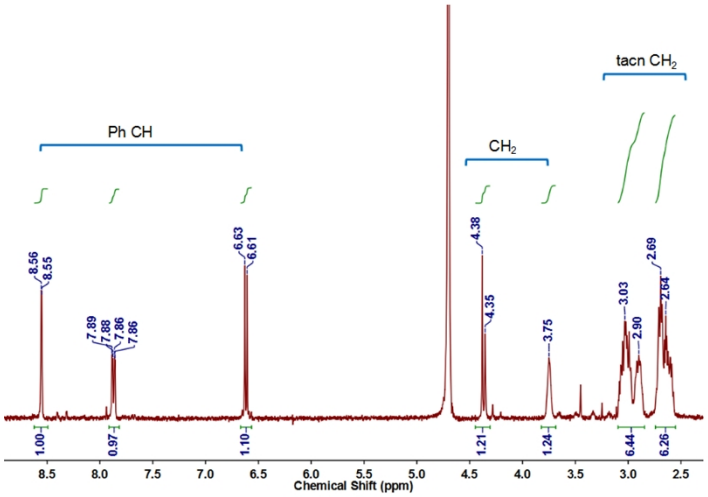


Figure S4. 400 MHz ^{1}H NMR spectroscopy of Zn(btacn)Cl_2 (D_2O, 300 K, ppm).

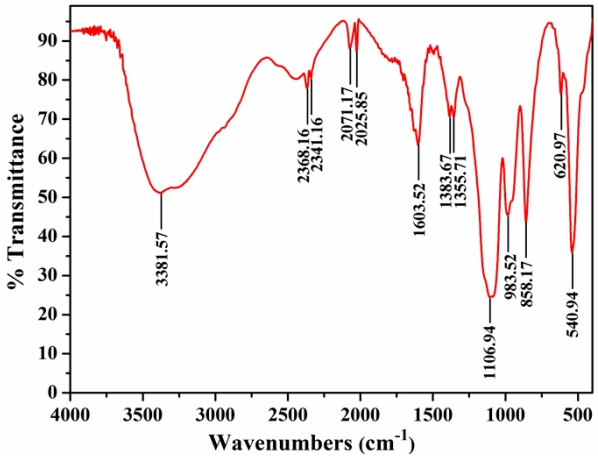


Figure S5. FT-IR pattern for Zn(btacn)Cl_2.

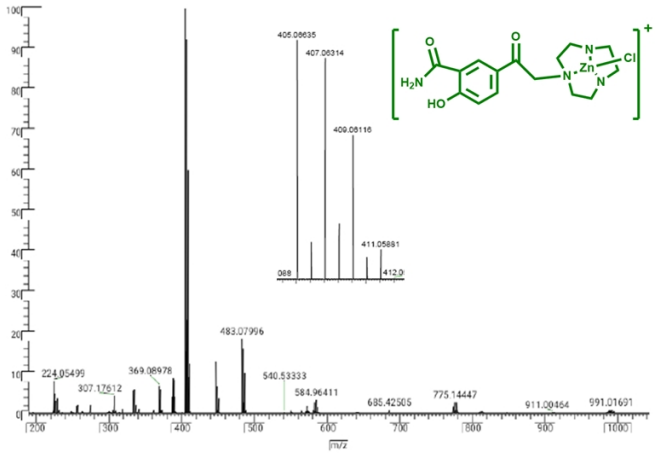


Figure S6. ESI-mass spectrum of Zn(btacn)Cl_2 in D_2O; Attributions: 405.066, $[Zn(btacn)Cl]^{+}$.

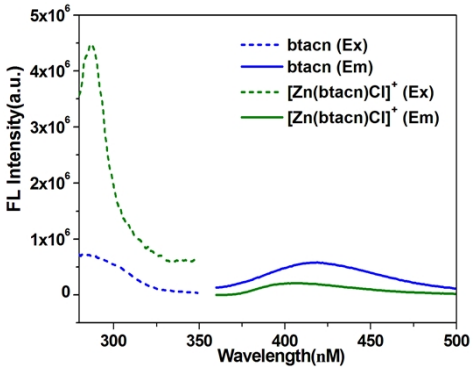


Figure S7. Excitation and emission spectra of btacn (blue) and $[Zn(btacn)Cl]^+$ (green); Solvents: H_2O, c: 5 μM for $[Zn(btacn)Cl]^+$, 200 μM for btacn, slit width: 4 nm.

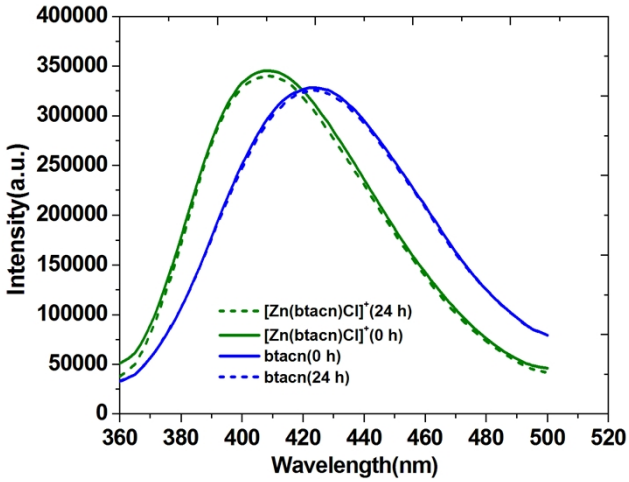
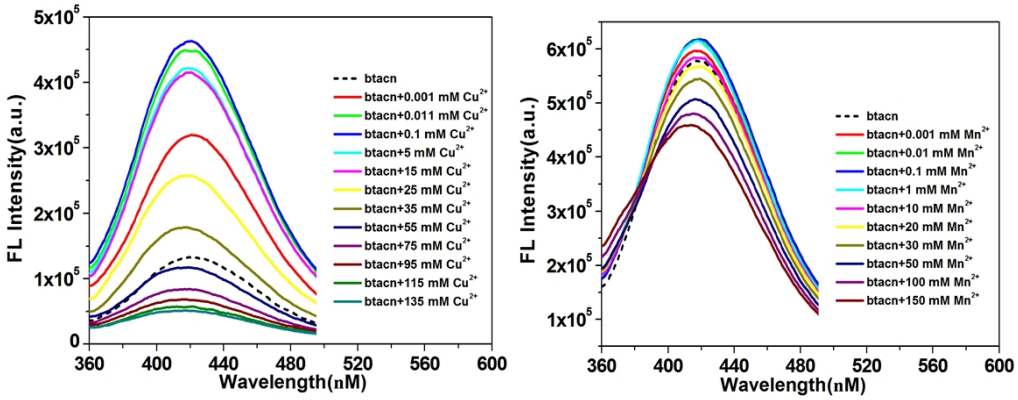
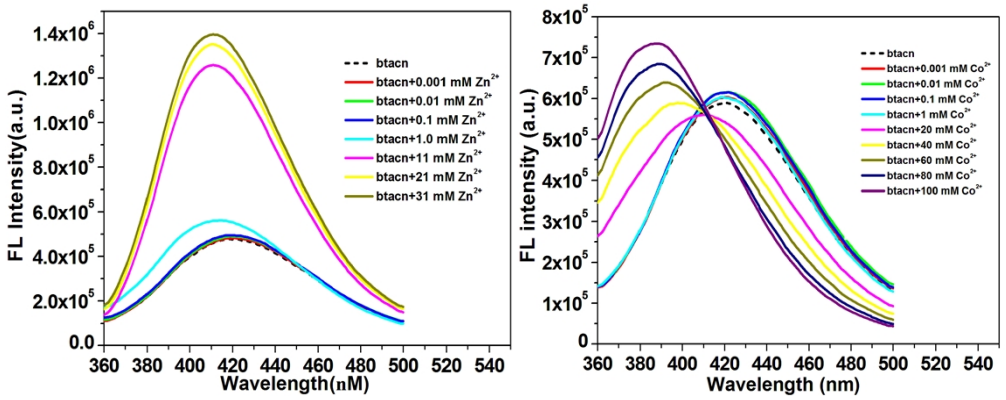


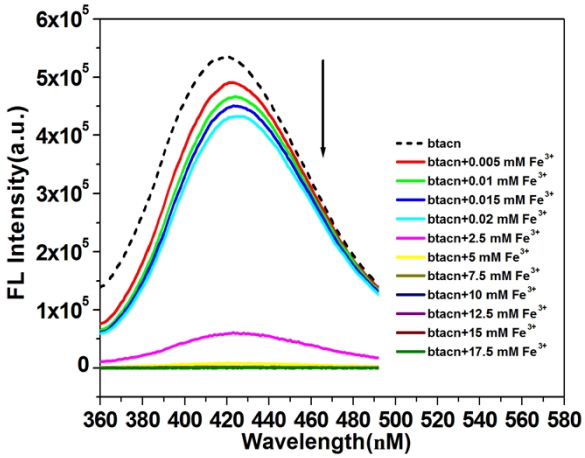
Figure S8. luminescence spectra of btacn (blue) and $[Zn(btacn)Cl]^+$ (green) for 0 h (solid) and 24 h (short dashed). Solvents: H_2O, c: 5 μM for $[Zn(btacn)Cl]^+$, 100 μM for btacn, λ_{ex}: 312 nm, slit width: 4 nm.



(a) (b)



(c) (d)

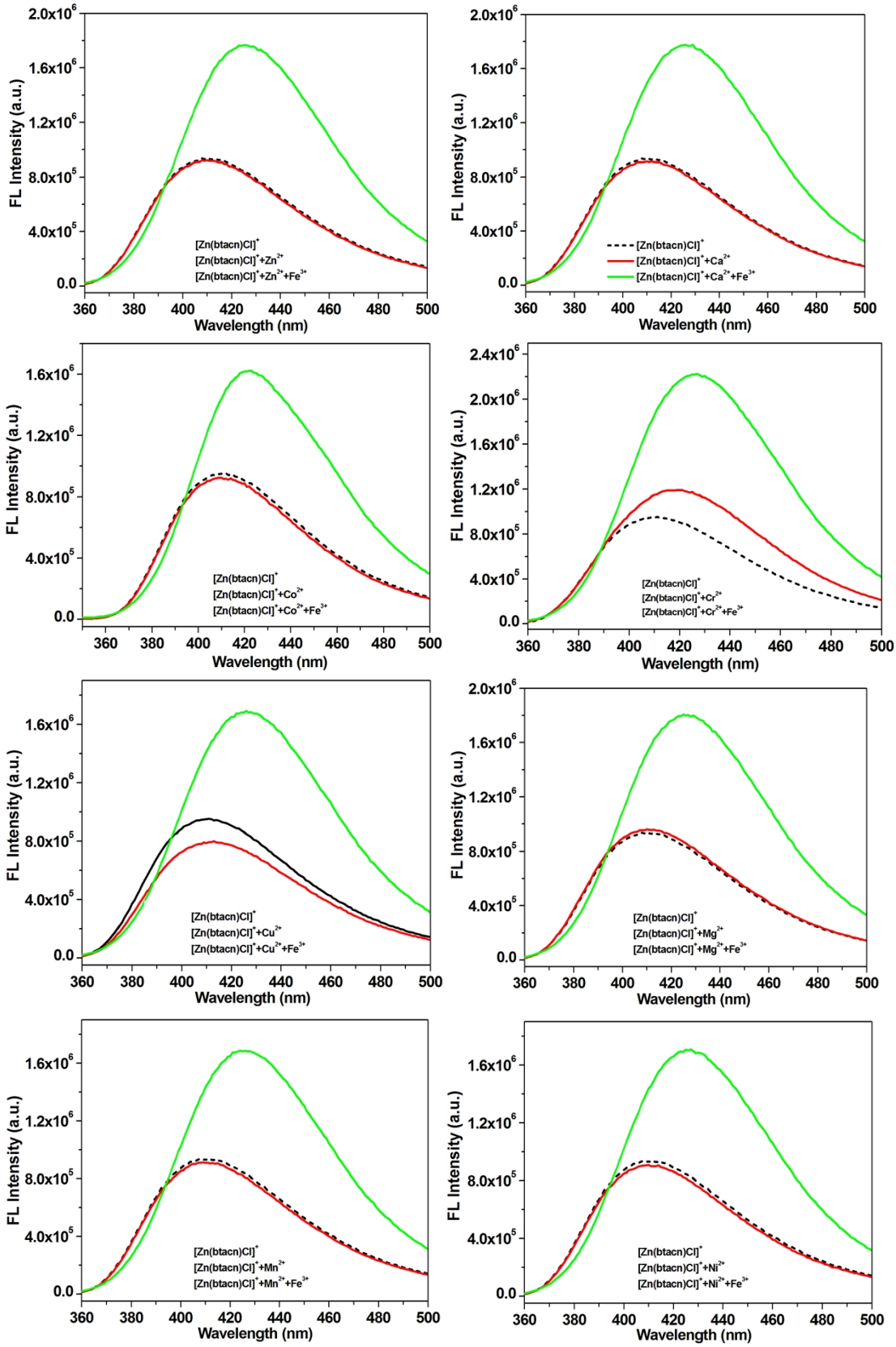


(e)

Figure S9. Fluorescence emission of btacn with addition of Cu^{2+} (a), Mn^{2+} (b), Zn^{2+} (c), Co^{2+} (d), Fe^{3+} (e). c: 200 μM for btacn except Cu^{2+} (50 μM for btacn), λ_{ex}: 312 nm, slit width: 4 nm.

Table S1. Comparison of $[Zn(btacn)Cl]^+$ with literature probes for Fe^{3+} ions.

S. No	Probe	LOD (M)	Ref
4	Mg-CP probe	4.7×10^{-4}	1
5	Zn-L-MOF probe	6.4×10^{-6}	2
6	Zn(II)-based MOF probe	2×10^{-6}	3
7	Ln(III)-MOF probe	10^{-6}	4
8	Europium-Based MOF probe	0.793×10^{-6}	5
9	{[Eu(Hdcppa)$(H_2O)_2$]·H_2O}n probe	10^{-6}	6
10	$[Zn(btacn)Cl]^+$ probe	1.6×10^{-7}	This work


FL Intensity (a.u.)
Wavelength (nm)
[Zn(btacn)Cl]+
[Zn(btacn)Cl]+Zn2+
[Zn(btacn)Cl]+Zn2++Fe3+
[Zn(btacn)Cl]+Ca2+
[Zn(btacn)Cl]+Ca2++Fe3+
[Zn(btacn)Cl]+Co2+
[Zn(btacn)Cl]+Co2++Fe3+
[Zn(btacn)Cl]+Cr2+
[Zn(btacn)Cl]+Cr2++Fe3+
[Zn(btacn)Cl]+Cu2+
[Zn(btacn)Cl]+Cu2++Fe3+
[Zn(btacn)Cl]+Mg2+
[Zn(btacn)Cl]+Mg2++Fe3+
[Zn(btacn)Cl]+Mn2+
[Zn(btacn)Cl]+Mn2++Fe3+
[Zn(btacn)Cl]+Ni2+
[Zn(btacn)Cl]+Ni2++Fe3+

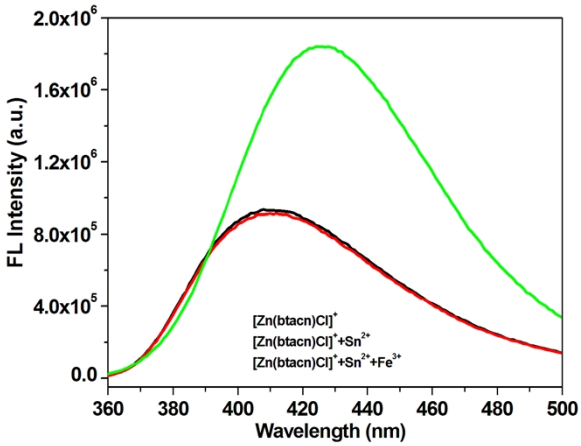


Figure S10. Comparison of the fluorescence intensity of $[Zn(btacn)Cl]^{+}$: blank as control, addition of other background ions, and followed by addition of Fe^{3+} ions. Solvents: H_2O, c: 40 μM for $[Zn(btacn)Cl]^{+}$, $[Fe^{3+}]$ and [background ion], λ_{ex}: 312 nm, λ_F: 405 nm, slit width: 4 nm. Background ions: Cr^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Sn^{2+}, Mg^{2+} and Ca^{2+}.

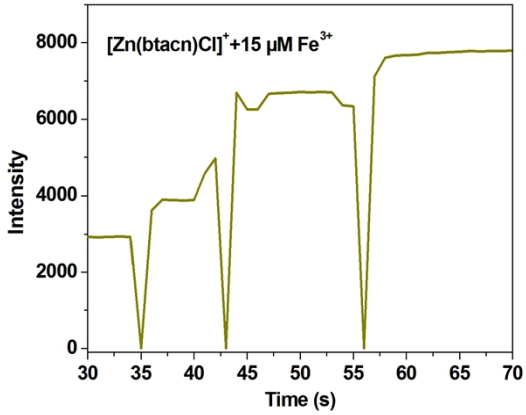
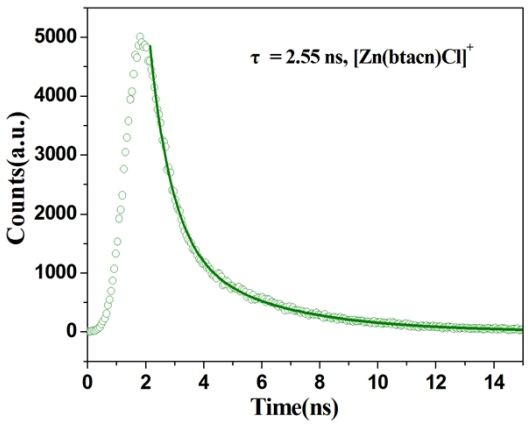
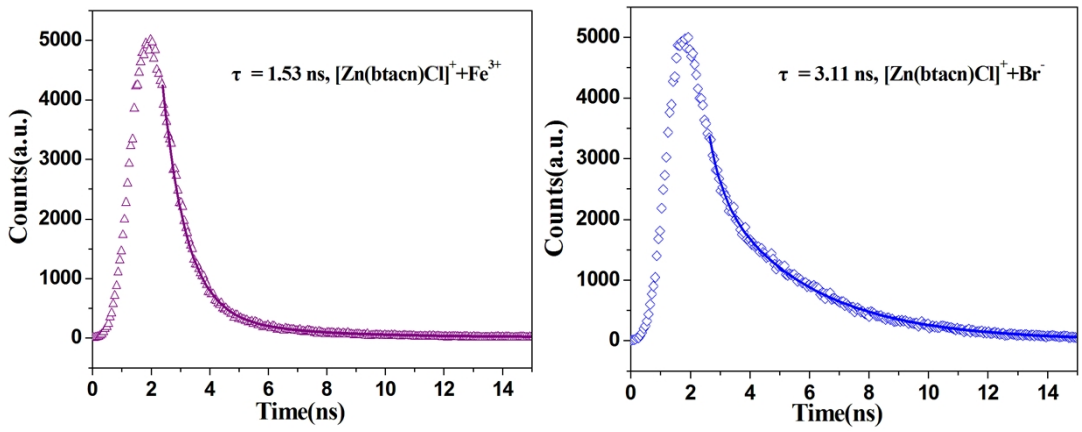


Figure S11. The variation of luminescent intensity of $[Zn(btacn)Cl]^{+}$ at 405 nm with immersion time in 15 μM $Fe(NO_3)_3$.



(a)



(b) (c)

Figure S12. Temporal fluorescence decay of 10 μM $[Zn(btacn)Cl]^+$ (a) and after added 100 μM Fe^{3+} ions (b), and after added 13 μM Br^- ions (c) in H_2O excited at 312 nm and monitored at 405 nm; The solid curve shows the best single exponential fit to the data; The data are obtained at 54.9 ps per point.

Table S2. Comparison of the lifetimes of $[Zn(btacn)Cl]^+$, $[Zn(btacn)Cl]^+$-Fe^{3+} and $[Zn(btacn)Cl]^+$-Br^-.

Compounds	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ (ns)
$[Zn(btacn)Cl]^+$	0.76	31.97	3.39	68.03	2.55
$[Zn(btacn)Cl]^+$-Br^-	0.46	4.73	3.24	95.27	3.11
$[Zn(btacn)Cl]^+$-Fe^{3+}	0.80	66.90	3.01	33.10	1.53

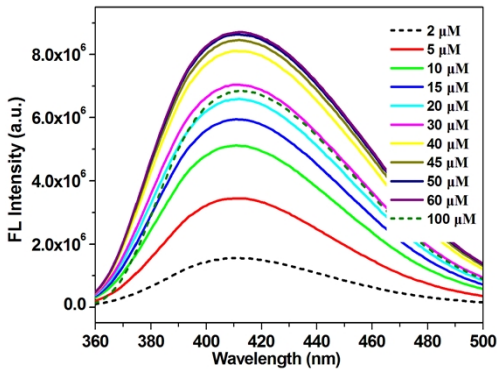


Figure S13. Fluorescence emission spectra of different concentrations of $[Zn(btacn)Cl]^+$; Solvents: H_2O; λ_{ex}: 312 nm; slit width: 4 nm.

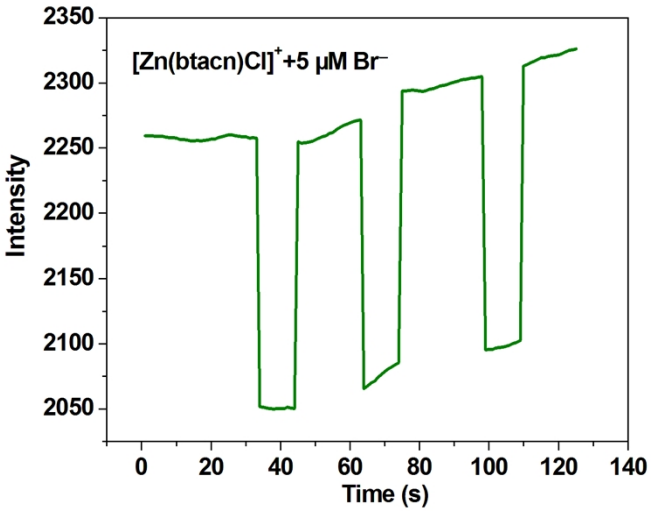


Figure S14. The variation of luminescent intensity of $[Zn(btacn)Cl]^+$ at 405 nm with immersion time in 5 μM KBr.

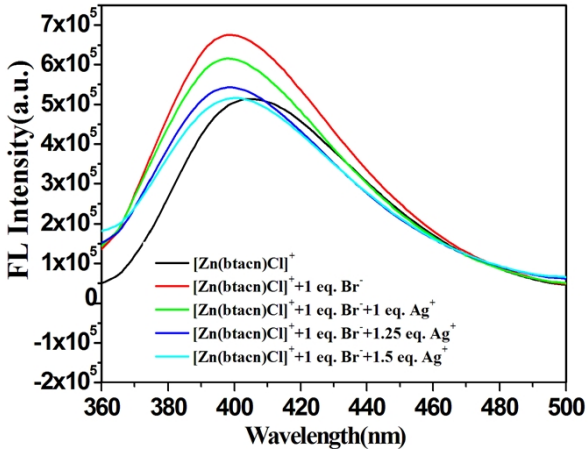


Figure S15. Fluorescence intensity of $[Zn(btacn)Cl]^+$ upon addition of 1.0 equiv Br^- ions in the presence of 0.0~1.5 equiv Ag^+ ions. Solvents: H_2O, c: 10 μM for $[Zn(btacn)Cl]^+$, λ_{ex}: 312 nm, slit width: 4 nm.

Reference:

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