Supporting Information

A new "on-off-on" fluorescent probe for sequential detection of Fe^{3+} and PPi based on 2-pyridin-2-ylethanamine and benzimidazo[2,1-a]benz[de]isoquinoline-7-one-12-carboxylic acid

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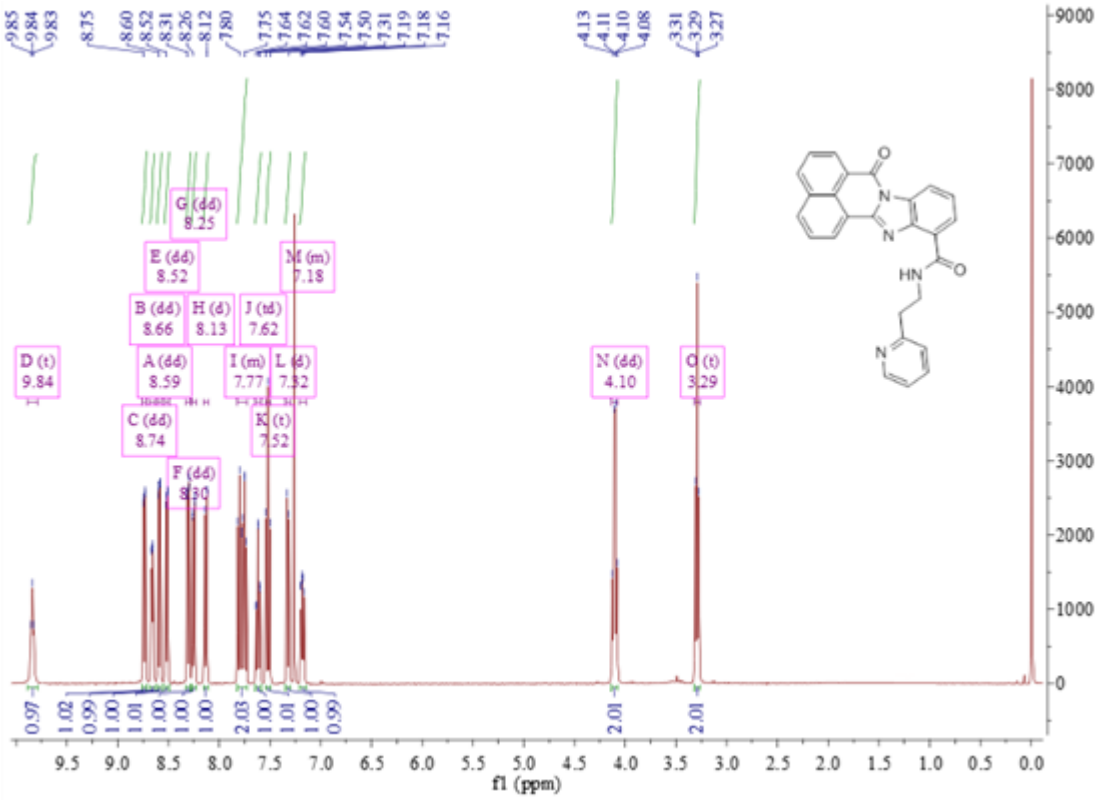


Fig. S1. ^{1}H NMR spectrum of **X**.

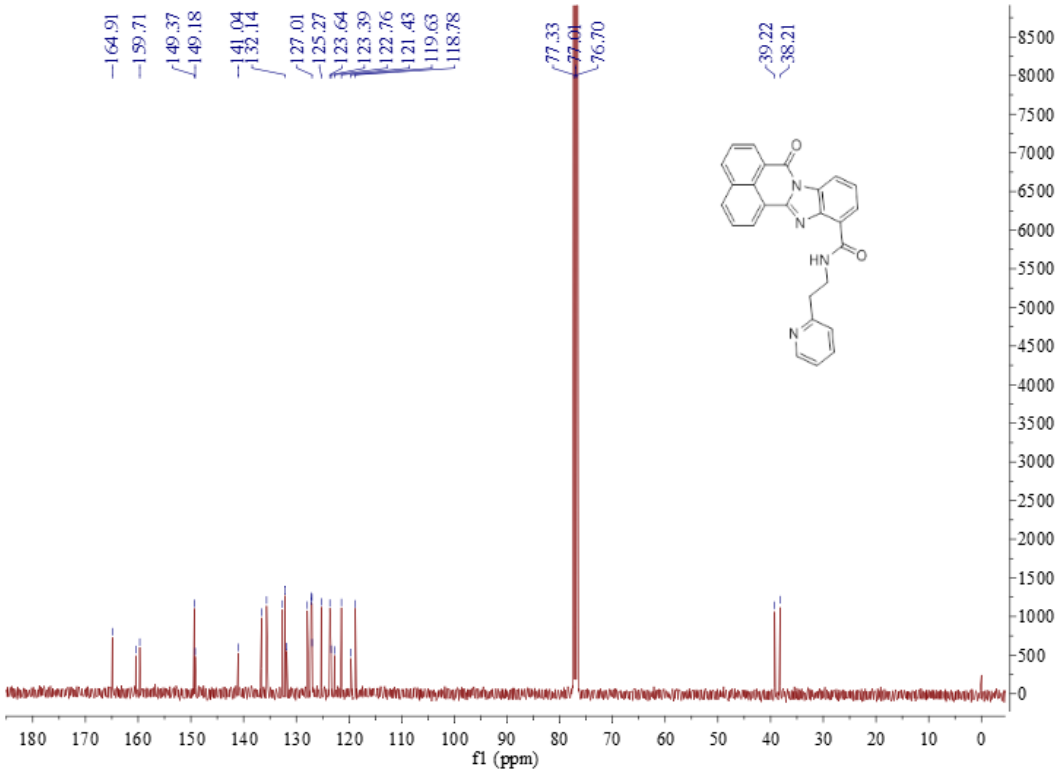


Fig. S2. ^{13}C NMR spectrum of **X**.

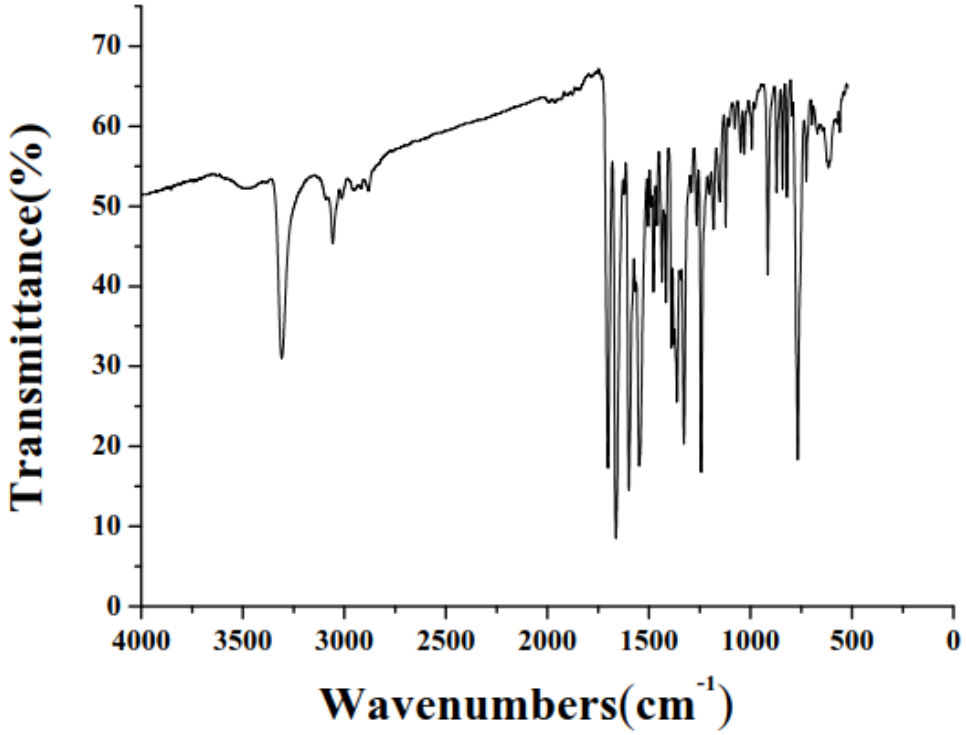


Fig. S3. The FTIR spectra of **X**.

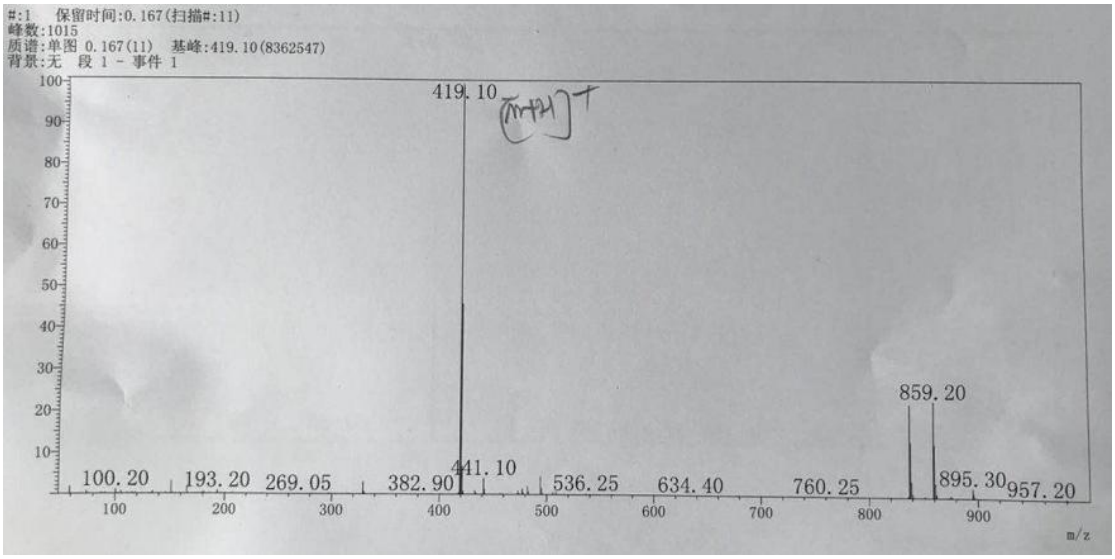


Fig. S4. ESI mass spectrum of complex **X**.

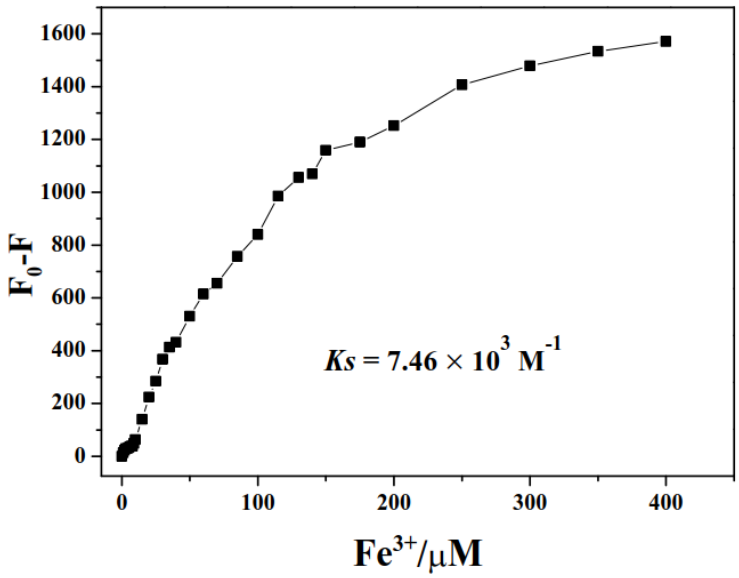


Fig. S5. the change of fluorescence emission intensity of **X** in DMF/H_2O solution (0 - 40 equiv.).

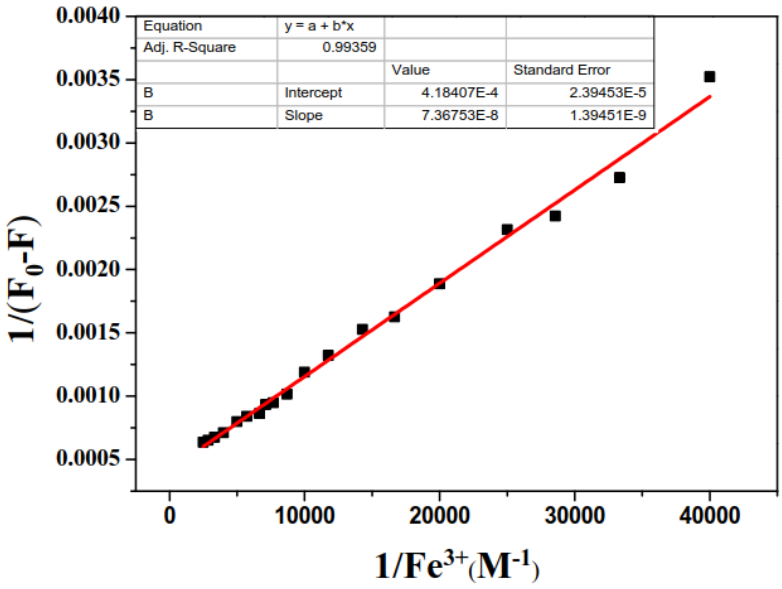


Fig. S6. Benesi-Hilderbrand plot of **X** with Fe^{3+}.

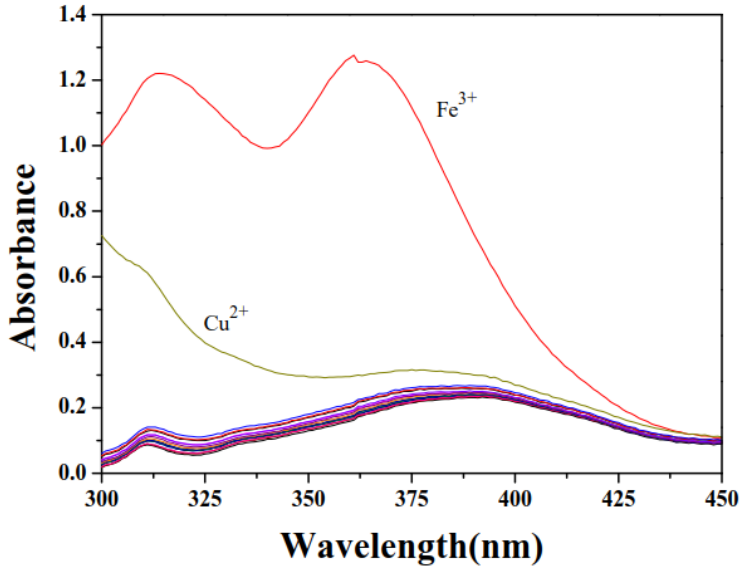


Fig. S7. Absorption spectrum of probe **X** in DMF/H_2O solution upon the addition of various metal ions (20 equiv.).

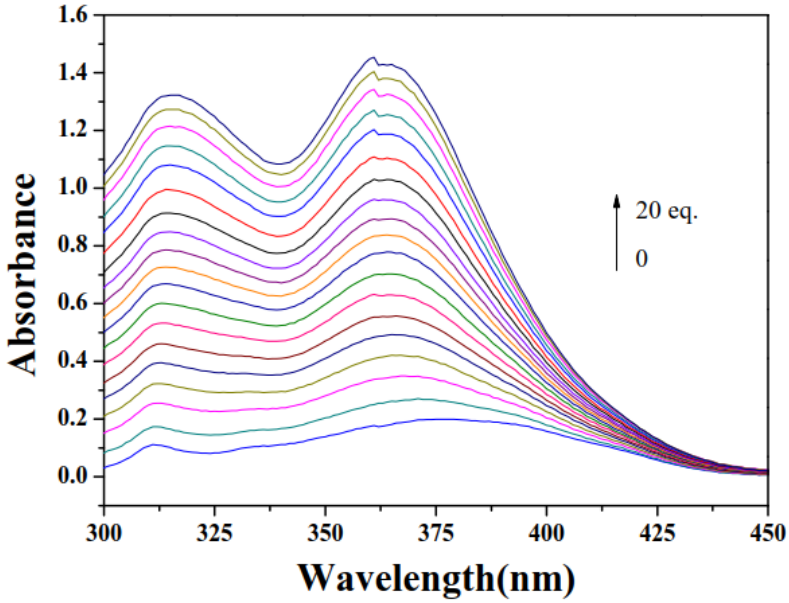


Fig. S8. Absorption titration spectra of probe **X** in DMF/H_2O buffer solution upon the addition of Fe^{3+} ions (0 - 20 equiv.).

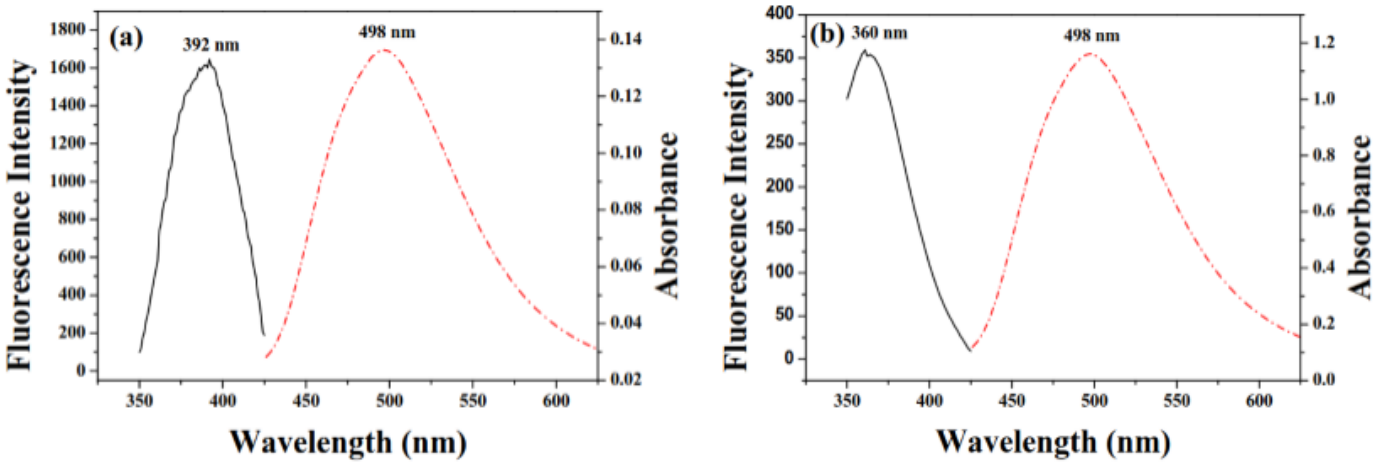


Fig. S9. (a) Excitation (λ_{em} = 498 nm) and emission (λ_{ex} = 392 nm) spectra of **X** (1.0×10^{-5} mol/L) in DMF-H_2O (v/v = 9:1, pH = 7.4) solution; (b) Excitation (λ_{em} = 498 nm) and emission (λ_{ex} = 360 nm) spectra of **X**-Fe^{3+} in DMF-H_2O (v/v = 9:1, pH = 7.4) solution (solid line: excitation spectrum; dash-dotted line: emission spectrum).

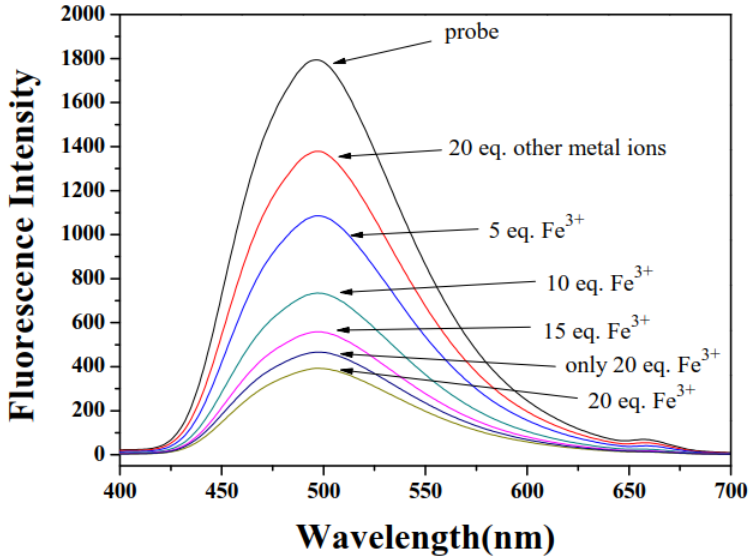


Fig. S10. Competition experiments: fluorescence emission spectra of probe X with addition of 20 equiv. of various metal ions (Na^+, Li^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+} and Al^{3+}) and Fe^{3+} (5 equiv., 10 equiv., 15 equiv., 20 equiv., respectively) in DMF/H_2O solution.

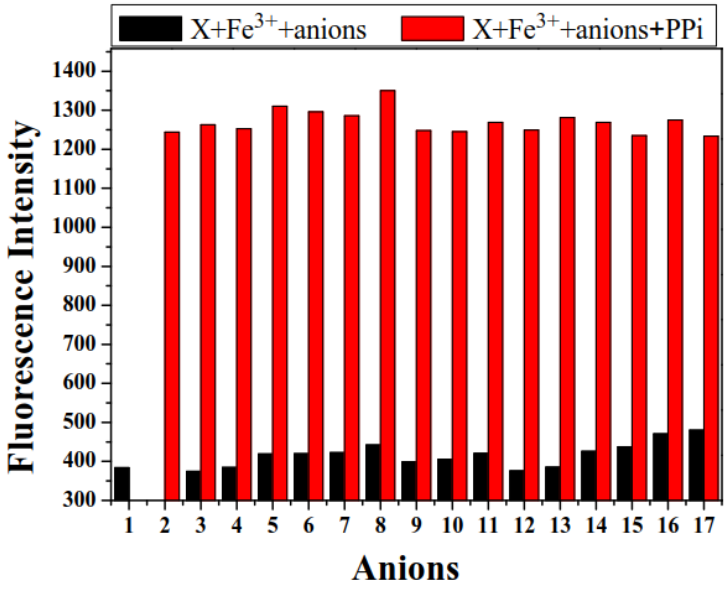


Fig. S11. The influence of single anions to the interaction between [X-Fe^{3+}] and PPi (1: the fluorescence of free **X**-Fe^{3+}, 2: addition of 20 equiv. of PPi to **X**-Fe^{3+}).

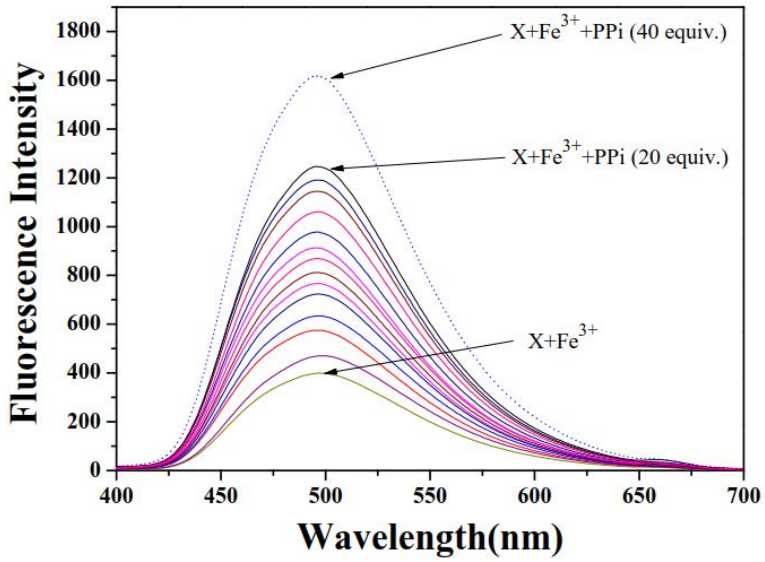


Fig. S12. Fluorescence titration spectrum of **X**-Fe^{3+} complex as a function of PPi concentration.

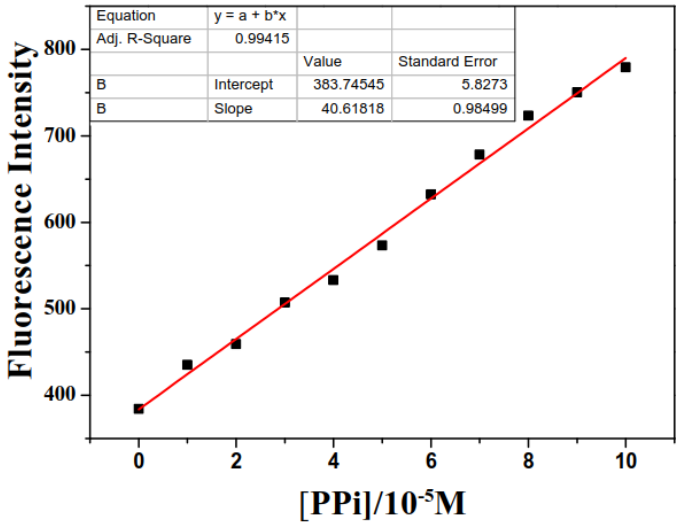


Fig. S13. The linear change ratio between fluorescence intensity (at 498 nm) and different concentration of PPi.

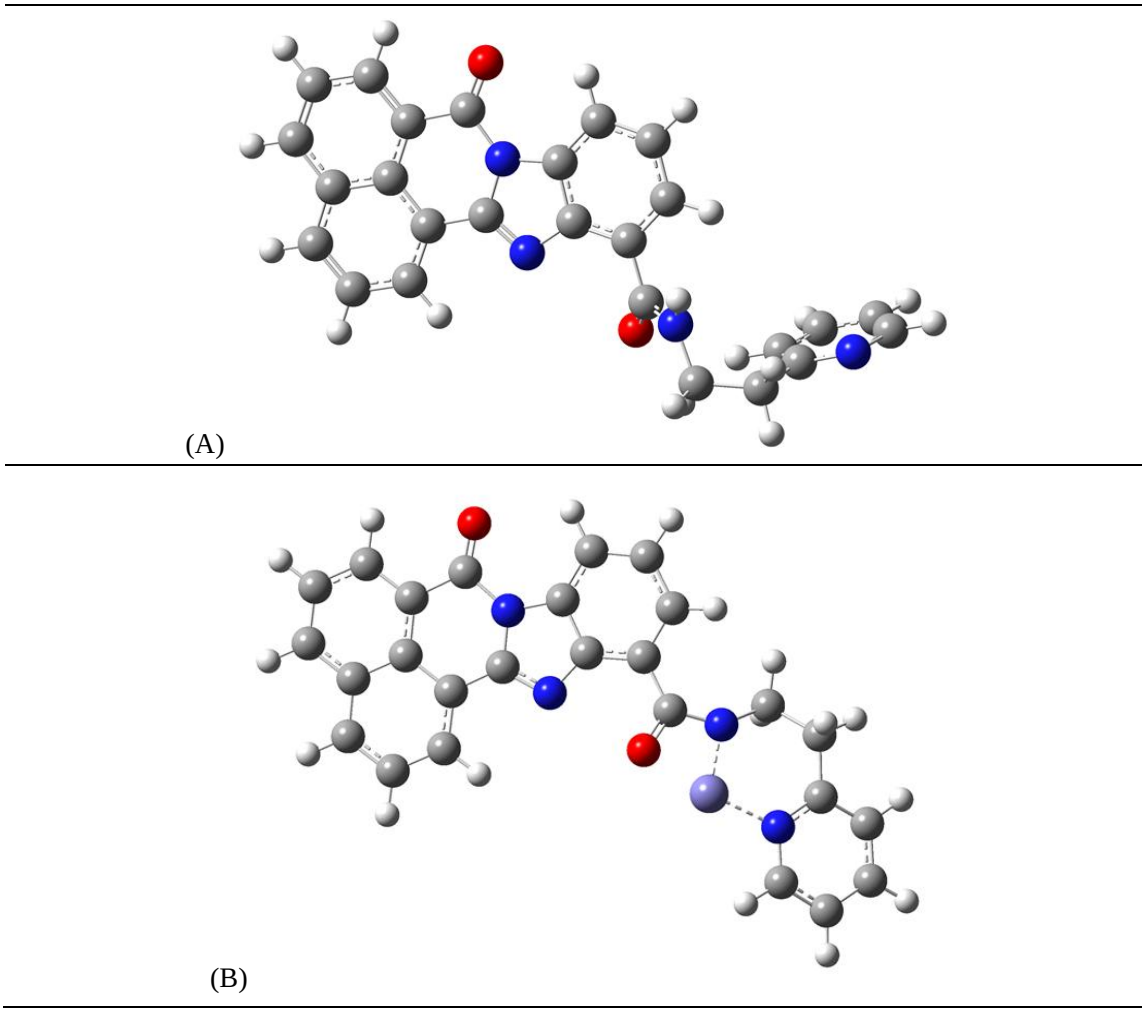
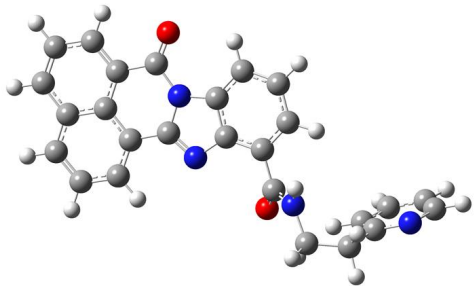


Fig. S14. The optimized geometry of **X** (A) and **X**-Fe^{3+} (B) complex at the B3LYP level of theory.

Table S1. XYZ coordinate of the optimized structure of **X**.

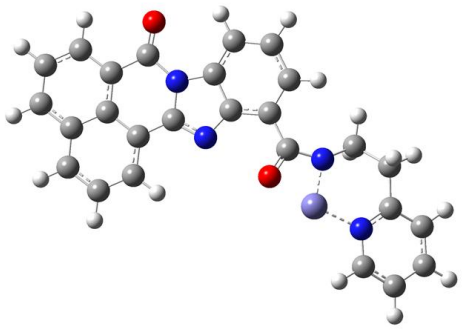


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.618220	-0.241364	0.309481
2	6	0	6.547555	-1.125127	0.086334
3	6	0	7.373327	1.282383	0.332956
4	6	0	6.074078	1.778212	0.170004
5	6	0	4.915103	0.818264	-0.074394
6	6	0	5.129498	-0.568231	-0.151191
7	6	0	5.774167	3.285281	0.246548
8	6	0	4.444676	3.746353	0.146192
9	6	0	3.265727	2.762338	-0.070469
10	6	0	3.501656	1.383197	-0.200883
11	6	0	3.950880	-1.528747	-0.463838
12	6	0	2.380016	0.374095	-0.448989
13	6	0	1.479181	-1.695683	-0.492699
14	6	0	0.503722	-0.788526	-0.170527
15	6	0	1.261063	-3.204372	-0.369557
16	6	0	-0.011933	-3.655647	0.023850
17	6	0	-1.146747	-2.634591	0.317872
18	6	0	-0.905214	-1.247998	0.221829
19	6	0	-2.042079	-0.256809	0.517781
20	6	0	-4.431814	0.000558	0.430076
21	6	0	-5.766511	-0.582928	0.924253
22	6	0	-6.930275	0.217411	0.317297
23	6	0	-7.840981	2.300368	-0.614380
24	6	0	-9.100000	1.730570	-0.839280
25	6	0	-9.337858	0.259352	-0.469364
26	6	0	-8.286329	-0.470577	0.085293
27	8	0	4.093051	-2.770091	-0.325079
28	8	0	-1.871185	0.982600	0.367918
29	7	0	2.668586	-0.982531	-0.940717
30	7	0	1.056713	0.575650	-0.243051
31	7	0	-3.331408	-0.792978	0.976816
32	7	0	-6.755832	1.506189	-0.009142
33	1	0	8.605595	-0.626082	0.463718
34	1	0	6.717737	-2.181846	0.076914
35	1	0	8.190919	1.957152	0.478887

36	1	0	6.573354	3.983368	0.381858
37	1	0	4.245191	4.795941	0.221774
38	1	0	2.264304	3.137406	-0.125544
39	1	0	2.049523	-3.894989	-0.580434
40	1	0	-0.200524	-4.704741	0.118230
41	1	0	-2.118793	-2.986121	0.594049
42	1	0	-3.428545	-1.736857	0.661651
43	1	0	-4.396457	-0.040576	-0.637317
44	1	0	-4.343333	1.017691	0.751630
45	1	0	-5.844223	-1.607129	0.621150
46	1	0	-5.806190	-0.523257	1.992968
47	1	0	-8.421312	-1.498417	0.345868
48	1	0	-10.290768	-0.198655	-0.631261
49	1	0	-9.887174	2.316111	-1.266870
50	1	0	-7.665407	3.319918	-0.882489

Table S2. XYZ coordinate of the optimized structure of **X**-Fe^{3+}.



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	6.565575	0.649489	1.040353
3	6	0	7.123858	-1.698501	0.908239
4	6	0	5.849933	-1.993228	0.401548
5	6	0	4.926743	-0.928726	0.198499
6	6	0	5.295534	0.383994	0.509234
7	6	0	5.435044	-3.313812	0.088862
8	6	0	4.150991	-3.581484	-0.378518
9	6	0	3.240861	-2.552009	-0.566198
10	6	0	3.621834	-1.228239	-0.304666
11	6	0	4.360284	1.517744	0.293308
12	6	0	2.727577	-0.134612	-0.508334
13	6	0	0.926706	1.032713	-0.573597
14	6	0	1.994165	1.959801	-0.392223
15	6	0	1.782673	3.302521	-0.178926
16	6	0	0.449654	3.727068	-0.198056
17	6	0	-0.609815	2.847992	-0.427828
18	6	0	-0.412164	1.481856	-0.617556
19	6	0	-1.530354	0.543987	-0.884730
20	6	0	-3.473027	1.343087	0.375472
21	6	0	-5.017170	1.339766	0.378917
22	6	0	-5.786260	0.106278	0.834105
23	6	0	-6.861240	-1.905125	0.381008
24	6	0	-7.560833	-1.863950	1.569586
25	6	0	-7.291927	-0.827349	2.463089
26	6	0	-6.403212	0.166260	2.096829
27	8	0	4.560757	2.637488	0.692825
28	8	0	-1.388478	-0.642482	-1.141680
29	7	0	3.193243	1.200085	-0.495880
30	7	0	1.422824	-0.243531	-0.662037
31	7	0	-5.953483	-0.962808	0.064277
32	1	0	6.816411	1.674350	1.294743
33	1	0	8.457509	-0.184297	1.632135

34	1	0	7.853540	-2.490625	1.054128
35	1	0	6.145390	-4.126317	0.222589
36	1	0	3.849852	-4.599453	-0.605982
37	1	0	2.239068	-2.767090	-0.924561
38	1	0	2.590392	4.001841	-0.005929
39	1	0	0.244796	4.781367	-0.038203
40	1	0	-1.614834	3.249276	-0.479861
41	1	0	-3.087460	0.724841	1.197927
42	1	0	-3.152021	2.377827	0.537995
43	1	0	-5.313195	2.111183	1.092497
44	1	0	-5.364695	1.631820	-0.619868
45	1	0	-6.190771	0.995724	2.765467
46	1	0	-7.787706	-0.805287	3.429707
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49	26	0	-4.309802	-0.908501	-1.569678
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