Supporting Information

A selective "turn-on" sensor for recognizing of In^{3+} and Zn^{2+} in respective system based on imidazo[2,1-*b*]thiazole

Yuankang Xu[a], Songfang Zhao[b,*], Yanxia Zhang[a], Hanyu Wang[a], Xiaofeng Yang[a], Meishan Pei[a], Guangyou Zhang[a,*]

[a] School of chemistry and chemical engineering, University of Jinan, Jinan 250022, China.

[b] Henan Sanmenxia Aoke Chemical Industry Co. Ltd., Sanmenxia 472000, China.

*Corresponding author:

Guangyou Zhang, Ph.D, Professor, E-mail address: chm_zhanggy@ujn.edu.cn.

Songfang Zhao, E-mail address: songfang2008@163.com.
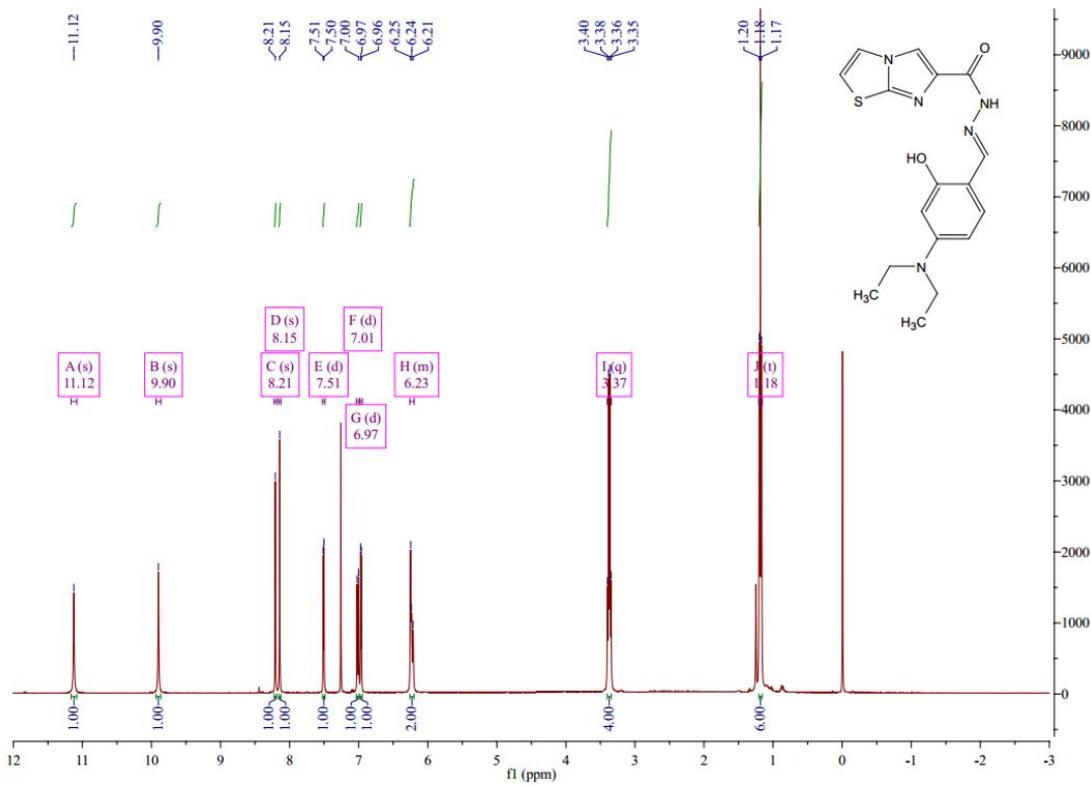
Fig. S1. ^{1}H NMR spectrum of **X**.
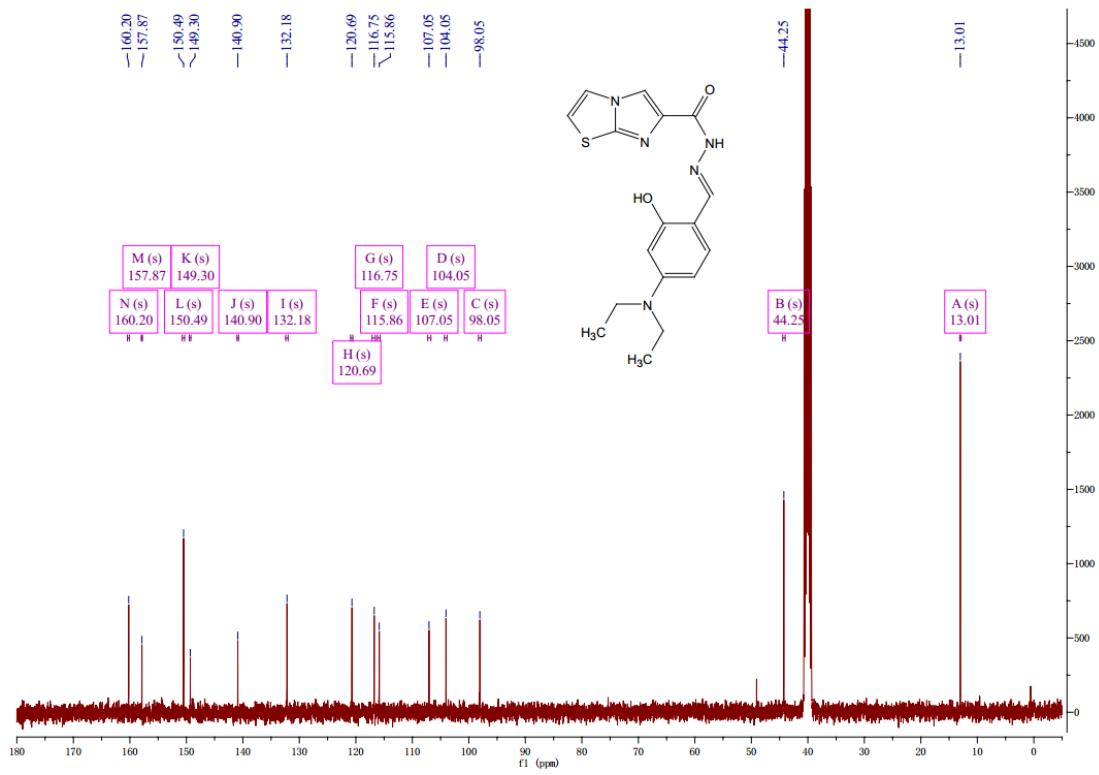

Fig. S2. ^{13}C NMR spectrum of **X.**
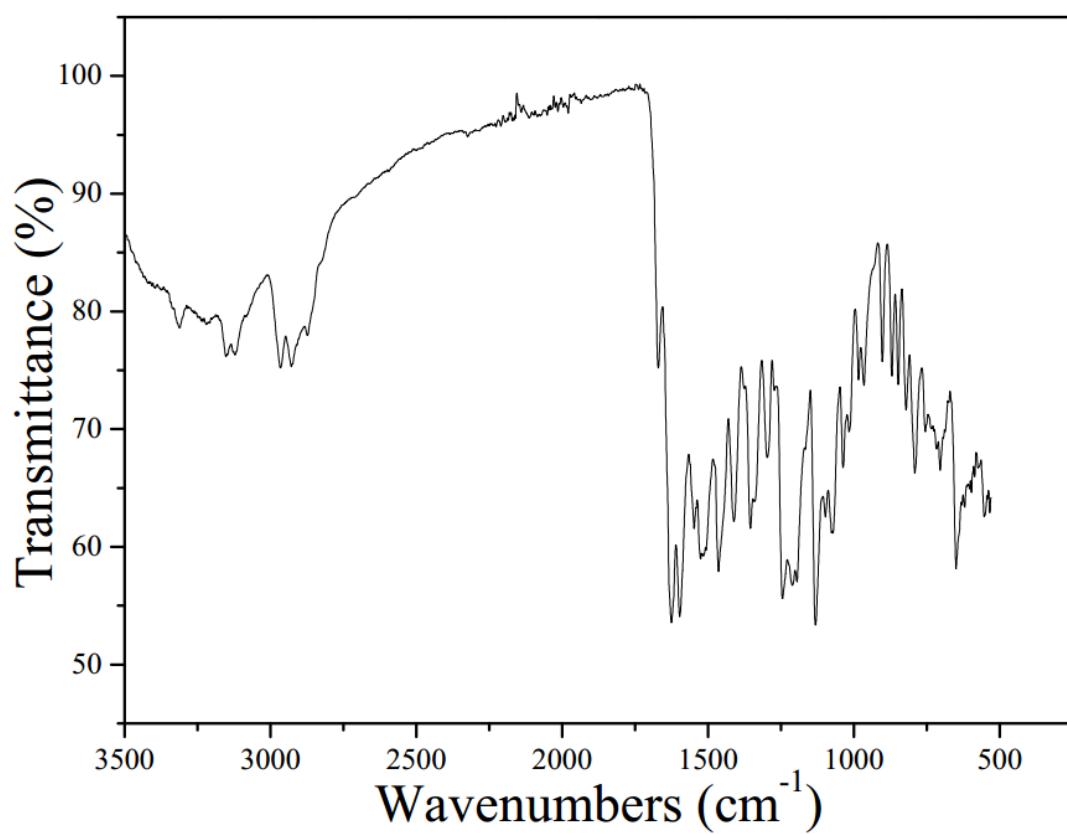
Fig. S3. The FTIR spectra of **X**.

+ESI Scan (1.192 min) Frag=135.0V 190715-X-1.d Subtract (2)

358.1278

Counts (%) vs. Mass-to-Charge (m/z)
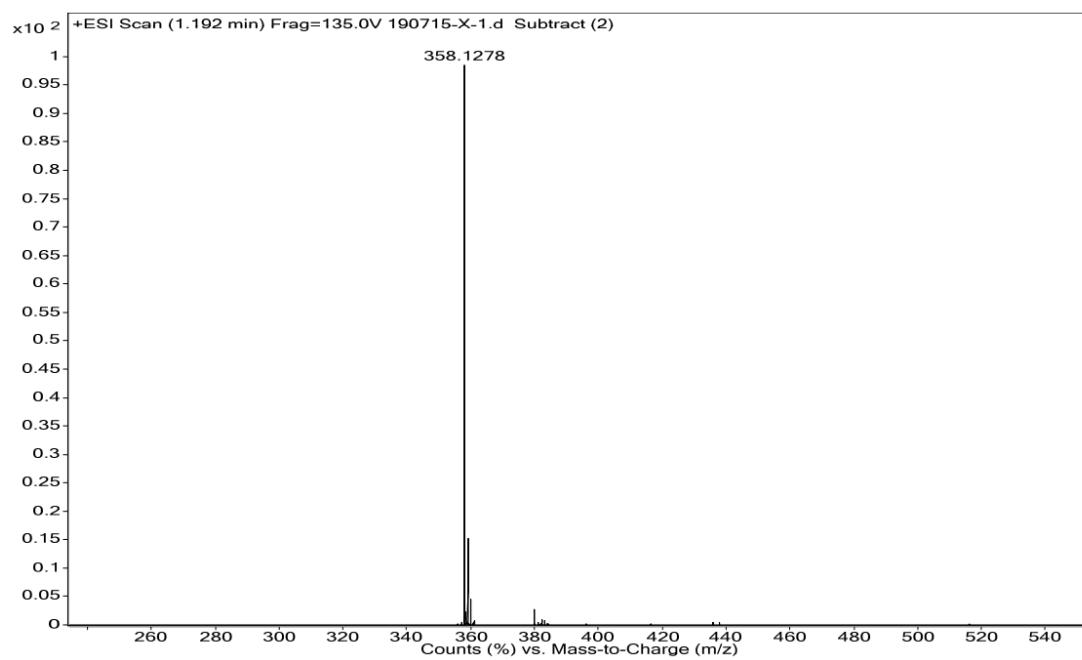
Fig. S4. ESI mass spectrum of **X**.
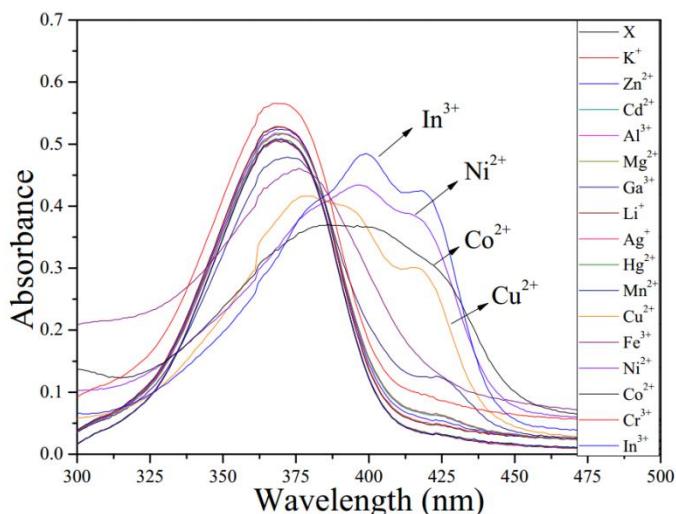
Fig. S5. Absorption spectra of **X** (1×10^{-5} M) upon the addition of various metal ions (7.5 equiv.) in DMF/H$_2$O buffer solution (v/v = 9:1, tris = 10 mM, pH = 7.4).
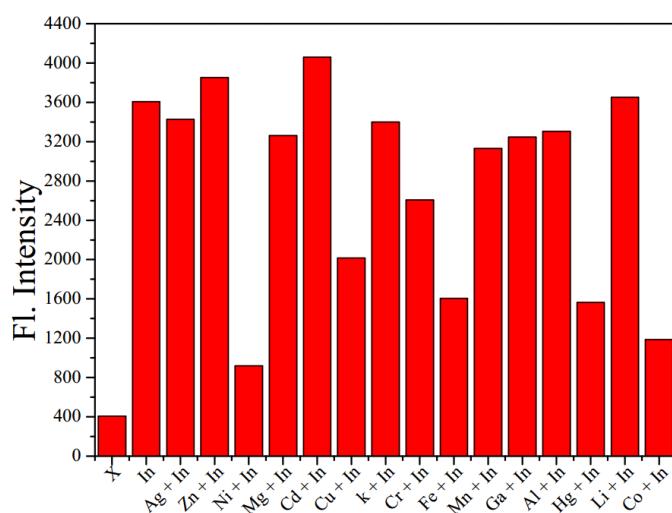
Fig. S6. Fluorescence intensity of **X** and its complexation with In^{3+} in the presence of other metal ions (Ag$^+$, Zn^{2+}, Ni^{2+}, Mg^{2+}, Cd^{2+}, Cu^{2+}, K$^+$, Cr^{3+}, Fe^{3+}, Mn^{2+}, Ga^{3+}, Al^{3+}, Hg^{2+}, Li$^+$ and Co^{2+}) in DMF/H$_2$O buffer solution (v/v = 9:1, tris = 10 mM, pH = 7.4).
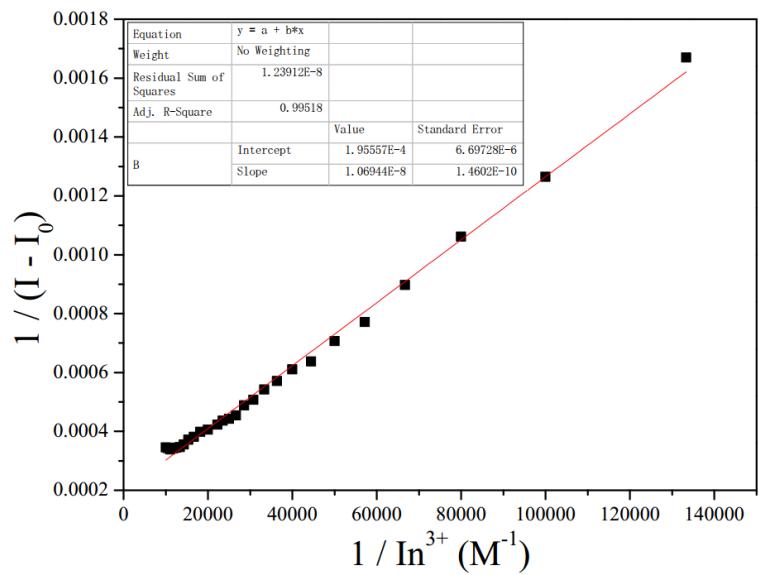
Fig. S7. Benesi-Hilderbrand plot of **X** with In^{3+}.
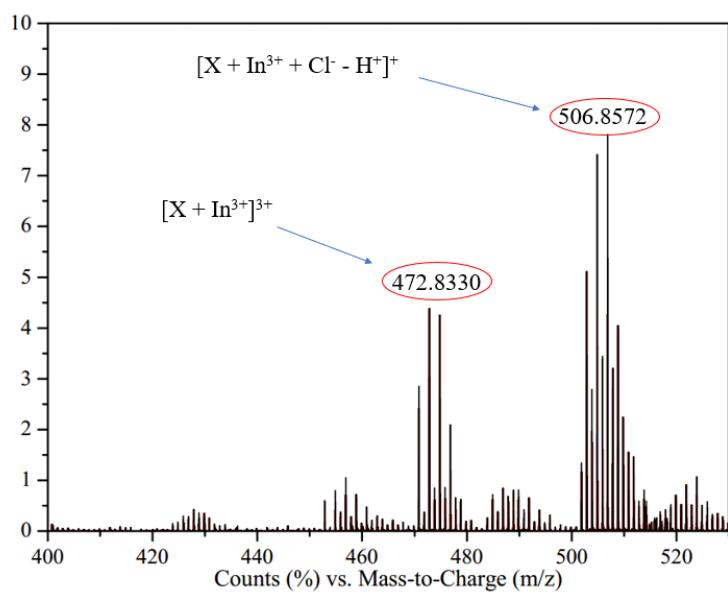
Fig. S8. ESI Mass spectrum of **X**$[In^{3+}]$.
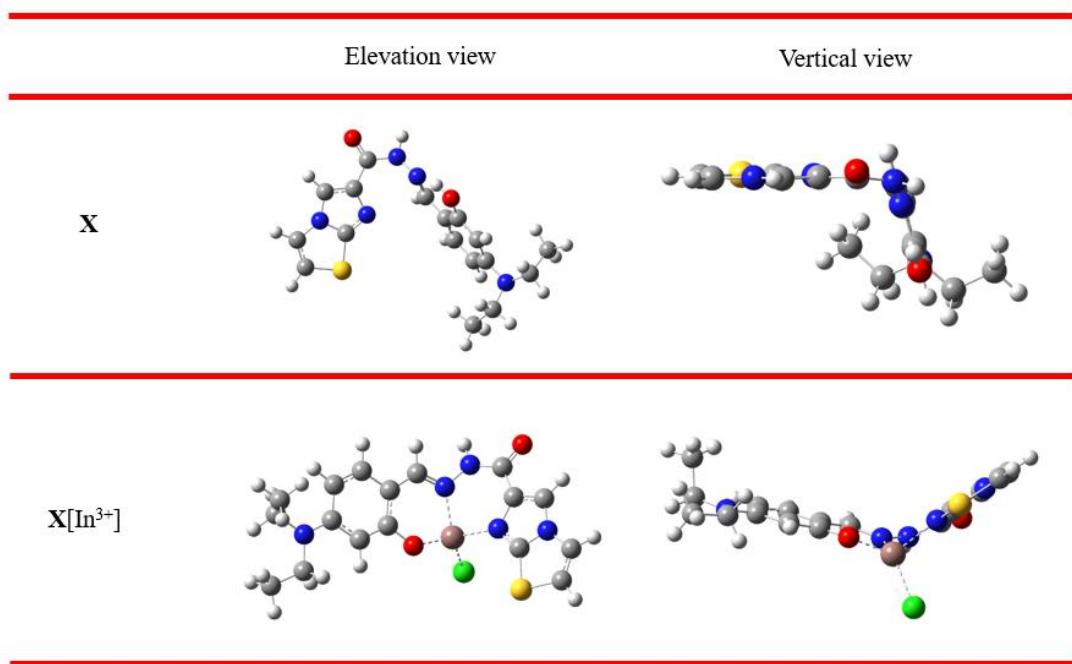
Figure S9. The optimized geometry of **X** and **X**[In^{3+}] at the B3LYP level of theory, where the light-gray, red, blue, white, brown and cyan spheres denote C, O, N, H, In and Cl atoms, respectively.
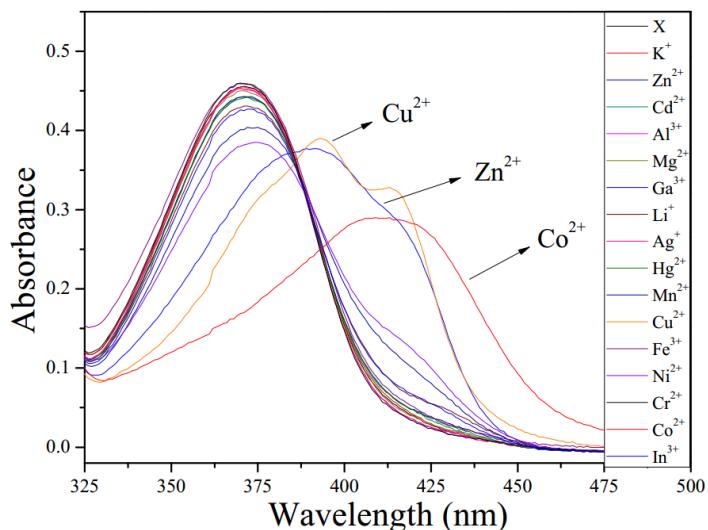

Fig. S10. Absorption spectra of **X** (1×10^{-5} M) upon the addition of various metal ions (7.5 equiv.) in EtOH/H$_2$O buffer solution (v/v = 9:1, tris = 10 mM, pH = 7.4).
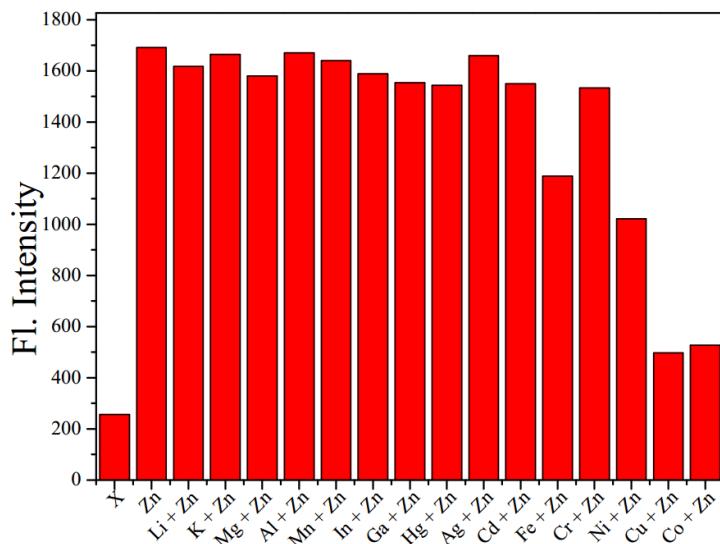
Fig. S11. Fluorescence intensity of **X** and its complexation with Zn^{2+} in the presence of other metal ions (Li^+, K^+, Mg^{2+}, Al^{3+}, Mn^{2+}, In^{3+}, Ga^{3+}, Hg^{2+}, Ag^+, Cd^{2+}, Fe^{3+}, Cr^{3+}, Ni^{2+}, Cu^{2+} and Co^{2+}) in EtOH/H_2O buffer solution (v/v = 9:1, tris = 10 mM, pH = 7.4).

Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of Squares	7.2369E-8	
Adj. R-Square	0.98616	
	Value	Standard Error
F Intercept	4.22861E-4	2.11303E-5
Slope	8.23876E-9	2.08007E-10
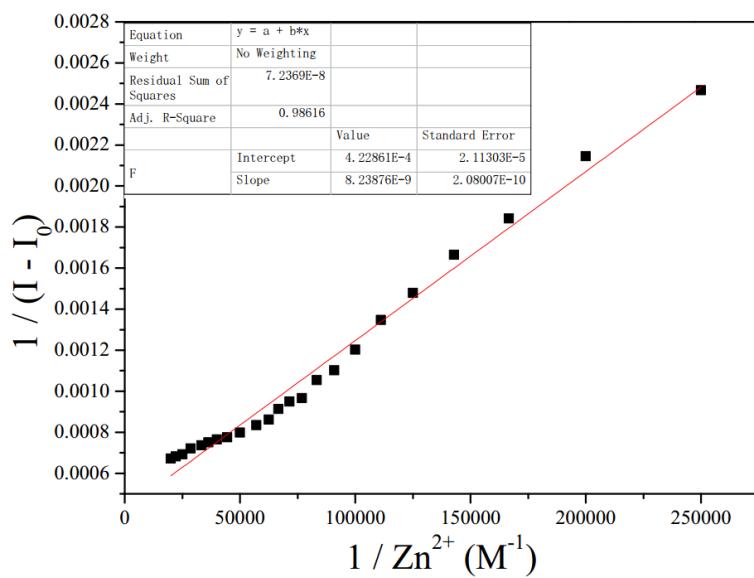
Fig. S12. Benesi-Hilderbrand plot of **X** with Zn^{2+}.
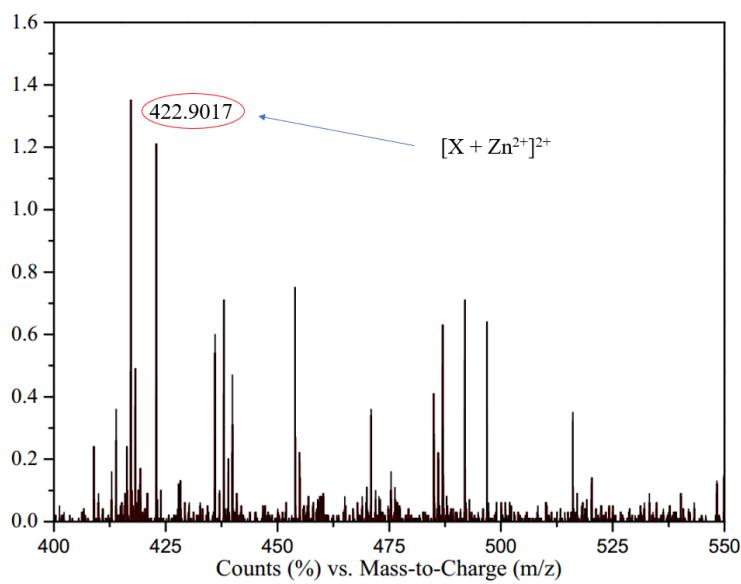
Fig. S13. ESI Mass spectrum of **X**[Zn^{2+}].
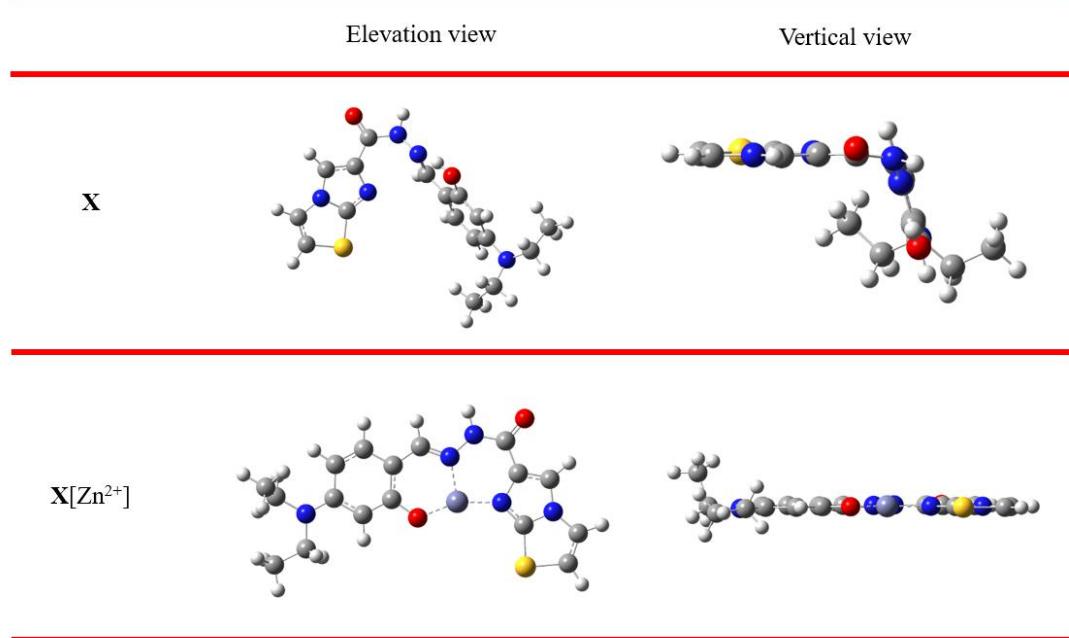
Figure S14. The optimized geometry of **X** and **X**[Zn^{2+}] at the B3LYP level of theory, where the light-gray, red, blue, white, dark-gray and cyan spheres denote C, O, N, H, Zn and Cl atoms, respectively.

No Fluorescence   Strong Fluorescence
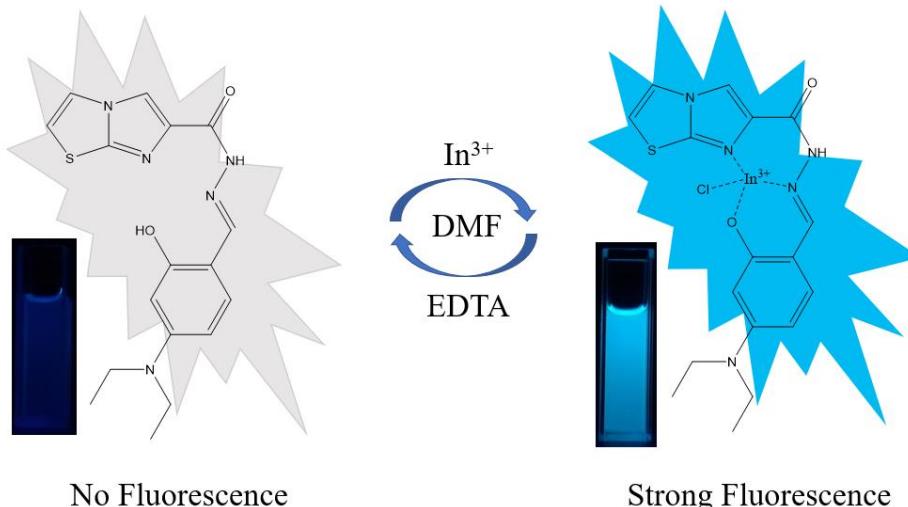
Scheme 2. The proposed binding mode of **X** with In^{3+}.

No Fluorescence   Strong Fluorescence
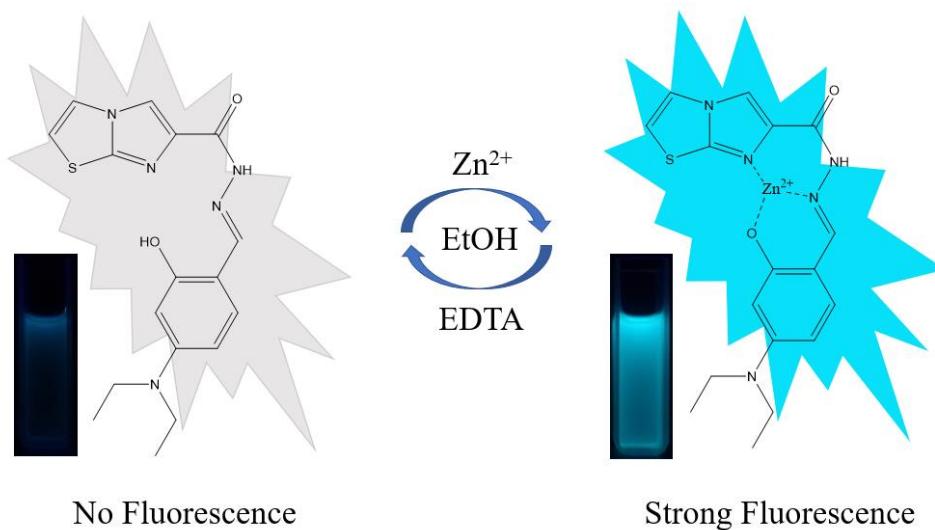
Scheme 3. The proposed binding mode of **X** with Zn^{2+}.

Table S1. Comparative study of the analytical performance of **X** with other previous sensors.

| sensor	Reaction media	Target ion	LOD (M)	Ka	Ref.
1	DMF/H$_2$O (v/v = 9/1)	In^{3+}	1.02×10^{-9}	1.01×10^5 M^{-1}	This work
2	MeOH	In^{3+}	7.9×10^{-6}	1.0×10^8 M^{-2}	[17]
3	EtOH	In^{3+}	6.1×10^{-7}	8.1×10^4 M^{-2}	[21]
4	MeOH	In^{3+}	2.0×10^{-6}	1.4×10^5 M^{-1}	[22]
5	DMF	In^{3+}	5.0×10^{-8}	2.0×10^{10} M^{-2}	[23]
6	EtOH/H$_2$O (v/v = 9/1)	Zn^{2+}	5.5×10^{-9}	2.65×10^5 M^{-1}	This work
7	EtOH/H$_2$O (v/v = 9/1)	Zn^{2+}	2.86×10^{-7}	1.81×10^5 M^{-1}	[25]
8	MeOH/H$_2$O (v/v = 1/9)	Zn^{2+}	7.95×10^{-7}	6.0×10^3 M^{-1}	[26]
9	EtOH	Zn^{2+}	4.0×10^{-8}	6.4×10^4 M^{-1}	[27]
10	EtOH/H$_2$O (v/v = 99/1)	Zn^{2+}	5.03×10^{-7}	85.7 M^{-2}	[29]

Table S2. Determination of In^{3+} concentrations in tap water samples.

sample	In^{3+} added (M)	In^{3+} recovered (M)	Recovery (%)	RSD (%)
1	1.0 × 10^{-5}	9.28 × 10^{-6}	92.8	0.74
2	2.0 × 10^{-5}	1.88 × 10^{-5}	94.1	2.36
3	3.0 × 10^{-5}	2.74 × 10^{-5}	91.2	2.27
4	4.0 × 10^{-5}	3.68 × 10^{-5}	92.3	3.51

Table S3. Determination of Zn^{2+} concentrations in tap water samples.

sample	Zn^{2+} added (M)	Zn^{2+} recovered (M)	Recovery (%)	RSD (%)
1	1.0 × 10^{-5}	9.73 × 10^{-6}	97.3	3.01
2	2.0 × 10^{-5}	2.08 × 10^{-5}	104.1	2.39
3	3.0 × 10^{-5}	3.19 × 10^{-5}	106.2	1.50

The specific configuration and test process

Stock solutions of the ions (In^{3+} and Zn^{2+}) were prepared with a concentration of 0.03 M in distilled water and tap water. The probe **X** was dissolved in ethanol/H$_2$O (v/v = 9 : 1) buffer solution (10 mM tris, pH = 7.4) and DMF/H$_2$O (v/v = 9 : 1) buffer solution (10 mM tris, pH = 7.4) at room temperature with the concentration of 1 × 10^{-5} M.

The fluorescence intensity was measured when the In^{3+} (distilled water) concentration were 1 × 10^{-5} M, 2 × 10^{-5} M, 3 × 10^{-5} M and 4 × 10^{-5} M. Then, the fluorescence intensity was measured with three times when the In^{3+} (tap water) concentration were 1 × 10^{-5} M, 2 × 10^{-5} M, 3 × 10^{-5} M and 4 × 10^{-5} M.

For example:

Determination of In^{3+} concentrations in tap water samples, sample 1, Table S2.

Fluorescence intensity: 751.3 (distilled water, 1 × 10^{-5} M); 1281 (distilled water, 2 × 10^{-5} M); 1829 (distilled water, 3 × 10^{-5} M); 2639 (distilled water, 4 × 10^{-5} M).

Linear equation: Y = 621.1X + 72.3

Fluorescence intensity (three times): 645.8 (tap water, 1 × 10^{-5} M); 654.5 (tap water, 1 × 10^{-5} M); 646.7 (tap water, 1 × 10^{-5} M).

The average of fluorescence intensity: (645.8 + 654.5 + 646.7) / 3 = 649

In^{3+} recovered (M) = (649 – 72.3) / 621.1 = 0.928; 9.28 × 10^{-6} M

Recovery = In^{3+} recovered (M) / In^{3+} added (M) = 9.28 × 10^{-6} / 1.0 × 10^{-5} = 92.8%

according to formula $\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2}$. The standard deviation (σ) was calculated to be 4.78.

RSD = σ / $\bar{x}$ = 4.78 / 649 = 0.0073, 0.73%

The calculation of other data was similar to the example.

Table S4. XYZ coordinate of the optimized structure of **X**.
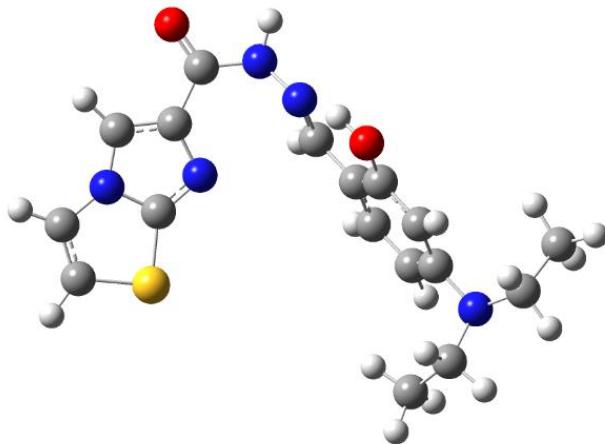
Standard orientation:
_____

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

_____

1	6	0	−5.286854	−1.689122	1.297058
2	6	0	−5.029600	−2.846596	0.505276
3	6	0	−4.245195	−0.756948	−0.580441
4	6	0	−4.389607	0.673399	1.158164
5	6	0	−3.481765	1.171424	0.203984
6	6	0	−2.663186	2.468481	0.342442
7	6	0	−0.170494	1.159687	−0.955533
8	7	0	−5.104271	−0.432312	0.532110
9	7	0	−3.424538	0.236037	−0.949725
10	16	0	−4.468550	−2.408646	−1.132110
11	8	0	−2.785476	3.182897	1.371143
12	7	0	−1.738967	2.872038	−0.727071
13	7	0	−0.473979	2.324584	−0.481918
14	6	0	1.220999	0.557498	−0.685874
15	6	0	2.251201	1.342095	0.147609
16	6	0	3.517459	0.794103	0.393001
17	6	0	3.878749	−0.592685	−0.170817
18	6	0	2.941266	−1.306666	−0.929288
19	6	0	1.549775	−0.704476	−1.198952
20	6	0	5.168273	−1.954254	1.327734
21	6	0	4.136916	−3.088863	1.184332
22	6	0	6.191465	−0.084469	0.223477
23	6	0	6.232026	0.739741	−1.076766
24	7	0	5.206989	−1.167506	0.086594
25	1	0	−5.139788	−3.851755	0.855155
26	1	0	−5.567763	−1.723522	2.328953

27	1	0	−4.525303	1.034849	2.156081
28	1	0	−1.671631	3.869490	−0.750669
29	1	0	−0.886282	0.614548	−1.534645
30	1	0	0.833986	−1.249617	−1.778061
31	1	0	3.192291	−2.270214	−1.321031
32	1	0	4.233248	1.339245	0.972109
33	8	0	1.915715	2.629823	0.671161
34	1	0	1.286207	3.058720	0.086895
35	1	0	6.135086	−2.372664	1.515100
36	1	0	4.889872	−1.320179	2.143419
37	1	0	4.415317	−3.722938	0.368648
38	1	0	4.108734	−3.661530	2.087747
39	1	0	3.170103	−2.670453	0.996965
40	1	0	5.913062	0.549607	1.039161
41	1	0	7.158278	−0.502878	0.410846
42	1	0	5.265214	1.158150	−1.264135
43	1	0	6.948618	1.528073	−0.977130
44	1	0	6.510429	0.105664	−1.892449

Table S5. XYZ coordinate of the optimized structure of **X**[In^{3+}].
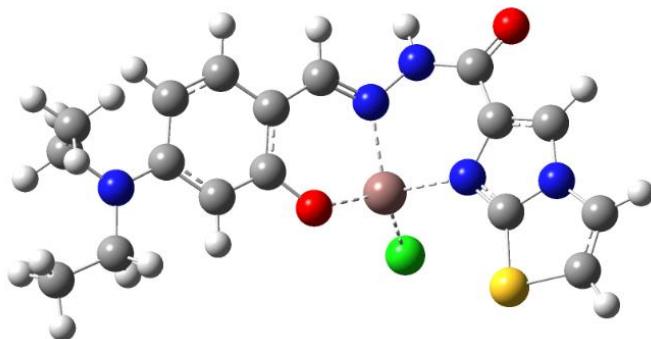
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	6.237351	−1.111169	0.104403
2	6	0	5.900047	−2.426783	0.124242
3	6	0	3.896381	−0.931753	0.055332
4	6	0	4.868171	1.105480	0.034367
5	6	0	3.500757	1.284462	0.004894
6	6	0	2.903405	2.663629	−0.033401
7	6	0	−0.789116	2.335051	−0.091511
8	6	0	−1.942531	1.527127	−0.101003
9	6	0	−2.020264	0.068346	−0.081086
10	6	0	−3.222850	−0.603361	−0.101810
11	6	0	−4.482661	0.101076	−0.151119
12	6	0	−4.421182	1.551995	−0.150763
13	6	0	−3.219212	2.210667	−0.131842
14	6	0	−5.659692	−2.073075	−0.150488
15	6	0	−7.026258	−2.752283	−0.304698
16	6	0	−6.964891	0.166868	−0.206641
17	6	0	−7.431265	0.579927	1.205484
18	16	0	4.091018	−2.700452	0.094673
19	7	0	5.100695	−0.271469	0.065571
20	7	0	2.875737	−0.026013	0.018259
21	8	0	3.690119	3.636644	−0.037985
22	7	0	1.535062	2.891704	−0.063755
23	7	0	0.514107	1.916691	−0.063674
24	8	0	−0.865739	−0.733998	−0.038136
25	7	0	−5.661859	−0.566500	−0.199356
26	1	0	7.233658	−0.690920	0.115299
27	1	0	6.553045	−3.286981	0.154006
28	1	0	5.643360	1.855868	0.034547
29	1	0	1.262980	3.875027	−0.089442

30	1	0	−0.949078	3.413696	−0.109409
31	1	0	−3.218664	3.298314	−0.137236
32	1	0	−5.330721	2.136961	−0.162299
33	1	0	−3.180573	−1.683605	−0.078735
34	1	0	−6.876238	1.037514	−0.863373
35	1	0	−7.708629	−0.483521	−0.665282
36	1	0	−8.394498	1.098208	1.133471
37	1	0	−7.568971	−0.294818	1.850892
38	1	0	−6.718374	1.254515	1.693799
39	1	0	−5.003830	−2.429263	−0.955475
40	1	0	−5.212206	−2.376778	0.806522
41	1	0	−7.481847	−2.562035	−1.282480
42	1	0	−6.869616	−3.834523	−0.226820
43	1	0	−7.733792	−2.471010	0.482004
44	49	0	0.878608	−0.049515	−0.021454
45	17	0	1.126325	−1.484262	0.000000

Table S6. XYZ coordinate of the optimized structure of **X**[Zn²⁺].
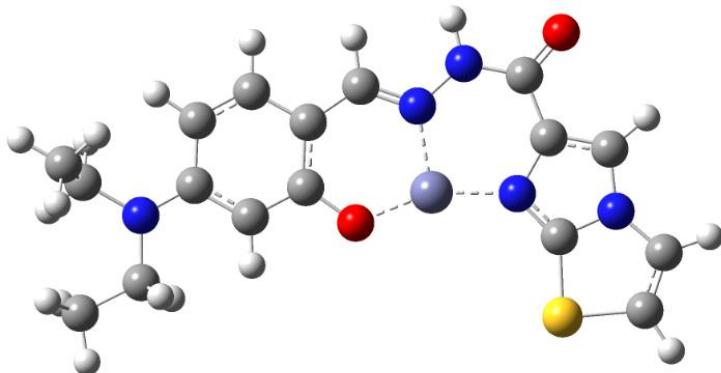
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	9.155514	−0.587574	−0.124890
2	6	0	9.502229	−2.358469	−0.107720
3	6	0	6.794288	−1.235770	−0.019087
4	6	0	6.525207	1.863029	−0.062636
5	6	0	5.087452	1.654306	−0.099225
6	6	0	3.445473	2.971061	−0.044245
7	6	0	−1.469868	3.072750	0.133254
8	6	0	−2.893709	1.329677	0.246067
9	6	0	−3.163982	−0.879914	0.332556
10	6	0	−5.163436	−1.201640	−0.003338
11	6	0	−6.499834	−0.246889	−0.115617
12	6	0	−6.543304	1.519982	−0.271853
13	6	0	−5.166845	2.256026	−0.307351
14	6	0	−7.716503	−2.790149	0.082132
15	6	0	−8.996326	−3.450589	−0.463278
16	6	0	−9.164387	0.955448	−0.277837
17	6	0	−10.463495	0.713459	0.512959
18	16	0	7.828092	−2.724789	−0.034339
19	7	0	7.726180	0.255221	−0.082492
20	7	0	4.856363	−0.518551	0.024669
21	8	0	4.082139	4.054808	−0.105230
22	7	0	2.007828	3.274832	−0.001821
23	7	0	0.251040	1.931793	0.109397
24	8	0	−2.002454	−1.705925	0.216551
25	7	0	−7.864524	−0.792929	−0.096571
26	1	0	10.028048	0.030078	−0.170614
27	1	0	10.396130	−2.945999	−0.133176
28	1	0	6.934056	2.851157	−0.025955

29	1	0	1. 786589	4. 249715	-0. 027442
30	1	0	-1. 630609	4. 130162	0. 102547
31	1	0	-5. 193490	3. 283629	-0. 604372
32	1	0	-7. 467604	2. 054893	-0. 338483
33	1	0	-5. 391706	-2. 238347	-0. 137622
34	1	0	-8. 662701	1. 815119	0. 114816
35	1	0	-9. 399652	1. 119639	-1. 308658
36	1	0	-11. 289730	1. 134303	-0. 021012
37	1	0	-10. 616179	-0. 338561	0. 634781
38	1	0	-10. 387203	1. 176500	1. 474558
39	1	0	-6. 871192	-3. 136420	-0. 475046
40	1	0	-7. 593813	-3. 047852	1. 113362
41	1	0	-9. 626228	-2. 702738	-0. 897838
42	1	0	-8. 735217	-4. 173512	-1. 207660
43	1	0	-9. 516760	-3. 934393	0. 336710
44	30	0	1. 763375	-0. 836095	0. 169945

The calculation process of detection limit:

Scan the blank sample solution 10 times and calculate the standard deviation (σ) according to formula $\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2}$. The standard deviation (σ) was calculated to be 0.48.

The fluorescence emission spectra were measured when the Zn^{2+} concentration were 1×10^{-7} M, 2×10^{-7} M, 3×10^{-7} M, 4×10^{-7} M, 5×10^{-7} M and 6×10^{-7} M, respectively. As shown in Fig 9 (b) inset, a good linear relationship ($R^2 = 0.9858$) between the fluorescence intensity at 463 nm and concentration of Zn^{2+} was obtained. The slope of the line is 26×10^7 M. based on 3σ/s equation, $LOD = \frac{3 \times 0.48}{26 \times 10^7} = 5.5 \times 10^{-9}$ M.