ELECTRONIC SUPPLEMENTARY INFORMATION

A fluorescent sensor for Zn^{2+} and NO_2^- based on the rational control of C=N isomerization

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Experimental section

Instruments

UV-vis spectra were recorded on a Shimadzu 3100 spectrometer; fluorescence measurements were carried out using an Edinburgh Instruments Ltd-FLS920 fluorescence spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV III 400 MHz NMR spectrometer with tetramethysilane (TMS) as an internal standard. Infrared spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer with KBr pellets.

Sample preparation

All tests described in this paper were carried out at room temperature (25 °C) with distilled water. In the experiments of titration with various metal ions, the sensor was dissolved in HEPES acetonitrile-H_2O (9:1) buffer solution to afford the test solution (1×10^{-5} M). Stock solutions (1×10^{-5} M) of the mental salts of LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, $PbCl_2$, $AgNO_3$, $MnCl_2$, $FeCl_3$, $CoCl_2$, $CrCl_3$, $SrCl_3$ and $AlCl_3$ were prepared in aquesous solution. Stock solutions (1×10^{-5} M) of the anion salts of CH_3COONa, $NaBF_4$, NaF, NaCl, NaBr, NaI, $NaNO_3$, $NaNO_2$, Na_2S, $NaHSO_3$, $Na_2S_2O_3$, $NaSO_4$, Na_3PO_4, Na_2HPO_4, NaH_2PO_4, $Na_4P_2O_7$, ATP, ADP and AMP in water were prepared for the sample tests.

Calculation of limit of detection (LOD)

The limit of detection was determined according to the following equation:

$LOD = 3\sigma/s$,

where LOD is the limit of detection; σ is the standard deviation of blank measurements; s is the slope between fluorescence intensity versus NO_2^- concentration. To testify the accurate detection level of ternary complex **L**+Zn^{2+}+Cl^- towards NO_2^-, the same titration experiment was repeated five times and the average value was applied.

Calculation of the fluorescence quantum yield

The fluorescence quantum yield of **L**, **L**+Zn^{2+}+Cl^- and **L**+Zn^{2+}+NO_2^- was determined according to the following equation:

$$\phi_u = \phi_s \frac{F_u A_s n_u^2}{F_s A_u n_s^2}$$

where ϕ is fluorescence quantum yield; F is integrated area under the corrected emission spectra; A is the absorbance at the excitation wavelength; n is the refractive index of the solution; the subscripts u and s refer to the unknown and the standard, respectively. 9,10-Diphenylanthracene in hexane solution was used as the standard, which has a quantum yield of 0.95.

Calculation of radiative decay rate constant (K_τ) and nonradiative decay rate constant ($K_{n\tau}$)

The fluorescence lifetime of **L**, **L**+Zn^{2+}+Cl^- and **L**+Zn^{2+}+NO_2^- in acetonitrile-H_2O (9:1) was measured by single photon counting, and it shows a good single-exponential decay. The radiative decay rate constant (K_τ) and nonradiative decay rate constant ($K_{n\tau}$) was determined according to the following equation:

$$\tau = (K_\tau + K_{n\tau})^{-1}$$
$$\phi = K_\tau \tau$$

Where τ is the lifetime; K_τ refers to the radiative decay rate constant; $K_{n\tau}$ refers to the nonradiative decay rate constant; ϕ refers to the emission fluorescence quantum yield.

Theoretical calculation

Structural optimizations from Density functional theory (DFT) were calculated with the Gaussian 09 program. In all cases, the structures were optimized using the B3LYP functional and the mixed basis sets 6-31+G(d) (C, H, O, N and Cl) and LANL2DZ (Zn). For all optimized structures, frequency calculations were carried out to confirm the absence of imaginary frequencies. The molecular structures were visualized and plotted with the GaussView 5.0 program.

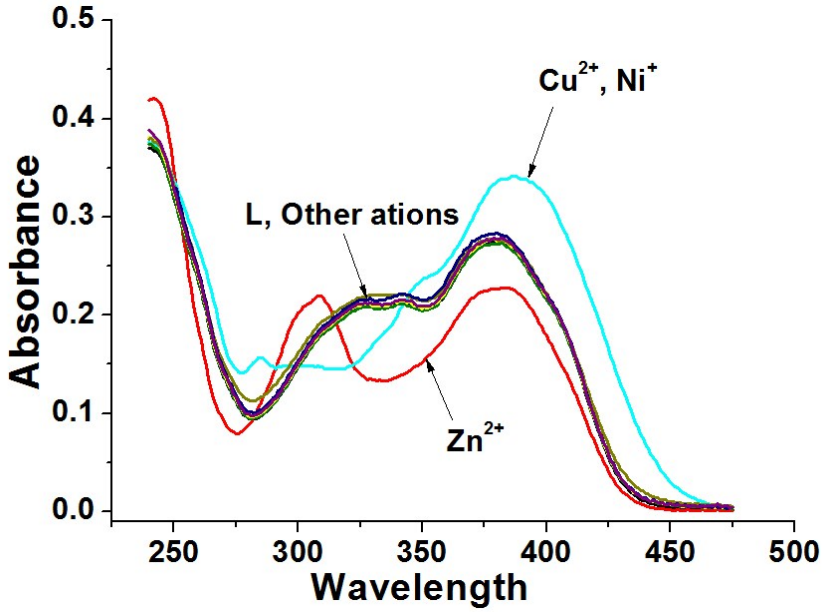


Figure S1. Absorption spectra of **L** (1×10^{-5} M) in acetonitrile-H_2O (9:1) containing HEPES (0.01 M, pH=7.4) buffer solution in the presence of various metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Mn^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Sr^{3+} and Al^{3+}).

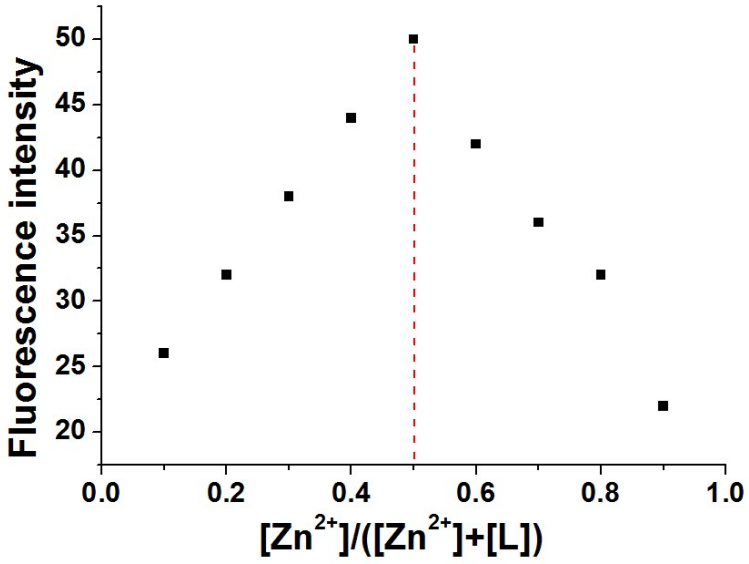


Figure S2. Job's plot of the **L**+Zn^{2+} complex in acetonitrile-H_2O (9:1) containing HEPES (0.01 M, pH=7.4) at 25 °C. The total concentration of **L** and Zn^{2+} was 0.1 mM. Excitation is at 370 nm, and emission is monitored at 495 nm.

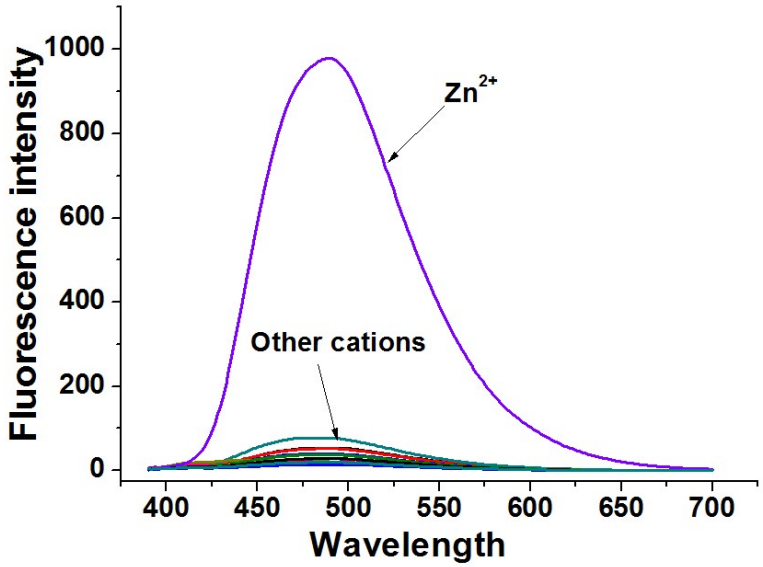


Figure S3. Fluorescence spectra of **L** (1×10^{-5} M) in acetonitrile–H_2O (9:1) containing HEPES (0.01 M, pH = 7.4) buffer solution in the presence of various metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Mn^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Sr^{3+} and Al^{3+}). Excitation wavelength is 370 nm.

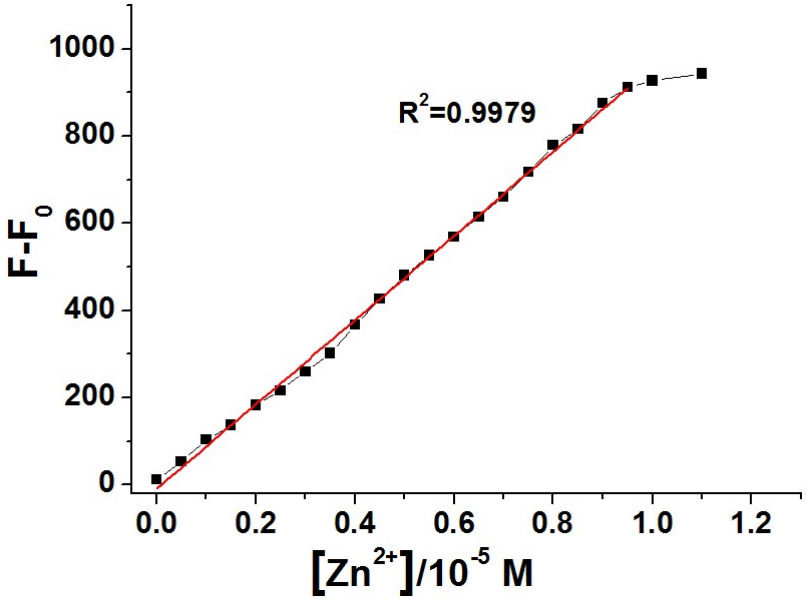


Figure S4. Change ratio of fluorescence of **L** (1×10^{-5}M) upon addition of Zn^{2+} (1×10^{-5} M) in acetonitrile-H_2O (9:1) containing HEPES (0.01 M, pH=7.4) at 25 °C. Excitation is at 370 nm, and emission is monitored at 495 nm. F_0 and F are the fluorescence intensities before and after addition of Zn^{2+}, respectively.

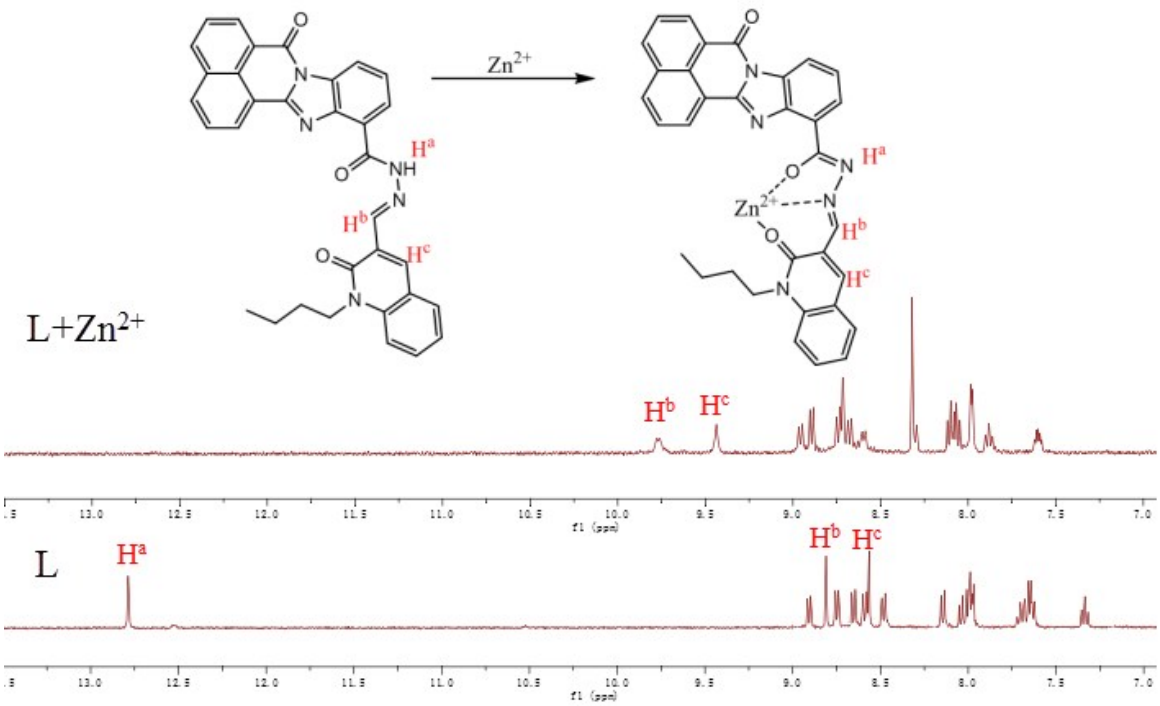


Figure S5. Partial ^{1}H NMR spectra of **L** (DMSO-d_6) and in the presence of $ZnCl_2$.

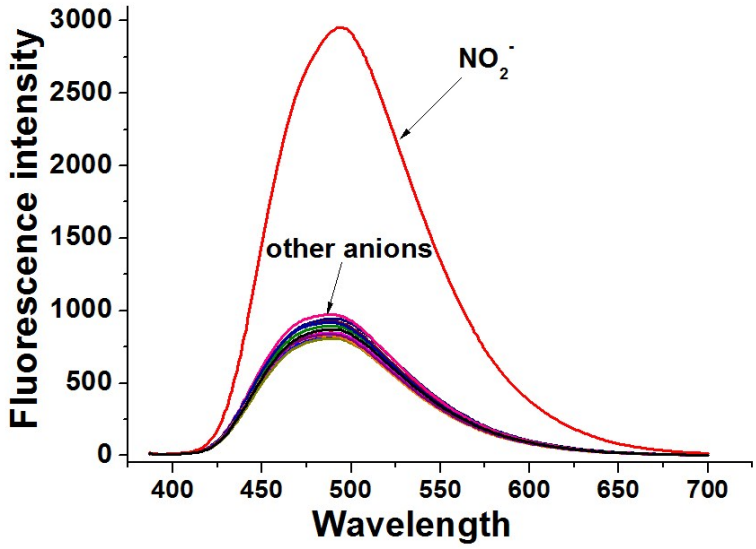


Figure S6. Fluorescence spectra of **L**+Zn^{2+}+Cl^{-} complex (1×10^{-5} M) in acetonitrile-H_2O (9:1) containing HEPES (0.01 M, pH=7.4) buffer solution in the presence of various anions (Ac^{-}, BF_4^{-}, F^{-}, Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, NO_2^{-}, S^{2-}, HSO_3^{-}, $S_2O_3^{2-}$, SO_4^{2-}, CrO_4^{-}, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$, PPi, ATP). Excitation wavelength is at 370 nm.

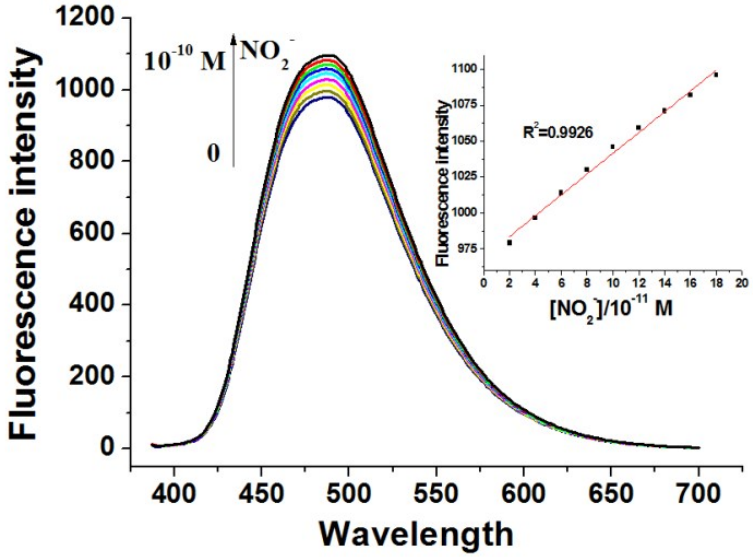


Figure S7. Fluorescence spectra of **L**+Zn^{2+}+Cl^- (1×10^{-5} M) in acetonitrile-H_2O (9:1, HEPES 0.01 M, pH=7.4) as the concentration of NO_2^- (1×10^{-11} M) increased from 0 to 10^{-10} M. Insert: Change ratio of fluorescence of **L**+Zn^{2+}+Cl^- (1×10^{-5}M) upon addition of NO_2^- (1×10^{-11} M). Excited at 370 nm.

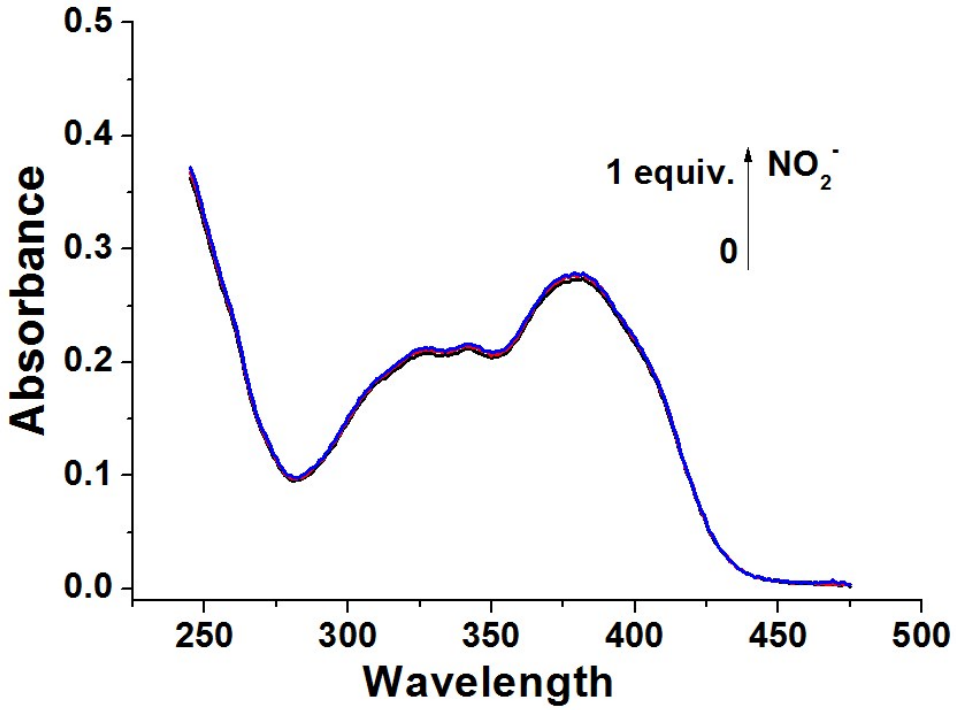


Figure S8. Changes in the absorption spectra of **L** (1×10^{-5} M) in acetonitrile-H_2O (9:1) containing HEPES (0.01 M, pH=7.4) upon titration with NO_2^- (1×10^{-5} M).

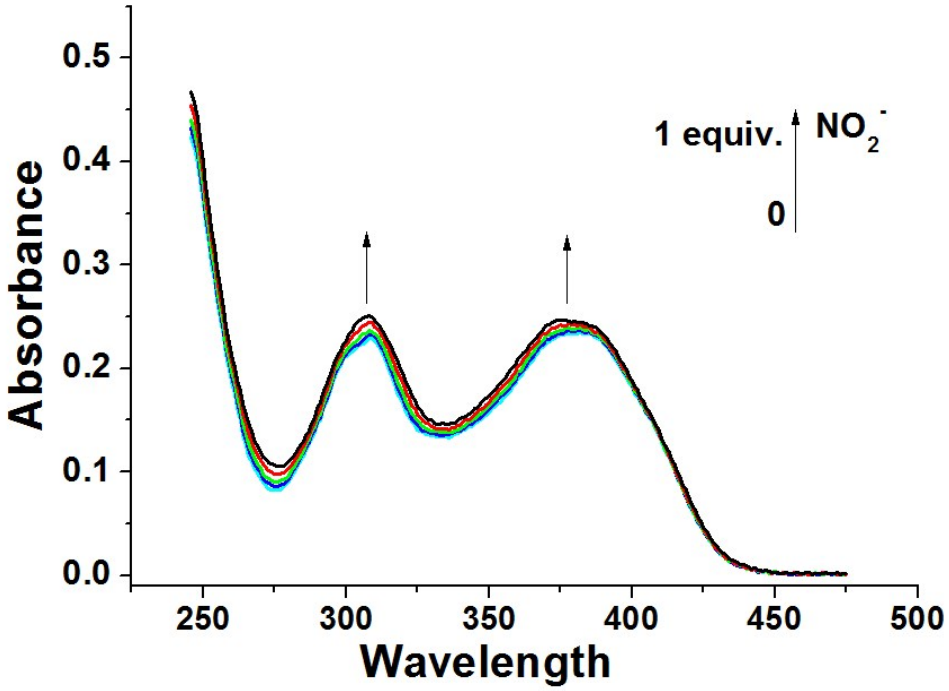


Figure S9. Changes in the absorption spectra of **L**+Zn^{2+}+Cl^- (1×10^{-5} M) in acetonitrile-H_2O (9:1) containing HEPES (0.01 M, pH=7.4) upon titration with NO_2^- (1×10^{-5} M).

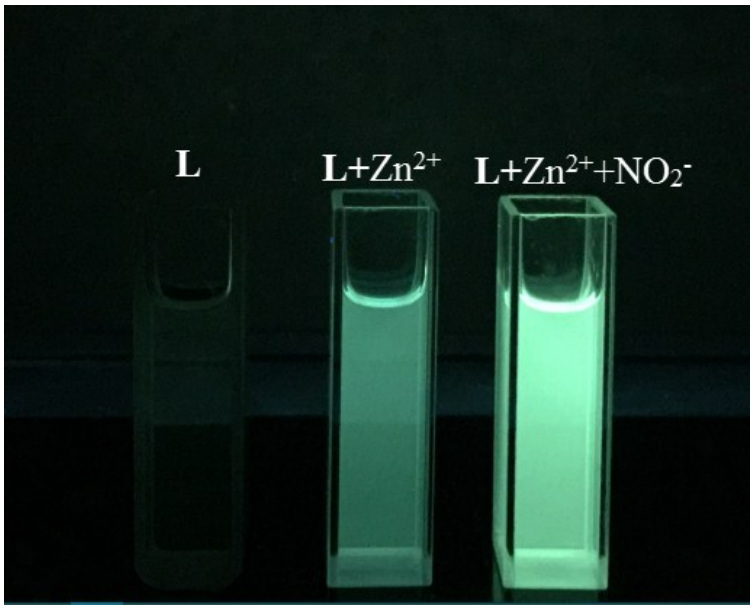


Figure S10. The fluorescence photo of **L** (1×10^{-5} M), **L**+Zn^{2+} (1×10^{-5} M) and **L**+Zn^{2+}+NO_2^- (1×10^{-5} M) in acetonitrile-H_2O (9:1) solution under UV-light. Excitation wavelength is at 365 nm.

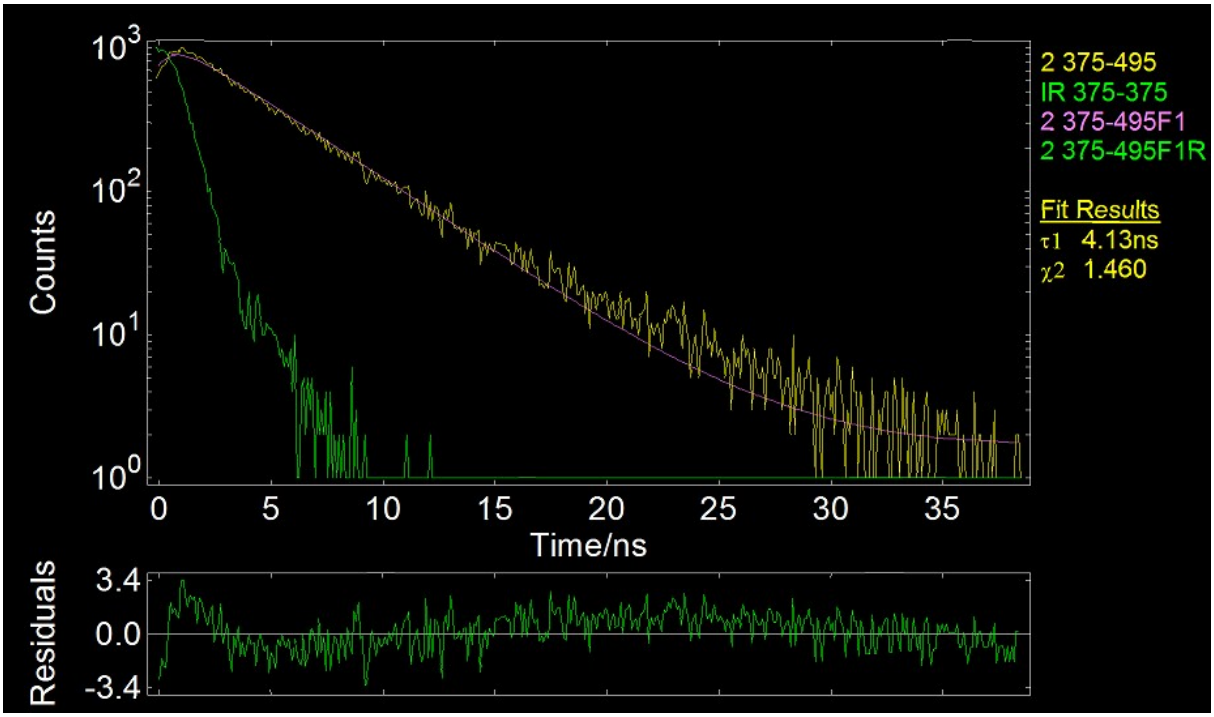


Figure S11. The fluorescence lifetime of the ternary complex **L**+Zn^{2+}+Cl^{-}.

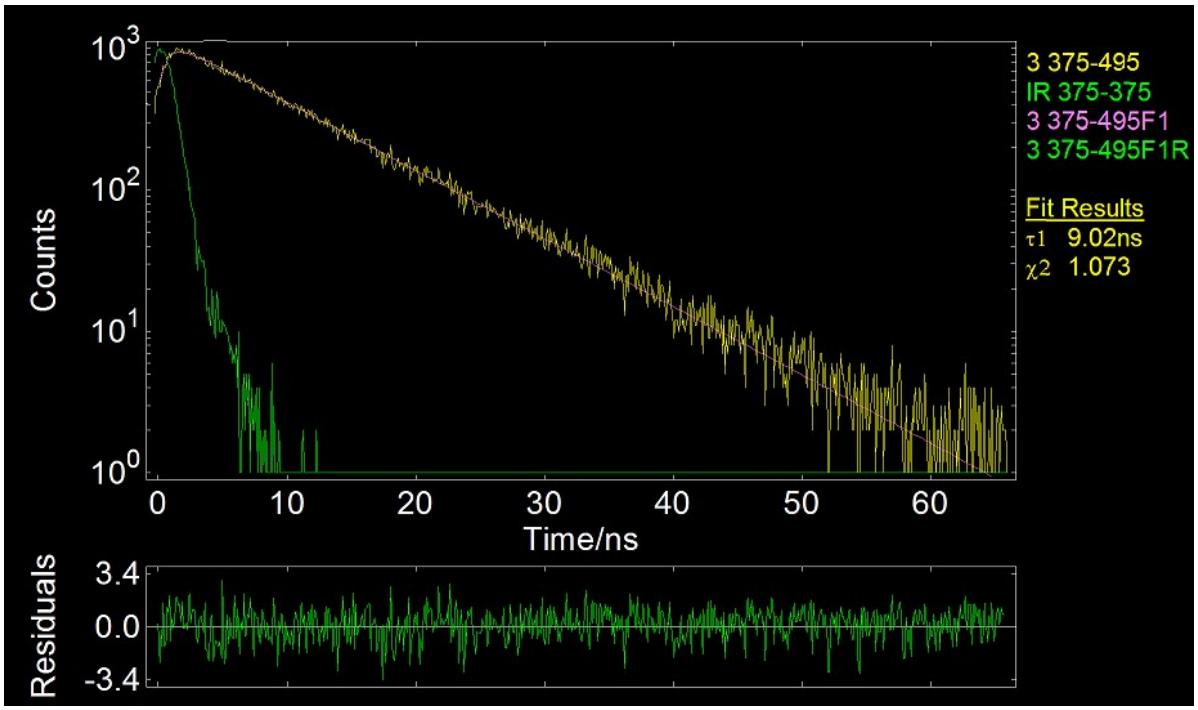


Figure S12. The fluorescence lifetime of **L**+Zn^{2+}+NO_2^{-}.

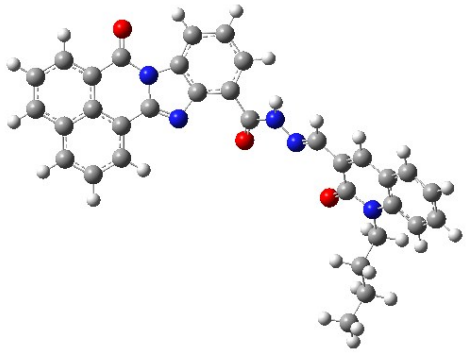
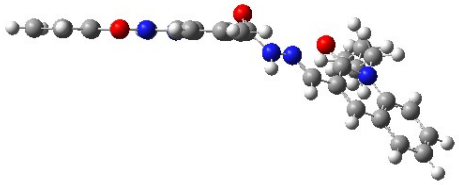
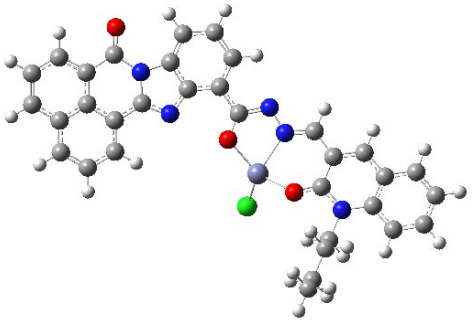
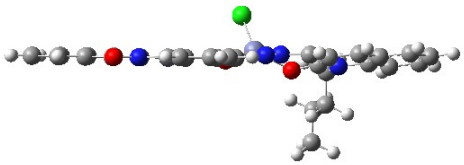
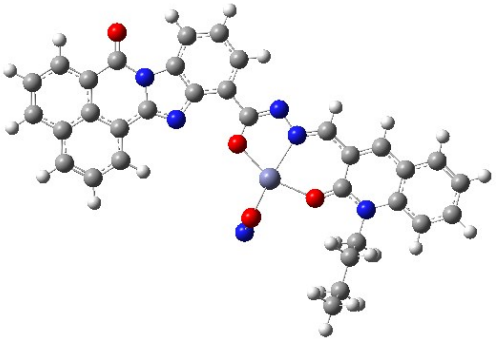
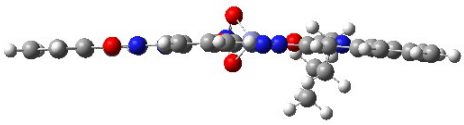
	Elevation view	Vertical view
L		
L+Zn^{2+}+Cl^{-}		
L+Zn^{2+}+NO_2^{-}		

Figure S13. Calculated structures of **L**, **L**+Zn^{2+}+Cl^{-} and **L**+Zn^{2+}+NO_2^{-} (B3LYP/6-31G(d), LANL2DZ), where the light-gray, red, white, dark-gray and cyan atoms denote C, N, O, H, Zn and Cl atoms, respectively.

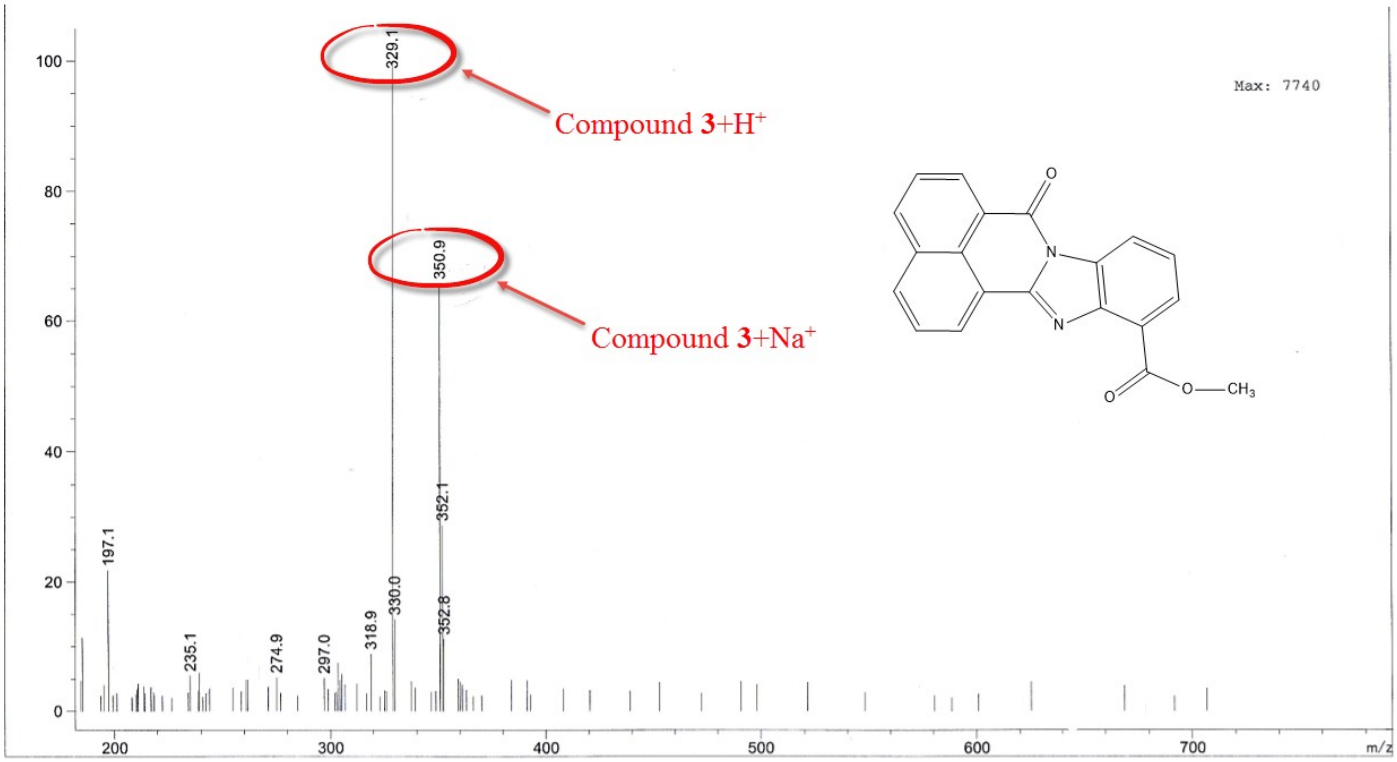


Figure S14. ESI mass spectra of the compound **3**.

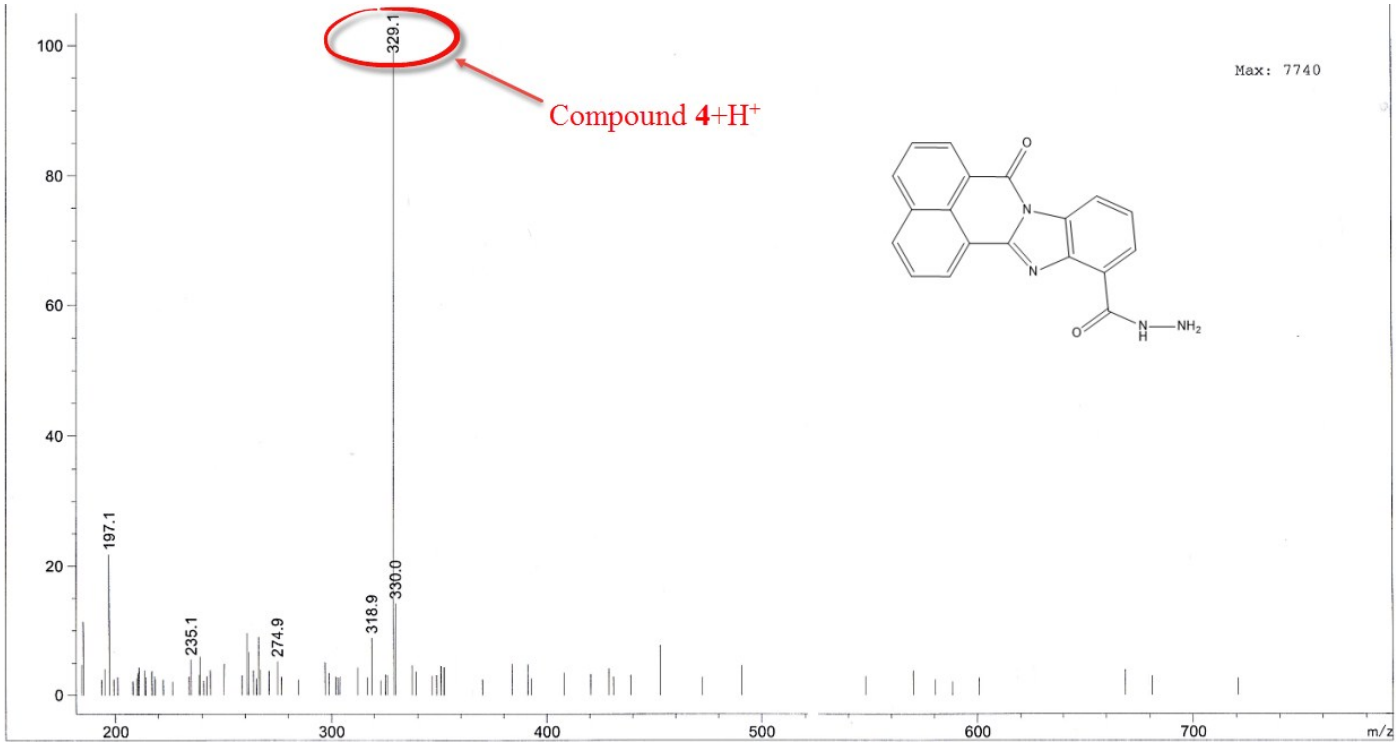


Figure S15. ESI mass spectrum of the compound **4**.

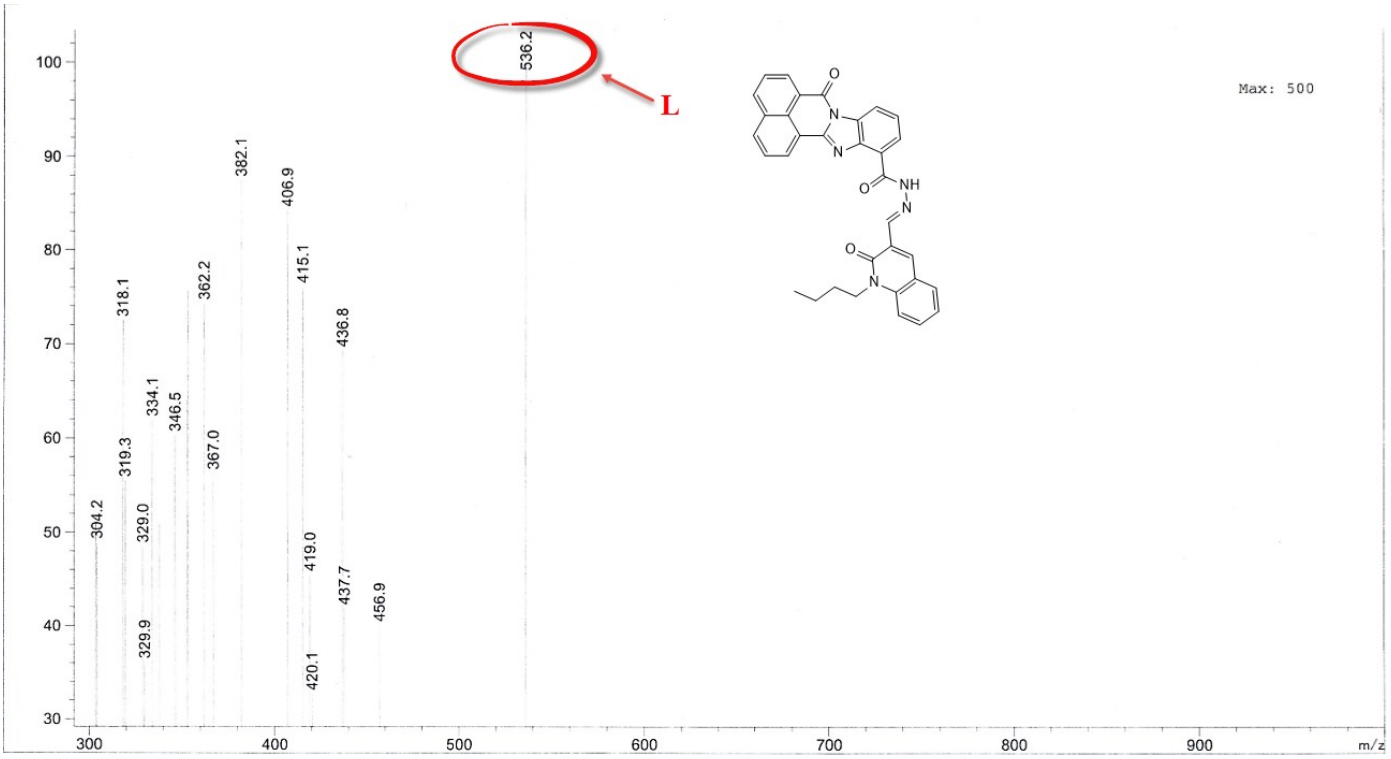


Figure S16. ESI mass spectrum of **L.**

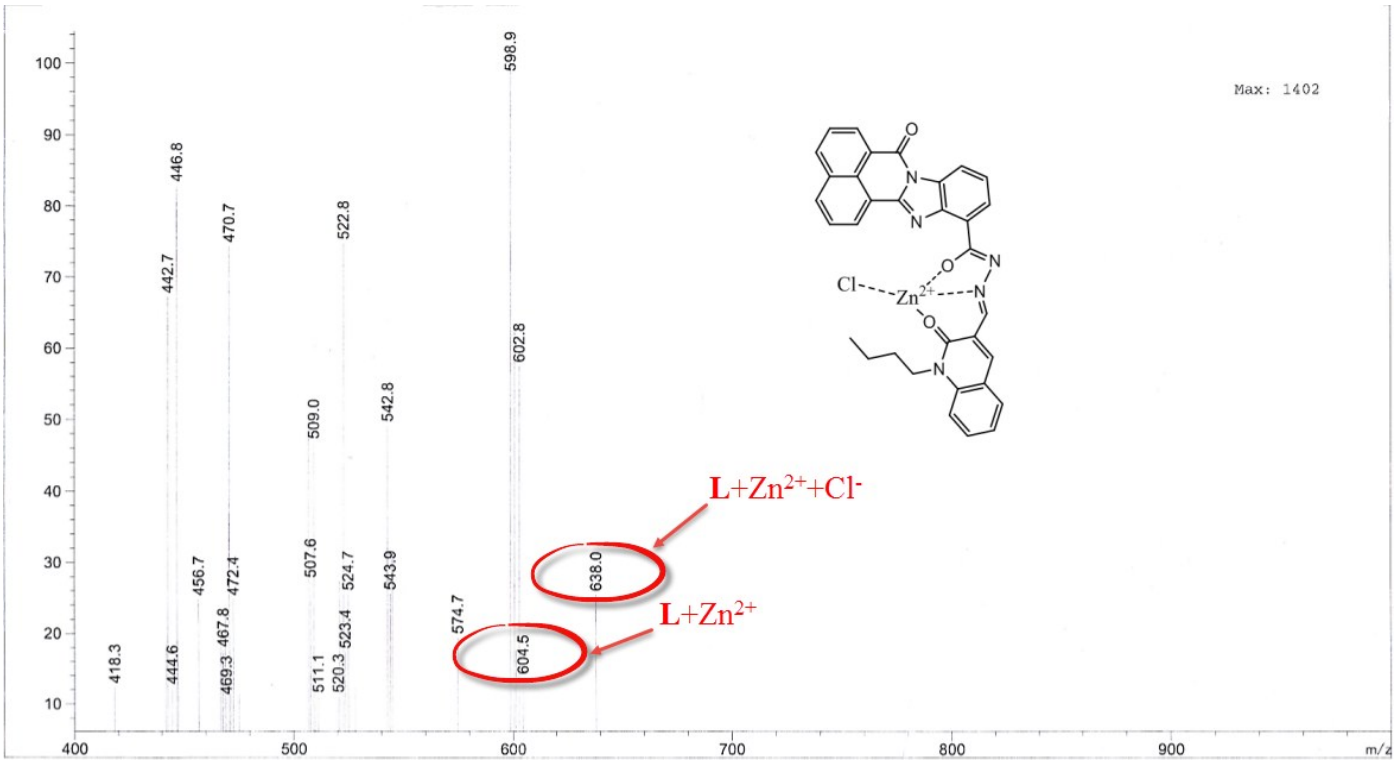


Figure S17. ESI mass spectra of **L**+Zn^{2+}+Cl^{-}

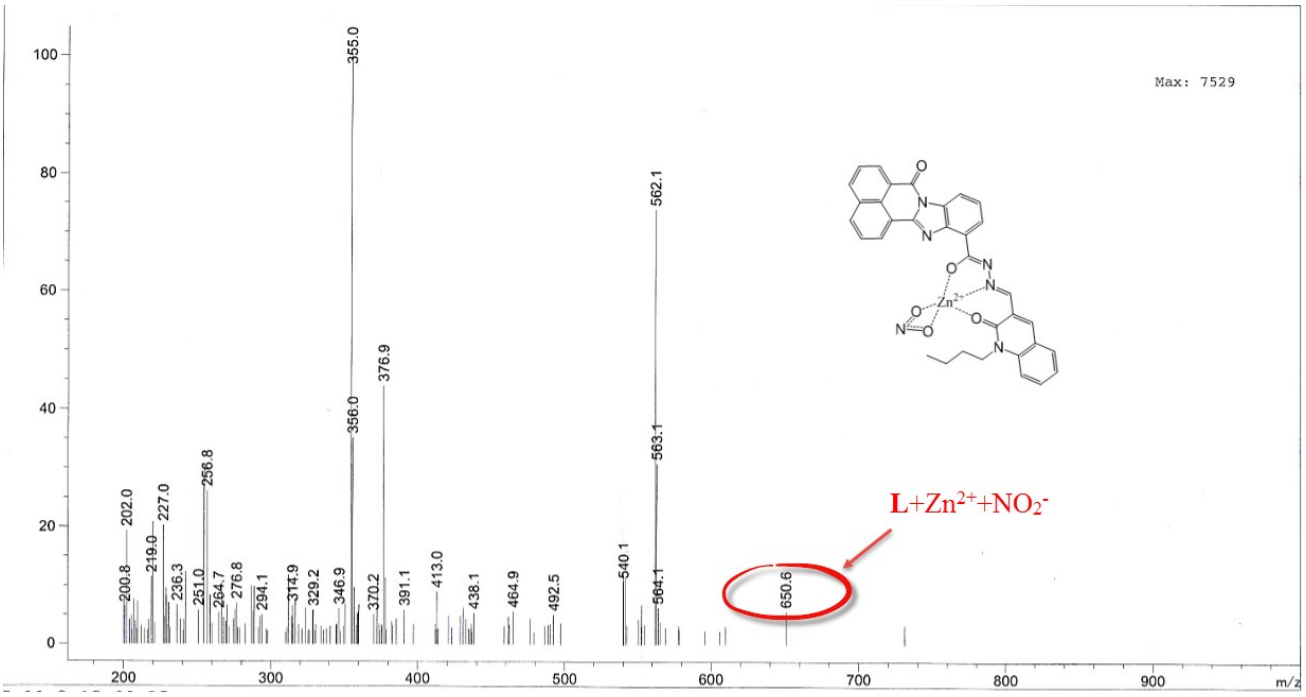


Figure S18. The mass spectra of **L**+Zn^{2+}+NO_2^-.

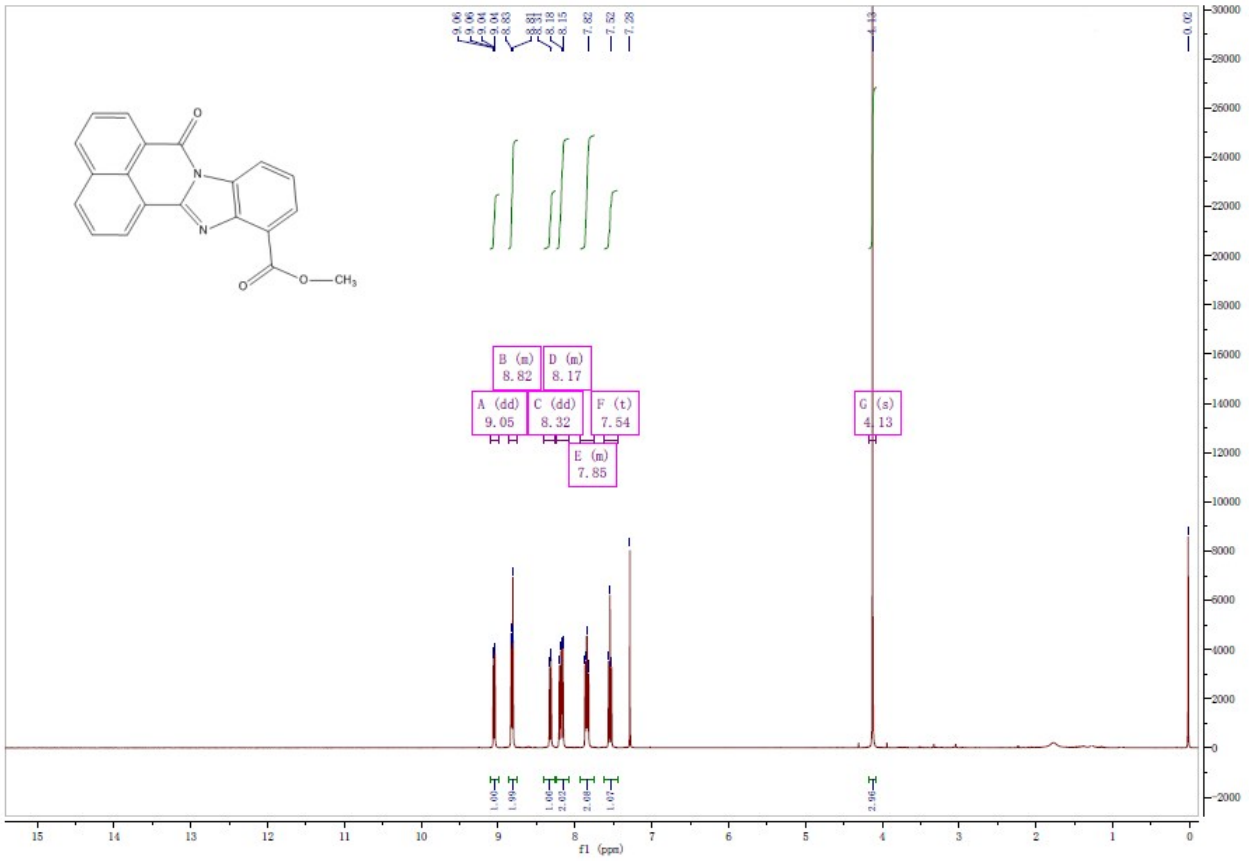


Figure S19. ^{1}H NMR spectra of compound **3** in $CDCl_3$.

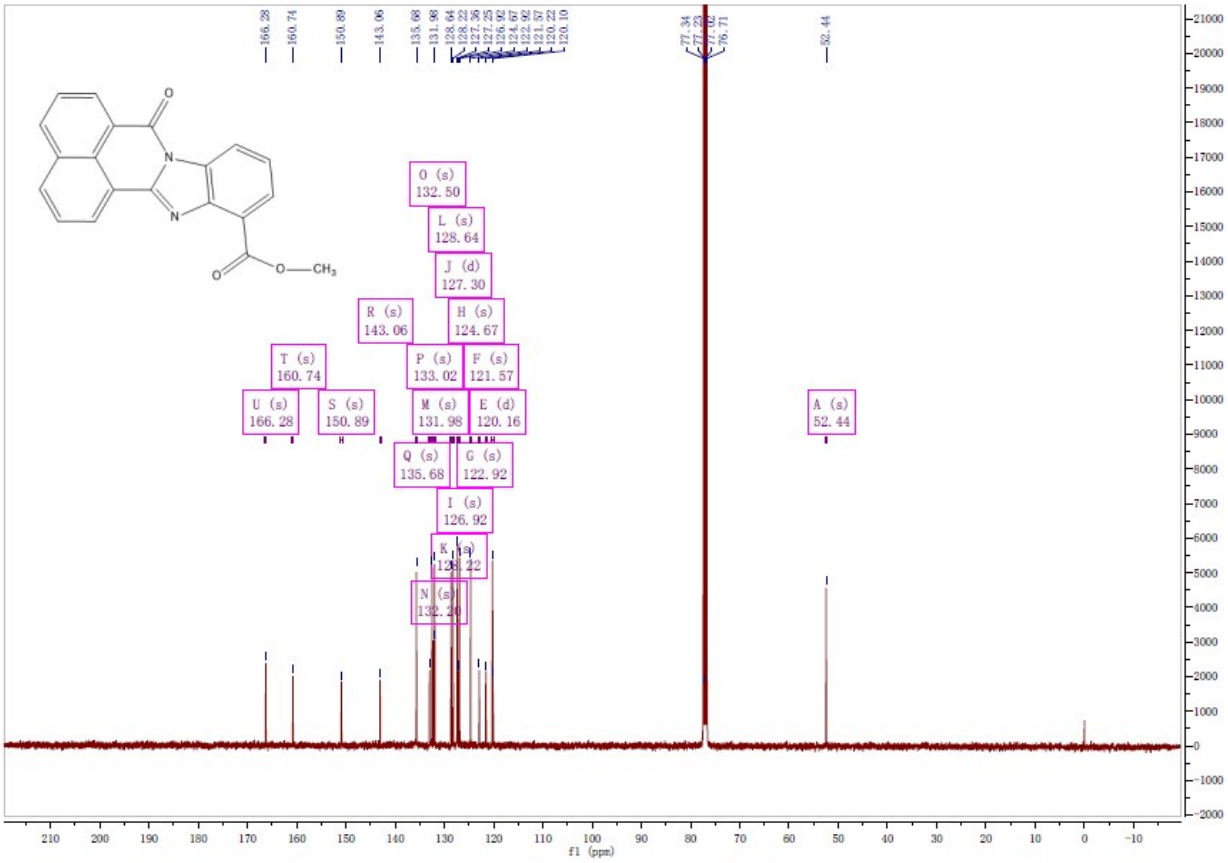


Figure S20. ^{13}C NMR spectra of compound **3** in $CDCl_3$.

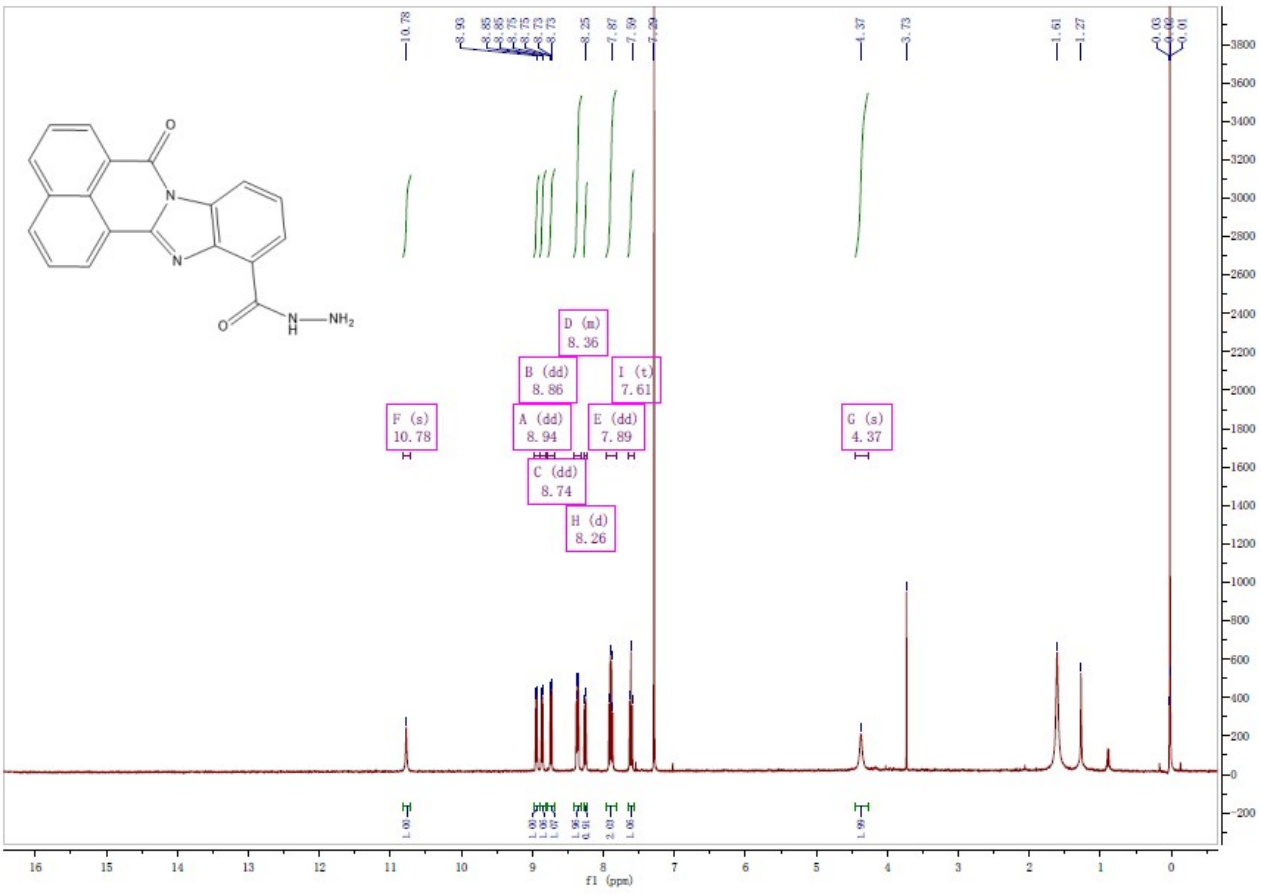


Figure S21. ^{1}H NMR spectra of compound **4** in $CDCl_3$.

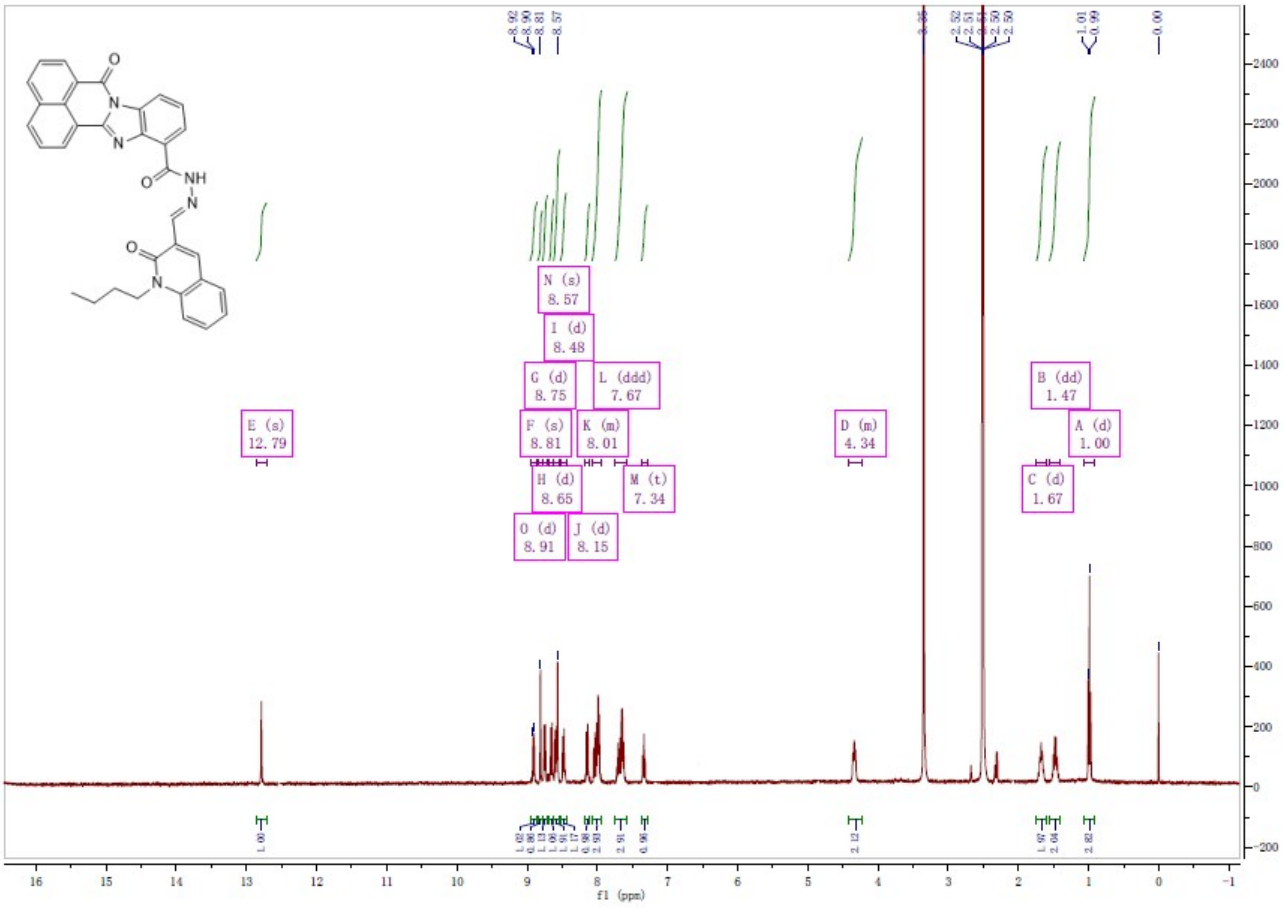


Figure S22. ^{1}H NMR spectra of **L** in DMSO.

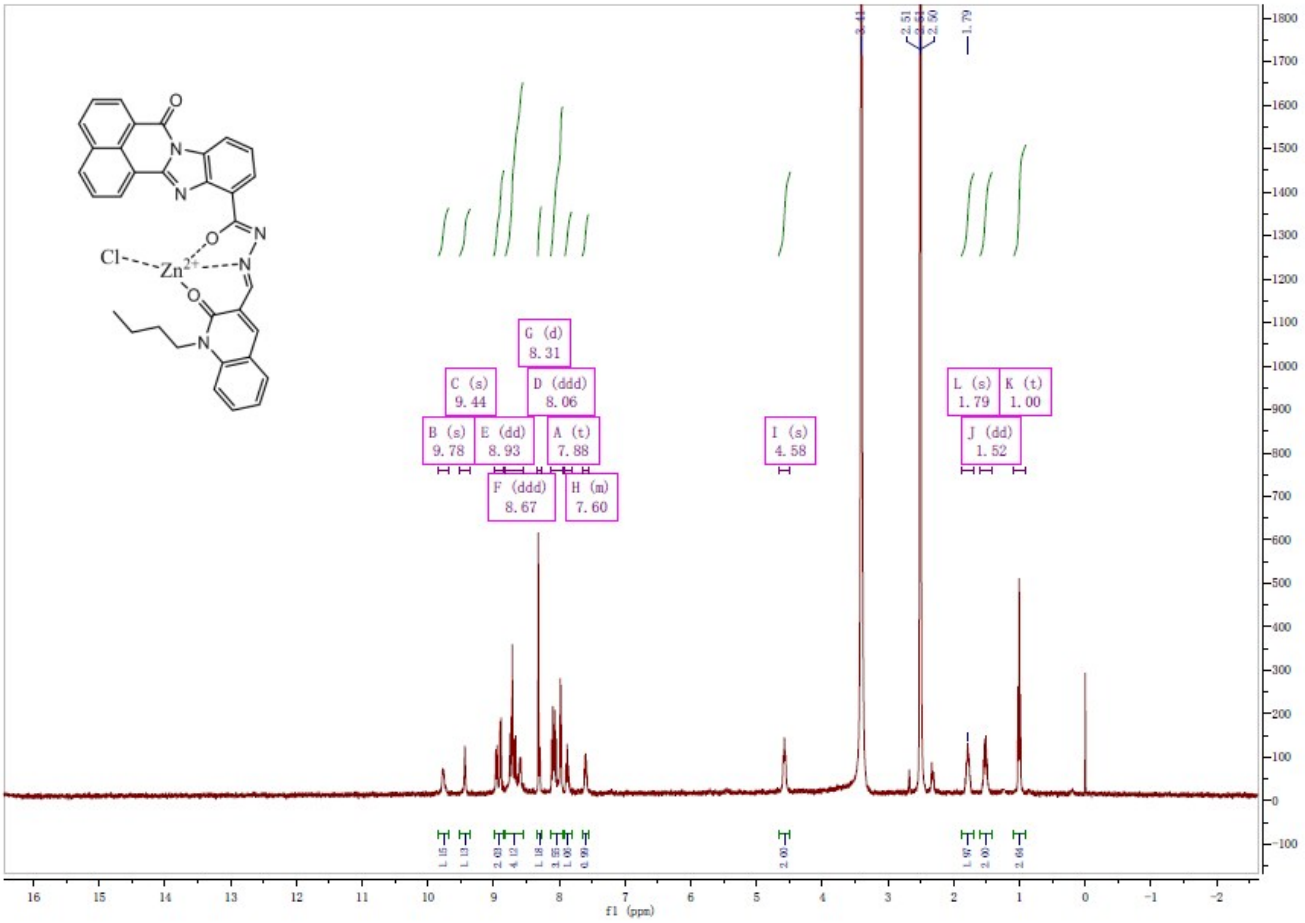


Figure S23. ^{1}H NMR spectra of **L**+Zn^{2+}+Cl^{-} in d6-DMSO.

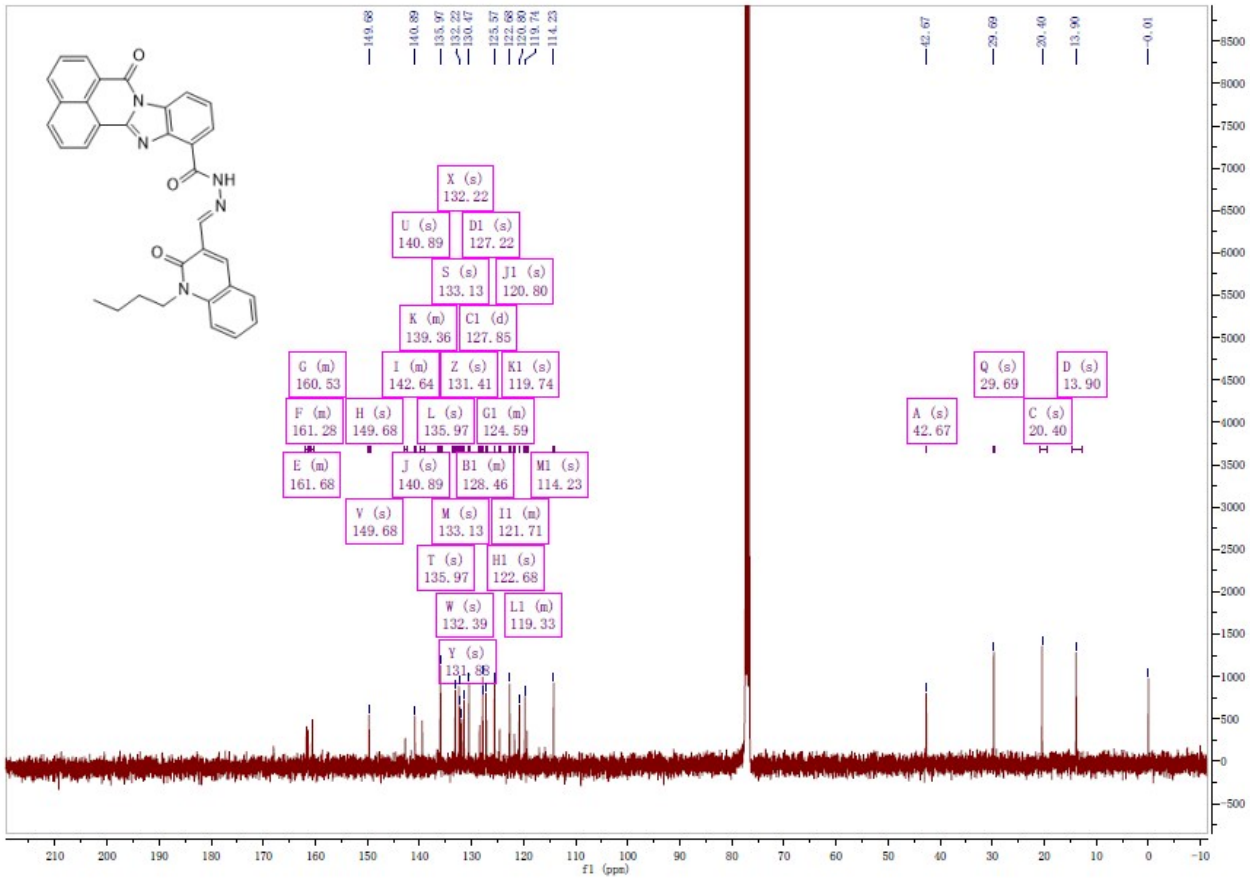


Figure S24. ^{13}C NMR spectra of **L** in d6-DMSO.

Table S1. XYZ coordination of the optimized structure of **L.**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.517509	2.663613	0.276041
2	6	0	5.030255	1.376838	0.213606
3	6	0	6.411332	1.138860	0.468512
4	6	0	7.260538	2.240343	0.793921
5	6	0	6.700027	3.543989	0.851018
6	6	0	5.358887	3.747578	0.596498
7	1	0	3.462655	2.816500	0.071855
8	6	0	6.964045	-0.173342	0.404609
9	6	0	8.634647	1.989490	1.047387
10	1	0	7.346931	4.381982	1.097931
11	1	0	4.942264	4.749421	0.640849
12	6	0	9.148612	0.710324	0.982055
13	6	0	8.310919	-0.375361	0.658668
14	1	0	9.280982	2.827868	1.295549
15	1	0	10.202070	0.534814	1.178481
16	1	0	8.702492	-1.385784	0.601522
17	6	0	4.194341	0.237391	-0.111892
18	6	0	6.122454	-1.348044	0.065625
19	7	0	4.772585	-1.042645	-0.178669
20	7	0	2.912192	0.234070	-0.366300
21	6	0	2.591142	-1.089351	-0.627034
22	6	0	3.732984	-1.918101	-0.510507
23	6	0	1.341872	-1.657796	-0.938243
24	6	0	3.694191	-3.297549	-0.701542
25	6	0	1.301472	-3.044294	-1.125323

26	6	0	2.450617	-3.844671	-1.014864
27	1	0	0.360089	-3.512617	-1.399951
28	1	0	2.369231	-4.914150	-1.185693
29	1	0	4.587400	-3.901566	-0.610688
30	6	0	0.123574	-0.793511	-1.118212
31	8	0	0.115749	0.243892	-1.745507
32	8	0	6.533154	-2.495551	-0.003340
33	7	0	-1.001541	-1.333661	-0.491780
34	7	0	-2.213574	-0.735492	-0.565500
35	6	0	-3.146016	-1.274321	0.138323
36	6	0	-6.766222	-1.134161	1.166521
37	6	0	-7.637283	-1.844890	2.017494
38	6	0	-8.960266	-1.468157	2.164707
39	6	0	-9.432284	-0.352903	1.455926
40	6	0	-8.600068	0.367355	0.609562
41	6	0	-7.252165	-0.013250	0.438642
42	1	0	-7.242910	-2.700539	2.560408
43	1	0	-9.622470	-2.022133	2.822840
44	1	0	-10.465989	-0.037881	1.569340
45	1	0	-8.998393	1.231016	0.092865
46	6	0	-5.396301	-1.501897	1.013971
47	1	0	-5.037619	-2.364508	1.573948
48	7	0	-6.383969	0.661738	-0.409654
49	6	0	-5.004541	0.359032	-0.545707
50	6	0	-4.527468	-0.817237	0.211172
51	8	0	-4.298096	1.052963	-1.262799
52	6	0	-6.848471	1.802470	-1.217439
53	1	0	-6.200270	1.836636	-2.093710
54	1	0	-7.866195	1.592615	-1.558532
55	6	0	-6.770113	3.140990	-0.473241
56	1	0	-7.363804	3.091326	0.448844
57	1	0	-5.728207	3.301291	-0.174294
58	6	0	-7.249930	4.305276	-1.345249
59	1	0	-8.295743	4.175071	-1.651457
60	1	0	-7.178391	5.255383	-0.805187
61	1	0	-6.644568	4.392849	-2.255011
62	1	0	-0.872365	-2.132628	0.129575
63	1	0	-2.933235	-2.161752	0.756986

Table S2. XYZ coordination of the optimized structure of **L**+Zn^{2+}+Cl^{-}**.**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.697594	2.443233	-0.314749
2	6	0	5.301586	1.210679	-0.075809
3	6	0	6.721439	1.099819	-0.000974
4	6	0	7.516987	2.272358	-0.170485
5	6	0	6.866432	3.511988	-0.411214
6	6	0	5.486521	3.593710	-0.482616
7	1	0	3.615223	2.495222	-0.371270
8	6	0	7.361637	-0.148881	0.235551
9	6	0	8.929311	2.157517	-0.094181
10	1	0	7.473236	4.404000	-0.541576
11	1	0	5.006971	4.548898	-0.670481
12	6	0	9.532599	0.935071	0.138723
13	6	0	8.748388	-0.220794	0.303296
14	1	0	9.535181	3.050436	-0.223091
15	1	0	10.613979	0.862387	0.194183
16	1	0	9.210272	-1.185942	0.484434
17	6	0	4.528590	0.009498	0.097805
18	6	0	6.578759	-1.389835	0.409401
19	7	0	5.173627	-1.201197	0.319936
20	7	0	3.205924	-0.109456	0.068405
21	6	0	2.957391	-1.437317	0.268695
22	6	0	4.168646	-2.165732	0.430881
23	6	0	1.714556	-2.137381	0.311555
24	6	0	4.209738	-3.533589	0.638314
25	6	0	1.767543	-3.538202	0.516674
26	6	0	2.973101	-4.209296	0.678380

27	1	0	0.835998	-4.088372	0.551061
28	1	0	2.967113	-5.282330	0.839280
29	1	0	5.151196	-4.053771	0.760615
30	6	0	0.446517	-1.447424	0.140813
31	8	0	0.362303	-0.193361	0.053871
32	8	0	7.038553	-2.498383	0.611692
33	7	0	-0.671998	-2.290388	0.096124
34	7	0	-1.769569	-1.577898	-0.106858
35	6	0	-2.920374	-2.219167	-0.058716
36	6	0	-6.623822	-1.762141	-0.225871
37	6	0	-7.789342	-2.567705	-0.316148
38	6	0	-9.040602	-1.993061	-0.332313
39	6	0	-9.152263	-0.590920	-0.251233
40	6	0	-8.033985	0.226841	-0.163375
41	6	0	-6.746177	-0.340678	-0.156845
42	1	0	-7.670109	-3.645970	-0.371663
43	1	0	-9.931417	-2.608097	-0.401545
44	1	0	-10.135985	-0.131277	-0.253285
45	1	0	-8.173981	1.296338	-0.086684
46	6	0	-5.336413	-2.330789	-0.199203
47	1	0	-5.242282	-3.413009	-0.252547
48	7	0	-5.590867	0.437300	-0.079019
49	6	0	-4.323622	-0.098905	-0.000209
50	6	0	-4.189256	-1.557449	-0.109626
51	8	0	-3.357256	0.683789	0.178312
52	6	0	-5.678727	1.924072	-0.058876
53	1	0	-4.752617	2.291201	-0.499556
54	1	0	-6.494319	2.210470	-0.725145
55	6	0	-5.863645	2.493365	1.351948
56	1	0	-6.765302	2.069275	1.813918
57	1	0	-5.013709	2.180337	1.970663
58	6	0	-5.959140	4.026205	1.336247
59	1	0	-6.802552	4.334255	0.702302
60	1	0	-5.056244	4.440228	0.867834
61	30	0	-1.440620	0.534527	-0.588531
62	1	0	-2.902597	-3.305387	0.049189
63	6	0	-6.129733	4.619276	2.738674
64	1	0	-6.193816	5.711327	2.696608
65	1	0	-7.043369	4.249705	3.219354
66	1	0	-5.283262	4.359098	3.385013
67	17	0	-1.460530	1.848475	-2.433522

Table S3. XYZ coordination of the optimized structure of **L**+Zn^{2+}+NO_2^-.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.808019	2.394412	-0.124675
2	6	0	5.391614	1.140822	-0.017279
3	6	0	6.808010	1.010567	0.064395
4	6	0	7.620119	2.185724	0.036665
5	6	0	6.987775	3.452924	-0.073749
6	6	0	5.613031	3.551148	-0.153054
7	1	0	3.726663	2.463939	-0.185716
8	6	0	7.430600	-0.267040	0.173331
9	6	0	9.030006	2.041272	0.121162
10	1	0	7.605946	4.346895	-0.095187
11	1	0	5.140732	4.525341	-0.238080
12	6	0	9.612387	0.794325	0.227404
13	6	0	8.810325	-0.364366	0.253270
14	1	0	9.648475	2.935350	0.100747
15	1	0	10.692425	0.700355	0.291142
16	1	0	9.255400	-1.350610	0.335892
17	6	0	4.595698	-0.071142	0.017923
18	6	0	6.627837	-1.518130	0.204316
19	7	0	5.239075	-1.315794	0.118104
20	7	0	3.292853	-0.169334	-0.032360
21	6	0	3.014536	-1.526879	0.034180
22	6	0	4.217916	-2.274049	0.130789
23	6	0	1.774134	-2.205653	0.026128
24	6	0	4.253919	-3.662171	0.217000
25	6	0	1.815997	-3.605894	0.116680
26	6	0	3.019279	-4.314803	0.207703
27	1	0	0.873024	-4.139135	0.113728

28	1	0	2.991891	-5.398739	0.272522
29	1	0	5.193320	-4.194537	0.287966
30	6	0	0.471893	-1.497932	-0.072519
31	8	0	0.456759	-0.236729	-0.231941
32	8	0	7.109555	-2.652806	0.296742
33	7	0	-0.621877	-2.287604	0.018608
34	7	0	-1.755558	-1.566536	-0.074159
35	6	0	-2.868872	-2.225559	0.007644
36	6	0	-6.623612	-2.003049	0.071038
37	6	0	-7.730237	-2.864927	0.250385
38	6	0	-9.020942	-2.373615	0.253757
39	6	0	-9.231970	-0.994192	0.084873
40	6	0	-8.168217	-0.122128	-0.097112
41	6	0	-6.847325	-0.611879	-0.120040
42	1	0	-7.540351	-3.925895	0.389703
43	1	0	-9.864268	-3.042709	0.393048
44	1	0	-10.242225	-0.595814	0.100927
45	1	0	-8.370011	0.935622	-0.204151
46	6	0	-5.287220	-2.483071	0.090213
47	1	0	-5.124562	-3.548236	0.239291
48	7	0	-5.744354	0.219078	-0.318282
49	6	0	-4.434389	-0.226755	-0.256979
50	6	0	-4.197823	-1.655559	-0.052907
51	8	0	-3.523977	0.620665	-0.389097
52	6	0	-5.921304	1.667026	-0.581207
53	1	0	-5.086646	1.970632	-1.212573
54	1	0	-6.838786	1.791034	-1.159970
55	6	0	-5.940772	2.508540	0.699807
56	1	0	-6.741296	2.156356	1.365033
57	1	0	-4.992413	2.356530	1.228301
58	6	0	-6.128454	4.002260	0.400951
59	1	0	-7.070592	4.152925	-0.146222
60	1	0	-5.325262	4.339030	-0.267914
61	30	0	-1.404300	0.602728	-0.362664
62	1	0	-2.805096	-3.307510	0.143458
63	7	0	-1.291005	3.128996	-0.726021
64	8	0	-1.336652	2.597911	0.418430
65	8	0	-1.291084	2.294271	-1.671964
66	6	0	-6.129157	4.861469	1.669637
67	1	0	-6.262458	5.921717	1.428487
68	1	0	-6.939323	4.568294	2.348786
69	1	0	-5.183122	4.759029	2.213715
