

SUPPLEMENTARY INFORMATION (SI)

A quinoline-based turn-off fluorescent cation sensor

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S1. Experimental

1. General

Mass spectrum was recorded on UPLC-Q-TOF mass spectrometer. ¹H NMR and ¹³C NMR spectra have been recorded on BRUKER Avance II 400 MHz and 100 MHz, respectively with TMS as internal standard using CDCl₃ as deuterated solvent. Data is reported as follow: chemical shift in ppm (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, dd=double doublet), coupling constant J (Hz) and assignment. The purity of the solid products was checked by elemental analysis performed on Thermoelectron FLASH EA1112, CHNS analyzer. UV-visible spectral studies were conducted on Shimadzu 1601 PC spectrophotometer with a quartz cuvette (path length, 1 cm). The absorption spectra have been recorded between 1100 and 200 nm. The cell holder of the spectrophotometer was thermostatted at 25°C for consistency in the recordings. The steady state fluorescence experiments were carried out on Cary Eclipse spectrofluorometer at ambient temperature. A slit width of 5 nm was used with $\lambda_{\text{ex}} = 320$ nm and $\lambda_{\text{em}} = 376$ nm. The titration experiment was accomplished by varying the concentration of metal ion and keeping the compound concentration constant (30 μM). In fluorescence titration experiment, working solutions were prepared by making dilution of compound stock (0.1mM) with HPLC grade methanol.

2. Computational Methods

All theoretical calculations were carried out by using the Gaussian 09 suite of programs.

The molecular geometry of **5** was optimized by DFT/B3LYP¹/6-311G* method. **5**:Hg²⁺ and **5**:Cu²⁺ geometries were optimized by DFT/MPW1PW91/GEN method in which 6-311G basis set was used for C, H, N and O with additional diffuse function for the donor atoms (N and O) and Stuttgart-Dresden basis set (SDD) for Hg and Cu. Energy values and properties of the systems were computed at the same level and considering solvent (methanol) effects by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model) modification² of the Tomasi's PCM formalism.³ The first 50 excited states were calculated by using time-dependent density functional theory (TD-DFT) calculations. The molecular orbital contours were plotted using Gauss view 5.0.9.

3. Chemicals

Metal salts used in the spectrophotometric studies were of analytical grade and bought from Sigma-Aldrich. The solvents used were also of analytical grade purchased from Thomas Baker.

4. Synthetic Procedure for 1-5.

(a) Synthesis of 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**1**). To the solution of benzaldehyde (1g, 9.4 mmol), urea (0.85g, 14mmol) and ethylacetoacetate (1.2ml, 9.4 mmol) in methanol, 2ml of conc. HCl was added and the solution was stirred at r.t for 24 hrs. The white solid separated in solution was filtered and washed 2-3 times with water. The recrystallization was done in hot ethanol.⁴

(b) Synthesis of 5-ethoxycarbonyl-6-methyl-4-phenylpyrimidine-2(1*H*)-one (**2**). A solution of **1** (0.5g, 1.97 mmol) in CH₂Cl₂ was stirred with pyridinium chlorochromate (1.3g, 5.90 mmol) for 18 hrs. The reaction mixture was filtered over celite to remove any suspension, and the residue

¹ L. J. Bartolotti and K. Fluchick, *Reviews in Computational Chemistry* Lipkowitz, K. B.; Boyd, B. D. Eds., VCH, New York, 1996, **7**, 187-216.

² (a) V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995; (b) M. Cossi, N. Rega, G. Scalmani, V. J. Barone, *Comp. Chem.*, 2003, **24**, 669-681.

³ S. Miertus, E. Scrocco and J. Tomasi, *J. Chem. Phys.* 1981, **55**, 117; (b) R. Cammi, B. Mennucci and J. Tomasi, *J. Phys. Chem., A* 2000, **104**, 5631-5637.

⁴ P. Biginelli, *Gazz. Chim. Ital.*, 1893, **23**, 360-416.

obtained after removal of the solvent was flash-chromatographed to obtain the corresponding pyrimidinone **2**.⁵

(c) Synthesis of 5-Ethoxycarbonyl-6-methyl-2-chloropyrimidines (**3**). 5-ethoxycarbonyl-6-methyl-4-phenylpyrimidin-2(1*H*)-one **2** (3 mmol) was taken in 10 ml of phosphorous oxychloride (POCl₃) and reaction mixture was refluxed at 105 °C for 45 min. The solvent was removed under reduced pressure and crude was purified by column chromatography using EtOAc / Hexane as eluent to give desired product **3**.⁶

(d) Synthesis of 7-chloroquinyl-1,4-butandiamine (**4**). A mixture of 4,7-dichloroquinoline (1g, 5.1 mmol) and butandiamine (5.0ml, 25.3 mmol) was heated to 110°C for 6h under inert atmosphere and then cooled to room temperature. Aqueous sodium hydroxide (1N) was then added and the mixture was extracted with dichloromethane. The organic layers were washed with water, brine, dried over sodium sulphate, and evaporated under reduced pressure. The yellow solid obtained was recrystallized from ethylacetate.⁷

(e) Synthesis of 5-Ethoxycarbonyl-6-methyl-4-phenyl-2-[(7-chloroquinolin-4-ylamino)butylamino]pyrimidine (**5**). To the stirred solution of **4** (1.1g, 4.41 mmol) in dry THF (50ml) mixture of **3** (1g, 2.01mmol) and potassium carbonate (2.78g, 20.15 mmol) in dry THF was added. The reaction mixture was stirred for 48hrs at room temperature. Then, the reaction mixture was filtered and THF was removed under vacuum. The residue was purified by column chromatography using MeOH / EtOAc as eluent to give desired product. The product was recrystallized from DCM/ Hexane. White solid. Rf: 0.4 (EtOAc). Yield: 77%. IR (KBr): $\nu_{\max}/\text{cm}^{-1}$, 3383 (NH), 2986 (C-H), 1708 (C=O), 1268(C-O). Found: C, 66.10; H, 5.63; N, 13.95. Calc. For C₂₇H₂₈N₅O₂Cl: C, 66.18; H, 5.72; N, 14.30%. ¹H NMR (300 MHz; CDCl₃; Me₄Si; ppm) δ_{H} : 0.94 (3H, t, *J* = 7.2 Hz, ester-CH₃), 1.80 (4H, q, *J* = 6.9 Hz, CH₂), 2.47 (3H, s, C6-CH₃), 3.37 (2H, q, *J* = 6.3 Hz, CH₂), 3.60 (2H, q, *J* = 7.2 Hz, CH₂), 4.05 (2H, q, *J* = 7.2 Hz, ester-CH₂), 5.06 (1H, s, NH), 5.45 (1H, s, NH), 6.38 (1H, d, *J* = 5.4 Hz, ArH), 7.3-7.58 (7H, m, ArH), 7.94 (1H, d, *J* = 2.1 Hz, ArH), 8.51 (1H, d, *J* = 5.4 Hz, ArH). ¹³C NMR (75 MHz; CDCl₃; Me₄Si;

⁵ K. Singh and K. Singh, *Aust. J. Chem.*; 2008, **61**, 910-913.

⁶ K. Singh, K. Singh, B. Wan, S. Franzblau, K. Chibale and J. Balzarini, *Eur. J. Med. Chem.*; 2011, **46**, 2290-2294.

⁷ J. K. Natarajan J. N. Alumasa, K. Yearick, K.A. Ekoue-Kovi, L.B. Casabianca, A.C.D. Dios, C. Wolf and P.D. Roebe, *J. Med. Chem.*, 2008, **51**, 3466-3469.

ppm) δ_C : δ 13.5, 22.9, 25.8, 27.4, 40.6, 42.9, 61.1, 99.0, 115.4, 117.0, 120.8, 125.2, 127.8, 128.2, 128.7, 129.4, 134.8, 139.0, 149.0, 149.6, 151.9, 161.2, 168.7. m/z (EI): 490.1 (M^+).

5. Calculation of Quantum Yield

Quantum yield of **5** and its complexes with Hg^{2+} , Fe^{3+} and Cu^{2+} was calculated using formula:

$$\Phi_u = \Phi_s F_u A_s / F_s A_u$$

Where, Φ_s is Quantum yield of standard

F_u and F_s are integrated fluorescence of standard and unknown respectively.

A_s and A_u are absorbance of standard and unknown respectively.

Quinine sulphate was used as standard whose quantum yield is 0.55 in 0.1N H_2SO_4 at λ_{ex} = 320 nm.⁸

⁸ Y. Li, H. Chong, X. Meng, S. Wang, M. Zhu, and Q. Guo, *Dalton Trans.*, 2012, **41**, 6189- 6194.

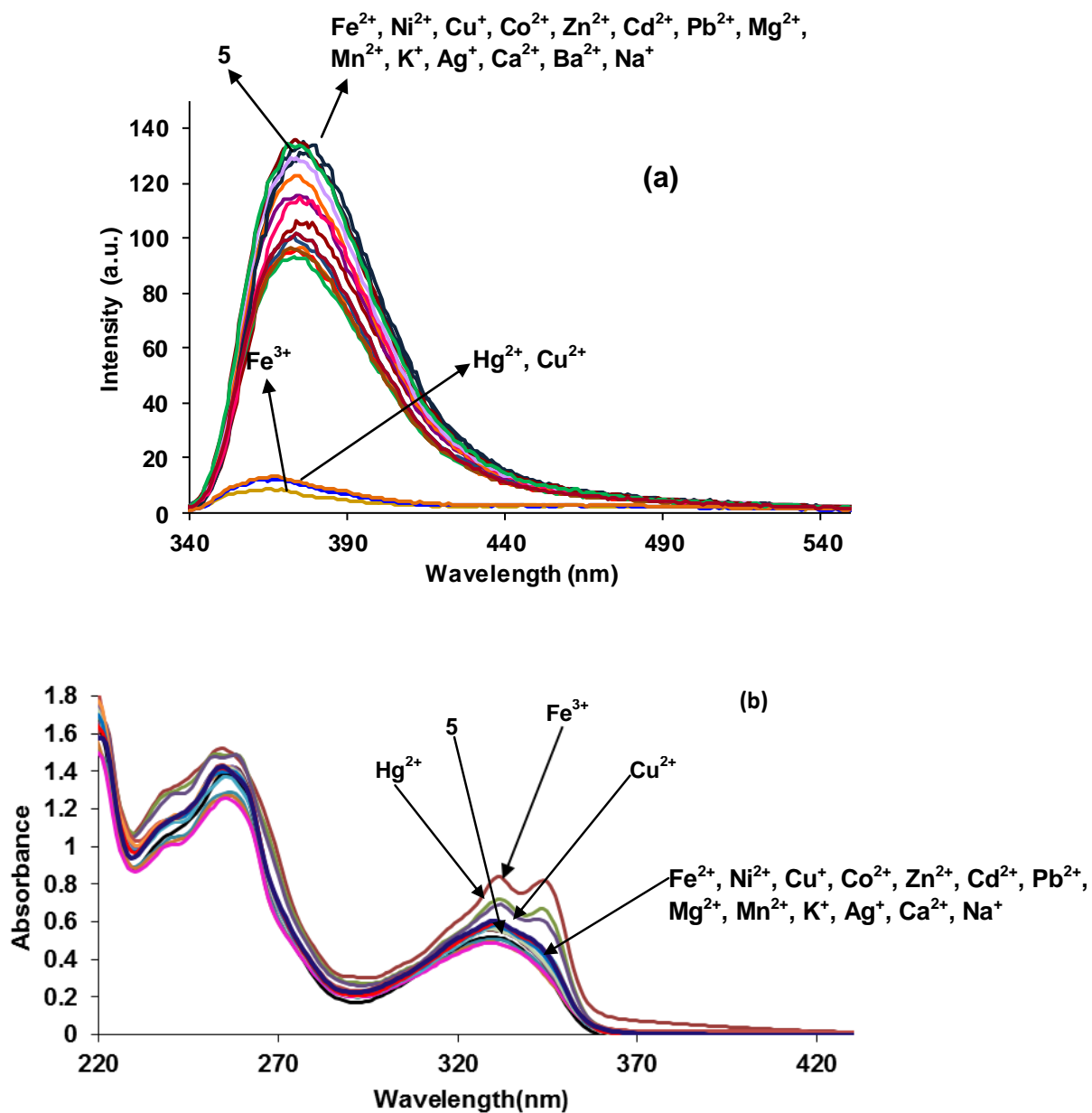
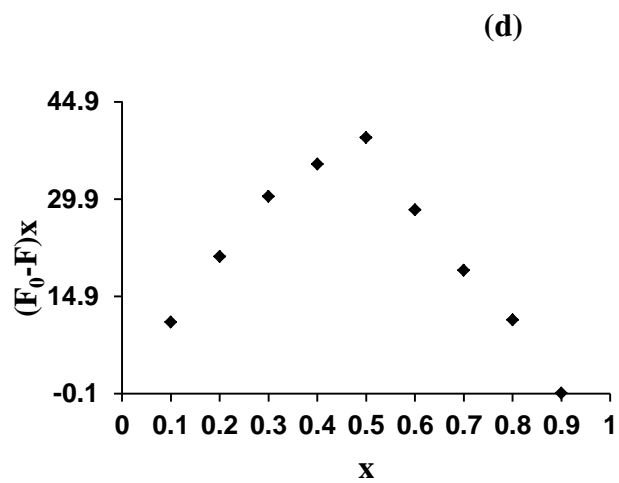
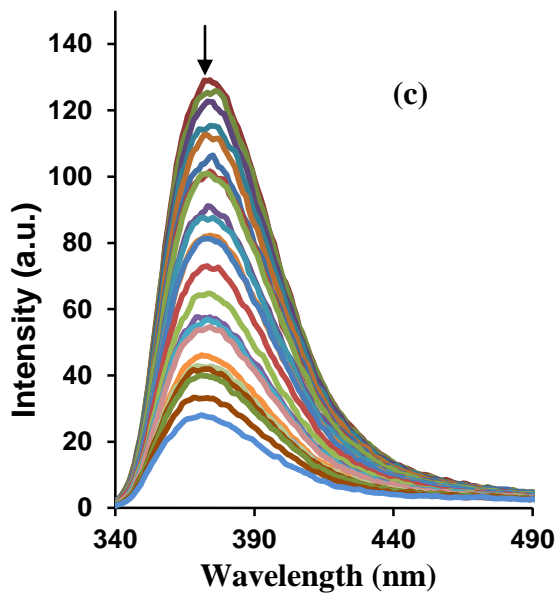
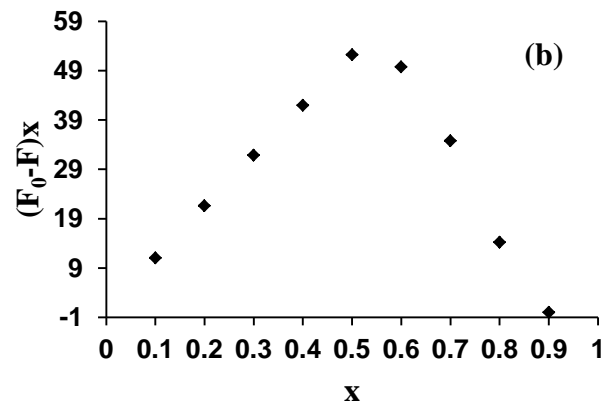
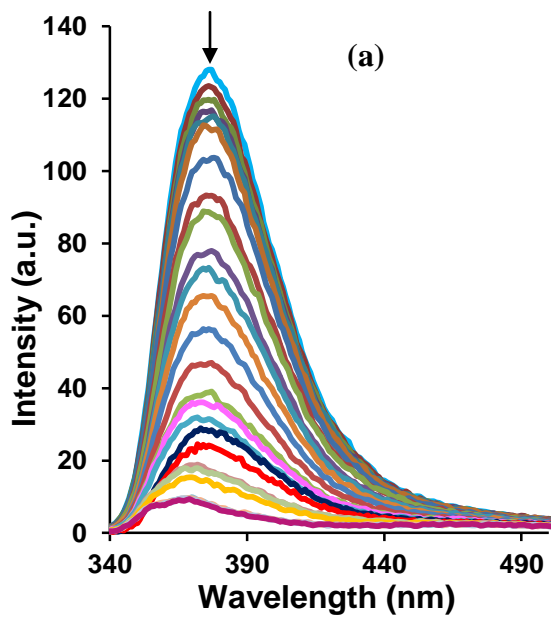


Fig. S1 (a) Emission spectra; (b) absorption spectra of **5** (30 μM) in CH_3OH in the presence of various metal ions (60 μM) in distilled H_2O .



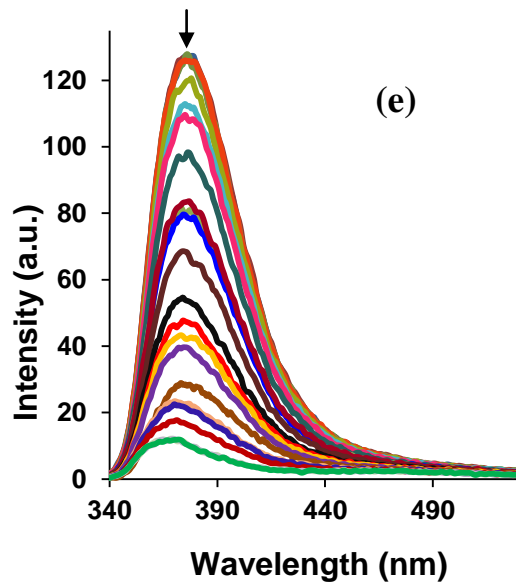


Fig. S2 Fluorescence spectra of **5** (30 μM) in CH_3OH upon addition of (a) Fe^{3+} (0-1.5 equiv.), ($\lambda_{\text{ex}} = 330 \text{ nm}$); (b) Job plot of Fe^{3+} complex formation. $x = [\text{5}]/[\text{5}] + [\text{Fe}^{3+}]$ is the mole fraction of the **5**. F_0 is the fluorescence, when $x = 1$ and F is the fluorescence at respective values of x ; (c) Cu^{2+} (0-1.5 equiv.), ($\lambda_{\text{ex}} = 330 \text{ nm}$); (d) Job plot of Cu^{2+} complex; (e) Hg^{2+} (0-1.5 equiv.).

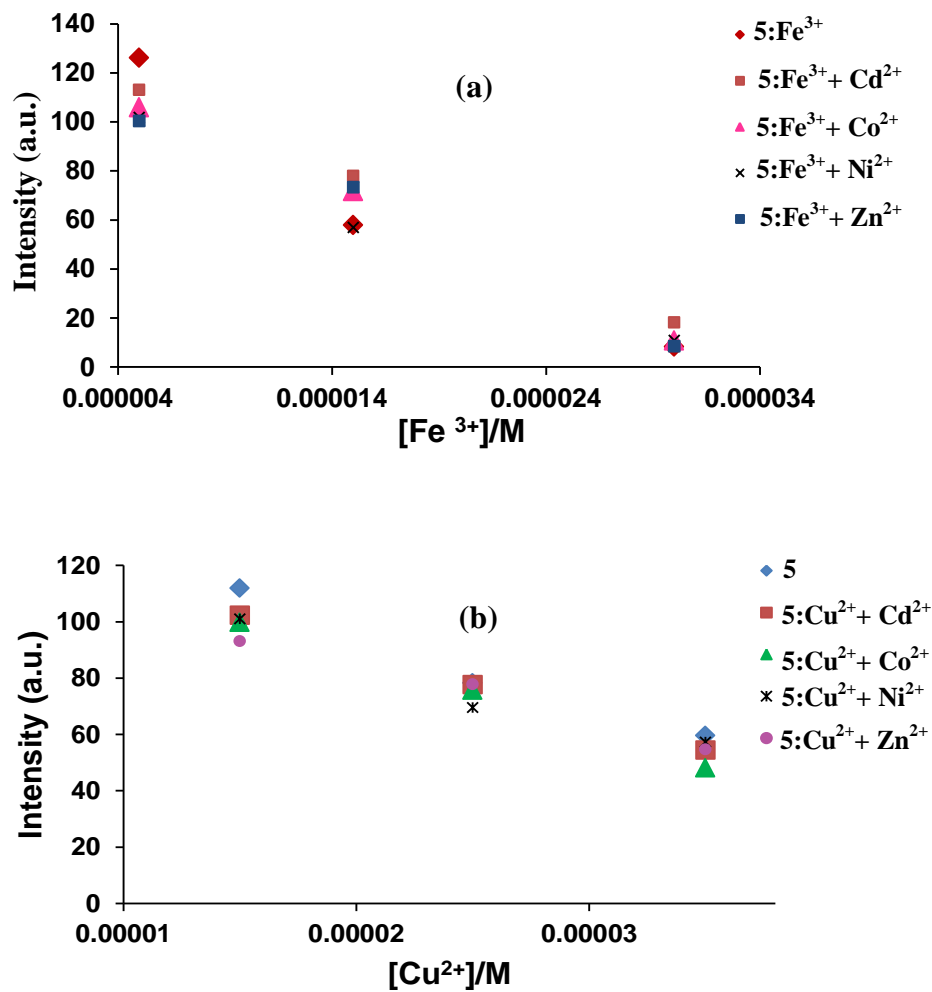


Fig. S3 Changes in the fluorescence intensity of **5** (30 μM in CH_3OH) at 376 nm upon titration with increasing concentration of (a) Fe^{3+} (5, 15 and 30 μM in distilled H_2O); (b) Cu^{2+} (15, 25 and 35 μM distilled H_2O) in the presence of other metal ions (30 μM in distilled H_2O) at pH 7.4.

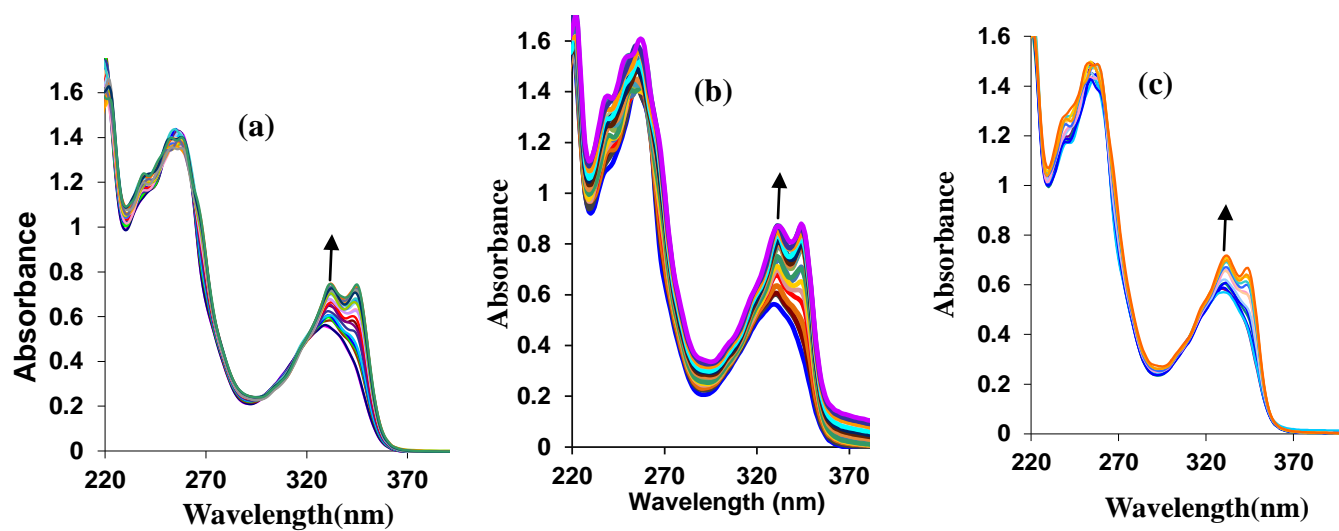


Fig. S4 UV-vis spectra of **5** (30 μ M) in CH₃OH titrated with (a) Hg²⁺ (0-1.5 equiv.); (b) Fe³⁺ (0-1.6 equiv.) and (c) Cu²⁺ (0-1.5 equiv.) in distilled H₂O.

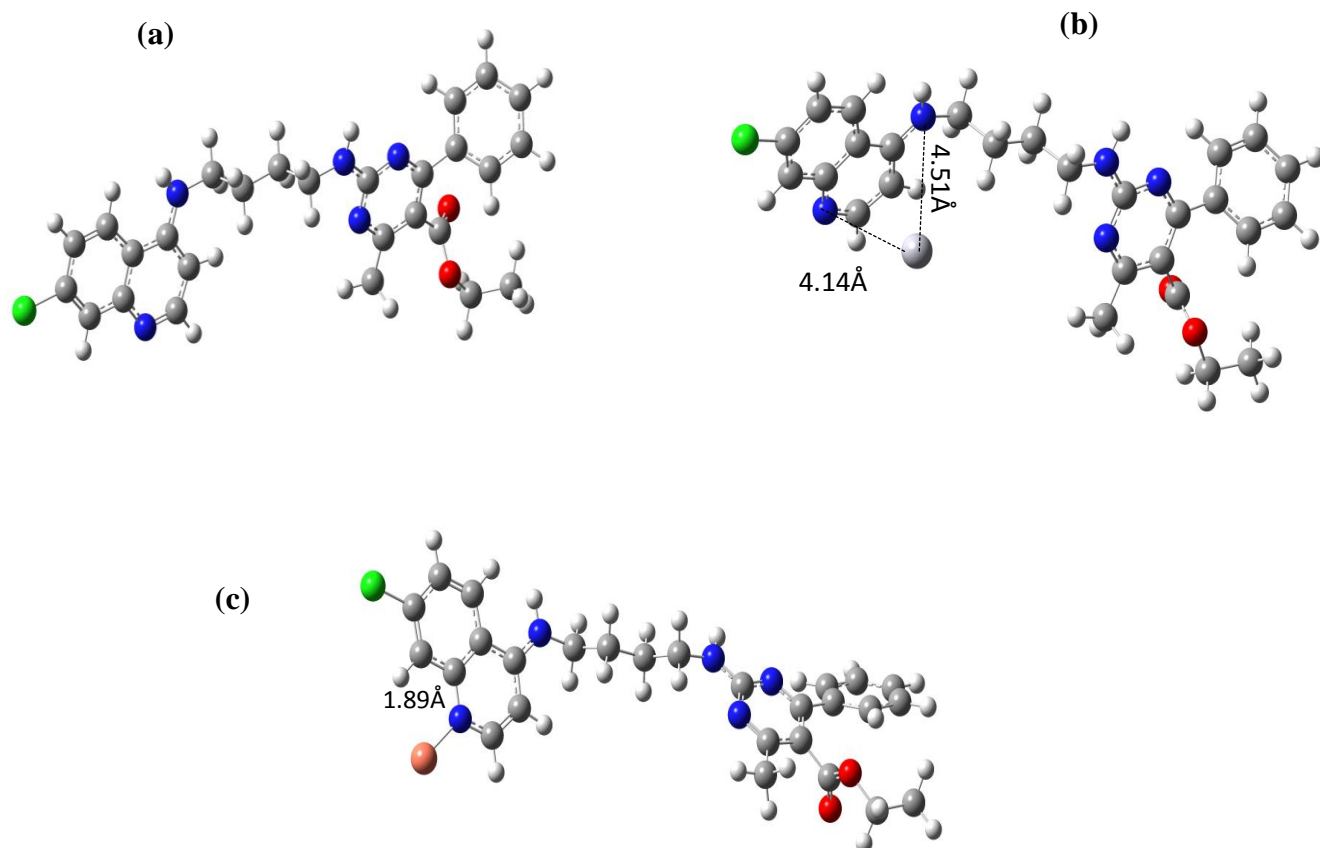


Fig. S5 Optimized structure of (a) **5**; (b) **5**: Hg^{2+} and (c) **5**: Cu^{2+} using Gaussian 09 program. All the bond distances are in Å (angstrom).

Table S1. (a) Selected data of electronic transitions in **5** by TDDFT method at the B3LYP/6-311G* level.^{[a][b]}

State	λ [nm (eV)]	f	Composition of band and CI coefficients
1	319.24 (3.88)	0.1529	H→L, 0.14; H→L+1, 0.67
12	250.43 (4.95)	0.4974	H→L+3, 0.19; H-2→L+2, 0.27; H-4→L+2, 0.24; H-4→L, 0.16; H-7→L+3, 0.10

[a] Calculations were carried out for the lowest 50 excited states, and only energies above 240 nm with $f > 0.15$ are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO.

(b) Cartesian coordinates from the optimized structure of **5** at B3LYP/6-311G*

E = -1930.54a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	2.964919	0.977070	-0.342418
2	6	0	4.306651	0.646077	-0.069131
3	6	0	4.656640	-0.719343	-0.171578
4	6	0	2.488478	-1.229316	-0.680556
5	7	0	2.061543	0.043895	-0.645526
6	7	0	3.747306	-1.647862	-0.463391
7	6	0	6.047798	-1.222114	-0.012083
8	6	0	7.136821	-0.546195	-0.573430
9	6	0	6.272742	-2.432946	0.652973

10	6	0	8.424070	-1.062361	-0.460207
11	6	0	7.561472	-2.938930	0.782284
12	6	0	8.641443	-2.255638	0.225308
13	1	0	9.257354	-0.533896	-0.912068
14	1	0	7.723555	-3.870702	1.314761
15	1	0	9.646569	-2.654049	0.320067
16	6	0	5.263769	1.660922	0.462164
17	8	0	5.870544	1.554062	1.499292
18	8	0	5.356345	2.742968	-0.349829
19	6	0	6.175258	3.844216	0.120072
20	6	0	7.630752	3.665535	-0.275021
21	1	0	6.066995	3.923732	1.202104
22	1	0	8.063105	2.794767	0.219996
23	1	0	7.729429	3.544348	-1.356602
24	1	0	8.207993	4.546313	0.021197
25	6	0	0.169514	-1.971485	-1.212972
26	6	0	-0.671402	-1.953584	0.071033
27	1	0	0.061879	-1.020696	-1.737347
28	1	0	-0.185024	-2.757766	-1.886756
29	6	0	-2.158042	-1.713516	-0.206136
30	1	0	-0.535104	-2.902814	0.604285
31	1	0	-0.280061	-1.168241	0.726130
32	1	0	-2.290613	-0.764250	-0.735535
33	1	0	-2.547308	-2.492571	-0.873978
34	7	0	1.585056	-2.198089	-0.980736

35	1	0	1.949985	-3.136951	-0.966775
36	6	0	-2.998154	-1.701163	1.080252
37	1	0	-2.615706	-0.951417	1.778363
38	1	0	-2.901731	-2.662762	1.593563
39	7	0	-4.420330	-1.465005	0.880816
40	1	0	-4.954200	-2.266922	0.590594
41	6	0	-4.980302	-0.237642	0.637326
42	6	0	-6.391431	-0.127457	0.360176
43	6	0	-4.254445	0.947899	0.678070
44	6	0	-7.277121	-1.231993	0.333535
45	6	0	-6.921942	1.175770	0.111354
46	6	0	-4.901966	2.171148	0.435373
47	1	0	-3.191231	0.952411	0.880469
48	6	0	-8.613916	-1.078945	0.049567
49	1	0	-6.924695	-2.231587	0.566663
50	6	0	-8.302228	1.313302	-0.186015
51	1	0	-4.313701	3.086920	0.469202
52	6	0	-9.114074	0.210353	-0.217956
53	1	0	-9.282003	-1.931175	0.037660
54	1	0	-8.679157	2.309589	-0.377421
55	7	0	-6.178148	2.317271	0.149076
56	17	0	-10.826187	0.389248	-0.586561
57	6	0	2.442040	2.388768	-0.274466
58	1	0	2.874743	3.001565	-1.067547
59	1	0	1.358951	2.372923	-0.384078

60	1	0	2.698463	2.868714	0.673674
61	1	0	5.426617	-2.968551	1.066583
62	1	0	6.975995	0.373972	-1.125033
63	1	0	5.736938	4.723582	-0.353125

Table S2. (a) Selected data of electronic transitions in **5:Hg²⁺** by TDDFT method at the B3LYP/GEN level.^{[a][b]}

State	λ [nm (eV)]	f	Composition of band and CI coefficients
10	318.20 (3.89)	0.1074	H-1→L+1, -0.11; H-1→L+2, -0.29; H→L+1, 0.57; H→L+2, -0.24
11	317.27 (3.90)	0.2290	H-1→L+1, -0.38; H-1→L+2, -0.38; H→L+2, 0.43
25	250.27 (4.95)	0.5858	H-5→L+1, 0.12; H-5→L+2, 0.15; H-2→L+1, 0.41; H-2→L+2, 0.49

[a] Calculations were carried out for the lowest 50 excited states, and only energies above 240 nm with $f > 0.10$ are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO.

(b) Cartesian coordinates from the optimized structure of **5:Hg²⁺** at MPW1PW91/GEN.

E= -2082.63a.u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.444446	-1.033011	0.240201
2	6	0	-5.790781	-0.552123	0.229885
3	6	0	-6.026911	0.760781	-0.280770
4	6	0	-3.785423	0.950344	-0.677280

5	7	0	-3.453098	-0.286383	-0.222160
6	7	0	-5.007447	1.503527	-0.716529
7	6	0	-7.359290	1.365138	-0.336043
8	6	0	-8.518859	0.588534	-0.566543
9	6	0	-7.477794	2.766889	-0.207016
10	6	0	-9.759844	1.200489	-0.655989
11	6	0	-8.722698	3.370000	-0.276501
12	6	0	-9.869613	2.589337	-0.499444
13	1	0	-10.643262	0.607785	-0.854647
14	1	0	-8.815275	4.441461	-0.155430
15	1	0	-10.842103	3.062967	-0.552848
16	6	0	-6.830480	-1.342515	0.957994
17	8	0	-7.187373	-0.984748	2.061092
18	8	0	-7.211378	-2.437292	0.312956
19	6	0	-8.149322	-3.349216	1.014860
20	6	0	-9.584928	-2.923227	0.799994
21	1	0	-7.877900	-3.358028	2.071558
22	1	0	-9.787604	-1.954060	1.260872
23	1	0	-9.829703	-2.882911	-0.263998
24	1	0	-10.249257	-3.656683	1.265181
25	6	0	-1.389128	1.352334	-1.265573
26	6	0	-0.530383	2.154310	-0.261276
27	1	0	-1.307839	0.281522	-1.077394
28	1	0	-1.051949	1.555943	-2.287654
29	6	0	0.956203	1.813650	-0.408244

30	1	0	-0.684604	3.227074	-0.429873
31	1	0	-0.879053	1.932758	0.753671
32	1	0	1.125428	0.746666	-0.221225
33	1	0	1.285049	2.014448	-1.434845
34	7	0	-2.787571	1.714526	-1.169815
35	1	0	-3.087935	2.622675	-1.506531
36	6	0	1.816971	2.644572	0.567891
37	1	0	1.531212	2.454252	1.604246
38	1	0	1.662962	3.711356	0.384529
39	7	0	3.243856	2.389178	0.404246
40	1	0	3.705661	2.950452	-0.298590
41	6	0	3.989925	1.473925	1.039893
42	6	0	5.411347	1.351069	0.785954
43	6	0	3.424666	0.598449	2.009612
44	6	0	6.135016	2.123212	-0.133935
45	6	0	6.125563	0.376438	1.557149
46	6	0	4.241437	-0.287722	2.698678
47	1	0	2.367470	0.622498	2.229727
48	6	0	7.506595	1.943591	-0.314186
49	1	0	5.658140	2.886127	-0.738993
50	6	0	7.522212	0.203919	1.362173
51	1	0	3.816686	-0.938698	3.452823
52	6	0	8.202236	0.979072	0.431888
53	1	0	8.041606	2.551561	-1.031709
54	1	0	8.028018	-0.538556	1.965239

55	7	0	5.558977	-0.411516	2.495763
56	17	0	9.894577	0.766196	0.198625
57	6	0	-4.103786	-2.384121	0.778100
58	1	0	-4.596528	-3.169852	0.198402
59	1	0	-3.026706	-2.535653	0.735584
60	1	0	-4.435081	-2.489574	1.816419
61	1	0	-6.586209	3.355805	-0.037828
62	1	0	-8.439467	-0.478844	-0.729786
63	1	0	-7.932380	-4.316468	0.564637
64	80	0	3.987736	-1.814063	-1.076749

Table S3. (a) Selected data of electronic transitions in **5:Cu²⁺** by TDDFT method at the B3LYP/GEN level.^{[a][b]}

State	λ [nm (eV)]	f	Composition of band and CI coefficients
40	305.59(4.05)	0.2675	H→L+2, -0.31; H→L+3, 0.55
50	276.78 (4.48)	0.2822	H-11→L, 0.19; H-10 →L, -0.22; H-3→L, 0.53; H-1→L+3, 0.15

[a] Calculations were carried out for the lowest 50 excited states, and only energies above 260 nm with $f > 0.03$ are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO

(b) Cartesian coordinates from the optimized structure of **5**:Cu²⁺ at MPW1PW91/GEN.

E= -2126.53a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	4.429817	1.301003	-0.722259
2	6	0	5.703188	0.759331	-0.338205
3	6	0	5.768761	-0.636804	0.011752
4	6	0	3.515636	-0.757697	-0.363024
5	7	0	3.350068	0.541881	-0.742389
6	7	0	4.657242	-1.367697	0.009539
7	6	0	7.010091	-1.304702	0.388784
8	6	0	8.256426	-0.909156	-0.143292
9	6	0	6.951876	-2.406982	1.268116
10	6	0	9.411652	-1.595837	0.204672
11	6	0	8.112729	-3.073948	1.628334
12	6	0	9.346055	-2.670024	1.098947
13	1	0	10.362591	-1.304345	-0.222161
14	1	0	8.067895	-3.904317	2.321094
15	1	0	10.251420	-3.193504	1.380316
16	6	0	6.831372	1.708783	-0.087056
17	8	0	7.125118	1.991501	1.054741
18	8	0	7.357210	2.211288	-1.197156
19	6	0	8.404003	3.251490	-1.040826

20	6	0	9.771761	2.625744	-0.877772
21	1	0	8.132477	3.872277	-0.185700
22	1	0	9.843884	2.058784	0.052889
23	1	0	10.011793	1.976104	-1.722725
24	1	0	10.525601	3.417083	-0.843155
25	6	0	1.080879	-1.171979	-0.792418
26	6	0	0.040028	-1.584911	0.257800
27	1	0	1.074438	-0.097048	-0.973128
28	1	0	0.872393	-1.677753	-1.744039
29	6	0	-1.391058	-1.347210	-0.241753
30	1	0	0.166084	-2.649833	0.495576
31	1	0	0.221236	-1.028260	1.184380
32	1	0	-1.553717	-0.281752	-0.442945
33	1	0	-1.543227	-1.873640	-1.192004
34	7	0	2.427491	-1.541214	-0.374500
35	1	0	2.608875	-2.503655	-0.105404
36	6	0	-2.432169	-1.849322	0.770480
37	1	0	-2.365380	-1.295134	1.711072
38	1	0	-2.231095	-2.896746	1.016145
39	7	0	-3.802842	-1.787905	0.271349
40	1	0	-4.131580	-2.611239	-0.205521
41	6	0	-4.674234	-0.771754	0.433453
42	6	0	-6.029926	-0.880486	-0.059287
43	6	0	-4.322531	0.422593	1.083696
44	6	0	-6.518908	-2.015942	-0.747852

45	6	0	-6.927101	0.202920	0.162821
46	6	0	-5.262187	1.423746	1.260666
47	1	0	-3.324123	0.584605	1.459864
48	6	0	-7.817667	-2.089505	-1.198778
49	1	0	-5.878289	-2.867087	-0.942285
50	6	0	-8.253335	0.115397	-0.303941
51	1	0	-4.975860	2.332378	1.774860
52	6	0	-8.692293	-1.008016	-0.971889
53	1	0	-8.174155	-2.965404	-1.722944
54	1	0	-8.936654	0.942152	-0.137042
55	7	0	-6.529825	1.346831	0.831395
56	17	0	-10.324138	-1.099534	-1.538577
57	6	0	4.278624	2.737964	-1.096190
58	1	0	4.894915	2.980448	-1.966380
59	1	0	3.236101	2.950173	-1.326133
60	1	0	4.600187	3.391936	-0.278676
61	1	0	5.994139	-2.709748	1.670402
62	1	0	8.315683	-0.106822	-0.868037
63	1	0	8.318226	3.825303	-1.962132
64	29	0	-7.758483	2.741840	1.158321

Complete Reference for Gaussian (Reference 13 in manuscript)

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