Supporting Information (SI)

A ferrocene-pyrene based '*turn-on*' chemodosimeter for Cr^{3+} - Application in Bioimaging

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Isolation of the hydrolytic by-products of the titration of 1 with Cr^{3+}

A solution of **1** (3.5 ml, 5.0 x 10^{-6} M) in (THF:water, 1:99 *v/v*) was titrated with increasing concentration (from 2.85 x 10^{-6} M to 5.0 x 10^{-4} M) of an aqueous solution of Cr^{3+} [$Cr(ClO_4)_3 6H_2O$). At the end of the titration, the solution was extracted with hexane (2 ml). Thin layer chromatography (TLC) revealed the presence of 1-ferrocenecarboxaldehyde upon comparison with authentic sample. Further, recording of the mass spectrum and ^{1}H NMR spectrum of the crude product showed the presence of 1-ferrocenecarboxaldehye and 1-aminopyrene, respectively (Fig S8-S9). Subsequently, the aqueous layer was extracted with ethyl acetate (2 ml). TLC analysis of the ethyl acetate layer revealed the presence of 1-aminopyrene upon comparison with authentic sample.

In order to isolate the by-products, to a solution of **1** (0.002 g) in THF:H_2O (1:99, *v/v*, 0.7 ml) an aqueous solution of $Cr(ClO_4)_3.6H_2O$ (0.1 M, 48 µl) was added and the solution stirred for two hours. After extractive workup of the reaction, as described above, 1-ferrocenecarboxaldehyde and 1-aminopyrene was isolated in quantity enough for recording the spectroscopic data as well as TLC comparison with authentic samples.

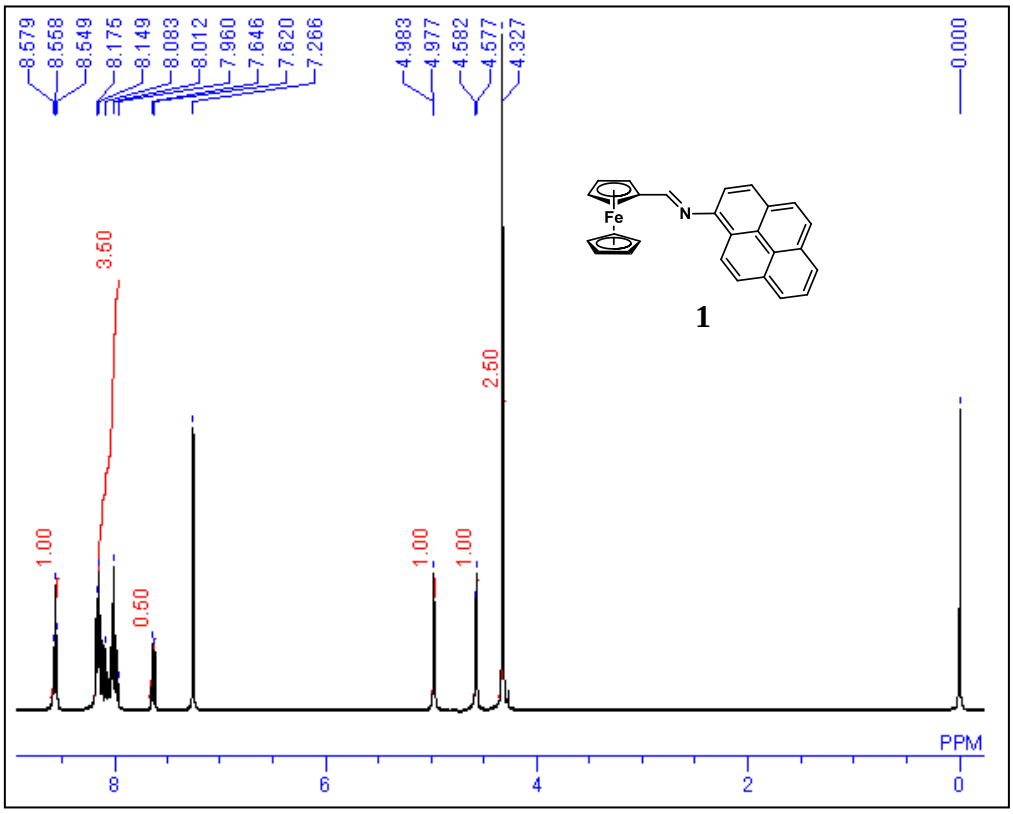

Fig. S1 ^{1}H NMR spectra of **1** in $CDCl_3$.

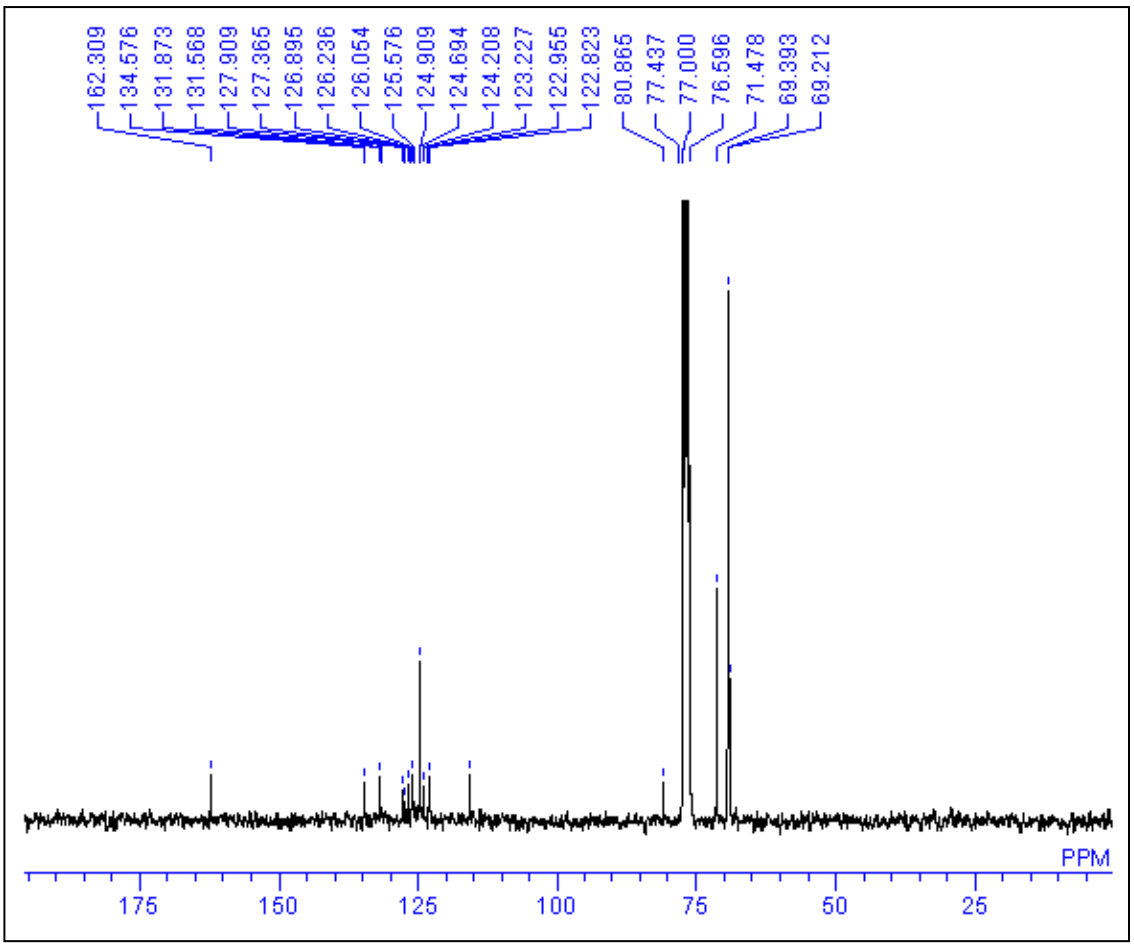

Fig. S2 ^{13}C NMR spectra of **1** in $CDCl_3$.

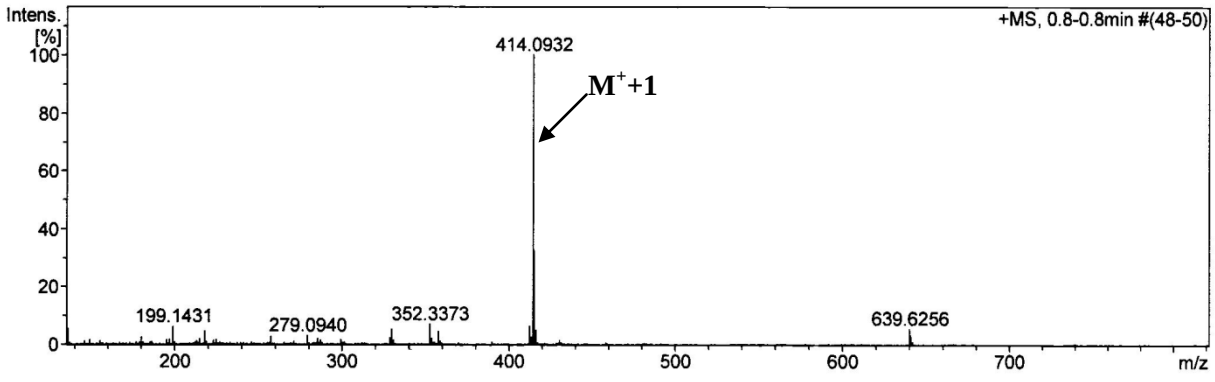

Fig. S3 Mass spectra of **1** (solid).

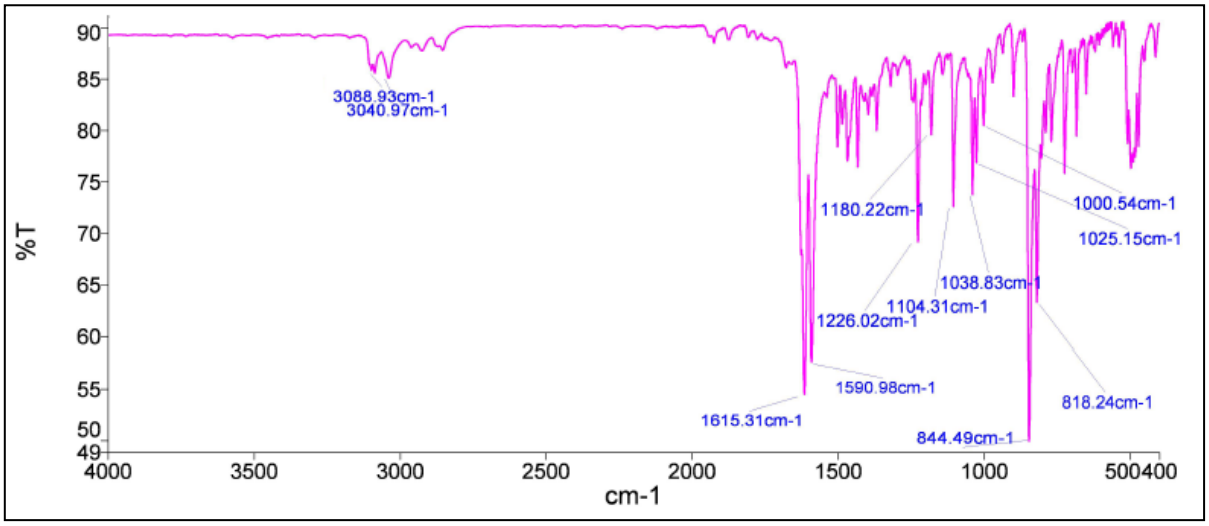

Fig. S4 IR (KBr) spectra of **1**.

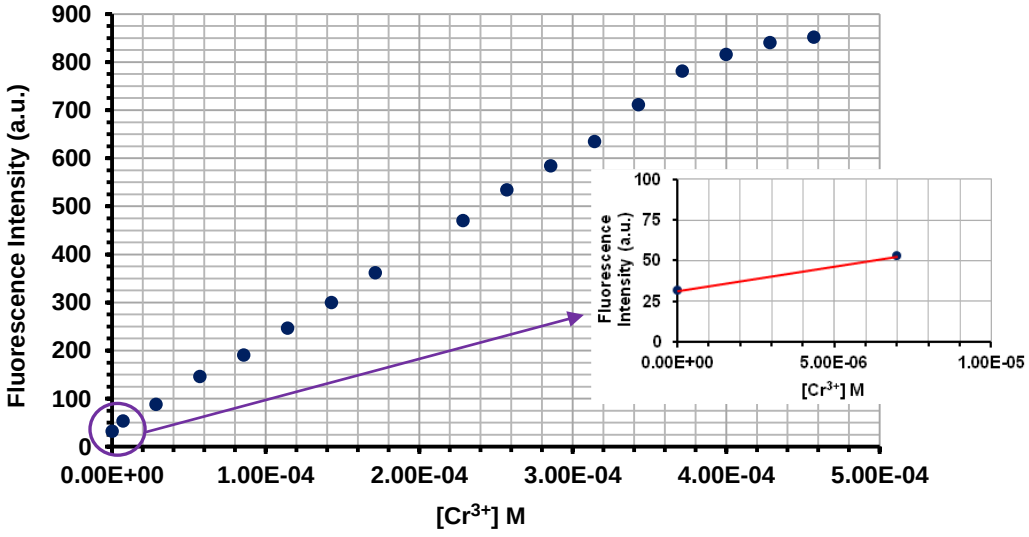

Fig. S5 Increase in the emission intensity at 442 nm of **1** (5 x 10^{-6} M, in THF) upon addition of increasing amount of Cr^{3+} (2.85 x 10^{-6} M - 5.0 x 10^{-4} M, in H_2O) in THF:H_2O. (The *v/v* ratio of THF and H_2O in the mixture was 1:99). Inset: Graph depicting 1 x 10^{-6} M concentration (detection limit) of Cr^{3+} to be the lowest to be detected by the chemodosimeter **1**.

Table S1. Selected data of electronic transitions in **1** by TD-DFT calculations using B3LYP/Gen method.

λ[nm/ (eV)]	f^a	Composition of bands and CI[b] coefficients
498 (2.49)	0.0129	H-2 → L+3, 0.42
406 (3.05)	0.6992	H → L, 0.67; H → L+1, 0.11
296 (4.18)	0.2721	H -3 → L, 0.47; H → L+4, 0.31
290 (4.28)	0.1043	H → L+4, 0.48
246 (5.04)	0.1534	H-5 → L+2, 0.48

[a]*f*- oscillator strength, [b]CI- configurational intergration coefficient, H - HOMO, L - LUMO.

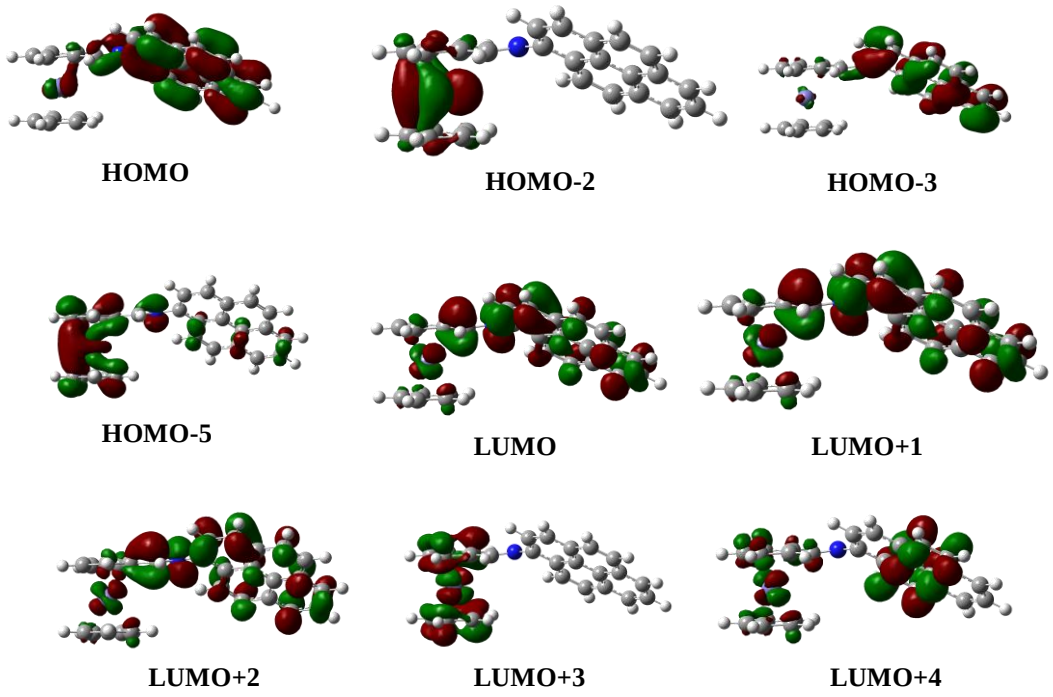

Fig. S6 Frontier molecular orbitals of **1** contributing to UV-visible absorption bands (isovalue=0.03).

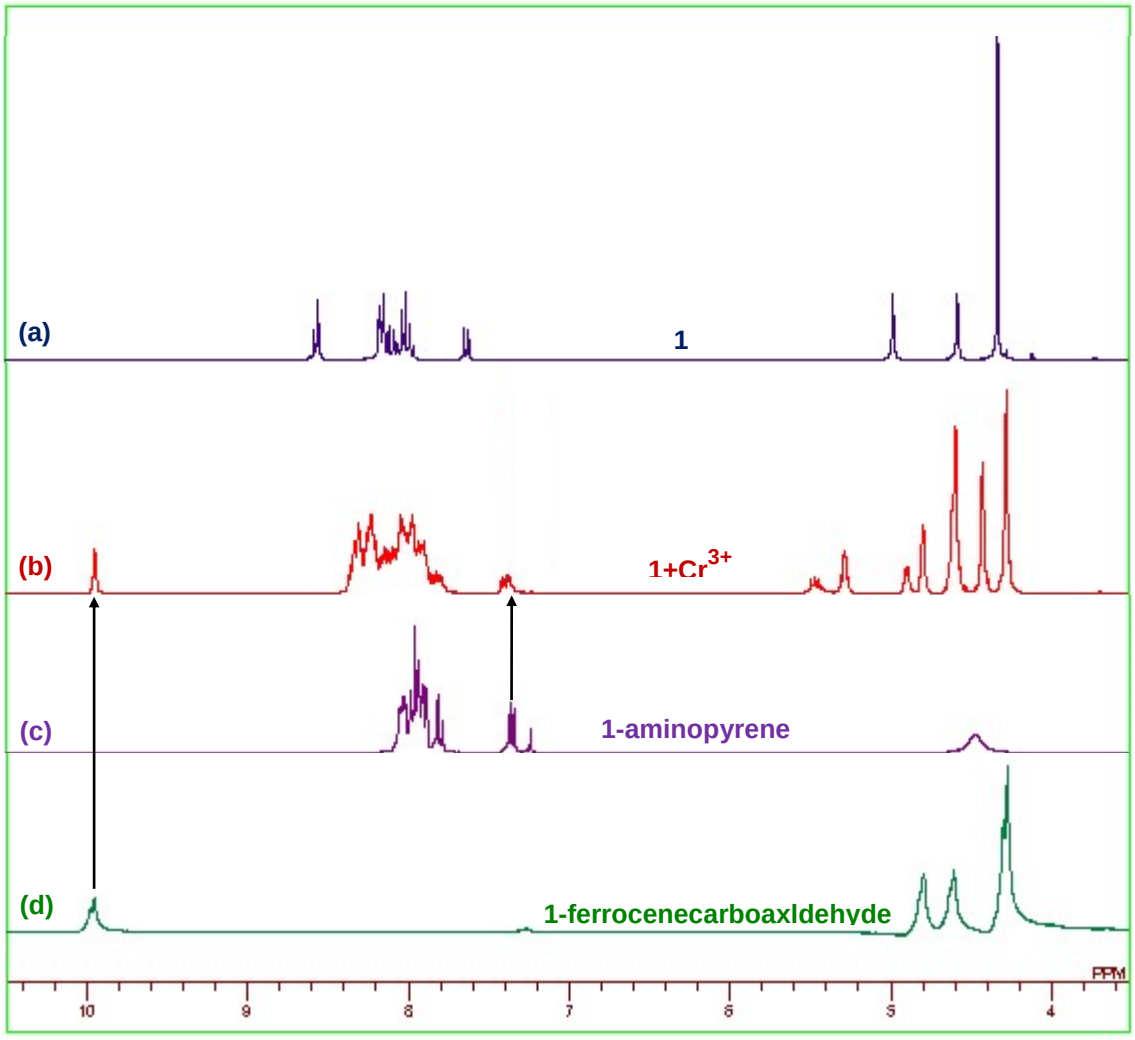

Fig. S7 ^{1}H NMR spectra of (a) **1**, (b) **1**+Cr^{3+}, (c) 1-aminopyrene and (c) 1-ferrocenecarboxaldehyde.

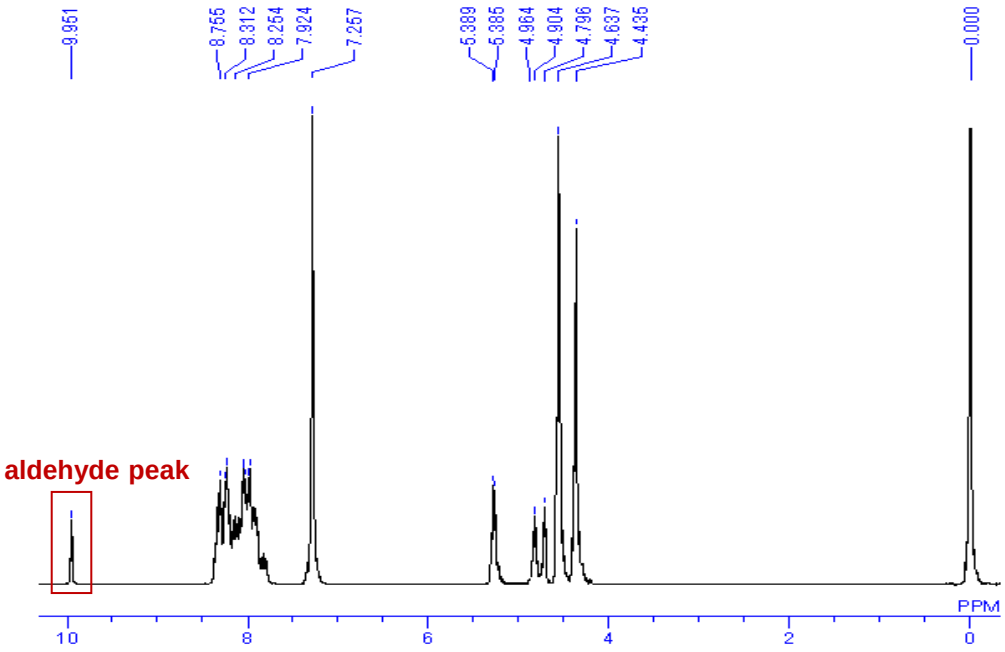

Fig. S8 Changes in the ^{1}H NMR spectrum of **1** (in $CDCl_3$) upon addition of Cr^{3+} (1 equiv., in CD_3CN) perchlorate salt, recorded after equilibration (24 h).

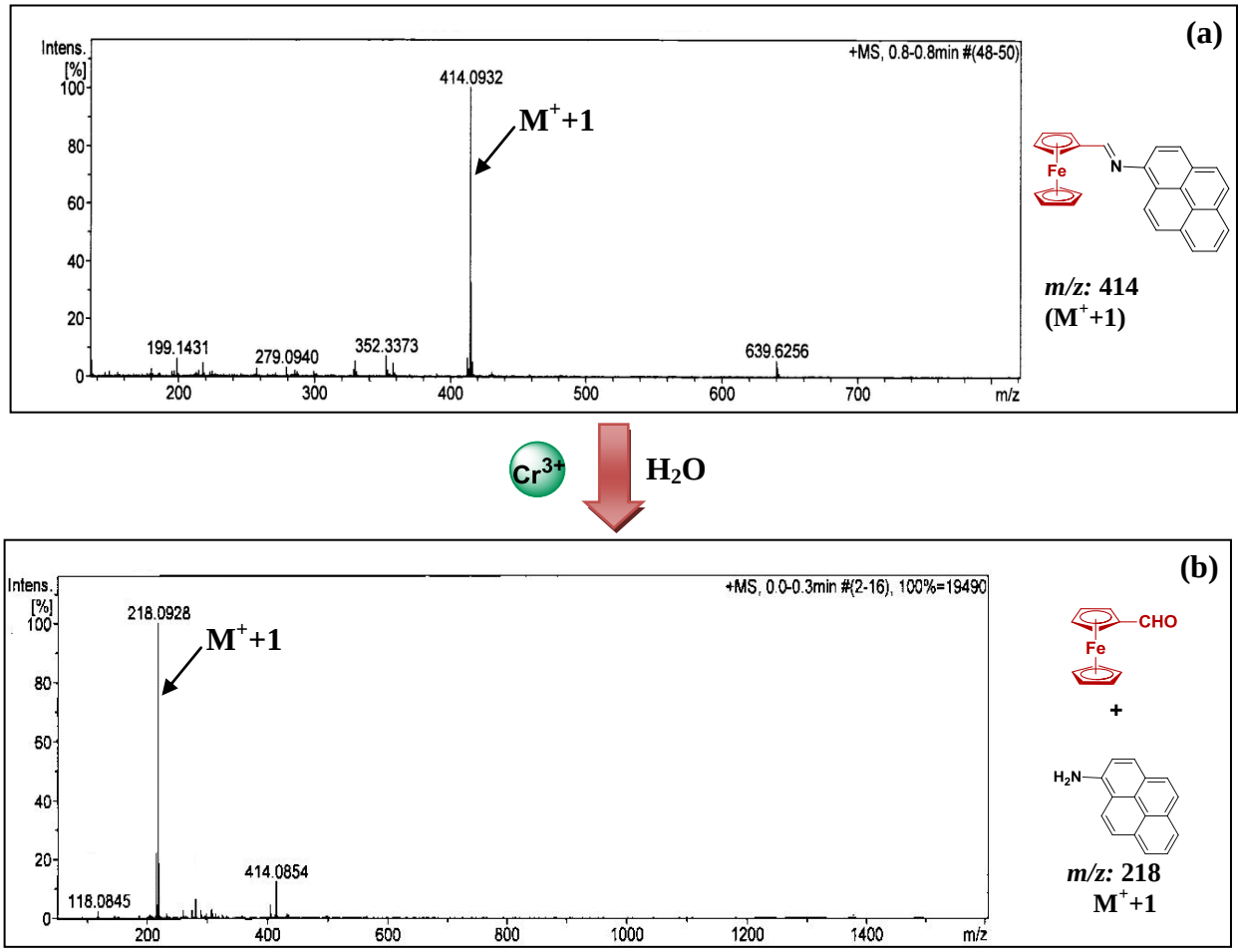

Fig. S9 Mass spectra of (a) **1** and (b) **1** upon addition of Cr^{3+} in THF:H_2O (1:99/*v*/*v*).

Table S2: Cartesian coordinates of **1**.

SCF Done: E (RB3LYP) = -1218.55825268 a.u. after 10 cycles.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	26	-4.020996	-0.253293	0.105144
2	6	-1.388339	1.471496	-0.14879
3	1	-1.262641	2.063628	0.770524
4	6	-2.763211	1.261395	-0.579942
5	6	-3.222745	0.462023	-1.681011
6	1	-2.583800	-0.106271	-2.342006
7	6	-4.642022	0.543843	-1.722785
8	1	-5.286336	0.029774	-2.423948
9	6	-5.076597	1.380011	-0.647087
10	1	-6.103356	1.611341	-0.396419
11	6	-3.923880	1.818463	0.062314
12	1	-3.913803	2.451574	0.940369
13	6	-2.979358	-1.487740	1.421653
14	1	-1.939027	-1.350119	1.685885
15	6	-3.467326	-2.246898	0.316436
16	1	-2.862484	-2.788181	-0.398824
17	6	-4.890966	-2.129179	0.295228
18	1	-5.553958	-2.564518	-0.440829
19	6	-5.281464	-1.296626	1.387472
20	6	-4.099689	-0.898280	2.083113
21	1	-4.058620	-0.244003	2.944113
22	7	-0.381876	1.004909	-0.783636
23	6	0.921758	1.312207	-0.373417
24	6	1.910411	0.294418	-0.433535
25	6	1.287113	2.607333	0.032643
26	6	3.246133	0.597753	-0.031748
27	6	1.604957	-1.039903	-0.866204
28	6	2.592301	2.904086	0.405367
29	1	0.537711	3.393512	0.018307
30	6	4.246240	-0.422073	-0.055871
31	6	3.591297	1.917654	0.394270
32	6	2.561489	-2.010639	-0.890107
33	1	0.589731	-1.250269	-1.184080
34	1	2.850422	3.917189	0.704759
35	6	3.912170	-1.743971	-0.481860

36	6	5.585593	-0.123317	0.345404
37	6	4.945805	2.189465	0.784855
38	1	2.314220	-3.014523	-1.227656
39	6	4.912039	-2.731560	-0.494167
40	6	6.550183	-1.143671	0.315841
41	6	5.898198	1.215753	0.764251
42	1	5.197172	3.198570	1.103130
43	6	6.214254	-2.431959	-0.098934
44	1	4.657278	-3.737741	-0.818229
45	1	7.569014	-0.917200	0.620879
46	1	6.919005	1.437201	1.066405
47	1	6.974675	-3.208214	-0.114849
48	1	-6.292221	-0.990989	1.623893

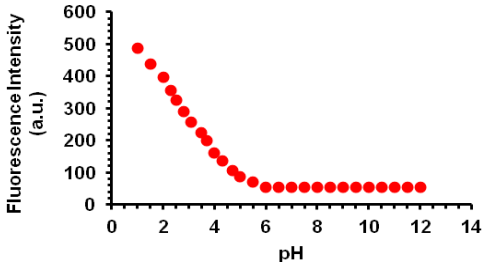

Fig. S10 Changes in the emission of **1** (5.0 x 10^{-6} M) upon pH titration with HCl (0.001 M) and NaOH (0.01 M) in THF:H_2O (1:99/*v/v*) at 442 nm.

Complete Reference 12

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.