Exploitation of a 1D coordination polymer as a fascinating portable kit for an eye-catching fluorometric response towards tri-positive cations sensing

Sourav Datta,[a,b] Sunanda Dey,[c] Chittaranjan Sinha,[c] Basudeb Dutta,*[a,d] Priyabrata Banerjee,*[b,e] and Mohammad Hedayetullah Mir*[a]

[a]Department of Chemistry, Aliah University, New Town, Kolkata 700 160, India.

[b]Electric Mobility & Tribology Research Group, CSIR-Central Mechanical Engineering Research Institute, Mahatma Gandhi Avenue, Durgapur 713 209, India.

[c]Department of Chemistry, Jadavpur University, Kolkata 700 032, India.

[d]Institute for Integrated Cell-Material Sciences, Kyoto University, Yoshida Ushinomiya-cho, Sakyo-ku, Kyoto 606-8501, Japan.

[e]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India.

Supporting Information

Experimental section

Materials

4-(1-Naphthylvinyl)pyridine (4-nvp) was purchased from TCI Chemicals (India) Pvt. Ltd and potassium thiocyanate (KSCN) was purchased from Alfa Aesar. High-purity cadmium(II) nitrate tetrahydrate was purchased from Sigma-Aldrich Co. All other chemicals were used for experiments including solvents were of AR grade and used without further purification.

General methods

During characterization, an infrared (IR) spectrum (4000–500 cm^{-1}) of the proposed compound was obtained using a KBr pellet by a Perkin Elmer Spectrum RX1 spectrometer. ^{1}H-NMR spectra were recorded on Bruker 400 MHz instruments respectively For NMR spectra using DMSO-d_6 solvent. For execution of solution state fluorescence experiments, the Varian Cary Eclipse fluorescence was employed. The scanning electron microscopy (SEM) analysis was carried out in sigma Zeiss oxford instrument. XPS measurements were performed by using an X–ray photoelectron spectroscopic (XPS, Omicron) method. Thermogravimetric Analysis (TGA) was performed using a NETZSCH STA 449F1 Jupiter instrument Perkin Elmer Pyris^{TM} 1 TGA analyzer in between the temperature range of 20–1000°C at ramping rate of 10.0 °C/min in an environment of N$_2$ atmosphere with an average flow rate of 20.0 mL/min.

Synthesis of compound

A solution of 4-nvp (0.046 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered to a solution of Cd(NO$_3$)$_2$·4H$_2$O (0.062 g, 0.2 mmol), in H2O (2 mL) using 2 mL solution of DMF followed by layering of KSCN (0.0194 g, 0.2 mmol) in 2 mL EtOH. The coloress block shaped crystals of [Cd(NCS)$_2$(4-nvp)$_2$]$_n$, (**1**) were obtained after five days (0.284 g, Yield 65%).

Single crystal X-ray crystallography

Proper shaped single crystal of compound **1** of suitable dimensions was used for single crystal X-ray diffraction (SCXRD) and data collection using a Bruker SMART APEX II diffractometer furnished with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The molecular arrangement of the single crystal was solved using the SHELX-97 package.[1] Non-hydrogen atoms of the diffracted compound were refined with anisotropic thermal parameters. All the

Hydrogen atoms were stayed in their geometrically perfect positions and constrained to ride on their parent atoms.The crystallographic data for compound **1** is summarized and depicted in Table S1, ESI†). The selected bond lengths and bond angles around the coordination atmosphere of the metal ion are also given in Table S2, ESI†.

General method for fluorometric sensing

The synthesized compound **1** was ground finely. Then 5 mg of it was deepened in 5 ml 1:1 CH_3CN/H_2O (v/v) and sonicated for 30 min to get the suspension of 1 mg/ml solution. Then, the suspension was used as a stock solution for photoluminescence measurements. All the required metal cations (K^+, Hg^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, Pd^{2+}, Al^{3+}, Na^+, Cd^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+} and Mg^{2+}) were made 1.0×10^{-4} M using in deionized water. To check the fluorescence selectivity and sensitivity of **1** towards metal ions, 100 μL stock solution of **1** was added into the solution of aforementioned metal ions.

Table S1. Crystal data and refinement parameters for compound **1**

Formula	$C_{36}H_{26}CdN_4S_2$ (**1**)
fw	691.13
crystsyst	triclinic
space group	$P\bar{1}$
a (Å)	5.9560(6)
b (Å)	9.0721(10)
c (Å)	15.5189(17)
α (deg)	73.890(3)
β (deg)	83.762(3)
γ (deg)	75.613(3)
V (Å^3)	779.64(15)
Z	1
D_{calcd}(g/cm^3)	1.472
μ(mm^{-1})	0.866
λ(Å)	0.71073
data[$I > 2\sigma(I)$]/params	3438/205
GOF on F^2	1.100
final R indices[$I > 2\sigma(I)$]^{a,b}	$R1 = 0.0623$ $wR2 = 0.1646$

$^a R1 = \Sigma||F_o| \quad |F_c||/ \Sigma|F_o|, ^b wR2 = [\Sigma w(F_o^2 \quad F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths and bond angles **1.**

Bond length (Å)	
Cd(1) - N(1)	2.367(4)
Cd(1) - N(1)d	2.367(4)
Cd(1) - N(2)	2.345(4)
Cd(1) - N(2)d	2.345(4)
Cd(1) - S(1)b	2.7461(12)
Cd(1) - S(1)c	2.7461(12)
Bond angle (°)	
N(1) - Cd(1) - N(1)d	180.00
N(1) - Cd(1) - S(1)b	89.92(9)
N(1) - Cd(1) - S(1)c	90.08(9)
N(1) - Cd(1) - N(2)	90.23(14)
N(1)d - Cd(1) - N(2)	89.77(14)
N(2) - Cd(1) - S(1)b	92.75(10)
N(2) - Cd(1) - S(1)c	87.25(10)
S(1)b - Cd(1) - S(1)c	180.00

Symmetry Code: b = -x, -y, 2-z; c = 1+x, y, z; d = 1-x, -y, 2-z

Table S3. Geometric features (distances, Å and angles, ^{0}) of the Hydrogen bonding and $\pi\cdots\pi$ stacking interactions in compound **1**.

Hydrogen bonding in 1(Å)				
D—H⋯A	Distance (Å) D—H	Distance (Å) H⋯A	Distance (Å) D⋅⋅A	Angle (°) ∠D—H⋯A
C(1)-H(1)⋯N(2)	0.9300	2.6000	3.270(6)	129.00
C(1)-H(1)⋯N(3)	0.9300	2.6200	3.036(7)	108.00
$\pi\cdots\pi$ **stacking interactions in 1(Å)**				
Cg(Ring I)⋯Cg(Ring J)	**Cg⋯Cg** **(Å)**			
Cg(2)⋯Cg(3)	4.191(4)			
C-H⋯π interactions in 1(Å)				
H⋯Cg(Ring J)	**H⋯Cg**			
H(12)⋯Cg(1)	2.95			
H(2)⋯Cg(2)	2.82			
H(4)⋯Cg(3)	2.99			

Cg(1) = Centre of gravity of the ring [N(1)-C(1)-C(2)-C(3)-C(4)-C(5)]
Cg(2) = Centre of gravity of the ring [C(8)-C(9)-C(10)-C(11)-C(12)-C(13)]
Cg(3) = Centre of gravity of the ring [C(14)-C(15)-C(16)-C(17)-C(9)-C(10)]
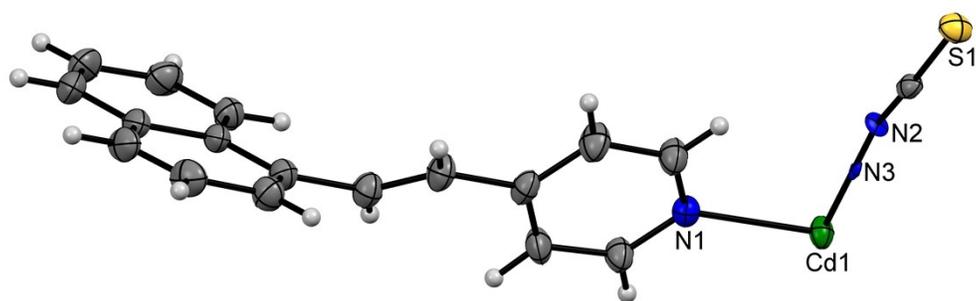
Fig. S1 Asymmetric unit of **1** with 30% thermal ellipsoid probability.
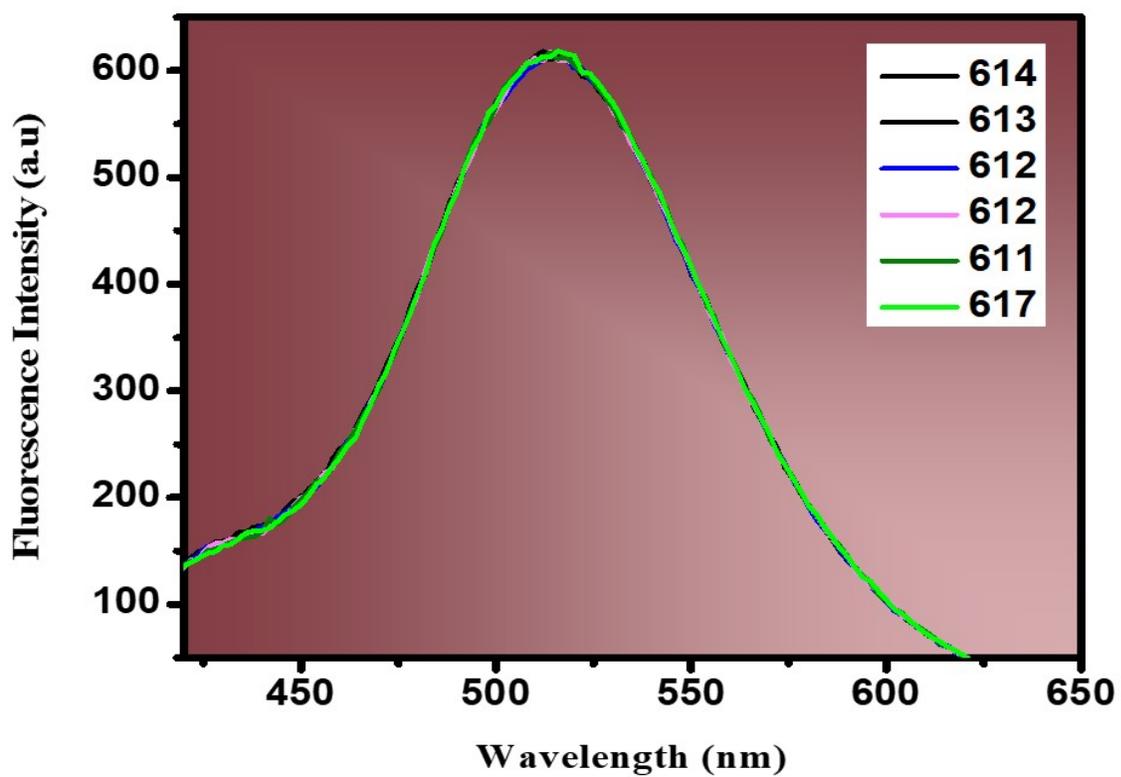
Fig. S2 Plot of blank titration of **1** using high concentration in 1:1 CH_3CN/H_2O (v/v), λ_{ex}, 400 nm.
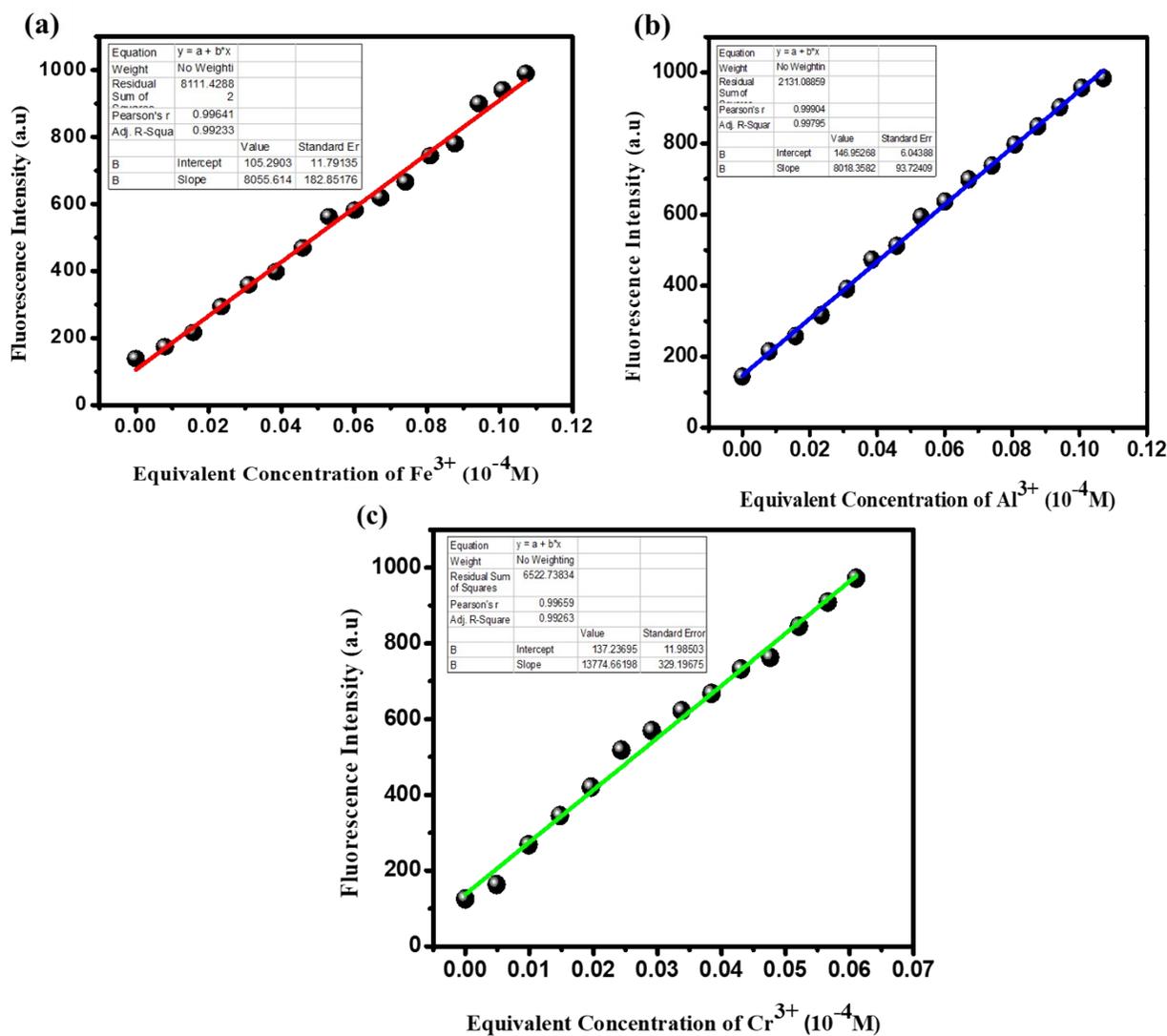
Fig. S3 Calculation of limit of detection (LOD) for M^{3+} (a) Fe^{3+}, (b) Al^{3+} and (c) Cr^{3+}.

Table S4. Limit of detection (LOD) for **1** for detection corresponding metal ions

Name	Standard Deviation (σ)	Slope (k)	Detection limit ($3\sigma/k$)
1+ Fe^{3+}	1.98	8055.61	73.7 nM
1+ Al^{3+}	1.98	8018.35	74.1 nM
1+ Cr^{3+}	1.98	13774.69	43.1 nM
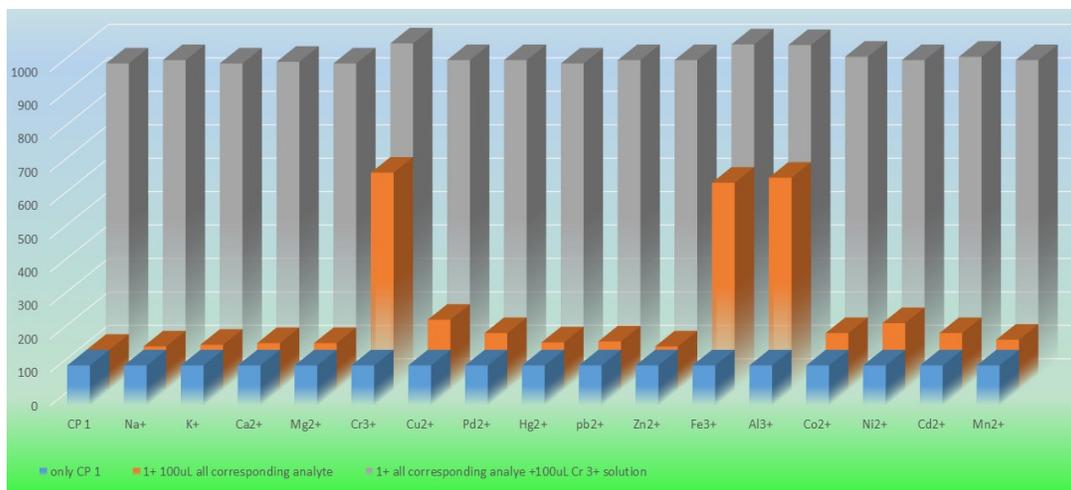
Fig. S4 Interference studies by various metal ions on Cr^{3+} ions sensitivity.
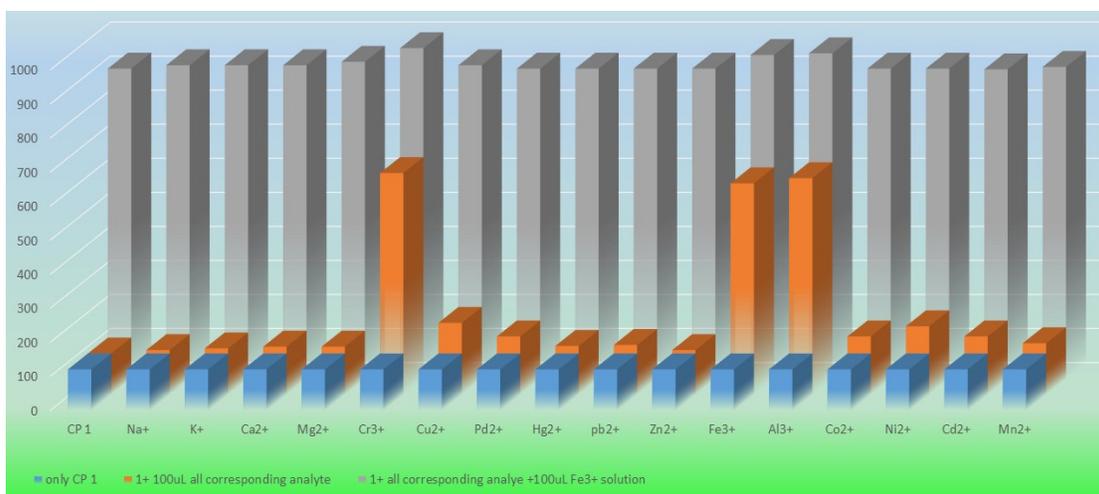
Fig. S5 Interference studies by various metal ions on Fe^{3+} ions sensitivity.
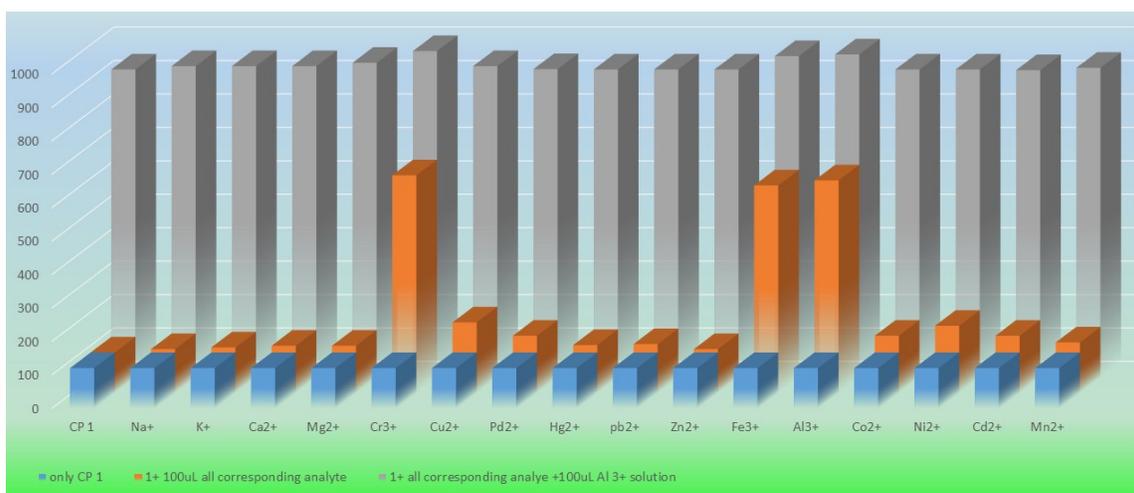
Fig. S6 Interference studies by various metal ions on Al^{3+} ions sensitivity.
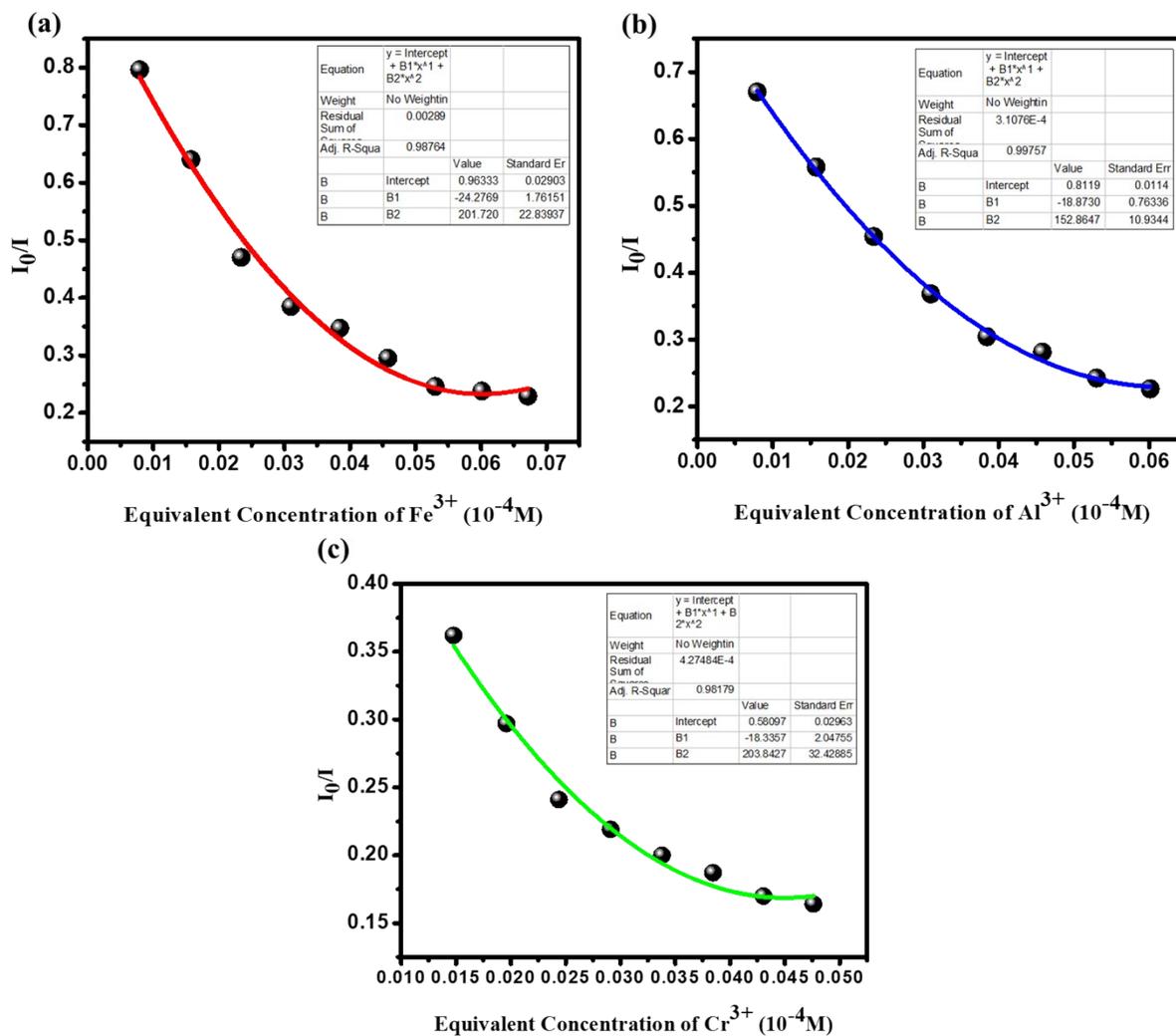
Fig. S7 Calculation of fluorescence enhancement constant (K_{sv}) according to modified Stern−Volmer (SV) equation for M^{3+} (a) Fe^{3+}, (b) Al^{3+} and (c) Cr^{3+}.
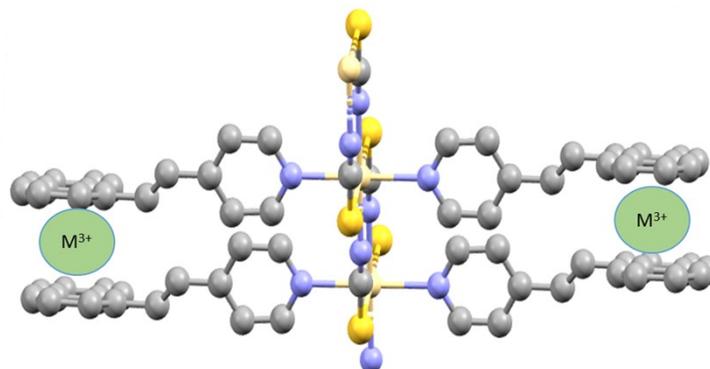
Fig. S8 Trivalent metals M^{3+} (Fe^{3+}, Al^{3+} and Cr^{3+}) locked between two adjacent dangling naphthalene moieties of **1**.
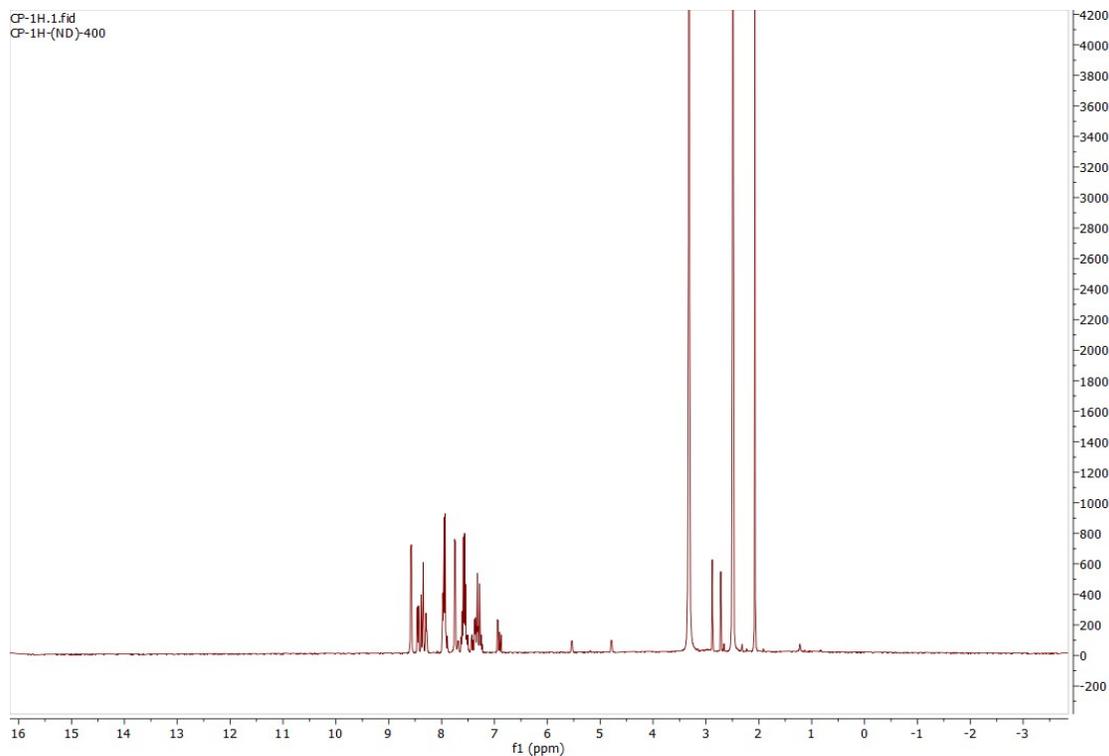
Fig. S9 ^{1}H NMR spectrum of compound **1** in DMSO-d_6.
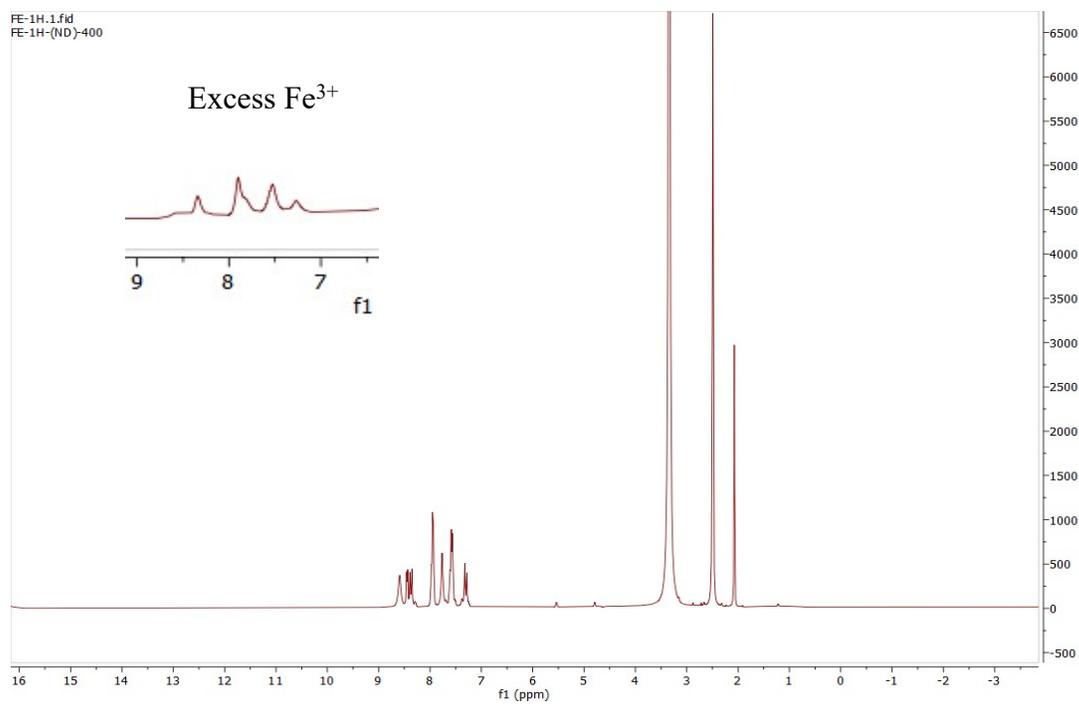
Fig. S10 ^{1}H NMR spectra (in DMSO-d_6) of compound **1** with Fe^{3+} and partial spectra (inset) of Compound **1** with excess Fe^{3+} (in DMSO-d_6).
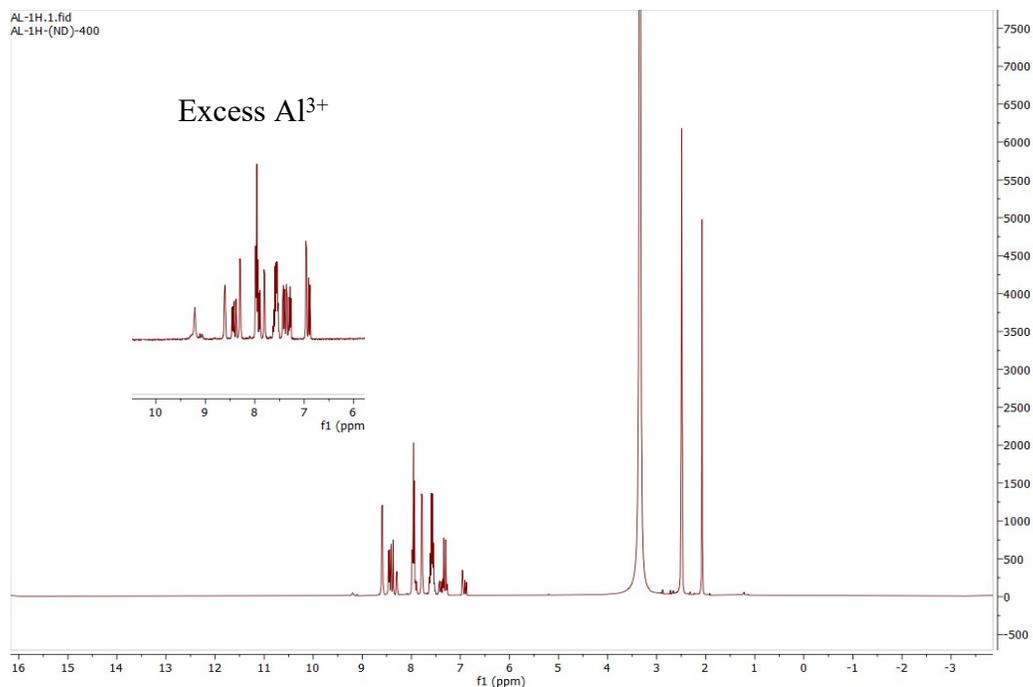
Fig. S11 1H NMR spectra (in DMSO-d_6) of compound **1** with Al^{3+} and partial spectra (inset) of Compound **1** with excess Al^{3+} (in DMSO-d_6).
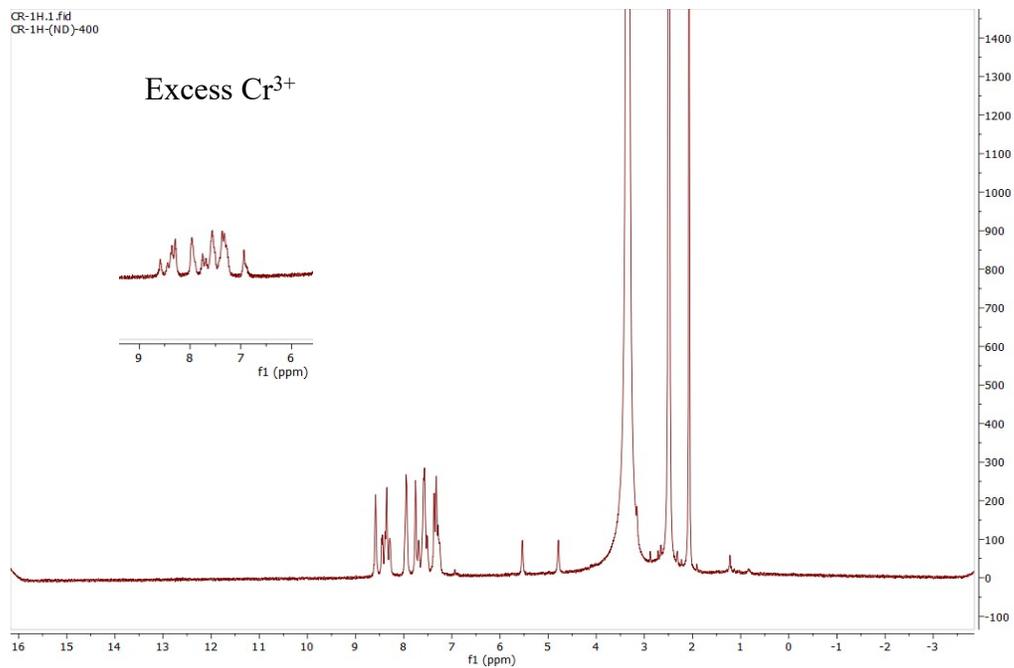
Fig. S12 ^{1}H NMR spectra (in DMSO-d_6) of compound **1** with Cr^{3+} and partial spectra (inset) of Compound **1** with excess Cr^{3+} (in DMSO-d_6).
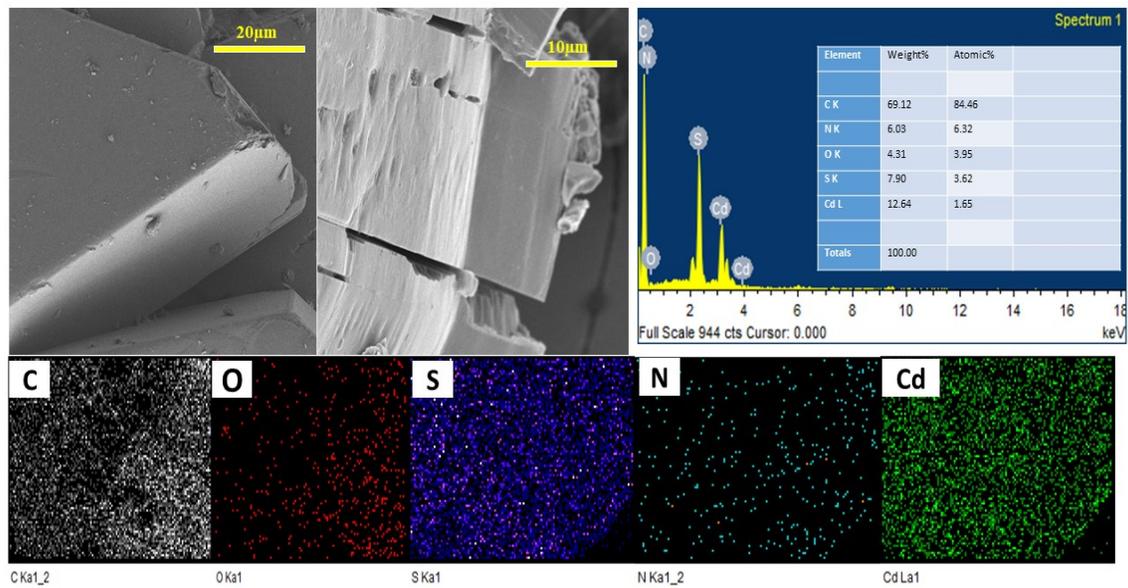
Fig. S13 SEM and EDX of compound **1.**

Element	Weight%	Atomic%
C K	69.12	84.46
N K	6.03	6.32
O K	4.31	3.95
S K	7.90	3.62
Cd L	12.64	1.65
Totals	100.00	
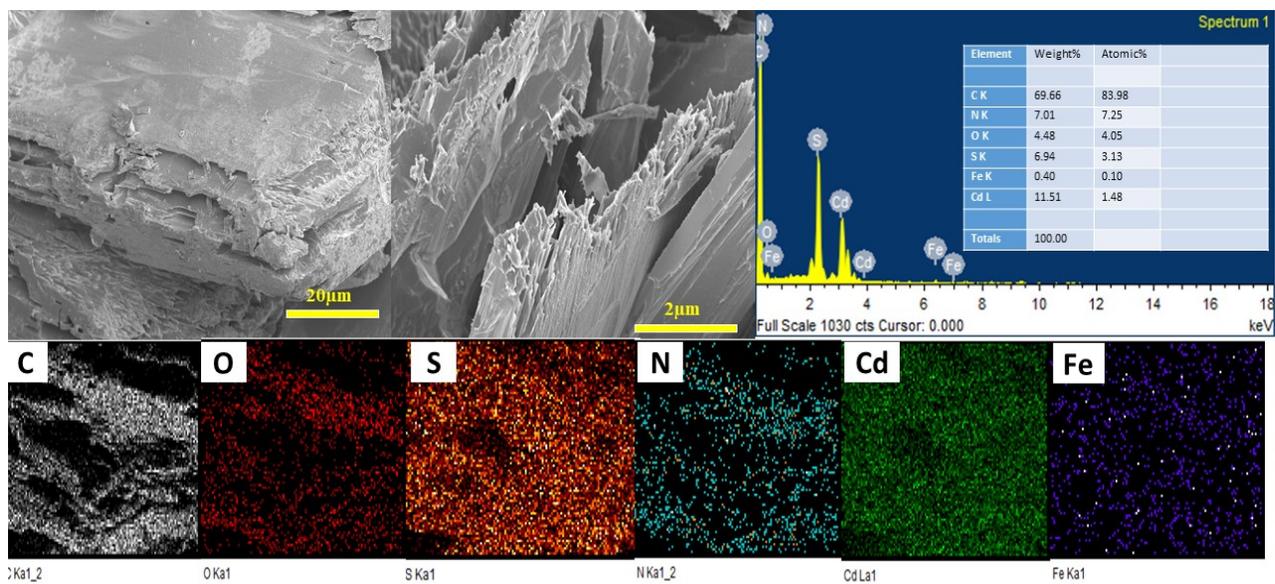
Fig. S14 SEM and EDX of compound **1** + Fe^{3+}.

Element	Weight%	Atomic%
C K	69.66	83.98
N K	7.01	7.25
O K	4.48	4.05
S K	6.94	3.13
Fe K	0.40	0.10
Cd L	11.51	1.48
Totals	100.00	

Element	Weight%	Atomic%
C K	60.57	80.91
N K	3.72	4.26
O K	7.07	7.09
S K	9.57	4.79
Cr K	1.32	0.41
Cd L	17.74	2.53
Totals	100.00	
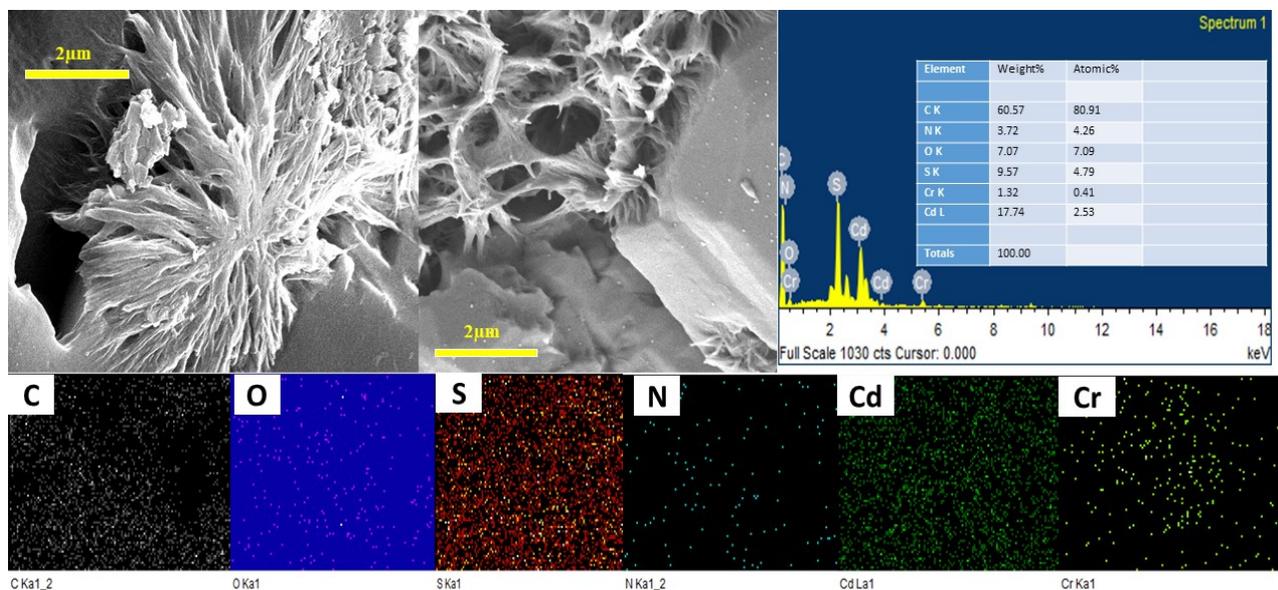
Fig. S15 SEM and EDX of compound **1** + Cr^{3+}.

Element	Weight%	Atomic%
C K	70.58	87.45
N K	1.08	1.14
O K	6.37	5.92
Al K	0.20	0.11
S K	7.50	3.48
Cd L	14.27	1.89
Totals	100.00	
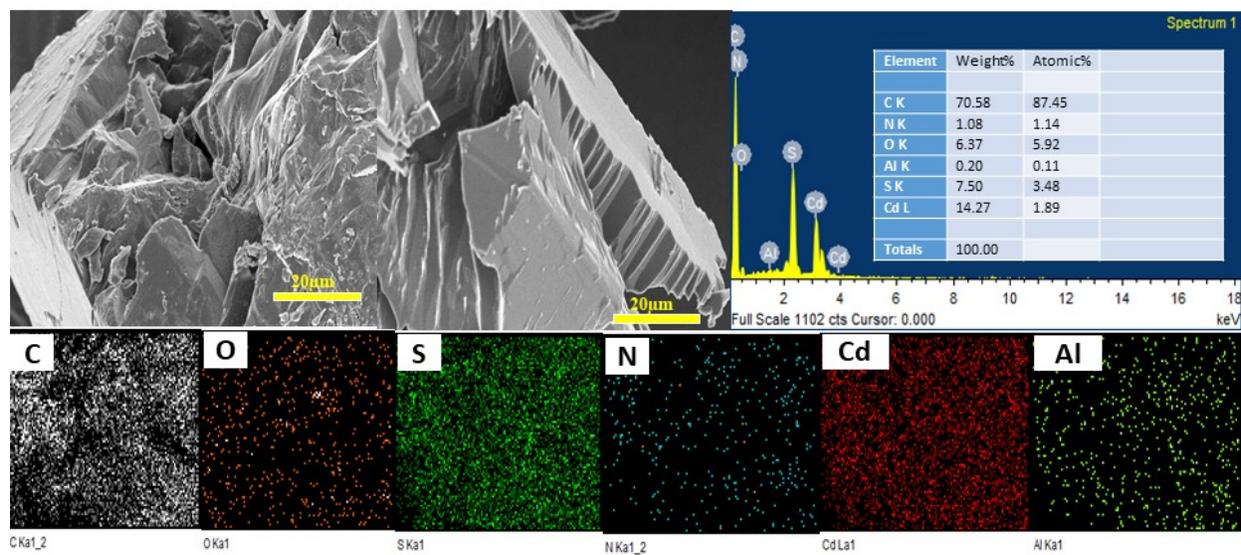
Fig. S16 SEM and EDX of compound **1** + Al^{3+}.
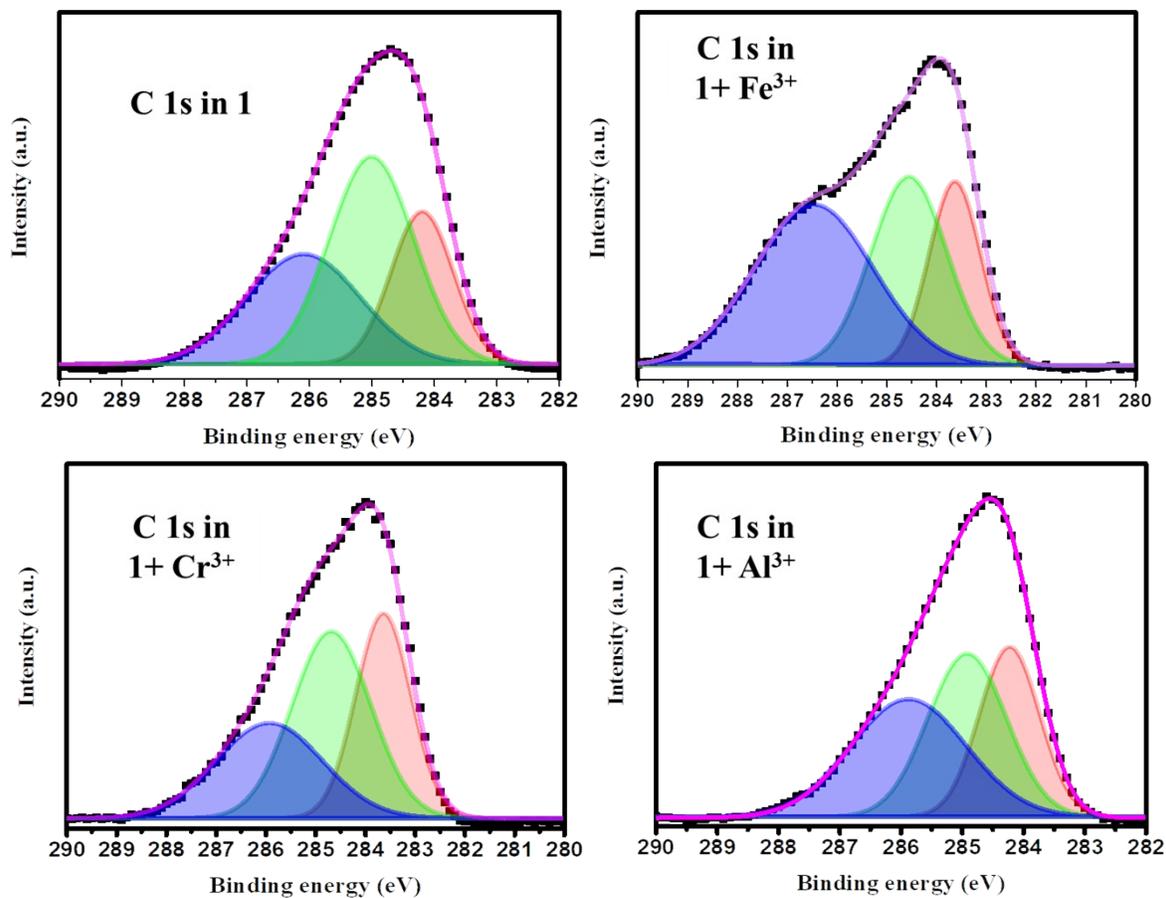
Fig. S17 High-resolution XPS spectra of C 1s in each cases.(C=C(blue), C-C (green), C-N(red)).
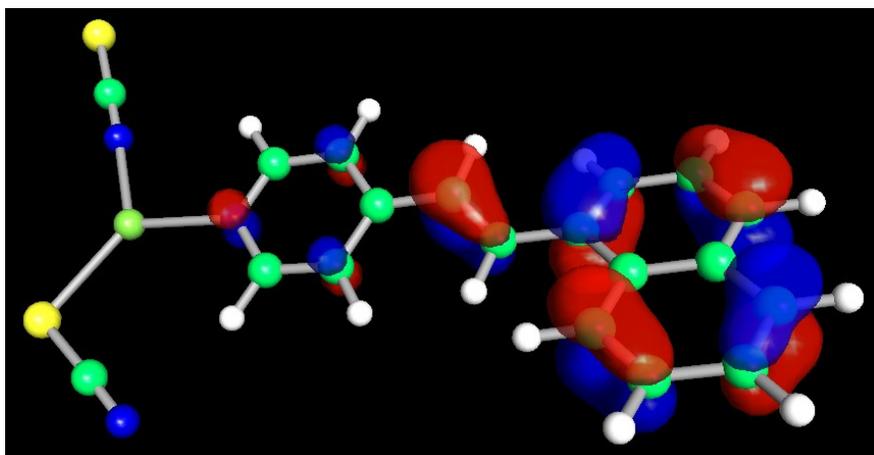
Fig. S18 HOMO of compound **1.**
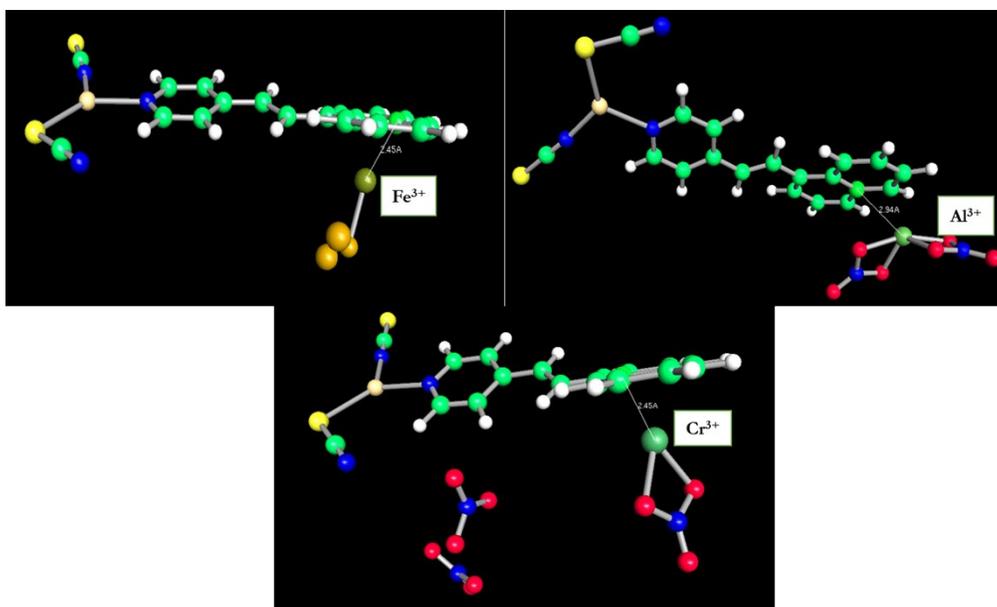
Fig. S19 Geometrically optimized structure of **1** in presence of metal ion in DFT computation.
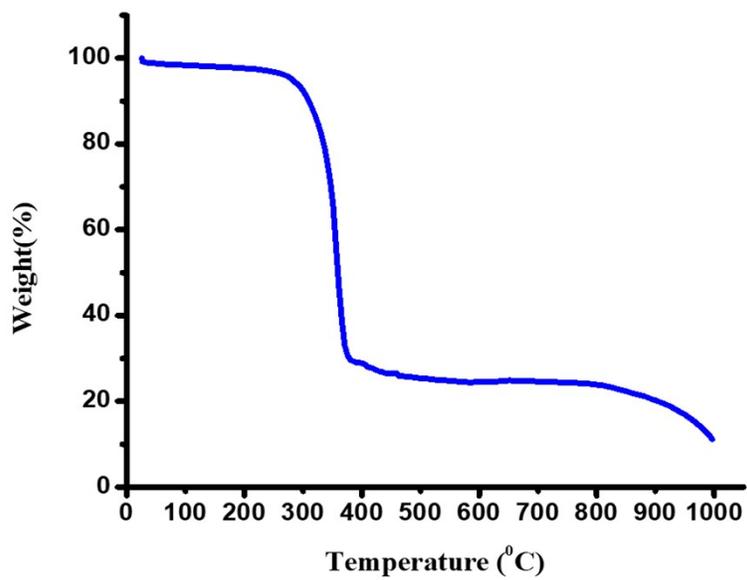
Fig. S20 TGA plot of **1** under nitrogen atmosphere.

Table S5. Comparison of recently published research work related to our present work

Sl. No.	Sensor Molecule	Synthesis Method Of sensor molecule	Concerned Cations	LOD	Detection medium	Real field application as a portable kit	Theoretical corroboration	Ref.
1.	[Zn(4-nvp)2(SCN)2]	Layering method at room temperature	Cr^{3+} (turn-on), Al^{3+} (turn-on), Fe^{3+} (turn-on)	2.53μM(Cr^{3+}), 2.67μM(Al^{3+}), 1.9 μM (Fe^{3+})	Water medium	No	No	2
2.	{[Me_2NH_2]$_{0.5}$[Co(DATRz)$_{0.5}$(NH_2BDC)]•xG}$_n$	Solvothermal at 120^{0}C temperature	Al^{3+} (turn-on)	0.65 μM(Al^{3+})	Water medium	No	No	3
3.	[Eu_2(ppda)$_2$(npdc)(H_2O)]·H_2O	Solvothermal at 160^{0}C temperature	Cr^{3+} (turn-off), Al^{3+} (turn-off), Fe^{3+} (turn-off), PO_4^{3-} (turn-off), TNP (turn-off)	61.7μM(Cr^{3+}), 109 μM(Al^{3+}), 16.6μM(Fe^{3+}), 14.2μM(PO_4^{3-}) 2.97 μM(TNP)	Water medium	No	NO	4
4.	[Co(H_2L)(TPY)(H_2O)]·H_2O	Solvothermal at 95^{0}C temperature	Al^{3+} (turn-on), Fe^{3+} (turn-off)	1.67 μM(Al^{3+}), --	Aqueous medium	No	Yes	5
5.	{[Co_3(BIBT)$_3$(BTC)$_2$(H_2O)$_2$]·solvents}$_n$	Solvothermal at 120^{0}C temperature	Cr^{3+} (turn-on), Al^{3+} (turn-on), Fe^{3+} (turn-on)	0.10μM(Cr^{3+}), 0.10μM(Al^{3+}), 0.13μM (Fe^{3+})	DMA medium	No	No	6
6.	Tb−TCPP	Solvothermal at 120^{0}C temperature	Cr^{3+} (turn-on), Al^{3+} (turn-on), Fe^{3+} (turn-on)	9.94nM(Cr^{3+}), 7.79nM(Al^{3+}), 16.4nM (Fe^{3+})	Aqueous medium	No	No	7
7.	[Cd(Hcip)(bpea)$_{0.5}$(H_2O)]$_n$	Solvothermal at 80^{0}C temperature	Cr^{3+} (turn-on), Al^{3+} (turn-on), Fe^{3+} (turn-off)	1.84μM(Cr^{3+}), 1.31μM(Al^{3+}), 3.24μM (Fe^{3+})	DMF medium	No	No	8
8.	[Cd(NCS)$_2$(4-nvp)$_2$]$_n$	Layering method at room temperature	Cr^{3+} (turn-on), Al^{3+} (turn-on), Fe^{3+} (turn-on)	43nM(Cr^{3+}), 74.1nM(Al^{3+}), 73.6nM (Fe^{3+})	Water medium	Yes	Yes	**This work**

References

1. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.,* 2015, **71**, 3–8.
2. B. Dutta, S. Dey, K. Pal, S. Bera, S. Naaz, K. Jana, C. Sinha and M. H.Mir, *New J. Chem*., 2020, **44**, 13163-13171.
3. S. Chand, G. Verma, A. Pal, S. C. Pal, S. Ma and M. C. Das, *Chem. Eur. J*., 2021, **27**, 11804-11810.
4. Z. Zhan, X. Liang, X. Zhang, Y. Jia and M. Hu, *Dalton Trans*., 2019, **48**, 1786-1794.
5. C. L. Zhang, Z. T. Liu, H. Xu, H. G. Zheng, J. Ma and J. Zhao, *Dalton Trans*., 2019, **48**, 2285-2289.
6. X. M. Tian, S. L. Yao, C. Q. Qiu, T. F. Zheng, Y. Q. Chen, H. Huang, J. L. Chen, S. J. Liu and H. R. Wen, *Inorg. Chem*., 2020, **59**, 2803-2810.
7. C. Fu, X. Sun, G. Zhang, P. Shi and P. Cui, *Inorg. Chem*, 2021, **60**, 1116-1123.
8. Y. E. Yu, Y. Wang, H. Yan, J. Lu, H. Liu, Y. Li, S. Wang, D. Li, J. Dou, L. Yang and Z. Zhou, *Inorg. Chem*, 2020, **59**, 3828-3837.