Electronic supplementary information (ESI)

Excited-state intramolecular proton transfer (ESIPT) active interwoven polycatenated coordination polymer for selective detection of Al^{3+} and Ag^{+} ions along with water detection in less polar solvents

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1. Experimental section:

1.1. Materials and synthesis

N, N′ donor 4-pmi was synthesized by the previous reported procedures[1]. Isoniazid and 4-pyridine carboxyldehyde for 4-pmi synthesis were purchased from Sigma-Aldrich Chemical Co. High purity cadmium (II) nitrate hexahydrate and 2,5-Dihydroxyterephthalic acid i.e. [H_2(dht)] were also purchased from Sigma-Aldrich Chemical Co. Inc. all the material used as received without any farther purification. Di-sodium salts of the acid was synthesized by the slow addition of solid $NaHCO_3$ to aqueous solution of 2,5-Dihydroxyterephthalic acid in a 1:1 ratio and allowed to evaporate until dryness. All other chemicals including solvents of AR grade and used as received.

1.2 Physical measurements.

Infrared spectra (4000−400 cm^{-1}) were taken on KBr pellet, using PerkinElmer Spectrum BX-II IR spectrometer. Thermal analysis (TGA) was carried out on a PerkinElmer Simultaneous thermal analyzer (STA 8000) under nitrogen atmosphere (flow rate: 10 cm^3 min^{-1}) at the temperature range 30−600 °C with a heating rate of 5 °C/min. PXRD patterns in different states of the samples were recorded on a Bruker D8 Discover instrument using Cu−Kα radiation (λ = 1.5406 Å), operating at 40 kV and 40 mA. UV-vis spectra are collected in PerkinElmer Lambda 35 instrument with integrating sphere attachment. Fluorescence measurements were done using Horiba Fluoromax$^+$ spectrofluorometer. Emission lifetime measurements were carried out by using time-correlated single photon counting set up from Horiba Jobin-Yvon. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using EZ time software. For photoexcitation, we used delta-diode of 370 nm as the light source.

1.3. Synthesis of $\{[Cd(4\text{-}pmi)(dht)(H_2O)]\cdot(H_2O)_3\}_n$

with an aqueous solution (20 mL) of Na_2dht (1 mmol, 0.242 g) was mixed with a methanolic solution (20 mL) of ((pyridin-4-yl)methylene)isonicotinohydrazide (4-pmi) (1 mmol, 0.226 g) and stirred for 30 min to make a homogenous solution. In a 20 ml crystal tube, 6mL of this mixed ligand solution was carefully layered over 3mL aqueous solution of $Cd(NO_3)_2\cdot 6H_2O$ (0.344 g, 20 mL) with a separation by 5mL of 1:1 water/MeOH buffer. After two weeks, block shaped yellow crystals, suitable for single X-ray diffraction analysis, is obtained at the junction of the layer (yield = 76% based on Cd). Crystals are separated and washed with a small amount of cold 1:1 water/methanol solution. IR spectra (4000–400$^-$

^{1}): ν (N–H), 3214 (stretch); ν (C=O), 1689 (stretch); ν (C=C,Ar), 1548; ν (-NHCO of amide), 1491, 1437; ν (C–O), 1294 (stretch).

1.4 Crystallographic data collection and refinement methods

The single crystal of compound **1** was mounted on thin glass fibers with commercially available super glue. Single crystal X-ray data collection of the crystal was done at room temperature using Bruker APEX III diffractometer, equipped with a micro focus, sealed tube X-ray source with graphite monochromated Mo−Kα radiation (λ= 0.71073 Å). The collected data was integrated using the SAINT program,[2] and the absorption corrections were made with SADABS.[3] The structure solved by SHELXS 2018[4] using the SIR-92 program and followed by successive Fourier and difference Fourier synthesis. Full matrix least squares refinements were performed on F^2 using SHELXL-2018[4] with anisotropic displacement parameters for all non-hydrogen atoms. Potential solvent accessible area or void space was calculated by removing of guest solvent molecule using PLATON[5] multipurpose crystallographic software. All the hydrogen atoms were fixed geometrically by HFIX command and placed in ideal positions in case of compound **1**. Calculations were carried out using SHELXL 2018,[4] SHELXS 2018,[4] PLATON v1.15,[5] Mercury Ver-3.6,[6] WinGX system Ver-1.80,[7] and TOPOS[8]. Data collection and structure refinement parameters along with crystallographic data for **1** are given in Table 1.

1.5 Sorption measurements

The adsorption isotherms of H_2 (at 77 K,1 bar), N_2 (at 77 K, 1 bar) and CO_2 (at 195 K,1 bar) were measured taking desolvated sample of compound **1**. High purity gases were used for the adsorption measurements (nitrogen, 99.999%; hydrogen, 99.999%; carbon dioxide, 99.95%). The ambient pressure (from 0 to 1 bar) volumetric adsorptions for H_2 and N_2 were carried out at 77 K for the desolvated sample, maintaining the temperature by a liquid-nitrogen bath, using Quantachrome Autosorb-iQ adsorption instrument. For CO_2 isotherms, dry ice-acetone cold bath was used. For the above purposes of gas adsorption, all the samples were placed in the sample tube and desolvated at 393 K under dynamic vacuum (1×10^{-6} bar) for about 4 hrs prior to measurement of the isotherms. Prior to isotherm data collection, the sample tubes were transferred to the analysis port and Helium gas (99.999% purity) was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve to measure dead volume. Then the analysis gas was introduced to the sample tube and the change of the pressure was monitored. The degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer controlled and automatic.

Table S1. Selected Bond Lengths (Å) and Bond Angles (°) for **1**.

Cd1-O1	2.437(2)	Cd1-O1W	2.303(2)
Cd1-O2	2.430(2)	Cd1-O3	2.266(2)
Cd1-O4	2.685(3)	Cd1-N1	2.335(2)
Cd1-N4^{a}	2.372(3)	O1-Cd1 -O1W	134.77(8)
O1 -Cd1-O2	53.46(9)	O1-Cd1-O3	93.91(8)
O1 -Cd1-O4	145.61(7)	O1-Cd1-N1	90.68(8)
O1-Cd1-N4^{a}	89.30(8)	O1W -Cd1-O2	81.32(8)
O1W -Cd1-O3	131.10(8)	O1W -Cd1-O4	79.62(7)
O1W -Cd1-N1	89.87(9)	O1W -Cd1- N4^{a}	90.23(8)
O2-Cd1-O3	146.80(8)	O2 -Cd1-O4	160.93(8)
O2-Cd1-N1	91.98(8)	O2-Cd1- N4^{a}	88.11(8)
O3-Cd1-O4	51.99(7)	O3-Cd1-N1	94.64(8)
O3-Cd1- N4^{a}	85.24(8)	O4-Cd1-N1	88.22(8)
O4-Cd1- N4^{a}	91.72(8)	N1-Cd1- N4^{a}	179.87(9)

Table S2. π-π interactions in **1**

Ring (i)→ring (j)	distance of centroid (i) from ring (j), (Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids, (Å)
R(1)→R(1)^{I}	4.192(2)	0.0(2)	3.9192(17)
R(1)→R(1)^{J}	4.870(2)	0.0(2)	3.7613(17)
R(2)→R(2)^{K}	4.197(3)	0.0(2)	3.6978(18)

Symmetry code: I = -x,1-y,1-z, J= 1-x,1-y,1-z, K = -x,-y,-z

R(i)/R(j) denotes the rings in the corresponding structures:

R(1) = N1/C1/C12/C4/C3/C2;

R(2)= N4/C9/C8/C7/C11/C10.

Table S3. Hydrogen bonding interactions in **1**

D–H···A	D–H	H···A	D···A	D–H···A
O1W –H1WA···O7	0.85	1.99	2.803(4)	159
O1W–H1WB···O5	0.85	2.00	2.832(5)	164
O5 –H5···O4	0.82	1.86	2.574(4)	146

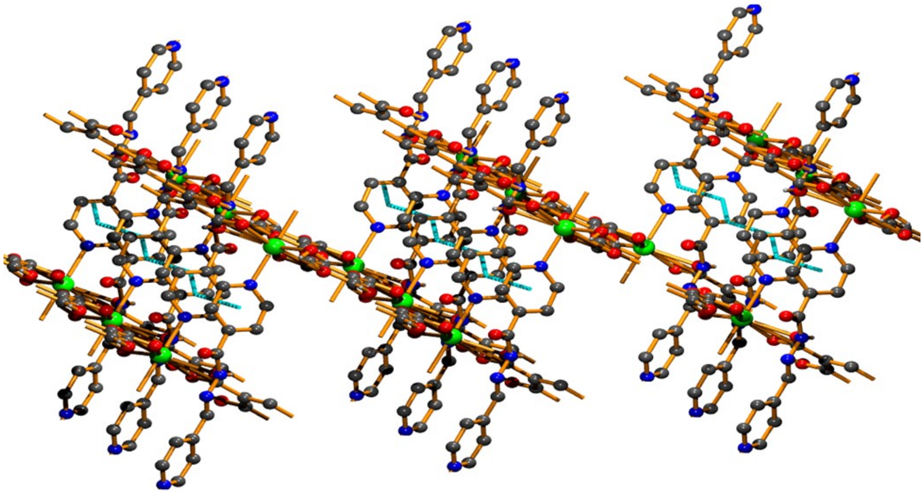

Fig. S1 View of the supramolecular 3D structure in **1** is provided, showing intermolecular π…π interactions (represented by cyan dotted lines)

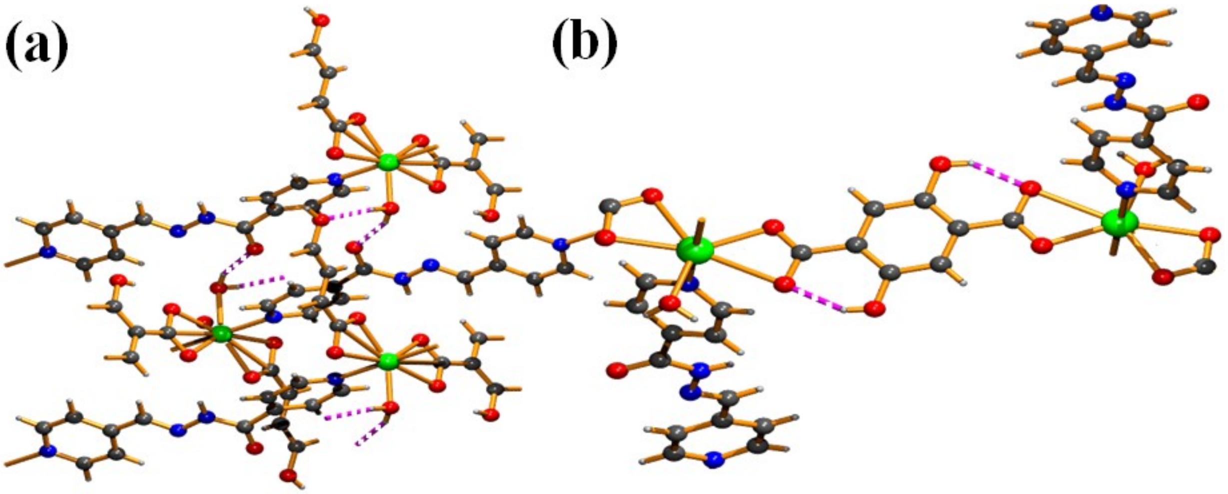

Fig. S2 (a) intermolecular and (b) intramolecular hydrogen bonding interactions: magenta dotted lines.

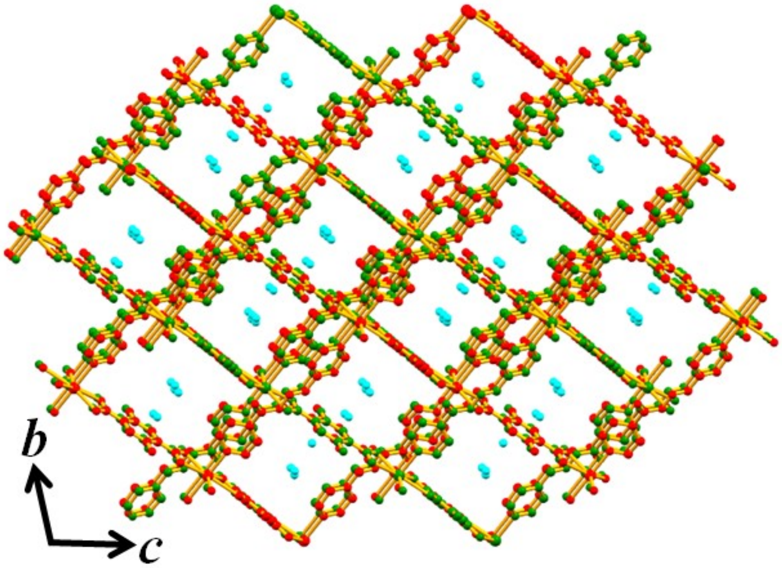

Fig. S3 The 3D architecture of compound **1** is displayed, featuring a 1D water channel along the *a*-axis. Cyan spheres symbolize lattice water molecules

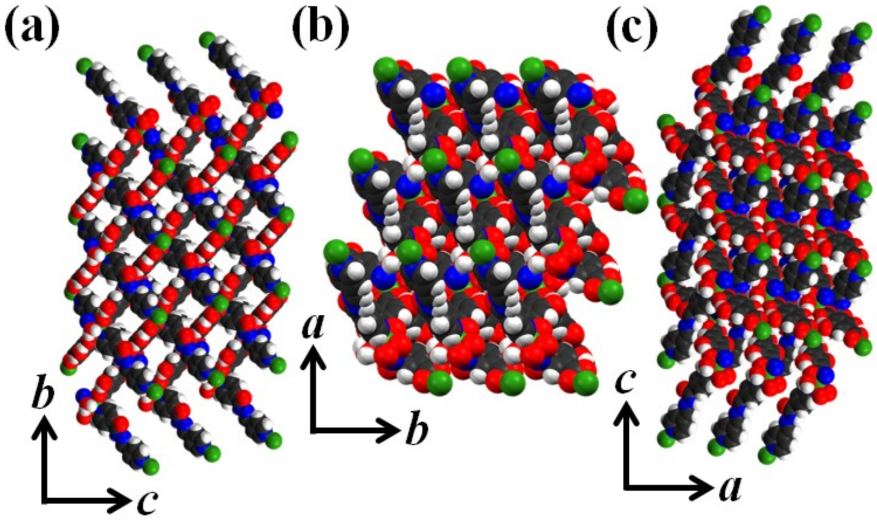

Fig. S4 Space-fill model of **1** along (a) *a* direction; (b) *c* direction; (c) *b* direction; Cd (green), H (white), N (blue), O (red) and C (black)

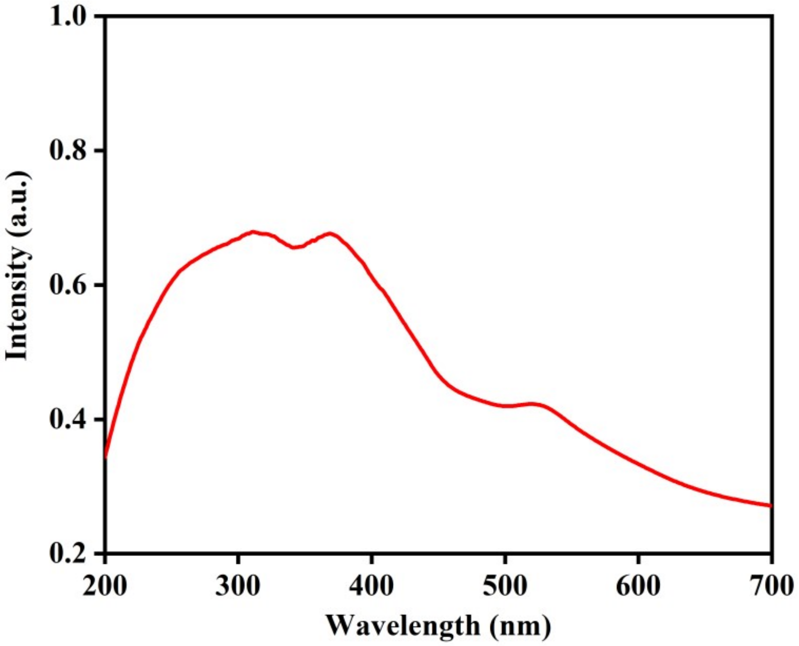

Fig. S5 UV-Vis spectra of compound **1**.

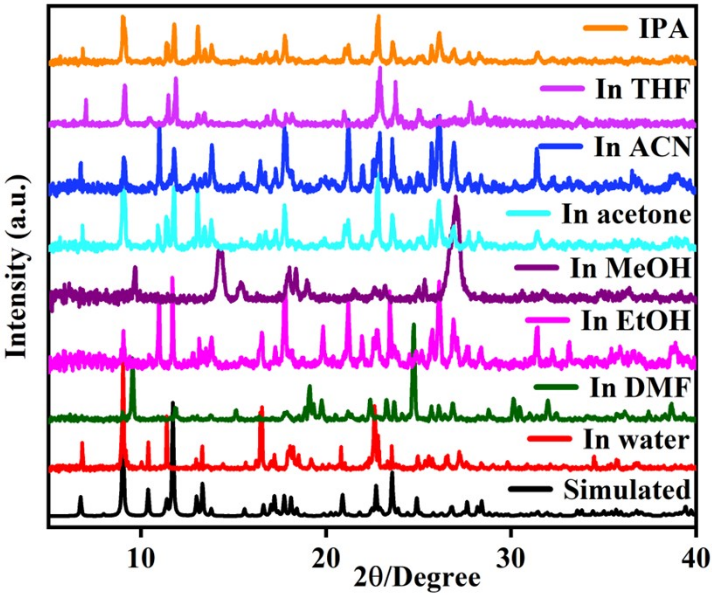

Fig. S6 PXRD patterns of the simulated form of compound **1** along with the PXRD patterns of **1´** after immersing it for 1 week in different solvents, as mentioned.

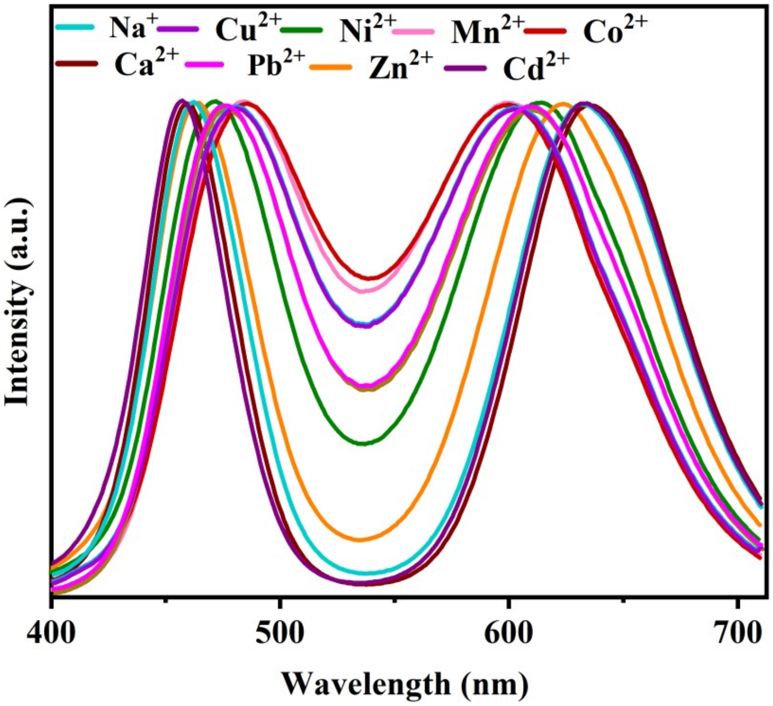

Fig. S7 Emission spectra of the compound **1** in different aqueous $M(NO_3)_x$ solution at λ_{ex} = 360. nm.

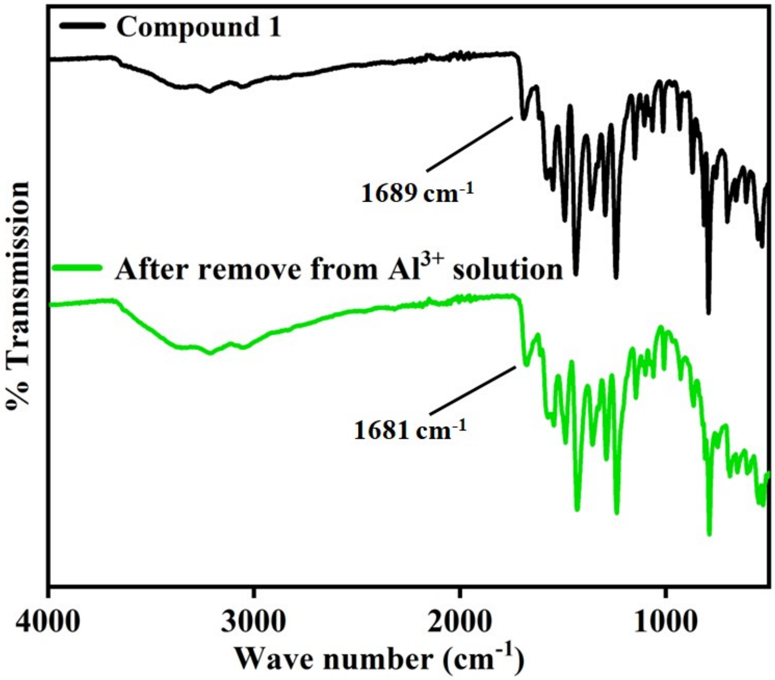

Fig. S8 Combined FT-IR spectra of **1** compare with compound **1** remove from aqueous Al^{3+} solution.

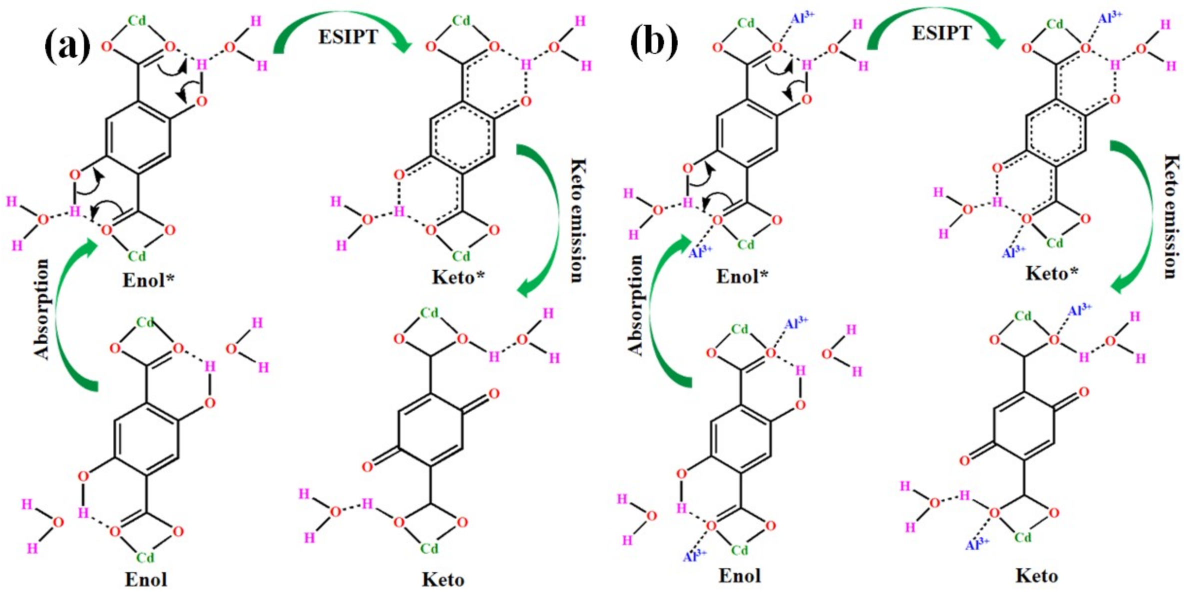

Fig. S9 The probable chemical formula of the keto and enol forms, along with their excited states for the ESIPT process (a) in water (b) in presence of Al^{3+} ion.

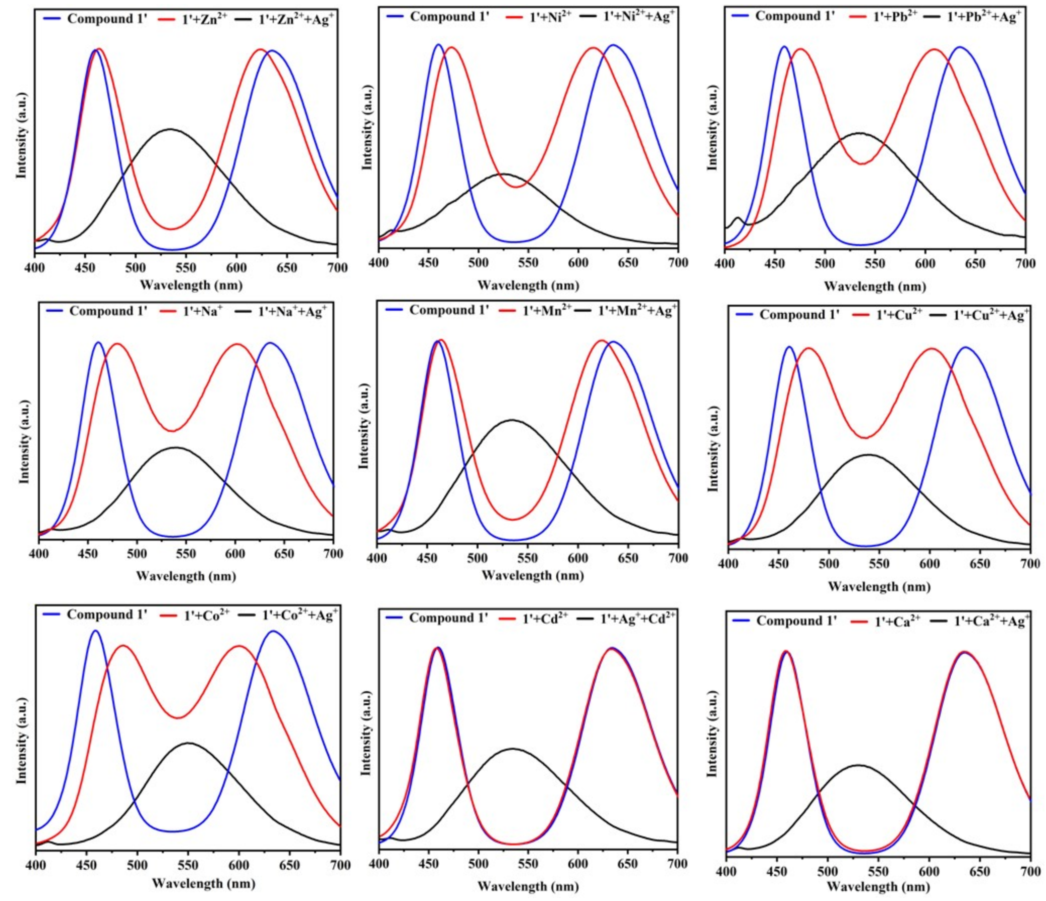

Fig. S10 Ag^+ sensing by compound **1** in the presence of interfering cations.

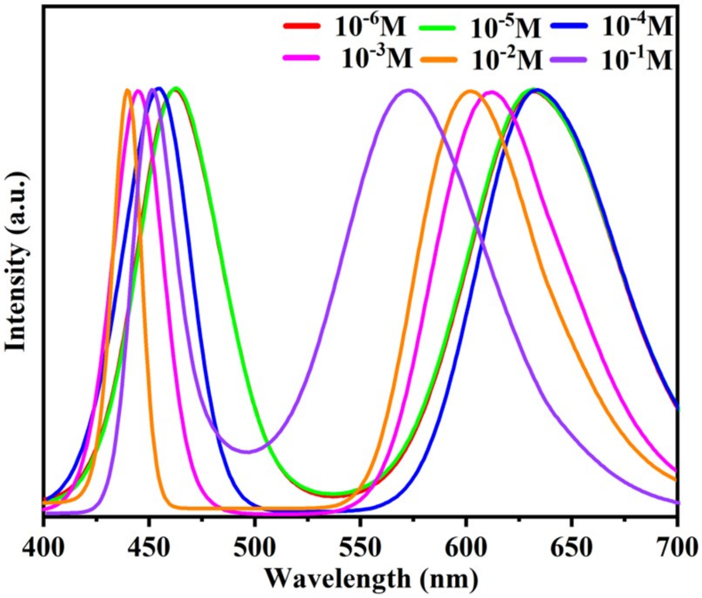

Fig. S11 PL spectra of compound **1** in Al^{3+} solution of different concentration.

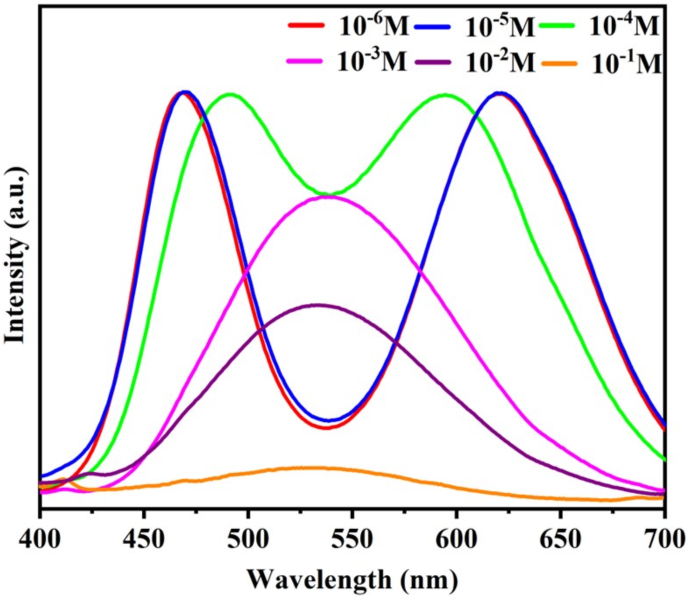

Fig. S12 PL spectra of compound **1** in Ag^{+} solution of different concentration.

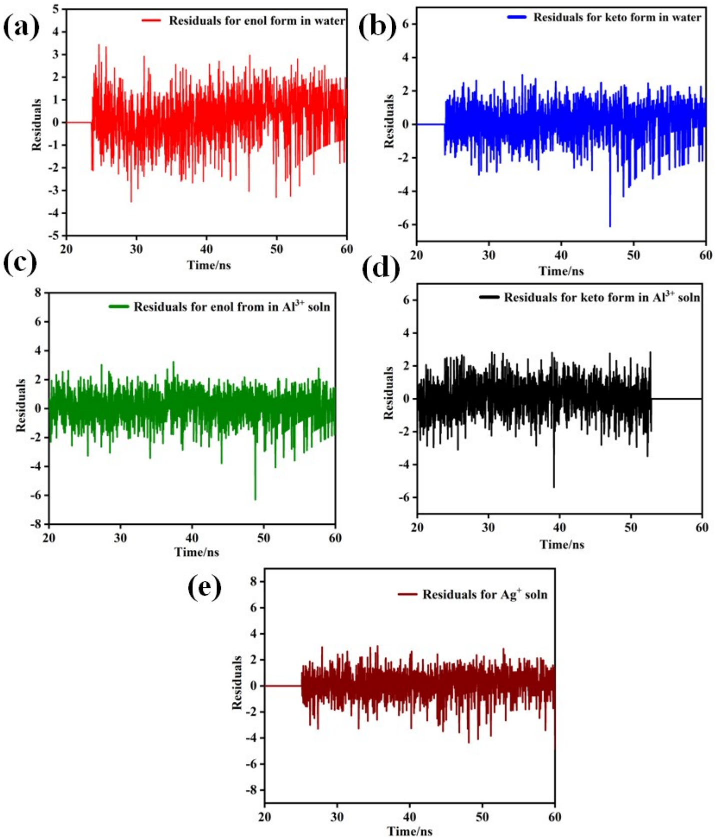

Fig. S13 Residuals for time-resolved fluorescence calculations for (a) enol form in water; (b) keto form in water; (c) enol form in Al^{3+} solution (aq); (d) keto form in Al^{3+} solution (aq); (e) Ag^{+} ion solution (aq).

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