Sunlight assisted SCSC dimerization of a 1D coordination polymer impacts the selectivity of Pd(II) sensing in water

Mohammad Hedayetullah Mir,*[a] Sambhunath Bera,[a] Samim Khan,[a] Suvendu Maity,[b] Chittaranjan Sinha[b] and Basudeb Dutta[a]

[a]Department of Chemistry, Aliah University, New Town, Kolkata 700 156, India.

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

Supporting Information

Experimental Procedures

Materials and general method

All chemicals purchased were reagent grade fand were used without further purification. Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin–Elmer 240C elemental analyzer. Infrared spectrum in KBr (4500–500 cm^{-1}) was recorded using a Perkin–Elmer FT-IR spectrum RX1 spectrometer. The PXRD data was collected on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2θ range of 5–50. Thermogravimetric analyses were performed on a Perkin–Elmer Pyris Diamond TG/DTA in the temperature range 30 800 °C under a nitrogen atmosphere. All ^{1}H NMR spectra were recorded on Bruker Avance III 400 MHz spectrometers with TMS as an internal reference in DMSO-*d6* solution.

Synthesis of the compounds

Synthesis of **1:** A solution of 4-nvp (0.046 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered onto a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.062 g, 0.2 mmol), in H_2O (2 mL) using a

2 mL 1 : 1 (= v/v) buffer solution of MeOH and H_2O followed by layering of 5-ssa (0.042 g, 0.2 mmol) neutralized with Et_3N (0.042 g, 0.4 mmol) in 2 mL EtOH. The brown color block shaped crystals of $[Cd(4\text{-nvp})_2(5\text{-ssa})]\cdot(4\text{-nvp})$ (**1**), were obtained after three days (0.056 g, yield 65%). Elemental analysis (%) calcd for $C_{58}H_{43}CdN_3O_7S$: C 67.08, H 4.17, N 4.05; found: C 67.05, H 4.09, N 4.13. IR (KBr pellet, cm^{-1}): 1611 $\nu_{as}(COO^-)$, 1428 $\nu_{sys}(COO^-)$ (Fig. S25, ESI†).

Synthesis of **1′**: The compound **1′** was synthesized by sunlight of **1:** Brown colored block-like single crystals of **1** (0.071 g, 0.1 mmol) were irradiated under sunlight for 2 h. IR (KBr pellet, cm^{-1}): 1616 $\nu_{as}(COO^-)$, 1430 $\nu_{sys}(COO^-)$ (Fig. S26, ESI†).

General X-ray Crystallography

Single crystals of **1** and **1′** having suitable dimensions, were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated MoK_α radiation (λ, 0.71073 Å). The crystal structure was solved using the SHELXT 2014/4 structure solution program package.[1] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Crystal data of **1**: Triclinic space group $P\bar{1}$, a = 11.134(3), b = 13.954(3), c = 15.979(4) Å, α = 84.307(7), β = 74.689(6), γ = 79.427(7), V = 2350.4(10)Å^3, Z = 2, ρ_{calcd} = 1.467g.cm^{-3}, μ = 0.569mm^{-1}, T = 273(2) K, $R1$ = 0.0496, $wR2$ = 0.1263with $I > 2\sigma(I)$, GOF = 1.086.

Crystal data of **1′**::Triclinic space group $P\bar{1}$, a = 11.0879(19), b = 13.986(2), c = 15.953(3) Å, α = 83.286(5), β = 73.056(5), γ = 79.719(5), V = 2322.9(7)Å^3, Z = 2, ρ_{calcd} = 1.489g.cm^{-3}, μ = 0.576mm^{-1}, T = 125(2) K, $R1$ = 0.0821, $wR2$ = 0.2100with $I > 2\sigma(I)$, GOF = 1.036.

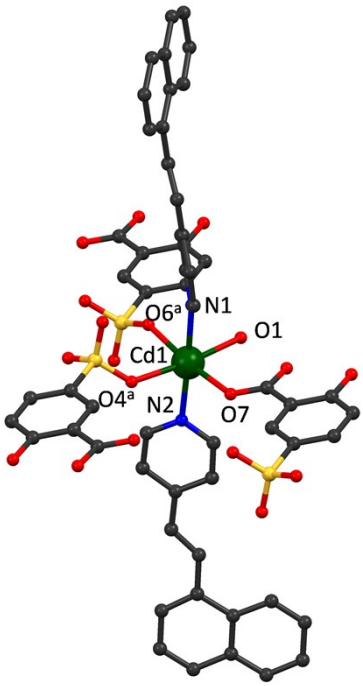

Fig. S1 A perspective view of the coordination mode of metal centre in **1**. Only relevant atoms are shown for the clarity. Symmetry transformation ª = -1+x,y,z.

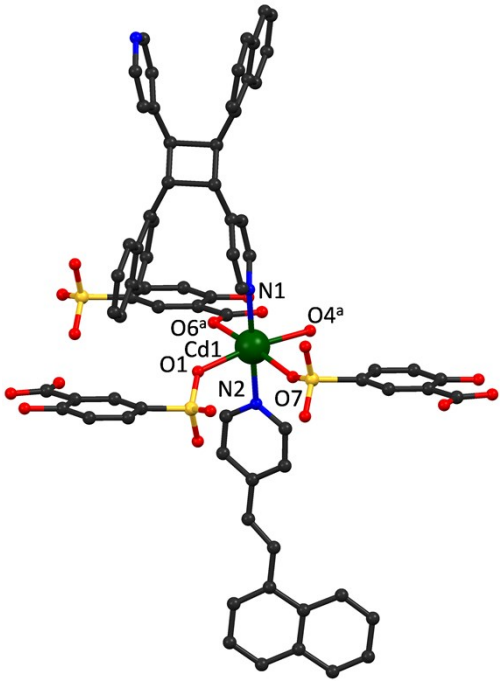

Fig. S2 A perspective view of the coordination mode of metal centre in **1′**. Only relevant atoms are shown for the clarity. Symmetry transformation ª = -1+x,y,z.

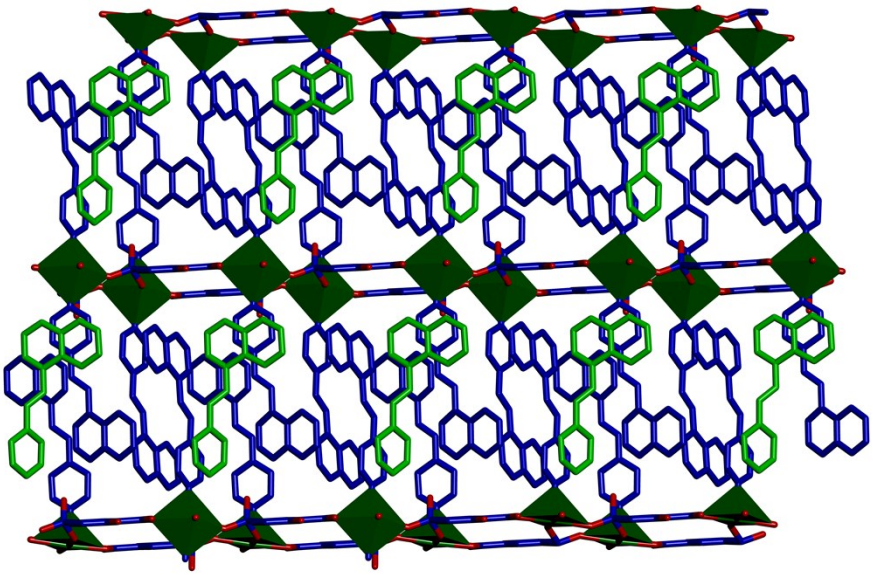

Fig. S3 2D supramolecular aggregate of **1** with free 4-nvp ligands. Only relevant atoms are shown for the clarity.

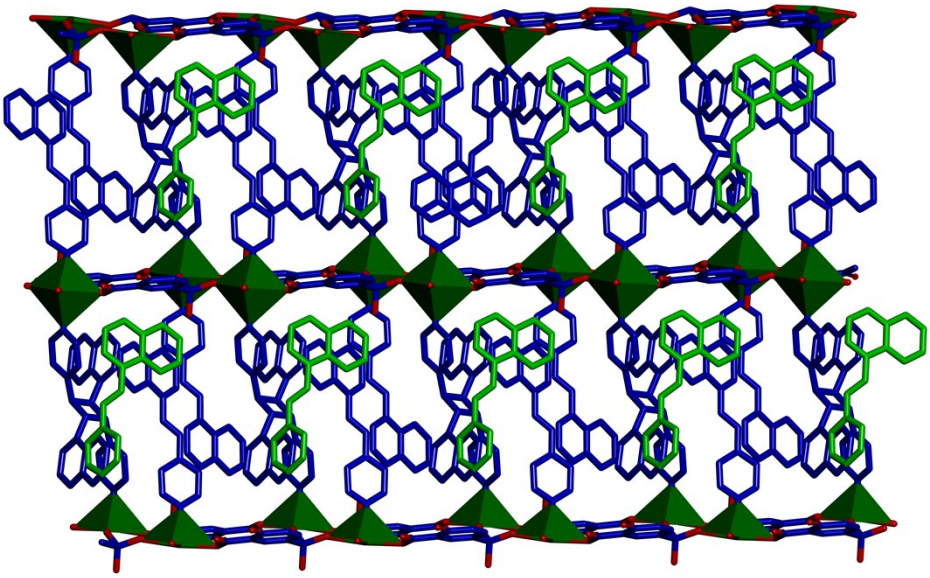

Fig. S4 2D architecture of **1′** with free 4-nvp ligands. Only relevant atoms are shown for the clarity.

Table S1. Selected bond lengths and bond angles in **1**

Cd(1) - O(1)	2.325(3)	O(1) - Cd(1) - N(1)	90.56(11)
Cd(1) - O(4)a	2.376(3)	O(1) - Cd(1) - O(6)c	92.44(9)
Cd(1) - O(7)	2.351(3)	O(7) - Cd(1) - O(4)a	83.32(9)
Cd(1) - O(6)c	2.333(3)	N(1) - Cd(1) - O(4)a	84.98(11)
Cd(1) - N(1)	2.279(3)	N(2) - Cd(1) - O(6)c	87.65(10)
Cd(1) - N(2)	2.281(3)	O(1) - Cd(1) - N(2)	90.51(10)
O(1) - Cd(1) - O(7)	93.01(9)	O(7) - Cd(1) - N(1)	87.14(10)
O(1) - Cd(1) - O(4)a	174.34(10)	O(7) - Cd(1) - O(6)c	174.02(9)
O(7) - Cd(1) - N(2)	94.78(10)	N(1) - Cd(1) - O(6)c	90.33(10)
N(1) - Cd(1) - N(2)	177.75(10)	O(4)a - Cd(1) - O(6)c	91.06(9)
N(2) - Cd(1) - O(4)a	94.08(9)		

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

Table S2. Selected bond lengths and bond angles in **2**

Cd(1) - O(1)	2.319(5)	O(1) - Cd(1) - N(1)	88.74(16)
Cd(1) - O(4)a	2.334(5)	O(1) - Cd(1) - O(6)d	90.04(16)
Cd(1) - O(7)	2.354(4)	O(7) - Cd(1) - O(4)a	84.72(15)
Cd(1) - O(6)d	2.333(4)	N(1) - Cd(1) - O(4)a	84.63(16)
Cd(1) - N(1)	2.294(5)	N(2) - Cd(1) - O(6)d	92.71(18)
Cd(1) - N(2)	2.308(5)	O(1) - Cd(1) - N(2)	91.65(16)
O(1) - Cd(1) - O(7)	93.45(15)	O(7) - Cd(1) - N(1)	85.30(15)
O(1) - Cd(1) - O(4)a	173.24(16)	O(7) - Cd(1) - O(6)d	171.76(16)
O(7) - Cd(1) - N(2)	94.65(18)	N(1) - Cd(1) - O(6)d	87.32(15)
N(1) - Cd(1) - N(2)	179.61(17)	O(4)a - Cd(1) - O(6)d	90.96(15)

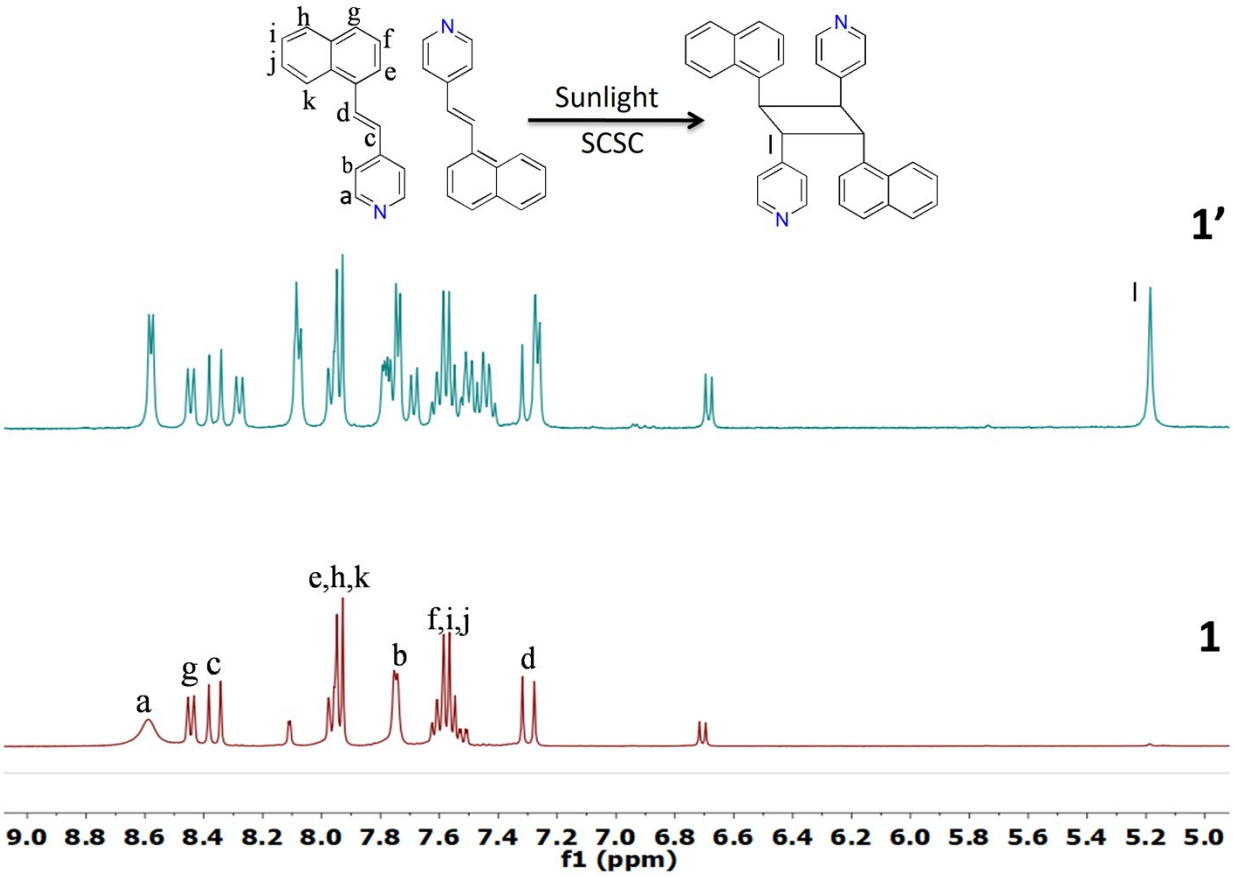

Fig. S5 Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6) of compound **1** (brown) and **1′** (green).

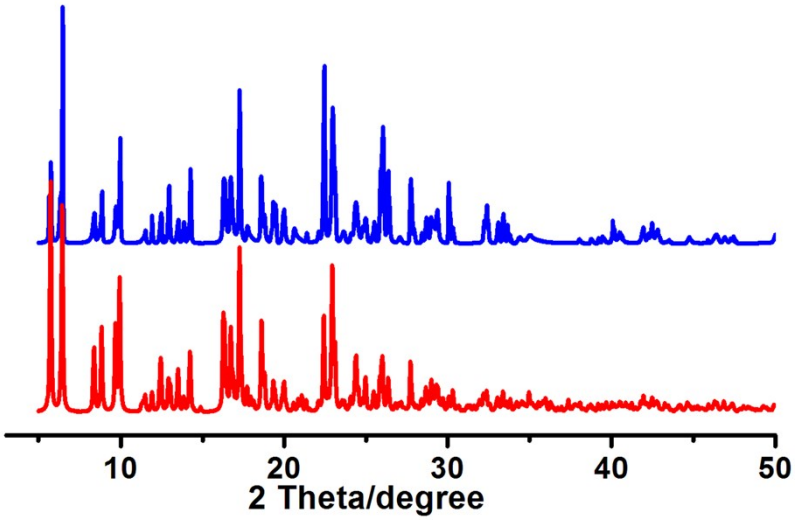

Fig. S6 PXRD patterns of a) simulated from the X-ray single structure of **1** (red) and b) as-synthesized **1** (blue).

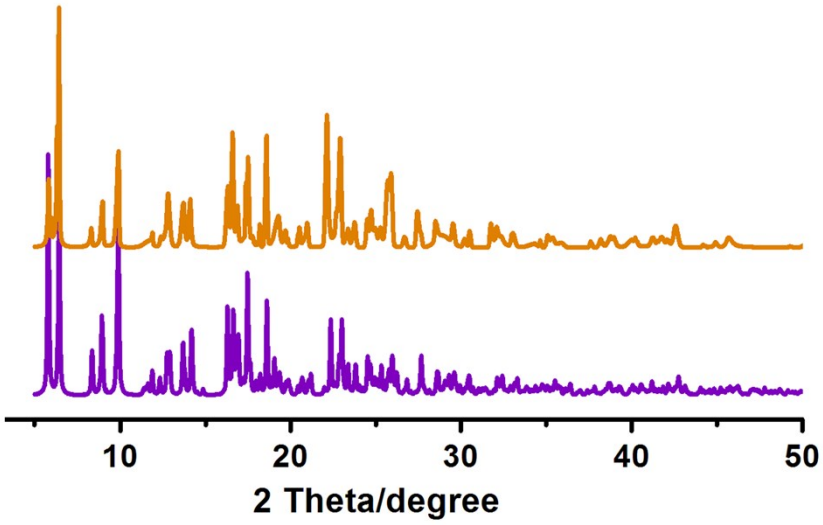

Fig. S7 PXRD patterns of a) simulated from the X-ray single structure of **1′** (violet) and b) as-synthesized **1′** (light brown).

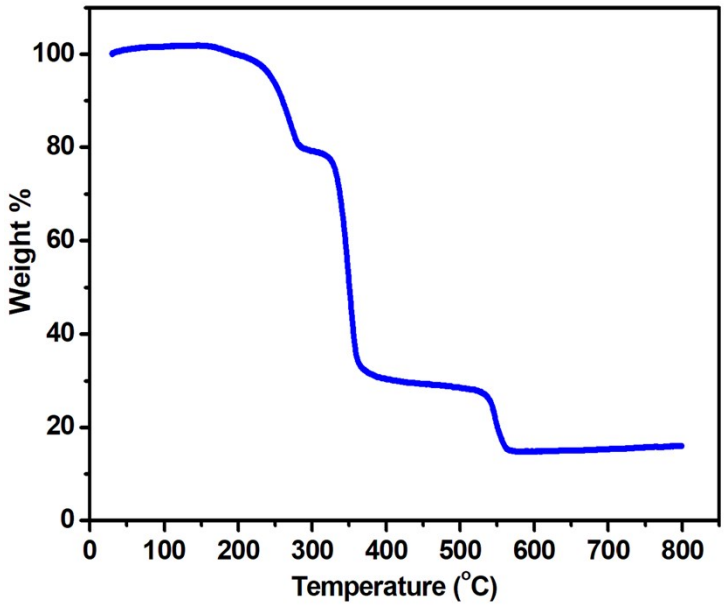

Fig. S8 TGA plot of compound **1** measured under N_2 atmosphere.

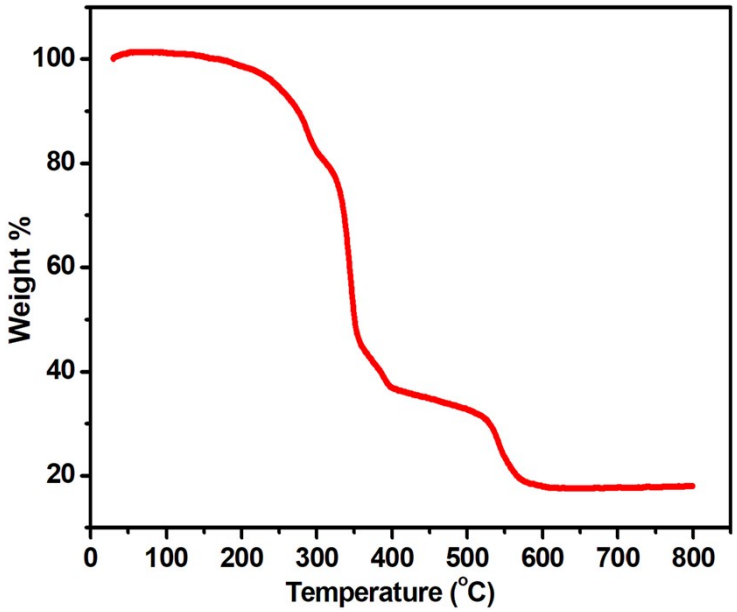

Fig. S9 TGA plot of compound **1′** measured under N_2 atmosphere.

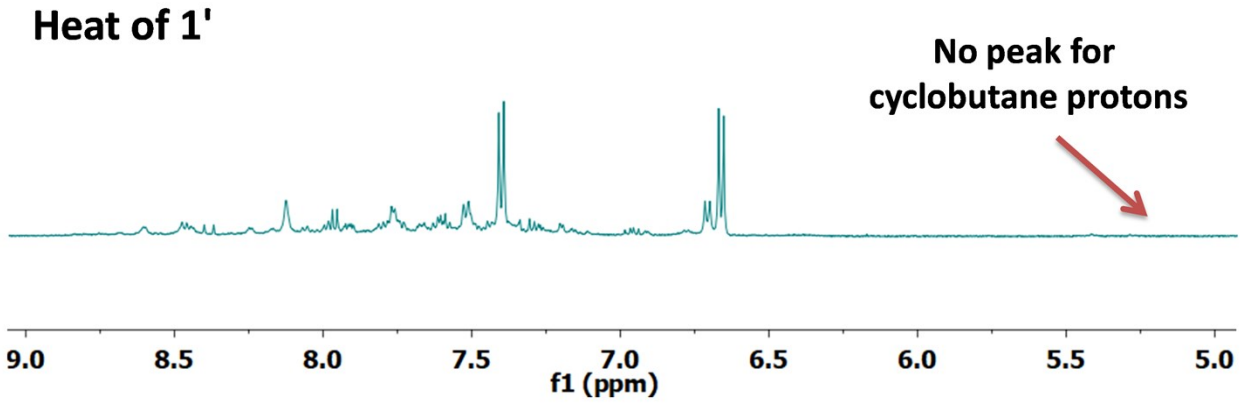

Fig. S10 Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6) of heated **1′** at 200 °C.

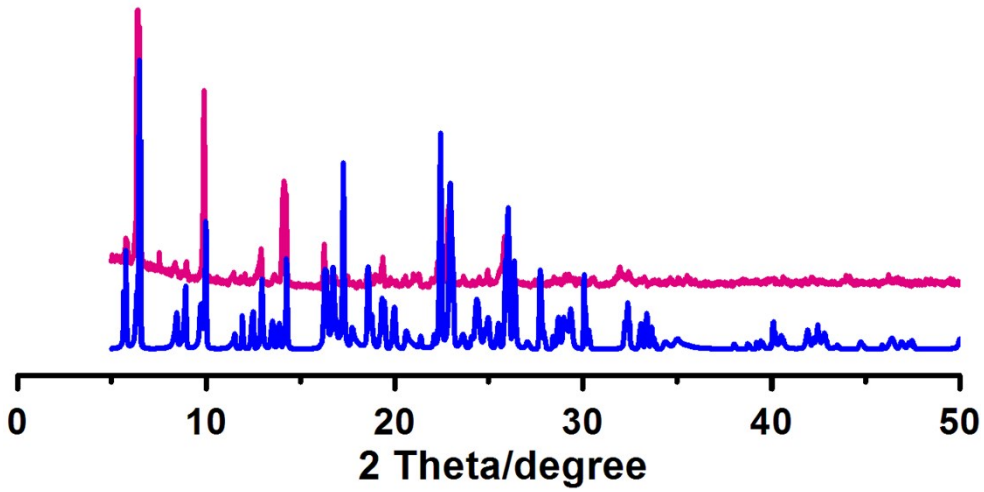

Fig. S11 PXRD patterns of a) as-synthesized **1** (blue) and b) heated **1′** (pink).

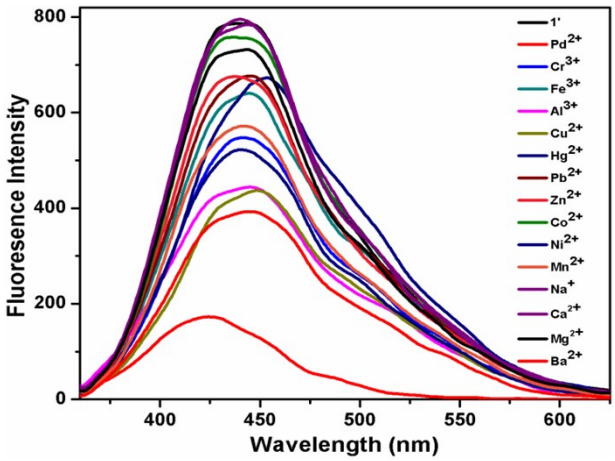

Fig. S12 Fluorescence spectra of **1′** in the presence of different metal ions and Pd^{2+}in H_2O.

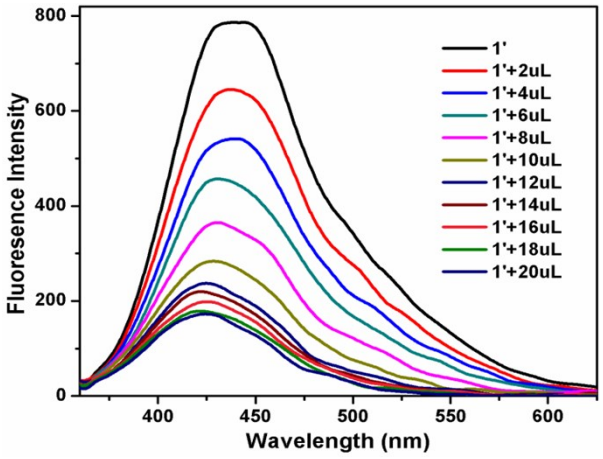

Fig. S13 Change of fluorescence intensity of **1′** upon addition of Pd^{2+} at an emission slit of 9 nm [all spectra were acquired at room temperature at excitation slit 340 nm].

Stern-Volmer equation:

$I0/I = K_{SV}[A] + 1$
Where, $I0$ = fluorescent intensity of **1** before the addition of the analyte
I = fluorescent intensity after the addition of the respective analyte
KSV = Stern-Volmer constant
[A] = molar concentration of the analyte (M^{-1}).

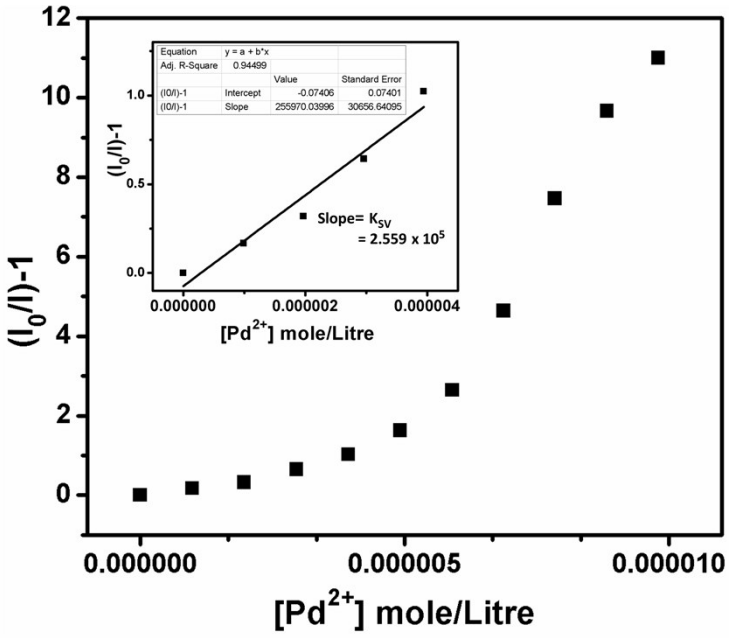

Fig. S14 Plot of the quenching efficiency of **1** dispersed in H_2O upon the addition of different concentrations of Pd^{2+}. Inset shows the linear relationship between $I_0/I - 1$ and concentration.

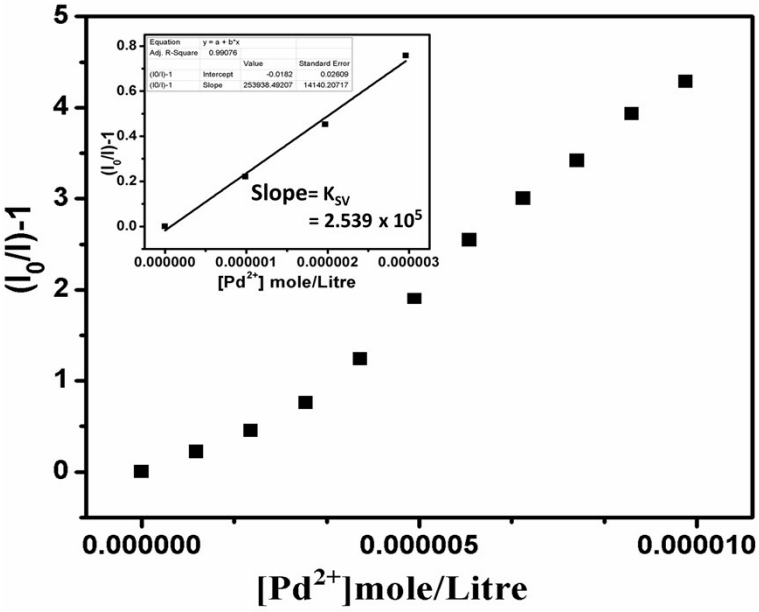

Fig. S15 Plot of the quenching efficiency of **1′** dispersed in H_2O upon the addition of different concentrations of Pd^{2+}. Inset shows the linear relationship between $(I_0/I) - 1$ and concentration.

Calculations for detection limit: LOD = 3σ/M Where σ = Standard deviation

M = Slope of Titration plot.

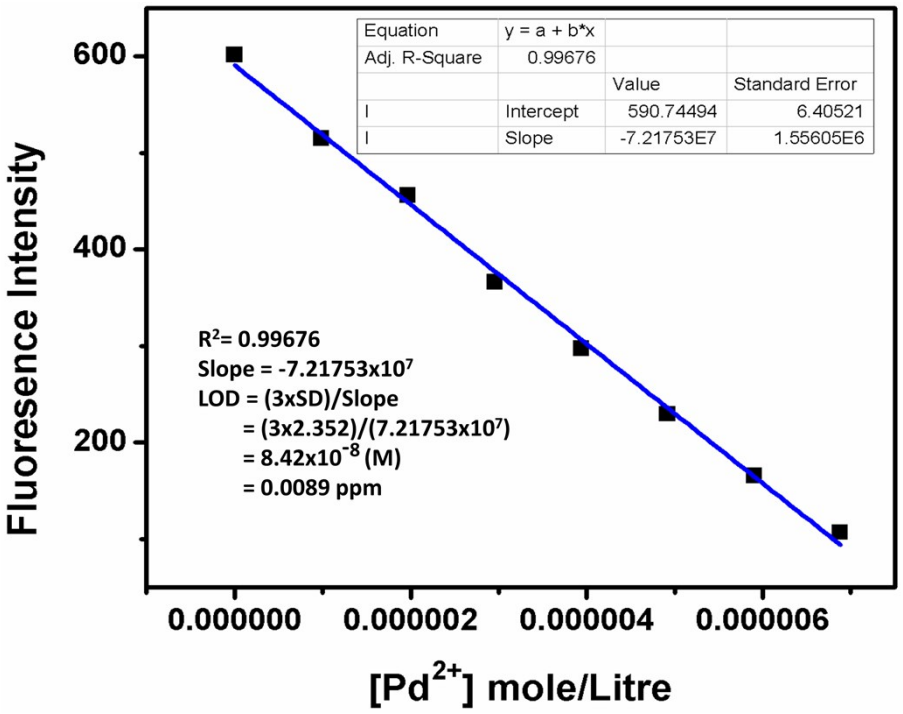

Fig. S16 The linear dynamic response of compound **1** for $Pd^{2+}$and the determination of the limit of detection (LOD) of Pd^{2+}.

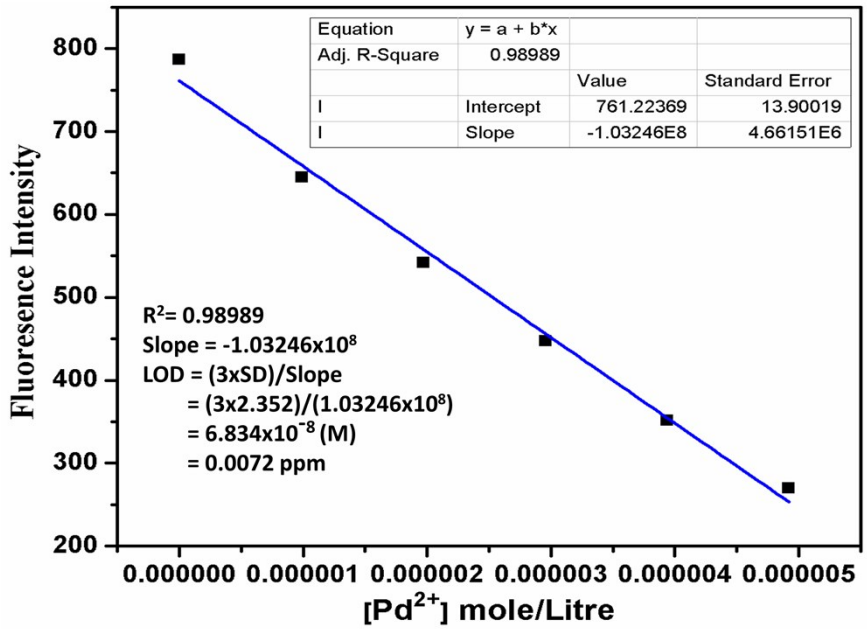

Fig. S17 The linear dynamic response of compound **1′** for $Pd^{2+}$and the determination of the limit of detection (LOD) of Pd^{2+}.

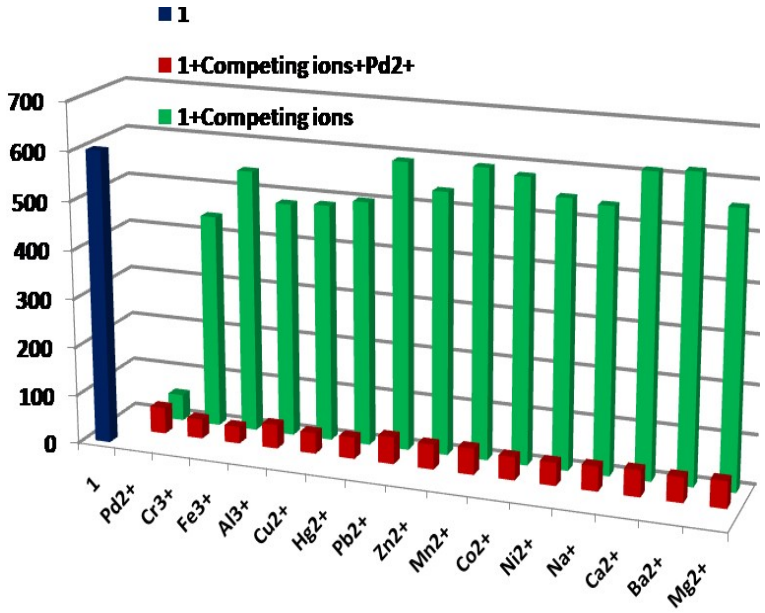

Fig. S18 Fluorescence intensity of **1**, its intensity diagram with Pd^{2+} along with competing ions and intensity change profile with various competing ions in H_2O medium.

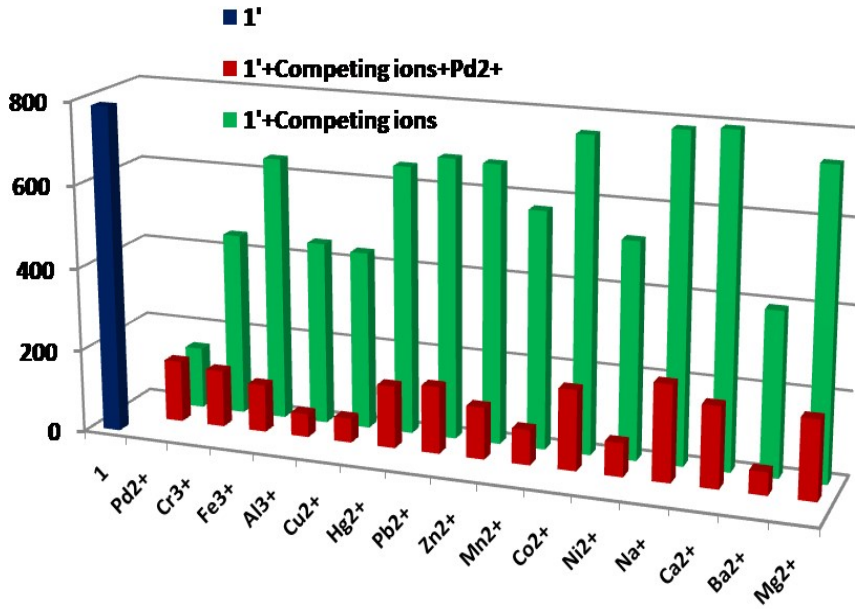

Fig. S19 Fluorescence intensity of **1′**, its intensity diagram with Pd^{2+} along with competing ions and intensity change profile with various competing ions in H_2O medium.

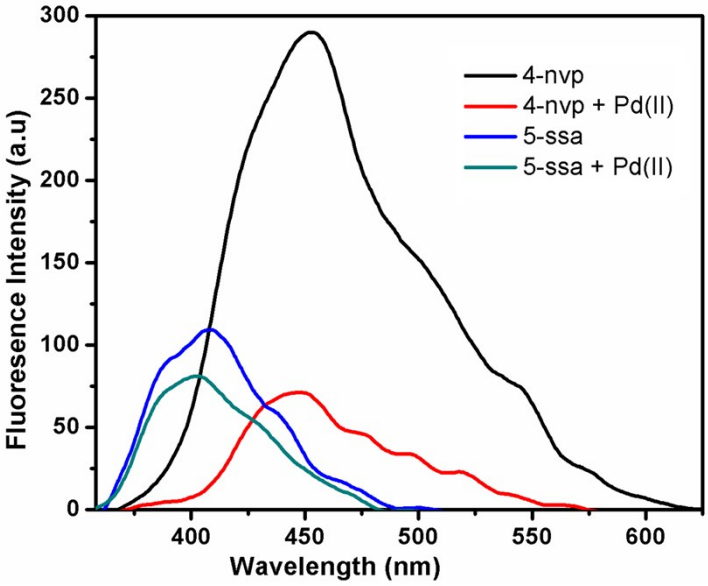

Fig. S20 Fluorescence spectra of components ligands and also in the presence of Pd^{2+}in H_2O.

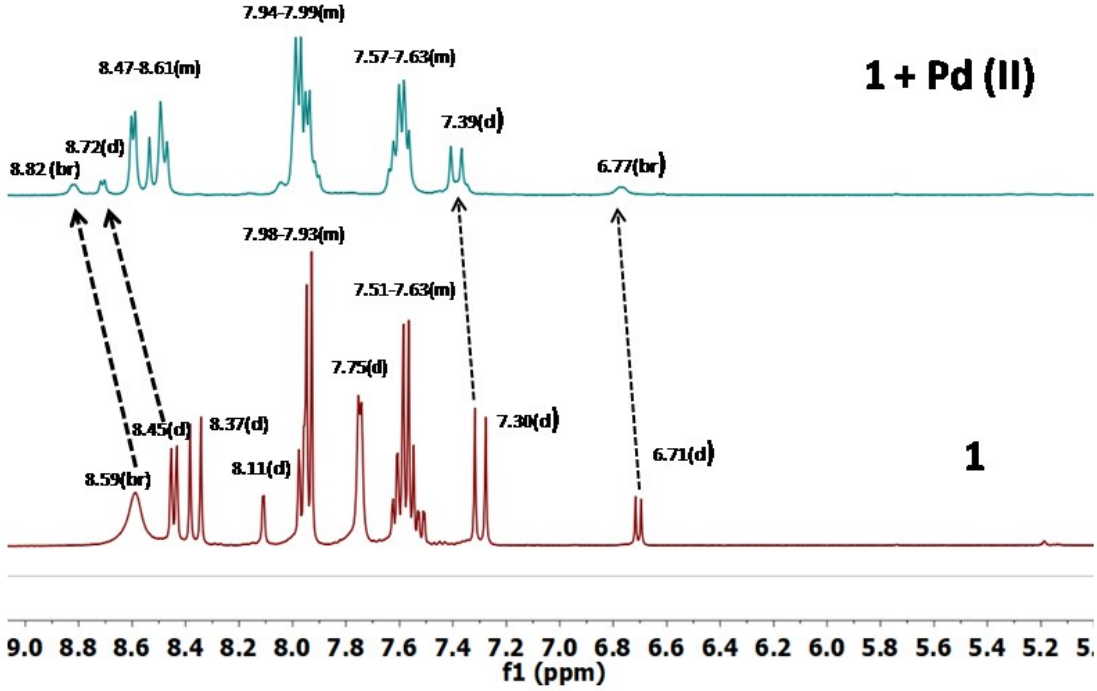

Fig. S21 Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6) of compound **1** and **1** with Pd^{2+}.

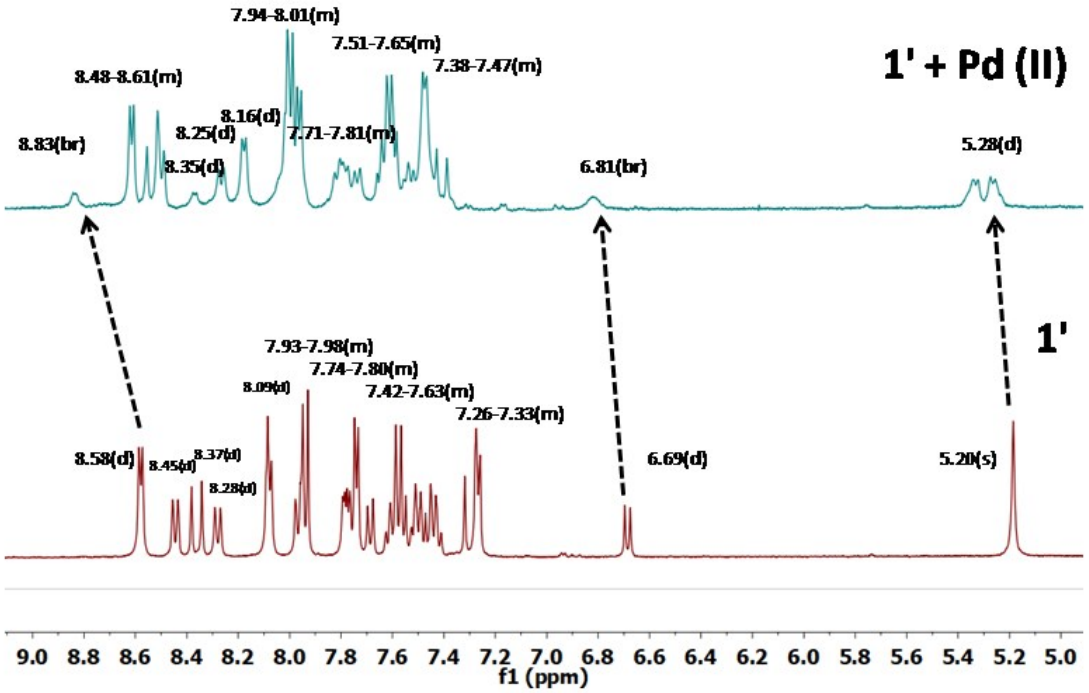

Fig. S22 Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6) of compound **1′** and **1′** with Pd^{2+}.

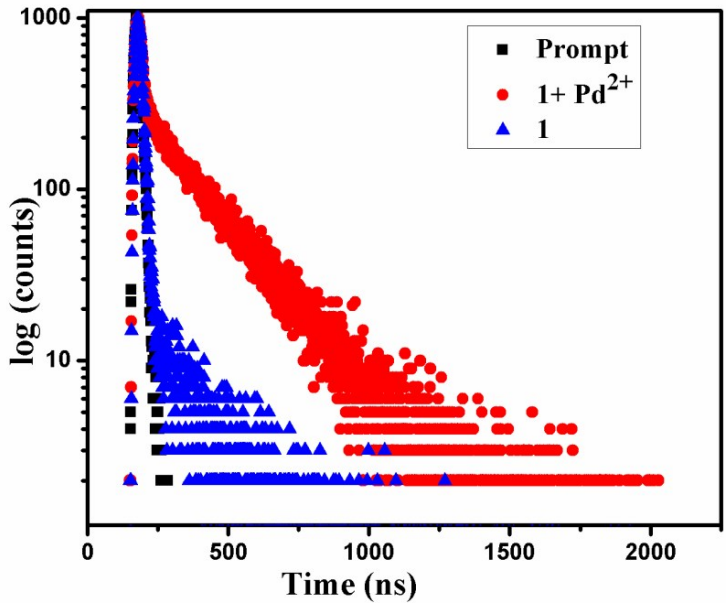

Fig. S23 Excited state decay profile of prompt, compound **1** and compound **1** with Pd^{2+} in H_2O.

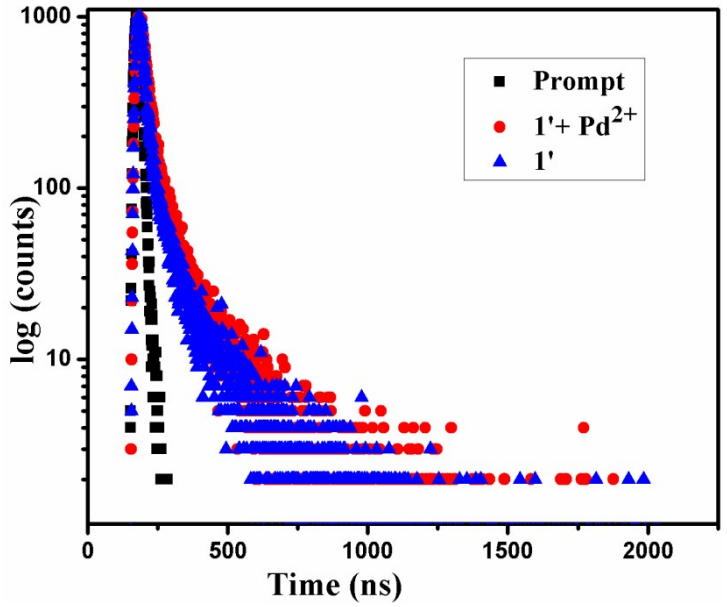

Fig. S24 Excited state decay profile of prompt, compound **1′** and compound **1′** with Pd^{2+} in H_2O.

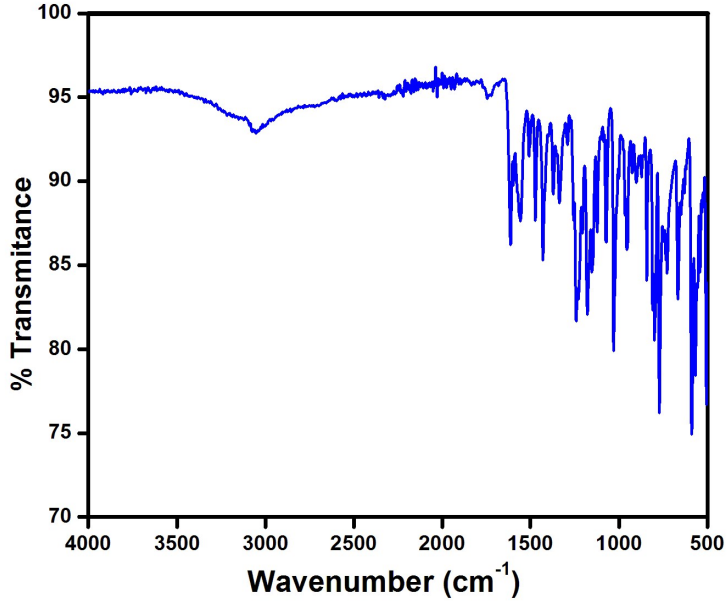

Fig. S25 IR spectrum of **1.**

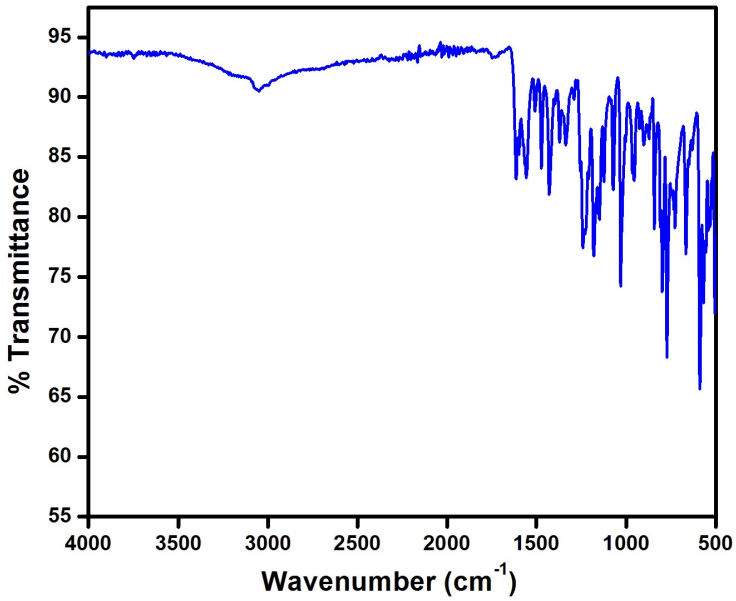

Fig. S26 IR spectrum of **1′.**

References

(1) G. M. Sheldrick, *Acta Cryst. A*, **2015**, *71*, 3-8.