Electronic Supplementary Material (ESI) for CrystEngComm.

One-dimensional Water Cages with Repeat unit of $(H_2O)_{24}$ Resembling Pagodane in 3D Coordination Polymer: Proton Conducting and Tunable Luminescence Emission by Absorption of Anionic Dyes

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Supporting Information

Details of synthesis procedures and characterization of coordination polymers by elemental analysis, IR spectra, PXRD, and TGA data, and proton conductivity, dye absorption and luminescence study.

General: Fourier transform IR (FTIR) spectra were recorded with an Perkin-Elmer instrument. Elemental analyses were obtained with a Perkin-Elmer instrument, series II, CHNS/O analyzer 2400. Thermogravimetric analysis (TGA) data were recorded under an Ar atmosphere at a heating rate of 5ºC min-1 with a Perkin-Elmer instrument, Pyris Diamond TG/DTA. Powder X-ray diffraction (XRD) data were recorded with a Bruker APEX-2 diffractometer at room temperature. The solid-state luminescence was recorded with a Spex Fluorolog-3 (model FL3-22) spectrofluorimeter.

Procedure for synthesis of ligand (L):

3-Amino pyridine (2 mmol) was added to 40 mL of a pyridine solution of (4-Carboxymethyl-phenyl)-acetic acid (1 mmol) and the solution were stirred for 15 min. After that triphenyl phosphite (9 mL, 2 mmol) was added slowly and the mixture was refluxed for 5 h. The volume of the solution mixture was reduced to 5 ml and then it was worked up with $CHCl_3$ and water.[1]
Yield = 90%, M.p = 222-224 ^{o}C.

Synthesis of Metal Complexes by Direct Reaction:

Preparation of $\{[Cd(L)(OAc)_2(H_2O)]\cdot 9H_2O\}_n$ (1) :

To a 4 ml methanolic solution of L (0.0173 g, 0.05 mmol), $Cd(OAc)_2$ (0.0 g, 0.05 mmol) in 4 ml methanol was added and it was mixed thoroughly. After that it was kept for slow evaporation and after 7-10 days colorless rod shaped crystals appeared.

Preparation of $\{[Cd_2(L)_2(OAc)_4]\cdot 2MeOH\}_n$ (2):

To a 4 ml anhydrous methanolic solution of L (0.0173 g, 0.05 mmol), $Cd(OAc)_2$ (0.0 g, 0.05 mmol) in 4 ml anhydrous methanol was added and it was mixed thoroughly. After that it was kept for slow evaporation and after 7-10 days colorless rod shaped crystals appeared.

Crystal Structure Determinations (1 and 2)

All the single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature (293 K) by the hemisphere method. The structures were solved by direct methods and refined by leastsquares methods on F^2 using SHELX-97.[2] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model. The H atoms attached to the O atom or N atoms are located wherever possible and refined using the riding model. In **1**, all the H-atoms on free water molecules located and refined using rding model, whereas in **2**, the H-atoms on MeOH molecules were not included in the refinement. PLATON was used for the calculation of volume occupied by the free water molecules in 1.[3]

Table S1: Crystallographic parameters for the complexes 1 and 2

	1	**2**
Formula	$C_{24}H_{44}CdN_4O_{16}$	$C_{50}H_{56}Cd_2N_8O_{14}$
Mol.Wt.	757.03	1217.83
T (k)	100(2)	100(2)
System	Monoclinic	Triclinic
Space group	C2/m	P-1
a (Å)	17.679(5)	10.1490(5)
b (Å)	27.134(7)	10.2936(5)
c (Å)	6.9113(18)	13.6107(7)
α (°)	90.00	104.922(4)
β (°)	94.222(8)	109.154(5)
γ (°)	90.00	95.153(4)
V (A^3)	3306.4(15)	1274.01(11)
Z	4	1
D(mg/m^3)	1.521	1.587
R1 [$I > 2\sigma(I)$]	0.0430	0.0373
wR2 (on F2, all data)	0.1306	0.0785

Table S2. Geometrical Parameters of Hydrogen Bonds in CP 1

Type	Donor	Acceptor	H···A(Å)	D···A(Å)	D-H···A(deg)
O-H···A	O2W	O3W	2.04(7)	2.822(5)	166(8)
O-H···A	O2W	O5W	1.81	2.7379	156
O-H···A	O3W	O201	1.88(4)	2.760(4)	178(7)
O-H···A	O4W	O2W	1.916(5)	2.793(4)	163.1(4)
O-H···A	O5W	O6W	1.88	2.7859	173
O-H···A	O5W	O21	2.022(4)	2.7927	157
O-H···A	O6W	O2W	1.85(6)	2.7653	162
O-H···A	O6W	O7W	1.85(6)	2.7309	175
O-H···A	O7W	O4W	1.85(2)	2.757(7)	179(8)
O-H···A	O7W	O4W	1.90(7)	2.774(7)	162(8)
N-H···A	N12	O201	1.96	2.818(4)	173

Table S3. Geometrical Parameters of Hydrogen Bonds in CP 2

Type	Donor	Acceptor	H···A(Å)	D···A(Å)	D-H···A(deg)
N-H···O	N(12A)	O(102)	1.98	2.822(4)	167
N-H···O	N(12B)	O(21A)	1.99	2.825(3)	165

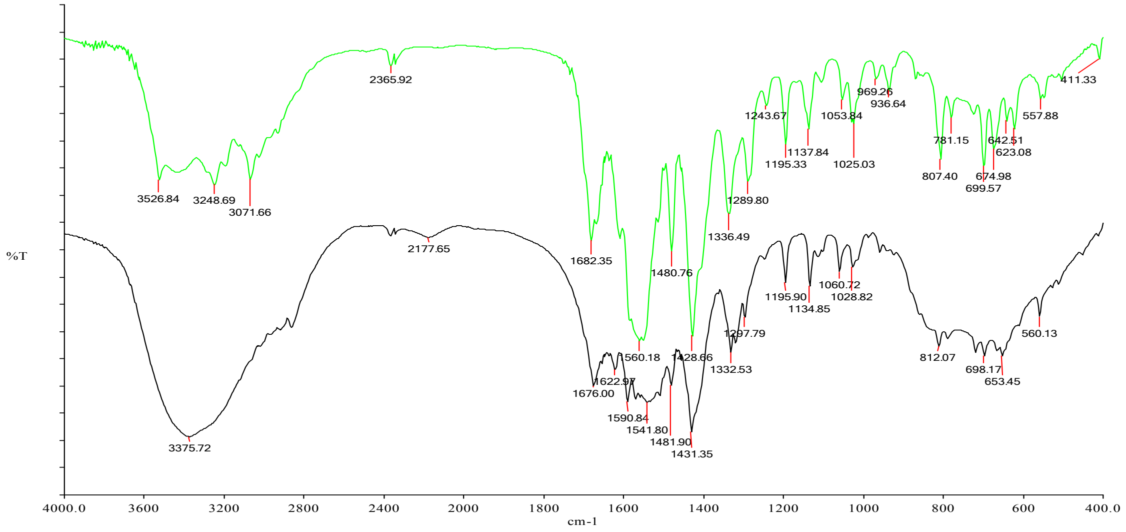


Figure S1. FTIR of Metal complex of **1** (black) and **2** (green)

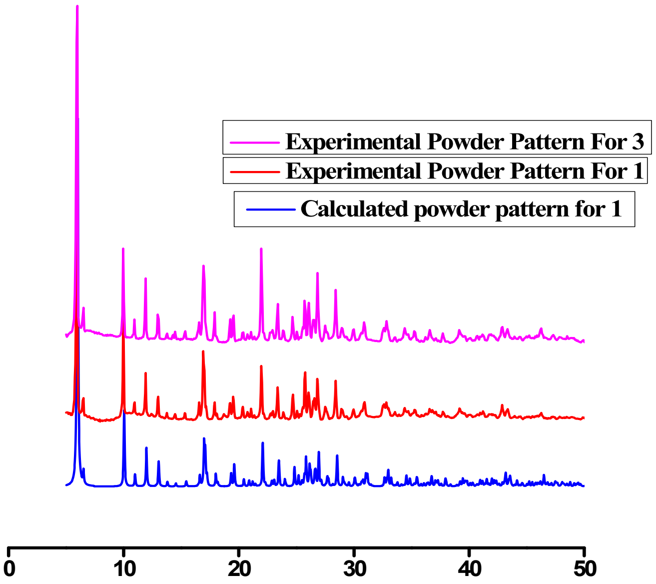


Figure S2. Comparison between Calculated PXRD pattern for **1** and Experimental PXRD pattern for **1** and **3**

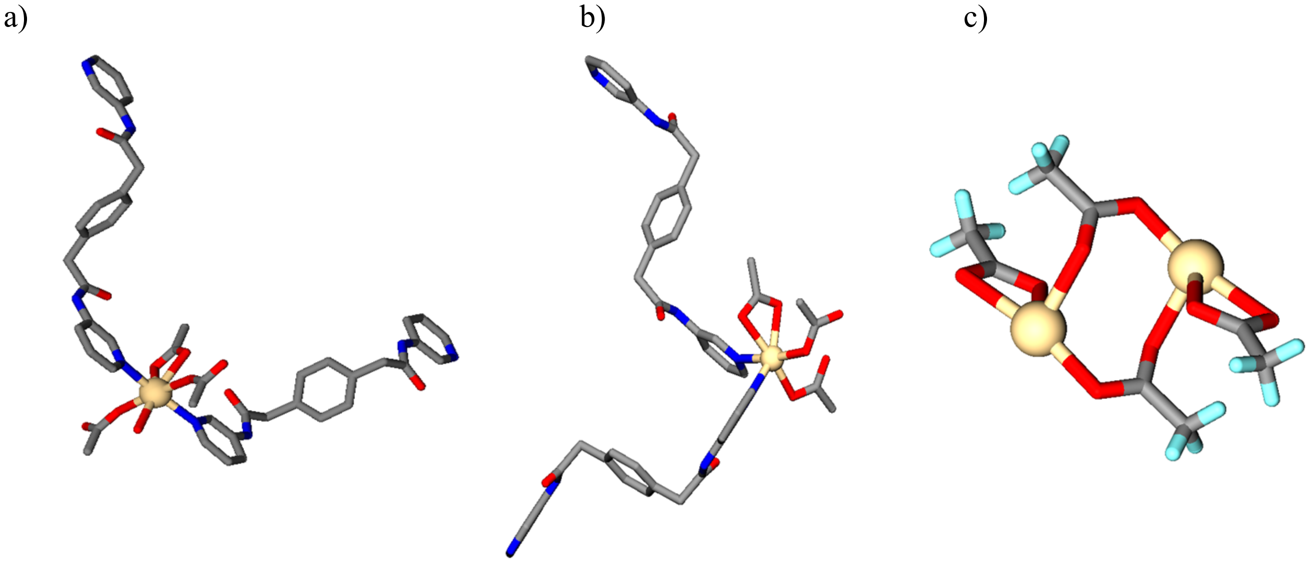


Figure S3. (a) & (b) Coordination environment of Cd(II) in CP **1**and Cd(II) in CP **2** respectively; (c) Formation $Cd_2(OAc)_4$ SBU with two Cd(II) ions in CP **2**

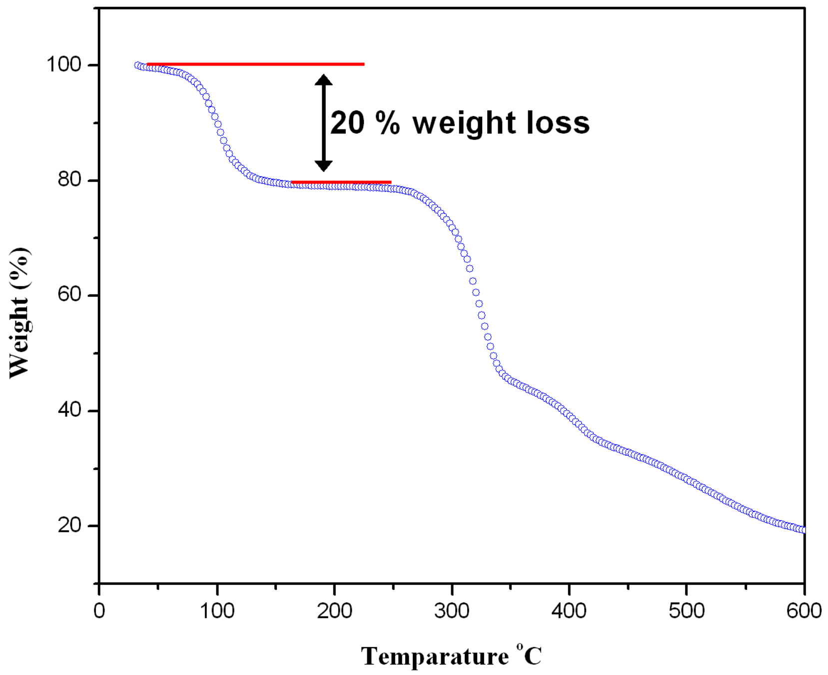


Figure S4. Thermal stability of Complexes **1**

Proton Conductivity Study:

The Proton Conductivities reported in this paper were measured using Solartron 1287 Electrochemical Interface with 1255B frequency response analyzer via a quasi-four-probe method. For this purpose, about 120 mg of the as-synthesized materials were pressed in a pellet maker to obtain uniform pellets of about 0.85 mm diameter, which was subject to humidification (98% RH) for 12 h and subsequently measured the proton conductivity. Resistances were measured from the semicircle of the Nyquist plots. The proton conductivities were measured by the following equation; $\sigma = L/(R.A)$ where σ = proton conductivity, L = thickness of the pellet, R = resistance of the pellet and A = area of the pellet = πr^2 where r = radius of the pellet.

For high-temperature proton conductivity measurements, the pellets were inserted within a humidification chamber, which was encircled with a controlled heating coil attached with an automated temperature controller. The heat flow within the temperature controller was controlled by a dimmerstat manually. The temperature of the chamber was monitored by an infrared temperature sensor attachment, having a sensing accuracy of ±0.5 °C.

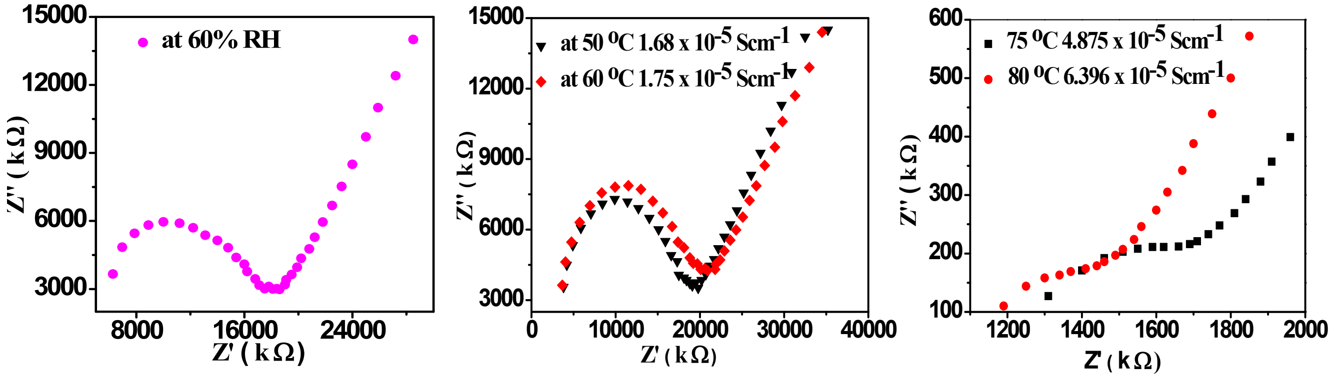
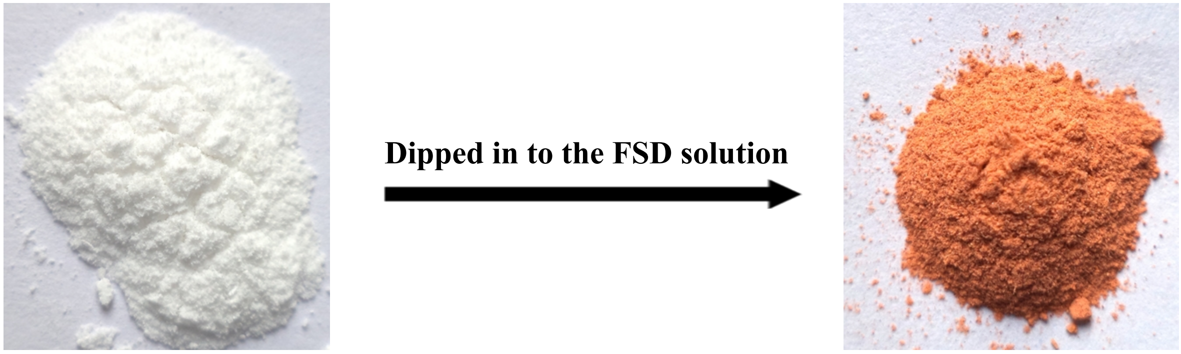


Figure S5. Nyquist plots of CP **1** (a) at 30 *°C* and 60 % RH; (b) at 50 and 60 *°C* at 98% RH; (c) at 75 and 80 *°C* at 98% RH

Dye absorption and Solid-state luminescences Study:



Before absorption

After absorption

Figure S6. Fluorescein doping in to the complex CP **1**

Elemental analysis for 1 and 3:

Elemental analysis for CP **1**, C_{24} H_{44} Cd N_4 O_{16}; calculated (%) C 38.07, H 5.86, N 7.40; observed (%) C 37.85, H 5.79, N 7.41

Elemental analysis for CP **3,** observed (%) C 41.67, H 5.46, N 8.18

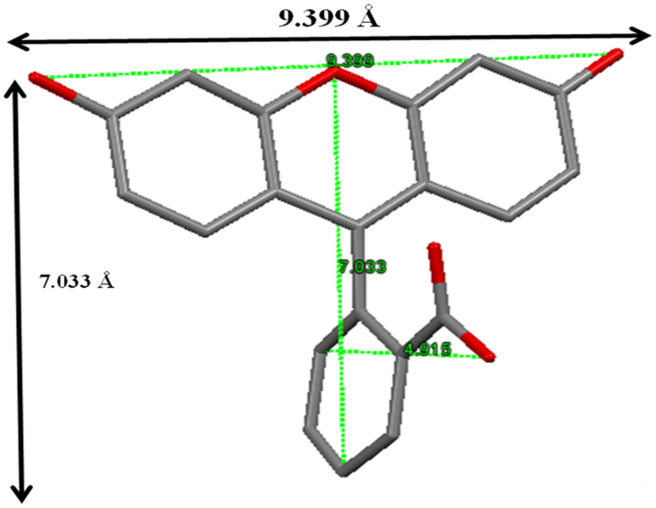


Figure S7. Molecular structure of Fluorescein with dimension of 9.399 × 7.033 Å^2

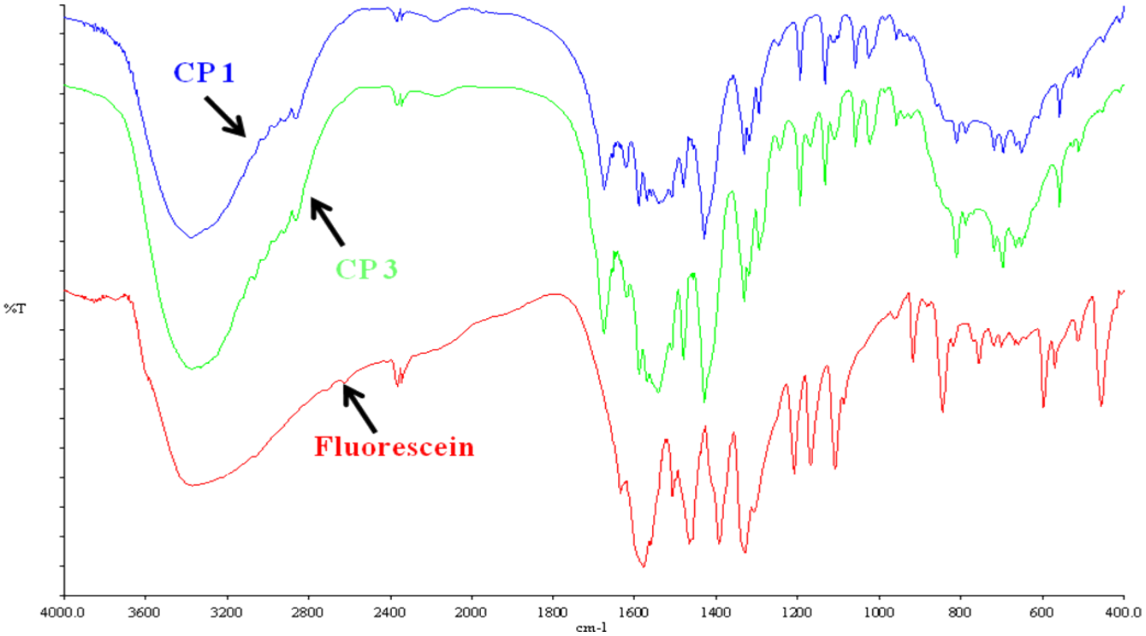
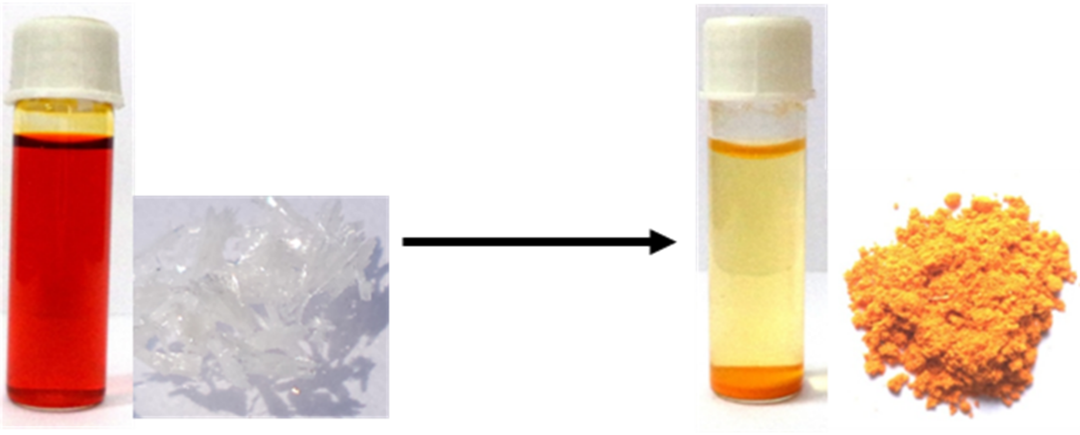


Figure S8. FTIR Fluorescein absorbed materials (**3**)



Before dye absorption

After dye absorption

Figure S9. Methyl Orange Dye Absorption Study

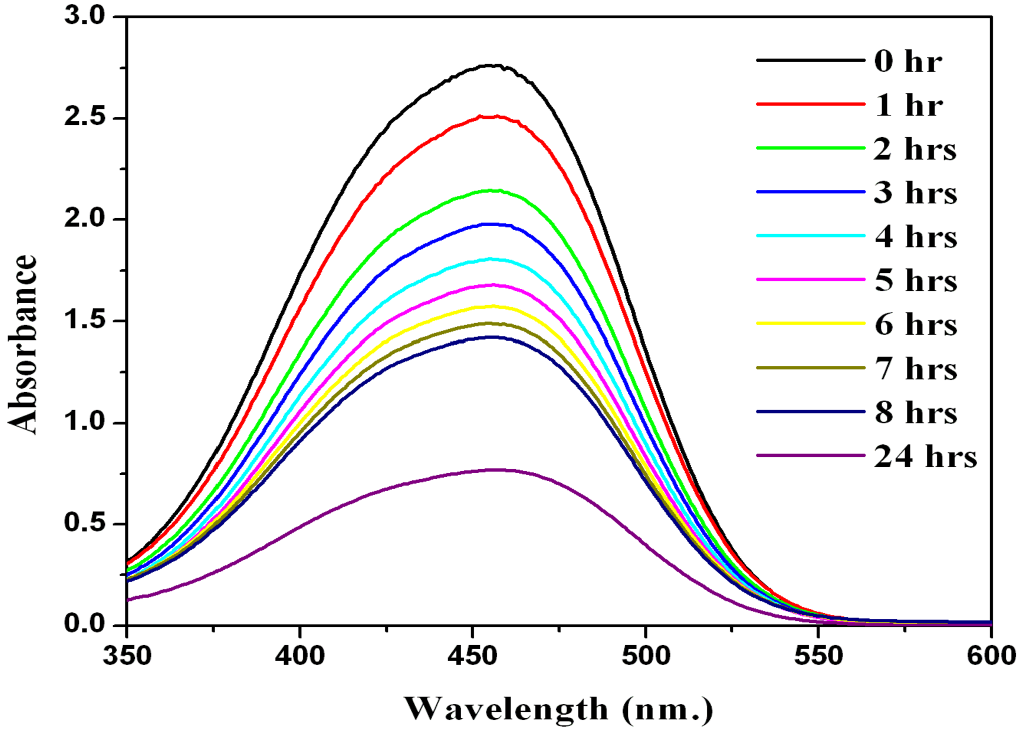


Figure S10. Monitoring of dye (Methyl orange) absorption by 1 at various time intervals using UV-visible spectroscopy

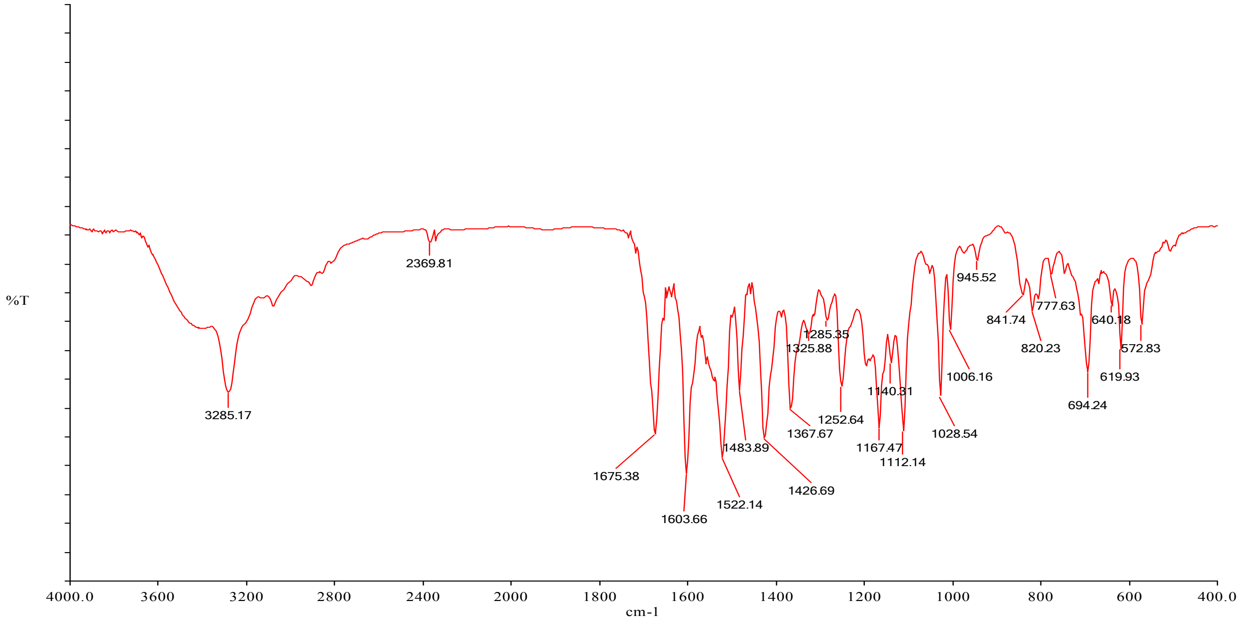


Figure S11. FTIR of the methyl orange absorbed CP **1**

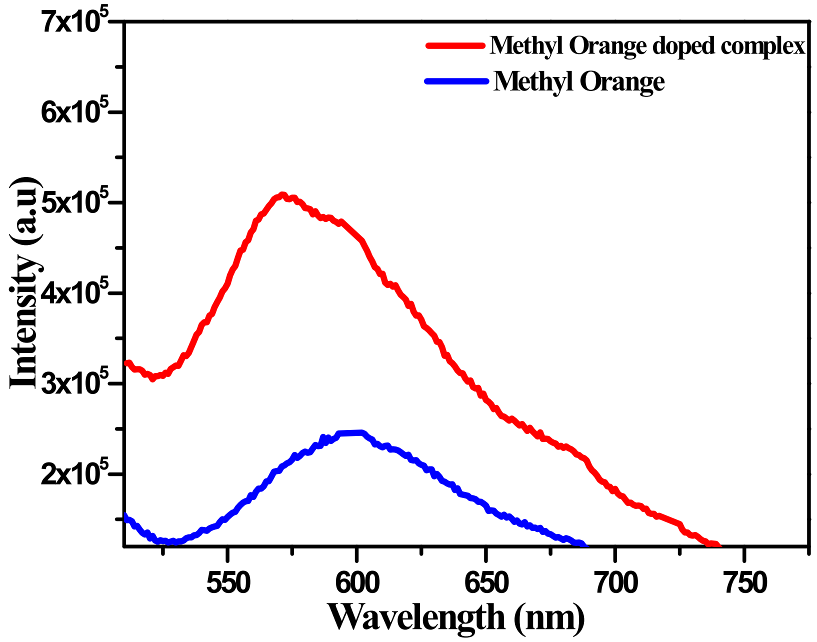


Figure S12. Solid state emission spectra of methyl orange and methyl orange doped spectra. Methyl orange doped CP **1** shows a broad range emission maximum at 570 nm having a blue sift compare to pure methyl orange which exhibits a broad range emission maximum at 597 nm. The emission intensity is almost doubled up for the dye absorbed materials compare to pure methyl orange.

References:

1. L. Rajput, S. Singha and K. Biradha, *Crystal Growth & Design*, 2007,**7**, , 2788
2. G. M. Sheldrick, SHELX-97, *Program for the Solution and Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.
3. A. L. Spek, *PLATON-A Multi Purpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2002.