Supporting Information

Tunable Emission from Porous Metal-Organic Frameworks by Employing an Excited-State Intramolecular Proton Transfer Responsive Ligand

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Experimental

Reagents

All reagents were obtained from commercial sources and used without further purification. High purity $Mg(NO_3)_2{\cdot}6H_2O$ and 2,5-dihydroxyterephthalic acid were purchased from Aldrich Chemical Co. and used as received.

Physical measurements

Elemental analysis was carried out using a Thermo Scientific Flash 2000 CHN analyzer. IR spectra were recorded using KBr pellets in the range 4000 - 400 cm^{-1} on Bruker IFS-66v spectrophotometer. Thermogravimetric analyses (TGA) were carried out under nitrogen (flow rate of 50 mL/min) with Metler Toledo TGA-850 TG analyzer in the temperature range between 25 - 650°C at a heating rate 3°C / min. Powder X-ray diffraction (PXRD) pattern were recorded on a Bruker D8 Discover instrument using Cu-Kα radiation.

Adsorption measurements: N_2 (77 K), CO_2 (195 K) and H_2 (77 K) adsorption study of the dehydrated sample of **1** was carried out using QUANTACHROME AUTOSORB-1C analyzer. In the sample chamber maintained at $T \pm 0.03$ K was placed the adsorbent sample (100-150 mg), which had been prepared at 493 K under a high vacuum (10^{-1} Pa) for 18 hours prior to measurement of the isotherms. The adsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state. All operations were computer-controlled and automatic.

Synthesis of $[Mg(DHT)(DMF)_2]_n$ (1)

A mixture of $Mg(NO_3)_2.6H_2O$ (0.128 g, 0.5 mmol), 2,5-dihydroxyterephthalic acid (0.099 g, 0.5 mmol) and 15 μL triethylamine and 8 mL N,N-dimethylformamide (DMF) was placed in a 23 mL teflon bomb and the whole reaction mixture was stirred for 1 h. Then Teflon bomb was subsequently placed in a steel autoclave and heated at 120 ºC under autogenous pressure for 72 h and then cooled to ambient temperature. Light yellow colored block shaped crystals were isolated by decanting the supernatant liquid and washed thoroughly several times with DMF. (Yield 80 %). IR (KBr cm^{-1}); ν(O-H), 3468; ν_{as}(OCO), 1609; ν_s(OCO), 1455. Anal. Calcd. for $C_{14}H_{18}MgN_2O_8$: C, 45.82; H, 4.90; N, 7.63. Found: C, 45.21; H, 5.01; N, 7.49%.

X-ray crystallography

A suitable single crystal for **1** was carefully selected under a polarizing microscope and fixed to a separate thin glass fiber by commercially available glue. X-ray single crystal structural data was collected by a Bruker Smart –CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source ($Mo_{K\alpha}$ radiation, 0.71073 Å) operating at 50 kV and 30 mA. The programme SAINT[1] was used for integration of diffraction profiles and an empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.[2] The structure was solved by direct method using SIR92 programme[3] and refined by full matrix least square method using SHELXL 97.[4] The hydrogen atoms were fixed by HFIX and placed in ideal positions. Potential solvent accessible area or void space was calculated using the PLATON 99[5] multipurpose crystallographic software. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non hydrogen atoms. All calculations were carried out using WinGX system, Ver 1.70.01.[6] The coordinates, anisotropic displacement parameters, and torsion angles for **1** is submitted as supplementary information in CIF format. Crystallographic data and structure refinement parameters for **1** are given in manuscript (ref. no. 8). Selected bond distances and angles of **1** are given in Table S1.

References

(1) SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc. Madison, Wisconsin, USA, 2004.

(2) Sheldrick, G. M. *Siemens Area Detector Absorption Correction Program*, University of Göttingen, Göttingen, Germany, 1994.

(3) Altomare, A.; Cascarano, G.; Giacovazzo C.; Gualaradi, A. *J. Appl. Cryst.* **1993**, *26,* 343.

(4) Sheldrick, G. M. SHELXL-97, *Program for Crystal Structure Solution and Refinement*; University of Göttingen, Göttingen, Germany, 1997.

(5) Spek, A. L. *J. Appl. Cryst.* **2003**, *36,* 7.

(6) Farrugia, L. J. *WinGX - A Windows Program for Crystal Structure Analysis*. *J. Appl. Crystallogr.* **1999**, *32*, 837.

Table S1. Bond distances (Å) and angles (°) for $[Mg(DHT)(DMF)_2]_n$ (**1**)..

Mg1-O1	2.072(5)	Mg1-O4	2.085(4)
Mg1-O2_a	2.049(4)	Mg1-O1_b	2.072(5)
Mg1-O4_b	2.085(4)	Mg1-O2_c	2.049(4)

O1-Mg1-O4	89.25(17)	O1-Mg1-O2_a	91.89(17)
O1-Mg1-O1_b	180.00	O1-Mg1-O4_b	90.75(17)
O1-Mg1-O2_c	88.11(17)	O2_a-Mg1-O4	83.86(16)
O1_b-Mg1-O4	90.75(17)	O4-Mg1-O4_b	180.00
O2_c-Mg1-O4	96.14(16)	O1_b-Mg1-O2_a	88.11(17)
O2_a-Mg1-O4_b	96.14(16)	O2_a-Mg1-O2_c	180.00
O1_b-Mg1-O4_b	89.25(17)	O1_b-Mg1-O2_c	91.89(17)
O2_c-Mg1-O4_b	83.86(16)		

Symmetry code: a = 2-x,y,3/2-z; b = 2-x,-y,1-z; c = x,-y,-1/2+z

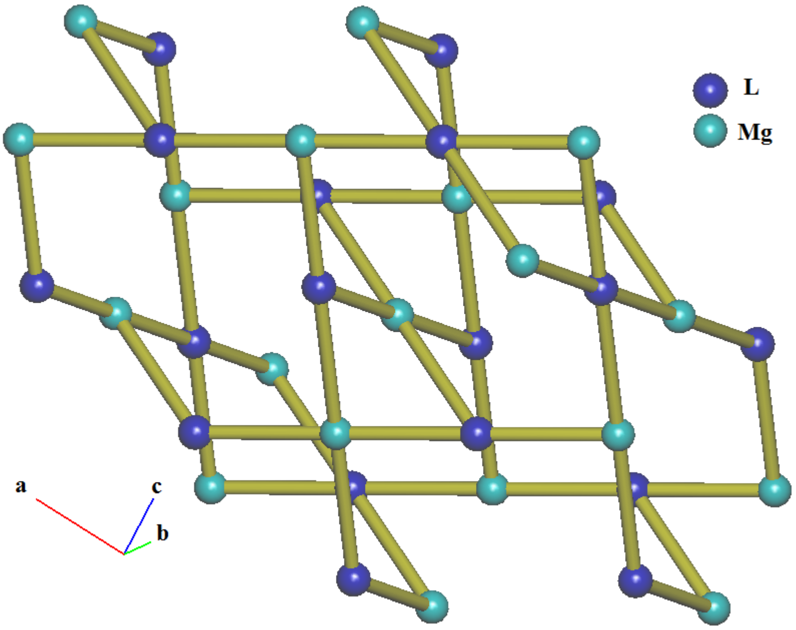

Fig. S1. 4-connected uninodal network topology of **1** analysis by the TOPOS. (See the references: (a) Blatov, V. A.; Shevchenko, A. P.; Serezhkin, V. N. *J. Appl. Crystallogr.* **2000**, *33*, 1193; (b) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; *Cryst. Eng. Comm.* **2004**, *6,* 377.)

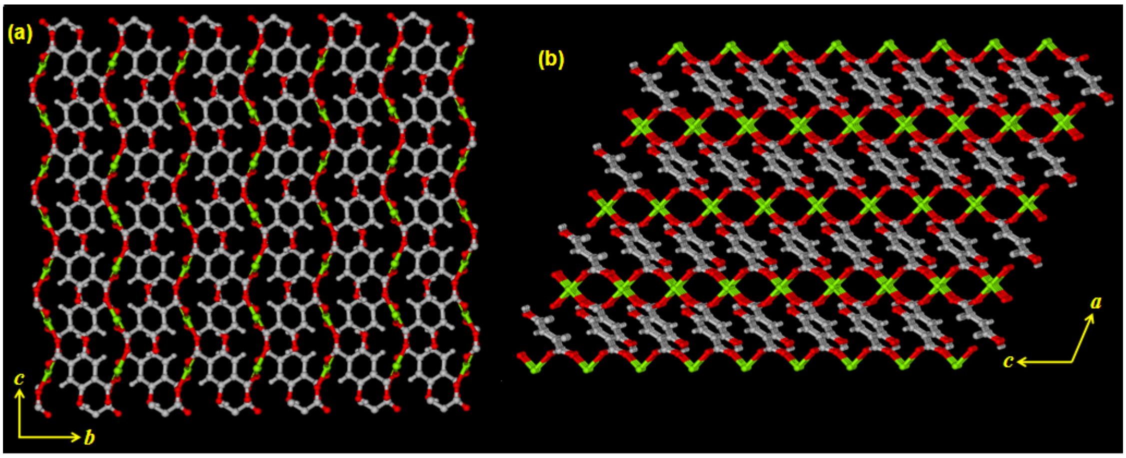

Fig. S2. View of the 3D framework (a) along crystallographic *a*-axis; and (b) along crystallographic *b*-axis.

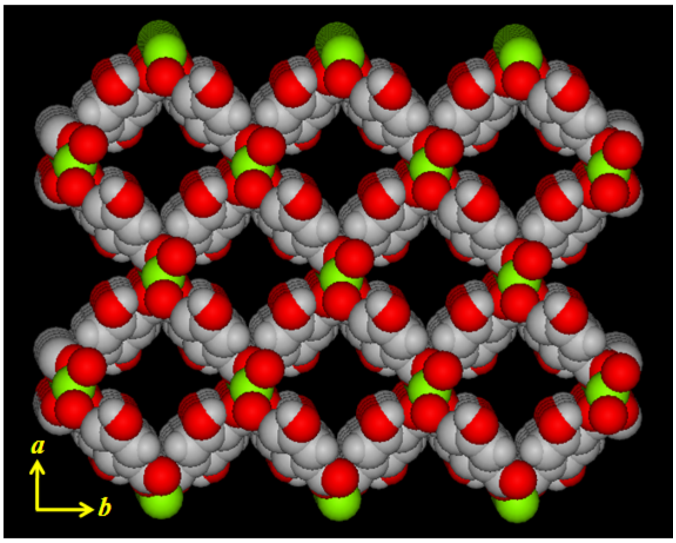

Fig. S3. CPK diagram of **1** showing the square shaped channels along the crystallographic *c*-axis.

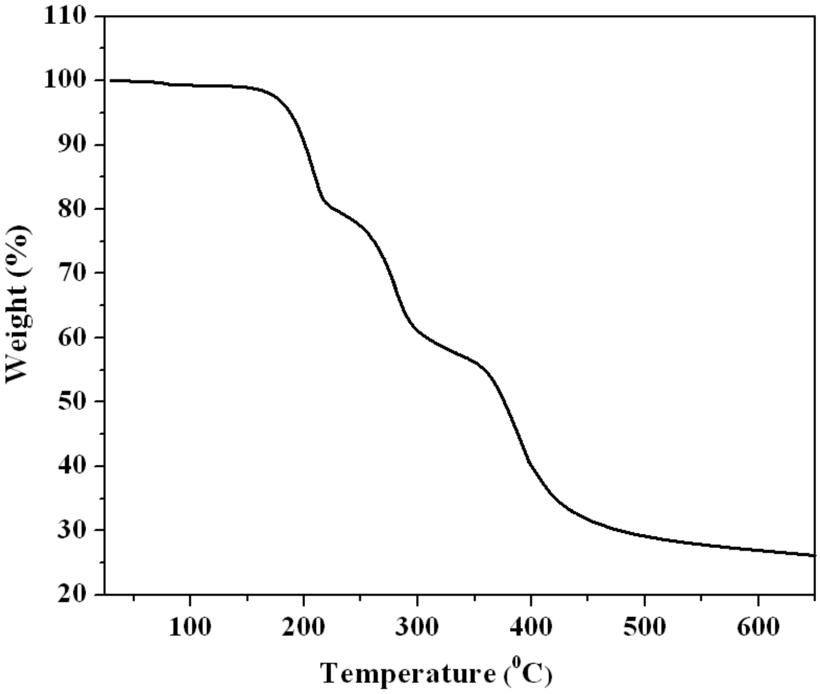

Fig. S4. TGA analysis of **1** under N_2 atmosphere.

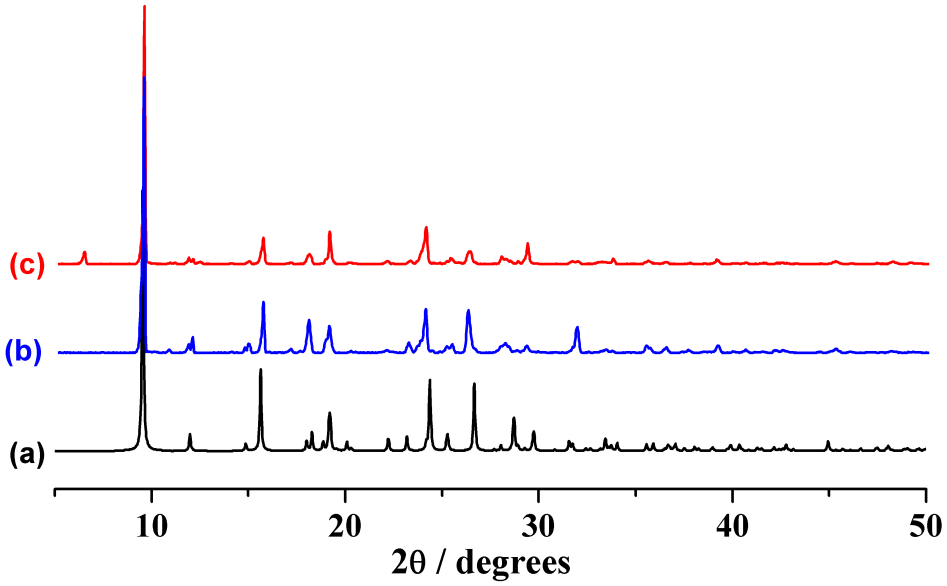

Fig. S5. PXRD pattern of **1** in different states; (a) simulated from X-ray single crystal data, (b) as-synthesized and (c) desolvated at 220 °C under high vacuum (10^{-1} Pa).

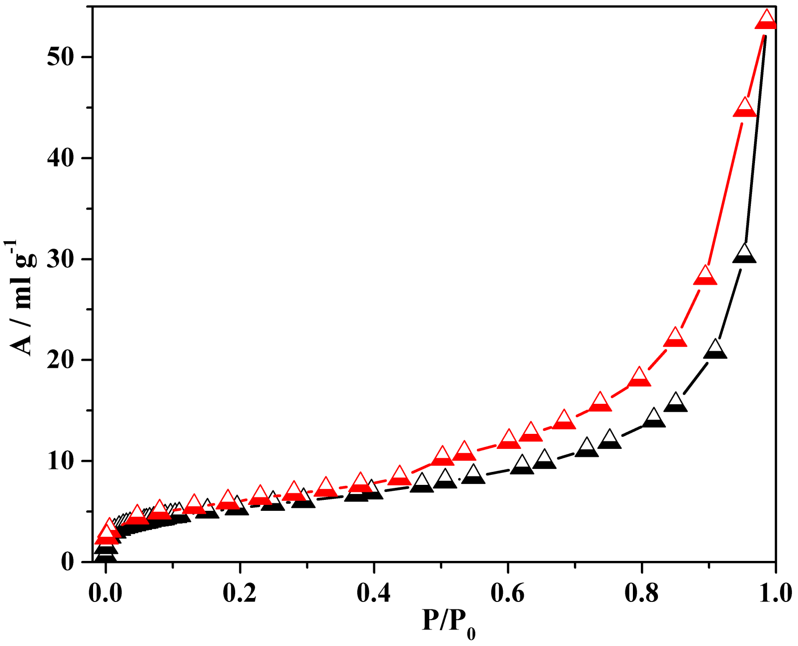

Fig. S6. N_2 sorption isotherm for the desolvated framework **1** at 77 K.

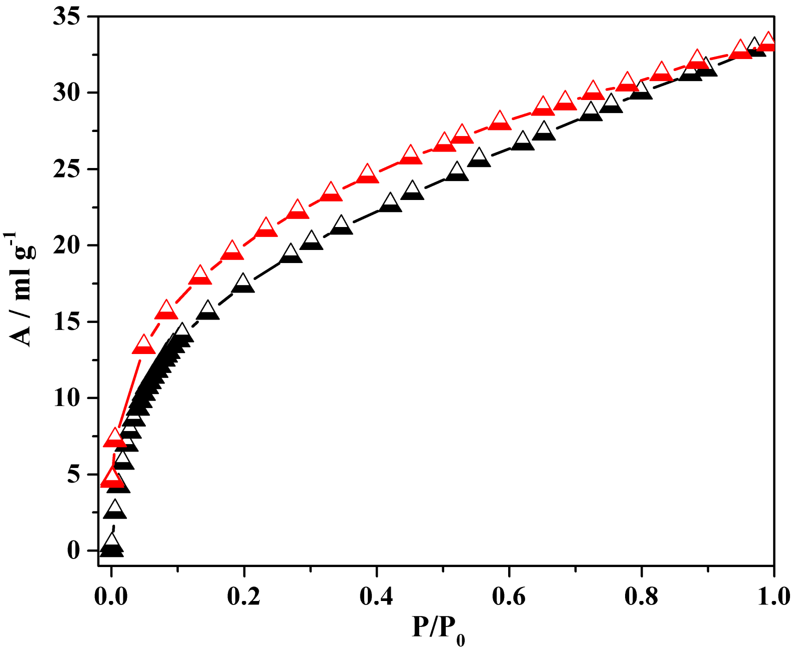

Fig. S7. H_2 sorption isotherm for the desolvated framework **1** at 77 K.

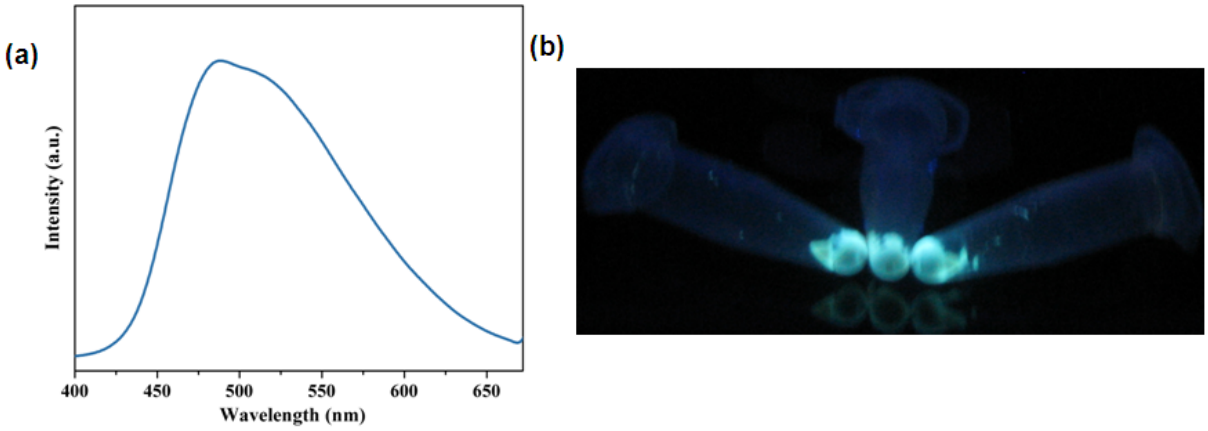

Fig. S8. (a) Solid state emission spectra of **1**; and (b) corresponding photographs of the as-synthesized MOF under UV irradiation.

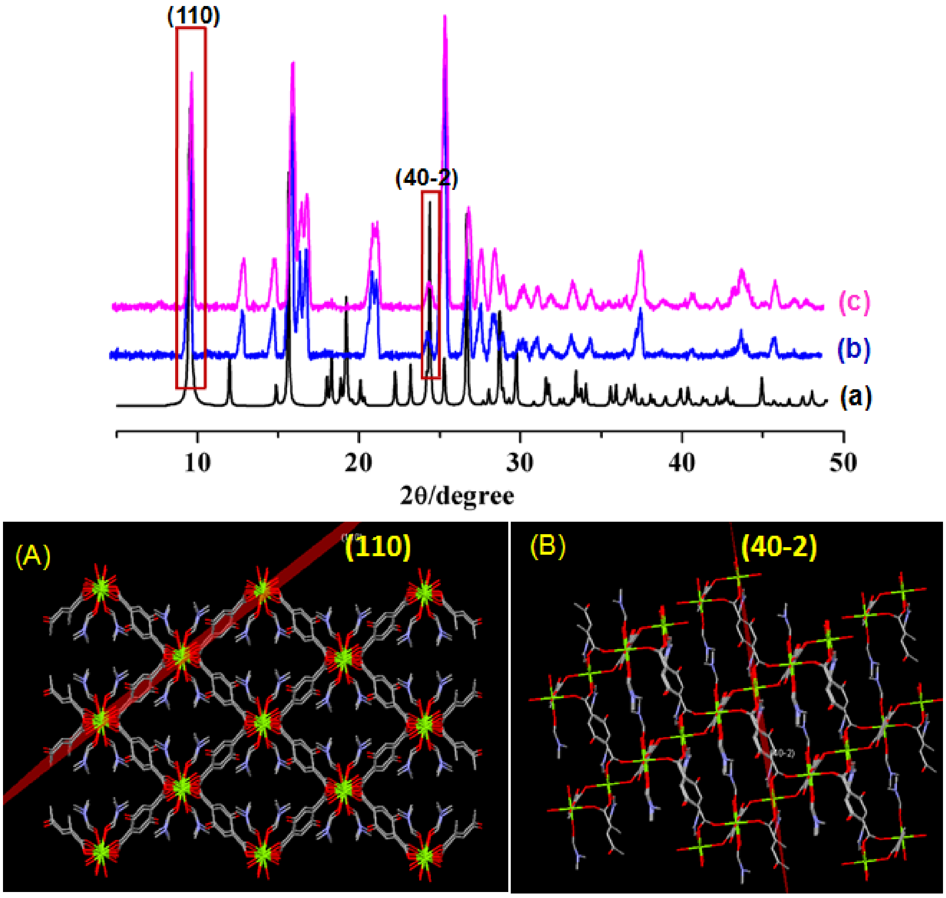

Fig. S9. (Top) PXRD pattern of **1** in different state: (a) assynthesized **1**; (b) isolated product of **1** after dissolved in water; and (c) **1** grinded with water. (Bottom) Extended structure of **1** with different crystallographic planes: (A) (110); and (B) (40-2) plane.

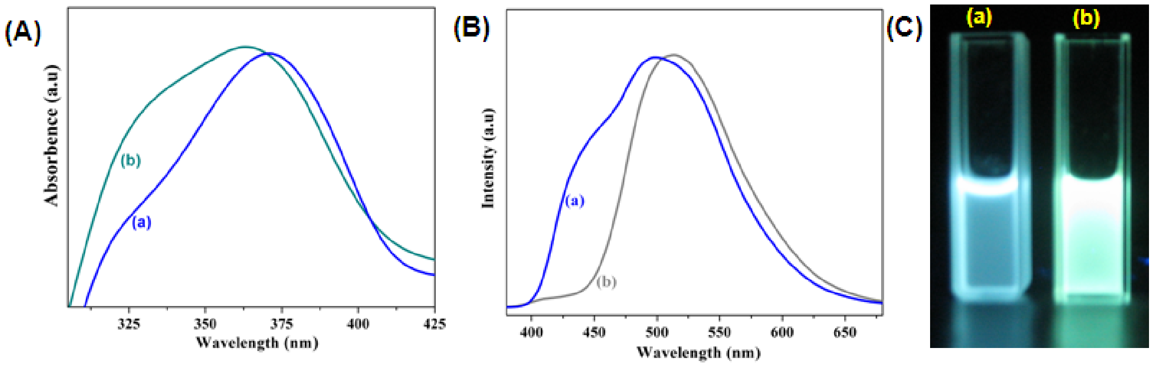

Fig. S10. (A) Normalized absorption spectra of DHT linker in different solvents (a) Ethanol, (b) DMF; (B) Corresponding normalized emission spectra of DHT linker (a) Ethanol, (b) DMF; (C) Corresponding photographs of the solution under UV irradiation (a) Ethanol, (b) DMF.

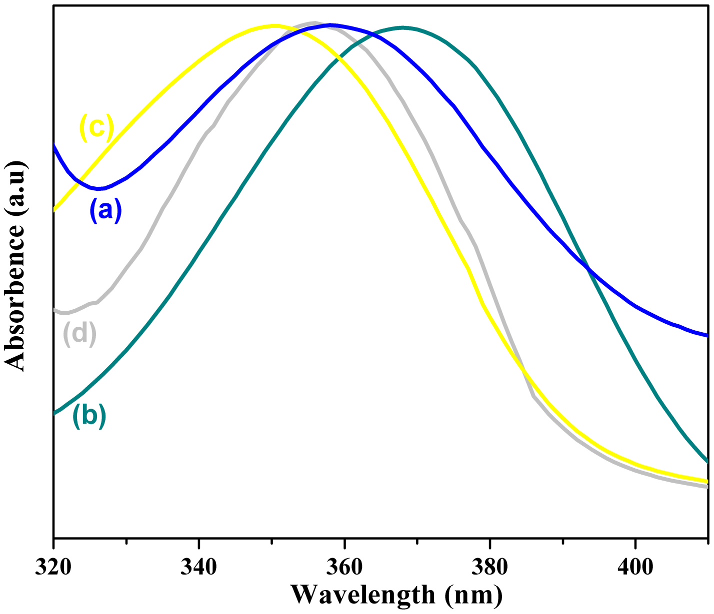

Fig. S11. Normalized absorption spectra of **1** in different solvents. (a) Ethanol, (b) DMSO, (c) H_2O and (d) DMF.

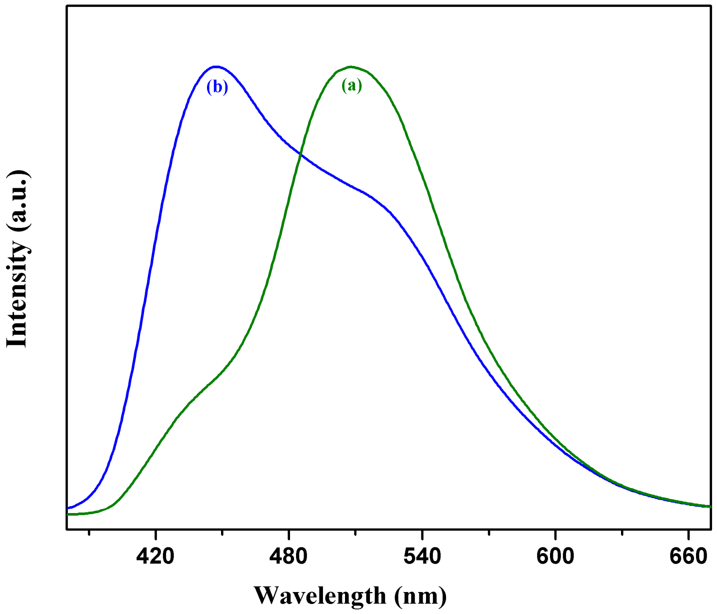

Fig. S12. Normalized emission spectra of **1;** (a) in DMSO; (b) in DMSO containing trifluoroacetic acid (TFA).

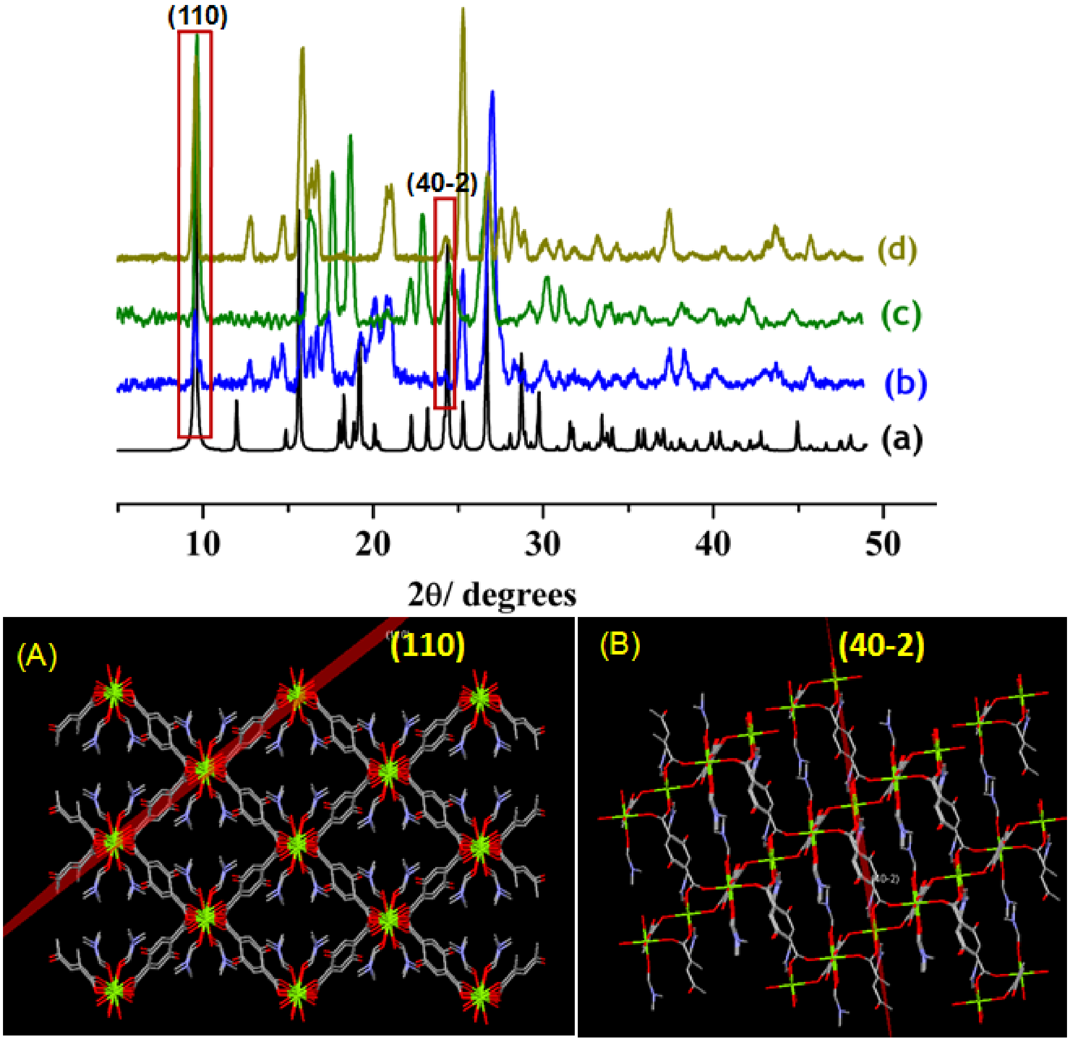

Fig. S13. (Top) PXRD pattern of **1** in different states, (a) assynthesized **1**; (b) **1** grinded with trifluoroacetic acid (TFA); (b) **1** grinded with DMSO; (c) **1** grinded with water. (Bottom) Extended structure of **1** with different crystallographic planes; (A) (110) and (B) (40-2) plane.

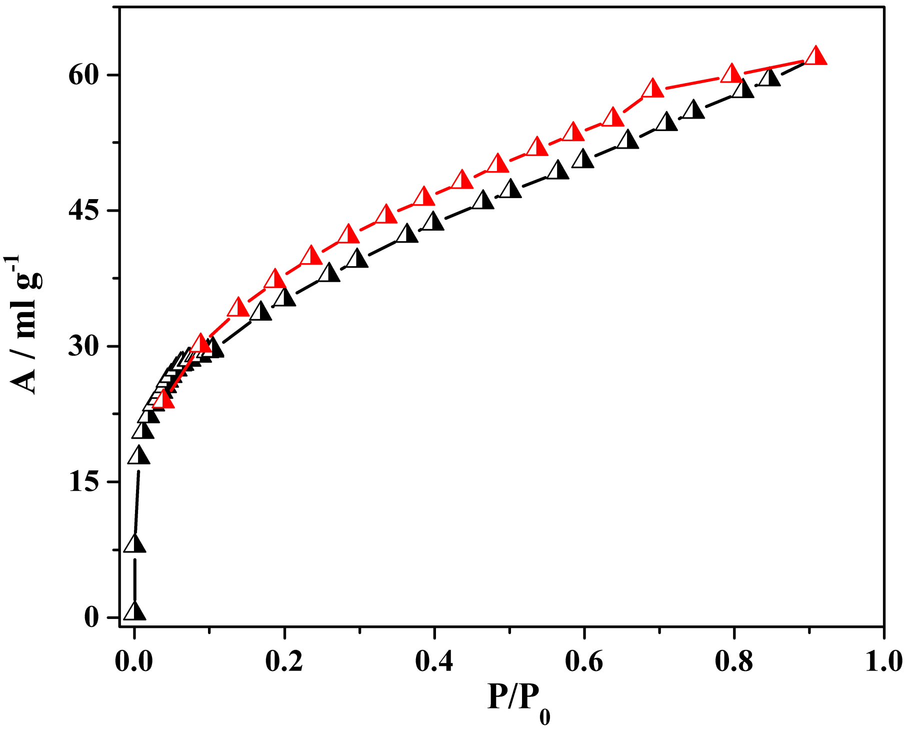

Fig. S14. CO_2 sorption isotherm for DMSO grinded sample of **1** at 195 K. (sample was degassed at 433 K).