

## **Electrochromic and Photochromic Behaviour in a Single Metal-Organic Framework Containing Redox-Active Linker**

### **Materials:**

The chemicals were purchased from the local suppliers. 1,4,5,8-naphthalenetetracarboxylic dianhydride (96%), 5-amino isophthalic acid (94%),  $ZrOCl_2 \cdot 8H_2O$  (98%), and formic acid ( $\geq 96\%$ ) were purchased from TCI and Sigma-Aldrich. N, N-dimethylformamide (DMF) (99.9%), Acetonitrile, Tetrabutyl ammonium hexafluorophosphate (TBAP) and glacial acetic acid (SRL) were purchased from Hychem Chemical local suppliers. ITOs were purchased from sinsil pvt ltd local suppliers. Deionized water was used throughout all experiments wherever is needed.

### **Synthesis of ligand (BINDI)**

N, N'-bis (5-isophthalic acid) naphthalenediimide (BINDI) was synthesized using reported literature procedure.<sup>1</sup> In acetic acid (25 ml) 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.810 g, 3 mmol) was taken and allowed stir for 10 min. Then amino isophthalic acid (1.096 g, 6 mmol) added and allowed to reflux for 24 h. After completion of reaction, the mixture was allowed to cool to room temperature and then precipitated from water. The filtered product was recrystallized from the DMF. The crystallized product was filtered off and washed with volatile solvent. The product was then dried in an oven at 80 °C.

### **Preparation of MOF**

MOF 1 was synthesized according to reported procedure the.<sup>1</sup> In DMF (3 ml),  $ZrOCl_2 \cdot 8H_2O$  (11.27 mg, 0.035 mmol) and BINDI (17.13 mg, 0.03 mmol) were taken in a 25 ml vial. To this 2 ml of formic acid was added and sonicated to get the uniform suspension. The vial was kept at 130 °C for 48 h to obtain rod shaped crystals. The crystals were washed with DMF and then with acetone for several times and allowed dry at 80°C for further use.

### **Preparation of ITO/MOF Film**

The MOF powder was finely grounded. The fine powder was taken 3 mg in 1 ml of methanol and sonicated for 3 h to get the uniform suspension. Before drop casting this suspension onto the ITO, the ITO was cleaned with soap water and then rinsed with deionized water. Then the ITO was sonicated in acetone for 15 min, after that washed with isopropanol and then dried in oven at 90 °C. After drying the ITO 100 µl of methanol suspension was drop casted onto it and allowed to dry at 80 °C overnight before performing the experiments.

## **Characterization**

**Thermal Gravimetric Analysis** The thermal stability of MOF was recorded under N<sub>2</sub> atmosphere using Shimadzu DTG-60 instrument from 30 °C - 800 °C by maintaining the rate at 10 °C/min. Up to 400 °C the sample has good thermal stability with mass loss below 100 °C with solvent loss.

**X-ray Powder Diffraction** The bulk phase purity of the material was conformed from the PXRD. The PXRD pattern was obtained using Rigaku Ultima-IV supplied with Cu K $\alpha$  source as the radiation (40 kV, 40 mA). The PXRD recorded in the 2 $\theta$  range from 4-40° with as step size of 2°/min.

**Nitrogen Adsorption** N<sub>2</sub> sorption isotherms were performed on Microtrac Bel - BEL SORP mini II model surface area analyzer. Prior to adsorption studies under dynamic vacuum the sample was activated at 100 °C for 4 h. The obtained values for BET surface area, pore size, and pore volume of the MOF were in good agreement with the reported values.

**Scanning Electron Microscopy** SEM images of as synthesised and after CV experiments were recorded on FEI Apreo LoVac instrument.

**Solid state photoluminescent studies** of 1 absorption measured on JASCO V-670 UV-VIS NIR spectrophotometer

**Electrochemical measurements**

Cyclic voltammetry (CV) and chronoamperometry were performed by an Autolab PGSTAT128N potentiostat. The UV and transmission studies were performed using the Ocean Optics UV-vis spectrophotometer (USB4000, Ocean Optics).

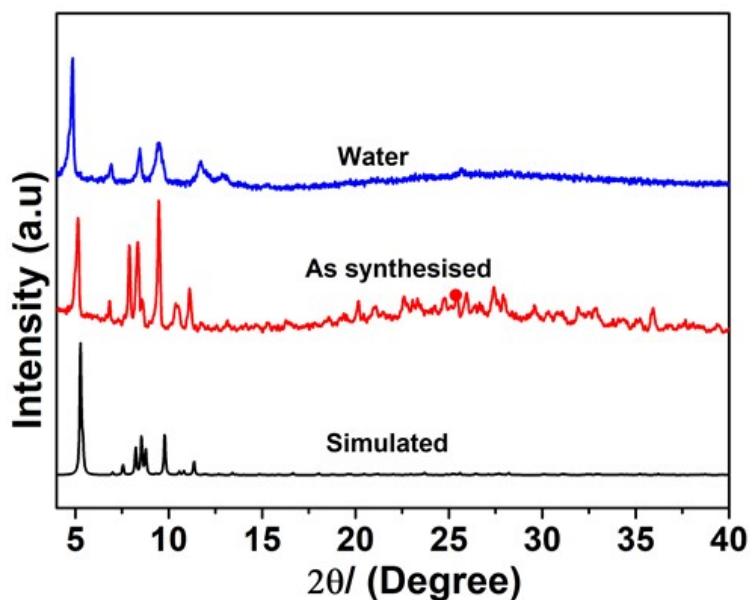


Fig S1. Comparison of as-synthesized material with the simulated one MOF stability is retained after exposed to water for 24 hr.

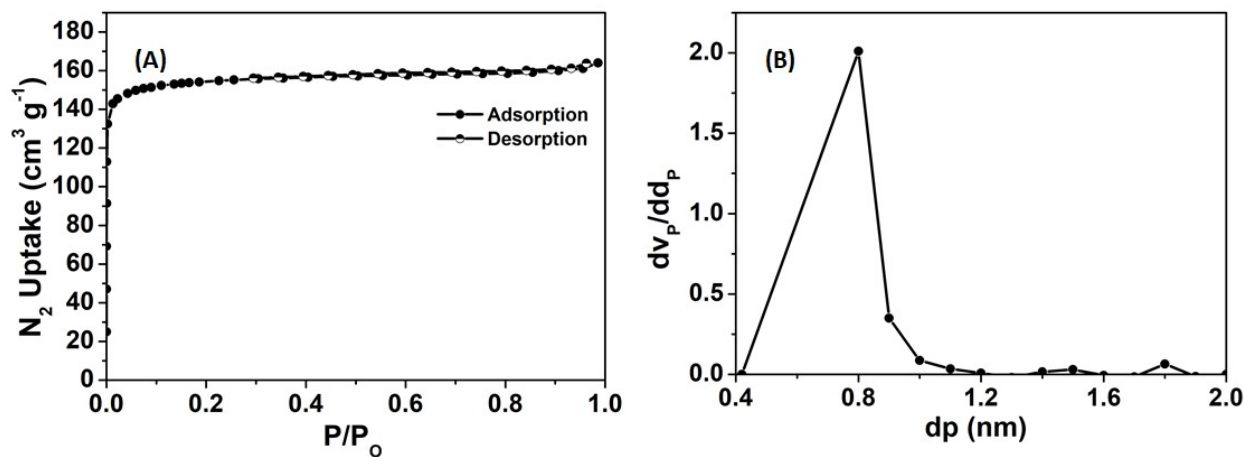


Figure S2. A) N<sub>2</sub> adsorption and desorption isotherm of **1**. B) pore diameter of **1** at 77 K.

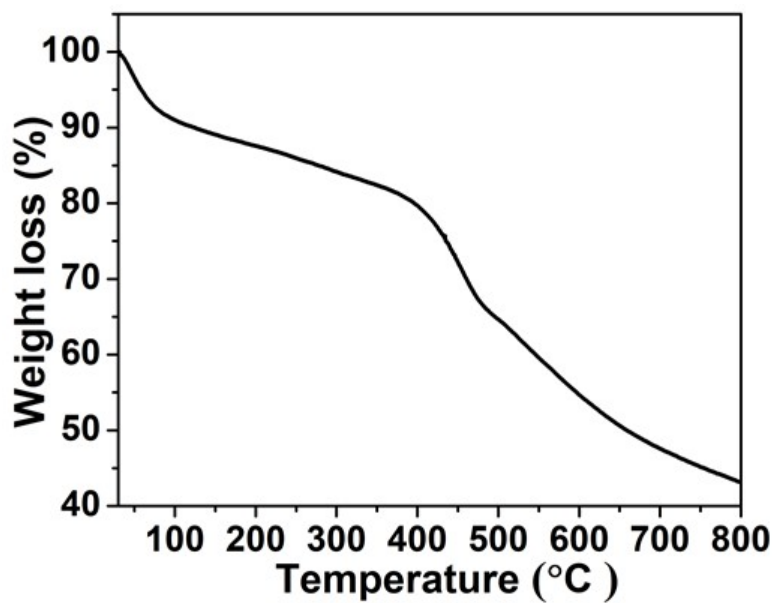


Figure S3. TGA of 1.

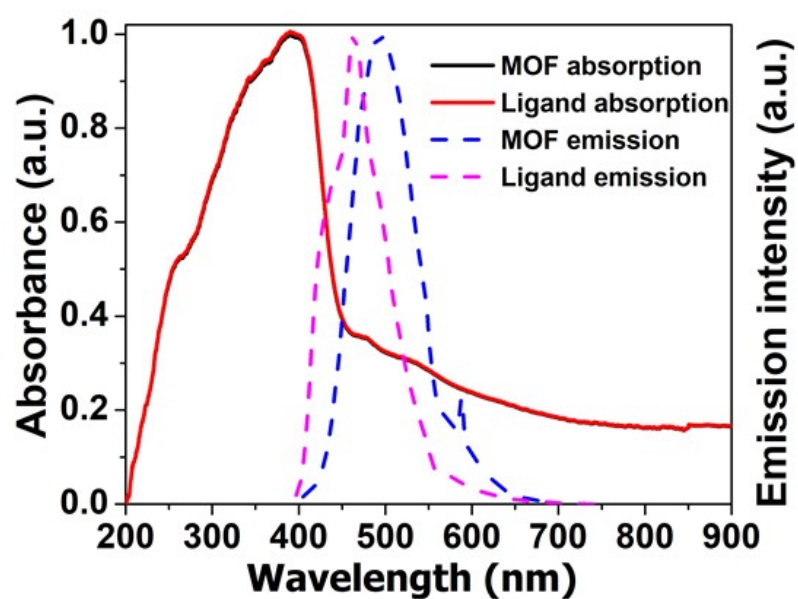


Figure S4. Solid state UV-absorbance and emission spectra of 1  $\lambda_{ex}$ = 395 nm and ligand  $\lambda_{ex}$ = 390 nm.

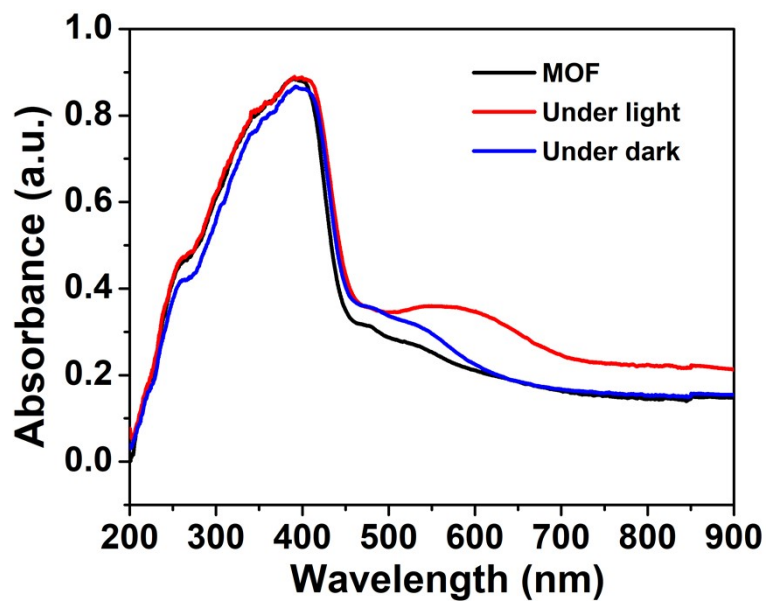


Figure S5. Absorbance spectra of **1** in after exposing to sunlight and dark conditions.

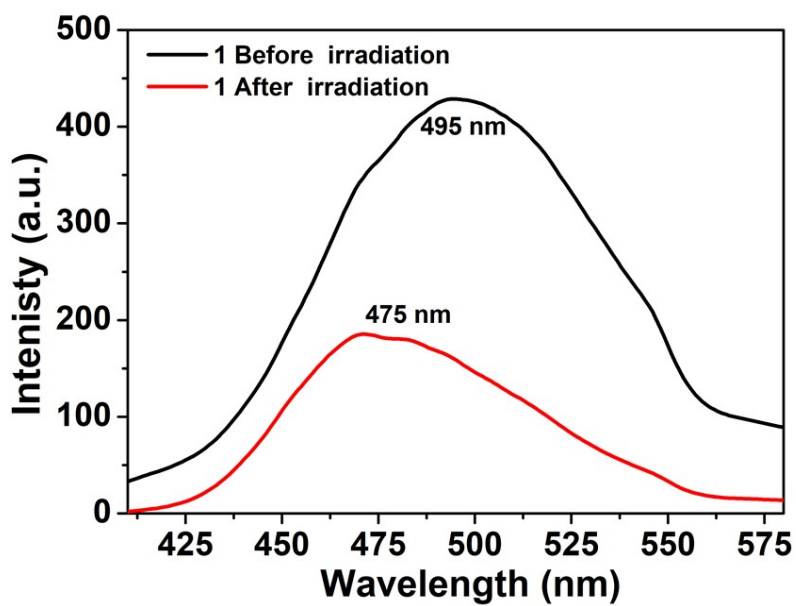


Figure S6: Emission spectra of **1** before and after irradiation under sunlight  $\lambda_{ex}$ = 395 nm.

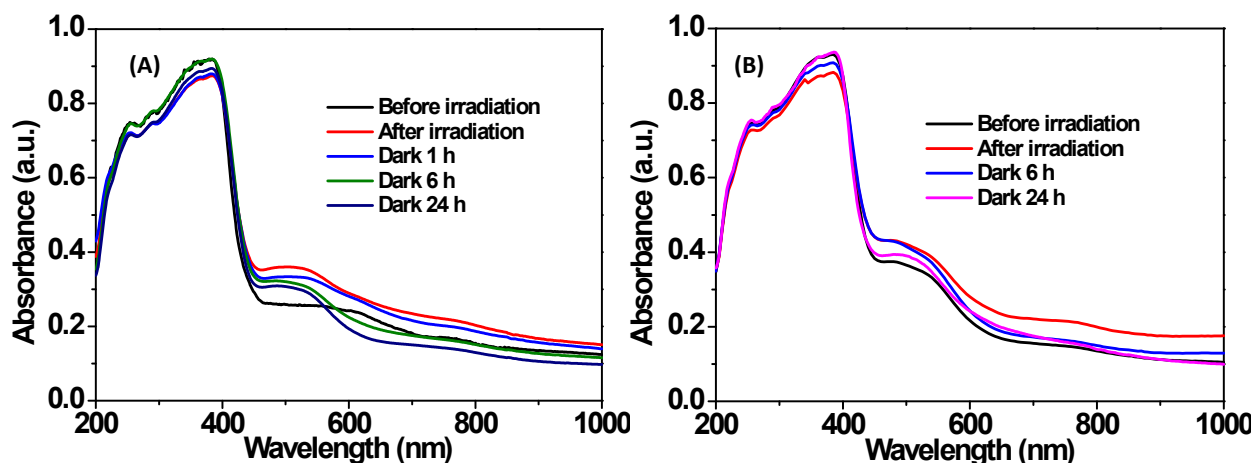


Figure S7. Time dependent Solid UV-DRS spectra of **1** under sunlight irradiation for 3 hr and keeping under dark for 24 h (A) Second cycle of irradiation and dark (B) 3<sup>rd</sup> cycle of irradiation and dark conditions.

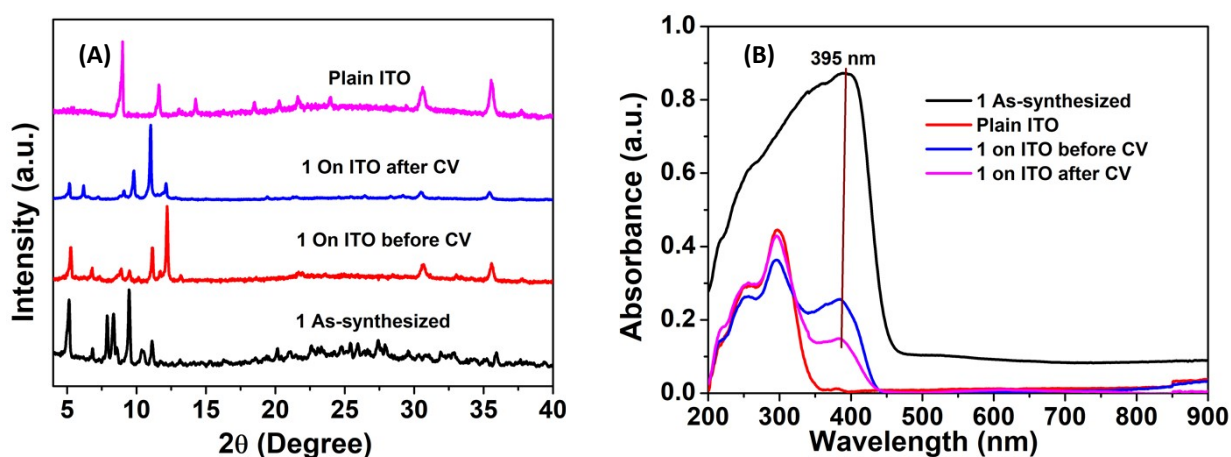


Figure S8. (A) Crystallinity of the MOF film before (red), and after (blue) a CV experiments performed in 0.1M TBAP. Pink colour pattern shows the plain ITO in to 0.1 M TBAPF<sub>6</sub>. (B) Solid state UV-Vis spectra of **1** and **1** on ITO film after and before the CV experiments.

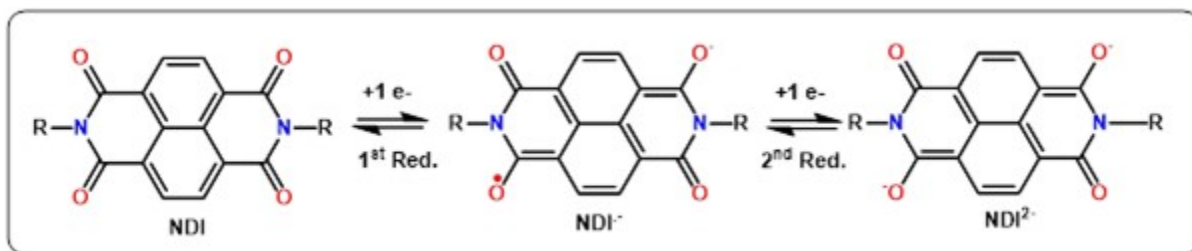


Figure S9: Stepwise redox mechanism for the reduction of NDI core.<sup>2</sup>

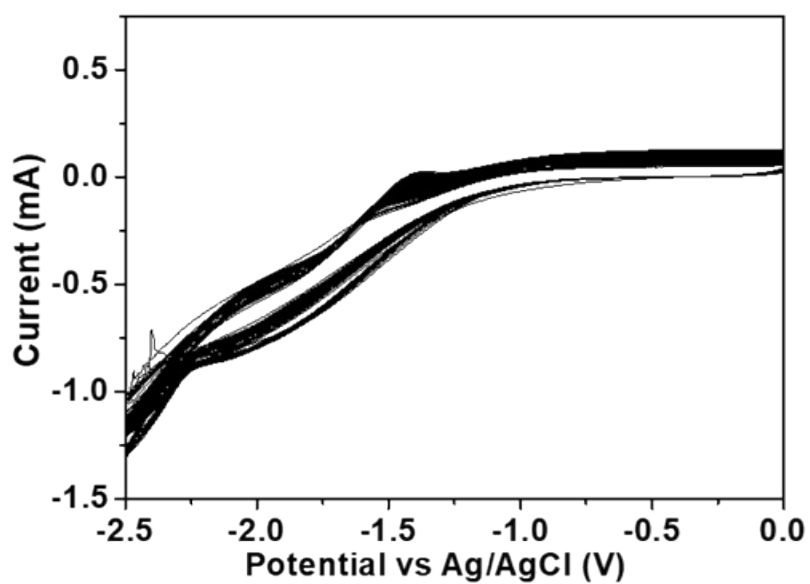


Figure S10. CV stability of Zr-NDI/ITO film recorded at 100 mV/s for 100 cycles

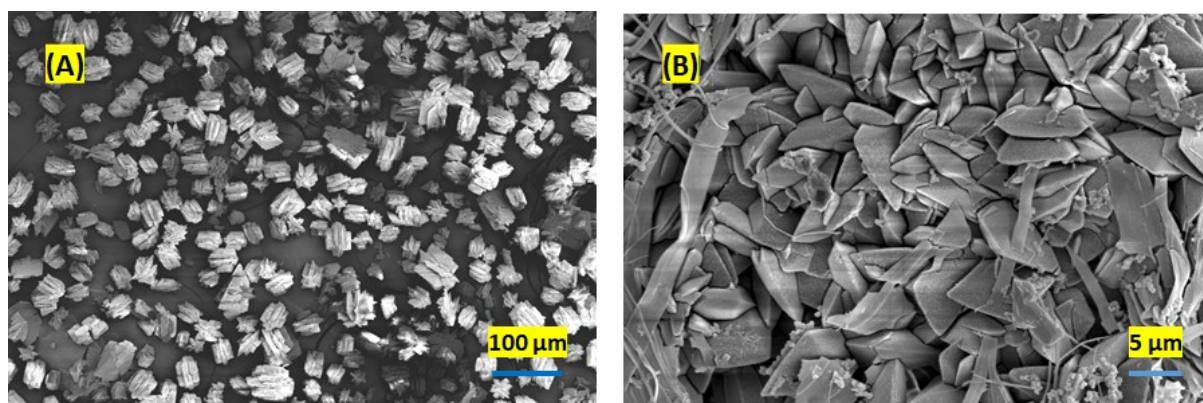


Figure S11. As synthesised MOF SEM images.

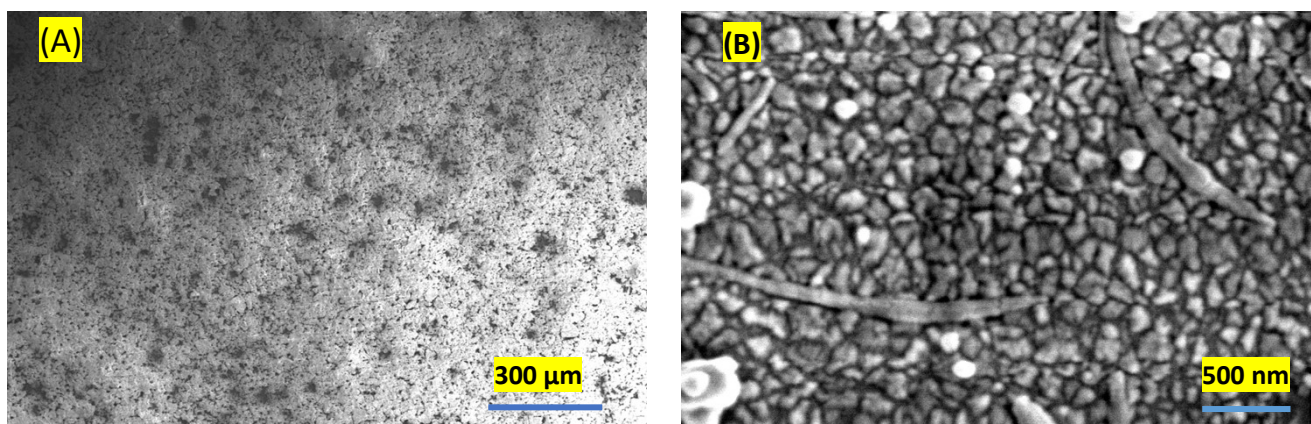


Figure S12. Morphology of the MOF film on ITO A) Before CV experiments and B) After CV experiments.

### References:

1. G. Radha, T. Leelasree, D. Muthukumar, S. Renjith and H. Aggarwal, *New J. Chem.*, 2021, **45**, 12931-12937.
2. S. Halder, S. Roy, C. Chakraborty, *Sol. Energy Mater. Sol. Cells*, 2022, **234**, 111429.