Electronic Supporting Information

Enhancement in electrical conductivity of a porous indium based metal–organic framework upon I₂ uptake: combined experimental and theoretical investigations

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1. Optical and Electronic properties:

Due to the slow and steady I_2 uptake of **1**, we are interested to explore the optical and electrical properties of **I₂@1** material. The diffuse reflectance spectra of **1** and **I₂@1** were collected at room temperature using Shimadzu UV/Vis/NIR spectrophotometer. Then the reflectance spectra were converted to a Kubelka–Munk function, from which the optical band gap was estimated. For a crystalline solid with a band gap (E_{bg}), the frequency dependence (v) of the absorption coefficient (κ) can be approximated using Eq. 1.

$$\kappa(v) = \frac{B_T\left(hv - E_{bg}\right)^n}{hv} \quad ----- (1)$$

Where B_T is a constant derived from the square of the averaged dipolar momentum matrix element and n is equal to 0.5 and 2 for direct and indirect band gap transitions, respectively. The absorption coefficient (κ) can be measured from the reflectance (R) and expressed as $\kappa = (1 - R)^2/(2R)$. Using the above equation 1, optical band gap of a material can be obtained by extrapolating to zero with the linear fit to a plot of $(\kappa hv)^{1/n}$ *vs* hv.

Table S1. Crystallographic parameters for compounds **1**.

| Parameters	Compound 1
Chemical formula	$C_7H_2In_{0.50}N_{0.50}O_4S$
Formula weight	246.56
Crystal System	Tetragonal
Space Group	$P4_322$
a(Å)	13.5642(13)
b(Å)	13.5642(13)
c(Å)	15.6425(12)
$\alpha(^0)$	90
$\beta(^0)$	90
$\gamma(^0)$	90
Volume ($Å^3$)	2878.0(6)
Z	8
Calculated density (g/cm^3)	1.138
θ range (^{0})	3.006 to 28.282
Absorption coefficient (mm^{-1})	0.992
Reflections collected	13786
Unique reflections	3579
Goodness-of-fit	1.071
Number of parameters	119
Final R indices [I>2sigma(I)]	$R_1 = 0.0364$, wR$_2 = 0.0959$

[a]$R_1 = \Sigma||F_0| - |F_c||/ \Sigma|F_0|$; wR$_2 = \{[w(F_0{}^2 - F_c{}^2)^2]/ [w(F_0{}^2)^2]\}^{1/2}$;

$w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$; $P = [\max(F_0{}^2,0) + 2(F_c)^2]/3$
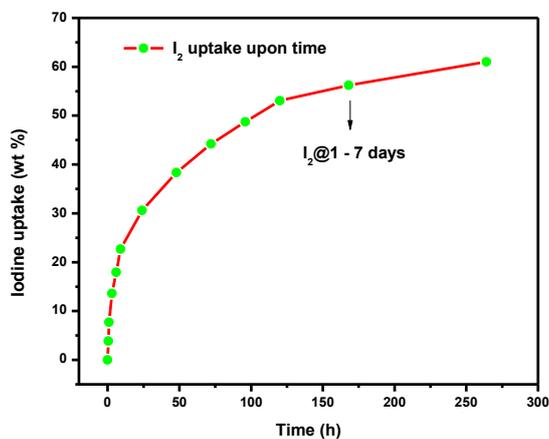
Figure S1. Gravimetric uptake of iodine as a function of time.

About 100 mg of compound **1** was exposed to the iodine vapors in closed glass flask. At each time interval we noted the incremental weight of **I₂@1**. Accordingly, we have calculated the wt. % of iodine present in compound **1**. In which about 56 weight % of iodine guests were incorporated in the pristine MOF in 7 days.
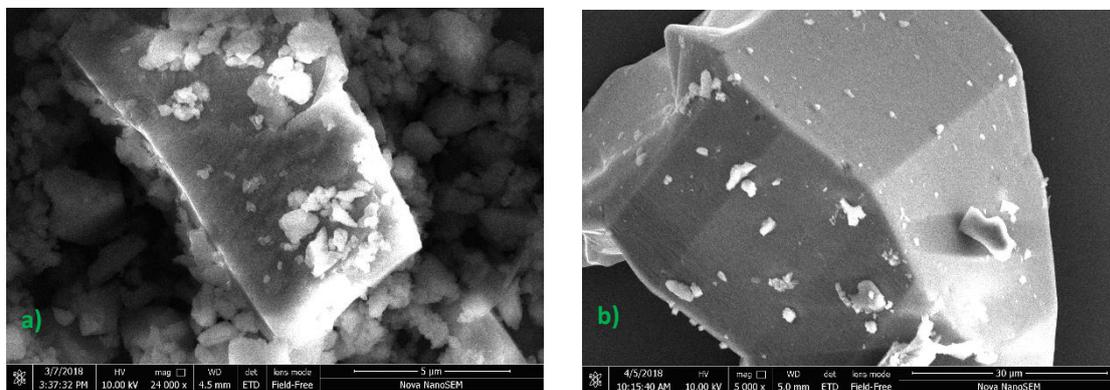
Figure S2. (a) and (b) are the SEM image of **1** before and after iodine uptake, respectively.
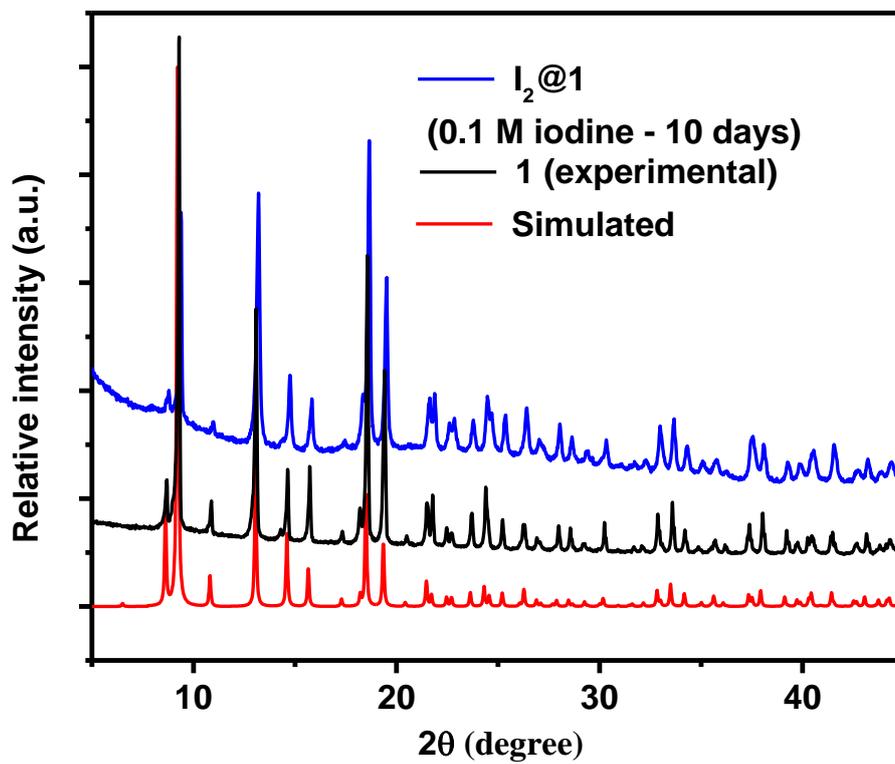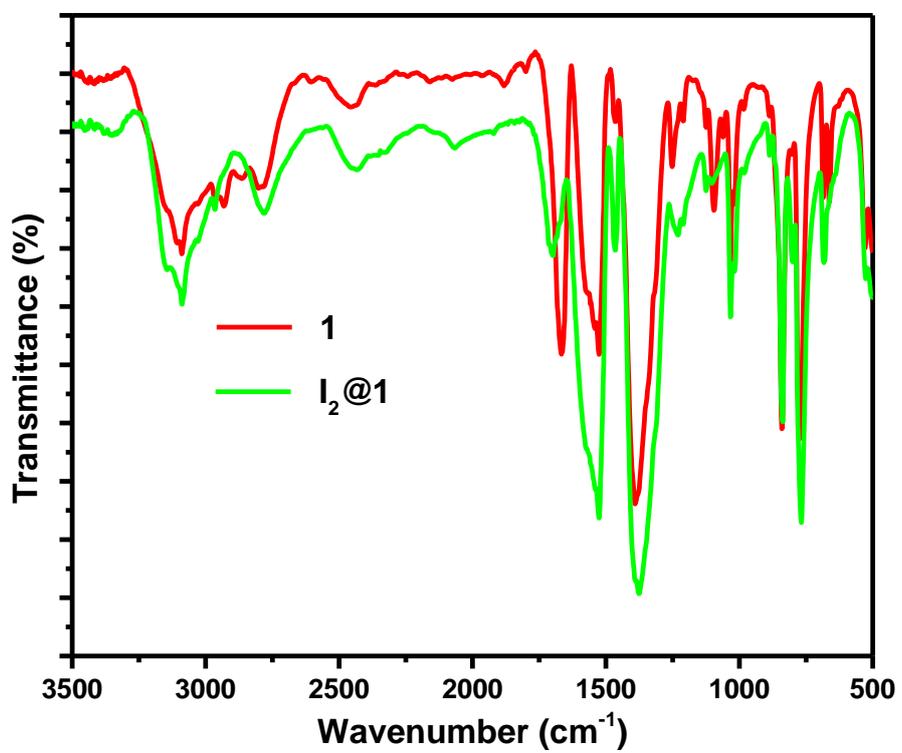
Figure S3. Powder XRD pattern of compound **1**.
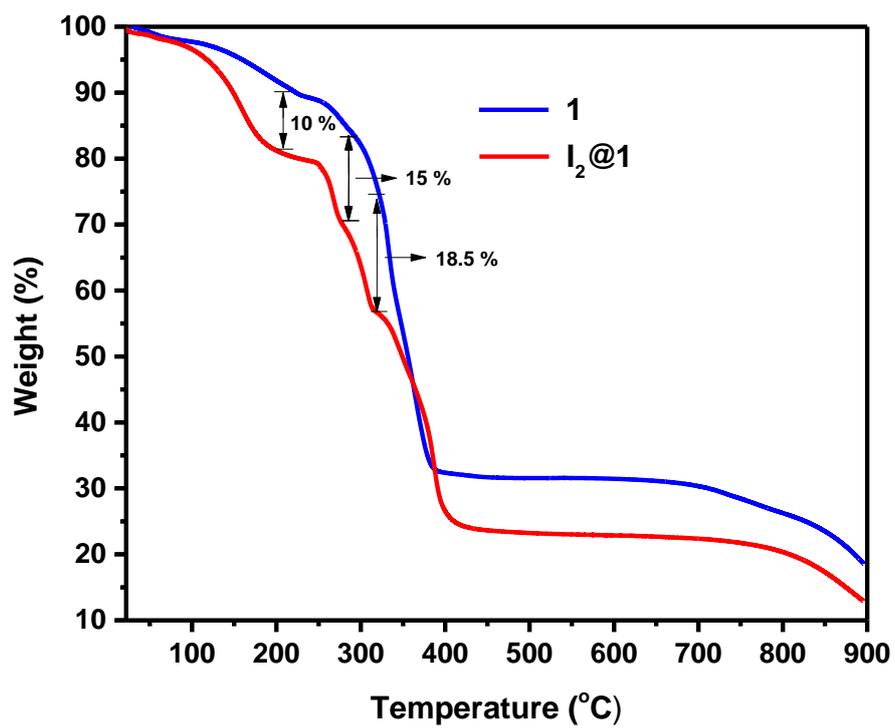
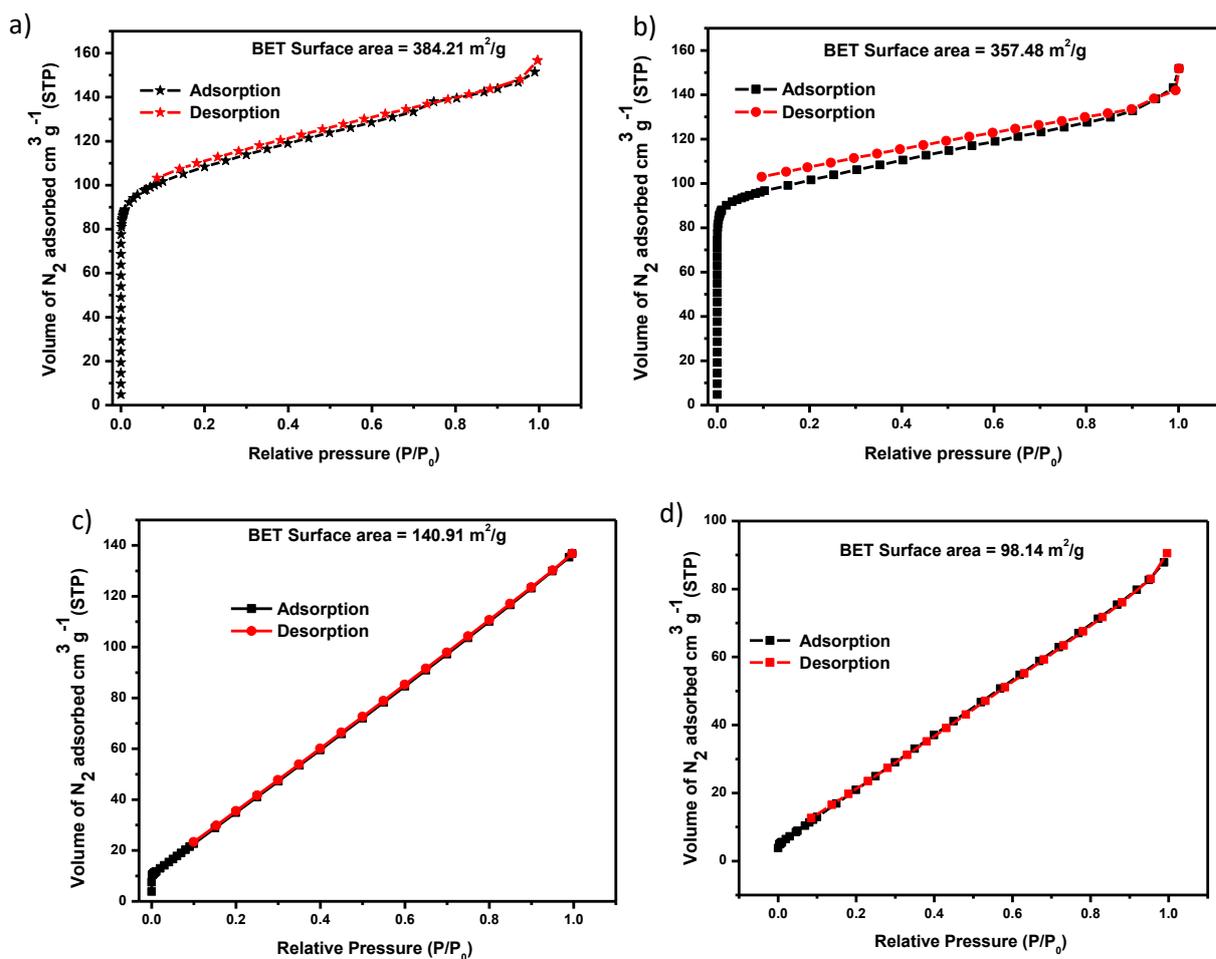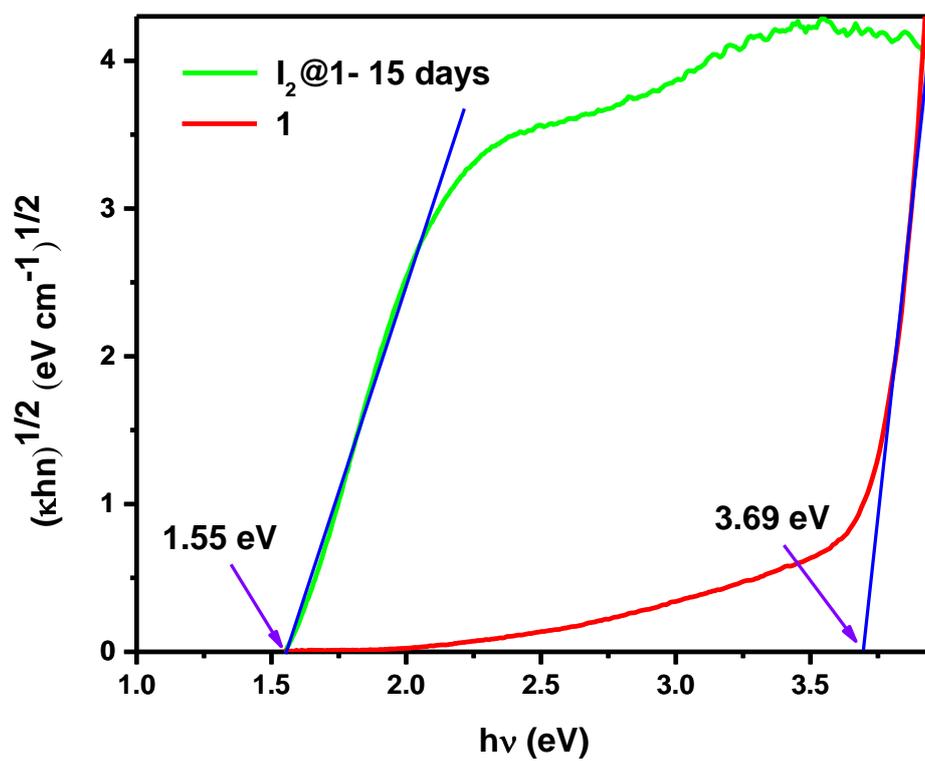**Figure S4.** IR spectra of compounds **1** and **I₂@1**.

Figure S5. TGA graph of **1** before and after iodine uptake.

Figure S6. a), b), c) and d) are N_2 adsorption profile at different time interval of iodine uptake **1** (pristine MOF), **I₂@1** - 3 days, **I₂@1 -** 5 days and **I₂@1 -** 7 days, respectively.

Figure S7. Tauc plots show the reduction of optical band gap of **1** upon iodine uptake.
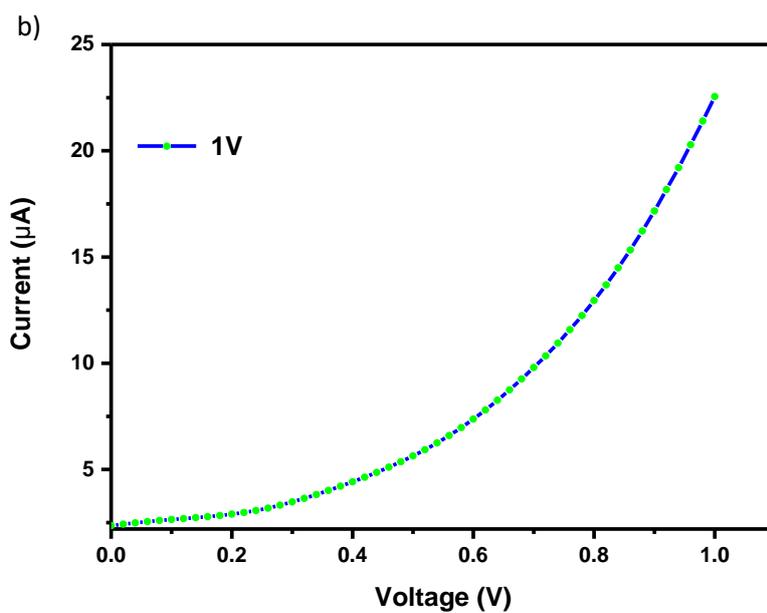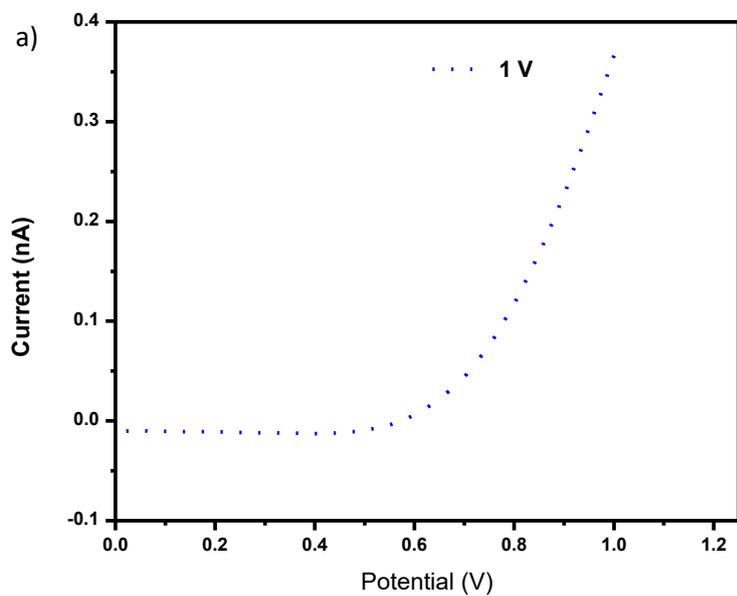
Figure S8. a) I-V graph for parent In-MOF measured using Keithley 6517B electrometer. b) I-V graph for parent In-MOF measured using KEYSIGHT B2987A Electrometer.

2. Unit cell of the In-MOF (1)

Unit cell of indium-based metal organic framework contains 16 atoms. It is crystallized in tetragonal crystal system with $P4_322$ space group. However, the full structure of this MOF was modeled using VESTA software.[1]
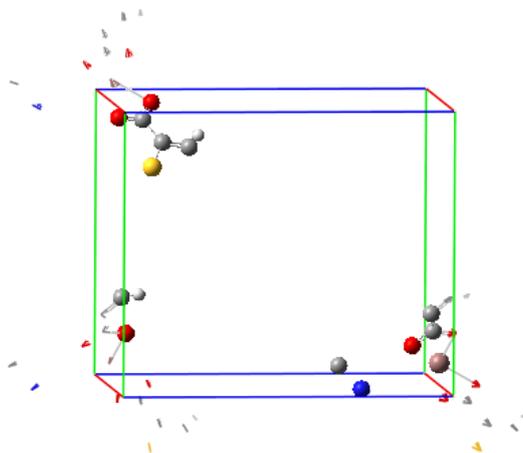

Figure S9. Unit cell of indium-based metal organic framework (In-MOF).

3. Optimized crystallographic parameters for compound 1

Cell Lengths(Å)	Cell Angles
a = 14.1588	α = 90
b = 14.1588	β = 90
c = 15.1995	γ = 90
Cell Volume = 3047.07 Å³	

Space group : 95 [P 43 2 2]
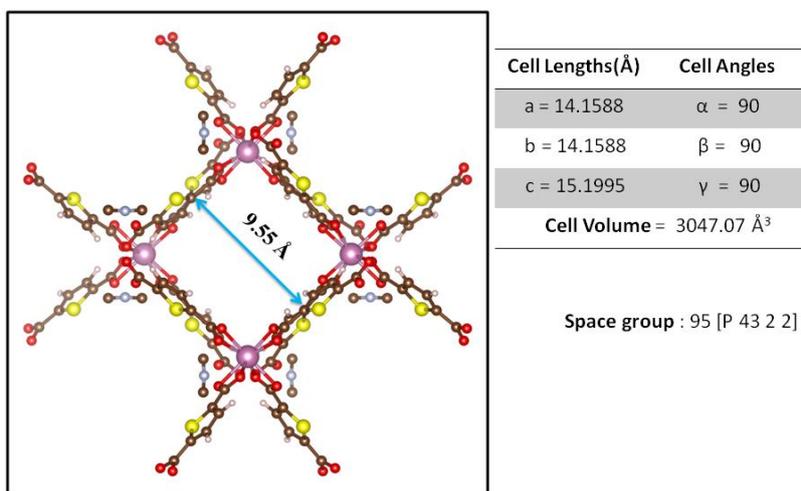
Figure S10. Optimized structure of In-TDC MOF and crystallographic parameters are presented.

4. Different conformation of iodine molecule inside 1 and their crystallographic parameters.

Conformation-I
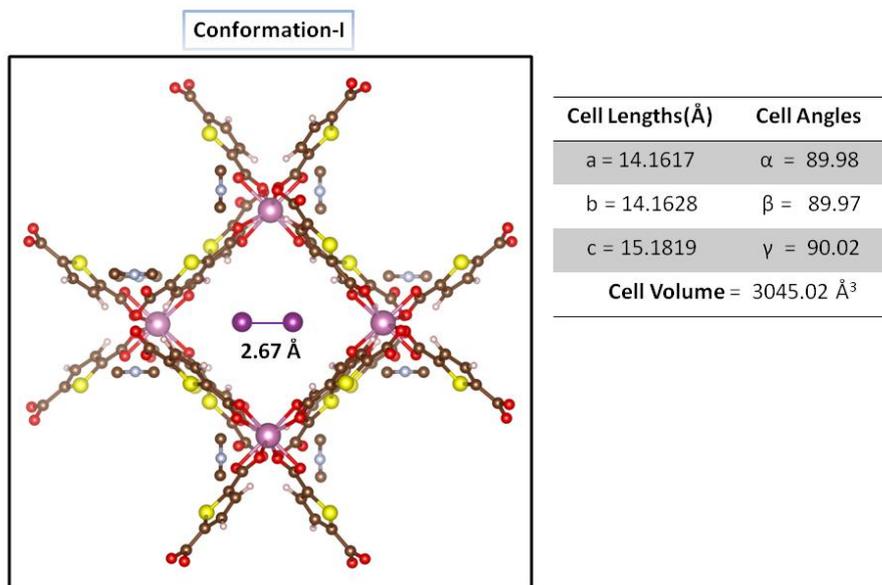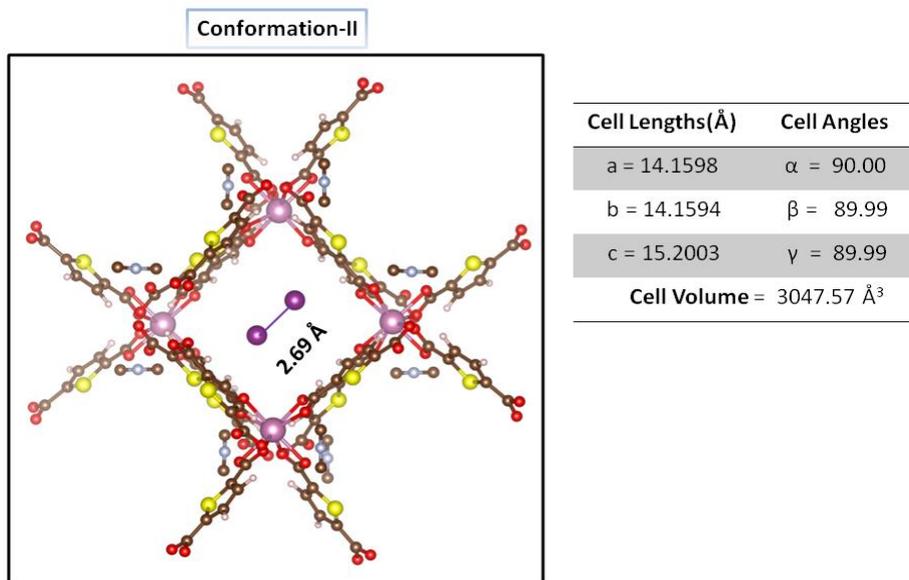
Cell Lengths(Å)	Cell Angles
a = 14.1617	α = 89.98
b = 14.1628	β = 89.97
c = 15.1819	γ = 90.02
Cell Volume = 3045.02 Å³	

Figure S11. Optimized structure of conformation-I of I$_2$@**1** and its crystallographic parameters.

Conformation-II

Cell Lengths(Å)	Cell Angles
a = 14.1598	α = 90.00
b = 14.1594	β = 89.99
c = 15.2003	γ = 89.99
Cell Volume = 3047.57 Å³	

Figure S12. Optimized structure of conformation-II of I$_2$@**1** and its crystallographic parameters.
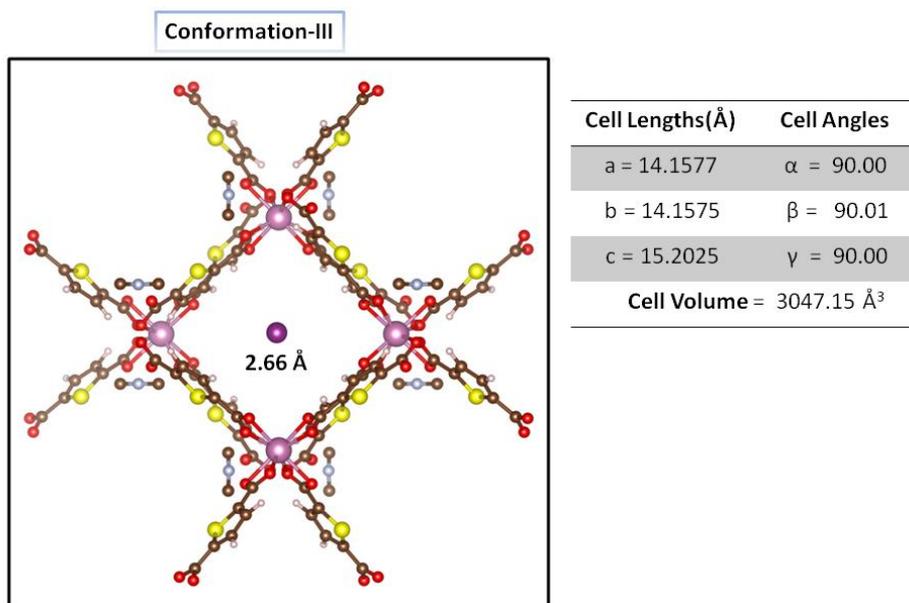
**Figure S13.** Optimized structure of conformation-III of I$_2$@**1** and its crystallographic parameters.

5. Calculated energies and binding energies (B.E.) of different conformations of iodine within the pore of 1.

Table S2. Computed energies and binding energies of three different conformation of I$_2$@**1.**

I$_2$@1	With_I$_2$ (eV)	In_TDC (eV)	B. E. (eV)	B.E. (kcal/mol)
Conformation-I	-849.61772203	-845.89943677	-1.05989733	-24.44
Conformation-II	-849.74204355	-845.89943677	-1.18421885	-27.31
Conformation-III	-849.54472409	-845.89943677	-0.98689936	-22.75

6. Interactive distances (Å) of iodine molecule with In-MOF (Conformation-II).
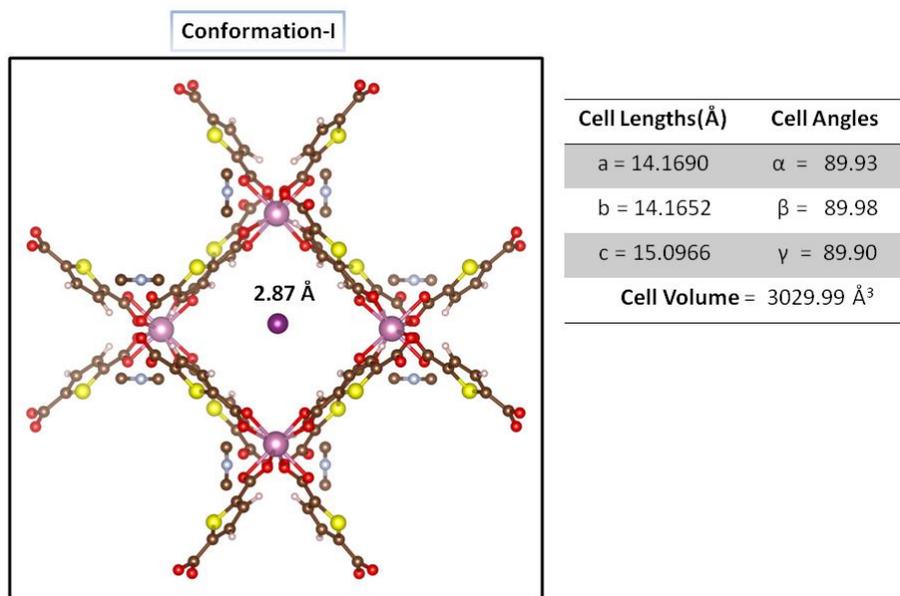
C1···I─I distance = 3.46 Å
C2···I─I distance = 3.20 Å
C3···I─I distance = 3.17 Å
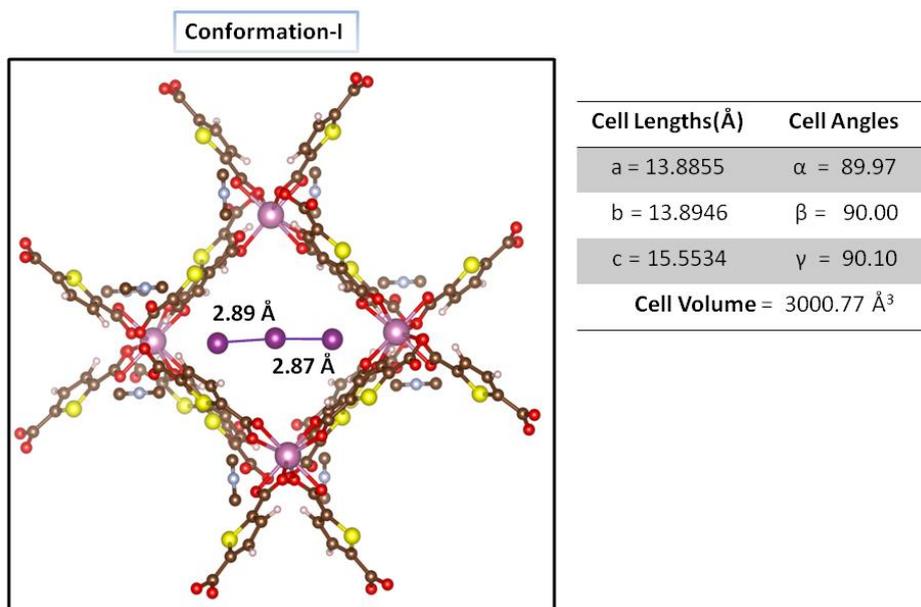C3─H···I─I distance = 3.15 Å
O···I─I distance = 3.59 Å
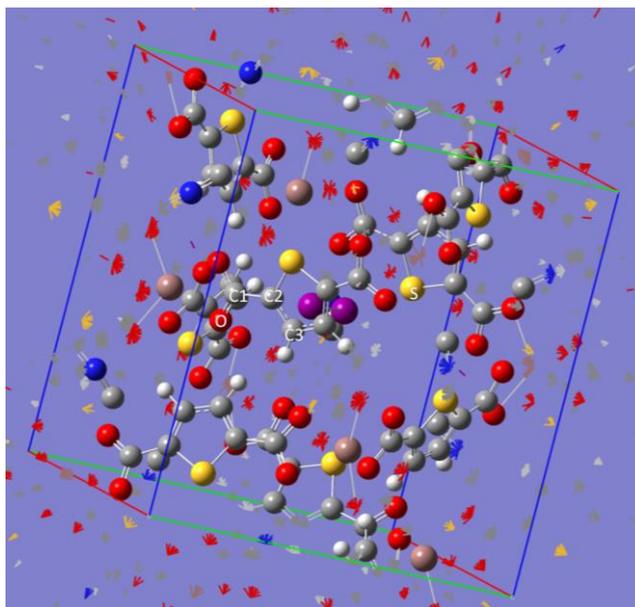
Figure S14. Different interactive distances of iodine molecule with the In-MOF (Conformation-II).

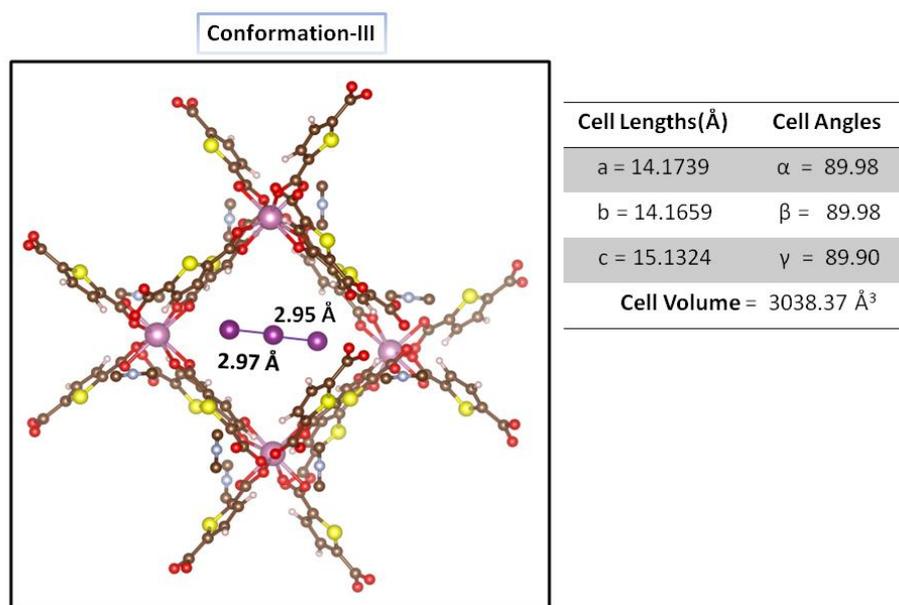## 7. Triiodide anion (I_3^-) as a guest for In-TDC.

We have also considered the tri-iodide anion as a guest molecule for In-TDC MOF. The tri-iodide anion can be incorporated in three different ways. However, several other conformations of this host-guest complex may exist. Interestingly, the following three different conformations have taken as they form relatively most stable aggregates. Both of these cases the crystallographic cell parameters have notable change. Therefore, it affects the cell volumes for each case. In case of conformation-III of I_3^-@1 has highest cell volume. Therefore, it suggests that the inclusion of tri-iodide anion into this MOF affects the inherent crystallographic properties.

Cell Lengths(Å)	Cell Angles
a = 14.1690	α = 89.93
b = 14.1652	β = 89.98
c = 15.0966	γ = 89.90
Cell Volume = 3029.99 Å³	

Figure S15. Optimized structure of conformation-I of I_3^-@1 and its crystallographic parameters.

Cell Lengths(Å)	Cell Angles
a = 13.8855	α = 89.97
b = 13.8946	β = 90.00
c = 15.5534	γ = 90.10
Cell Volume = 3000.77 Å³	

Figure S16. Optimized structure of conformation-II of I_3^-@1 and its crystallographic parameters.

Conformation-III

Cell Lengths(Å)	Cell Angles
a = 14.1739	α = 89.98
b = 14.1659	β = 89.98
c = 15.1324	γ = 89.90
Cell Volume = 3038.37 Å³	

2.95 Å
2.97 Å

Figure S17. Optimized structure of conformation-III of I_3^-@1 and its crystallographic parameters.

8. Calculated energies and binding energies (B.E.) of different conformations of triiodide ion (I_3^-@1) within the pore of 1.

Binding energies for these systems (for all these conformations) are also computed which reflects that conformation-II forms relatively more favorable host-guest interaction. In Conformation-II, Iodide ion weakly interact with (thiophene) C-H bonds (average C-H…I distance = 2.83 Å). However, the negative charge and larger size of this tri-iodide anion demonstrate that their probability of forming such type of complex is less than compare to **I₂@1**. The computed binding energies are all positive and hence they are unstable with respect to **I₂@1**.

Table S3. Computed energies and binding energies of three different conformation of I_3^-@1.

| I_3^-@1	With_I_3^- (eV)	In_TDC (eV)	B. E. (eV)	B.E. (kcal/mol)
Conformation-I	-852.42251175	-846.0335380	0.92605750	21.36
Conformation-II	-852.5380000	-846.0335380	0.81056925	18.70
Conformation-III	-852.20350680	-846.0335380	1.14506245	26.41

9. Band path and band structures:

For band structure calculations Path Γ-X-M-Γ is taken. Band structure calculations were performed for the both the systems (compound 1 and conformation-II of $I_2@1$). From the analyses of the band structures of these systems reveal that both have 0.4 eV band gap. These results cannot explain the real situation. However, when the band gaps are calculated using their density of states, those results provide significant relevance with the experimental results. Therefore, it is useful to interpret the band gaps from their density of states.
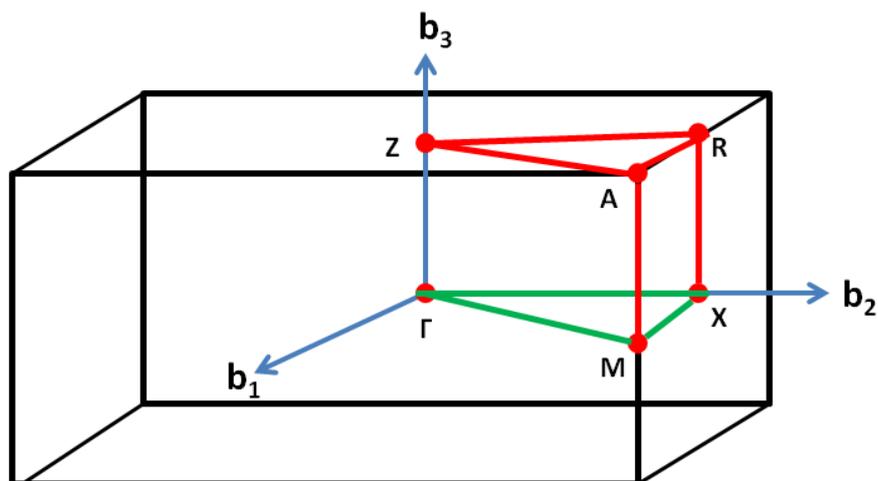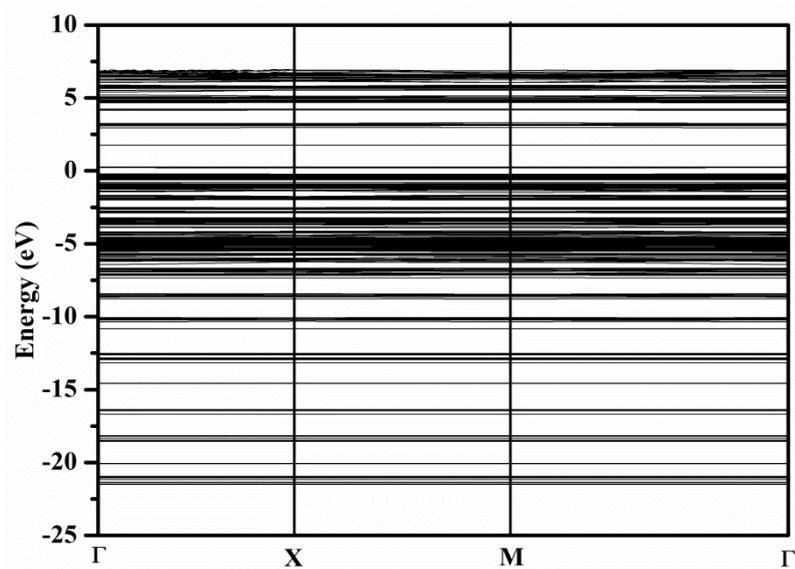

Figure S18. Brillouin zone of tetragonal lattice. Path: Γ-X-M-Γ is taken for band structure calculations.

10. Band structure of In-MOF (compound 1).
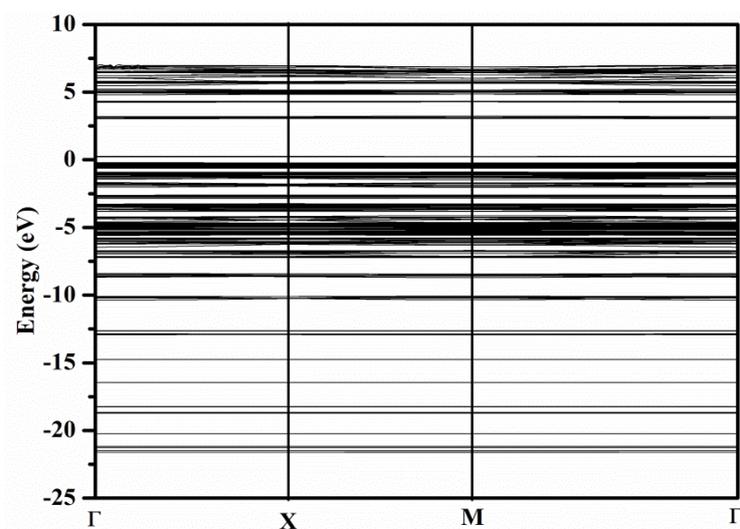
Figure S19. Band structure of compound **1**.

11. Band structure of Conformation-II of I$_2$@1

Figure S20. Band structure of conformation-II of I$_2$@1.

References:

1. Momma, K; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272-1276.