

## Supporting Information

### From insulator to semiconductor: Effect of host-guest interactions on charge transport in M-MOF-74 metal-organic frameworks

*Sydney M. Angel,<sup>a</sup> Nicholas S. Barnett,<sup>a</sup> A. Alec Talin,<sup>b</sup> Michael E. Foster,<sup>b</sup>*

*Vitalie Stavila,<sup>b</sup> Mark D. Allendorf,<sup>b</sup> Monica C. So<sup>a\*</sup>*

<sup>a</sup> Department of Chemistry and Biochemistry, California State University Chico, Chico, California, 95973, United States

<sup>b</sup> Sandia National Laboratories, Livermore, CA 94551, United States

\*Corresponding author: [mso@csuchico.edu](mailto:mso@csuchico.edu)

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## I. Syntheses

All metal precursors, terephthalic acids, and solvents were analytical grade purity and purchased from Sigma Aldrich.

*Cu-MOF-74*: Copper nitrate trihydrate (1.18 g, 24.6 mmol) and 2,5-dihydroxyterephthalic acid (dhtp) (0.44 g, 11.2 mmol) were added into a 20:1 (v/v) solution of *N, N*-dimethylformamide (DMF) and 2-propanol in a 100 mL screw cap jar. The mixture was sonicated for 15 minutes until a homogenous solution was achieved. The solution was capped tightly and placed in an 80°C oven for 18 hours. The solution was then cooled to room temperature in a fume hood. The mother liquor was decanted and the precipitate was washed with 30 mL of DMF one time followed by 30 mL of methanol four times over 48 hours. The sample was dried with nitrogen gas before activation in vacuum at 150°C for 6 hours.

*Mn-MOF-74*: Manganese (II) chloride tetrahydrate (0.8784 g, 4.44 mmol) and dhtp (0.2664 g, 1.345 mmol) were added to a 15:1:1 (v/v/v) solution of DMF-ethanol-water (120 mL : 8 mL : 8 mL) in a 250 mL screw cap jar. (A glass rod was used to crush the reagents in some cases.) The mixture was sonicated for 10 minutes until a homogenous solution was achieved. The solution was then capped tightly and placed in a 135°C oven for 24 hours, then cooled to room temperature in a fume hood. The mother liquor was decanted and washed with 30 mL of methanol six times over 72 hours. The sample was dried with nitrogen gas before activation under dynamic vacuum at 150°C for 6 hours.

*Zn-MOF-74*: Zinc nitrate hexahydrate (1.021 g, 3.43 mmol) and dhtp (0.250 g, 1.30 mmol) were added to 50 mL of DMF and 3 mL of water in a 100 mL screw cap jar. The mixture was sonicated for 15 minutes until a homogenous solution was achieved. The solution was then capped tightly and placed in a 100°C oven for 24 hours, then cooled to room temperature in a fume hood. The

mother liquor was decanted and washed with 30 mL of DMF three times followed by 30 mL of methanol three times. The last methanol wash was left overnight. The sample was dried with nitrogen gas in vacuum before activation at 150°C for 6 hours.

*Mg-MOF-74*: Magnesium nitrate hexahydrate (0.476 g, 1.11 mmol) and dhtp (0.111 g, 0.56 mmol) were added into a 15:1:1 (v/v/v) solution of DMF-ethanol-water in a 100 mL screw cap jar. The mixture was sonicated for 15 minutes until a homogenous solution was achieved. The solution was then capped tightly and placed in a 125°C oven for 24 hours, then cooled to room temperature in a fume hood. The mother liquor was decanted and washed with 30 mL of DMF one time followed by 30 mL of methanol three times. The last methanol wash was left overnight. The sample was dried with nitrogen gas in vacuum before activation at 150°C for 6 hours.

*Nano-Mn-MOF-74*: dhtp (0.0401g, 0.2024 mmol) and 7 mL of DMF were sonicated until a homogenous solution was achieved. The solution was then added dropwise to manganese(II) nitrate tetrahydrate (0.1305g, 0.5199 mmol). At the beginning of sonication, 0.17 mL of TEA was added then the sample was sonicated for 2 hours at room temperature. The mixture was then centrifuged at 3,000 rpm for 5 minutes before replacing the mother liquor with 7 mL of fresh DMF and sonicating. The sample was centrifuged for another 5 minutes at 3,000 rpm before repeating the process with fresh DMF. After the last DMF wash, the sample was placed in a 4:9:6 (v/v/v) mixture of DMSO/ethanol/ethylene glycol. A 6 mL aliquot of the solution was used to print onto a fluorine-doped tin oxide (FTO) slide.

## II. Guest Molecule Infiltration

Toluene was dried by passage through alumina and molecular sieves in a commercially available solvent-purification system. All guest infiltration experiments were performed in a N<sub>2</sub>-

filled MBraun 130-BG glove box. 7,7,8,8-tetracyanoquinodimethane and (cyclohexane-1,4-diylidene)dimalononitrile were recrystallized from a hot solution of methanol before infiltration experiments were initiated.

#### A. TCNQ Infiltration

The TCNQ was first recrystallized in hot methanol and dried under vacuum before being used in the infiltration. The M-MOF-74s were then submerged in 20 mL of a dry toluene solution saturated with 5 mM TCNQ and left undisturbed for 12-48 hours in a glovebox. The mother liquor color remained yellow to a dark yellow during the infiltration process. After infiltration, the mother liquor was exchanged 5 times with fresh toluene or until the solution was clear. The MOF powders were then dried under nitrogen gas before activation at 150°C for 6-12 hours. The samples were stored in a dry box prior to conductivity measurements.

#### B. H<sub>4</sub>TCNQ Infiltration

The H<sub>4</sub>TCNQ was recrystallized in hot methanol and dried before being used in the infiltration. The Cu-MOF-74 and Mn-MOF-74 powders were submerged in 20 mL of a dry toluene solution saturated with 5 mM H<sub>4</sub>TCNQ and was kept in a glovebox for a minimum of 18 hours. The mother liquor color remained clear during the infiltration process. After infiltration, the mother liquor was exchanged several times with fresh toluene. The MOF powders were then dried under nitrogen gas before activation at 120°C for 6 hours under vacuum. The samples were stored in a dry box prior to conductivity measurements.

### III. Characterization methods

Powder x-ray diffraction (PXRD) data were obtained using a Rigaku SmartLab X-Ray diffractometer equipped with a HyPix-3000 high energy resolution 2D HPAD detector. Experiments were conducted in continuous scanning mode with the goniometer in the  $2\theta$  orientation. The samples were dried and ground into a fine powder, deposited on a microscope slide, and mounted on a flat sample stage. Typically, data were collected from  $5^\circ < 2\theta < 40^\circ$  with a step size of  $0.01^\circ$  and a scan rate of 5 degrees per minute.

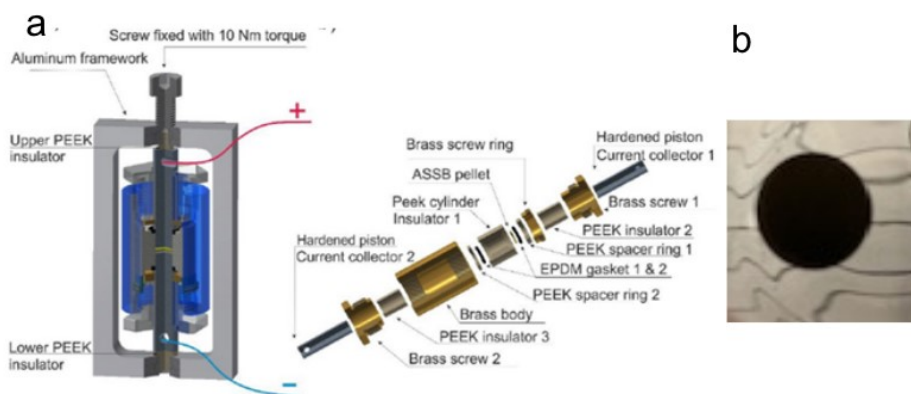
Scanning electron microscopy images were obtained using a Japanese Electron Optics Ltd JSM-7600F with a Thermal Field Emission Scanning Electron Microscope. To avoid charging, samples were sputter-coated with gold. Measurements were carried out using an acceleration voltage of 10 kV with a magnification of  $2000\times$  and a working distance of 8.0 mm.

Raman spectra were collected on a Renishaw inVia Raman Microscope Sox objective by taking spectra between  $1100\text{-}2400\text{ cm}^{-1}$  with 10 accumulations using a 532 nm laser excitation source and  $\sim 50\text{ }\mu\text{W}$  power at the sample.

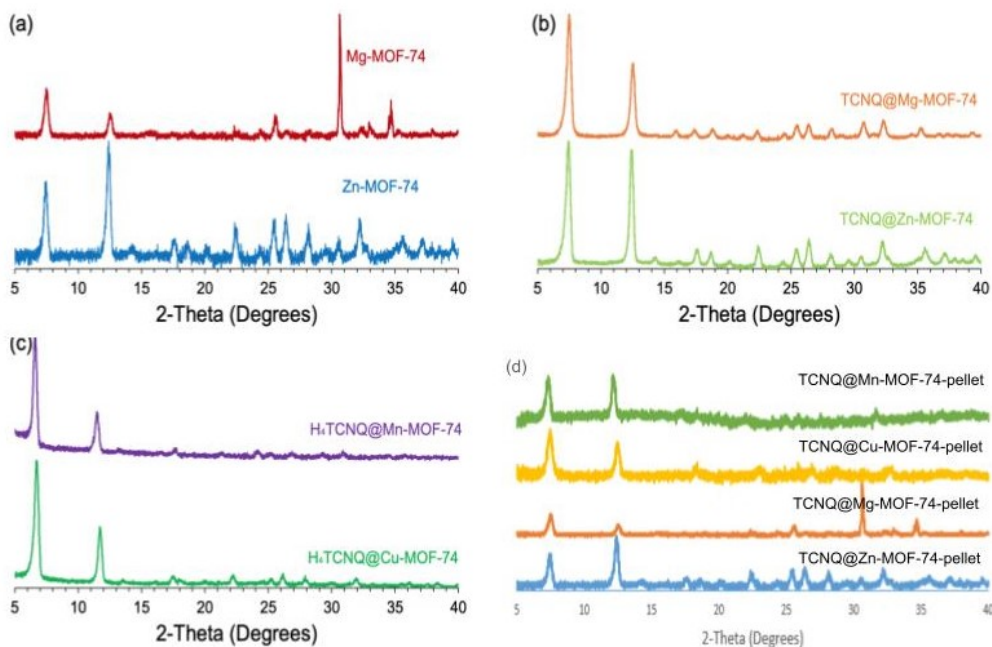
Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

UV-vis spectra were collected on a UV-3600 Shimadzu UV-VIS-NIR spectrophotometer at a wavelength of 900-2000 nm. Diffuse reflectance spectra (DRS) were obtained using an ASD Quality Spec Pro UV-Vis spectrometer equipped with a fiber optic mug light attachment. The spectra were scanned in the range of 350 to 2500 nm. For DRS measurements, Mn-MOF-74 films were printed using a solution of nano-Mn-MOF-74 onto FTO-coated glass substrates (precleaned using an Ozone ProCleaner for a total of 8 passes) using a FUJIFILM Dimatix Materials Printer DMP-2800 Series.

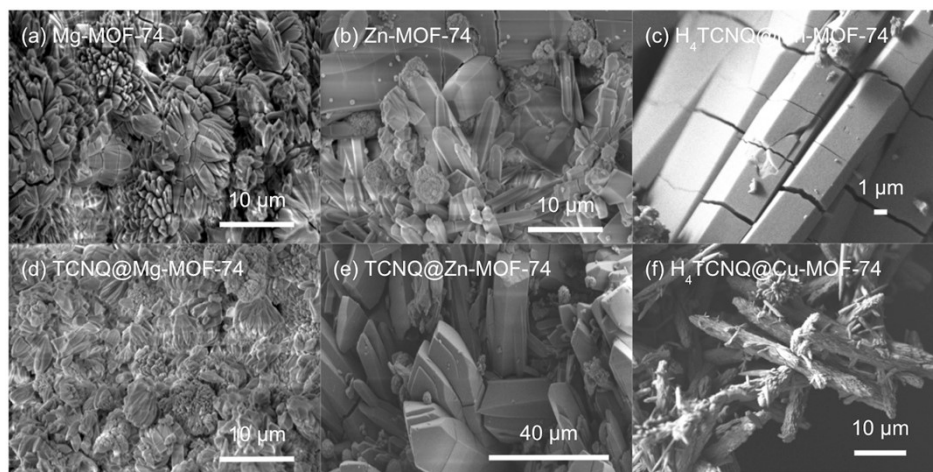
Two-point probe electrical conductivity measurements were performed in an argon filled glovebox (<1 ppm O<sub>2</sub>) using a Gamry PCI4750-333041 potentiostat connected to the device as shown in Figure S1. Measurements were taken on the powder by pressing them into pellets with 3 tons of force for 2 minutes using 50 mg of material with 0.5 mm of thickness.



**Figure S1.** Conductivity measurement apparatus using (a) pellet pressing set-up to make (b) a pressed pellet of TCNQ@M-MOF-74.



**Figure S2.** PXRD of (a) M-MOF-74 (M = Mg, Zn), (b) TCNQ@M-MOF-74 (M = Mg, Zn), (c) H<sub>4</sub>TCNQ@M-MOF-74 (M = Cu, Mn), and (d) TCNQ@M-MOF-74-pellet (M = Mn, Cu, Mg, Zn).



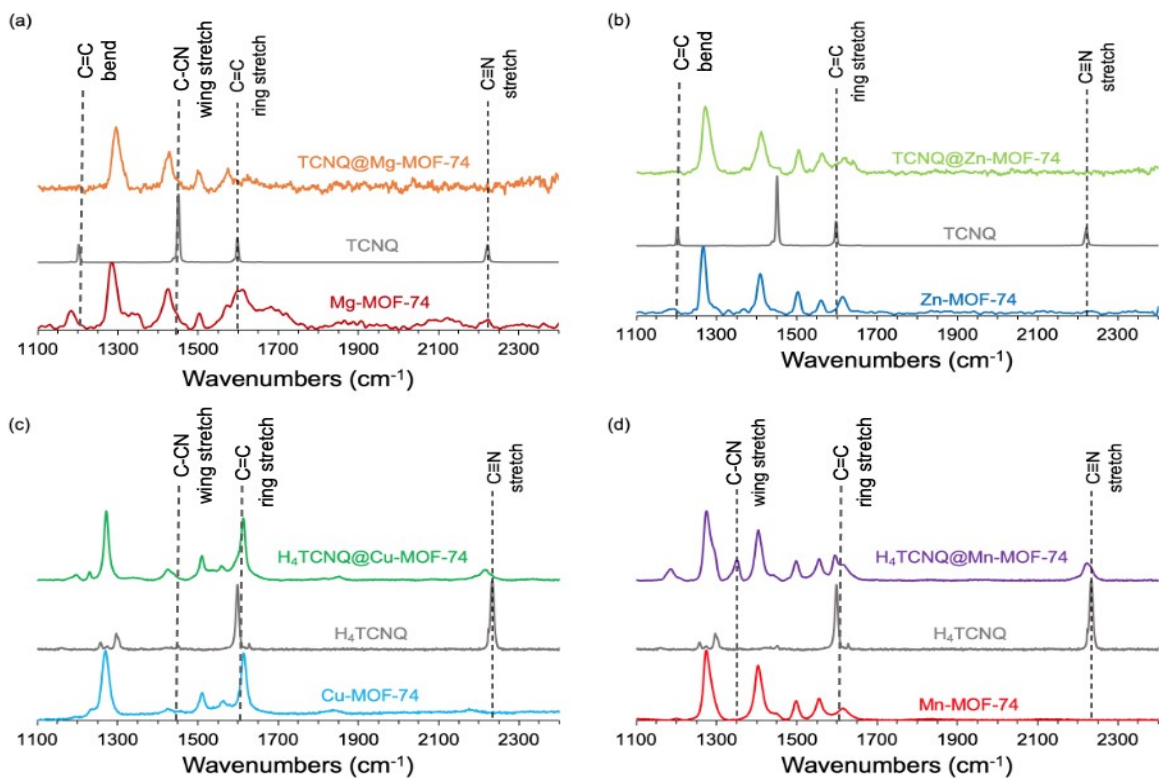
**Figure S3.** SEM of (a) Mg-MOF-74, (b) Zn-MOF-74, (c) H<sub>4</sub>TCNQ@Mn-MOF-74, (d) TCNQ@Mg-MOF-74, (e) TCNQ@Zn-MOF-74, and (f) H<sub>4</sub>TCNQ@Cu-MOF-74.

### Elemental Analysis

The elemental analysis (C, H, N) was performed by Galbraith Laboratories. For both TCNQ and H<sub>4</sub>TCNQ infiltrated samples the best match was obtained for a TCNQ (H<sub>4</sub>TCNQ) : Cu<sub>2</sub>(dobdc) ratio of 1:6 and TCNQ (H<sub>4</sub>TCNQ) : Mn<sub>2</sub>(dobdc) ratio of 1:3.

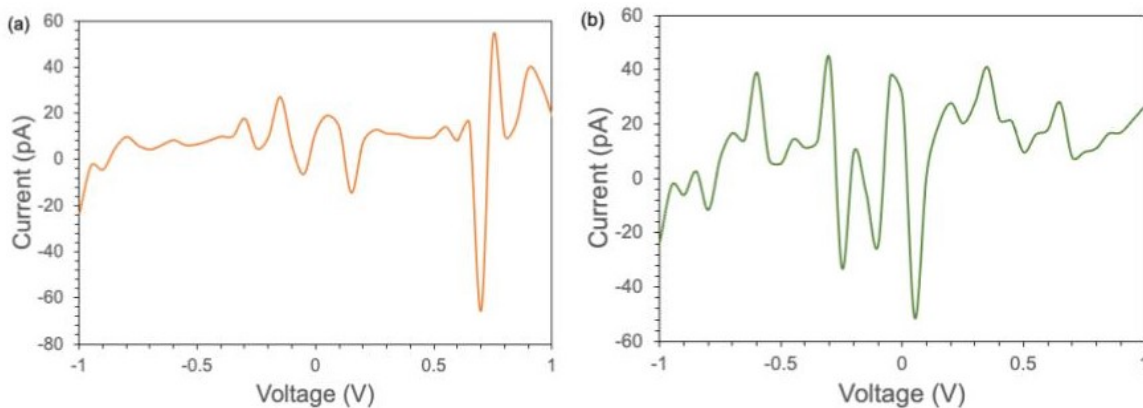
Sample	% Carbon		% Nitrogen		% Hydrogen	
	<i>Exp.</i>	<i>Calc.</i>	<i>Exp.</i>	<i>Calc.</i>	<i>Exp.</i>	<i>Calc.</i>
TCNQ@Cu-MOF-74	30.4	45.4	2.36	10.6	2.72	7.60
TCNQ@Mn-MOF-74	35.0	46.91	4.53	11.0	2.77	7.80
H <sub>4</sub> TCNQ@Cu-MOF-74	30.3	4.50	2.36	10.5	2.72	1.51
H <sub>4</sub> TCNQ@Mn-MOF-74	34.9	4.66	4.52	10.9	2.76	1.55

**Table S1.** Elemental analysis data.

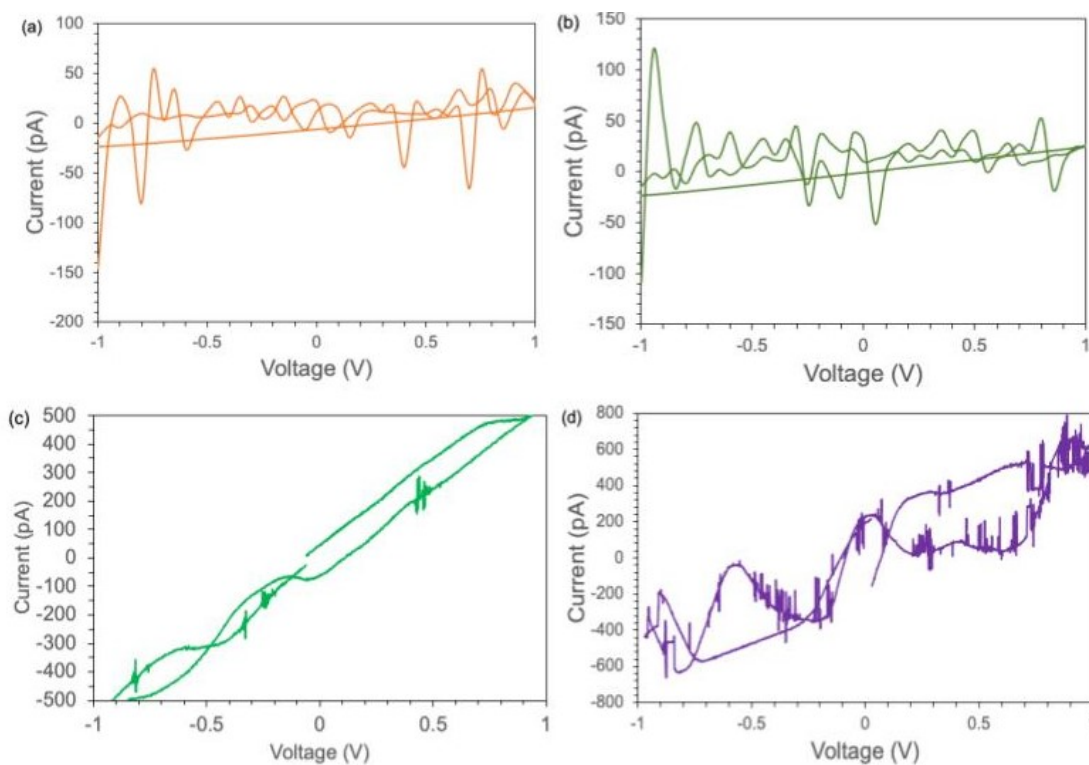


**Figure S4.** Raman spectra of (a) Mg-MOF-74, TCNQ, and TCNQ@Mg-MOF-74, (b) Zn-MOF-74, TCNQ, and TCNQ@Zn-MOF-74, (c) Cu-MOF-74, H<sub>4</sub>TCNQ, and H<sub>4</sub>TCNQ@Cu-MOF-74, as well as (d) Mn-MOF-74, H<sub>4</sub>TCNQ, and H<sub>4</sub>TCNQ@Mn-MOF-74.





**Figure S5.** IV curves at room temperature for (a) TCNQ@Mg-MOF-74 and (b) TCNQ@Zn-MOF-74 show practically zero conductivity.

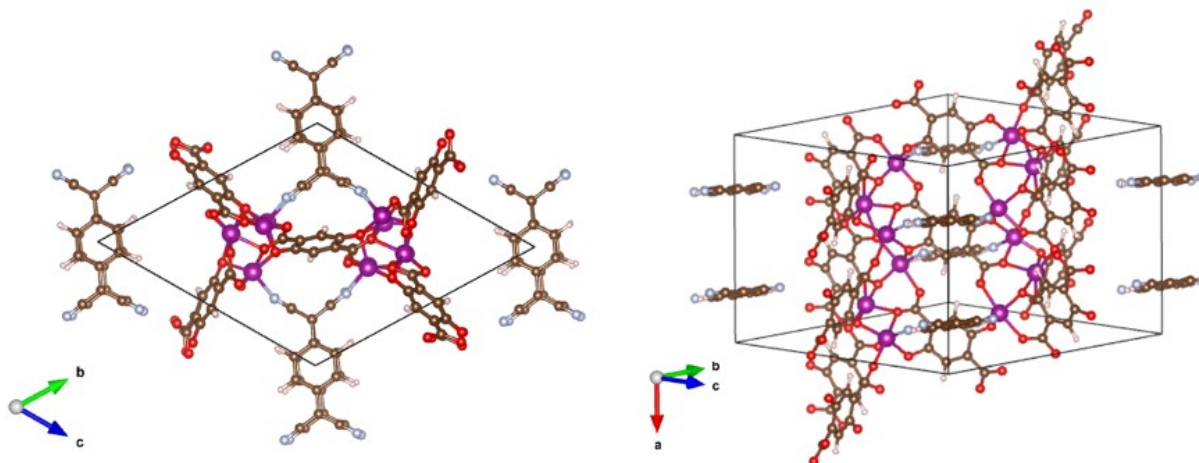


**Figure S6.** IV curves at room temperature for (a) H<sub>4</sub>TCNQ@Mg-MOF-74, (b) H<sub>4</sub>TCNQ@Zn-MOF-74, (c) H<sub>4</sub>TCNQ@Cu-MOF-74, and (d) H<sub>4</sub>TCNQ@Mn-MOF-74 show no conductivity.

#### IV. Computational Details

All density functional theory (DFT) calculations were done using the *Vienna ab initio simulation package* (VASP).<sup>1</sup> Geometric optimizations (unit cell and atomic positions) were performed with a single  $k$ -point, energy cutoff of 400 eV, and using the HSE06 hybrid functional.<sup>2</sup> The optimizations were carried out until all atomic forces were less than 0.01 eV/atom. All systems were modeled in the antiferromagnetic state (spin polarized calculations), which was achieved by initializing alternating up/down spin states along the secondary building units (SBUs). (Note that the ferromagnetic state was considered but was higher in energy.) Single-point calculations were then performed on the optimized structures with a  $2 \times 2 \times 2$   $k$ -point grid; these calculations were used to determine the density-of-states (DOS) and Bader charges.

The TCNQ@M-MOF-74 (M = Mn and Cu) binding energies (BE) were computed in the usual fashion ( $BE = TCNQ@MOF - 2*TCNQ - MOF$ ); the factor of two ( $2*TCNQ$ ) results because there were two TCNQs per cell (1 TCNQ: 6 metal ions). Several different binding orientations were considered; however, orientating the TCNQ molecule such that all the nitrogen atoms can interact with the open-metal-sites (OMS) of the MOF resulted in the lowest energy structures. (Note, not all computational space was considered but it is chemically intuitive to align all the TCNQ nitrogen atoms with the MOF OMS.) The optimized structure for TCNQ@Mn-MOF-74 is shown in Figure S7; images of the Cu system are omitted because they look visually similar. The predicted binding energies and MOF metal (M) to TCNQ nitrogen atom (N) distance analysis (see Table S2) indicates that TCNQ can covalently bond to the MOF framework. These DFT calculations provided theoretical binding motifs of TCNQ within the M-MOF-74 framework.



**Figure S7.** HSE06 optimized structure of TCNQ@Mn-MOF-74.

<i>MOF Metal (M)</i>	<i>Binding Energy (eV)</i>	<i>Avg. M --- N (Å)</i>	<i>Min. M --- N (Å)</i>	<i>Max. M --- N (Å)</i>	<i>TCNQ Bader Charge</i>
<i>Mn</i>	-1.82	2.234	2.169	2.321	-0.76
<i>Cu</i>	-0.41	2.700	2.670	2.758	-0.06

**Table S2.** HES06 predicted binding energies, average, minimum, and maximum distances (Å) between the metal atoms (M) in the MOF and the TCNQ nitrogen atoms (N) of TCNQ@M-MOF-74 (M = Mn, Cu). The binding energy is found to be significantly larger for the Mn version (-1.8 vs. -0.41) due to the smaller average binding distance (MOF metal atom to TCNQ's N atom). There may also be stability differences associated with the change in the metal atoms' coordination environment; however, the TCNQ@Cu-MOF-74 binding energy is significant.

#### References:

1. Kresse, G., Furthmüller, *J. Comp. Mat. Sci.* **1996**, *6*, 15–50.
2. Krukau, A. V., Vydrov, O. A., Izmaylov, A. F., & Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 224106.