

## Electronic Supplementary Information

### **Growth of ZIF-8 on molecularly ordered 2-methylimidazole/single-walled carbon nanotubes to form highly porous, electrically conductive composites**

James E. Ellis<sup>a</sup>, Zidao Zeng<sup>a</sup>, Sean I. Hwang<sup>a</sup>, Shaobo Li<sup>b</sup>, Tian-Yi Luo<sup>a</sup>, Seth C. Burkert<sup>a</sup>, David L. White<sup>a</sup>, Nathaniel L. Rosi<sup>a</sup>, Jeremiah J. Gassensmith<sup>b, c</sup>, Alexander Star<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, United States

<sup>b</sup> Department of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, TX 75080, United States

<sup>c</sup> Department of Bioengineering, University of Texas at Dallas, Richardson, TX 75080, United States

### Table of Contents

Material section.....	2
Experimental section .....	2
Characterization section.....	4
Figure S1. Photograph of ZIF-8/SWCNT water-based syntheses.....	7
Figure S2. Raman spectroscopy of pristine ox-SWCNTs (black), ox-SWCNTs saturated with 2mIM (red), and material 1 (blue).....	8
Table S1. Zeta potential of SWCNTs and SWCNTs in 2mIM (10 mM).....	9
Figure S3. TEM of material 1 .....	10
Figure S4. PXRD of material 1 .....	11
Figure S5. TEM and PXRD of ZIF-8/SWCNT composite synthesized by adding ox-SWCNT to zinc salt solution first, then adding 2mIM solution.....	12
Figure S6. TEM of material 2 .....	13
Figure S7. Time study of ZIF-8/SWCNT (material 3) growth mechanism .....	14
Figure S8. PXRD of material 4 (black), ZIF-L ([Zn <sup>2+</sup> ] = 20 mM; Zn:2mIM = 1:8; no ox-SWCNT) (red), material 3, which is representative of ZIF-8/SWCNT (blue).....	15
Figure S9. TEM of material 4 .....	16
Figure S10. TEM of material 6 after 24 hours .....	17
Figure S11. SEM of material 7 after 24 hours .....	18
Figure S12. TEM of material 6 after 90 hours .....	19

Figure S13. XRD of material 6 (black), material 5, which is representative of dia(Zn) pattern (red), and material 2, which is representative of ZIF-8/SWCNT pattern. ....	20
Figure S14. ZIF-L and dia(Zn).....	21
Figure S15. HRTEM of material 6 after (A) 24 hours and (B) 90 hours. ....	22
Table S2. Reagent parameters and product composition of synthesized products.....	23
Figure S16. CO <sub>2</sub> vs. N <sub>2</sub> uptake of ZIF-8/SWCNT composite (material 2) at 298 K. ....	24
Figure S17. Chemiresistor device with interdigitated gold electrodes. ....	25
Table S3. BET surface area and conductivity of conductive MOFs and MOF composites.....	26
ESI references .....	27

## Material section

Zinc nitrate hexahydrate (reagent grade, 98%), zinc acetate (99.99%), and 2-methylimidazole (99%) were purchased from Sigma-Aldrich. Oxidized single-walled carbon nanotubes (P3-SWNT) were purchased from Carbon Solutions, Inc. P3-SWCNTs contain 1-3 atomic% of oxygen and a residual metal content of 5-7%. The typical diameter of a P3-SWNT is  $1.55 \pm 0.1$  nm. However, they often form bundles with typical diameter of 4 – 5 nm and length of 500 nm – 1.5  $\mu$ m.

## Experimental section

### *ZIF/SWCNT synthesis with excess ox-SWCNT (material 1)*

To 6 ml of 0.5 mg/ml unsaturated CNT, 10 ml of 1344 mM 2mIM was added, followed by 5 ml addition of 84 mM zinc nitrite. The vial was shaken for 20 seconds and left unstirred for 4 hours. Solution was black when collected. Sample was centrifuged and washed with water twice. Black supernatant was observed and removed during water wash.

*Preparation of 2mIM-saturated ox-SWCNT*

1904 mg 2mIM was dissolved in 15 ml of nanopure water and was added into 5 ml of 0.5 mg/ml CNT. The mixture was set for 2 hours before filtration with 0.2  $\mu\text{m}$  pore size filter membrane. CNT was transferred into vial together with the filter membrane and 5 ml of nanopure water was added. Slight sonication was done for a couple of seconds to resuspend the CNT and the filter membrane was removed. Another 15 minutes sonication was done before further synthesis with this CNT.

*ZIF/SWCNT synthesis with Zn:2mIM 1:40 ratio,  $[\text{Zn}^{2+}] = 20 \text{ mM}$  (materials 2 and 3)*

To the 3 ml of 2mIM-saturated ox-SWCNT solution (0.1 mg/ml), 8 ml of 2-methylimidazole solution (1500 mM) was added. 4 ml of the zinc precursor (zinc nitrite or zinc acetate) solution (75 mM) was added after. The vial was shaken for 20 seconds after all the precursors were added and set overnight for 24 hours. Then the sample was centrifuged and washed with water twice and stored in water.

*ZIF/SWCNT synthesis with Zn:2mIM 1:40 ratio,  $[\text{Zn}^{2+}] = 10 \text{ mM}$  (material 6)*

To 3 ml of 2mIM-saturated ox-SWCNT solution (0.05 mg/ml), 8 ml of 2-methylimidazole solution (750mM) was added. 4 ml of the zinc precursor (zinc acetate) solution (37.5 mM) was added after. The vial was shaken for 20 seconds after all the precursors were added and left unstirred. The sample was centrifuged and washed with water twice and stored in water.

*ZIF/SWCNT synthesis with Zn:2mIM 1:40 ratio,  $[\text{Zn}^{2+}] = 6.6 \text{ mM}$  (material 7)*

To 50  $\mu\text{L}$  of ox-SWCNT (4 mg/mL), 6 mL of 2-methylimidazole solution (400 mM) was added. 3 mL of the zinc precursor (zinc acetate) solution (20 mM) was added after. The vial was shaken for 20 seconds after all the precursors were added and left unstirred. The sample was centrifuged and washed with water.

*ZIF/SWCNT synthesis with Zn:2mIM 1:8 ratio,  $[\text{Zn}^{2+}] = 20 \text{ mM}$  (materials 4 and 5)*

To 3 ml of 2mIM-saturated ox-SWCNT solution (0.1 mg/ml), 8 ml of 2-methylimidazole solution (300 mM) was added. 4 ml of the zinc precursor (zinc nitrite or zinc acetate) solution (75 mM) was added after. The vial was shaken for 20 seconds after all the precursors were added and collected after 24 hours. The sample was centrifuged and washed with water twice and stored in water.

## **Characterization section**

*Raman spectroscopy.* Raman spectra were collected from an XplorA Raman AFM-TERS system with a 638 nm (24 mW) laser at 10% laser intensity and 1 s exposure time averaged over 10 accumulations. Sample were prepared by dropcasting concentrated solutions on glass slides.

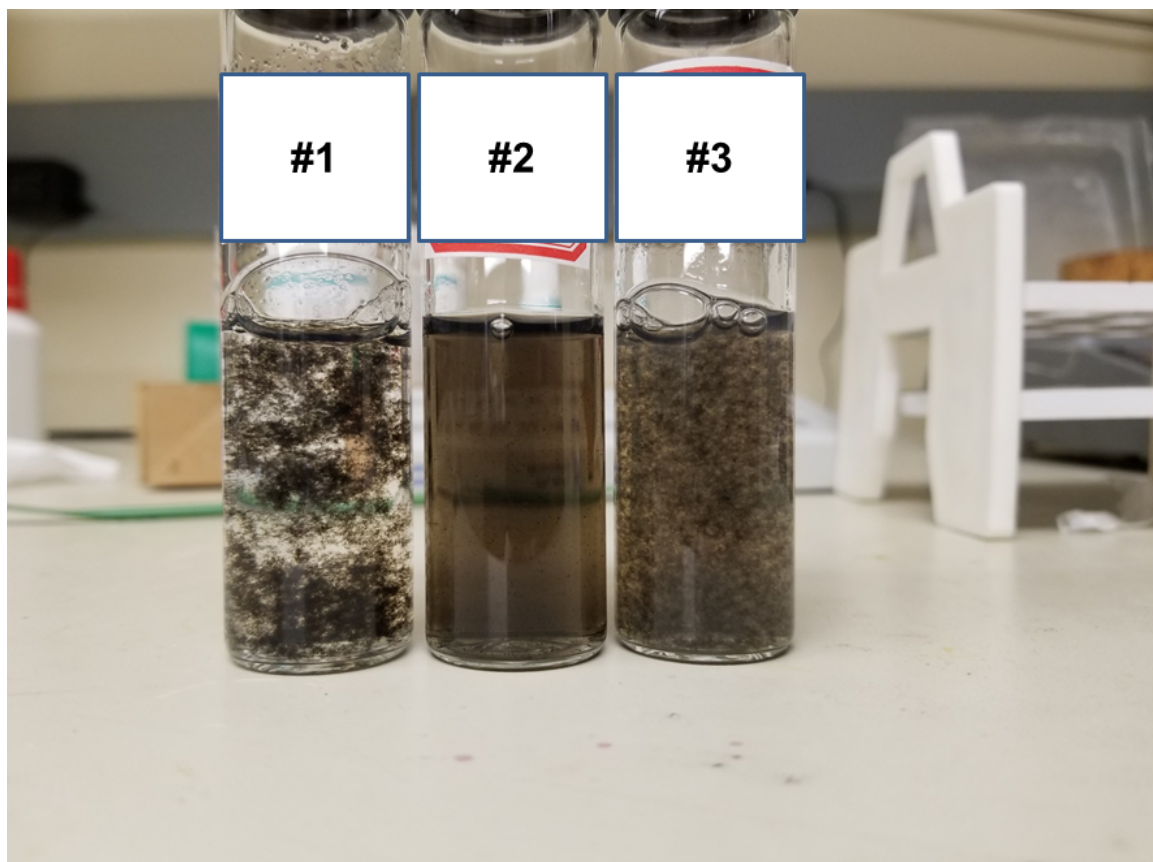
*Electron microscopy.* Transmission electron microscopy (TEM) samples were prepared by dropcasting 7  $\mu\text{L}$  of diluted samples in water on TEM sample grids (carbon film, 400 mesh copper grid; Electron Microscopy Sciences). The TEM instrument model used was FEI Morgagni. Scanning electron microscopy (SEM) of ZIF-8/SWCNT was performed on a copper foil substrate. The SEM instrument model used was ZEISS Sigma 500 VP. HRTEM images were taken with Thermo Fisher Titan Themis G2 200 Probe Cs corrected scanning transmission electron microscope.

*Powder x-ray diffraction (PXRD).* PXRD was performed on a Bruker D8 XRD system equipped with LynxEye detector. Each sample was dropcast on a glass slide before measuring.  $2\theta$  angles between  $5^\circ$  and  $50^\circ$  were measured at  $0.02^\circ$  intervals with a rate of 0.3 seconds/point. The X-ray source was Cu  $K\alpha$  held at 40 kV and 40  $\mu$ A with a 0.2 mm aperture slit width.

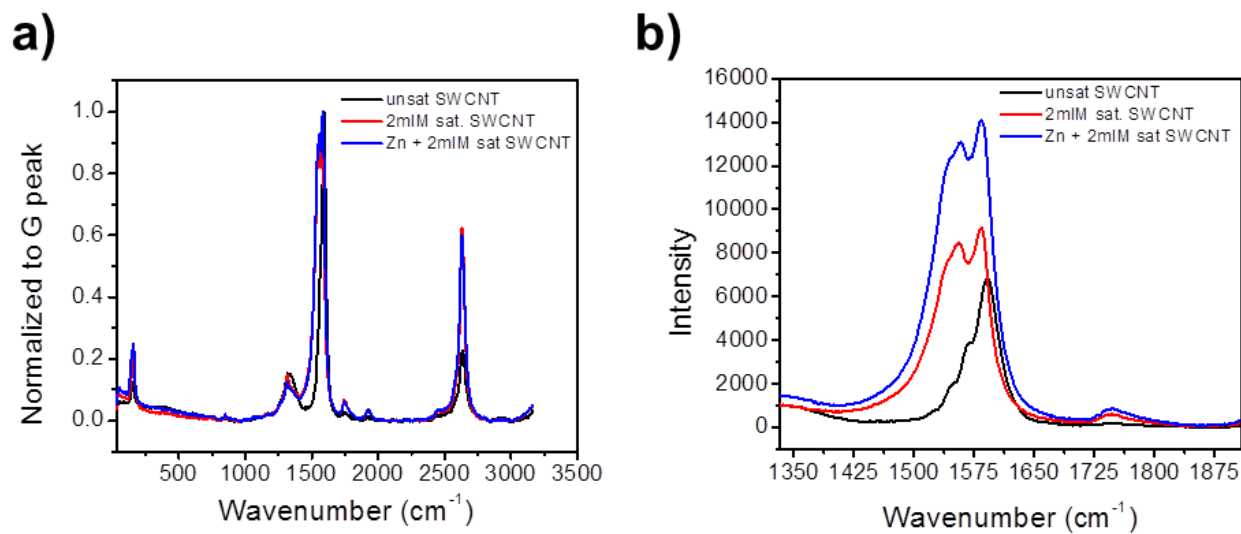
*Gas adsorption experiments.* Gas adsorption isotherms were collected using a Quantachrome Autosorb-1 instrument. A 9 mm stem diameter sample cell equipped with Cell Seal™ assembly was first evacuated on an outgassing station at room temperature and backfilled with  $N_2$  gas. Once removed from outgassing station, the empty cell capped with a Cell Seal™ valve was weighed on a balance. Approximate 40 mg of ZIF-8-nanotube sample was loaded to the sample cell. The sample cell was then evacuated at  $80^\circ C$  for 12 hours using an outgassing station. The cell was allowed to cool to room temperature, backfilled with  $N_2$  gas and removed from the outgassing station. The loaded sample cell capped with a Cell Seal™ valve was weighed. The weight of empty cell was subtracted from that of loaded cell to calculate the sample weight. The sample cell was then installed to analysis station to perform the gas adsorption experiments. A liquid  $N_2$  bath was used for  $N_2$  adsorption experiments at 77 K. A water–ethylene glycol bath was used for  $N_2$  and  $CO_2$  experiments at 298 K. UHP grade  $N_2$  and  $CO_2$  gas adsorbates (99.999%) were used. Brunauer–Emmett–Teller (BET) surface area was calculated based on  $N_2$  77K isotherm data.

*Electrical characterization:* A 2 x 2 mm  $SiO_2$  chip with 4 interdigitated gold electrode was used to collect the I-V characteristics of ZIF-8/SWCNT. ZIF-8/SWCNT in water was dropcast above the chip such that the entire surface was covered with a very thick layer of ZIF-8/SWCNT. The I-V characteristics were collected with a Keithly 2400 sourcemeter and LabView software.

*Gas sensing experiment:* The gas sensing experimental data was collected using a custom-made system. Up to 8 packaged chips were inserted into a printed circuit board with 8 through-hole soldered 40-pin zero insertion force (ZIF) connectors. The packages were then capped with a stainless-steel gas manifold. The current measurements were taken at 50 mV using a Keithley 2602B SourceMeter and a Keithley 3706A System Switch. Dry air (Ultra Zero Grade) from a gas cylinder (Matheson Tri-Gas) was delivered to the gas manifold at a total flow rate of 1,000 sccm using a Bronkhorst EL-FLOW Prestige mass flow controller (MFC). The Keithley systems and Bronkhorst MFC were interfaced and controlled through LabView 2016 software. The saturated ethanol vapor was generated by bubbling the dry air stream through a glass bubbler with liquid ethanol. A manually controlled three-way valve was used to either direct the air stream directly toward the manifold or the bubbler. The manifold was initially purged with dry air for 30 minutes. The sensors were then exposed to ethanol vapor for 5 minutes and then purged with dry air for 5 minutes. There was an additional purging period of 30 minutes after the last ethanol exposure.



**Figure S1.** Photograph of ZIF-8/SWCNT water-based syntheses. Solution #1: ox-SWCNT solution is added to zinc salt solution first, then 2mIM is added. Solution #2: ox-SWCNT is added to 2mIM solution first, then zinc salt is added. Solution #3: ox-SWCNT is added to zinc salt and 2mIM solution simultaneously.

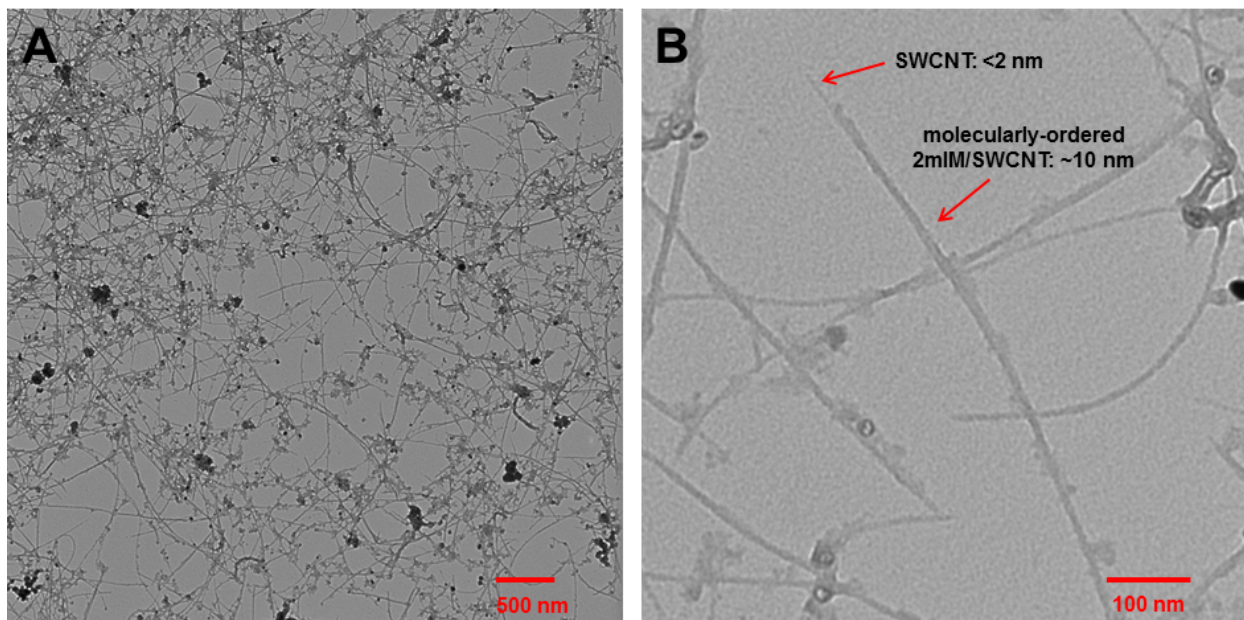


**Figure S2.** Raman spectroscopy of pristine ox-SWCNTs (black), ox-SWCNTs saturated with 2mIM (red), and material **1** (blue). a) Raman spectra normalized to each G peak; b) G peak.

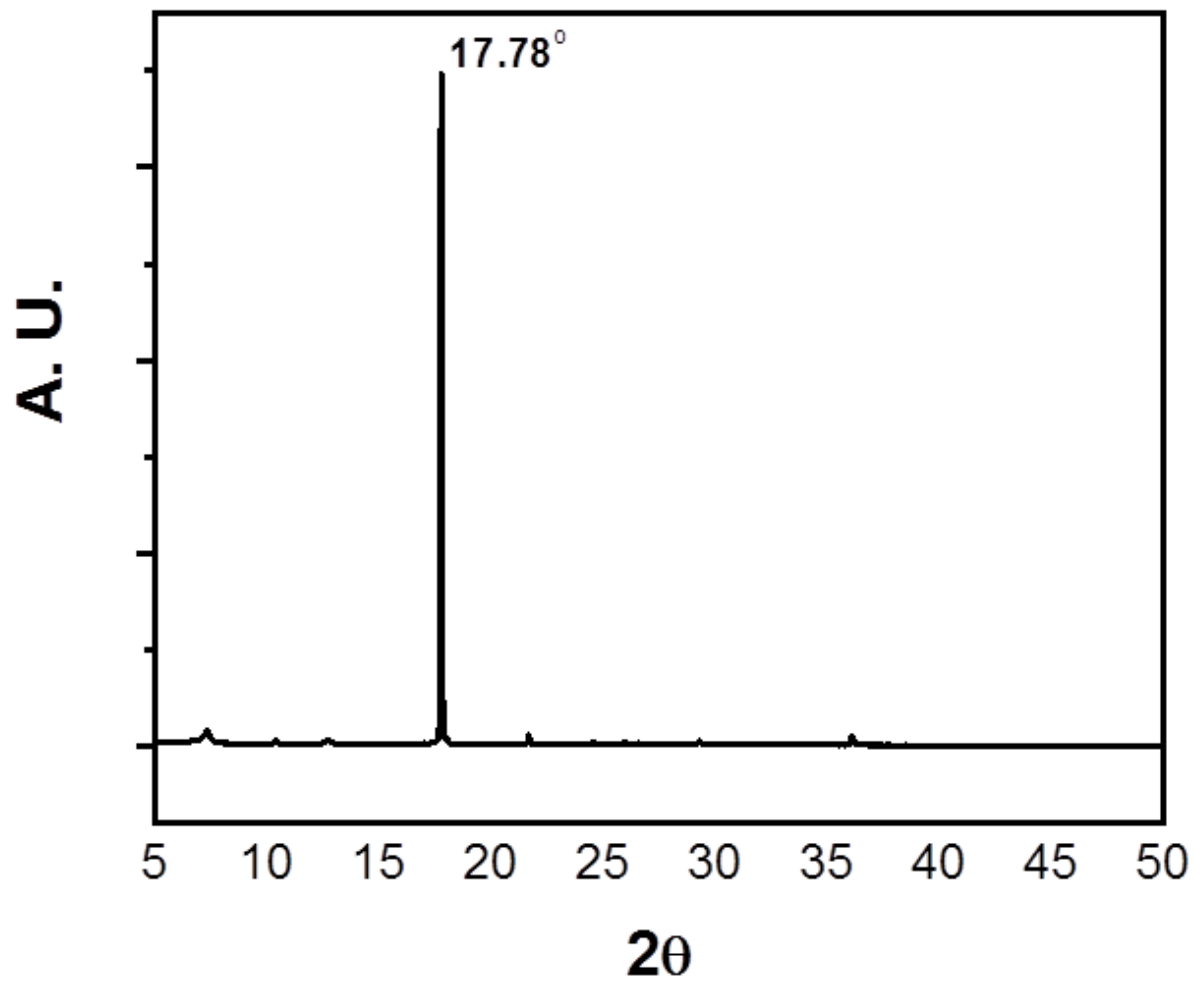


**Table S1.** Zeta potential of SWCNTs and SWCNTs in 2mIM (10 mM)

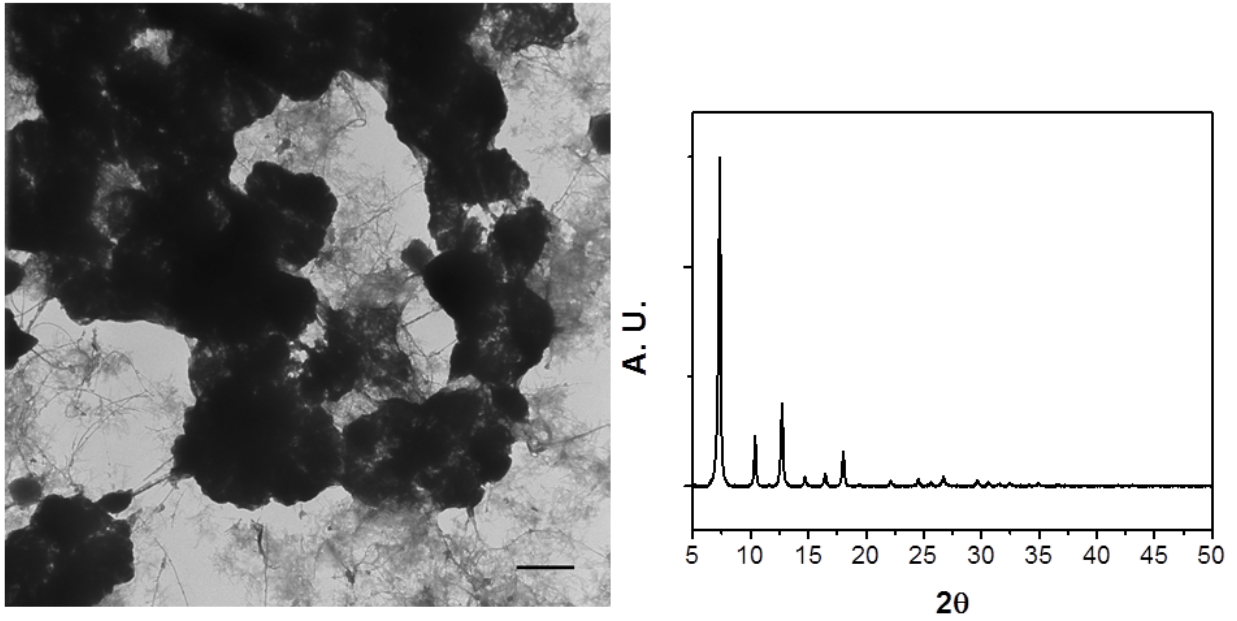
<b>Material</b>	<b>Mean zeta potential (mV)</b>	<b>Standard deviation (mV)</b>
<b>SWCNTs</b>	-40.1	±0.4
<b>SWCNTs/2mIM</b>	-43.8	±1.5



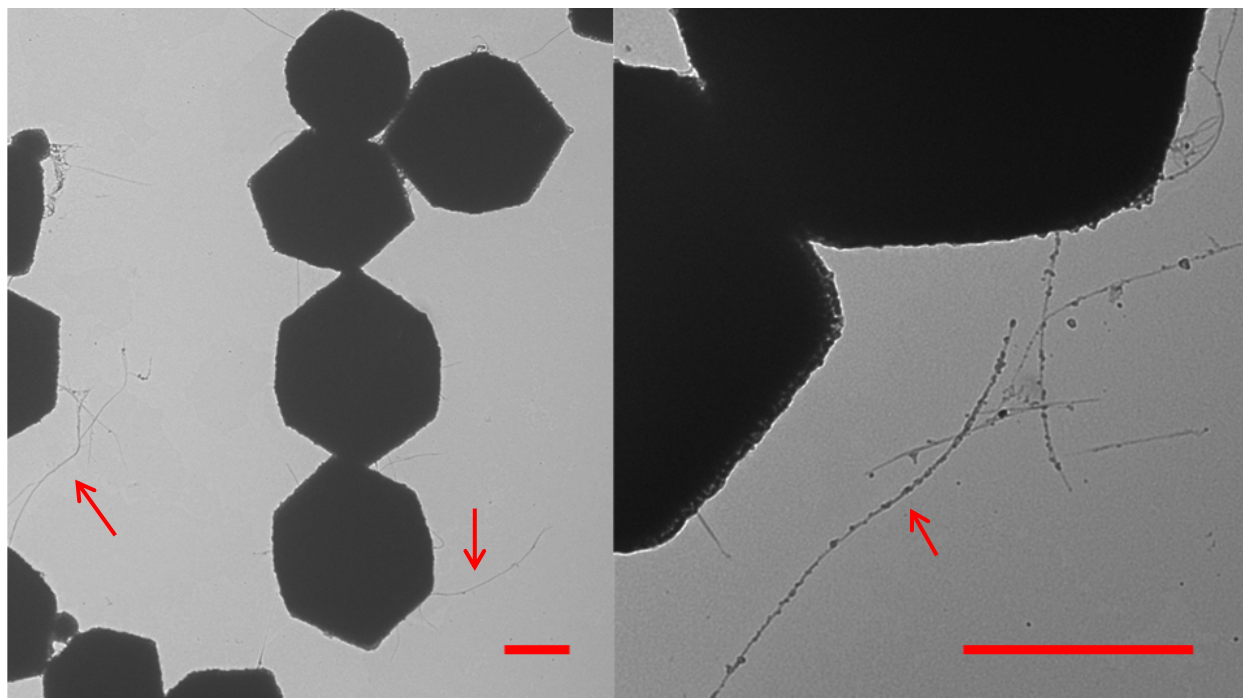
**Figure S3.** TEM of material **1**. Scale bars for panels A and B are 500 nm and 100 nm, respectively. Arrows in panel B highlight the size difference between SWCNT and molecularly-ordered 2mIM/SWCNT. The diameter of the SWCNT is less than 2 nm, while the molecularly-ordered 2mIM/SWCNT has a diameter of approximately 10 nm.



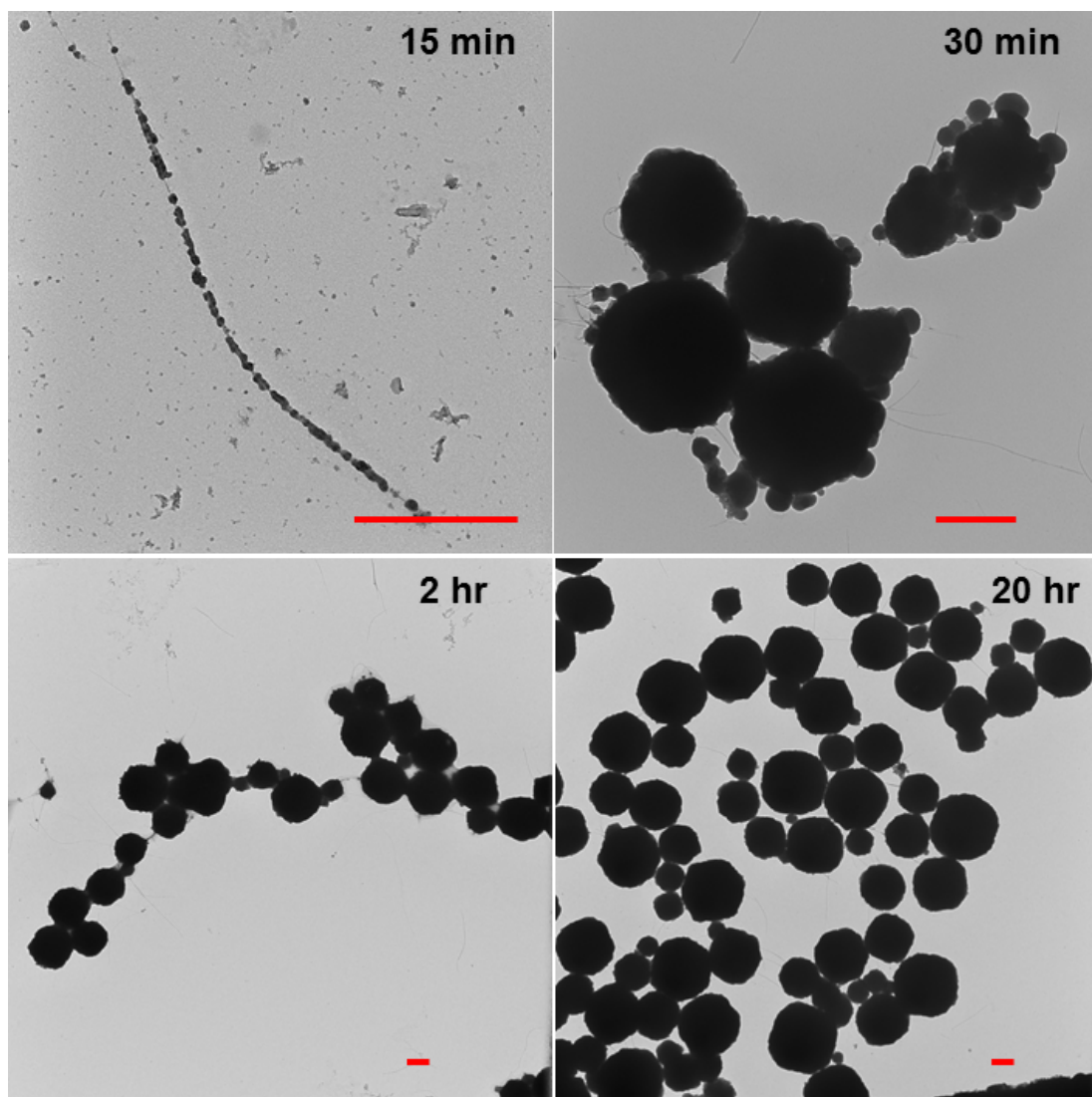
**Figure S4.** PXRD of material 1. 2mIM is added to ox-SWCNTs first, then zinc nitrate is added. d-spacing is 4.98 Å.



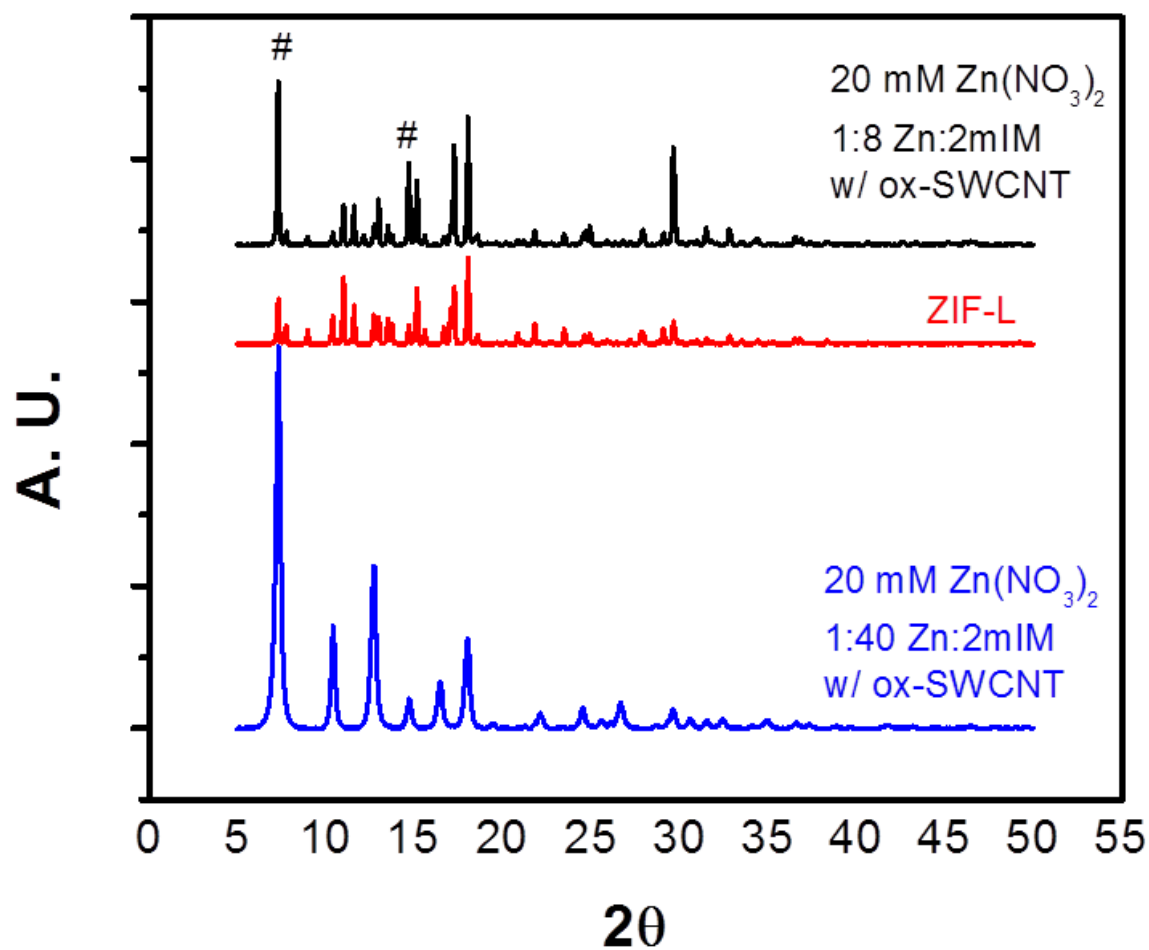
**Figure S5.** TEM and PXRD of ZIF-8/SWCNT composite synthesized by adding ox-SWCNT to zinc salt solution first, then adding 2mIM solution. Scale bar is 1 μm.



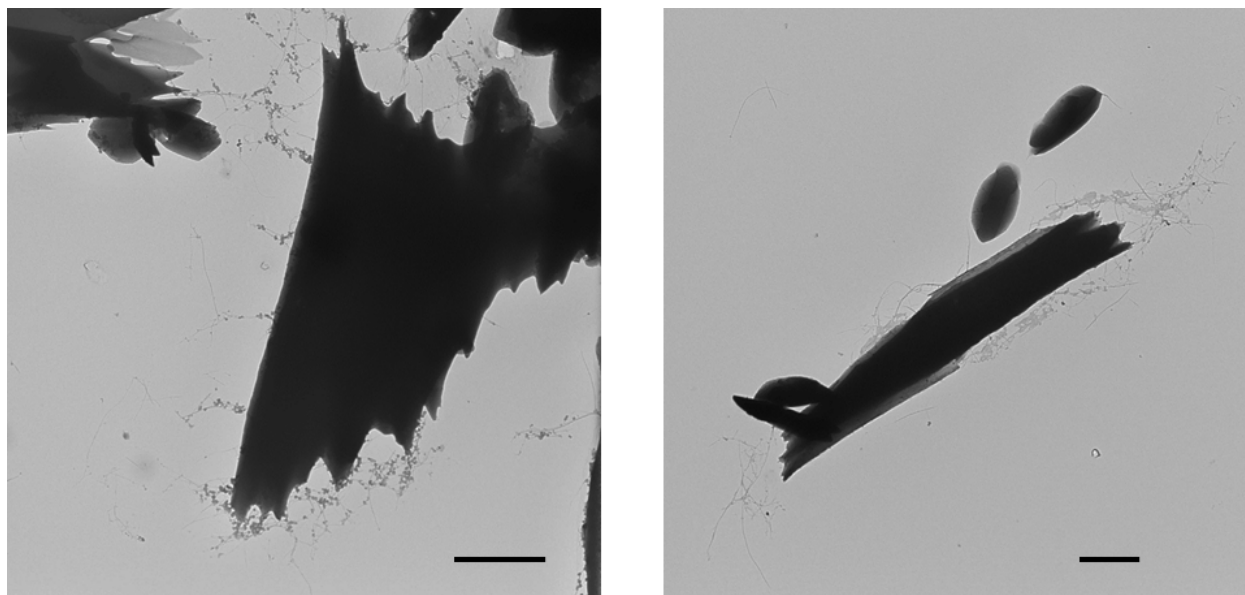
**Figure S6.** TEM of material **2**. Red arrows highlight exposed SWCNTs threading the ZIF-8 crystals. Scale bars are 1  $\mu\text{m}$ .



**Figure S7.** Time study of ZIF-8/SWCNT (material **3**) growth mechanism. TEM of ZIF-8/SWCNT reaction was taken at four time points: 15 minutes, 30 minutes, 2 hours, and 20 hours. The scale bars in all TEM images are 500 nm.



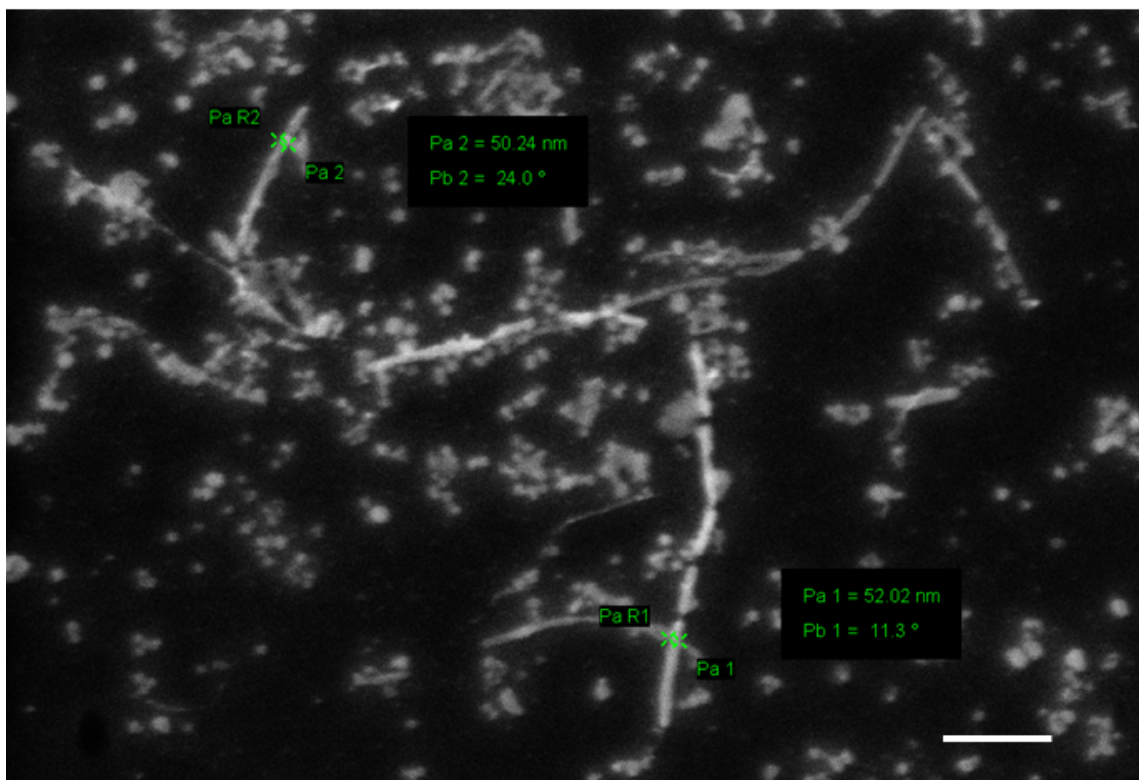
**Figure S8.** PXRD of material 4 (black), ZIF-L ( $[\text{Zn}^{2+}] = 20 \text{ mM}$ ; Zn:2mIM = 1:8; no ox-SWCNT) (red), material 3, which is representative of ZIF-8/SWCNT (blue). Zinc nitrate hexahydrate is the zinc source. (#) symbol indicates the ZIF-8 features in the top diffraction pattern.



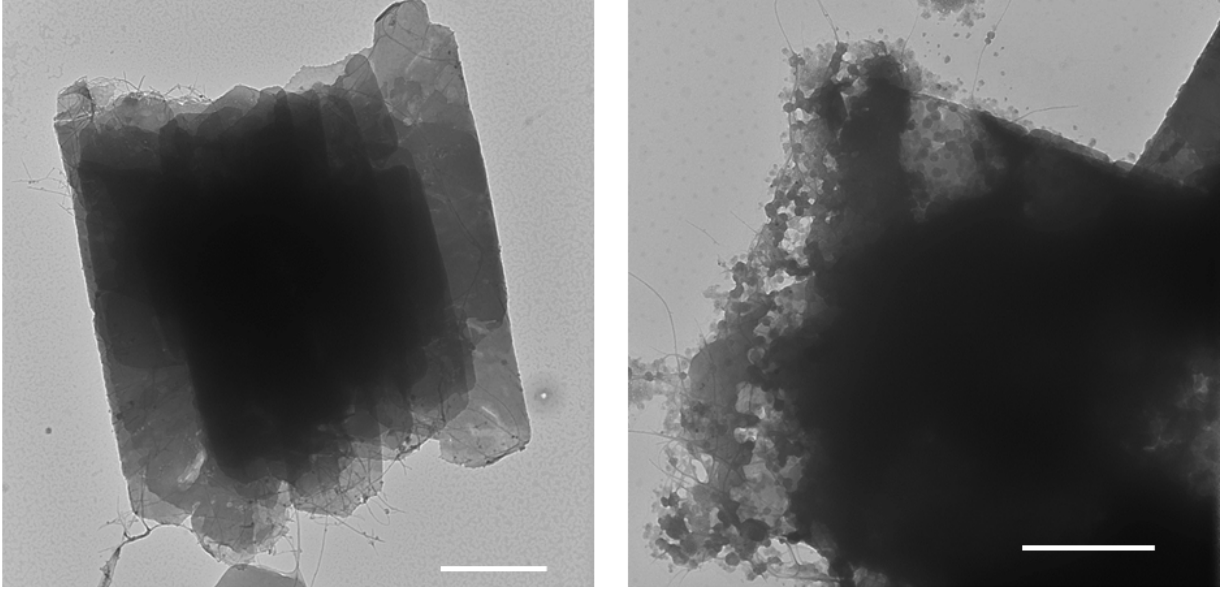
**Figure S9.** TEM of material 4. Zinc source is zinc nitrate hexahydrate. Scale bar is 1  $\mu\text{m}$ .



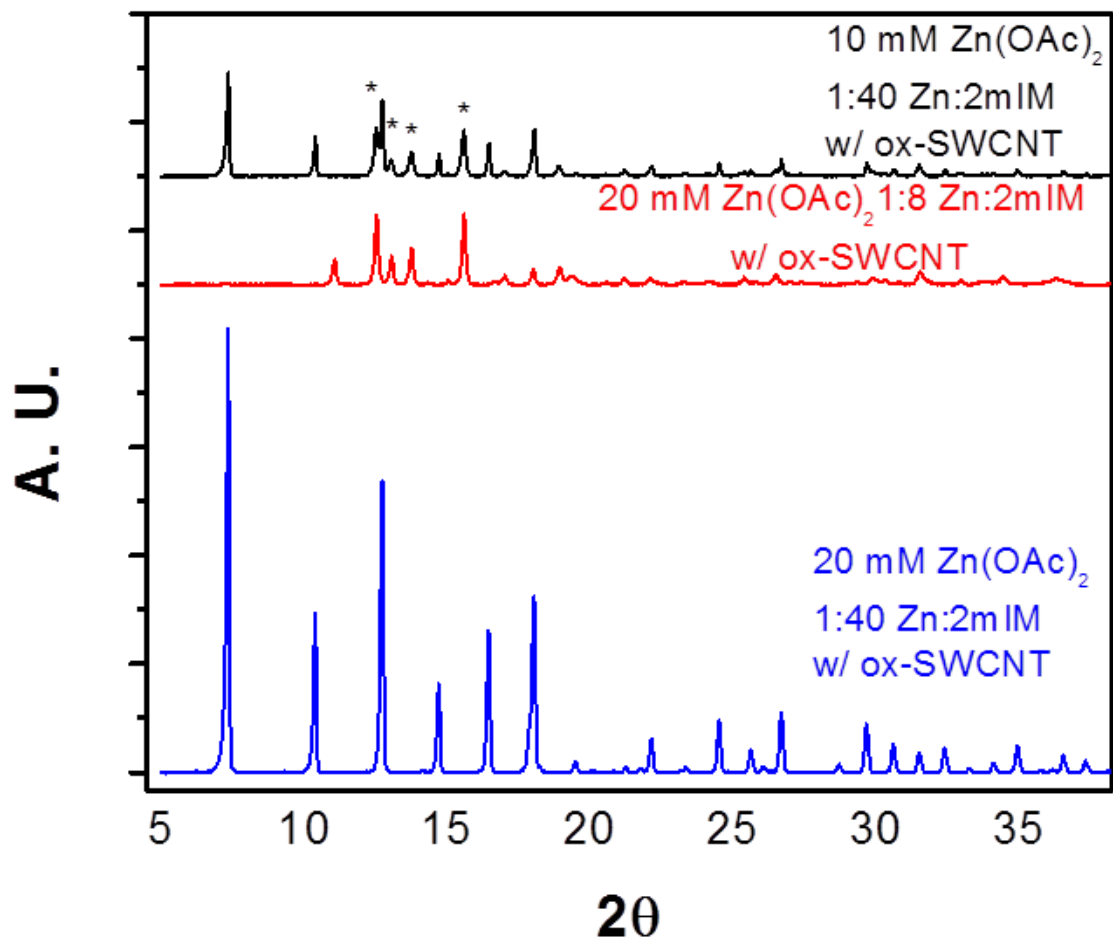




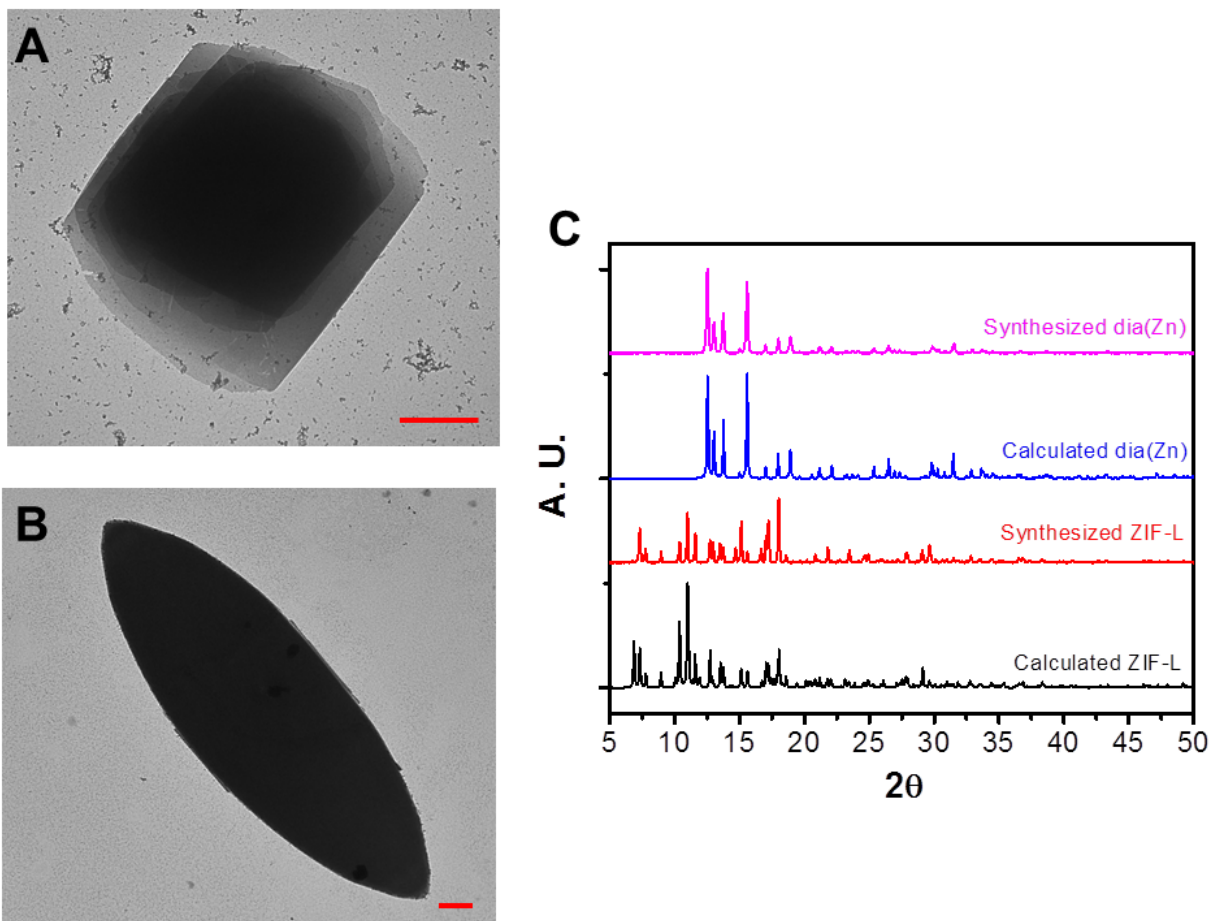
**Figure S11.** SEM of material 7 after 24 hours. Zinc acetate is the zinc source. Scale bar is 500 nm.



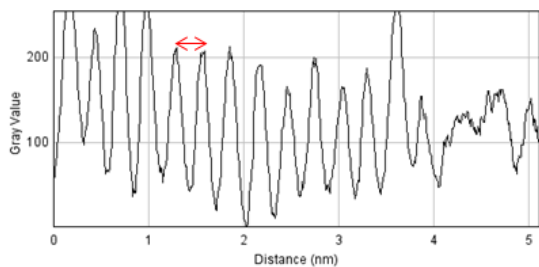
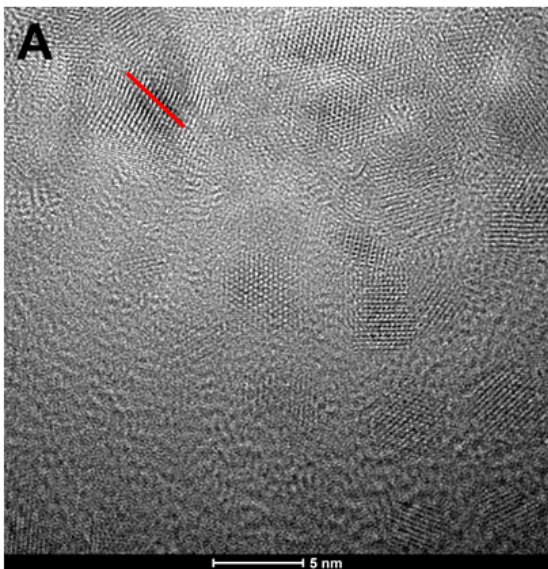
**Figure S12.** TEM of material **6** after 90 hours. Scale bars are 1  $\mu\text{m}$ .



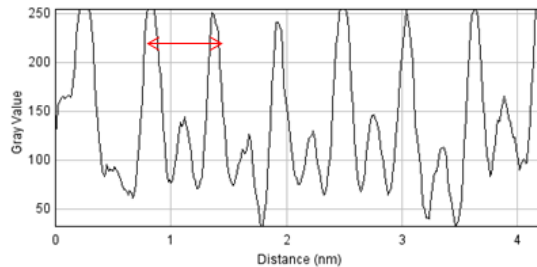
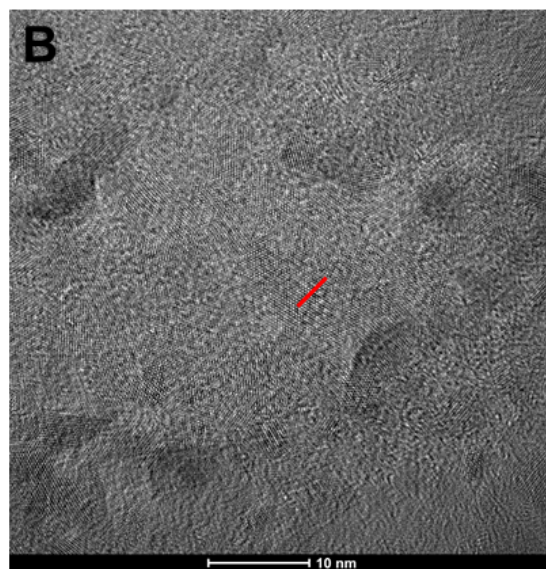
**Figure S13.** XRD of material 6 (black), material 5, which is representative of dia(Zn) pattern (red), and material 2, which is representative of ZIF-8/SWCNT pattern. Asterisks indicate dia(Zn) peaks in the top diffraction pattern.



**Figure S14.** ZIF-L and dia(Zn). (A) TEM of dia(Zn), (B) TEM of ZIF-L, (C) calculated and experimental PXRD of dia(Zn) and ZIF-L.



d-spacing = 0.29 nm

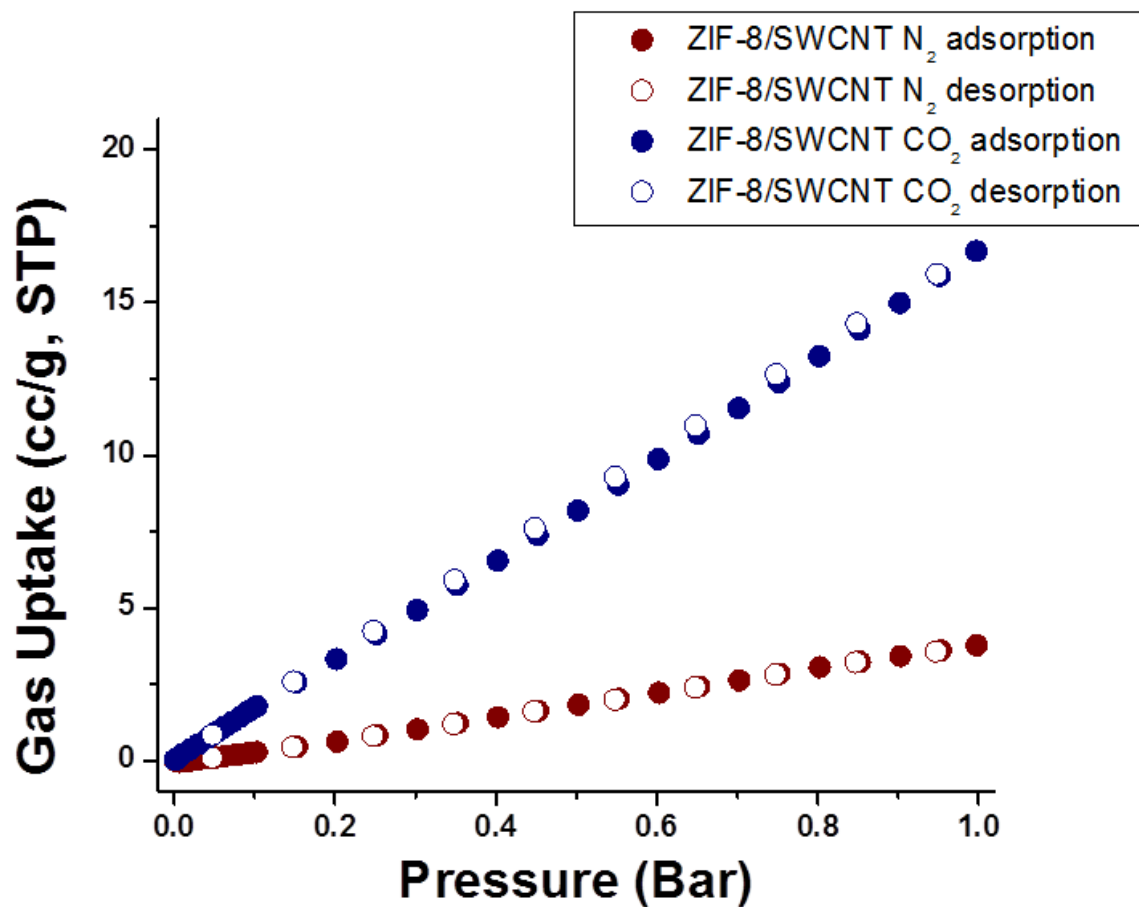


d-spacing = 0.56 nm

**Figure S15.** HRTEM of material **6** after (A) 24 hours and (B) 90 hours. The crystal lattice spacing was measured for each image (red lines). The d-spacing in figure A and B is 0.29 nm and 0.56 nm, respectively. These d-spacing correspond to the  $2\theta=31^\circ$  peak of ZIF-8 and the  $2\theta=15.6^\circ$  of dia(Zn).

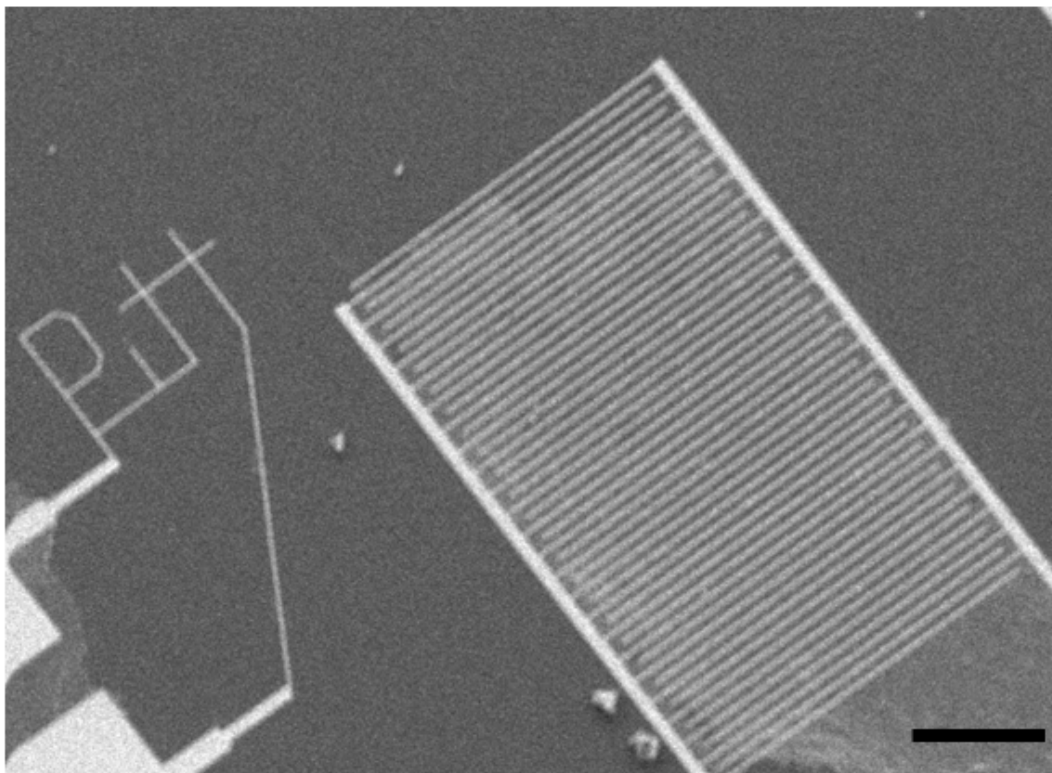
**Table S2.** Reagent parameters and product composition of synthesized products

Material	Zinc source	[Zn] (mM)	Zn:2mIM mol. ratio	Zn:SWCNT (mmol:mg)	Product composition according to PXRD
1	Zn(NO <sub>3</sub> ) <sub>2</sub>	20	1:32	1:7.5	Molecularly-ordered 2mIM/SWCNT
2	Zn(OAc) <sub>2</sub>	20	1:40	1:1	ZIF-8/SWCNT
3	Zn(NO <sub>3</sub> ) <sub>2</sub>	20	1:40	1:1	ZIF-8/SWCNT
4	Zn(NO <sub>3</sub> ) <sub>2</sub>	20	1:8	1:1	ZIF-8@ZIF-L/SWCNT
5	Zn(OAc) <sub>2</sub>	20	1:8	1:1	dia(Zn)/SWCNT
6	Zn(OAc) <sub>2</sub>	10	1:40	1:1	ZIF-8@dia(Zn)/SWCNT
7	Zn(OAc) <sub>2</sub>	6.6	1:40	1:3.3	ZIF-8/SWCNT
ZIF-L	Zn(NO <sub>3</sub> ) <sub>2</sub>	20	1:8	No CNT	ZIF-L
dia(Zn)	Zn(OAc) <sub>2</sub>	20	1:8	No CNT	dia(Zn)



**Figure S16.** CO<sub>2</sub> vs. N<sub>2</sub> uptake of ZIF-8/SWCNT composite (material 2) at 298 K.





**Figure S17.** Chemiresistor device with interdigitated gold electrodes. Interdigitated electrode length is  $7\ \mu\text{m}$ . The width and height of the electrodes are  $500\ \mu\text{m}$  and  $65\ \text{nm}$ , respectively. Scale bar is  $100\ \mu\text{m}$ .

**Table S3.** BET surface area and conductivity of conductive MOFs and MOF composites.

<b>material</b>	<b>surface area (m<sup>2</sup>/g)</b>	<b>conductivity (S/cm)</b>	<b>reference</b>
Ni <sub>3</sub> (HITP) <sub>2</sub> (2-D)	625	2	S1
HKUST-1/activated carbon (77 wt%)	1170	0.076	S2
NU-1000/oligothiophene	1600	1.3 x 10 <sup>-7</sup>	S3
NU-1000/Ni(IV) bis(dicarbollide)	1260	2.7 x 10 <sup>-7</sup>	S4
oxidized Fe <sub>2</sub> (BDT) <sub>3</sub>	614	1.8	S5
ZIF-8/rGO (20 wt%)	720	.64	S6
MIL-101(Cr)/PEDOT	803	1.1 x 10 <sup>-3</sup>	S7
HKUST-1/TCNQ	214	0.07	S8
(NBu <sub>4</sub> ) <sub>2</sub> Fe <sub>2</sub> <sup>III</sup> (dhbq) <sub>3</sub>	not microporous	0.16	S9
ZIF-8/SWCNT (0.40 ± 0.09%)	1792	0.054	this work
ox-SWCNT	not microporous	85	this work

## ESI references

- S1. D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Er, C. R. Wade, C. K. Brozek, A. Aspuru-Guzik and M. Dinca, *J. Am. Chem. Soc.*, 2014, **136**, 8859-8862.
- S2. O. Fleker, A. Borenstein, R. Lavi, L. Benisvy, S. Ruthstein and D. Aurbach, *Langmuir*, 2016, **32**, 4935-4944.
- S3. T. C. Wang, I. Hod, C. O. Audu, N. A. Vermeulen, S. T. Nguyen, O. K. Farha and J. T. Hupp, *ACS Appl. Mater. Interfaces*, 2017, **9**, 12584-12591.
- S4. C. W. Kung, K. Otake, C. T. Buru, S. Goswami, Y. Cui, J. T. Hupp, A. M. Spokoyny and O. K. Farha, *J. Am. Chem. Soc.*, 2018, **140**, 3871-3875.
- S5. L. S. Xie, L. Sun, R. Wan, S. S. Park, J. A. DeGayner, C. H. Hendon and M. Dinca, *J. Am. Chem. Soc.*, 2018, **140**, 7411-7414.
- S6. D. Kim, D. W. Kim, W. G. Hong and A. Coskun, *J. Mater. Chem. A*, 2016, **4**, 7710-7717.
- S7. B. Le Ouay, M. Boudot, T. Kitao, T. Yanagida, S. Kitagawa and T. Uemura, *J. Am. Chem. Soc.*, 2016, **138**, 10088-10091.
- S8. A. A. Talin, A. Centrone, A. C. Ford, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, H. P. Yoon, F. Leonard and M. D. Allendorf, *Science*, 2014, **343**, 66-69.
- S9. L. E. Darago, M. L. Aubrey, C. J. Yu, M. I. Gonzalez and J. R. Long, *J. Am. Chem. Soc.*, 2015, **137**, 15703-15711.