Electronic Supporting Information

Exchange of coordinated carboxylates with azolates as a route to obtain a microporous zinc–azolate framework

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Materials:

All materials, unless otherwise specified, were purchased and used as received.

Zinc (II) nitrate hexahydrate (98%, $Zn(NO_3)_2 \cdot 6H_2O$), Sulfuric acid-d2 (99.5%, D_2SO_4), and Dimethyl sulfoxide-d6 (99.9%, DMSO-d6) were purchased from Sigma Aldrich (St. Louis, MO). 1,5-Dihydrobenzo[1,2-d:4,5-d']bis([1,2,3]triazole (97%, H_2BBTA) was purchased from Chemsoon (Shanghai, China). 2,5-Dihydroxyterephthlalic acid (97%, dhbdc), Methanol (MeOH, 99.8%), and *N,N*-Dimethylformamide (DMF, 98%) were purchased from Fisher.

Synthesis:

Zn-MOF-74 (CPO-27-Zn, Zn_2(dobdc)). Zn-MOF-74 was prepared according to the published literature[1] with slight modification. $Zn(NO_3)_2 \cdot 6H_2O$ (4.52 g, 15 mmol) and dhbdc (1.00 g, 5 mmol) were placed in a 500 mL bottle with 100 mL DMF. The solution was sonicated for 5 minutes to dissolve. 5 mL of water was added, and the solution was sonicated for another minute. The bottle was then capped tightly and placed in an oven for approx. 21.5 hours. Then, the DMF solution was decanted, and the resulting solid was washed 3× with 100 mL DMF, 3× with 100 mL methanol, and stored in about 100 mL of methanol in a fume hood.

SALE parameter screening: First, we tested the addition of a 2:1 theoretical mass ratio of H_2BBTA:dobdc in a solution of MOF-74 in DMF, a solvent in which the linker is soluble. After heating for 24 hours at 100 ºC, the mother liquor was decanted, the MOF was washed three times with DMF, and the ^1H NMR spectra revealed an exchange of 46%. This process was repeated three more times, and each day resulted in about a 10% increase in $BBTA^{2-}$ linker incorporation, with up to 76% after 96 h (Figure 2). Intending to increase the incorporation further, we then carried out the procedure using a 5:1 mass ratio of H_2BBTA:dobdc monitored over 120 hours. Indeed, after four days, we observed a higher exchange (90%) for the higher concentration, likely due to a greater shift in the equilibrium process favoring $BBTA^{2-}$ incorporation. We elected to move forward with a 96-hour timeframe, as we only observed a 3% increase in linker exchange between the fourth and fifth cycles. We chose to add a 40 mg/mL concentration of H_2BBTA in several cycles as opposed to one cycle in high excess in order to mitigate the formation of side products; potential leaching of Zn(II) ions from the framework would readily react with excess $BBTA^{2-}$ in solution to form the unwanted MFU-4.[2] We also tested H_2BBTA equivalences of 1, 1.5, and 2.5, finding lower exchanges than the 5 eqv. sample for each. We then tested this SALE procedure at temperatures of 80 ºC, 100 ºC, and 120 ºC. While we observed a lower linker exchange after one day with a temperature of 80 ºC, there was negligible difference of linker exchange between samples held at 100 and 120 ºC.

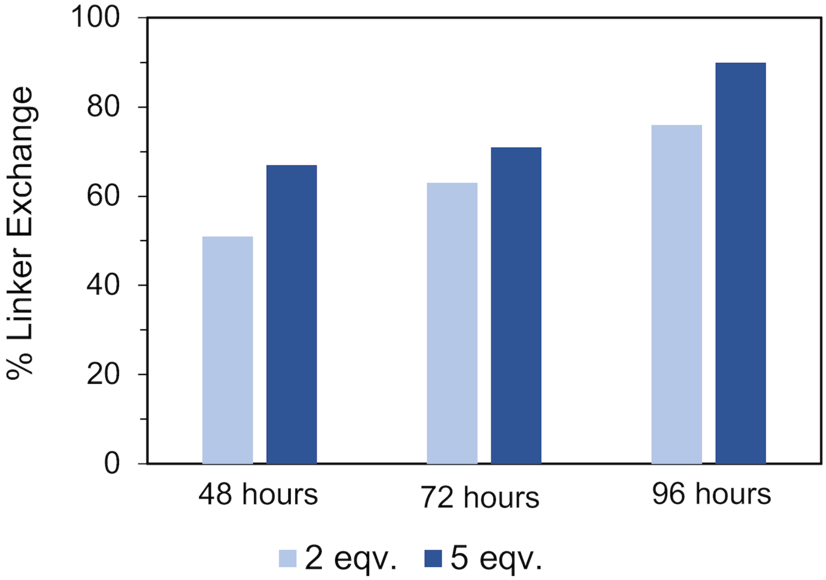

Figure S1. H_2BBTA incorporation into MOF-74 as a function of synthesis time and linker ratio during SALE. Linker exchange was calculated *via* ^1H NMR integration from digested samples run at 100 ºC with 40 mg ml^{-1} of added H_2BBTA.

NU-250 and NU-251: Zn-MOF-74 (60 mg, 0.18 mmol) that was stored in 100 mL of methanol, was isolated from solvent and washed three times with several milliliters of DMF. A 40 mg/mL solution of H_2BBTA (179 mg, 1.07 mmol) dissolved in 4.45 mL DMF was sonicated for 30 seconds and filtered through a 0.2 μm PFTE Whatman filter. The H_2BBTA solution was then added to the rinsed Zn-MOF-74 in a glass screwcap vial which was sealed and placed on an aluminum heating block at 100 ºC for 24 hours. After the solution was cooled to room temperature, the liquid was decanted and the remaining solid was washed three times with several mL of DMF. Another 4.45 mL solution of 40 mg/mL H_2BBTA in DMF was added to the washed solid, and the cycle was repeated three more times for a total of four days. The resulting material was washed three times with several mL of DMF, three times with several mL of methanol, and then stored in methanol. Linker exchange was quantified through ^{1}H NMR spectroscopy, prepared by digesting ~1 mg of dried MOF in 7 drops of deuterated sulfuric acid (D_2SO_4, Sigma Aldrich), sonicating for 5 minutes, and adding 0.7 mL of dimethyl sulfoxide-d6 (DMSO-d6, Sigma Aldrich). Calculations were obtained by integrating the resulting ^{1}H NMR spectrum peaks of both dobdc^{4-} and BBTA (Figure S2) utilizing MestReNova 14.2 software.

Instrumentation

Nuclear Magnetic Resonance (NMR). ^{1}H NMR spectra of samples were obtained using a Bruker Avance III 500 MHz (IMSERC-Northwestern University). Sample data was acquired with TopSpin^{TM} software by Bruker.

Scanning Electron Microscopy (SEM). SEM images were collected using a JEOL JSM-7900FLV scanning electron microscope. Samples were drop-cast, left to dry, and blown with compressed air. Prior to imaging, the samples were coated with 18nm of osmium oxide using an SPF Osmium Coater (NUANCE Center-Northwestern University).

Powder X-ray diffraction (PXRD). PXRD measurements were taken on a STOE-STADI-P (IMSERC-Northwestern University) run on pure CuKα1 radiation (λ = 1.54056 Å). Samples were prepared by drop-casting in methanol onto a PXRD mask and drying in air for at least 15 minutes. Data was collected from 0-40 º 2θ with a step size of 4.005 and time/PSD step set to 20 seconds.

Nitrogen Adsorption. Samples were first activated at 150 ºC for 12-24 hours (NU-250) or 150 ºC for 10 hours and 265 ºC for 10 hours (MOF-74) under vacuum on a Micromeritics ASAP 2420. N_2 isotherms were then measured on the same instrument at 77 K. Pore-size distributions were calculated using a DFT carbon slit-pore model.

CO_2 Adsorption. Carbon dioxide isotherms were measured on activated samples using a Micromeritics ASAP 2020 surface area analyzer. An ISO Controller (Micromeritics) was utilized to regulate the temperatures at which the isotherms were collected (273, 283, and 298 K). Isosteric heat of adsorption (Q_{st}) values for CO_2 were calculated using the Clausius-Clapeyron equation (Eq. 1)[3,4] utilizing the MicroActive software.

$$\Delta H_{ads}(n) = -R \cdot \ln\left(\frac{p_2}{p_1}\right)\frac{T_1 \cdot T_2}{(T_2 - T_1)} \qquad \text{(Eq. 1)}$$

Proton Nuclear Magnetic Resonance (^{1}H NMR)

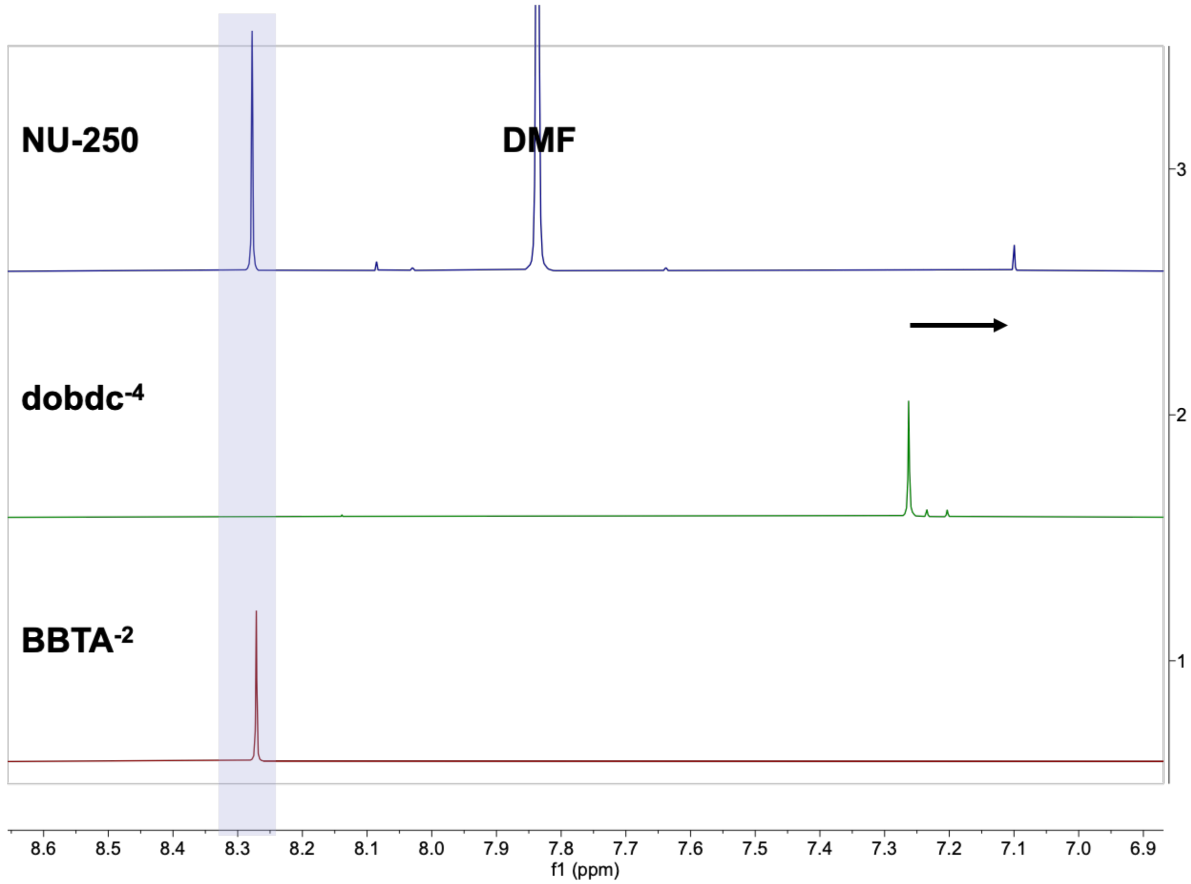

Figure S2. ^{1}H NMR spectra of digested NU-250 (top), dobdc^{4-} linker (middle), and BBTA^{2-} linker (bottom). The arrow indicates an upfield shift in the peak of the dobdc^{4-} linker after incorporation into the MOF framework due to shielding effects.

Table S1. Linker exchanges after 1 day as calculated by ^{1}H NMR integration.

Temperature	**80ºC**				**100ºC**			
H_2BBTA equivalence	1×	1.5×	2×	2.5×	1×	1.5×	2×	2.5×
% Exchange	4%	10%	17%	19%	6%	15%	27%	9%

Scanning Electron Microscopy (SEM)

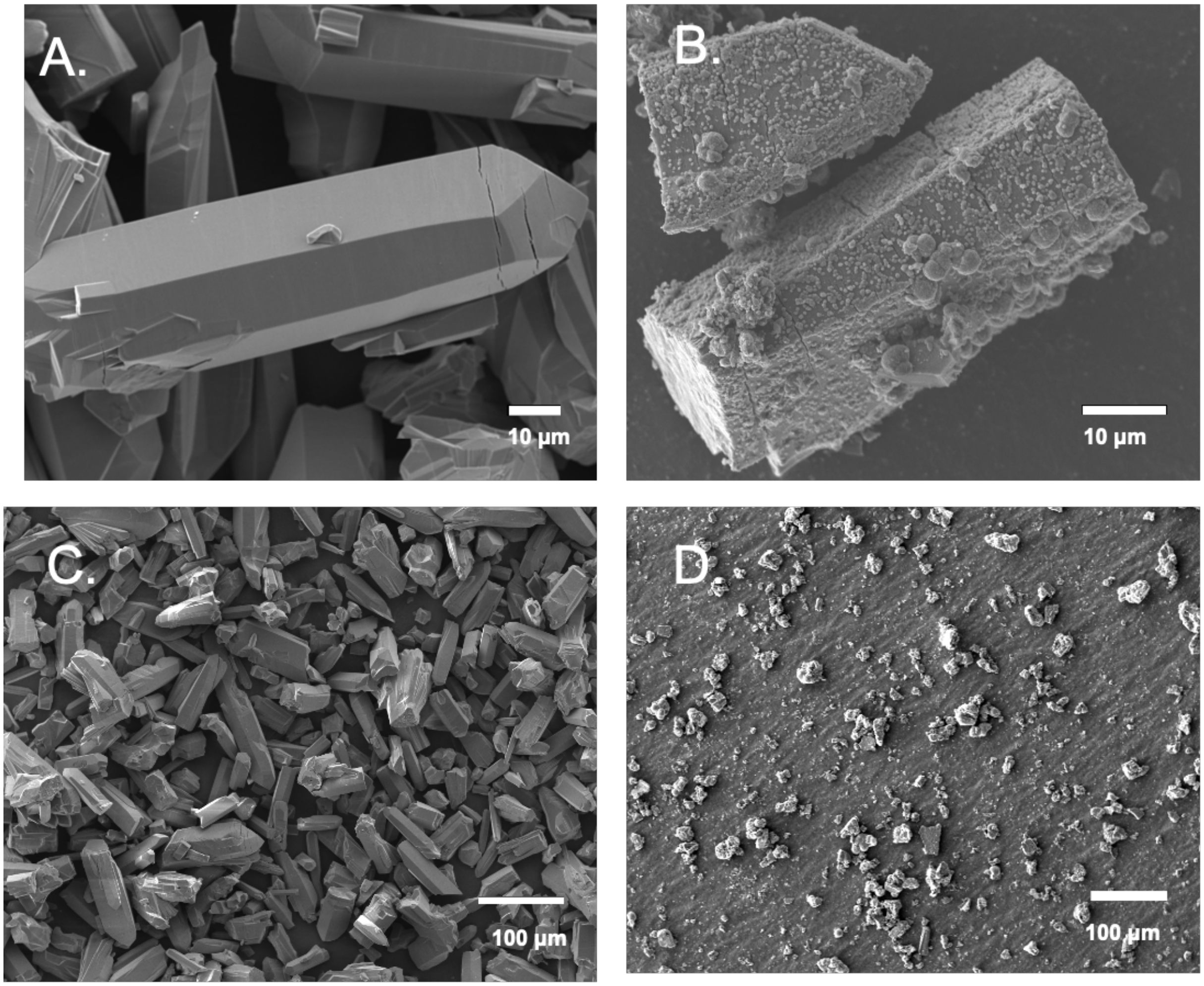

Figure S3. SEM images of MOF-74 (A, C) and NU-250 (B, D).

Carbon Dioxide Isotherms

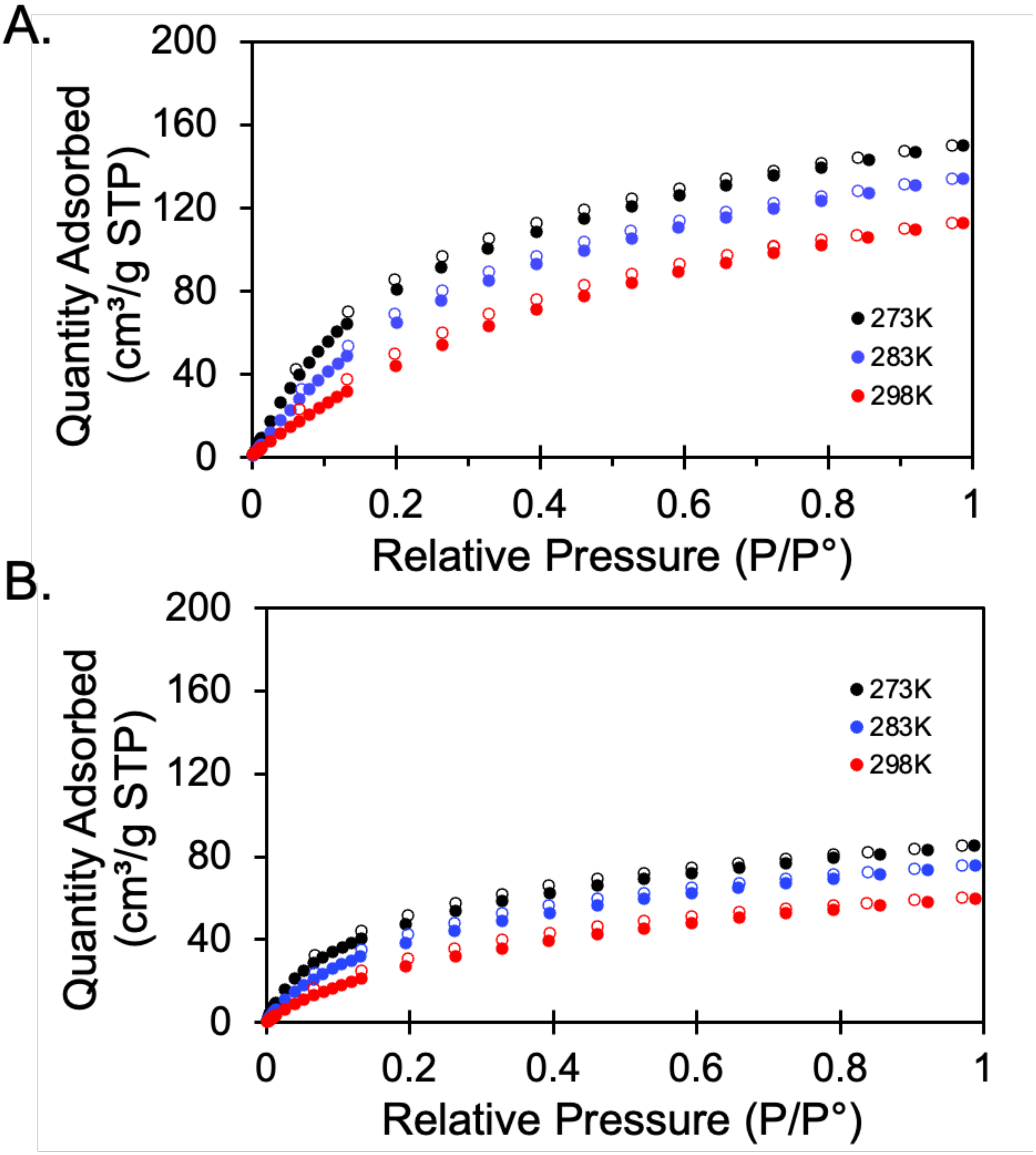

Figure S4. Representative CO_2 adsorption (open circles) and desorption (closed circles) isotherms for A) MOF-74 and B) NU-250.

Single Crystal XRD

Single-crystal X-ray crystallographic analyses were carried out using a Rigaku Cu-synergy Hybrid Photon Counting (HPC) detector equipped with a Cu Kα ($\lambda = 1.54178$ Å) microsource. The single crystals were mounted on MicroMesh (MiTeGen) with paratone oil at 100 K under a nitrogen cryostream. The structures were determined by intrinsic phasing (SHELXT 2014/5)[5] and refined by full-matrix least-squares refinement on F2(SHELXL-2017/1)[6] using the Olex2[7] software package. Crystallographic details and refinement results are summarized below. Crystallographic data in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-2145009. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

Table S2: Crystal data and structure refinement for NU-251

Empirical formula	$C_{10}H_{10}N_4O_4Zn$
Formula weight	315.59
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2/c
a/Å	24.4357(10)
b/Å	9.0502(4)
c/Å	13.1766(4)
α/°	90
β/°	94.775(4)
γ/°	90
Volume/Å^3	2903.9(2)
Z	8
ρ_{calc}g/cm^3	1.444
μ/mm^{-1}	2.508

F(000)	1280.0
Crystal size/mm^3	0.06 × 0.02 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.26 to 159.844
Index ranges	$-30 \leq h \leq 30$, $-11 \leq k \leq 9$, $-16 \leq l \leq 16$
Reflections collected	9848
Independent reflections	3000 [R_{int} = 0.0509, R_{sigma} = 0.0517]
Data/restraints/parameters	3000/0/175
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1208
Final R indexes [all data]	R_1 = 0.0622, wR_2 = 0.1289
Largest diff. peak/hole / e Å^{-3}	0.78/-0.56

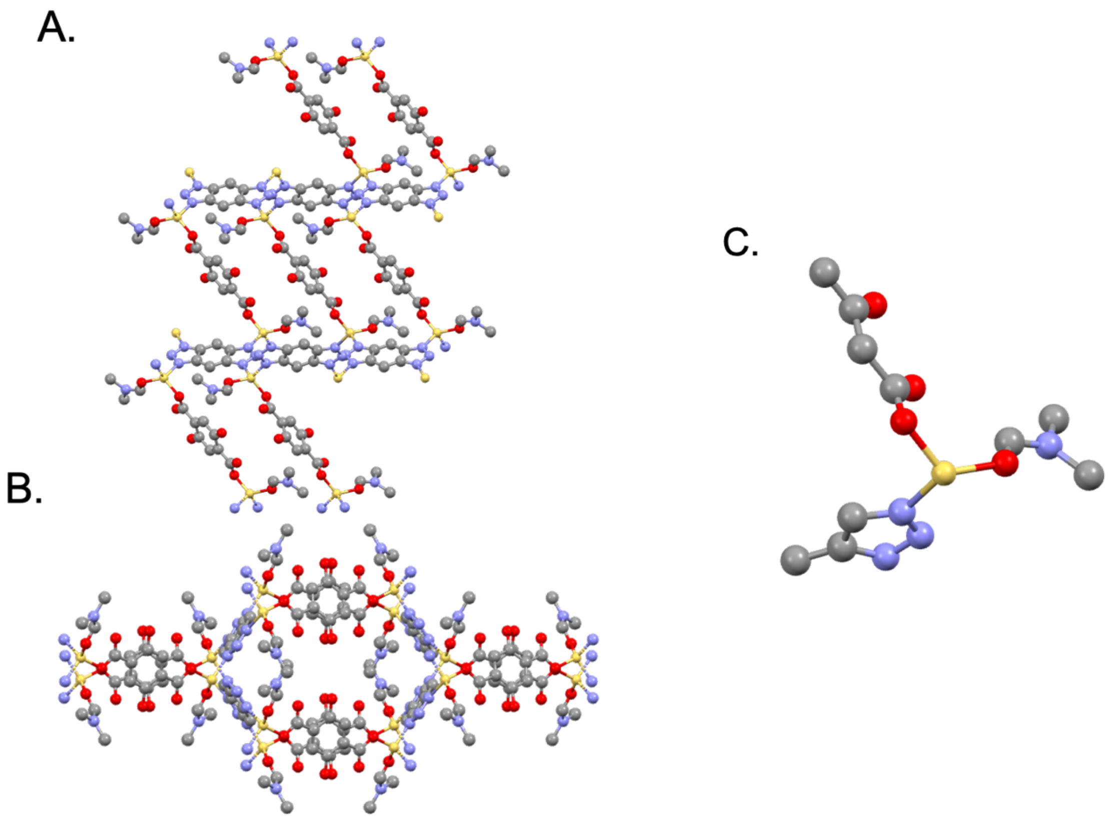

Figure S5. Crystal structure representations as viewed from A) the *b*-axis and B) the *c*-axis and C) the asymmetric unit of NU-251 obtained from single crystal X-ray diffraction. (Hydrogens omitted for clarity)

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