

Supporting Information for

Gram-Scale Synthesis of MIL-125

Nanoparticles and their Solution Processability

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Experimental Methods

Materials. All commercial chemicals were used as received unless stated otherwise. Titanium(IV) methoxide (95%, Sigma-Aldrich), titanium(IV) ethoxide (Strem Chemicals), titanium(IV) butoxide (TCI Chemicals), titanium(IV) isopropoxide (97%, Sigma-Aldrich), titanocene dichloride (TCI Chemicals), 1,4-benzenedicarboxylic acid (terephthalic acid, Sigma-Aldrich), 2-amino-1,4-benzenedicarboxylic acid (2-aminoterephthalic acid, Sigma-Aldrich), methanol (ACS grade, Fisher Scientific), *N,N*-dimethylformamide (DMF, ACS grade, Fisher Scientific), benzoic acid (JT Baker), *p*-toluic acid (MCB), 4-fluorobenzoic acid (Sigma-Aldrich), glacial acetic acid (ACS grade, Fisher Scientific), and tetrabutylammonium hexafluorophosphate (98%, Sigma-Aldrich, recrystallized 3× from ethanol).

Characterization Sample purity was verified by powder X-Ray diffraction (PXRD) with a Bruker D2 Phaser benchtop diffractometer and infrared spectroscopy (IR) using a Bruker Alpha II compact IR with an ATR attachment in a N₂ glovebox. UV-vis-NIR spectra were collected on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer in the range of 190-2200 nm or a Shimadzu Biospec-1601 and all samples were collected with a baseline solvent mixture matching the sample medium. Photoluminescence data was collected on a Horiba Jobin Yvon Fluoromax-4 Fluorimeter with an excitation wavelength of 280 nm. No fluorescence was observed in pure solvent. Gaussian fittings were performed in Igor Pro Version 6.37 using the Multipeak Fitting 2 package. For N₂ sorption experiments, samples were washed twice with DMF, MeOH, acetone, and hexanes as recommended from Howarth et al.¹. Samples were suspended in analysis tubes before being dried on a Schlenk at ambient temperature. Then, samples were degassed under high vacuum at 140 °C on a Micromeritics ASAP 2020, and degassing was considered complete when the outgas rate fell below 2.5 μtorr/min. All solution-state electrochemical data was collected using a Biologic SP200 in a N₂-filled glovebox. For acid digestion ¹H-NMR, samples were washed with methanol (3×, 10 mL) before being dried under vacuum and digested in a 20% DCI/D₂O in DMSO-d₆ mixture in air. Undissolved solids were separated by centrifugation, and the supernatant was analyzed using a Bruker Advance III-HD 600 NMR spectrometer. Scanning electron microscopy (SEM) was performed using a FEI Helios 600i instrument with 5.0 kV energy and 0.69 nA current. SEM samples were prepared by drop-casting MIL-125 suspensions onto clean silicon substrates and drying under N₂ flow. Particle sizing was performed in ImageJ using the line tool to determine crystal diameter, and histograms created in Igor Pro 6.37. The polydispersity index (PDI) was calculated by dividing the standard deviation of the Gaussian fit by the mean particle size.

Modulated Synthesis of MIL-125 NPs A two-neck round-bottom flask fitted with a reflux condenser was charged with H₂BDC (0.352 g, 2.12 mmol) and dry DMF (5 mL). The reaction was then allowed to stir at 110 °C for 30 min, ensuring that cool water was flowing through the condenser for the entire duration of the synthesis. After complete dissolution of the linker, methanol (1.5 mL) and modulator were added, and the solution continued to stir under reflux for an additional 30 min. Next, the Ti(IV) source (1.23 mmol) was added by syringe and the reaction was vigorously stirred at 110 °C under reflux. Once a precipitate was observed, aliquots (< 500 μL) were taken from the reaction mixture and centrifuged at 13200 rpm for 3 min, then washed sequentially with 3 mL of cold DMF and MeOH before crystallinity was confirmed by PXRD. Once the reaction was deemed complete by PXRD, an excess (~20 mL) of cold DMF was added to the reaction mixture to halt the reaction. The final nanoparticles were collected by centrifugation and subsequently washed with 15 mL of cold DMF twice and then MeOH twice, and finally suspended and sonicated in fresh MeOH. For the scaled reaction, all reactants are simply increased by 3- or 10-fold.

Controlled Addition of Water to MIL-125 NP Syntheses. All manipulations were performed under an N₂-atmosphere with Schlenk techniques. Otherwise, the procedure was analogous to the modulated synthesis of MIL-125 NPs described above. All glassware was heated and dried at 120 °C and cycled 3× between vacuum and N₂ before use. MilliQ H₂O was added to DMF before modulator addition in concentrations 0.1, 0.25, 0.50, 1.0, or 2.0% v/v to DMF.

Synthesis of 38 nm NH₂-MIL-125 NPs In a manner analogous to the synthesis of MIL-125 NPs, dry DMF (5 mL) was combined in a small glass vial with H₂O (5 μL). H₂BDC-NH₂ (0.364 g, 2.12 mmol) along with the dry, de-aerated DMF was added into a multi-neck round-bottom flask fitted with a reflux condenser. The reaction stirred at 110 °C in an oil bath under N₂ for 30 minutes, until the linker dissolved, ensuring that cool water was flowing through the condenser over the course of the reaction. Next, benzoic acid (1.18 g, 9.7 mmol) was added to the flask followed by methanol (1.5 mL) and stirred for 30 minutes. The Ti(IV) source (1.23 mmol) was added, and the reaction was left to stir. Aliquots (500 μL) were taken periodically and centrifuged at 13200 rpm for 3 minutes. After, they were washed with DMF and MeOH and PXRD was taken to confirm crystallinity. Once crystallinity was confirmed, the rest of the reaction mixture was collected, and the same washing procedure was performed before drying the particles on a Schlenk line under vacuum and storing them in a scintillation vial until use.

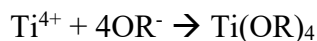
Synthesis of 105 nm NH₂-MIL-125 NPs In a modified procedure from Romero-Angel et al.,² a multi-neck RBF was fitted with a condenser and heated to 110 °C with an oil bath under N₂, taking care to make sure that the condenser had cool water flowing through it for the entire duration of the reaction. The flask was charged with H₂BDC-NH₂ (0.3802 g, 2.12 mmol) and DMF (5 mL) and left to stir for 30 minutes. Dodecanoic acid (2.12g, 10.6 mmol) was then added followed by methanol (1.5 mL) and left to stir for 30 minutes. The Ti(IV) source (1.23 mmol) was then added with a syringe through a septum while stirring. Aliquots (500 μL) were taken periodically to check for crystallinity by PXRD. Aliquots were centrifuged for 3 minutes at 13200 rpm and washed with DMF and MeOH. After the product was confirmed to be crystalline by PXRD, the reaction mixture was collected and washed by the same procedure used for the aliquots. The particles were then dried on a Schlenk line under vacuum and stored in a scintillation vial until use.

UV-Vis-NIR Photodoping of MIL-125 NPs. Concentrations of MIL-125 nanoparticle dispersions in methanol were determined by sonicating a “stock” solution and drying a 1 mL aliquot to determine the mass of an ensemble of activated nanoparticles. The concentrations of the “stock” solutions were thereby determined to be ~20-30 mg/mL. A concentration of 0.025 mg/mL was deemed sufficient for achieving optical densities below 1.0 by UV-vis spectroscopy. Correspondingly, an amount of “stock” MIL-125 solution was washed with methanol (6×, 10 mL) and dried under vacuum at 110 °C to reach the final concentration of 0.025 mg/mL. The activated nanoparticles were redispersed in dry MeOH (10 mL) in an N₂ glovebox and sonicated for 30 min. to avoid particle aggregation. To a clean custom-made air-free quartz cuvette, 3.0 mL of the MIL-125 dispersion was transferred. Finally, the cuvette was irradiated for intermittent time intervals to record optical absorption spectra until no further changes are noted in the UV-vis traces. For observation of Ti(III) *d-d* transitions, the procedure was identical, except that the concentration of MIL-125 NPs was increased to 0.10 mg/mL.

Open Circuit Voltage Measurements. Prior to electrochemical experiments, DMF was freeze-pump-thawed 6× and brought into an N₂ glovebox. The MIL-125 NPs were suspended in a 3-mL

0.1-M TBAPF₆/DMF solution with 0.5 mL methanol and transferred to a quartz cuvette fitted with a standard three-electrode cell with a platinum working electrode, a silver wire pseudo-reference electrode, and a platinum wire counter electrode. All electrodes were cleaned with dilute HNO₃ before use. At the end of all electrochemistry experiments, 10 mg of ferrocene was added to the solution to provide a quantitative measurement of E_{1/2} versus Ag. For in situ photodoping while measuring OCV, the silver wire was shielded from the 308 nm LED to avoid photochemical degradation.

Computational Methods. An experimentally obtained crystal structure for MIL-125 was geometrically optimized using GGA@PBEsol³ as implemented by the Vienna *ab initio* Simulation Package (VASP)^{4,6}. Optimizations used a projector-augmented plane wave basis set with an energy cutoff of 500 eV, and electronic and ionic convergence criteria were set to 10⁻⁶ eV and 0.005 eV, respectively. All structures were optimized using a Γ -centered $2 \times 2 \times 2$ *k*-grid. The relaxed geometry of pristine MIL-125 has a puckered titanium octamer, giving it D_{2d} symmetry. To simulate electronic excitation, an electron was added to the pristine structure and the system was allowed to optimize under the same criteria as above. Photo-doping was simulated by adding a hydrogen to one of the μ^2 -oxo bridges and allowing the structure to relax. DFT calculations for the different Ti(OR)₄ precursors were geometrically optimized using the B3LYP functional and the 6-31G(d,p) basis sets as implemented in Gaussian09. The total energies of the Ti⁴⁺, OR⁻ and Ti(OR)₄ species were calculated individually and included the zero-point vibrational energy. Metal-ligand dissociation energies were computed by subtracting the individual Ti⁴⁺ and OR⁻ energies from the Ti(OR)₄ product according to the following balanced chemical reaction:



Summary of Particle Sizes and Sizing Methods

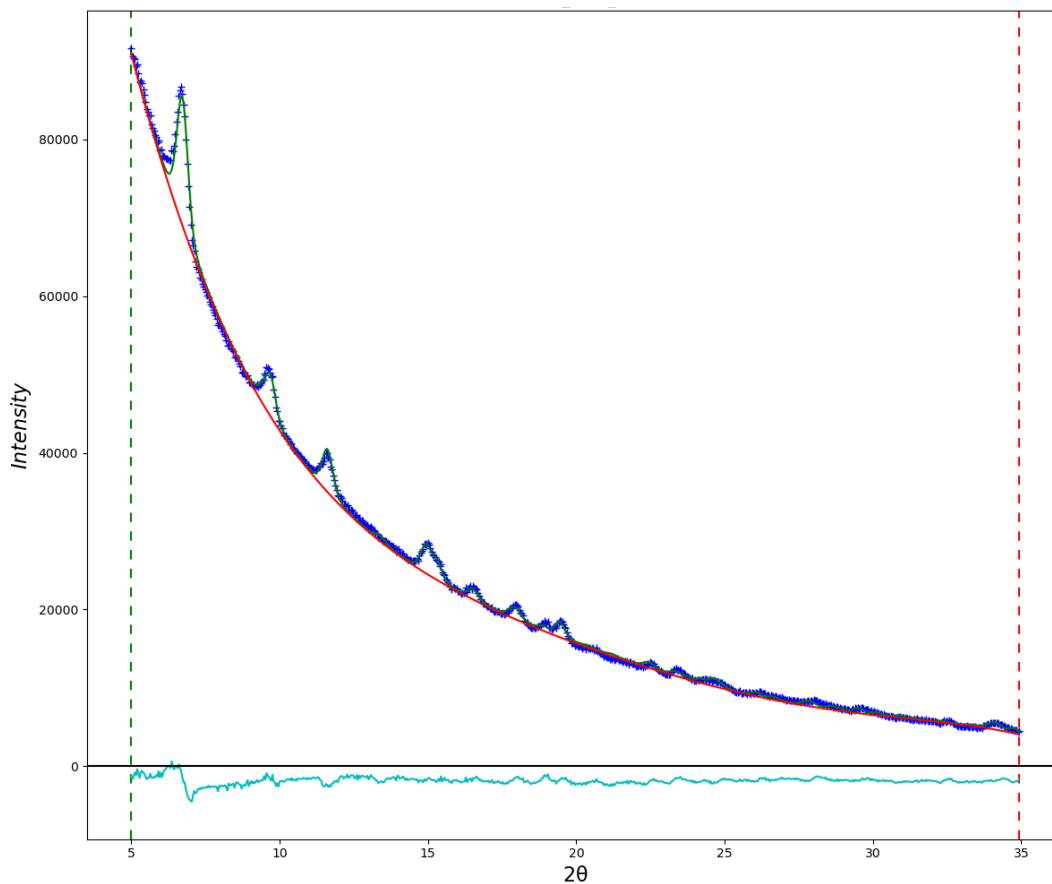


Figure S1: Rietveld refinement results of MIL-125 nanoparticles. Results suggest phase purity of the nanocrystals

Table S1: Comparison of crystal sizes by varying benzoic acid modulator equivalents (Mod:BDC) from PXRD and SEM.

Mod:BDC	Scherrer Size (nm)	SEM Size (nm)
0	91.06	424
2.5	55.05	217
3	50.38	92.7
5	41.30	78.9
7	84.55	289
10	92.81	383

Table S2: Comparison of crystal sizes by varying Ti(IV) source anion identity from PXRD and SEM.

Ti(IV) source	Anion pKa	Scherrer Size (nm)	SEM Size (nm)
Ti(OMe) ₄	15.50	43.49	42.7
Ti(OEt) ₄	16.0	34.51	54.9
Ti(OBu) ₄	16.95	41.30	78.9
Ti(O ⁱ Pr) ₄	17.1	47.24	80.4
TiCp ₂ Cl ₂	-	42.96	59.5

Table S3: Dissociation energies calculated for various Ti(IV) precursors. Calculations were done using the method outlined in the *Computational Methods* section.

Ti (IV) source	Dissociation Energy (Ha)
Ti(OMe) ₄	4.02
Ti(OEt) ₄	3.99
Ti(OBu) ₄	3.98
Ti(O ⁱ Pr) ₄	3.98

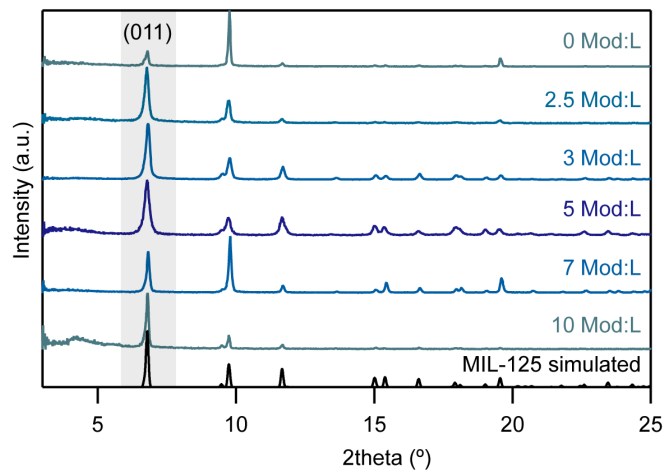


Figure S2: PXR D pattern for all MIL-125 NCs synthesized with benzoic acid equivalents. The first reflection (011) is highlighted to emphasize peak widening.

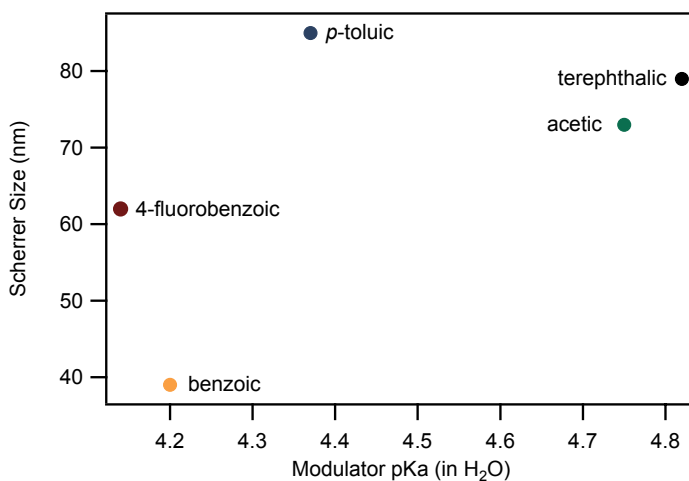


Figure S3: Nanocrystal sizes of MIL-125 versus modulator pKa using 5 equivalents of modulator.

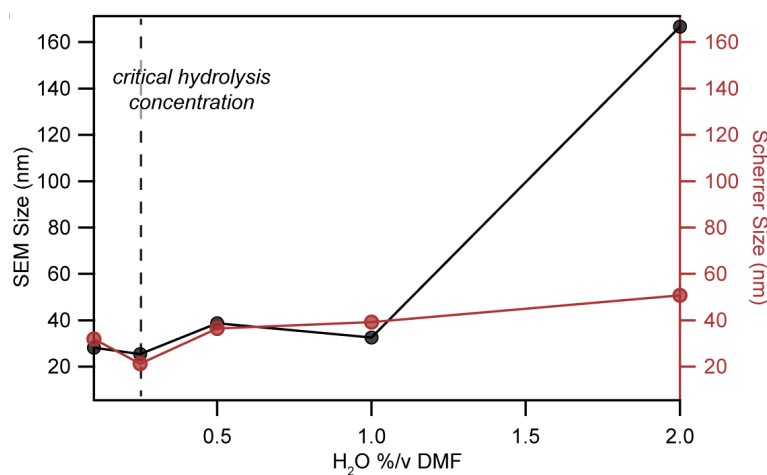


Figure S4: Nanocrystal sizes of MIL-125 versus water content relative to DMF volume in the reaction solution.

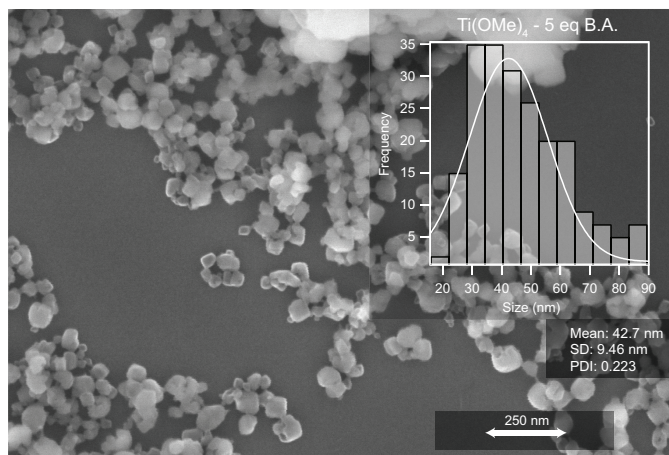


Figure S5: SEM image and sizing histogram for MIL-125 NCs synthesized with 5 eq of benzoic acid to linker and using Ti(OMe)₄ as a Ti⁴⁺ source.

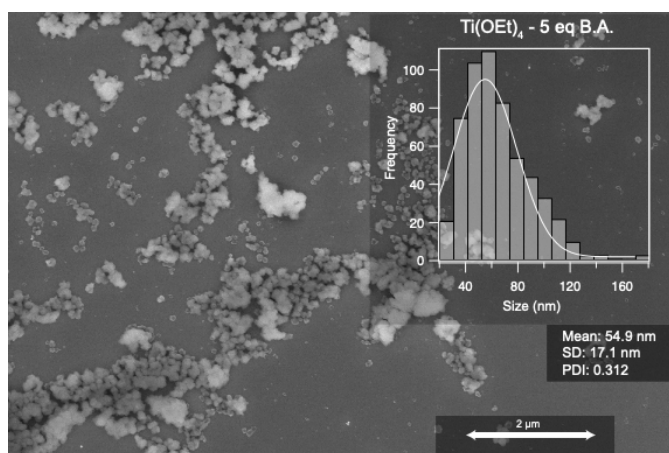


Figure S6: SEM image and sizing histogram of MIL-125 NCs synthesized with 5 eq of benzoic acid equivalents for each linker and using Ti(OEt)₄ as a Ti⁴⁺ source.

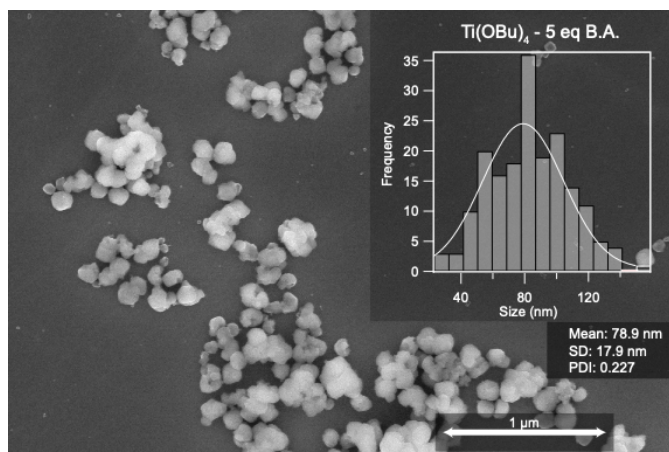


Figure S7: SEM image and sizing histogram for MIL-125 NCs synthesized with 5 eq of benzoic acid equivalents for each linker and using Ti(OBu)₄ as a Ti⁴⁺ source.

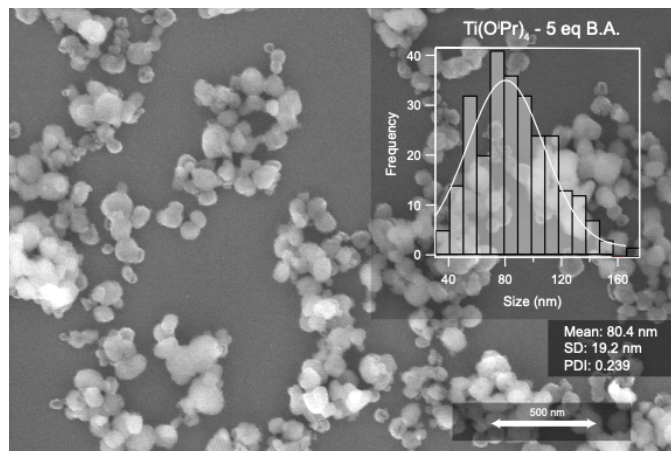


Figure S8: SEM image and sizing histogram for MIL-125 NCs synthesized with 5 eq of benzoic acid equivalents for each linker and using Ti(OiPr)₄ as a Ti⁴⁺ source.

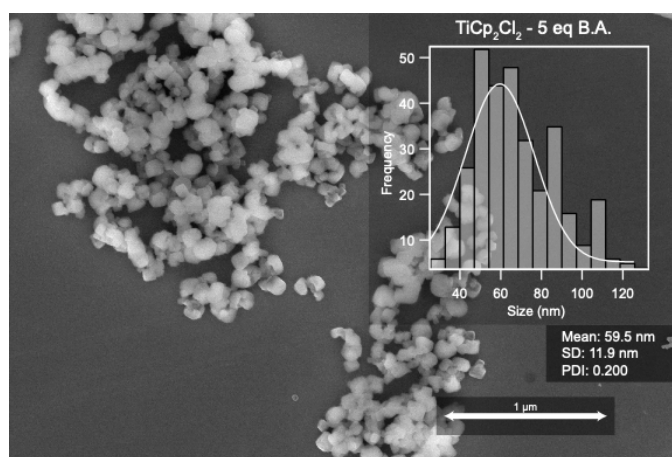


Figure S9: SEM image and sizing histogram for MIL-125 NCs synthesized with 5 eq of benzoic acid equivalents for each linker and using TiCp₂Cl₂ as a Ti⁴⁺ source.

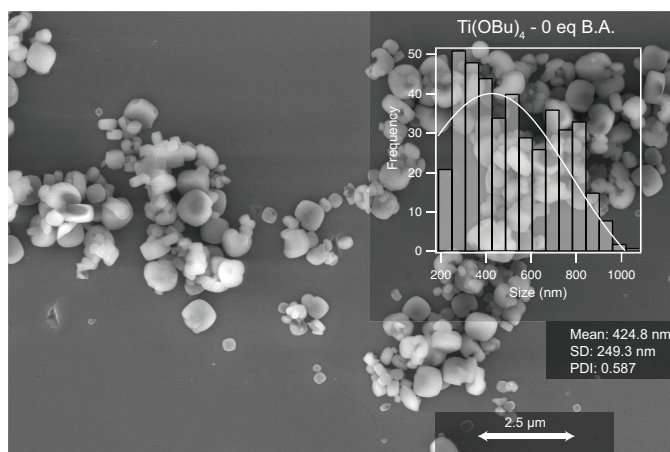


Figure S10: SEM image and sizing histogram for MIL-125 NCs synthesized with 0 eq of benzoic acid for each linker and using Ti(OBu)₄ a Ti⁴⁺ source.

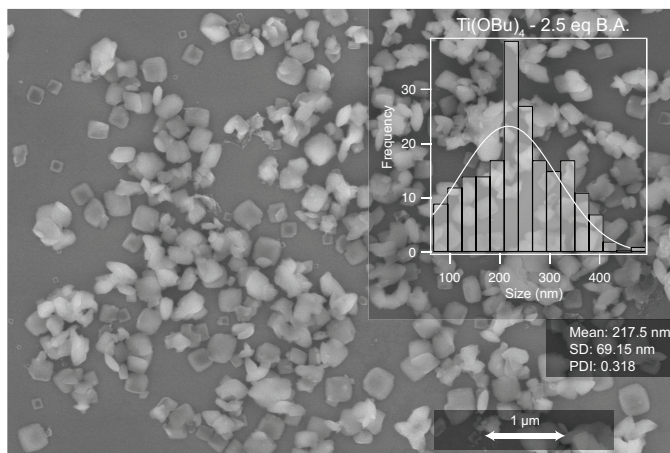


Figure S11: SEM image and sizing histogram for MIL-125 NCs synthesized with 2.5 eq of benzoic acid for each linker and using Ti(OBu)₄ a Ti⁴⁺ source.

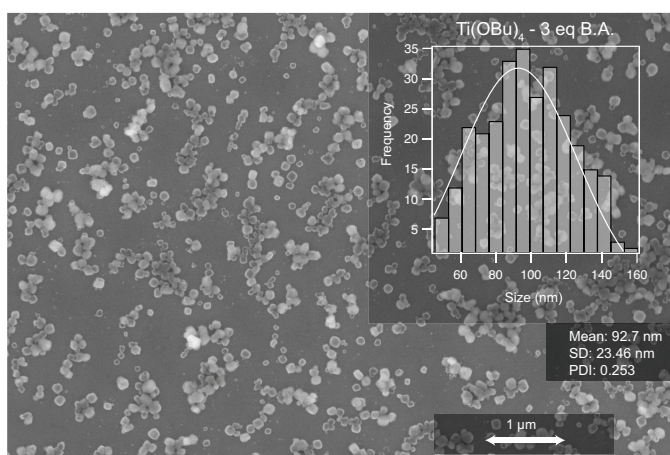


Figure S12: SEM image and sizing histogram for MIL-125 NCs synthesized with 3 eq of benzoic acid for each linker and using Ti(OBu)₄ a Ti⁴⁺ source.

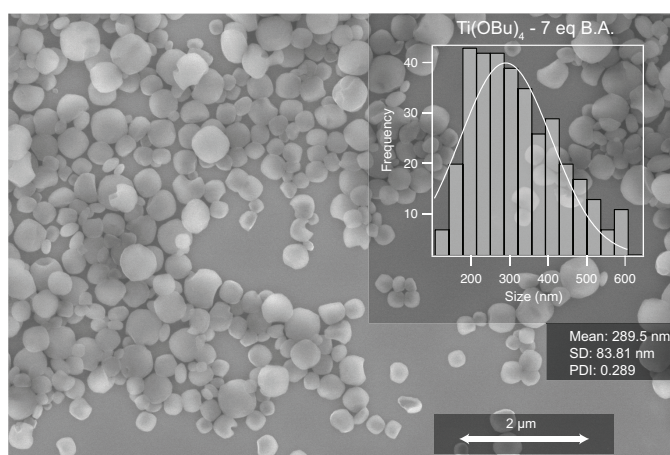


Figure S13: SEM image and sizing histogram for MIL-125 NCs synthesized with 7 eq of benzoic acid for each linker and using Ti(OBu)₄ a Ti⁴⁺ source.

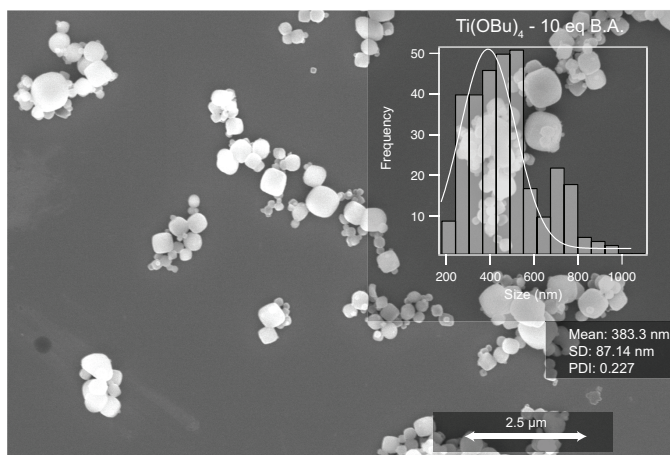


Figure S14: SEM image and sizing histogram for MIL-125 NCs synthesized with 10 eq of benzoic acid for each linker and using Ti(OBu)₄ a Ti⁴⁺ source.

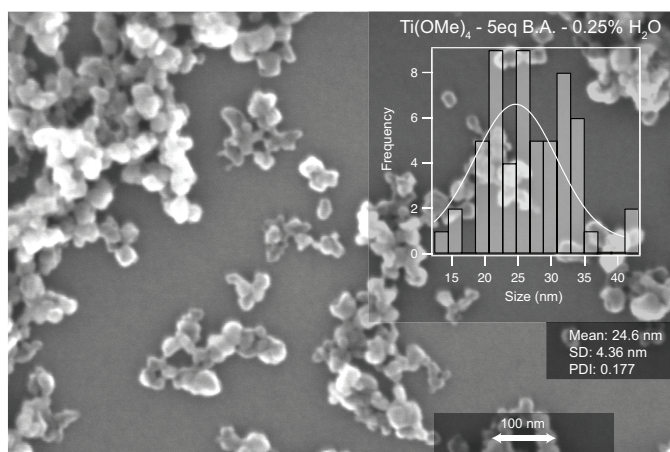


Figure S15: SEM image and sizing histogram for MIL-125 NCs synthesized with 5eq of benzoic acid for each linker, using Ti(OBu)₄ a Ti⁴⁺ source, and 0.25% H₂O relative to DMF in the reaction.

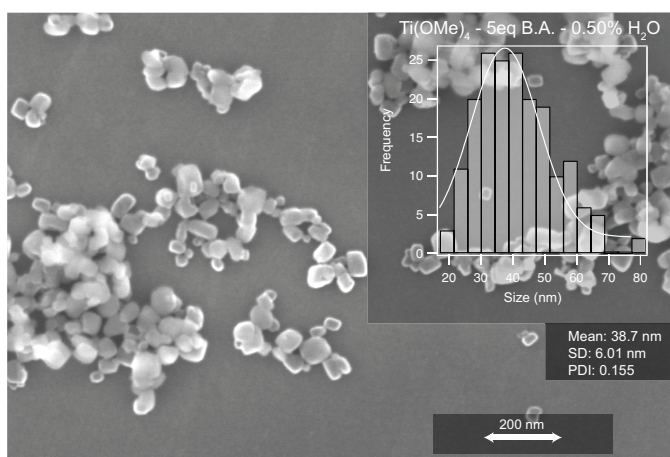


Figure S16: SEM image and sizing histogram for MIL-125 NCs synthesized with 5eq of benzoic acid for each linker, using Ti(OBu)₄ a Ti⁴⁺ source, and 0.50% H₂O relative to DMF in the reaction.

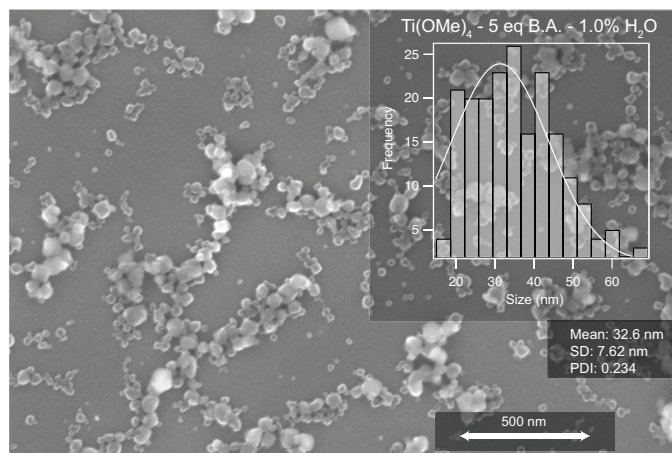


Figure S17: SEM image and sizing histogram for MIL-125 NCs synthesized with 5eq of benzoic acid for each linker, using Ti(OBu)₄ a Ti⁴⁺ source, and 1.0% H₂O relative to DMF in the reaction.

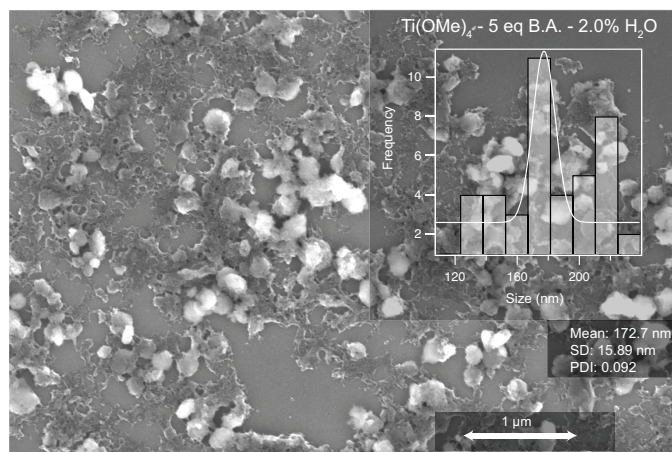


Figure S18: SEM image and sizing histogram for MIL-125 NCs synthesized with 5eq of benzoic acid for each linker, using Ti(OBu)₄ a Ti⁴⁺ source, and 2.0% H₂O relative to DMF in the reaction.

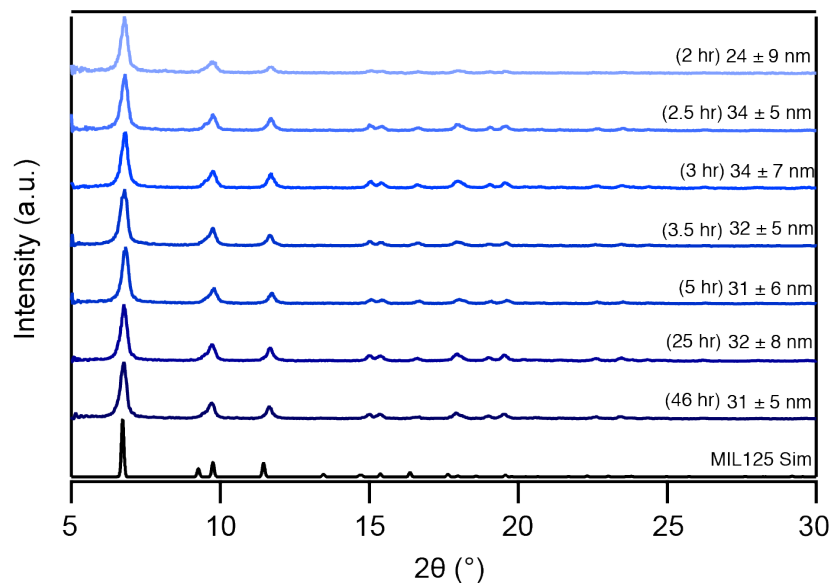


Figure S19: PXRD patterns of nano-MIL-125 at different times over the course of 46 hours at 110°C. Notably, the size of the particles, by Scherrer analysis, is not changed after 46 hours of reflux.

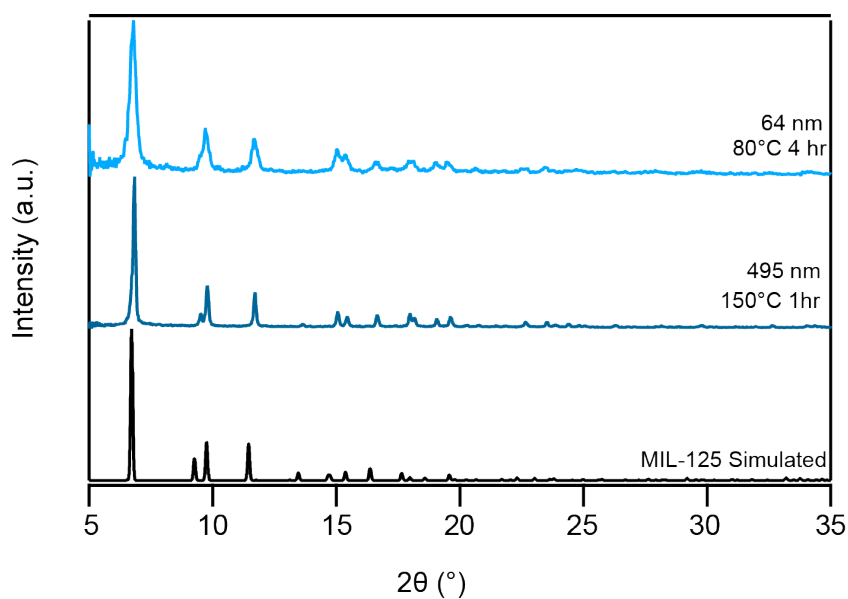


Figure S20: PXRD patterns of MIL-125 synthesized at different temperatures. The 150°C synthesis produced large crystalline particles in 1hr. The 80°C synthesis produced smaller crystalline particles in 4hrs.

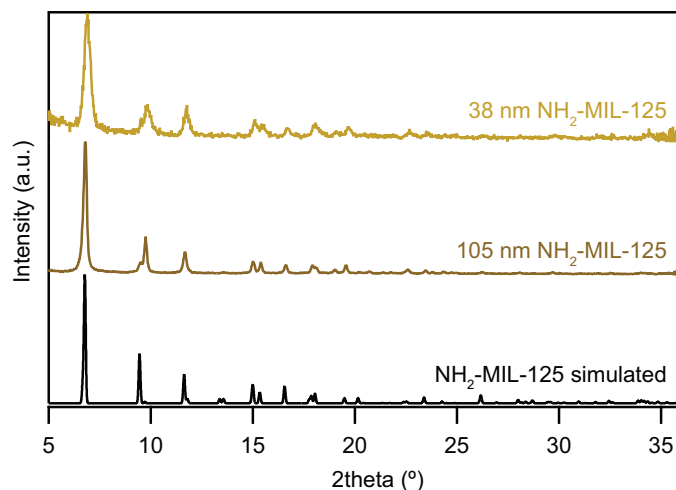


Figure S21: PXRD patterns for all modulated NH₂-MIL-125 NCs synthesized using the reflux method with benzoic acid (38 nm) and dodecanoic acid (105 nm).

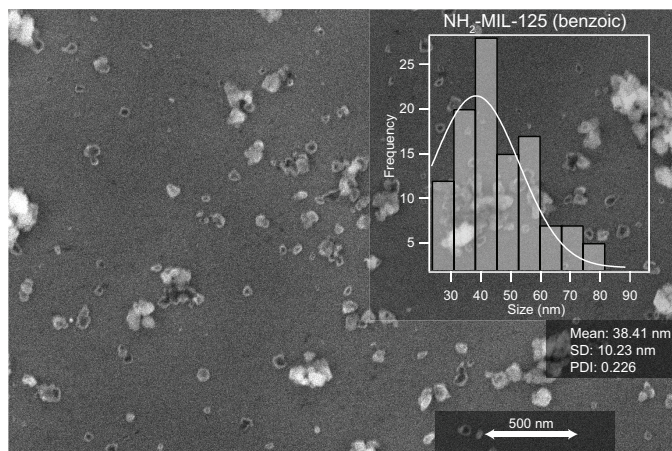


Figure S22: SEM image and sizing histogram for NH₂-MIL-125 NCs synthesized with benzoic acid.

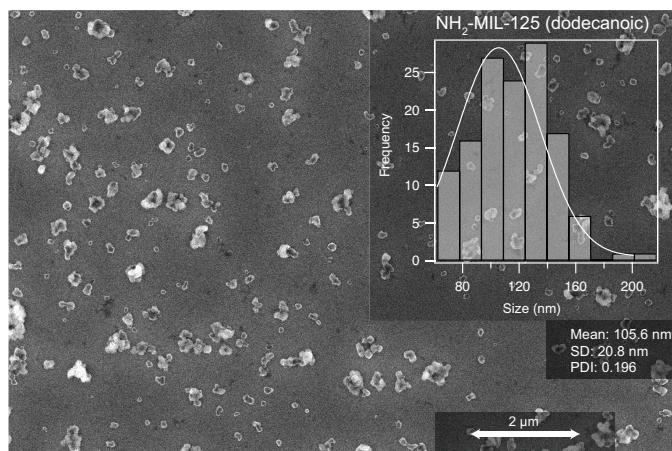


Figure S23: SEM image and sizing histogram for NH₂-MIL-125 NCs synthesized with dodecanoic acid.

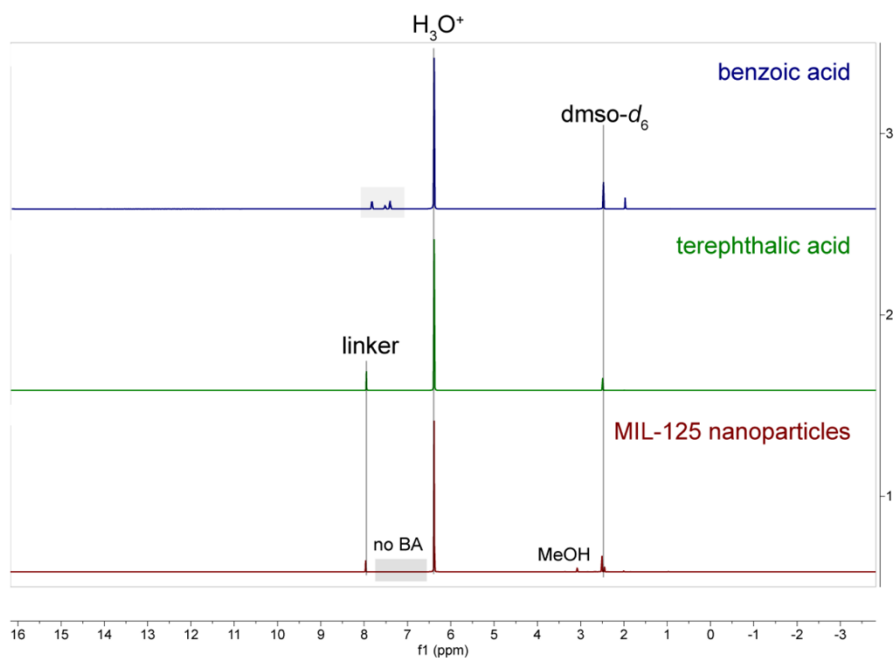


Figure S24: Acid digestion ^1H -NMR of MIL-125 nanocrystals, linker, and modulator. No benzoic acid shifts were detected in the digested nanocrystals.

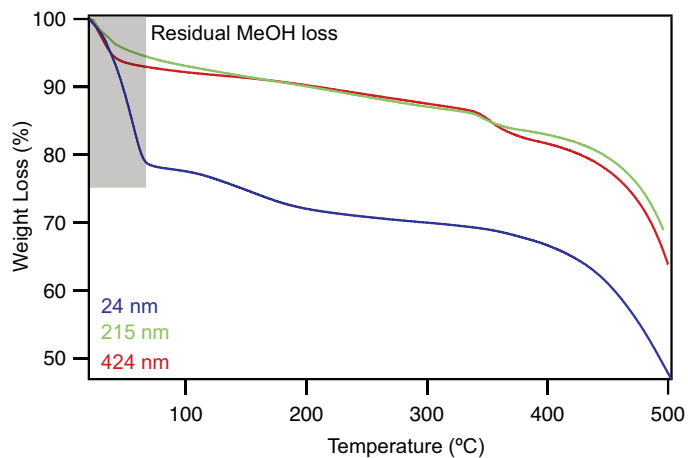


Figure S25: Thermogravimetric analysis for three sizes of MIL-125 NCs. Residual MeOH is highlighted in the first weight loss below 100 °C.

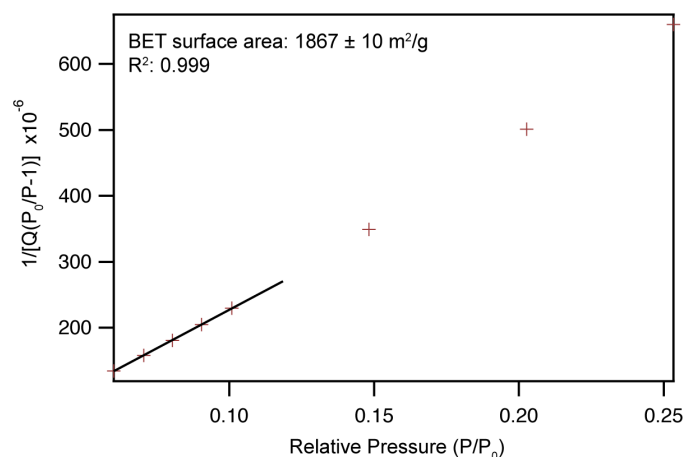
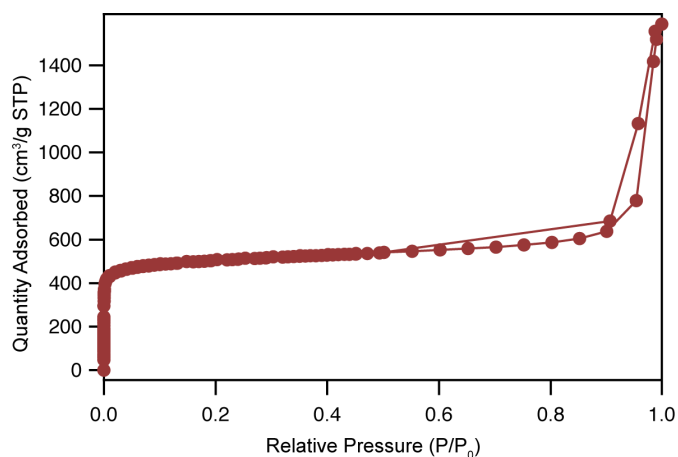


Figure S26: Gas adsorption/desorption isotherms and BET analysis for 34-nm MIL-125 NCs.

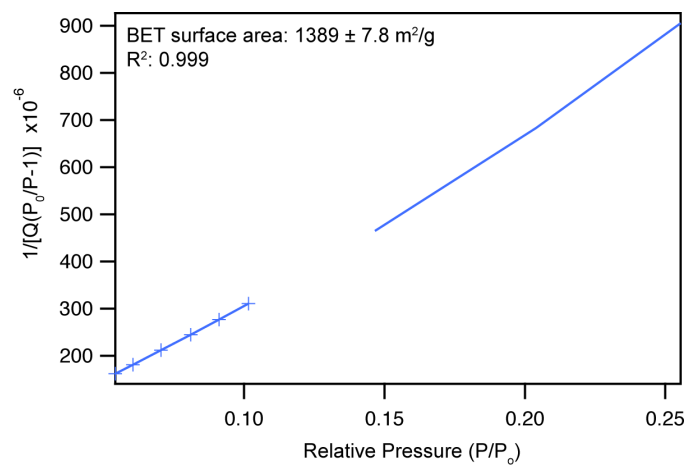
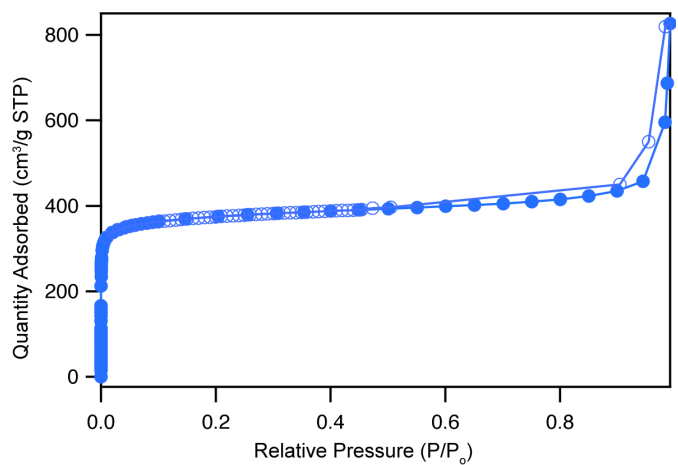


Figure S27: Gas adsorption/desorption isotherms and BET analysis for 80-nm MIL-125 NCs.

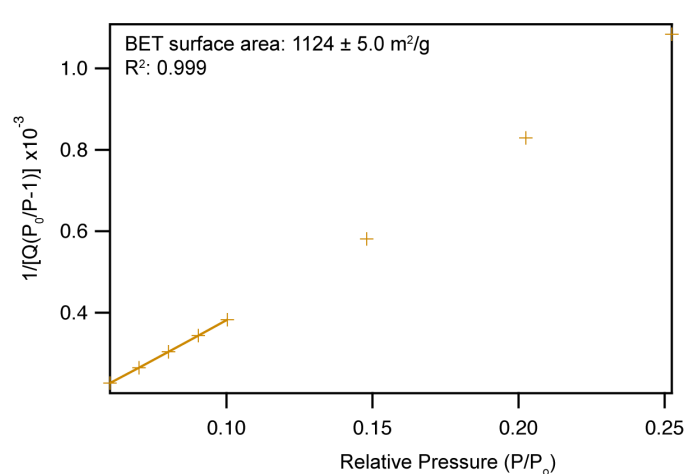
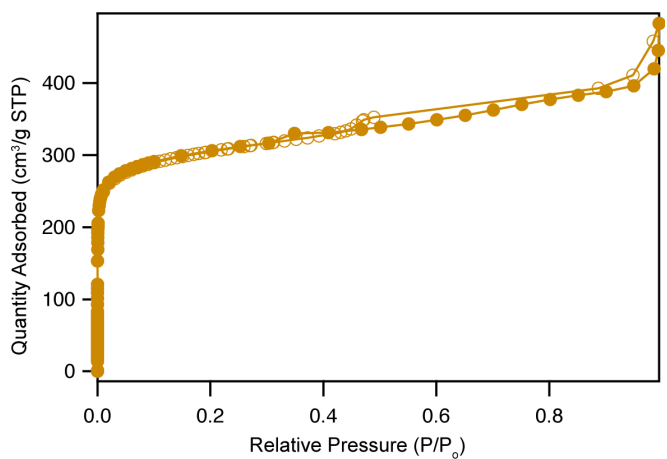


Figure S28: Gas adsorption/desorption isotherms and BET analysis for 217-nm MIL-125 NCs.

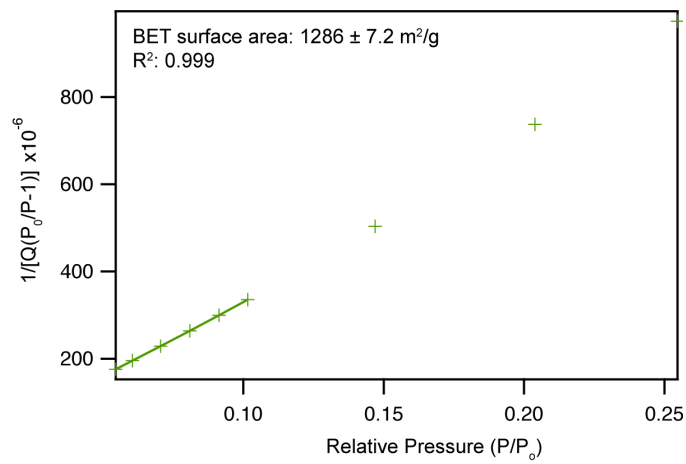
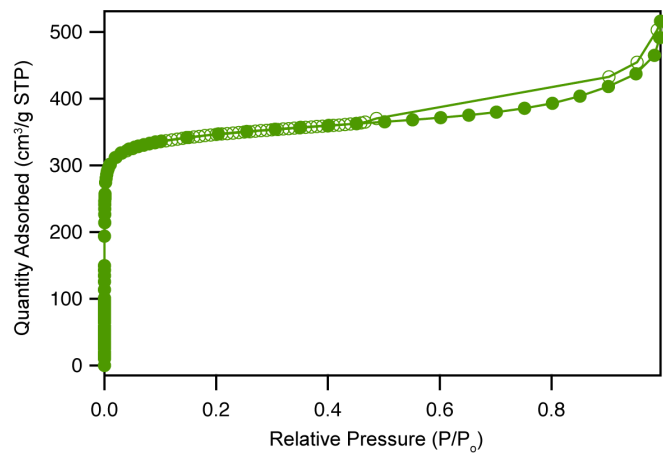


Figure S29: Gas adsorption/desorption isotherms and BET analysis for 424-nm MIL-125 NCs.

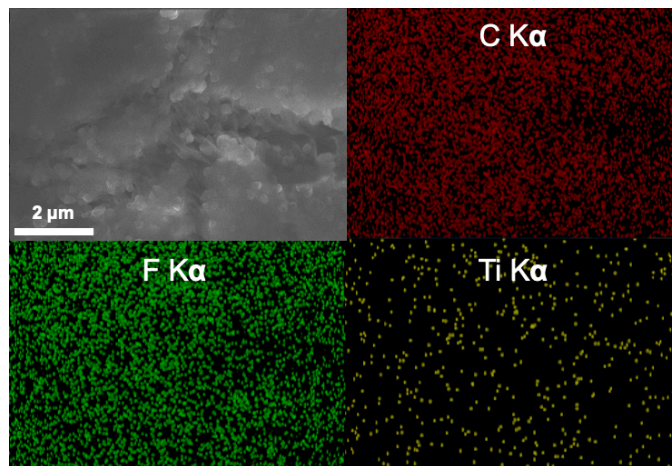


Figure S30: SEM-EDX imaging of carbon, fluorine, and titanium in a 25 wt% MIL-125 MMM.

Table S4: SEM-EDX data results from measuring carbon, fluorine, and titanium in a 25 wt% MIL-125 MMM.

Element	Apparent Concentration	wt %
C	1.51	56.58
F	3.29	34.50
Ti	0.26	8.92
Total		100.0

$$8.92(\text{Ti}) / 3.450 (\text{F}) = 25.85 \text{ wt\% MIL-125 in PVDF MMM}$$

Table S5: Dynamic light scattering (DLS) results of 25, 75, and 424 nm MIL-125 methanolic colloids.

SEM Size (nm)	Hydrodynamic Diameter (nm)	Std. Dev.	PDI	Std. Dev	Zeta Potential (mv)	Std. Dev.
25	84.64	0.5919	0.119	0.003	-25.6	0.597
75	150.9	0.5132	0.087	0.006	-31.6	1.36
424	515.5	2.281	0.135	0.005	-34.0	0.78

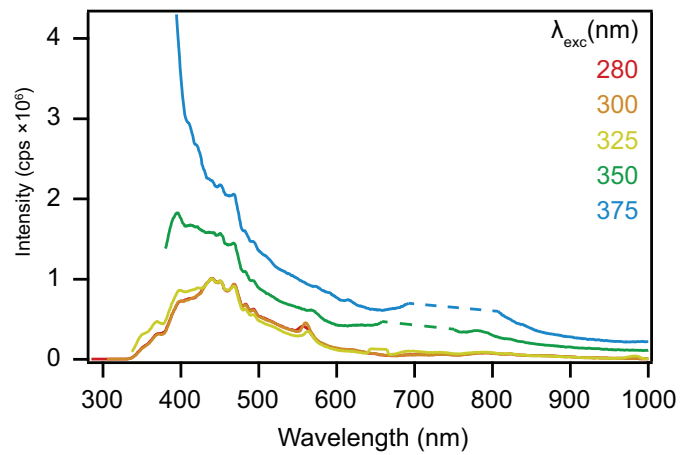


Figure S31: Solution fluorescence spectroscopy of a 0.025 mg/mL methanolic colloid of MIL-125 excited at varying wavelengths.

References

- (1) Howarth, A. J.; Peters, A. W.; Vermeulen, N. A.; Wang, T. C.; Hupp, J. T.; Farha, O. K. Best Practices for the Synthesis, Activation, and Characterization of Metal–Organic Frameworks. *Chem. Mater.* **2017**, *29* (1), 26–39. <https://doi.org/10.1021/acs.chemmater.6b02626>.
- (2) Romero-Angel, M.; Castells-Gil, J.; Rubio-Giménez, V.; Ameloot, R.; Tatay, S.; Martí-Gastaldo, C. Surfactant-Assisted Synthesis of Titanium NanoMOFs for Thin Film Fabrication. *Chem. Commun.* **2021**. <https://doi.org/10.1039/D1CC02828F>.
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