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Supporting Information

Metal-Organic Framework (MOF) Morphology Control by Design

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Supporting Information

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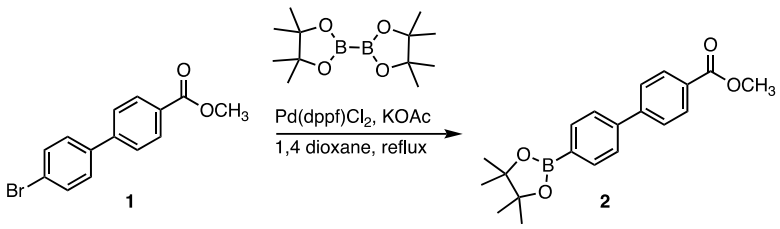
SI 1. Materials:

Terephthalic acid (H_2BDC, 98.0%), 2-aminoterephthalic acid ($H_2BDC\text{-}NH_2$, 99.0%), biphenyl-3-carboxylic acid (97.0%), and isophthalic acid (>99%) were purchased from Sigma Aldrich. 3-tert-Butylbenzoic acid (>98.0%) was purchased from Oakwood Products. 2,6-Naphthalenedicarboxylic acid (H_2NDC, >98.0%) was purchased from TCI. 4-Carboxycinnamic acid (H_2CCA, >95%), [1,1'-biphenyl]-3,4'-dicarboxylic acid (**A1**, 98.0%) and [1,1':3',1''-Terphenyl]-4,4''-dicarboxylic acid (**A2**, 98.0%), were purchased from Ambeed. 1,3,5-Tris(4-carboxyphenyl)benzene (H_3BTB (**A5**), 97%) was purchased from Alfa Aesar. Fumaric acid (H_2FMA, purified), N,N-dimethylformamide (DMF, ACS grade), methylene chloride (DCM, HPLC grade, 99.9%), and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, ACS grade) were purchased from Fisher Scientific. N,N-diethylformamide (DEF, 99.0%) was purchased from Acros Organics and purified by storage on activated charcoal for ~10 days followed by removal of impurities via silica gel column. 5'-Bromo-[1,1':3',1''-terphenyl]-4,4'-dicarboxylic acid (**A3**), [1,1':3',1''-terphenyl]-4,4',5'-tricarboxylic acid (**A4**), and [1,1':3',1'':4'',1'''-quaterphenyl]-4,4''',5'-tricarboxylic acid (**A7**) were synthesized according to the literature procedure.[1] 5'-Bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylic acid (**A6**) was synthesized through the procedure described below.

SI 2. Synthesis of the A6 additive

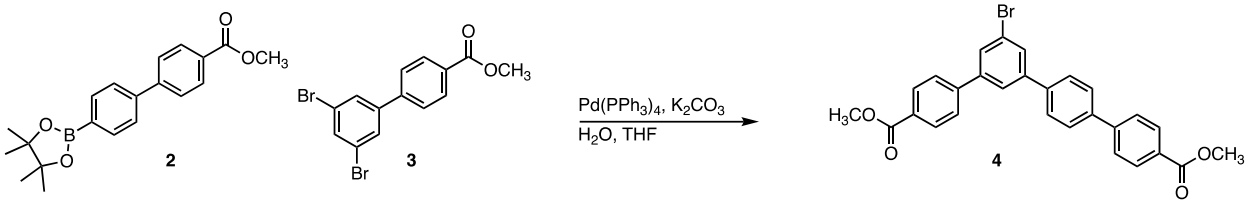
Step-I:



Scheme S1: Synthesis of methyl 4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-carboxylate (**2**)

Procedure: The compound **1** was purchased from Combi-Blocks and used without further purification. Compound **2** was synthesized according to the literature procedure.[1]

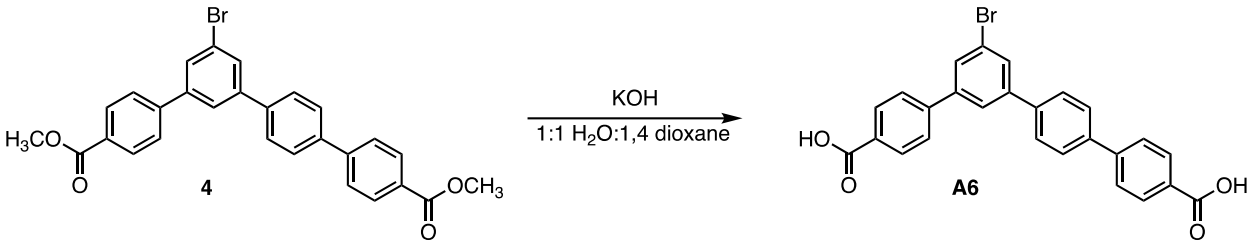
Step-II



Scheme S2: Synthesis of dimethyl 5'-bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylate (**4**)

Procedure: Synthesis of **4** was adapted from the literature with additional modifications.[1] Methyl 4-pinacolatoboronbiphenyl (**2**) (0.729 g, 2.16 mmol) and methyl 3',5'-dibromo-biphenyl-4-carboxylate (**3**) (0.726 g, 1.96 mmol), K_2CO_3 (0.947 g, 6.85 mmol), THF (25 mL), and H_2O (5 mL) were added in a pressure vessel equipped with a magnetic stir bar. The reaction mixture was sparged with N_2 gas for one hour. Afterwards $Pd(PPh_3)_4$ (0.227 g, 0.196 mmol) was added to the mixture and the vessel was sealed for 48 h at 62 °C. Once the reaction mixture had cooled to room temperature the solvent was removed under reduced pressure. The residue was dissolved in DCM (75 mL) and washed with H_2O (3 × 25 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was subjected column chromatography (80/20 hexanes/ethyl acetate) to obtain a white solid yield (14%, 0.139 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 4H), 7.81 – 7.67 (m, 12H), 3.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.34, 52.40, 123.67, 124.97, 127.12, 127.34, 127.88, 128.00, 129.32, 129.42, 129.77, 129.82, 130.35, 130.41, 139.35, 139.92, 142.73, 143.26, 144.14, 144.89, 166.93, 167.07; HRMS calculated for $C_{28}H_{21}BrO_4$ $[M+H]^+$: 501.0696 found: 501.0684.

Step-III:



Scheme 3: Synthesis of 5'-bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylic acid (**A6**)

Procedure: Synthesis of **A6** was adapted from the literature.[1] Compound **4** (0.122 g, 0.243 mmol), KOH (0.206 g, 3.67 mmol), 1,4 dioxane (5 mL), and H_2O (5 mL) were added into a pressure vessel. The resultant suspension was heated to 100 °C and stirred for 13 h. After the solution was cooled, solvent was removed under reduced pressure. The crude product was dissolved in water and acidified with conc. HCl until the pH was 2. The target compound was collected by filteration to produce a light brown solid yield (84%, 0.970 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, *J* = 8.0 Hz, 5H), 7.94 (d, *J* = 8.9 Hz, 6H), 7.86 (dd, *J* = 8.1, 3.1 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 123.32, 124.59, 126.89, 127.46, 127.66, 127.93, 128.83, 129.04, 129.90, 130.08, 130.15, 130.43, 138.24, 138.88, 142.10, 142.54, 142.70, 143.64, 167.18, 167.25; HRMS calculated for $C_{26}H_{17}BrO_4$ $[M-H]^-$: 471.0237 found: 471.0222.

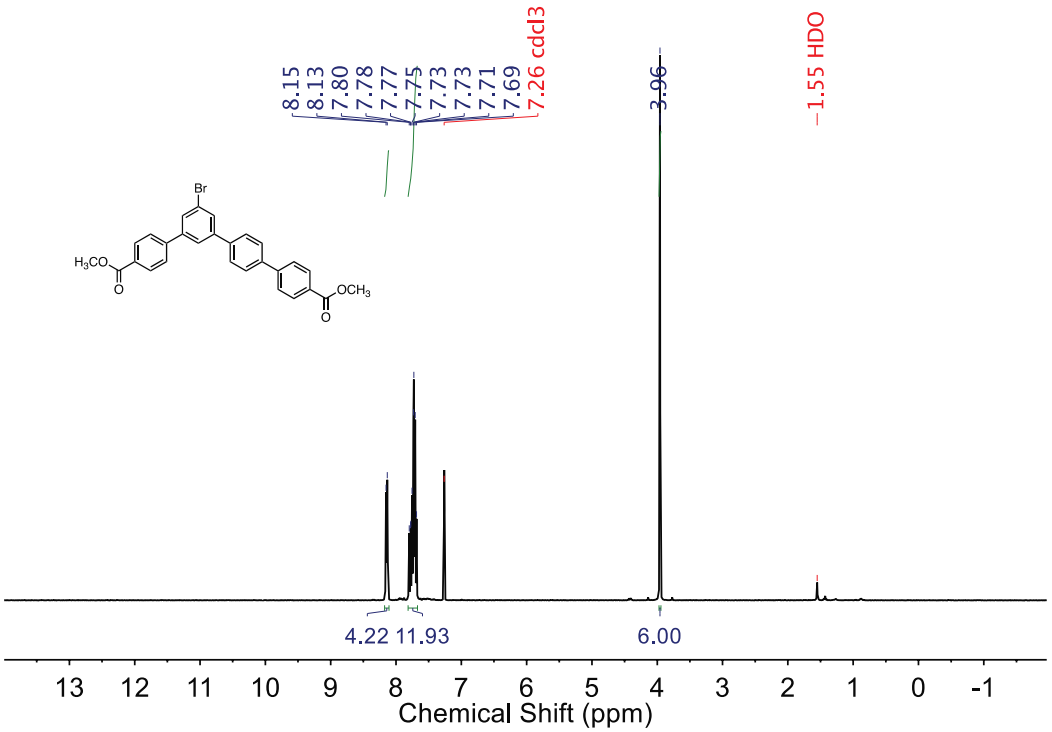


Figure S1: ^{1}H (400 MHz) NMR spectrum of dimethyl 5'-bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylate (**4**) in DMSO-d_6.

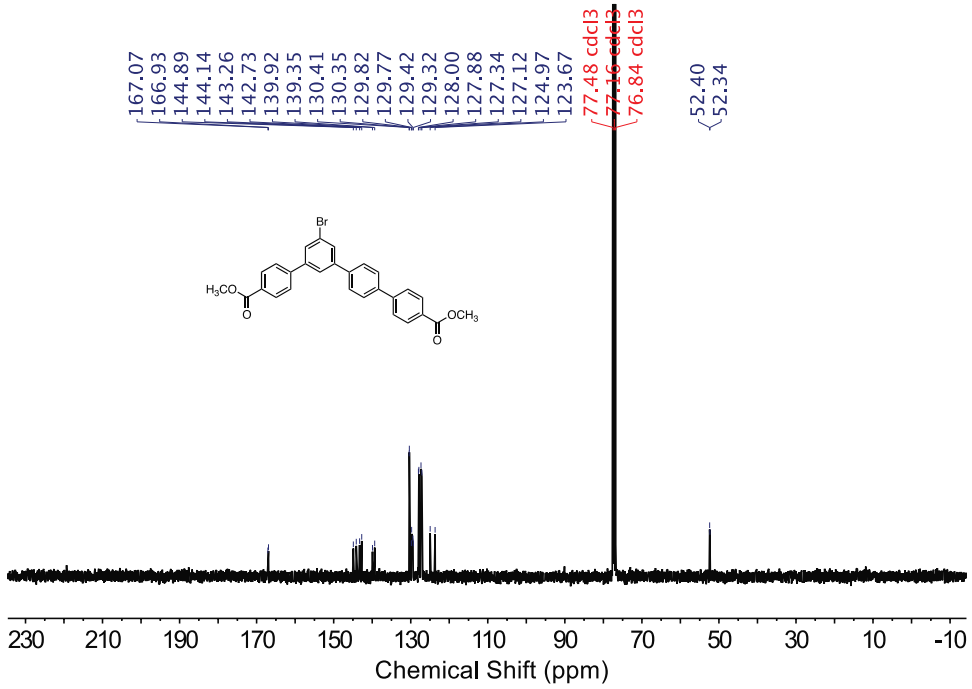


Figure S2: ^{13}C (100 MHz) NMR spectrum of dimethyl 5'-bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylate (**4**) in DMSO-d_6.

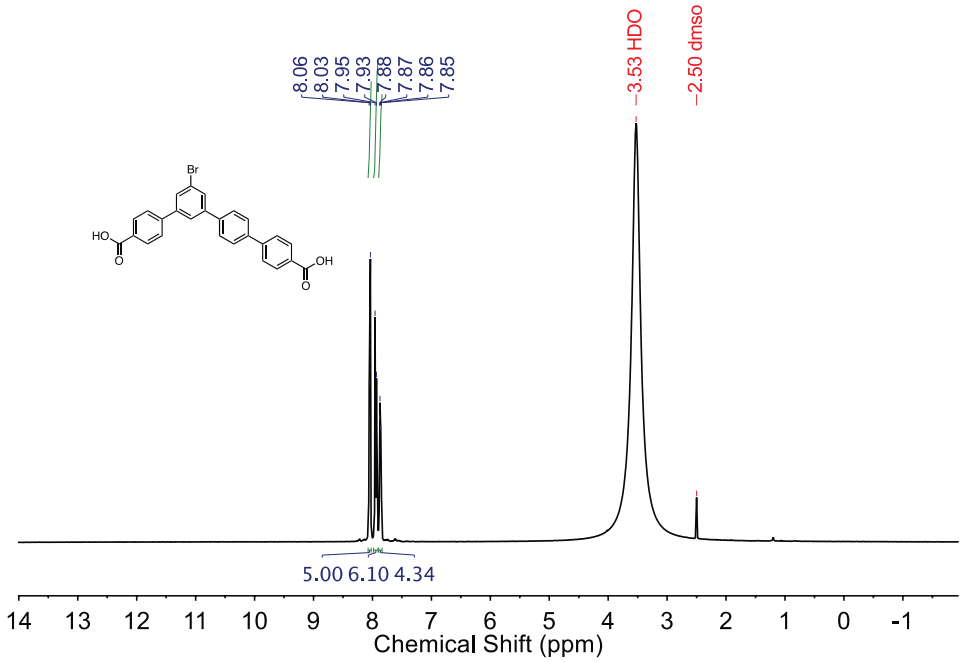


Figure S3: ^{1}H (400 MHz) NMR spectrum of 5'-bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylic acid (**A6**) in DMSO-d_6.

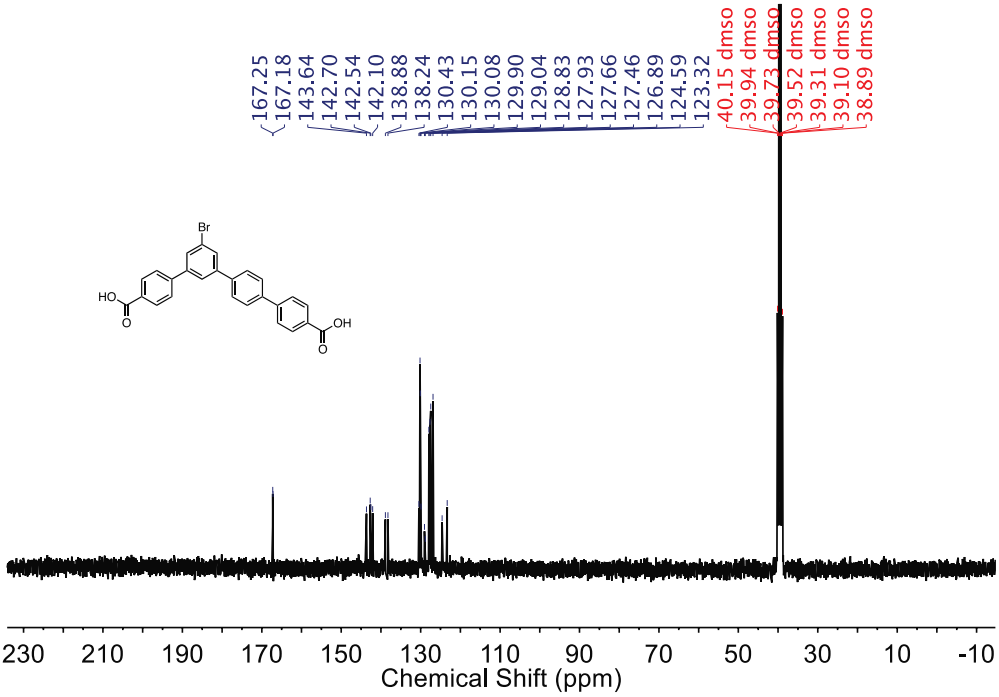
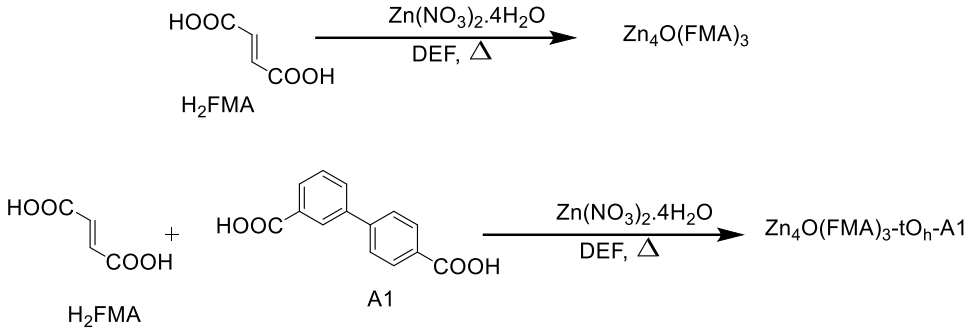


Figure S4: ^{13}C (100 MHz) NMR spectrum of 5'-bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylic acid (**A6**) in DMSO-d_6.

SI 3. MOF new morphologies synthesis and activation procedures

SI 3a. Synthesis, solvent exchange, and activation procedures for $Zn_4O(FMA)_3$ cubic and non-cubic morphology crystals:



Scheme S4. Synthetic process for cubic and non-cubic morphologies of $Zn_4O(FMA)_3$.

$Zn_4O(FMA)_3$: H_2FMA (11.67 mg, 0.100 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (27.94 mg, 0.106 mmol), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The resulting colorless cubic morphology crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (5.03 mg), is ~25% based on H_2FMA.

$Zn_4O(FMA)_3$-tO_h(A1): H_2FMA (25.04 mg, 0.216 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (75.03 mg, 0.287 mmol), **A1** additive (15.01 mg, 0.0619 mmol (22.3 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The resulting colorless truncated octahedral (tO_h) morphology crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (15.43 mg), is ~33% based on H_2FMA.

As synthesized cubic and non-cubic morphology samples of $Zn_4O(FMA)_3$ and $Zn_4O(FMA)_3$-tO_h(A1) were digested in DCl/DMSO-d_6 solution (Figure S6) and analyzed by NMR spectroscopy. In $Zn_4O(FMA)_3$-tO_h(A1) sample, the peaks corresponding to FMA and A1 were observed (Figure S7). Incorporation of A1 does not yield new phase as confirmed through PXRD (see details and Figure 2 in the main manuscript) and so the linker must occupy defect sites.

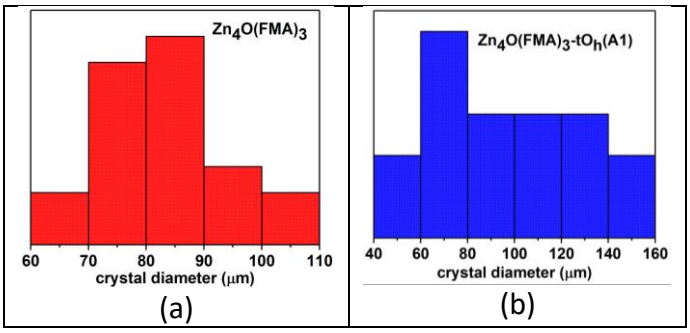


Figure S5: Histogram plot for different morphologies of $Zn_4O(FMA)_3$.

Table S1: Tabulated crystal size distributions range and median values for different morphologies of $Zn_4O(FMA)_3$.

Sample name	Mean (μm)	Median (μm)	Standard deviation (μm)
$Zn_4O(FMA)_3$	82	82	10
$Zn_4O(FMA)_3$-tO_h(A1)	96	94	30

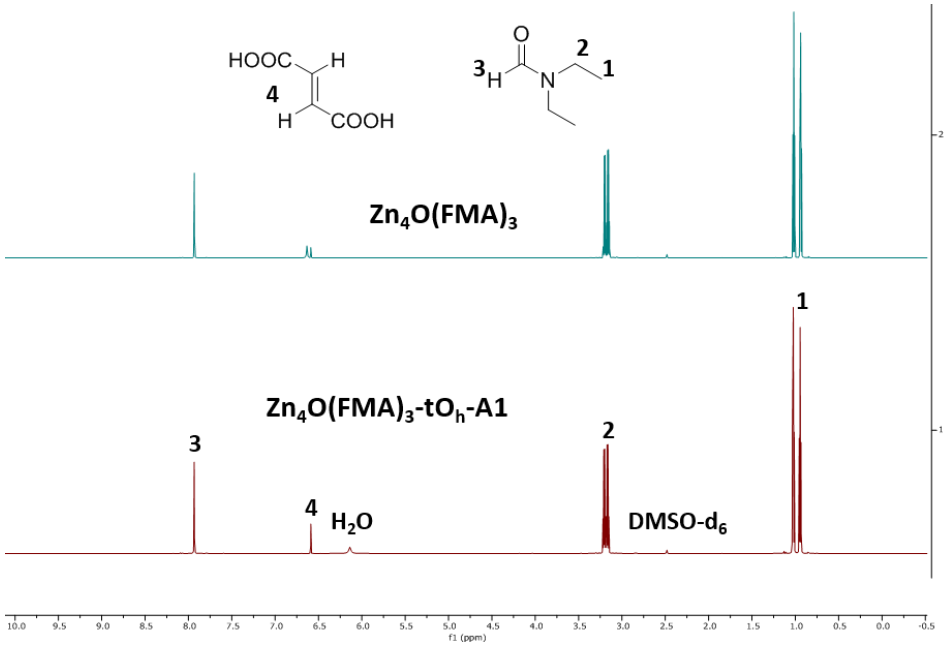


Figure S6: ^{1}H-NMR spectrum for as synthesized $Zn_4O(FMA)_3$ and $Zn_4O(FMA)_3$-tO_h(A1) samples after digesting in DCl/DMSO-d_6 solution.

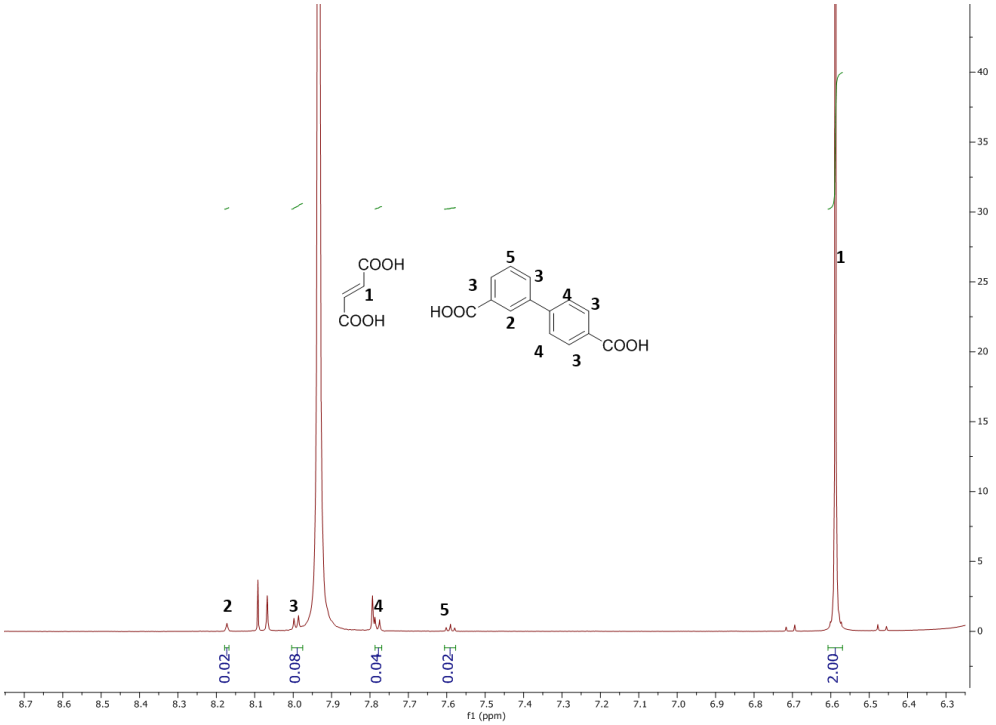


Figure S7: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared $Zn_4O(FMA)_3$-tO_h(A1) sample after digesting in DCl/DMSO-d_6 solution. From the integration, the molar ratio and mol% of A1 is estimated to be 1.00:0.02 (FMA:A1) and ~2 mol%.

Solvent exchange and activation: As synthesized $Zn_4O(FMA)_3$-tO_h(A1) crystals were washed with DMF and exchanged with DCM. The crystals were soaked in 20 mL of DCM 3 times over 24 h. The crystals were then immersed in *n*-hexane over 1 h replacing the solvent every 20 min. Once the solvent exchange is complete, the material was isolated by decanting the n-hexane and the crystals were evacuated under dynamic vacuum (0.05 Torr) for 24 h at room temperature and the BET surface area was determined at 77 K (Figure S8).

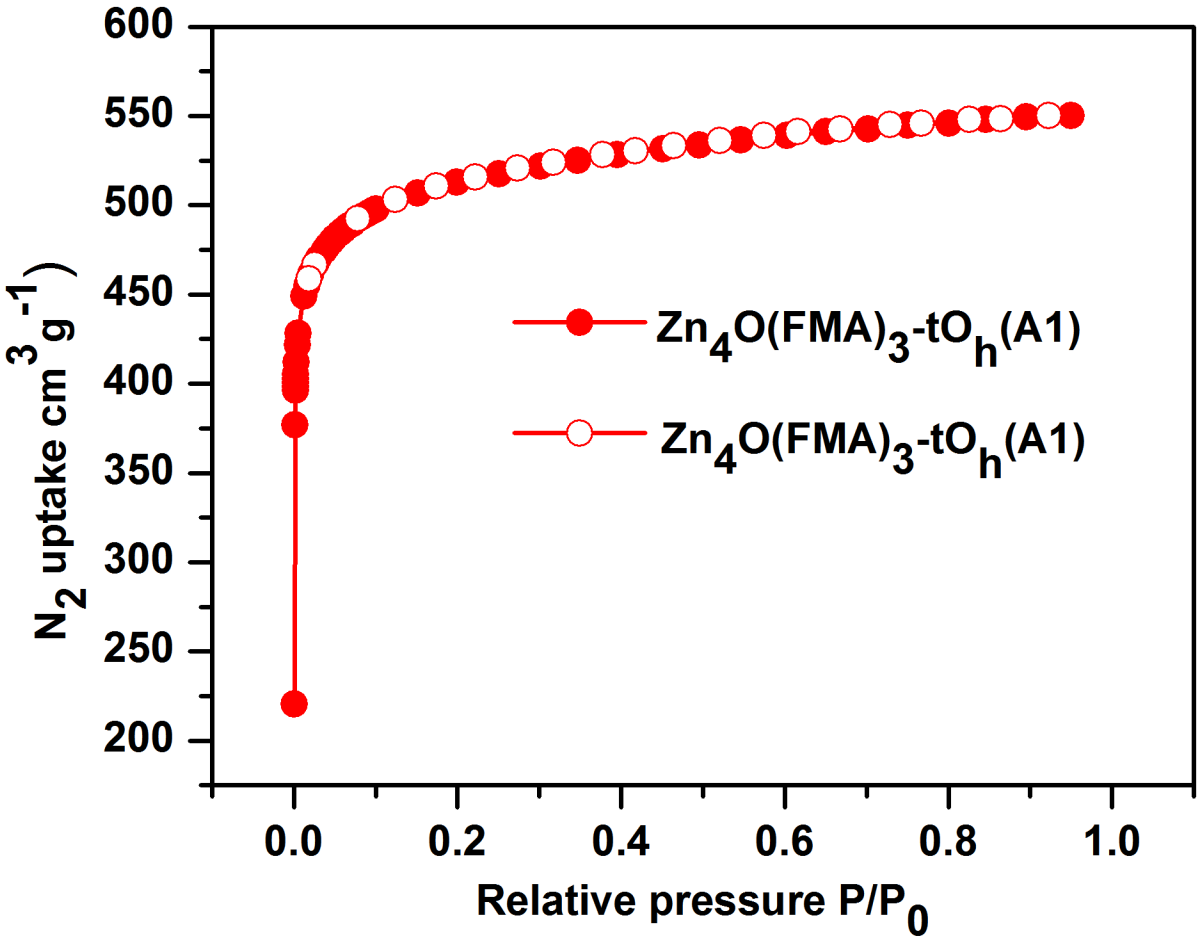
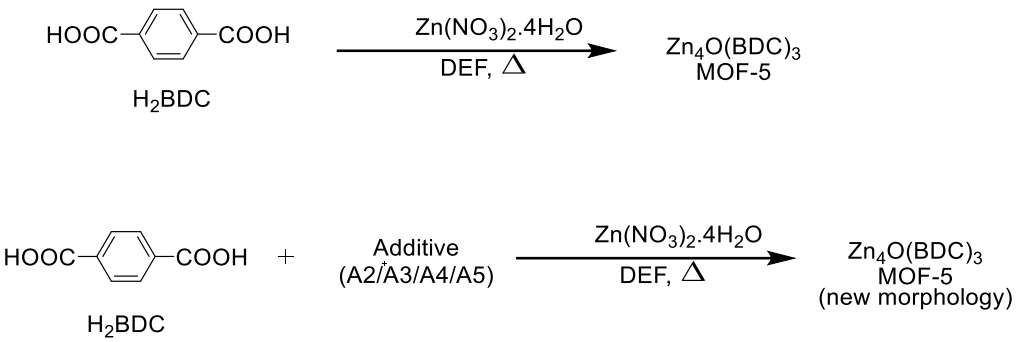


Figure S8: N_2 sorption isotherm for $Zn_4O(FMA)_3$-tO_h(A1) (adsorption data are shown with filled symbols while desorption data are shown with empty symbols).

SI 3b. Synthesis, solvent exchange, and activation procedures for MOF-5 cubic and non-cubic morphology crystals:



Scheme S5. Synthetic process for cubic and non-cubic morphologies of MOF-5.

MOF-5: H_2BDC (100.0 mg, 0.602 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (500.0 mg, 1.92 mmol), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The resulting colorless cubic morphology crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (56.83), is ~37% based on H_2BDC.

MOF-5-R_d(A2): H_2BDC (25.01 mg, 0.150 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (250.0 mg, 0.956 mmol), A2 additive (20.06 mg, 0.0631 mmol (29.6 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (17.19 mg), is ~39% based on H_2BDC.

MOF-5-R_d(A3): H_2BDC (25.04 mg, 0.150 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (250.0 mg, 0.956 mmol), A3 additive (20.07 mg, 0.0505 mmol (25.0 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (17.17 mg), is ~39% based on H_2BDC.

MOF-5-R_d(A4): H_2BDC (100.0 mg, 0.602 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (500.0 mg, 1.92 mmol), A4 additive (15.01 mg, 0.0414 mmol (6.4 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (54.67 mg), is ~36% based on H_2BDC.

MOF-5-O_h(A5): H_2BDC (100.0 mg, 0.602 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (500.0 mg, 1.92 mmol), A5 additive (10.04 mg, 0.0228 mmol (3.6 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (58.31), is ~38% based on H_2BDC.

As synthesized cubic and non-cubic morphology samples of MOF-5 were digested in DCl/DMSO-d_6 solution (Figure S10) and analyzed by NMR spectroscopy. In all new morphology samples, the peaks corresponding to BDC and additive (A2/A3/A4/A5) were observed (Figure S11-S14). Incorporation of these

additives does not yield new phases as confirmed through PXRD (see details and Figure 3 in the main manuscript) and so the linkers must occupy defect sites.

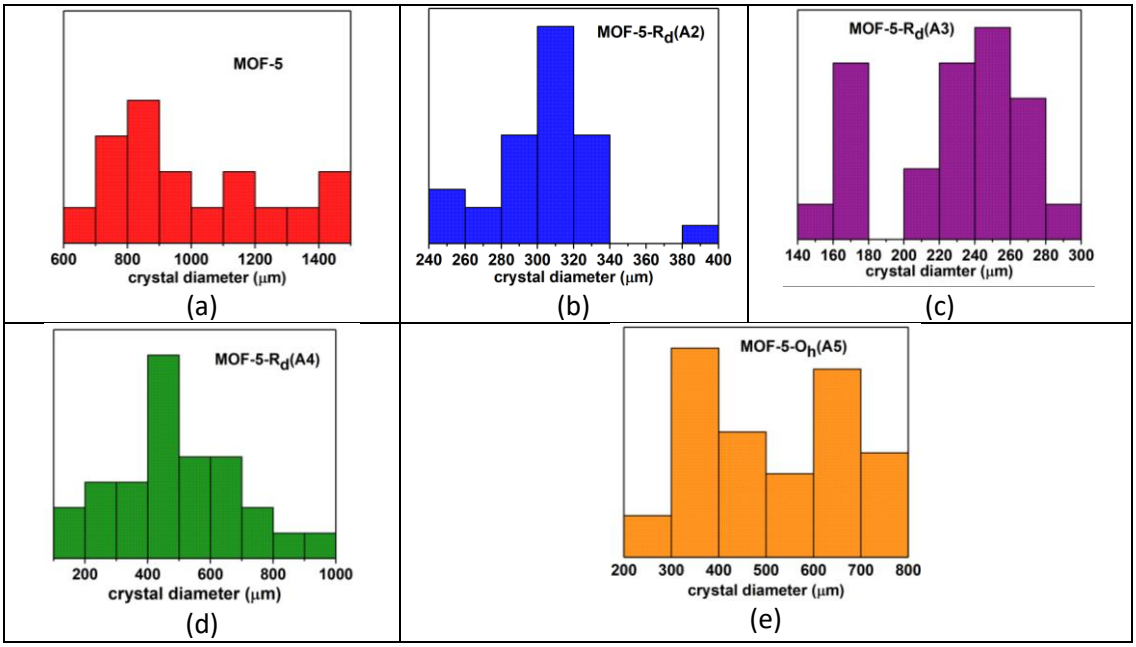


Figure S9: Histogram plot for different morphologies of MOF-5.

Table S2: Tabulated crystal size distributions range and median values for different morphologies of MOF-5.

Sample name	Mean (μm)	Median (μm)	Standard deviation (μm)
MOF-5	870	852	274
MOF-5-R_d(A2)	303	305	29
MOF-5-R_d(A3)	224	235	41
MOF-5-R_d(A4)	500	481	194
MOF-5-O_h(A5)	516	497	145

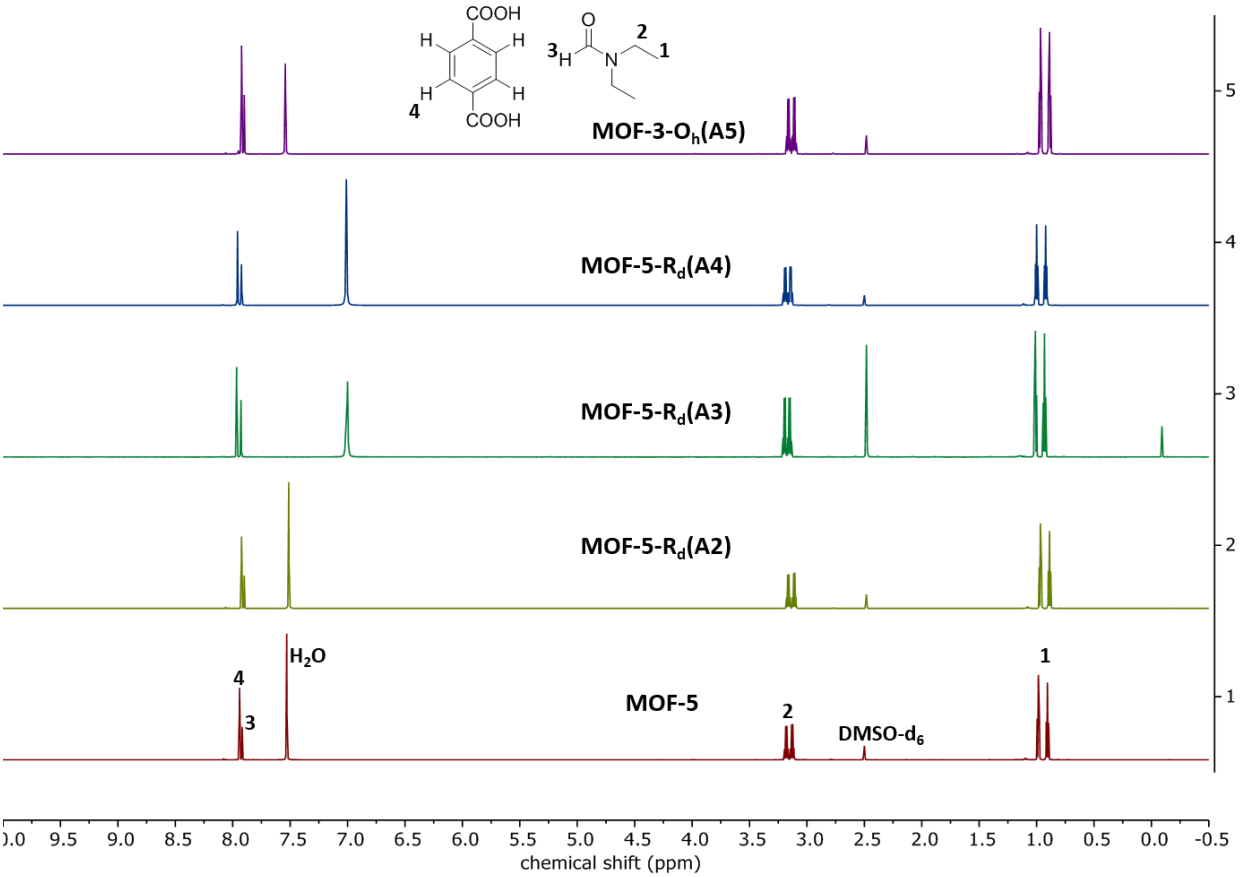


Figure S10: ^{1}H -NMR spectra for as synthesized IRMOF-3, MOF-5-R_d(A2), MOF-5-R_d(A3), MOF-5-R_d(A4), and MOF-5-O_h(A5) samples after digesting in DCl/DMSO-d_6 solution.

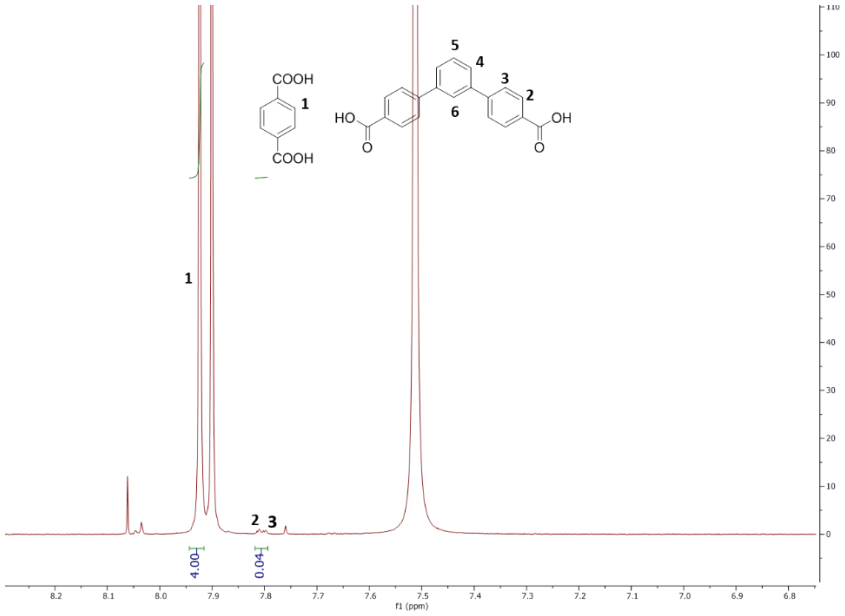


Figure S11: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared MOF-5-R_d(A2) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A2 were observed at <1 mol%.

Figure S12: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared MOF-5-R_d(A3) sample after digesting in DCl/DMSO-d_6 solution. From the integration, the molar ratio and mol% of A3 have been estimated to be 1.00:0.01 (BDC:A3) and 1 mol%.

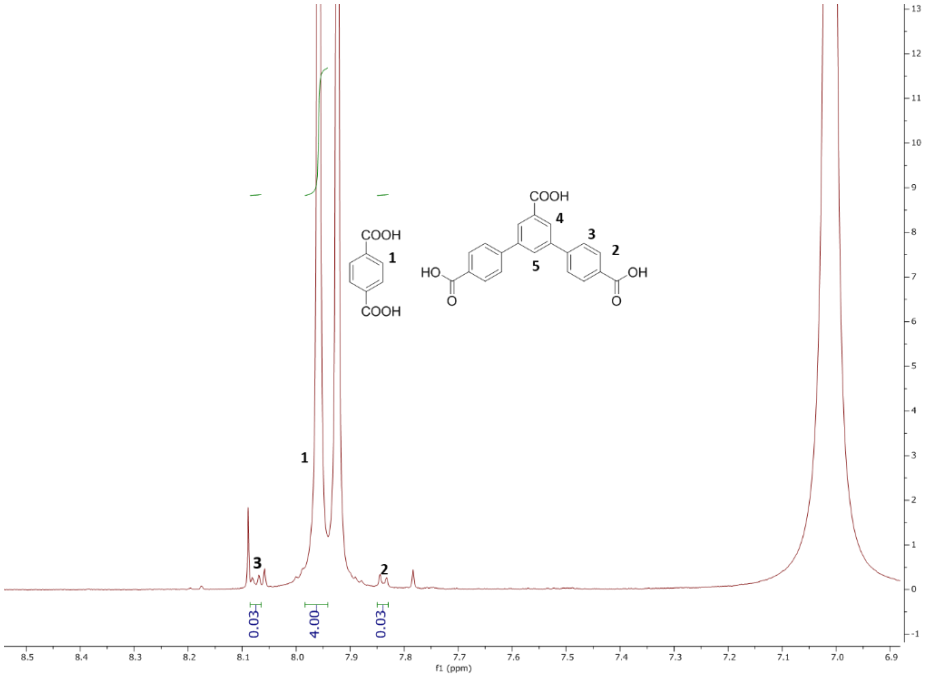


Figure S13: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared MOF-5-R_d(A4) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A4 were observed at <1 mol%.

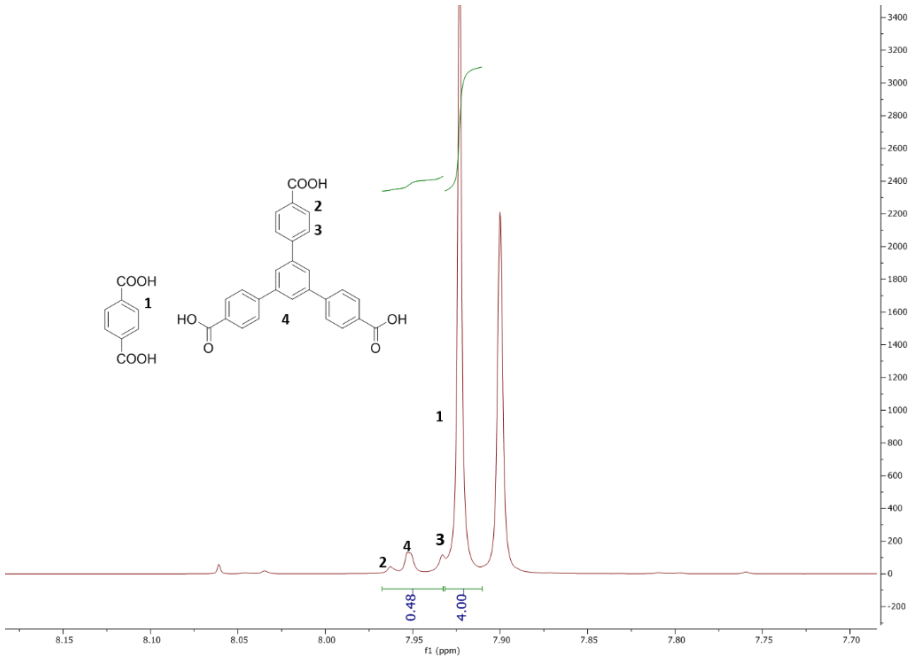


Figure S14: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared MOF-5-O_h(A5) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A5 were observed at <1 mol%.

Solvent exchange and activation: As synthesized MOF-5-R_d(A2) crystals were washed with DMF and exchanged with DCM. The crystals were soaked in 20 mL of DCM 3 times over 24 h. The crystals were then immersed in *n*-hexane over 1 h replacing the solvent every 20 min. Once the solvent exchange is complete, the material was isolated by decanting the n-hexane and the crystals were evacuated under dynamic vacuum (0.05 Torr) for 24 h at room temperature and the BET surface area was determined at 77 K (Figure S15).

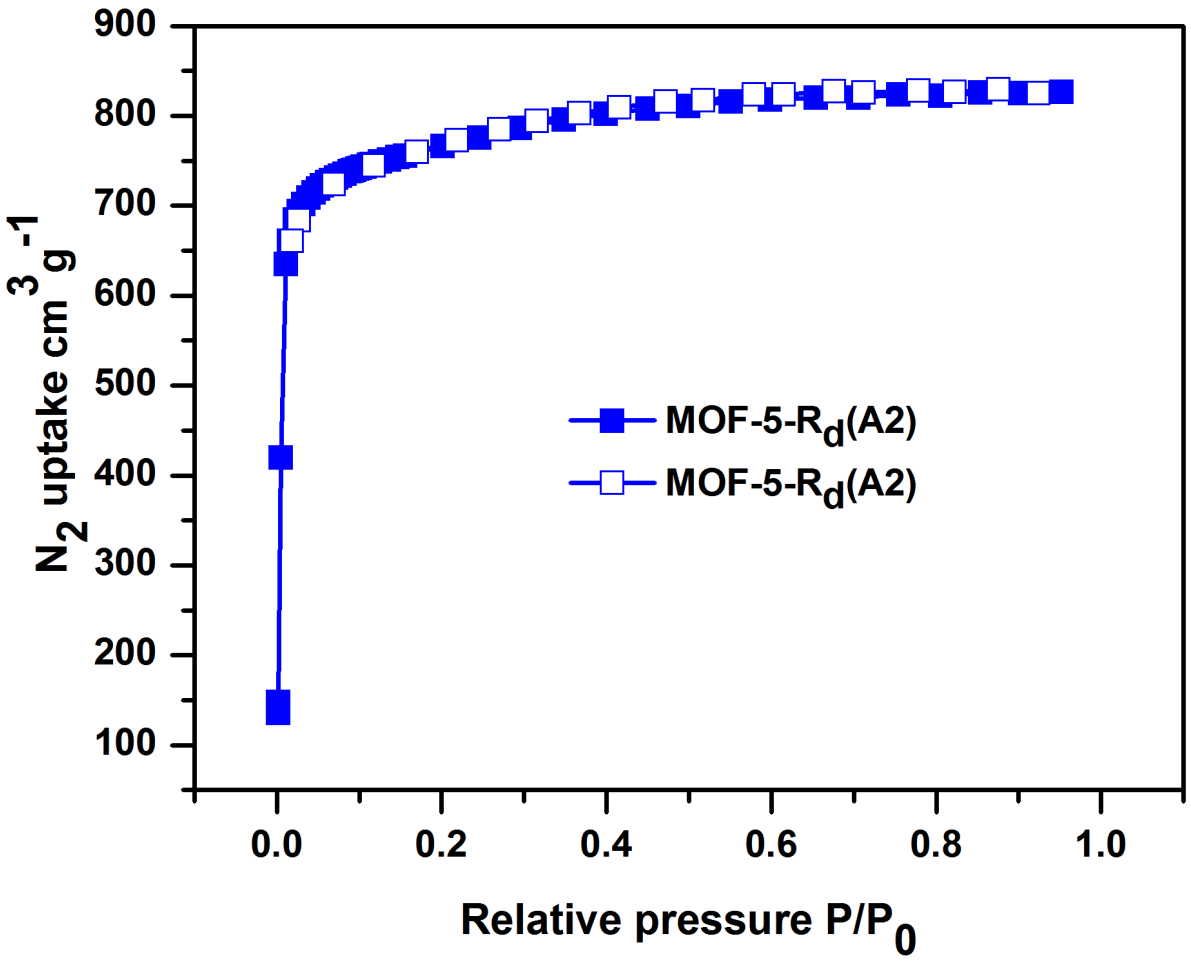
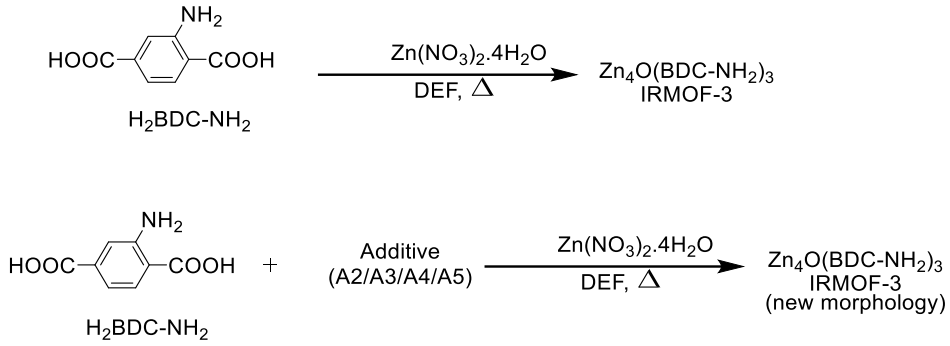


Figure S15: N_2 sorption isotherm for MOF-5-R_d(A2) (adsorption data are shown with filled symbols while desorption data are shown with empty symbols).

SI 3c. Synthesis, solvent exchange, and activation procedures for IRMOF-3 cubic and non-cubic morphology crystals:



Scheme S6. Synthetic process for cubic and non-cubic morphologies of IRMOF-3.

IRMOF-3: H_2BDC-NH_2 (75.06 mg, 0.414 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (300.0 mg, 1.15 mmol), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 16 hours. The resulting orange color cubic morphology crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (45.06 mg), is 40% based on H_2BDC-NH_2.

IRMOF-3-tO$_h$(A2): H_2BDC-NH_2 (25.10 mg, 0.138 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (250.0 mg, 0.956 mmol), A2 additive (20.40 mg, 0.0641 mmol (31.7 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 16 hours. The resulting light yellow color crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (15.63 mg), is ~42% based on H_2BDC-NH_2.

IRMOF-3-R$_d$(A3): H_2BDC-NH_2 (25.40 mg, 0.140 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (250.0 mg, 0.956 mmol), A3 additive (20.40 mg, 0.0513 mmol (26.8 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 16 hours. The resulting light yellow color crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (15.18 mg), is ~41% based on H_2BDC-NH_2.

IRMOF-3-tO$_h$(A4): H_2BDC-NH_2 (75.00 mg, 0.414 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (300.0 mg, 1.15 mmol), A4 additive (15.10 mg, 0.0457 mmol (9.9 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 16 hours. The resulting light yellow color crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (45.76 mg), is ~41% based on H_2BDC-NH_2.

IRMOF-3-O$_h$(A5): H_2BDC-NH_2 (75.01 mg, 0.414 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (300.0 mg, 1.15 mmol), A5 additive (5.03 mg, 0.0115 mmol (2.5 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 100 °C for 24 hours. The yield of the reaction, determined from the weight of the solvent-free material (45.77), is ~41% based on H_2BDC-NH_2.

As synthesized cubic and non-cubic morphology samples of IRMOF-3 were digested in DCl/DMSO-d_6 solution (Figure S17) and analyzed by NMR spectroscopy. In all new morphology samples, the peaks corresponding to BDC-NH_2 and additive (A2/A3/A4/A5) were observed (Figure S18-S21). Incorporation of these additives does not yield new phases as confirmed through PXRD (see details and Figure 3 in the main manuscript) and so the linkers must occupy defect sites.

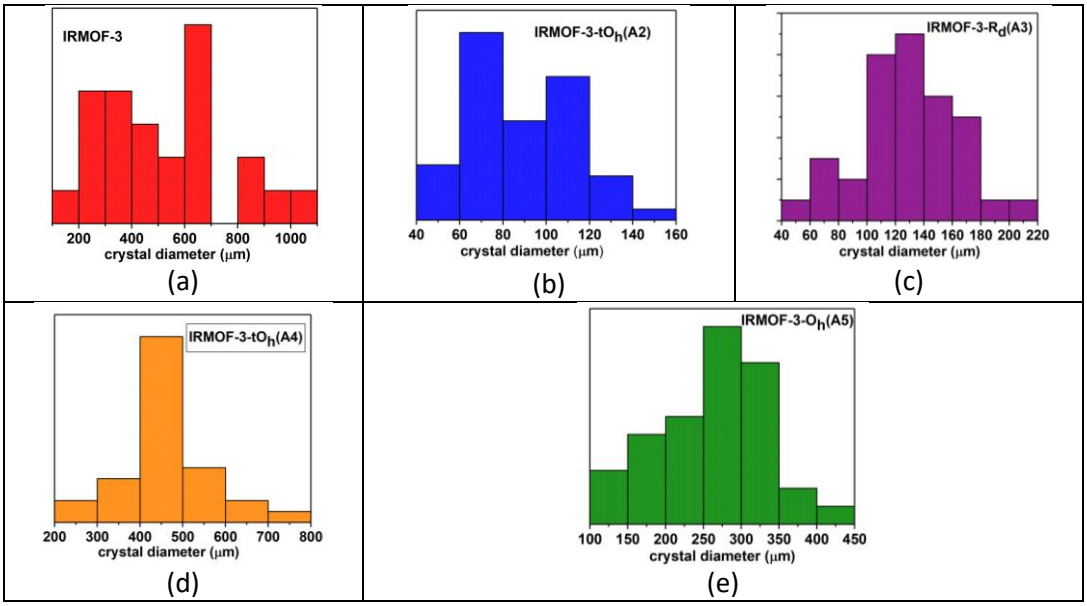


Figure S16: Histogram plot for different morphologies of IRMOF-3.

Table S3: Tabulated crystal size distributions range and median values for different morphologies of IRMOF-3.

Sample name	Mean (μm)	Median (μm)	Standard deviation (μm)
IRMOF-3	510	476	239
IRMOF-3-tO$_h$(A2)	89	82	23
IRMOF-3-R$_d$(A3)	129	130	35
IRMOF-3- tO$_h$ (A4)	458	339	105
IRMOF-3-O$_h$(A5)	265	264	71

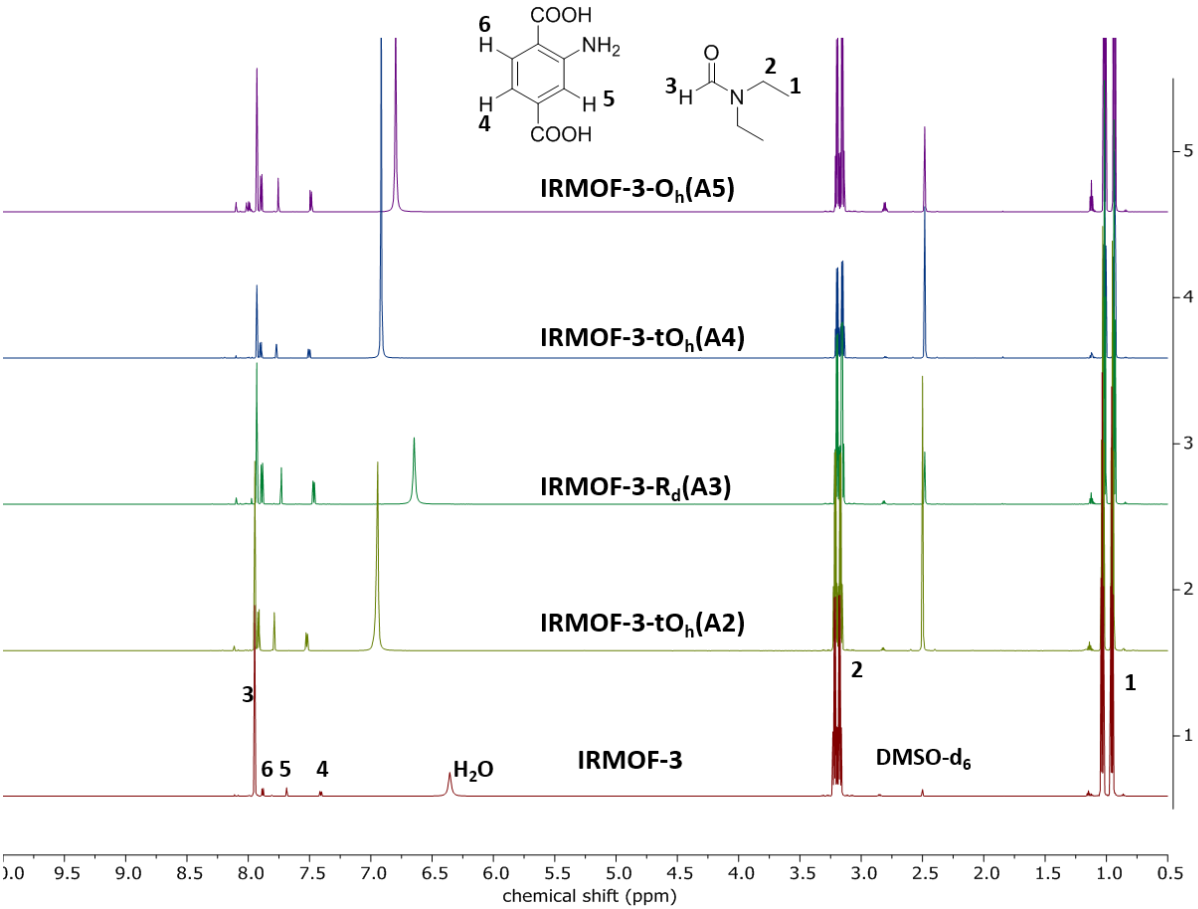


Figure S17: Proton NMR spectrum for as synthesized IRMOF-3, IRMOF-3-R_d(A2), IRMOF-3-R_d(A3), IRMOF-3-R_d(A4), and IRMOF-3-R_d(A5) samples after digesting in DCl/DMSO-d_6 solution.

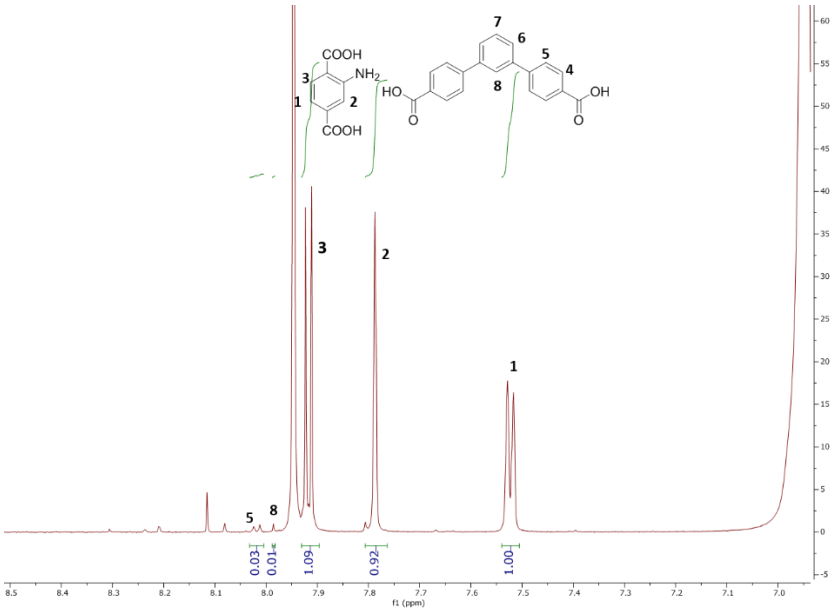


Figure S18: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared IRMOF-3-R_d(A2) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A2 were observed at >1 mol%.

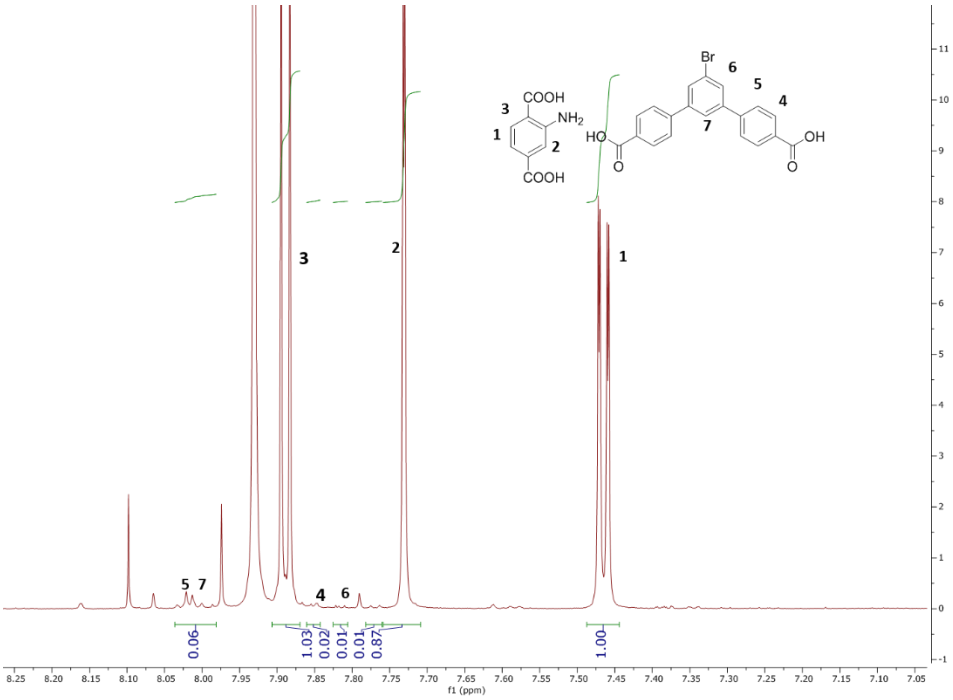


Figure S19: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared IRMOF-3-tO_h(A3) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A3 were observed at >1 mol%.

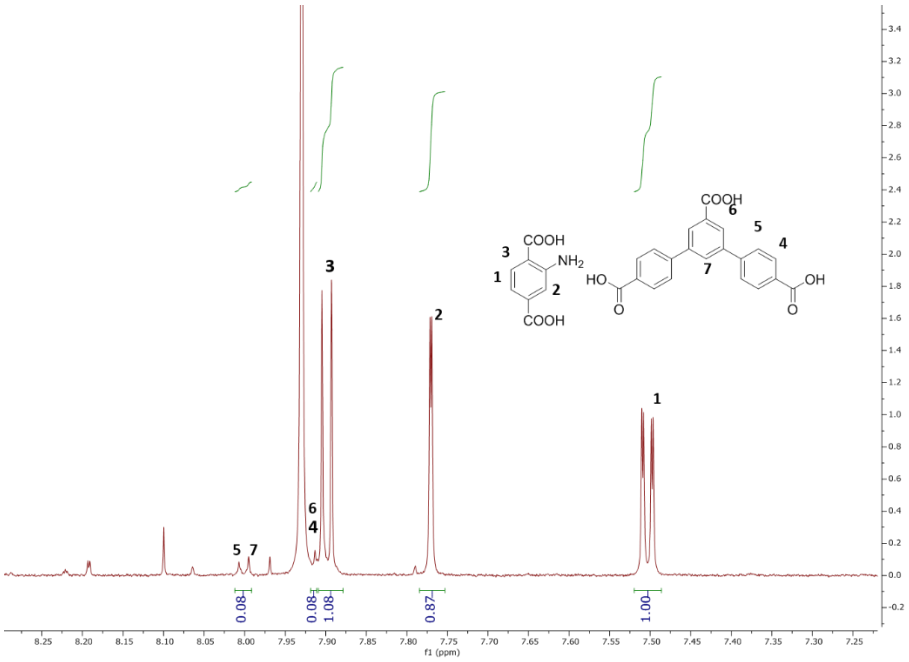


Figure S20: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared IRMOF-3-tO_h(A4) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A4 were observed at <1 mol%.

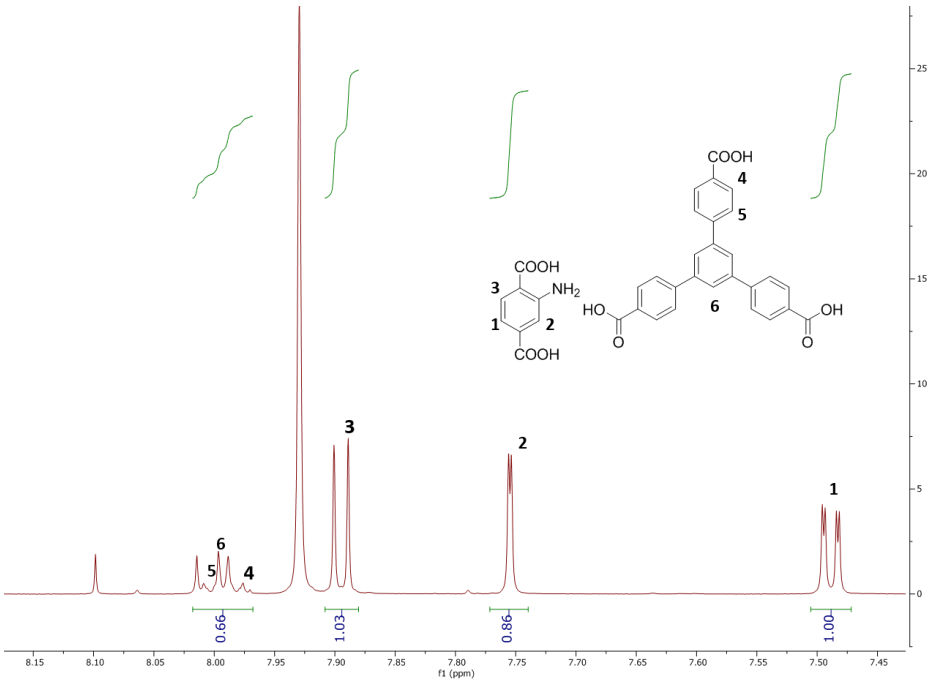


Figure S21: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared IRMOF-3-O_h(A5) sample after digesting in DCl/DMSO-d_6 solution. In this sample the peaks corresponding to A5 were observed at <1 mol%.

Solvent exchange and activation: As synthesized IRMOF-3-tO$_h$(A2) crystals were washed with DMF and exchanged with DCM. The crystals were soaked in 20 mL of DCM 3 times over 24 h. The crystals were then immersed in n-hexane over 1 h replacing the solvent every 20 min. Once the solvent exchange is complete, the material was isolated by decanting the n-hexane and the crystals were evacuated under dynamic vacuum (0.05 Torr) for 24 h at room temperature and the BET surface area was determined at 77 K (Figure S22).

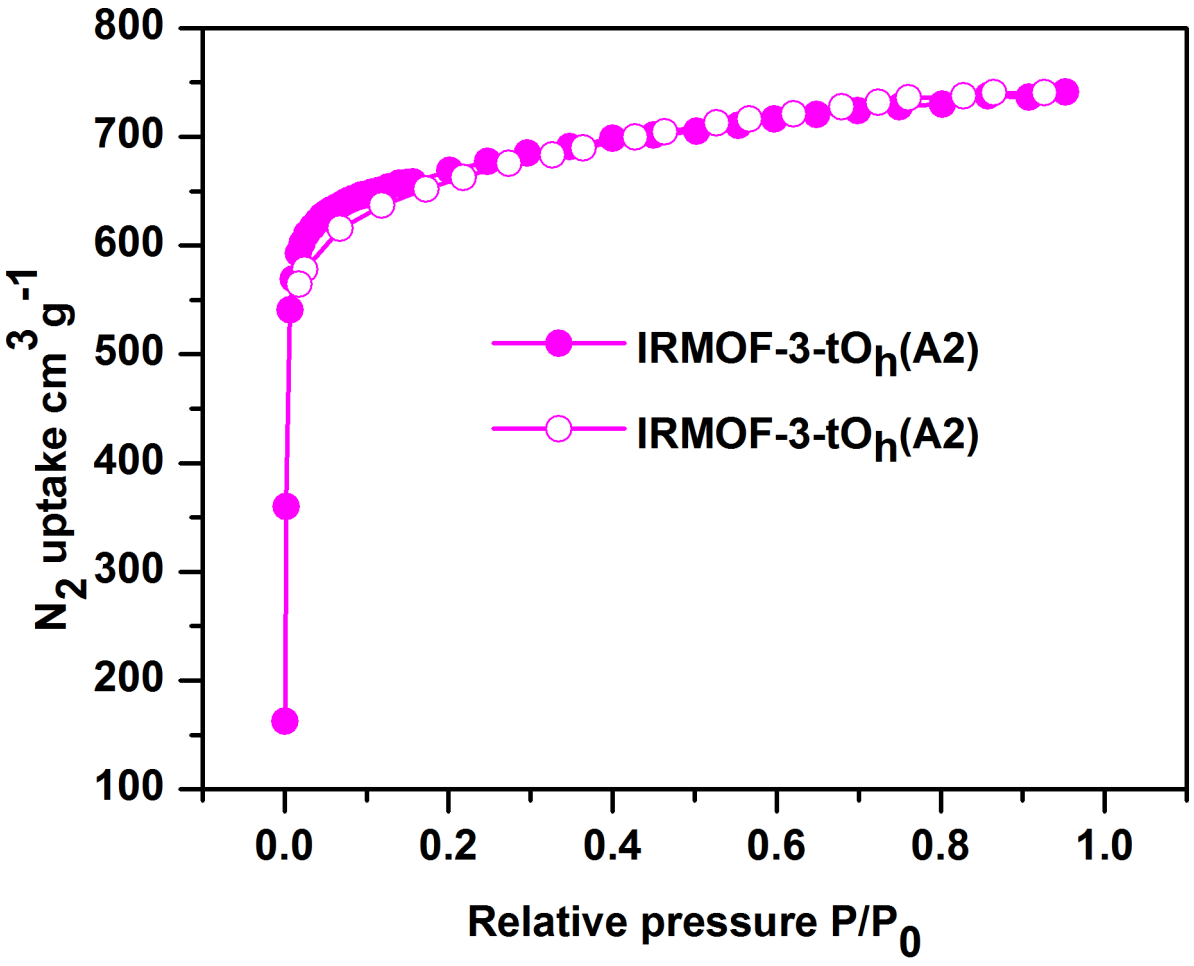
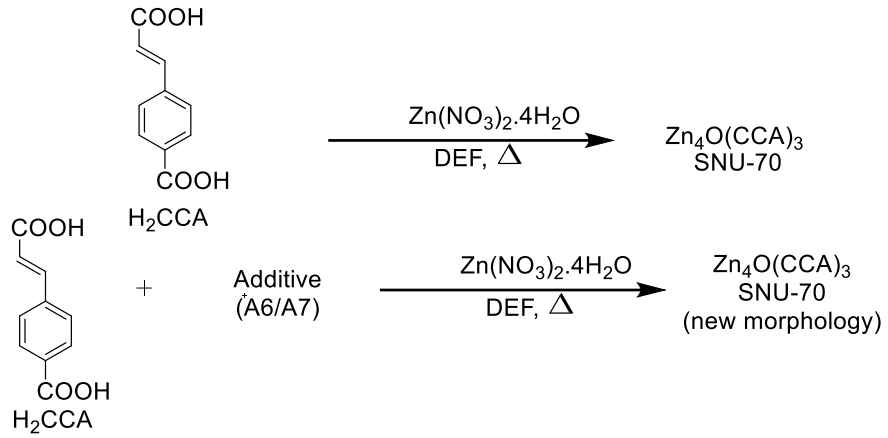


Figure S22: N_2 sorption isotherm for IRMOF-3-tO$_h$(A2) (adsorption data are shown with filled symbols while desorption data are shown with empty symbols).

SI 3d. Synthesis, solvent exchange, and activation procedures for SNU-70 cubic and non-cubic morphology crystals:



Scheme S6. Synthetic process for cubic and non-cubic morphologies of SNU-70.

SNU-70: H_2CCA (37.50 mg, 0.195 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (75.02 mg, 0.286 mmol), and 12.5 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 105 °C for 12 hours. The resulting colorless cubic morphology crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (13.43 mg), is ~24% based on H_2CCA.

SNU-70-R_d(A6): H_2CCA (37.51 mg, 0.195 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (75.01 mg, 0.286 mmol), A6 additive (6.74 mg, 0.0142 mmol (6.8 mol%)), and 12.5 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 105 °C for 18 hours. The resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.68 mg), is ~25% based on H_2CCA.

SNU-70-R_d(A7): H_2CCA (37.50 mg, 0.195 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (75.02 mg, 0.286 mmol), A7 additive (6.76 mg, 0.0154 mmol (7.3 mol%)), and 12.5 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 105 °C for 18 hours. The resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.83 mg), is ~25% based on H_2CCA.

SNU-70-tO_h(A7): H_2CCA (60.04 mg, 0.313 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (300.0 mg, 1.147 mmol), A7 additive (12.74 mg, 0.0291 mmol (8.5 mol%)), and 12.5 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The mixture was heated to 105 °C for 18 hours. The resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (23.07 mg), is 26% based on H_2CCA.

As synthesized cubic and non-cubic morphology samples of SNU-70 were digested in DCl/DMSO-d_6 solution (Figure S24) and analyzed by NMR spectroscopy. In all new morphology samples, the peaks

corresponding to CCA and additive (A6/A7) were observed (Figure S25-S27). Incorporation of these additives does not yield new phases as confirmed through PXRD (see details and Figure 4 in the main manuscript) and so the linkers must occupy defect sites.

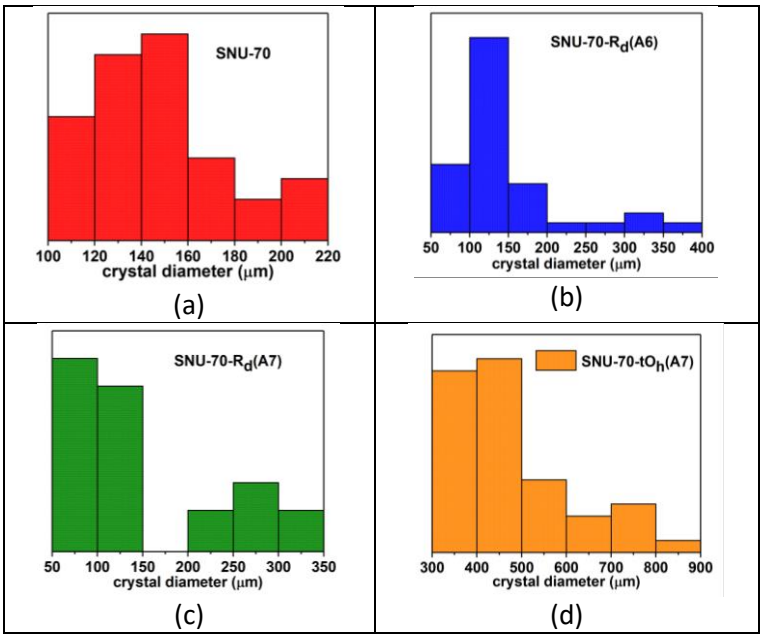


Figure S23: Histogram plot for different morphologies of SNU-70.

Table S4: Tabulated crystal size distributions range and median values for different morphologies of SNU-70.

Sample name	Mean (μm)	Median (μm)	Standard deviation (μm)
SNU-70	138	140	37
SNU-70-R_d(A6)	148	130	74
SNU-70-R_d(A7)	145	100	73
SNU-70-tO_h (A7)	473	450	138

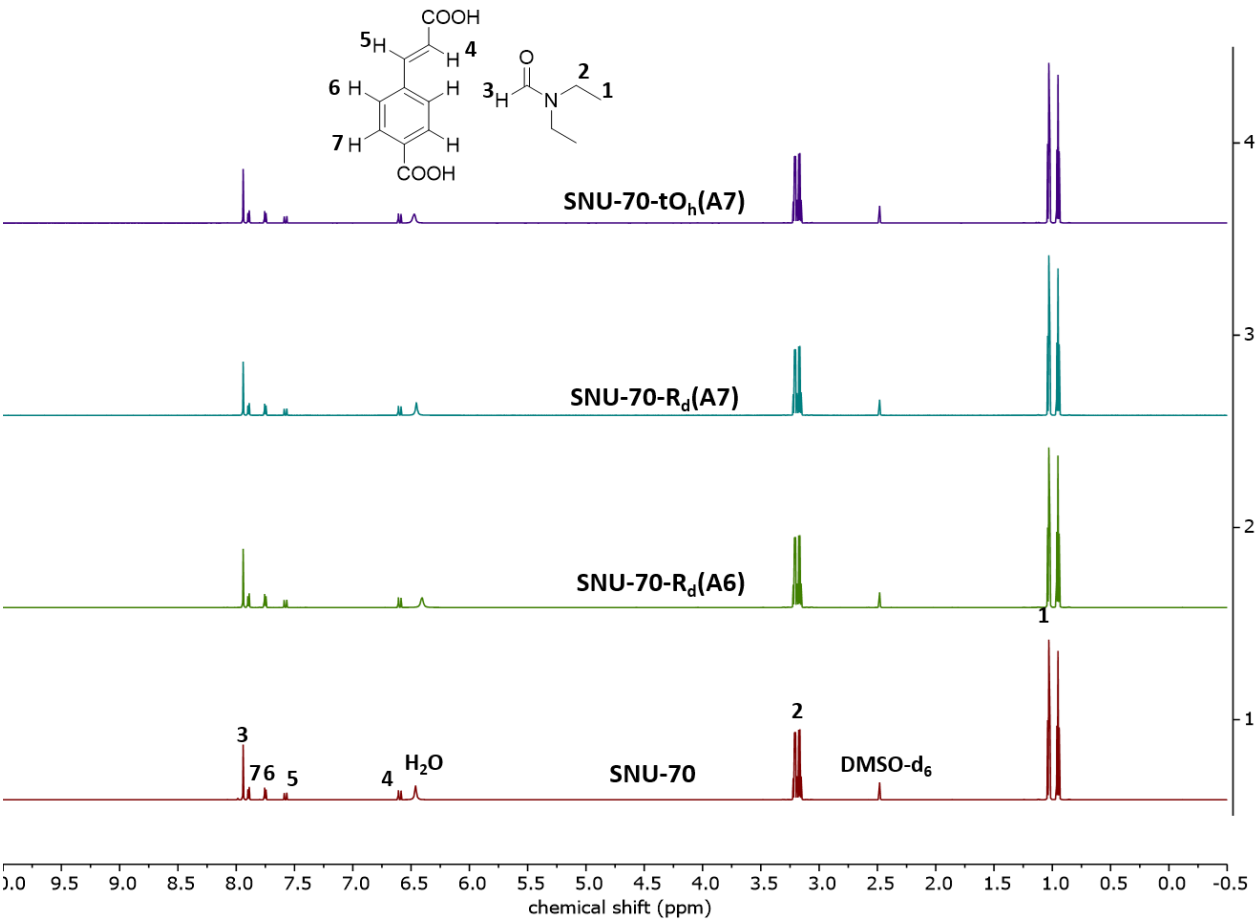


Figure S24: Proton NMR spectrum for as synthesized SNU-70, SNU-70-R_d(A6), SNU-70-R_d(A7), and SNU-70-tO_h(A7) samples after digesting in DCl/DMSO-d_6 solution.

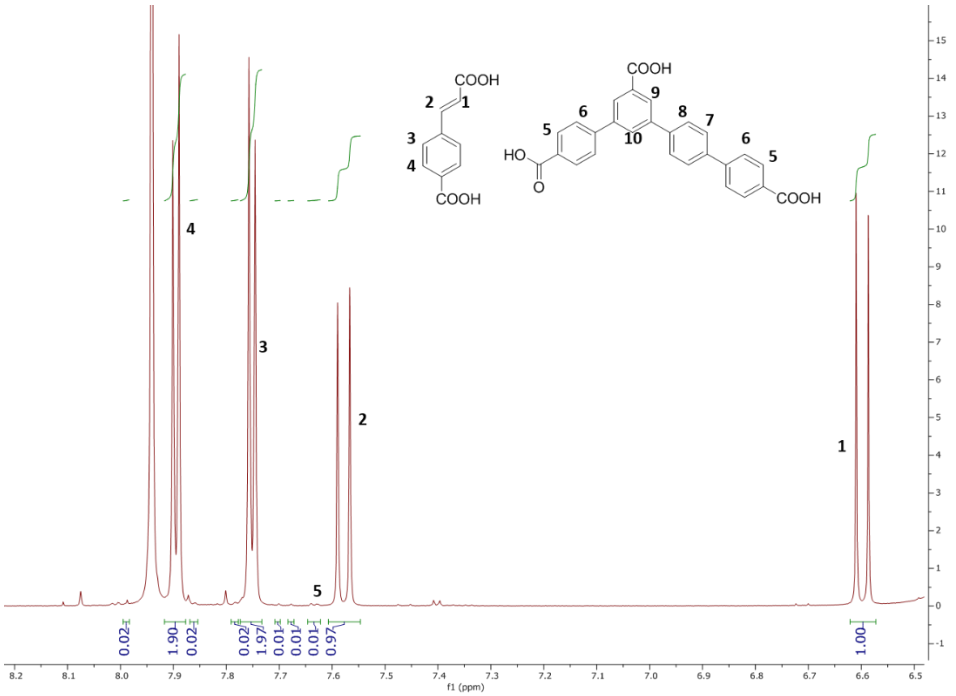


Figure S25: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared SNU-70-R_d(A6) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A6 were observed at <1 mol%.

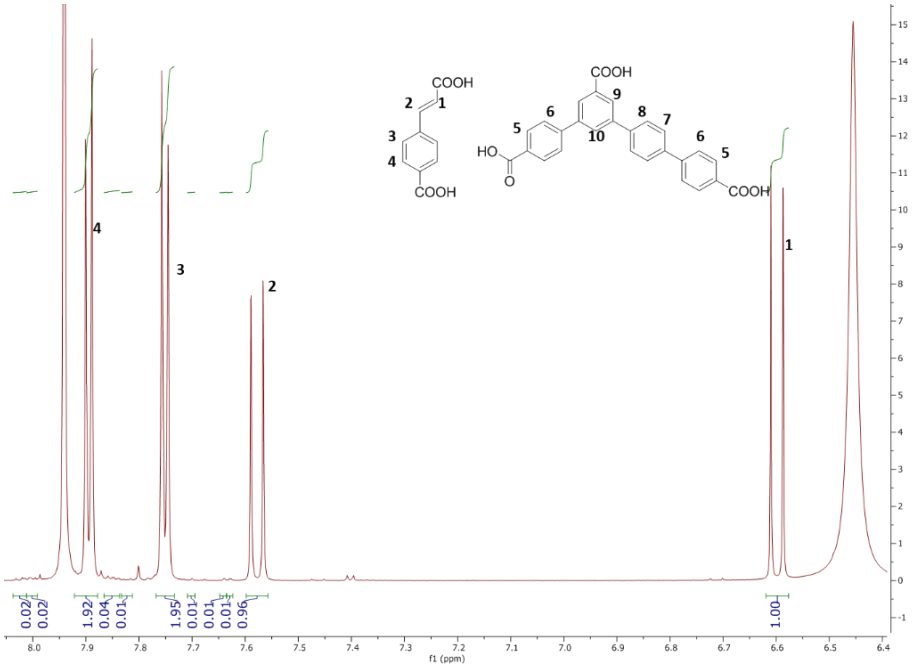


Figure S26: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared SNU-70-R_d(A7) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A7 were observed at <1 mol%.

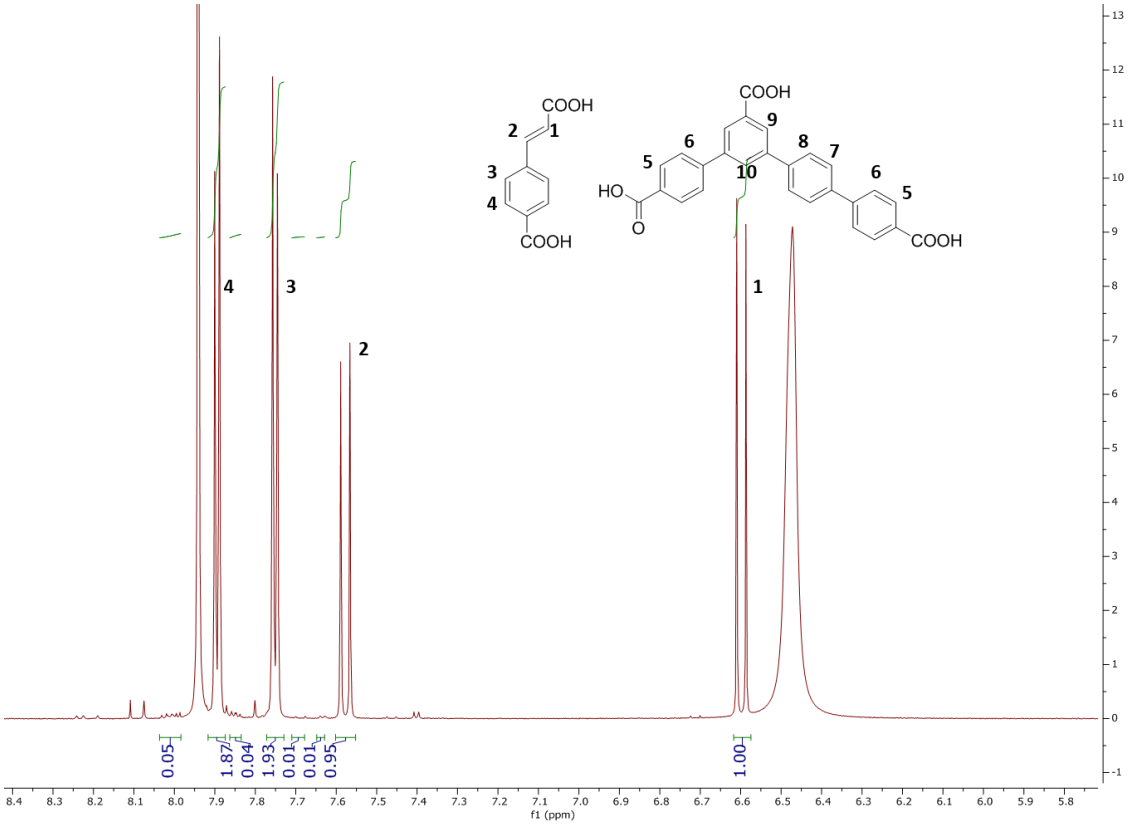


Figure S27: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared SNU-70-tO_h(A7) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A7 were observed at <1 mol%.

Solvent exchange and activation: As synthesized SNU-70-R_d(A7) and SNU-70-tO_h(A7) crystals were washed with DMF and exchanged with DCM. The crystals were soaked in 20 mL of DCM 3 times over 24 h. The crystals were then immersed in n-hexane over 1 h replacing the solvent every 20 min. Once the solvent exchange is complete, the material was isolated by decanting the *n*-hexane and the crystals were evacuated under dynamic vacuum (0.05 Torr) for 24 h at room temperature and BET surface areas were determined at 77 K (Figure S28).

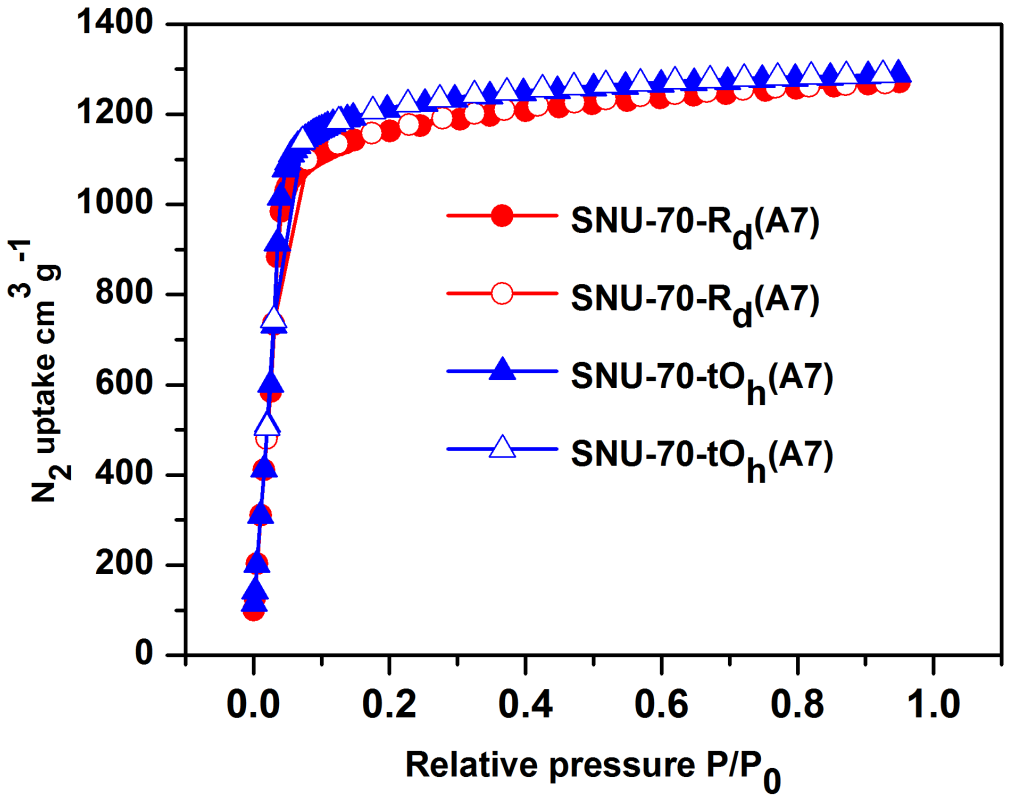
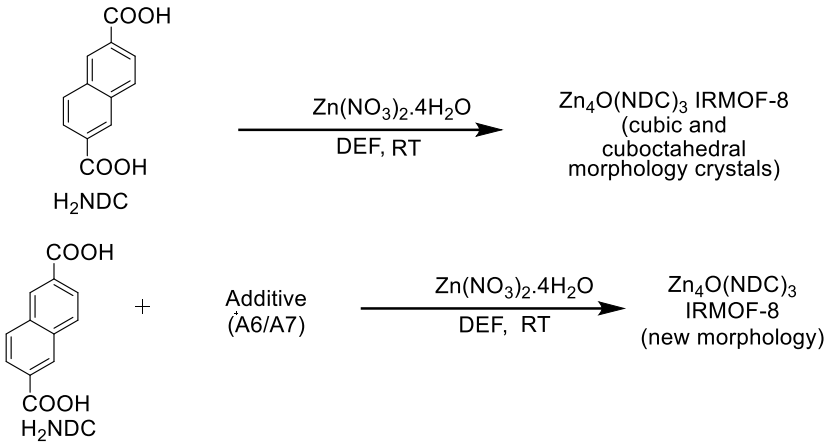


Figure S28: N_2 sorption isotherm for SNU-70-R_d(A7) and SNU-70-tO_h(A7) (adsorption data are shown with filled symbols while desorption data are shown with empty symbols).

SI 3e. Synthesis, solvent exchange, and activation procedures for IRMOF-8 cubic and non-cubic morphology crystals:

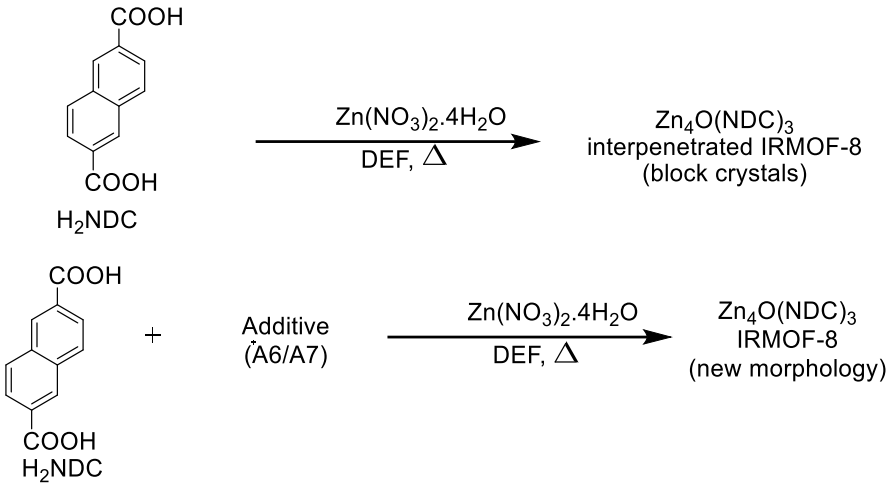


Scheme S7. Synthetic process for cubic and non-cubic morphologies of IRMOF-8 at room temperature.

IRMOF-8-RT: H_2NDC (12.24 mg, 0.0566 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (109.0 mg, 0.416 mmol), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The solution was incubated at room temperature for 7 days, after which time crystals had grown on the walls of the vial. These resulting crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.07 mg), is ~34% based on H_2NDC.

IRMOF-8-RT-R_d(A6): H_2NDC (12.46 mg, 0.0576 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (109.0 mg, 0.416 mmol), A6 additive (3.03 mg, 0.00638 mmol (10.1 mol%)) and 12.5 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The solution was incubated at room temperature for 12 days, after which time crystals had grown on the walls of the vial. These resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.18 mg), is 35% based on H_2NDC.

IRMOF-8-RT-R_d(A7): H_2NDC (12.24 mg, 0.0566 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (109.0 mg, 0.416 mmol), A7 additive (3.04 mg, 0.00693 mmol (10.9 mol%)) and 12.5 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. The solution was incubated at room temperature for 12 days, after which time crystals had grown on the walls of the vial. These resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.08 mg), is 37% based on H_2NDC.



Scheme S8. Synthetic process for cubic and non-cubic morphologies of IRMOF-8 at elevated temperatures.

IRMOF-8-HT: H_2NDC (12.23 mg, 0.0565 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (109.0 mg, 0.416 mmol), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. After the mixture was heated to 85 °C for 24 hours. These resulting colorless block morphology crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.21 mg), is ~35% based on H_2NDC.

IRMOF-8-HT-R_d(A6): H_2NDC (12.25 mg, 0.0566 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (109.0 mg, 0.416 mmol), A6 additive (3.02 mg, 0.00638 mmol (10.2 mol%)) and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. After the mixture was heated to 85 °C for 24 hours. These resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.03 mg), is ~34% based on H_2NDC.

IRMOF-8-HT-R_d(A7): H_2NDC (12.21 mg, 0.0564 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (109.0 mg, 0.416 mmol), A7 additive (3.04 mg, 0.00693 mmol (10.9 mol%)) and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. After the mixture was heated to 85 °C for 24 hours. These resulting colorless crystals were analyzed using optical microscopy. The yield of the reaction, determined from the weight of the solvent-free material (6.06), is ~34% based on H_2NDC.

As synthesized IRMOF-8-HT, IRMOF-8-HT-R_d(A6), and IRMOF-8-HT-R_d(A7) samples were digested in DCl+DMSO-d_6 solution (Figure S30) and analyzed by NMR spectroscopy. In all new morphology samples, the peaks corresponding to NDC and additive (A6/A7) were observed (Figure S31 and S32). Incorporation of these additives does not yield new phases as confirmed through PXRD (see details and Figure 4 in the main manuscript) and so the linkers must occupy defect sites.

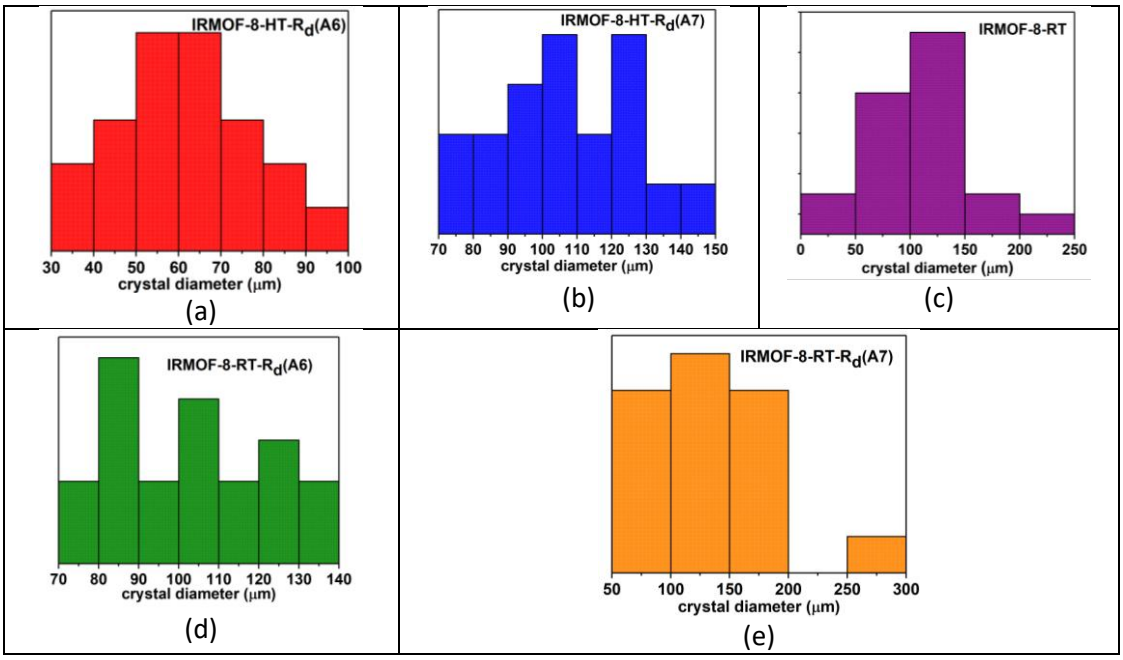


Figure S29: Histogram plot for different morphologies of IRMOF-8.

Table S5: Tabulated crystal size distributions range and median values for different morphologies of IRMOF-8.

Sample name	Mean (μm)	Median (μm)	Standard deviation (μm)
IRMOF-8-HT-R_d(A6)	61	60	16
IRMOF-8-HT-R_d(A7)	107	106	20
IRMOF-8-RT	112	112	43
IRMOF-8-RT-R_d(A6)	99	103	29
IRMOF-8-RT-R_d(A7)	132	126	52

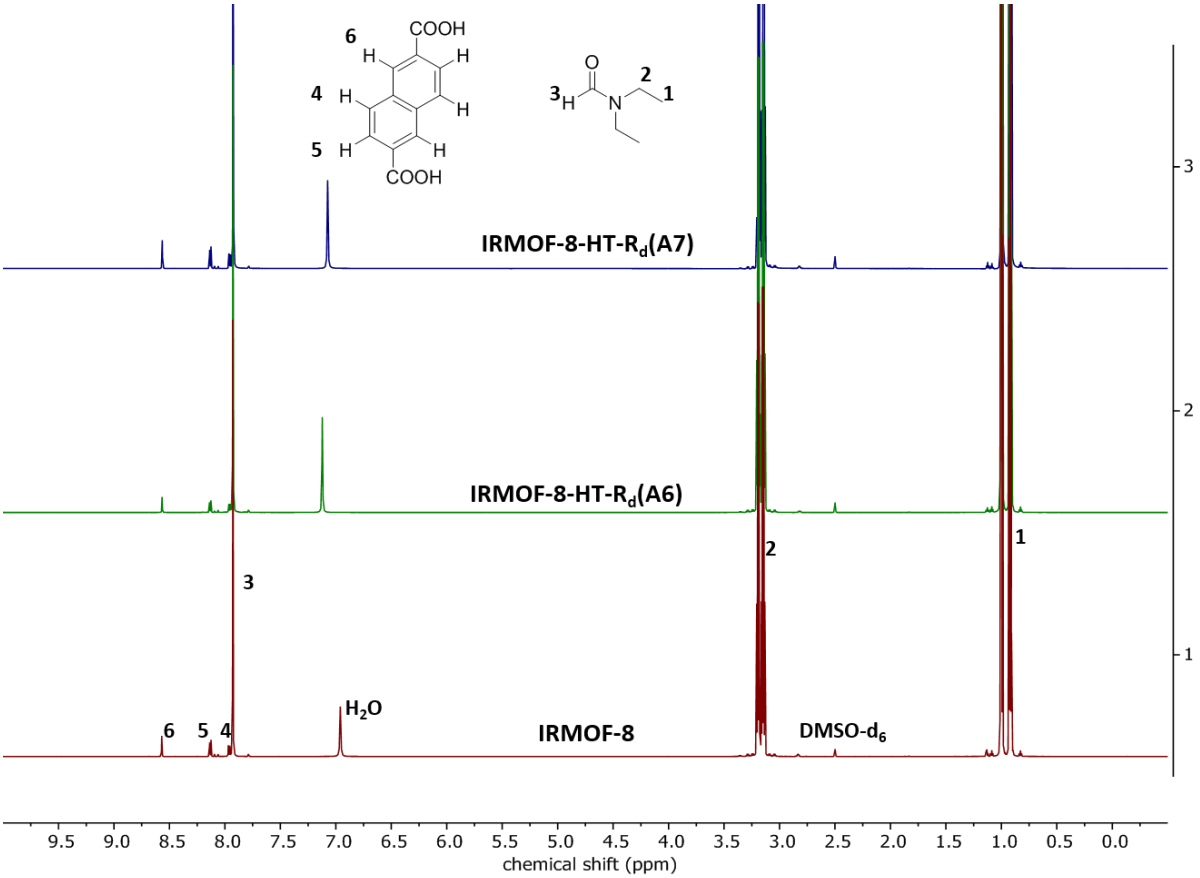


Figure S30: ^{1}H-NMR spectrum for as synthesized IRMOF-8-HT, IRMOF-8-HT-R_d(A6), and IRMOF-8-HT-R_d(A7) samples after digesting in DCl/DMSO-d_6 solution.

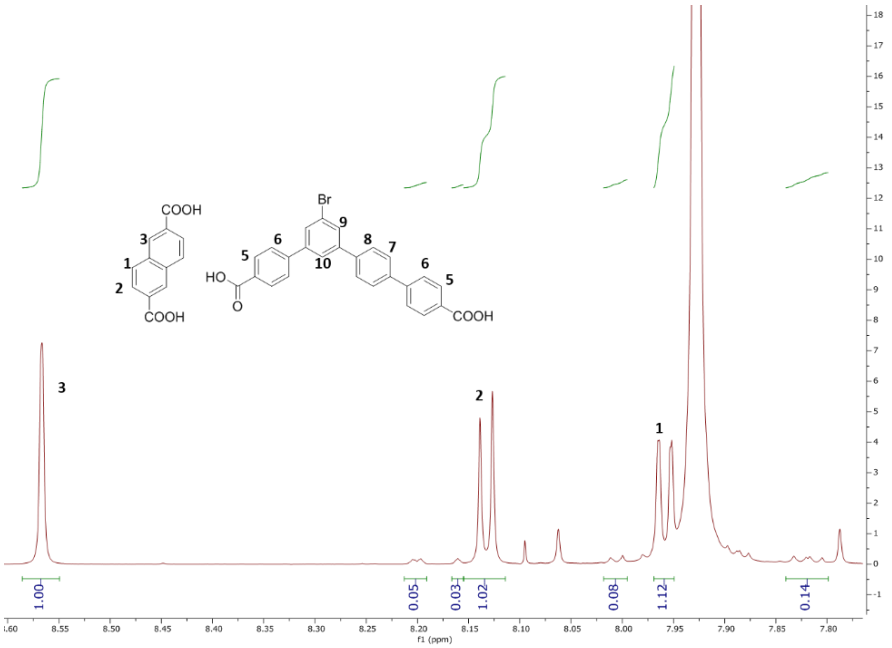


Figure S31: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared IRMOF-8-R_d(A6) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A6 were observed at <1 mol%.

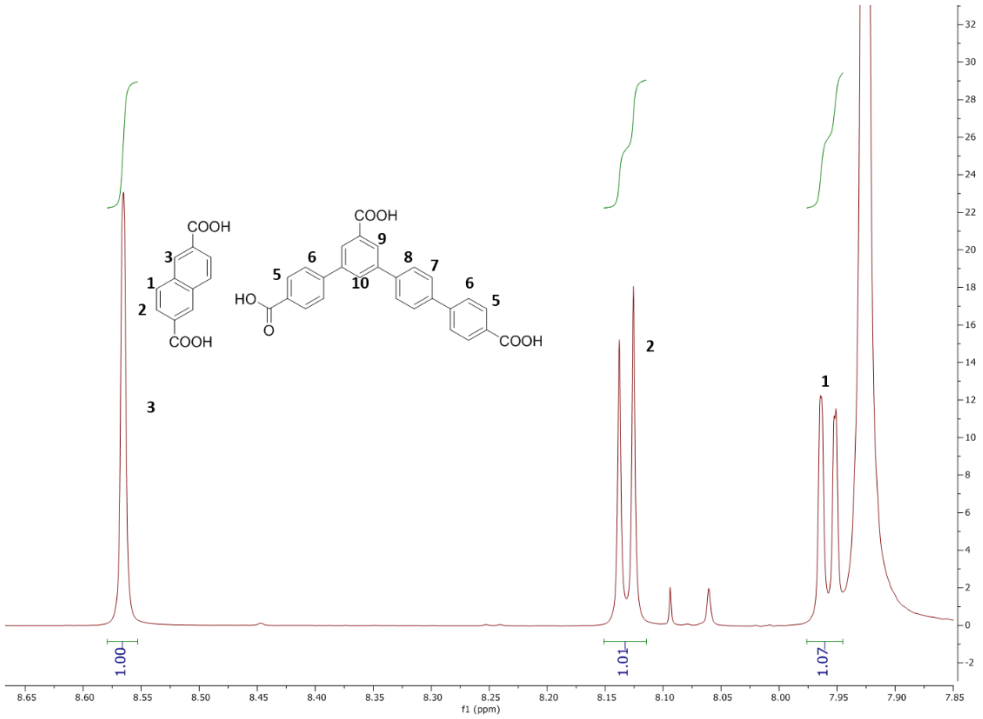


Figure S32: Aromatic region enlarged ^{1}H-NMR spectrum for an as prepared IRMOF-8-R_d(A7) sample after digesting in DCl/DMSO-d_6 solution. In this sample, the peaks corresponding to A7 were observed at <1 mol%.

Solvent exchange and activation: Initially as synthesized IRMOF-8-HT-R_d(A6) crystals were washed with DMF and exchanged with DCM. The crystals were soaked in 20 mL of DCM 3 times over 24 h. The crystals were then immersed in n-hexane over 1 h replacing the solvent every 20 min. Once the solvent exchange is complete, the material was isolated by decanting the n-hexane and the crystals were evacuated under dynamic vacuum (0.05 Torr) for 24 h at room temperature and the BET surface area was determined at 77 K (Figure S33).

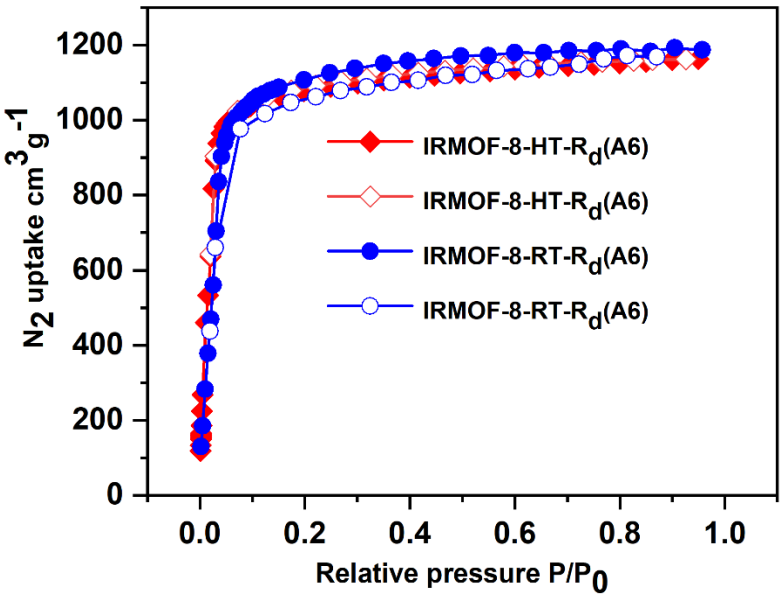


Figure S33: N_2 sorption isotherm for IRMOF-8-RT-R_d(A6) and IRMOF-8-HT-R_d(A6) (adsorption data are shown with filled symbols while desorption data are shown with empty symbols).

SI 4. MOF new morphologies synthesis validation with mismatched additives

Addition of additives which did not match the carboxylate C to C bond distance for any selected MOF initial reagent mixture resulted in no change in cubic morphology (See below Table S1). For instance, the addition of isophthalic acid, *m*-terphenyl-4,4'-dicarboxylic acid, and 5'-bromo-[1,1':3',1'':4'',1'''-quaterphenyl]-4,4'''-dicarboxylic acid at ~10-50 mol% level into initial ($Zn_4O(FMA)_3$ MOF reagent mixture resulted in cubic crystal morphology. These results are also mirrored in other MOFs (MOF-5, IRMOF-3, SNU-70 and IRMOF-8) in the presence of C to C distance mismatched additives in the initial MOF reagents mixture.

Table S6. Synthetic conditions of MOF new morphologies using mismatched additives

S. No.	Linker/ $Zn(NO_3)_2{\cdot}4H_2O$ (mg (mmol)/ mg (mmol)	Additive mg, mmol (mol%)	Solvent (DEF)	Temperature/ time	Observation
$Zn_4O(FMA)_3$					
1	11.67 (0.100)/ 27.06 (0.106)	isophthalic acid 2.00, 0.0121 (10.7)	10 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
2	11.67 (0.100)/ 27.06 (0.106)	isophthalic acid 10.04, 0.0604 (37.7)	10 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
3	11.67 (0.100)/ 27.06 (0.106)	A2 7.23, 0.0227 (18.5)	10 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
4	11.63 (0.100)/ 27.07 (0.106)	A2 31.89, 0.100 (50.0)	10 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
5	1.18 (0.0101)/ 3.03 (0.0115)	A6 1.02, 0.00215 (17.6)	1 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
6	1.23 (0.0105)/ 2.78 (0.0106)	A6 4.76, 0.0105 (50.0)	1 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
7	11.63 (0.100)/ 28.03 (0.106)	3-tert-butylbenzoic acid 7.47, 0.0419 (30.0)	10 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
8	11.63 (0.100)/ 28.03 (0.106)	biphenyl-3-benzoic acid 8.53, 0.0430 (30.0)	10 mL	100 °C/ 24 h	no change in $Zn_4O(FMA)_3$ cubic morphology
MOF-5					
9	100.0 (0.602)/ 500.0 (1.92)	isophthalic acid 50.01, 0.302 (33.4)	10 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology

10	100.0 (0.602)/ 500.0 (1.92)	isophthalic acid 100.0, 0.602 (50.0)	10 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
11	100.0 (0.602)/ 500.0 (1.92)	A1 14.57, 0.0601 (9.1)	10 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
12	100.0 (0.602)/ 500.0 (1.92)	A1 72.58, 0.300 (33.4)	10 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
13	10.02 (0.0603)/ 50.02 (0.192)	A6 5.73, 0.0121 (16.7)	1 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
14	10.05 (0.0604)/ 50.04 (0.192)	A6 28.36, 0.0599 (50.0)	1 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
15	100.0 (0.602)/ 500.0 (1.92)	3-tert-butylbenzoic acid 45.85, 0.257 (30.0)	1 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
16	100.0 (0.602)/ 500.0 (1.92)	biphenyl-3-benzoic acid 50.34, 0.254 (30.0)	1 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
IRMOF-3					
17	75.27 (0.414)/ 300.0 (1.15)	isophthalic acid 35.27, 0.212 (33.9)	10 mL	100 °C/ 24 h	no change in IRMOF-3 cubic morphology
18	75.27 (0.414)/ 300.0 (1.15)	isophthalic acid 75.03, 0.414 (50.0)	10 mL	100 °C/ 24 h	no change in MOF-5 cubic morphology
19	75.27 (0.414)/ 300.0 (1.15)	A1 9.69, 0.0400 (8.8)	10 mL	100 °C/ 24 h	no change in IRMOF-3 cubic morphology
20	75.27 (0.414)/ 300.0 (1.15)	A1 50.04, 0.206 (33.2)	10 mL	100 °C/ 24 h	no change in IRMOF-3 cubic morphology
21	7.57(0.0418)/ 30.07 (0.115)	A6 4.03, 0.00851 (16.9)	1 mL	100 °C/ 24 h	no change in IRMOF-3 cubic morphology
22	7.53(0.0416)/ 30.06 (0.115)	A6 19.57, 0.0413 (49.8)	1 mL	100 °C/ 24 h	no change in IRMOF-3 cubic morphology
23	75.61 (0.414)/ 300.0 (1.15)	3-tert-butylbenzoic acid 32.72, 0.184	10 mL	100 °C/ 24 h	no change in IRMOF-3 cubic morphology

		(30.0)			
24	75.56(0.414)/ 300.0 (1.15)	biphenyl-3-benzoic acid 36.53, 0.184 (30.0)	10 mL	100 °C/ 24 h	no change in IRMOF-3 cubic morphology
SNU-70					
25	37.51 (0.195)/ 75.17 (0.286)	isophthalic acid 4.03, 0.0245 (11.2)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
26	37.53 (0.195)/ 75.01 (0.286)	isophthalic acid 20.07, 0. 122 (38.4)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
27	37.54 (0.195)/ 75.08 (0.286)	A1 5.03,0.0207 (9.6)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
28	37.57 (0.196)/ 75.06 (0.286)	A1 25.05, 0.103 (34.4)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
29	37.51 (0.195)/ 75.03 (0.286)	A2 7.63, 0.0240 (11.0)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
30	37.56 (0.195)/ 75.04 (0.286)	A2 38.15,0.120 (38.1)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
31	37.66 (0.195)/ 75.04 (0.286)	3-tert-butylbenzoic acid 15.07, 0.0849 (30.0)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
32	37.58 (0.195)/ 75.04 (0.286)	biphenyl-3-benzoic acid 16.83, 0.0849 (30.0)	12.5 mL	105 °C/ 16 h	no change in SNU-70 cubic morphology
IRMOF-8					
33	12.43 (0.0574)/ 109.0 (0.416)	isophthalic acid 2.07, 0.0126 (18.0)	10 mL	85 °C/ 24 h	*non-interpenetrated IRMOF-8 cubic morphology crystals were obtained
34	12.43 (0.0574)/ 109.0 (0.416)	isophthalic acid 9.44, 0.0575 (50.0)	10 mL	85 °C/ 24 h	*non-interpenetrated IRMOF-8 cubic morphology crystals were obtained

35	12.43 (0.0574)/ 109.0 (0.416)	A1 2.89, 0.0119 (17.2)	10 mL	85 °C/ 24 h	*non-interpenetrated IRMOF-8 cubic morphology crystals were obtained
36	12.42 (0.0574)/ 109.0 (0.416)	A1 13.32, 0.0550 (49.1)	10 mL	85 °C/ 24 h	*non-interpenetrated IRMOF-8 cubic morphology crystals were obtained
37	12.47 (0.0576)/ 109.0 (0.416)	A2 3.50, 0.0109 (15.8)	10 mL	85 °C/ 24 h	*non-interpenetrated IRMOF-8 cubic morphology crystals were obtained
38	12.33 (0.0571)/ 109.0 (0.416)	A2 17.52, 0.0551 (49.1)	10 mL	85°C/ 24 h	*non-interpenetrated IRMOF-8 cubic morphology crystals were obtained
39	37.66 (0.195)/ 75.04 (0.286)	3-tert-butylbenzoic acid 4.41, 0.0248 (30.0)	10 mL	85°C/ 24 h	interpenetrated IRMOF-8 (CSD refocode: IDIXAU) needle morphology crystals morphology Obtained
40	37.58 (0.195)/ 75.04 (0.286)	biphenyl-3-benzoic acid 4.87, 0.0246 (30.0)	10 mL	85°C/ 24 h	interpenetrated IRMOF-8 (CSD refocode: IDIXAU) needle morphology crystals morphology Obtained

*Addition of diagonal cluster spacing C to C distance mismatched additives effectively suppresses the formation of an interpenetrated IRMOF-8 framework (Confirmed from indexing obtained crystals through single crystal X-ray diffraction analysis reveal that cell parameters consistent with reported single crystal X-ray structure for non-interpenetrated IRMOF-8 (CSD refcode: EDUTUS).

SI 5. In situ crystal growth monitoring

Data acquisition was conducted with the 20 mL vial at 100 °C. H_2BDC (25.08 mg, 0.150 mmol), $Zn(NO_3)_2{\cdot}4H_2O$ (250.0 mg, 0.956 mmol), A3 additive (20.07 mg, 0.0505 mmol (25.0 mol%)), and 10 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and solution was clarified by filtration. This solution was inserted into the preheated block and held for the duration of synthesis (~24 hours). The camera was externally hooked up to a desktop computer with the software package DSLR Remote Pro for time-lapse shooting. Specific parameters for time-lapse/ bulb shooting include: 1 frame every 30 seconds for 24 hours, F stop 6.3.

In situ camera setup

The camera setup comprises the following components: Canon EOS 5DS DSLR camera, Canon MP-E 65mm f/2.8 1.5-5x Macro lens, circular aluminum block with a hole in the center (drilled for 20 mL vial), 4 x 4 x 1/8'' quartz plate, heating tape capable of 313 Watts of power, J-KEM Scientific temperature controller model 210, a thermocouple, red silicone rubber, 1 band clamp, ring light for overhead illumination, and focused fiber optic light source for bottom illumination.

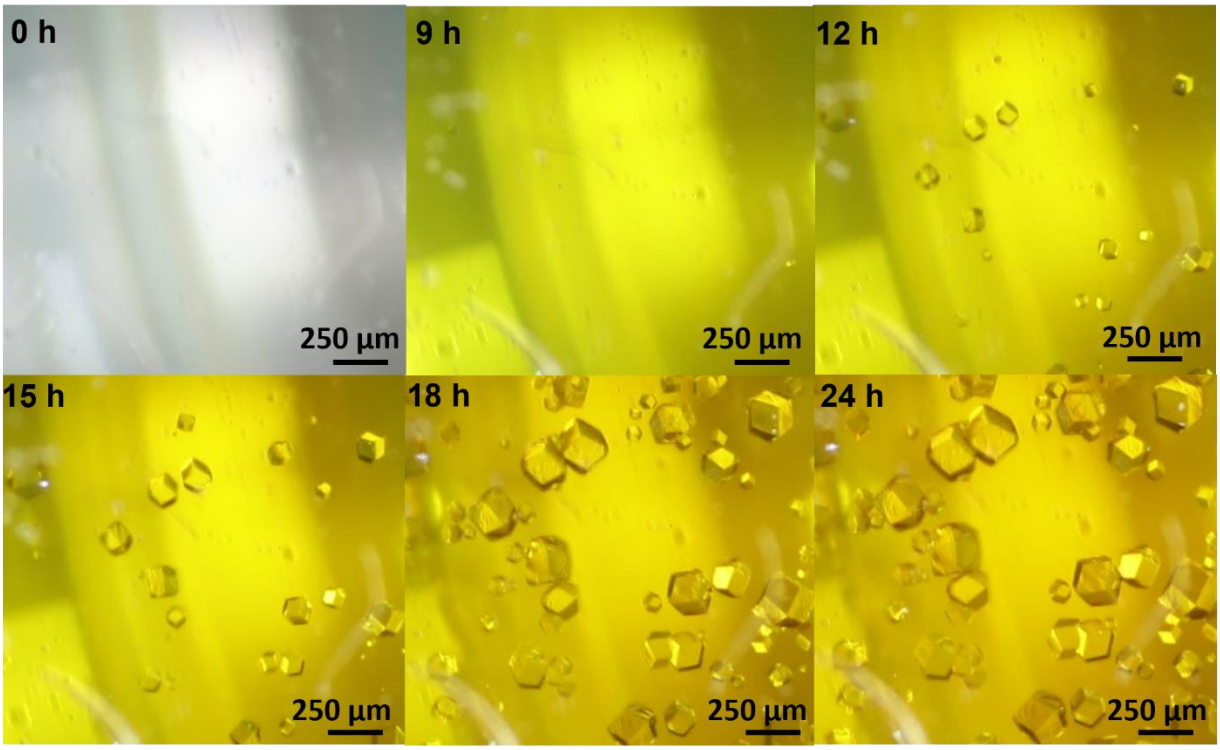


Figure S34. Optical images showing crystal growth of MOF-5-R_d-A3 in presence of A3 additive in DEF during reaction at 100 °C.

SI 6. Instrumental details

Optical microscopy

Inverted Leica DMIL LED optical microscopy was used to determine morphologies and suitable images collected and represented in Figure 2, 3 and 4.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) data of all samples of MOF-5 were collected on a PANalytical Empyrean diffractometer in Bragg-Brentano geometry using Cu-Kα radiation (λ = 1.54187 Å), operating at 45 kV and 40 mA. The incident beam was equipped with a Bragg-BrentanoHD X-ray optic using fixed slits/soller slits. The detector was a silicon-based linear position sensitive X'Celerator Scientific operating in 1-D scanning mode. Data were collected from 5 to 50° 2θ using a step size of 0.0083° and a count time of at least 10 s per step. Powder patterns were processed using Data Viewer PANalytical and OriginPro 8 software.

Single crystal X-ray diffraction

Cell parameters were evlauated using a Rigaku XtaLAB Synergy-S X-ray diffractometer configured with a kappa goniometer geometry. X-ray intensities were measured at 298 K (room temperature) with the HyPix-6000HE detector placed 32 mm from the sample.

Gas sorption measurements

Sorption experiments were carried out using a NOVA e series 4200 surface area analyzer (Quantachrome Instruments, Boynton Beach, Florida, USA). N_2 (99.999%) was purchased from Cryogenic Gases and used as received. For N_2 measurements, a glass sample cell was charged with ~30 mg sample and analyzed at 77 K. Sorption isotherms were collected in the NOVAwin software.

^{1}H-NMR and ^{13}C-NMR measurements

^{1}H NMR measurements were carried out on Varian MR400 (400 MHz (9.4 Tesla)) and Varian Vnmrs 700 (700 MHz (17.6 Tesla)) spectrometers. ^{13}C NMR measurements were carried out on Varian MR400 (100 MHz (9.4 Tesla). Compounds 1-4 and **A6** were dissolved in DMSO-d_6 solution (500 µL DMSO-d_6) and all MOFs new morphologies were digested in DCl/DMSO-d_6 solution (500 µL DMSO-d_6 + 50 µL of 35 wt % DCl in D_2O).

SI 7. References

[1] Barnard, R. A.; Dutta, A.; Schnobrich, J. K.; Morrison, C. N.; Ahn, S.; Matzger, A. J. *Chem. Eur. J.,* 2016, **21**, 5954-5961.