Supporting Information for

Orthogonal Ternary Functionalization of a Mesoporous Metal-Organic Framework via Sequential Postsynthetic Ligand Exchange

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1. General procedures

All purchased chemicals were used without further purification except where otherwise stated. All DMF used for washing crystals was pre-dried over 4Å molecular sieves.

X-Ray powder diffraction patterns were collected using a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu K α , (λ = 1.5406 Å) with a scan speed of 0.10 sec/step from 2.5 to 20° at a step size of 0.02°. The data were analyzed using the EVA program from the Bruker Powder Analysis Software package. The simulated powder patterns were calculated using Materials Studio based on single crystal data of N₃-bMOF-100.

¹H-NMR spectra were obtained using Bruker Avance III 300/400/500 MHz spectrometers. Chemical shifts are in parts per million using the residual solvent peak (Chloroform-*d*, DMSO-*d*₆) as references.

Microspectrophotometric experiments were performed on a CRAIC QDI 2010 microspectrophotometer equipped with a 420 nm filter. The sampling area was fixed at 31 \times 31 μ m, and the integration time was fixed at 971.60 ns for all acquired fluorescence spectra.

Optical microscopic images were obtained using an Olympus BH-2 microscope.

LC-MS analyses were performed on a Shimadzu LCMS-2020 instrument. The LC method used was 6 minute running time with a constant ratio of 1:1 acetonitrile:water at a constant flow rate of 0.2 mL/min. In this method the samples do not pass through a chromatographic column; therefore, there is virtually no separation of the components. So in Section 5, the chromatograms are omitted, the mass spectra represent the samples' composition. The ionization interface was simultaneous ESI & APCI.

2. Syntheses of substituted H₂-BPDC ligands

2.1 dimethyl 2-amino-1,1'-biphenyl-4,4'-dicarboxylate (Compound 1)

Compound **1** was synthesized according to the literature. ¹ H NMR (400 MHz, CDCl₃) δ 8.13 (m, 2H), 7.55 (m, 2H), 7.48 (dd, J = 7.9, 1.4 Hz, 1H), 7.45 (d, J = 1.4 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.86 (s, 2H).

2.2 2-amino-1,1'-biphenyl-4,4'-dicarboxylic acid (Compound 2)

Compound **1** (990 mg, 3.47 mmol) was dissolved in THF (35 mL) and MeOH (25 mL). The resulting solution was then mixed with a solution of KOH (2 g, 35.7 mmol) in DI H₂O (40 mL). The reaction mixture was heated to reflux overnight. After all the volatiles were removed *in vacuo*, it was diluted with DI H₂O and acidified with 1M HCl solution until pH = 2. The precipitates were collected via centrifugation, washed with DI H₂O, and dried in air. Compound **2** was collected as a yellow solid (857 mg, 96 %). ¹H NMR (400 MHz, DMSO- d_6) δ 12.92 (s, 2H), 8.01 (m, 2H), 7.57 (m, 2H), 7.41 (d, J = 1.5 Hz, 1H), 7.21 (dd, J = 7.9, 1.5 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 5.15 (s, 2H).

2.3 2-azido-1,1'-biphenyl-4,4'-dicarboxylic acid (Compound 3)

$$\mathsf{HOOC} \overset{\mathsf{N}_3}{\longleftarrow} \mathsf{COOF}$$

Compound **3** was synthesized according to the literature.¹ ¹H NMR (400 MHz, DMSO- d_6) δ 13.26 (s, 2H), 8.03 (m, 2H), 7.85 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.65 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H).

S3

2.4 methyl 4-bromo-3-formylbenzoate (Compound 4)

Compound **4** was synthesized according to the literature.² ¹H NMR (300 MHz, CDCl₃) δ 10.39 (s, 1H), 8.54 (d, J = 2.2 Hz, 1H), 8.09 (dd, J = 8.3, 2.2 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 3.95 (s, 3H).

2.5 dimethyl 2-formyl-1,1'-biphenyl-4,4'-dicarboxylate (Compound 5)

Compound **4** (729 mg, 3 mmol), 4-Methoxycarbonylphenylboronic acid (810 mg, 4.5 mmol), Pd(dppf)Cl₂ (66 mg, 0.09 mmol), and Cs₂CO₃ (2.93 g, 9 mmol) were mixed with DMF (10 mL) and stirred at 90 °C for 16 hours. DI H₂O (100 mL) was added and the mixture was extracted with DCM (25 mL, 3x). The organic layer was washed with DI H₂O (125 mL), brine (125 mL), and dried over MgSO₄. After filtration, the solution was concentrated and purified via column chromatography over 230-400 mesh silica gel (DCM : hexanes = 2 : 1 to DCM) to yield compound **5** as a yellow-white solid (465mg, 52 %). ¹H NMR (300 MHz, CDCl₃) δ 9.98 (s, 1H), 8.69 (d, J = 1.8 Hz, 1H), 8.31 (dd, J = 8.0, 1.8 Hz, 1H), 8.17 (m, 2H), 7.55 (d, J = 8.1 Hz, 1H), 7.48 (m, 2H), 3.99 (s, 3H), 3.97 (s, 3H).

2.6 2-formyl-1,1'-biphenyl-4,4'-dicarboxylic acid (Compound 6)

Compound **5** (239 mg, 0.8 mmol) was dissolved in THF (3 mL) and then mixed with a clear solution of LiOH·H₂O (201 mg, 4.8 mmol) in DI H₂O (1 mL) and MeOH (1 mL). The reaction mixture was stirred at room temperature for 24 hrs. Thereafter, all the volatiles were removed *in vacuo*, the reaction mixture was diluted with DI H₂O and acidified with 1M HCl solution. The precipitates were collected via filtration and dried *in vacuo*. Compound **6** was collected as an off-white solids (205 mg, 95 %). ¹H NMR (400 MHz, DMSO- d_6) δ 13.26 (s, 2H), 9.92 (s, 1H), 8.46 (d, J = 1.7 Hz, 1H), 8.27 (dd, J = 8.0, 1.7 Hz, 1H), 8.08 (m, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.63 (m, 2H).

3. Solvothermal MOF syntheses

bMOF-100 crystals were synthesized based on the literature protocol.³ N₃-bMOF-100 crystals were synthesized based on the literature protocol.¹ The assynthesized materials were washed as described in the following sections.

The mass of MOFs used for subsequent experiments was determined after the DMF-washed crystals were dried under Ar flow to the point that they become free-flowing solids.

4. Ligand exchange experiments

4.1 Ligand exchange on bMOF-100

bMOF-100 (6 mg) was washed with DMF(6x) in a 1.5 mL centrifuge tube. After removing most of the solvent while keeping the crystals wet, a DMF solution of compounds **2** or **3** or **6** (0.05 M, 0.5 mL) was added. The tube was placed in a 75 °C oven for 24 hours.

The crystals were imaged after the reaction (Figures S1-S3).

PXRD patterns were collected to assess the crystallinity after reaction (Figure S4). For PXRD sample preparation, the crystals were washed with DMF (3x), soaked in DMF at 75 °C for 30 minutes, washed with DMF (3x), soaked in DMF at 75 °C for another 30 minutes, and finally washed with DMF again (3x).

For 1 H NMR analysis, after following steps in the previous paragraph, the crystals were washed with DCM (3x), soaked in DCM at room temperature for at least 1 hour, washed with DCM (3x), and then dried under argon flow. Then, the crystals were dissolved in DMSO- d_6 (0.7 mL) and DCI in D₂O (37%, 0.006 mL) for 1 H NMR analysis to determine the ligand composition and exchange percentage (Figure S5).

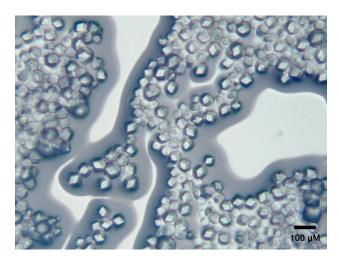


Figure S1. bMOF-100 crystals after ligand exchange with compound 2

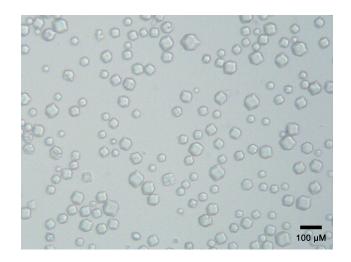


Figure S2. bMOF-100 crystals after ligand exchange with compound 3.

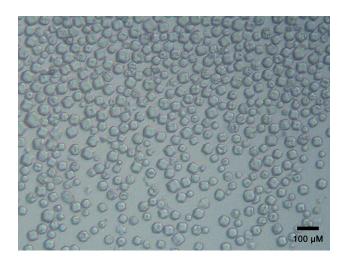


Figure S3. bMOF-100 crystals after ligand exchange with compound **6**.

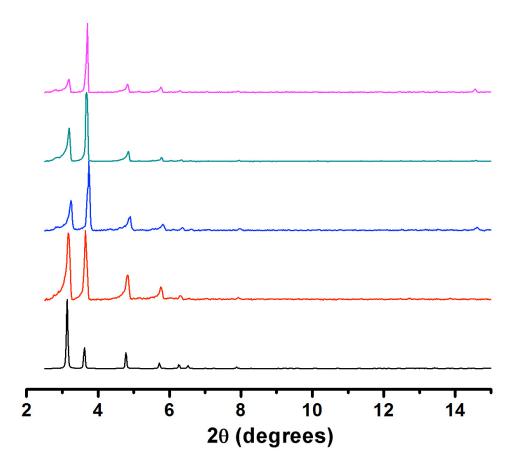


Figure S4. PXRD patterns for as-synthesized bMOF-100 crystals (red) and after ligand exchange with compounds **2** (magenta), **3** (cyan), and **6** (blue). The pattern simulated from single crystal data is shown in black.

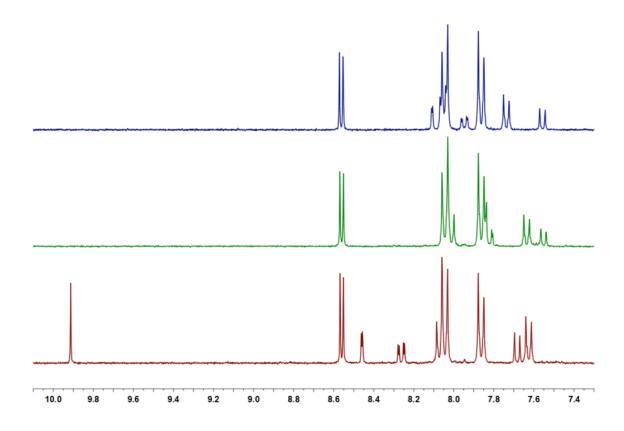


Figure S5. ¹H NMR spectra of dissolved crystals after ligand exchange with compounds **2** (blue), **3** (green), and **6** (red). The integration values of non-overlapping peaks for the two ligands were compared to determine the amount of ligand exchange.

4.2 Ligand exchange on N₃-bMOF-100

4.2.1 difunctionalization

N₃-bMOF-100 (6 mg) was washed with DMF (6x) in a 1.5 mL centrifuge tube. After removing most of the solvent while keeping the crystals wet, a DMF solution of **2** or **6** (0.05 M, 0.5 mL) was added. The tube was incubated in a 35 °C thermomixer (600 rpm) for various time periods.

For PXRD sample preparation, the crystals were washed with DMF (3x), soaked in DMF at 75 °C for 30 minutes, washed with DMF (3x), soaked in DMF at 75 °C for another 30 minutes, and finally washed with DMF again (3x).

For 1 H NMR analysis, after following steps in the previous paragraph, the crystals were washed with DCM (3x), soaked in DCM at room temperature for at least 1 hour, washed with DCM (3x), and then dried under argon flow. Then, the crystals were dissolved in DMSO- d_6 (0.7 mL) and DCI in D₂O (37%, 0.006 mL) for 1 H NMR analysis to determine the ligand composition and exchange percentage (Figures S6 and S8).

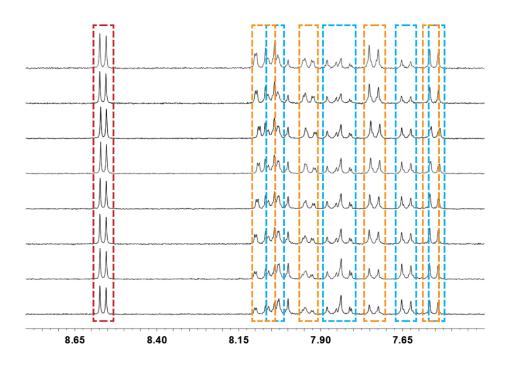


Figure S6. ¹H NMR spectra of dissolved N₃-bMOF-100 crystals after ligand exchange with compound **2** (red: adenine; blue: N₃-BPDC; yellow: NH₂-BPDC). The integration values of non-overlapping peaks for the two ligands were compared to determine the amount of ligand exchange.

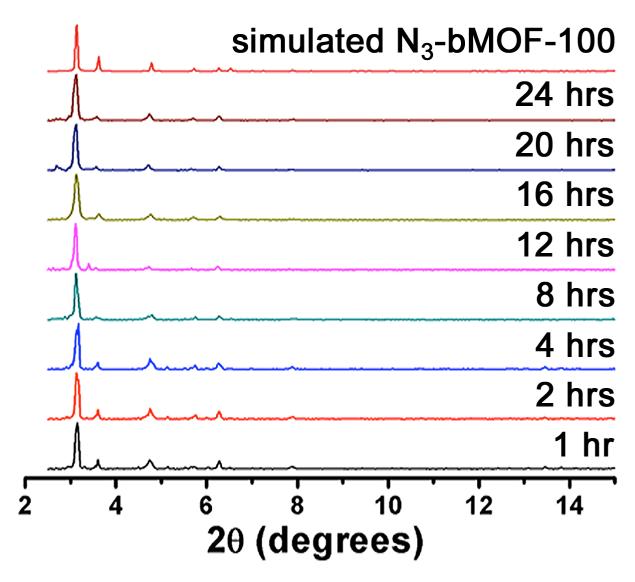


Figure S7. Enlarged Figure 2E, comparing MOFs at different exchange time points with simulated pattern.

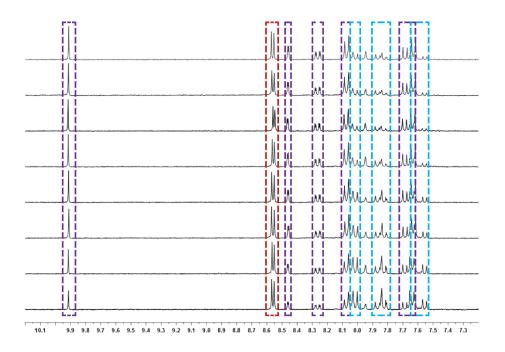


Figure S8. ¹H NMR spectra of dissolved N₃-bMOF-100 crystals after ligand exchange with compound **6** (red: adenine; blue: N₃-BPDC; purple: F-BPDC). The integration values of non-overlapping peaks for the two ligands were compared to determine the amount of ligand exchange.

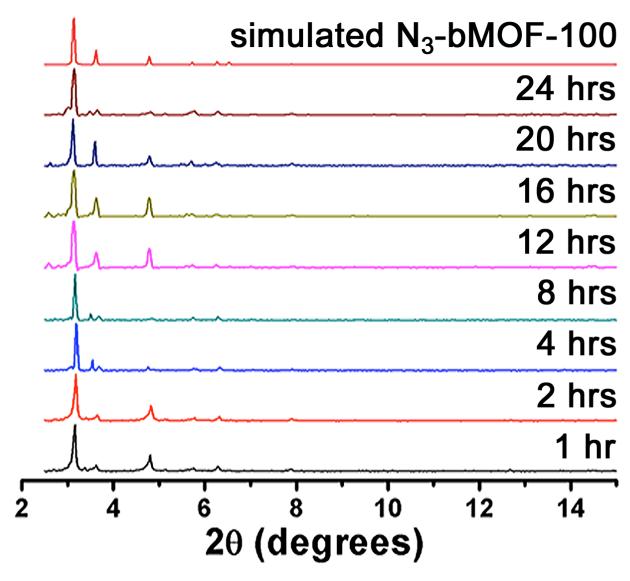


Figure S9. Enlarged Figure 2B, comparing MOFs at different exchange time points with simulated pattern.

4.2.2 trifunctionalization

4.2.2.1 N₃-bMOF-100 exchanged with H₂-F-BPDC and then H₂-NH₂-BPDC

N₃-bMOF-100 (6 mg) was washed with DMF (6x) in a 1.5 mL centrifuge tube. After removing most of the solvent while keeping the crystals wet, a DMF solution of **6** (0.05 M, 0.5 mL) was added. The tube was incubated in a 35 °C thermomixer (600 rpm) for 4 hours. The crystals were washed with DMF (3x), soaked in DMF at 75 °C for 30 minutes, washed with DMF (3x), soaked in DMF at 75 °C for another 30 minutes, and then washed again with DMF (3x). Then, the supernatant was removed and the crystals were added to a DMF solution of **2** (0.05 M, 0.5 mL) and incubated in a 35 °C thermomixer (600 rpm) for 1, 2, 4, or 6 hour(s).

For PXRD sample preparation, the crystals were washed with DMF (3x), soaked in DMF at 75 °C for 30 minutes, washed with DMF (3x), soaked in DMF at 75 °C for another 30 minutes, and finally washed with DMF again (3x).

For 1 H NMR analysis, after following steps in the previous paragraph, the crystals were washed with DCM (3x), soaked in DCM at room temperature for at least 1 hour, washed with DCM (3x), and then dried under argon flow. Then, the crystals were dissolved in DMSO- d_6 (0.7 mL) and DCI in D₂O (37%, 0.006 mL) for 1 H NMR analysis to determine the ligand composition and exchange percentage (Figure S10).

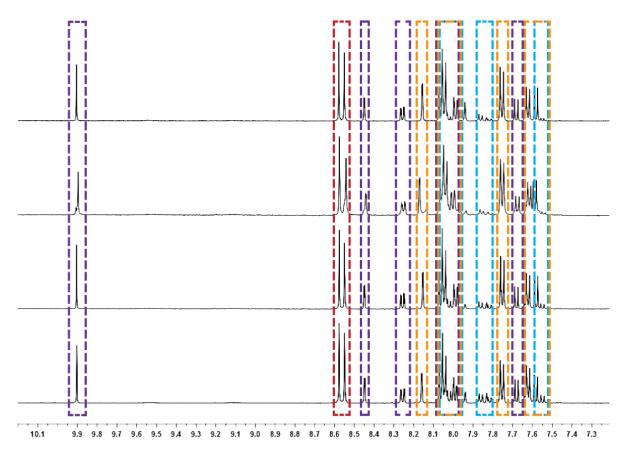


Figure S10 ¹H NMR spectra of dissolved N₃-bMOF-100 crystals after ligand exchange with compound **6** and then **2**. From top to bottom: 6, 4, 2, 1 hour(s) exchange with compound **2** (red: adenine; blue: N₃-BPDC; purple: F-BPDC; yellow: NH₂-BPDC). The integration values of non-overlapping peaks for the three ligands were compared to determine the composition. We note that no peaks were observed that correspond to the imine adduct of F-BPDC and NH₂-BPDC.

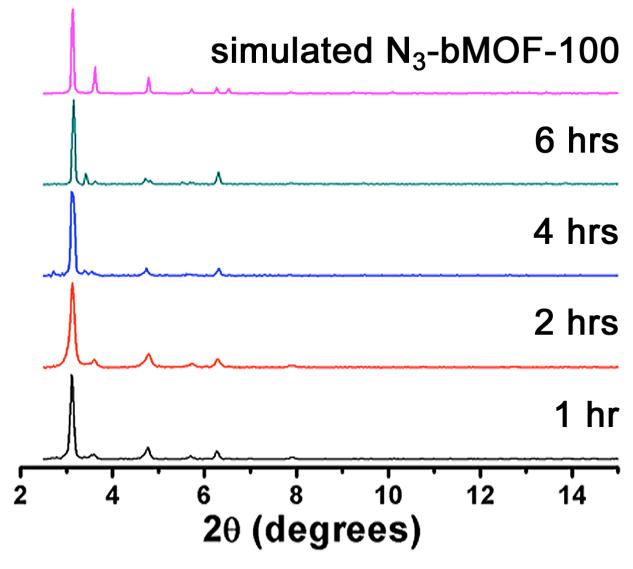


Figure S11. Enlarged Figure 3B, comparing MOFs at different exchange time points with simulated pattern.

4.2.2.2 N₃-bMOF-100 exchanged with H₂-NH₂-BPDC and then H₂-F-BPDC

 N_3 -bMOF-100 (6 mg) was washed with DMF (6x) in a 1.5 mL centrifuge tube. After removing most of the solvent while keeping the crystals wet, a DMF solution of **2** (0.05 M, 0.5 mL) was added. The tube was incubated in a 35 °C thermomixer (600 rpm) for 6 hours. The crystals were washed with DMF (3x), soaked in DMF at 75 °C for 30 minutes, washed with DMF (3x), soaked in DMF at 75 °C for another 30 minutes, and then washed again with DMF (3x). Then, the supernatant was removed and the crystals were added to a DMF solution of **6** (0.05 M, 0.5 mL) and incubated in a 35 °C thermomixer (600 rpm) for 1, 2, 4, or 6 hour(s).

For PXRD sample preparation, the crystals were washed with DMF (3x), soaked in DMF at 75 °C for 30 minutes, washed with DMF (3x), soaked in DMF at 75 °C for another 30 minutes, and finally washed with DMF again (3x).

For 1 H NMR analysis, after following steps in the previous paragraph, the crystals were washed with DCM (3x), soaked in DCM at room temperature for at least 1 hour, washed with DCM (3x), and then dried under argon flow. Then, the crystals were dissolved in DMSO- d_6 (0.7 mL) and DCl in D₂O (37%, 0.006 mL) for 1 H NMR analysis to determine the ligand composition and exchange percentage (Figure S12).

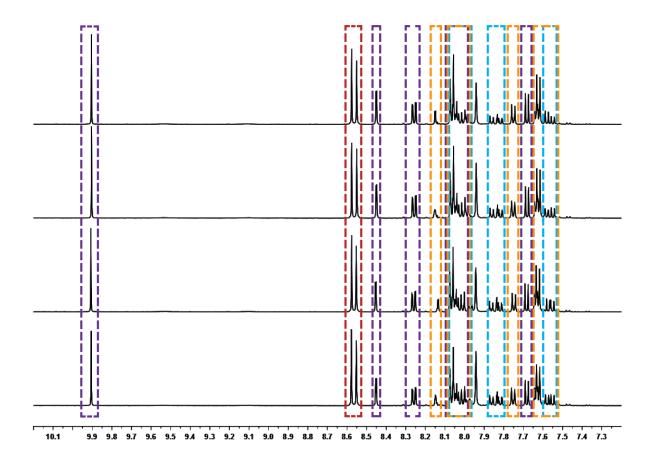


Figure S12. ¹H NMR spectra of dissolved N₃-bMOF-100 crystals after ligand exchange with compound **2** and then **6**. From top to bottom: 6, 4, 2, 1 hour(s) exchange with compound **6** (red: adenine; blue: N₃-BPDC; purple: F-BPDC; yellow: NH₂-BPDC). The integration values of non-overlapping peaks for the three ligands were compared to determine the composition. We note that no peaks were observed that correspond to the imine adduct of F-BPDC and NH₂-BPDC.

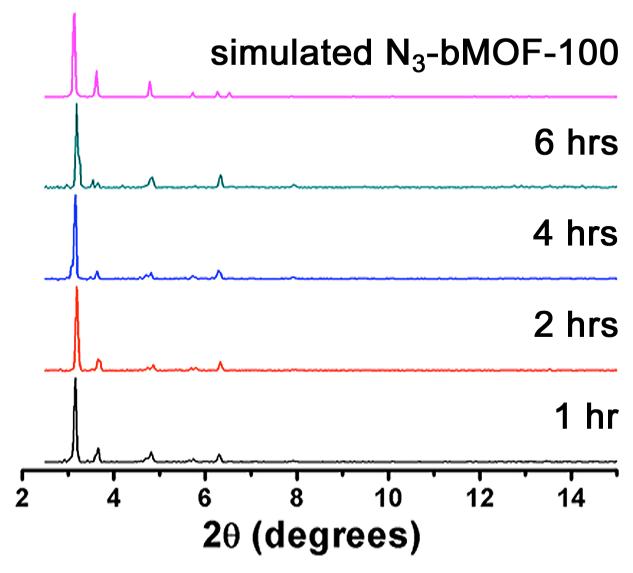


Figure S13. Enlarged Figure 3E, comparing MOFs at different exchange time points with simulated pattern.

5. Postsynthetic incorporation of DBCO carboxyrhodamine 110 and BHQ-1 amine

5.1 Estimation of the molecular geometry of the dye and quencher

Models of the two molecules were created in ChemBio3D Ultra 11.0 and then imported into Scigress as c3xml files. Geometry optimization was done using B88LYP DFT functional and DGauss double zeta double valence polarization (DZVP) basis set. Then, the molecule was fitted into an orthorhombic box, considering the atoms' van der Waals radii. The dimensions of the orthorhombic box are used to estimate the molecule's size (Figures S14, S15).

DBCO carboxyrhodamine 110 has a long flexible spacer chain between the DBCO and dye components. Therefore, the calculated box is not rigid, but is an approximation of the maximum possible molecular dimensions.

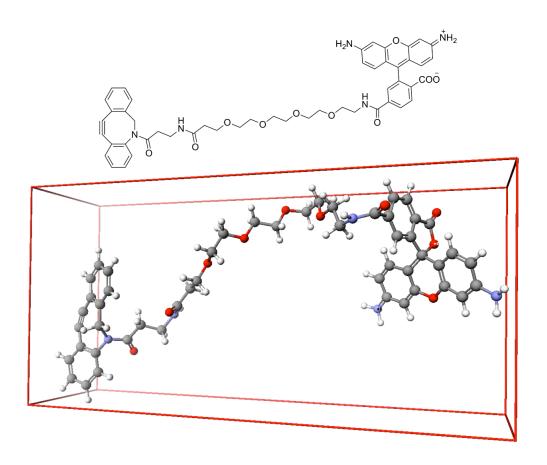


Figure S14. Structure and optimized geometry of DBCO carboxyrhodamine 110 (box dimensions: $8.489 \text{ Å} \times 15.283 \text{ Å} \times 31.636 \text{ Å}$).

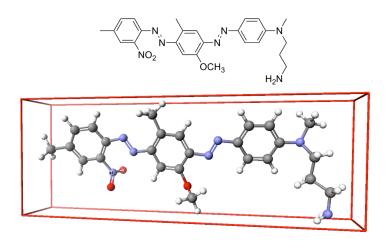


Figure S15. Structure and optimized geometry of BHQ-1 amine (box dimensions: $3.882 \text{ Å} \times 8.527 \text{ Å} \times 23.761 \text{ Å}$).

5.2 DBCO carboxyhodamine 110 incorporation.

 N_3 -bMOF-100 (3 mg, containing 1.08×10^{-3} mmol N_3 groups) was washed with DMF (6x) in a 1.5 mL centrifuge tube. After removing most of the solvent while keeping the crystals wet, a DMF solution of **6** (0.05 M, 0.5 mL) was added. The tube was incubated in a 35 °C thermomixer (600 rpm) for 4 hours. The crystals were washed with DMF (3x), soaked in DMF at 75 °C for 30 minutes, washed with DMF (3x), soaked in DMF at 75 °C for another 30 minutes, and then washed with DMF (3x). Then, the supernatant was removed and the crystals were added to a solution of DBCO carboxyrhodamine 110 (1 mg, 1.58×10^{-3} mmol) in DMF (0.2 mL) and incubated in a 25 °C thermomixer (600 rpm) for 16 hours.

5.3 LC-MS characterization of DBCO carboxyrhodamine 110 incorporation.

After reaction, the supernatant was analyzed via LC-MS. The molecular weight of DBCO carboxyrhodamine 110 is 879.35 g/mol. In positive ion mode, m/z = 880 can be assigned to $[M+H]^+$, and m/z = 441 can be assigned to $[M+2H]^{2+}$. In negative ion mode, m/z = 878 can be assigned to $[M-H]^-$. In the negative mode, there are no peaks that correlate to the degradation product of the MOFs (e.g. H_2 - N_3 -BPDC or H_2 -F-BPDC) (Figure S16).

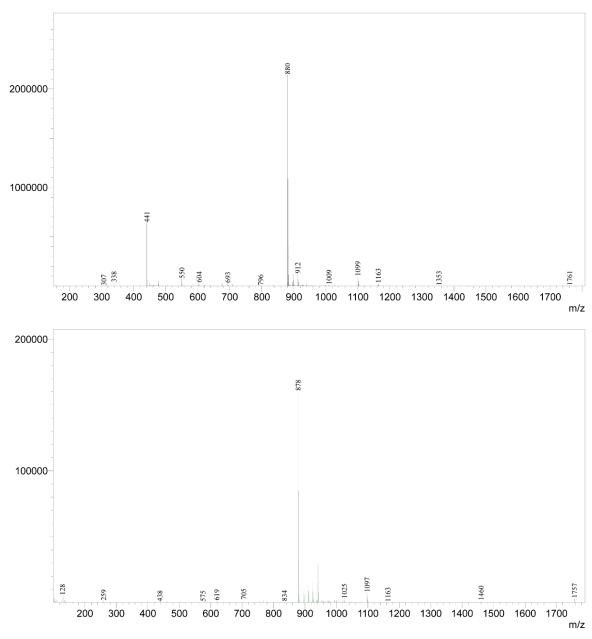


Figure S16. Mass spectra of supernatant after DBCO carboxyrhodamine 110 incorporation reaction (top: positive; bottom: negative).

After analysis of the supernatant, the crystals were washed with DMF (4x). The supernatant from the fourth wash was analyzed via LC-MS. A small amount of DBCO carboxyrhodamine 110 was present (note that the peak intensities are very low compared to Figure S16).

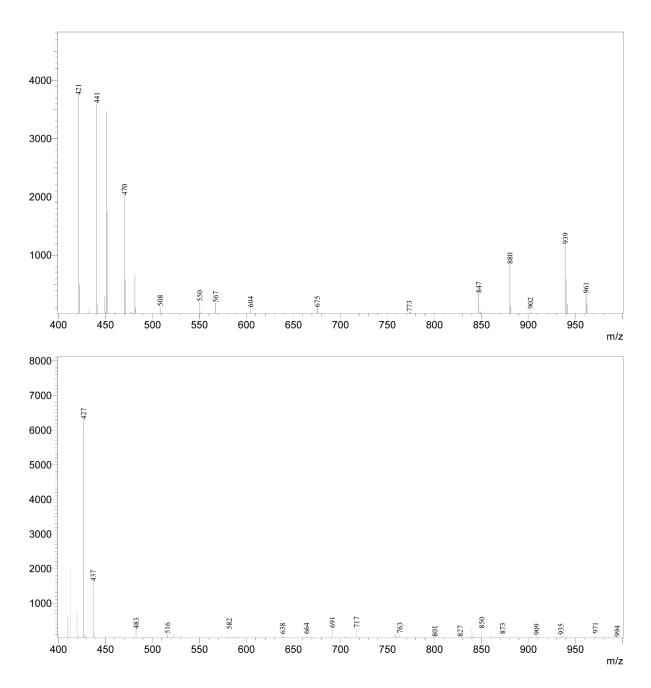


Figure S17. Mass spectra of supernatant after the fourth DMF wash after DBCO carboxyrhodamine 110 incorporation reaction (top: positive; bottom: negative).

Finally, the crystals were soaked again in DMF for 12 additional hours. The (fifth) supernatant was analyzed via LC-MS. No DBCO carboxyrhodamine 110 was present. Therefore, there is no significant leakage and any dye remaining associated with the MOF is most likely covalently attached through the postsynthetic 'click' modification.

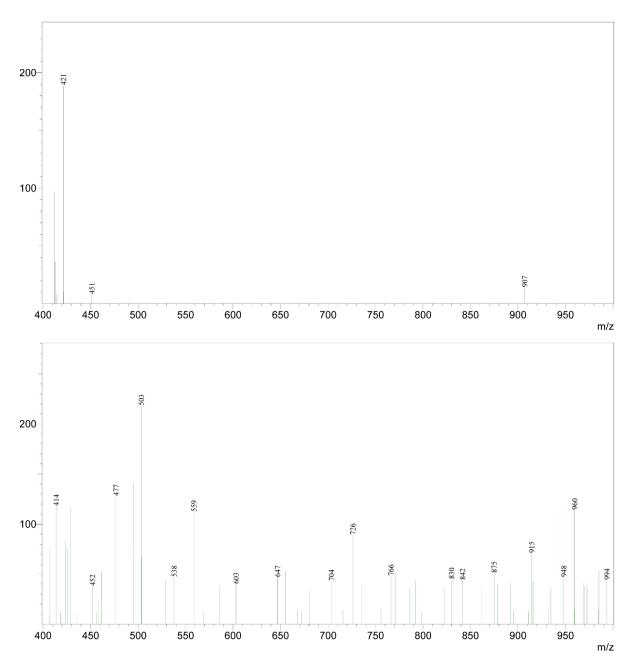


Figure S18 Mass spectra of the fifth supernatant after 12-hour leakage test (top: positive; bottom: negative).

~20-30 crystals were digested with a few drops of 1M NaOH/DI H_2O in 0.15 mL DMF; the resulted solution was analyzed via LC-MS. In the negative mode, m/z = 1161 can be assigned to the [M-H]⁻ of the click product; m/z = 269 can be assigned to the [M-H]⁻ of unreacted H_2 -F-BPDC (not affected by the 'click' reaction). There is no significant peak corresponding to H_2 - N_3 -BPDC (m/z = 282).

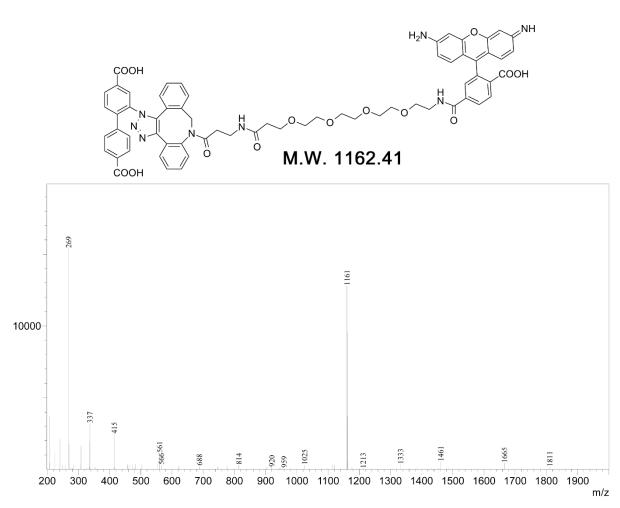


Figure S19. Mass spectrum of digested N_3 /F-bMOF-100 after reaction with DBCO carboxyrhodamine 110 (negative mode).

5.4 BHQ-1 amine incorporation.

After performing the 'click' reaction to incorporate the dye and after performing the dye leakage test through multiple DMF washes (see above), the MOF crystals were soaked in a solution of BHQ-1 amine (2mg, 4.21×10⁻³ mmol) in DMF (0.2 mL) and incubated in a 25 °C thermomixer (600 rpm) for 16 hours.

5.5 LC-MS characterization of BHQ-1 amine incorporation.

After reaction, the supernatant was analyzed via LC-MS. The molecular weight of BHQ-1 amine is 475.23. In positive mode, m/z = 476 can be assigned to $[M+H]^+$. In negative mode, m/z = 1161 (dye-BPDC product) and m/z = 269 (H₂-F-BPDC) indicate that MOF is degrading to some extent, possibly due to the basic nature of BHQ-1 amine.

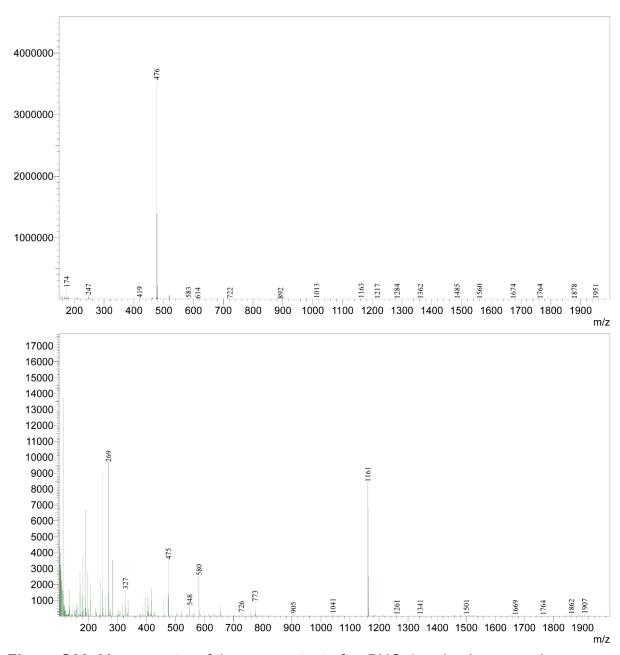


Figure S20. Mass spectra of the supernatant after BHQ-1 amine incorporation reaction (top: positive; bottom: negative).

After analysis of the supernatant, the crystals were washed with DMF (8x). The supernatant from the eighth wash was analyzed via LC-MS. Only a very small amount of BHQ-1 amine was present (m/z = 476, positive mode) (note that the intensities are very low compared to Figure S20).

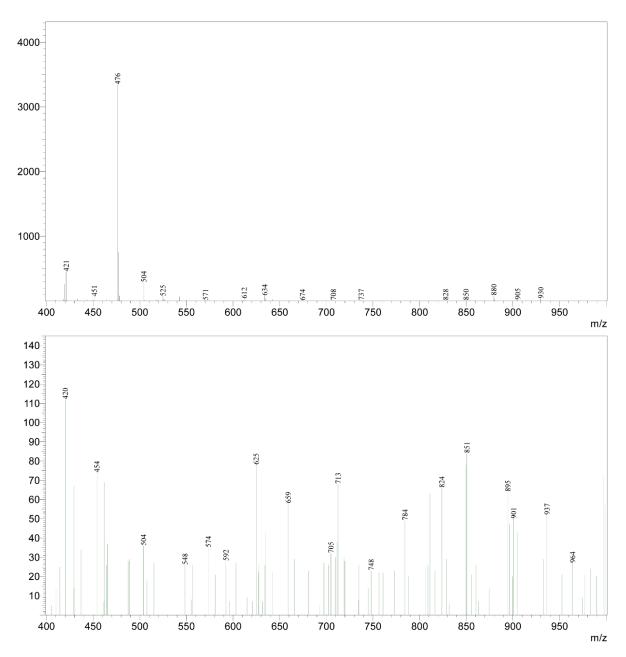


Figure S21. Mass spectra of supernatant after the eighth DMF wash after BHQ-1 amine incorporation reaction (top: positive; bottom: negative).

Finally, the crystals were soaked again in DMF for 8 hours. Then, then the (ninth) supernatant was analyzed via LC-MS. Only a very small amount of BHQ-1 amine was present (m/z = 476, positive mode). We concluded that most of the quencher is likely covalently attached to the MOF through the postsynthetic aldehyde-amine condensation reaction.

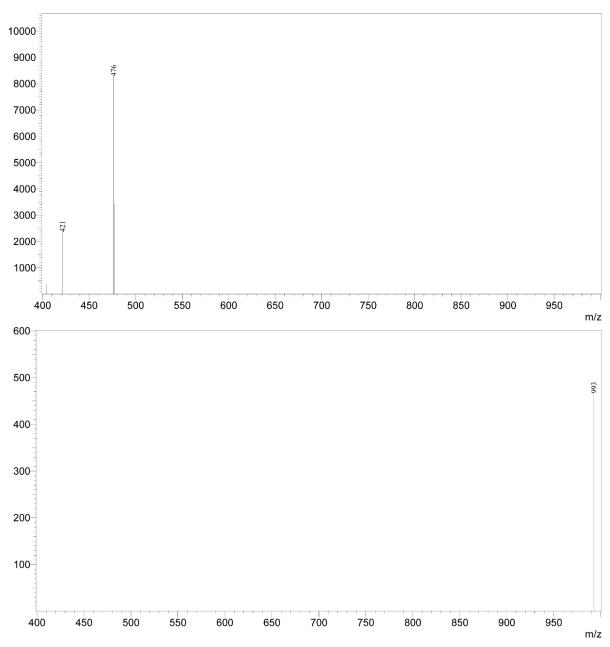


Figure S22. Mass spectra of the ninth supernatant after 8-hour leakage test (top: positive; bottom: negative)

We note that the dissolution conditions could reverse the formation of the imine linkage, releasing free BHQ-1 amine. To confirm imine formation between BHQ-1 amine and F-BPDC in the MOF sample, we attempted to reduce the imine bonds to permanent secondary amines. ~20-30 crystals were treated with a few drops of 1M NaBH₄/MeOH in 0.15 mL MeOH for 10 minutes. Then, the crystals were dissolved with 1M NaOH/H₂O and some DMF for LC-MS analysis. In the positive mode, m/z = 730 can be assigned to $[M+H]^+$ of the secondary amine (reduced imine product). m/z = 476 can be assigned to $[M+H]^+$ of BHQ-1 amine; its presence indicates the incomplete reduction of the imine. Some imine may have degraded into the original BHQ-1 amine and F-BPDC, which is indeed found in the negative mode (m/z = 269). Also, in the negative mode, m/z = 1162 can be assigned to the $[M-H]^-$ (1161 rounded up by software).

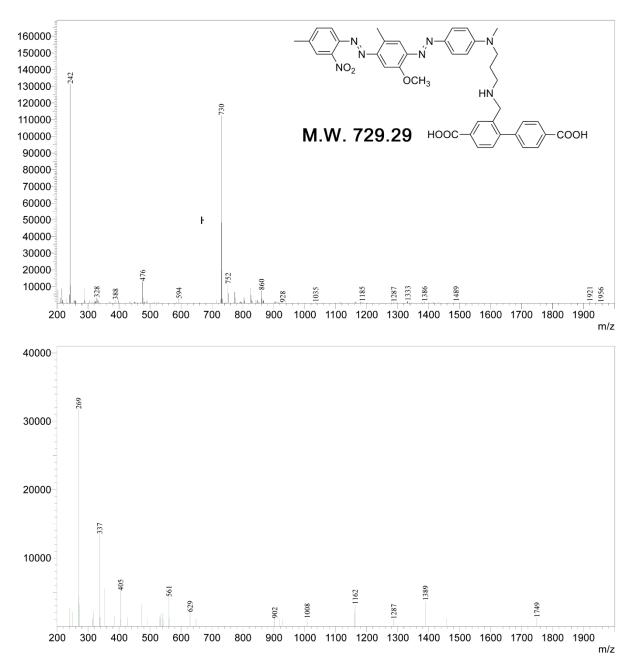


Figure S23. Mass spectra of digested N₃/F-bMOF-100 after reaction with DBCO carboxyrhodamine 110 and BHQ-1 amine (top: positive mode; bottom: negative mode).

5.6 Picture of MOFs before and after dye/quencher incorporation

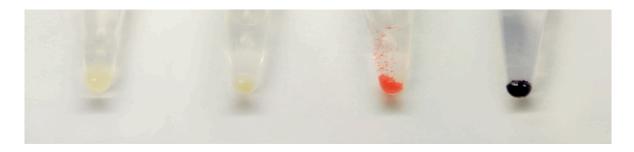


Figure S24 From left to right: N_3 -bMOF-100, N_3 /F-bMOF-100, dye-incorporated, dye/quencher-incorporated.

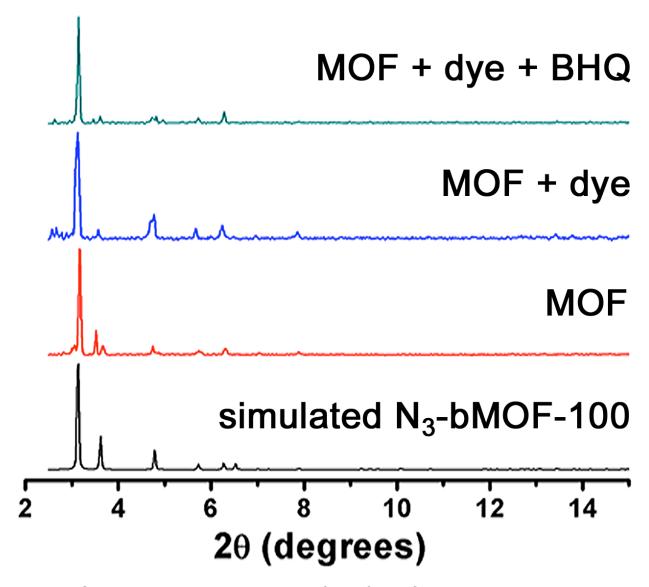


Figure S25. Enlarged Figure 4B, PXRD of modified MOFs compared to simulated pattern.

6. Microspectrophotometry.

Using methods described in previous sections, all the MOFs used for microspectrophotometric experiments were properly washed with DMF and dried *in vacuo*. N_3 /F-bMOF-100 (abbreviated as MOF in this section), N_3 /F-bMOF-100 with carboxyrhodamine 110 (abbreviated as MOF + dye), N_3 /F-bMOF-100 with carboxyrhodamine 110 and BHQ-1 amine (abbreviated as MOF + dye + BHQ), and ground samples of the latter two were placed on glass slides for microspectrophotometric measurements.

Aside from the spectra and images shown in Figure 4, two other parallel samplings were performed. The results are shown below.

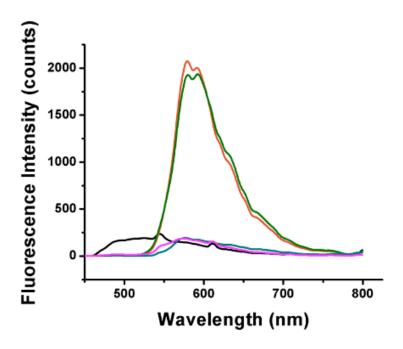


Figure S26. Fluorescence spectra excited at 420 nm (black: MOF; orange: MOF + dye; olive: MOF + dye (ground); cyan: MOF + dye + BHQ; magenta: MOF + dye + BHQ (ground)).

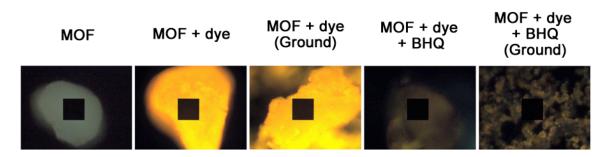


Figure S27. Microscopic images of the materials. The black squares represent the 31 × 31 μm sampling area for spectroscopy.

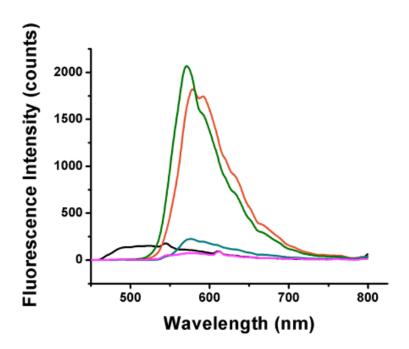


Figure S28. Fluorescence spectra excited at 420 nm (black: "MOF"; orange: MOF + dye; olive: MOF + dye (ground); cyan: MOF + dye + BHQ; magenta: MOF + dye + BHQ (ground)).

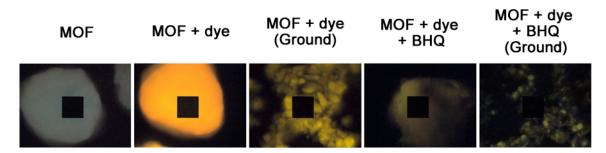


Figure S29. Microscopic images of the materials. The black squares represent the 31 \times 31 μ m sampling area for spectroscopy.

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