Electronic Supplementary Material (ESI) for Chemical Communications.


Supporting Information for

# A Supramolecular Approach for Designing Emissive Solid-State Carbazole Arrays

L. M. Lifshits,[a] B. C. Noll,[b] J. K. Klosterman.[a]

a: Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University, 141 Overman Hall, Bowling Green OH 43403

b: Bruker AXS, Inc. 5465 East Cheryl Parkway, Madison, WI 53711-5373

## Contents

1. General information
2. Materials
3. Ligand synthesis
4. NMR spectra
5. MOFs syntheses
6. Single crystal X-Ray diffraction analyses
7. Powder X-Ray diffraction patterns
8. TGA analyses
9. IR analyses
10. Photophysical measurements
11. Crystallographic Data Tables
12. References

**1. General information**

Proton ($^{1}H$), carbon ($^{13}C$), COSY, HSQC and HMBC NMR experiments were performed on Bruker AVANCEIII 500 MHz NMR. Chemical shifts are given in parts per million (ppm) and referenced to solvent signals for $CDCl_3$ (7.26 ppm) or DMSO-$d_6$ (2.50 ppm) for $^{1}H$ NMR, and $CDCl_3$ (77.00 ppm) or DMSO-$d_6$ (39.52 ppm) in $^{13}C$ NMR.

Silica gel (60Å, 40-63 μm) was used as stationary phase for column chromatography. IR spectra were obtained on Shimadzu FTIR-8400S spectrophotometer with spectroscopic grade KBr as a pellet supporter. Melting points (uncorrected) were measured with Laboratory devices, Inc. Melt-Temp II with a thermocouple. HRMS (ESI+) spectra were obtained in the University of Michigan Mass Spectrometry lab, 3411 Chemistry, 930 N University Ave, Ann Arbor, MI 48103. Elemental analysis for C, H and N content was carried out in the Atlantic Microlab, 6180 Atlantic Blvd., Suite M, Norcross, GA 30071 with instrument nominal accuracy ± 0.3%.

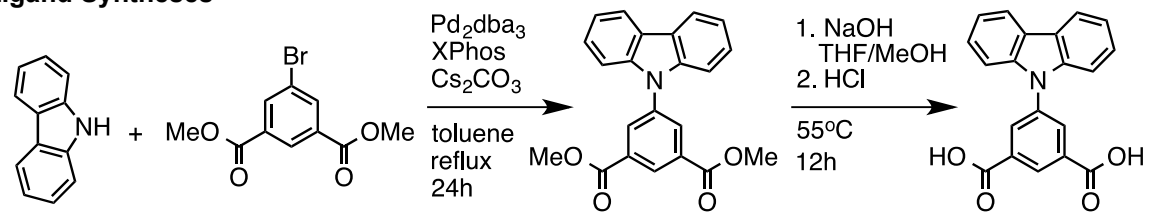
Powder X-Ray diffraction measurements were carried out with a Bruker D8 Advance PXRD with a 2.2kW Cu anode long fine focus ceramic X-Ray tube and LinxEye detector. Single crystal diffraction measurements were carried out in the Bruker AXS, Inc. on a Bruker D8 Venture system equipped with a multilayer mirror monochromator and a Cu K$\alpha$ sealed tube ($\lambda$=1.54178Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were collected for absorptions effects using the multi-scan method (SADABS). The structures were solved and refined with the Bruker SHELXTL Software Package. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1061880 – 1061883 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

UV-Vis absorption spectra were recorded with Shimadzu UV-2401 PC spectrophotometer (equipped an integrating sphere for diffuse reflectance measurements of solids). Fluorescence measurements were performed on Horiba Fluorolog FL3-11 spectrofluorometer. Steady state emission spectra were collected using a 450W xenon lamp with computer controlled excitation shutter with excitation and observation at the reported wavelength maximum. Lifetime decays were then measured using time-correlated single photon counting (TCSPC) with a 340nm NanoLED. Absolute quantum yields of solids and **1a** in cyclohexane solution were measured at Hamamatsu absolute PI quantum yield spectrometer C11347. Measurements were repeated on three different batches of freshly prepared samples and observed standard deviations were within instrumental error (±0.01).

**2. Materials**

All reagents were purchased from commercial suppliers (Aldrich, Alfa Aesar, BDH, EMD, Matrix Scientific, Strem Chemicals, VWR) and used without further purification. Solvents were purchased from commercial suppliers and used without further purification. Dry solvents were purified using an MBraun Solvent Purification System and stored over molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories. The spectrophotometric measurements of solutions were carried out in solvents of spectrophotometric quality from EMD.

**3. Ligand Syntheses**




**Scheme S1.** Ligand **1b** synthesis.

*Dimethyl 5-(9H-carbazol-9-yl)-isophthalate* **(1a)**
Adapted from literature protocols.[1] Carbazole **2** (0.40 g, 2.40 mmol) was mixed with dimethyl 5-bromoisophthalate **3** (0.55 g, 2.00 mmol), dipalladium(0) trisdibenzylideneacetone ($Pd_2dba_3$) (0.05 g, 0.06 mmol), $Cs_2CO_3$ (1.63 g, 5.00 mmol) and 2-dicyclohexylphosphino-2',4',6'-triisopropylphenyl (XPhos) (0.05 g, 0.10 mmol) in the round bottom flask. The flask was evacuated and refilled with nitrogen. Compounds mixture was dissolved in degased toluene (16 mL), then heated to 112°C and kept at that temperature. Reaction was monitored by ESI-MS until full conversion of starting materials to the product was observed after 24 hours of refluxing. Reaction was quenched with saturated aqueous solution of EDTA and $NaHCO_3$ (16 mL), extracted with EtOAc (3x100 mL), washed with $H_2O$ deionized, dried over $MgSO_4$ (anhydrous), filtered. Solvent was removed under reduced pressure. Column chromatography was performed to purify crude product. Gradient column was found to be the most effective way of separation: starting from solvents mixture as eluent (dichloromethane:hexane, v:v = 1:3) to pure dichloromethane. Dimethyl 5-(*9H*-carbazol-9-yl)-isophthalate **1a** was obtained as a yellowish solid (0.55 g, 77% yield). M.p. 186-189 °C.
$^1$H NMR (500 MHz, $CDCl_3$, δ): 8.78 (t, J = 1.5 Hz, 1H), 8.46 (d, J = 1.5 Hz, 2H), 8.16 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 3.99 (s, 6H).
$^{13}$C NMR (125 MHz, $CDCl_3$, δ): δ 165.49, 140.39, 138.52, 132.58, 132.10, 129.28, 126.26, 123.67, 120.59, 120.49, 109.38, 52.70.
HRMS-ESI$^+$ (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{17}NO_4$, 360.1230; found 360.1231.

*5-(9H-carbazol-9-yl)-isophthalic acid* (**1b)**
Dimethyl 5-(*9H*-carbazol-9-yl)-isophthalate **1a** (1.20 g, 3.34 mmol) was dissolved in THF (50 mL) and MeOH (30 mL) was added. After that NaOH aqueous was added (80 mL of 1.8M solution). Reaction mixture was heated to 55$^0$C and kept at that temperature. Reaction completion was monitored by TLC, which showed full conversion after 12 hours. After that reaction mixture was cooled down and organic solvents were removed under reduced pressure. Aqueous layer was acidified with HCl (4M) until white precipitate occurred. Precipitate was washed with $H_2O$ deionized and dried under high vacuum. 5-(*9H*-carbazol-9-yl)-isophthalic acid **1a** was obtained as a yellowish solid (1.00 g, 95% yield). Yield of ligand **1b** after all steps: 73%. M.p. 340 °C dec.
$^1$H NMR (500 MHz, DMSO-$d_6$, δ): 13.63 (bs, 2H), 8.57 (t, J = 1.5 Hz, 1H), 8.32 (d, J = 1.5 Hz, 2H), 8.28 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H).
$^{13}$C NMR (125 MHz, DMSO-$d_6$, δ): 165.95,139.85, 137.69, 133.54, 131.02, 128.61, 126.60, 123.07, 120.78, 120.68, 109.41.
HRMS-ESI$^-$ (*m/z)*: $[M-H]^-$ calcd for $C_{20}H_{13}NO_4$, 330.0772; found 330.0770.

**4. NMR spectra**

Assignments of signals based on 2D NMR experiments (COSY, HMBC, HSQC).

**4.1 Ligand 1a**

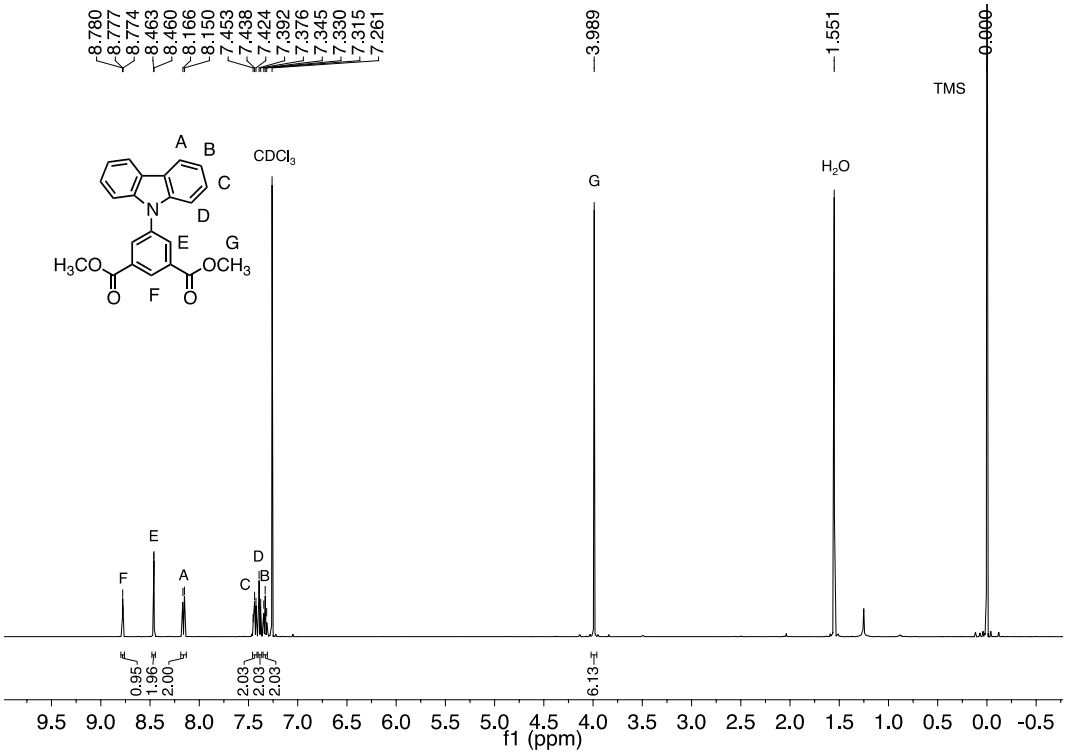



**Figure S1.** 500 MHz $^{1}$H NMR Spectrum of **1a** $CDCl_3$ at 298 K.

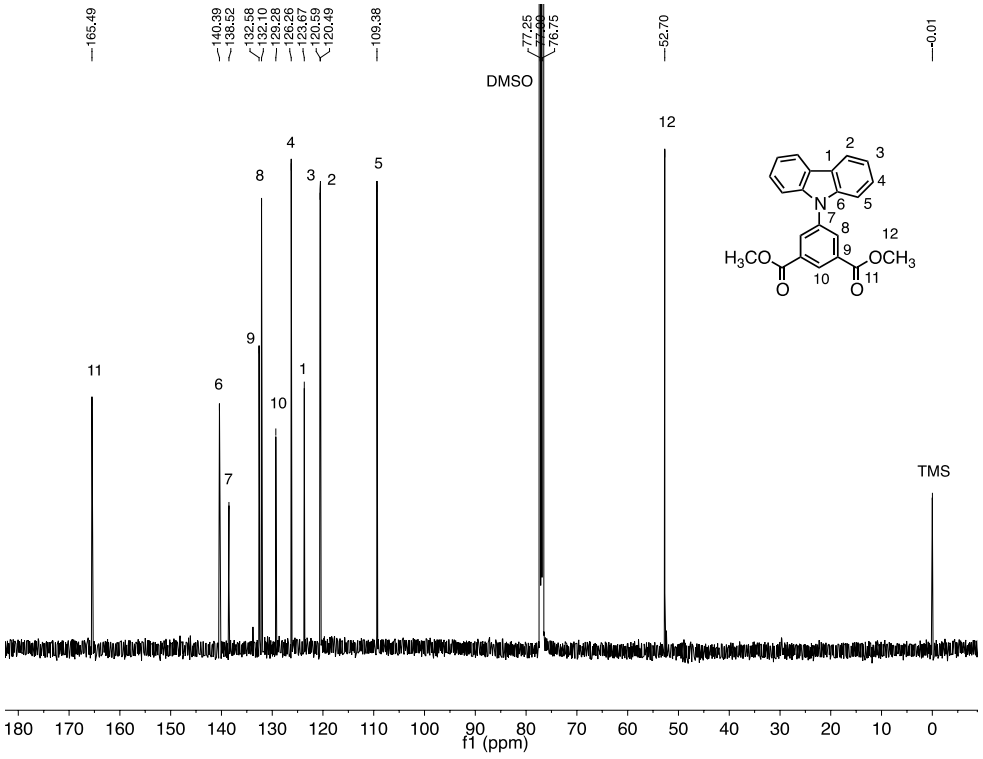



**Figure S2.** 125 MHz $^{13}$C NMR Spectrum of **1a** in $CDCl_3$ at 298 K.

## 4.2 Ligand 1b

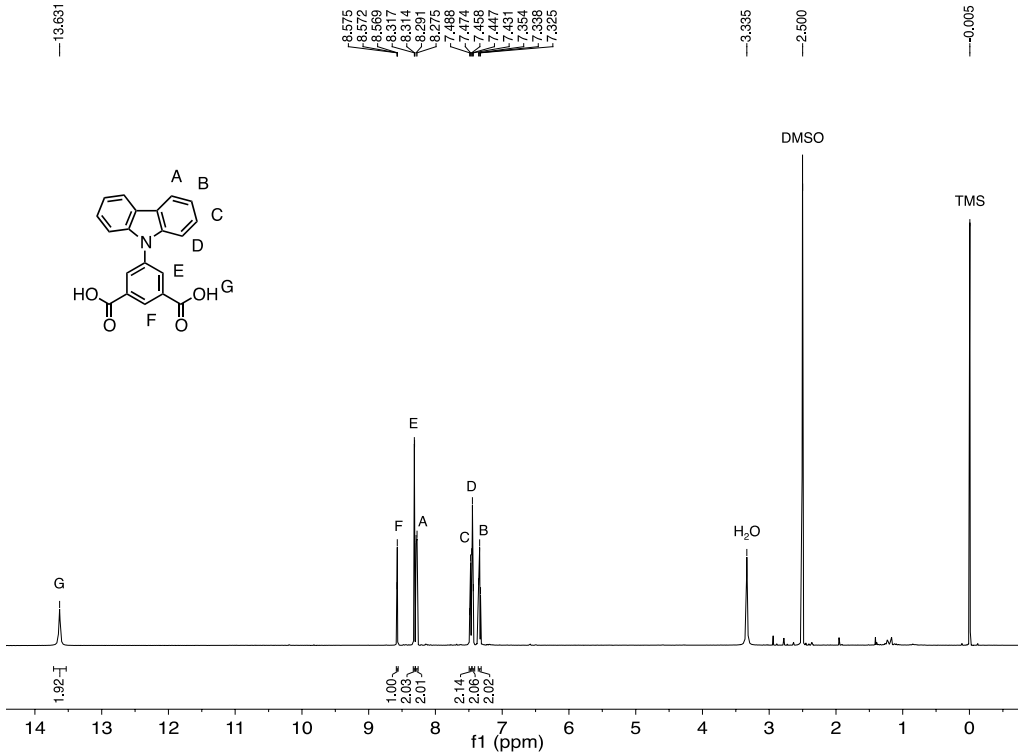



**Figure S3.** 500 MHz $^{1}$H NMR Spectrum of **1b** in DMSO-$d_6$ at 298 K.

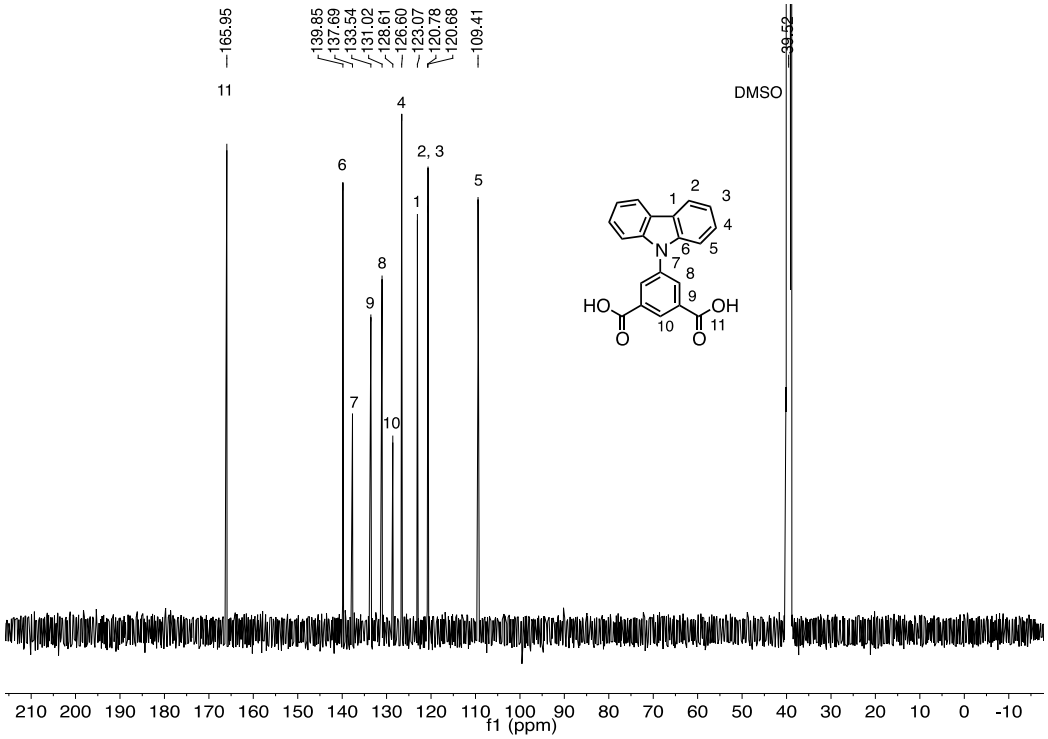



**Figure S4.** 125 MHz $^{13}$C NMR Spectrum of **1b** in DMSO-$d_6$ at 298 K.

**5. MOFs syntheses**

*General procedure:* Metal salts were dissolved in the specified solvent mixture and added to a solution of **1b** in the same solvent mixture. The reaction solution was well-stirred, separated into vials of 2mL size and placed in the isothermal oven. Crystals' appearance in the vials was monitored. Obtained crystals were collected, evaluated under microscope and washed with suitable solvents. Crystals were dried in air and/or under high vacuum as required.

**CuCbz MOF:** $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.08 g, 0.36 mmol) was dissolved in 1:1 NMP:EtOH solvent mixture (11.5 mL) and added to the solution of **1b** (0.10 g, 0.30 mmol) in the same solvent mixture (11.5 mL). Vials with reaction mixture were placed in the isothermal oven at 85°C. First crystals (green uniform rhombohedra platelets) appeared after 4 hours in the oven. Crystals were collected after 5 days in the oven. Crystals were washed with 1:1 NMP:EtOH (3 times), with EtOH (3 times), dried in air and then under high vacuum to give CuCbz MOF as green crystals (0.05 g, 34% yield).
Anal. Calcd for $C_{25}H_{20}N_2O_5Cu$: C, 61.03; H, 4.10; N, 5.69, O, 16.26; Cu, 12.92. Found: C, 60.74; H, 4.16; N, 5.64.

*Notes:* the procedure above was successfully reproduced at different scales from 0.01 g to 0.30 g of ligand **1b**. Crystalline powder was obtained when reaction was scaled up to 0.40 g of **1b**. Smaller but more uniform crystals were obtained after 4 days in the oven when vials were kept at 55°C instead of 85°C. Crystals obtained at either 55°C or 85°C are of SXRD quality.

**CoCbz MOF:** $Co(NO_3)_2 \cdot 6H_2O$ (0.10 g, 0.36 mmol) was dissolved in 1:3 DMF:MeOH solvent mixture (11.5 mL) and added to the solution of **1b** (0.10 g, 0.30 mmol) in the same solvent mixture (11.5 mL). Vials with reaction mixture were placed in the isothermal oven at 70°C. First crystals (purple uniform rhombohedra platelets) appeared overnight. Crystals were collected after 5 days in the oven. Crystals were washed with 1:1 DMF:MeOH (3 times), with MeOH (3 times), dried in air and then under high vacuum to give CoCbz MOF as purple crystals (0.12 g, 44% yield).
Anal. Calcd for $C_{45}H_{35}N_3O_{11}Co_2$: C, 59.28; H, 3.86; N, 4.60, O, 19.30, Co, 12.92. Found: C, 58.44; H, 4.40; N, 4.90.

*Notes:* the procedure above was successfully reproduced at different scales from 0.01 g to 0.30 g of ligand **1b**. The best conditions for SXRD quality crystals were found to be 1:6 DMF:MeOH and 70°C. The conditions for the best total yield were found to be 1:3 DMF:MeOH, 85°C, 5 days.

**ZnCbz MOF:** $Zn(NO_3)_2 \cdot 6H_2O$ (0.10 g, 0.36 mmol) was dissolved in DMF:EtOH (v:v = 1:1) solvent mixture (11.5 mL) and added to the solution of **1b** (0.10 g, 0.30 mmol) in the same solvent mixture (11.5 mL). Vials with reaction mixture were placed in the isothermal oven at 55°C. First crystals (clear uniform prisms) appeared after 4 days in the oven and kept appearing during next days. Crystals were collected after 9 days in the oven. Crystals were washed with 1:1 DMF:EtOH (3 times), with MeOH (3 times), dried in air and then under high vacuum to give ZnCbz MOF as colorless crystals (0.10 g, 33 % yield).
Anal. Calcd for $C_{51}H_{48}N_5O_{12}Zn_2$: C, 58.13; H, 4.59; N, 6.64, O, 18.22, Zn, 12.41. Found C, 57.70; H, 4.35; N, 6.65.

*Notes:* the procedure above was successfully reproduced at different scales from 0.01 g to 0.20 g of ligand **1b**. The best conditions for SXRD quality crystals were found to be 1:1 DMF:EtOH, 55°C, 4 days or 1:1 DMF:MeOH, room temperature, 1 month. The conditions for the best total yield were found to be 1:1 DMF:EtOH, 55°C, 9 days.
New peaks slowly appear over several hours in the PXRD trace for crystals of ZnCbz MOF washed in EtOH, presumably due to solvent lose. Thus all reported photophysical measurements were immediately performed on fresh crystals washed with DMA, which exhibited structural integrity for ~2 days in air due to the lower volatility. It is important to note that photophysical measurements of freshly EtOH washed crystals were similar to DMA washed crystals indicating that the majority of the carbazole materials remains intact.

## 6. Single crystal X-Ray diffraction analyses

**Table S1.** Crystallographic data for **1a**

| | |
|---|---|
| Chemical formula | $C_{22}H_{17}NO_4$ |
| $M_r$ | 359.36 |
| Crystal system, space group | Triclinic, *P-1* |
| Temperature (K) | 130(2) |
| *a*, *b*, *c* (Å) | 7.3977 (5), 11.6656 (7), 20.3981 (13) |
| α, β, γ (°) | 76.247 (3), 83.564 (3), 88.301 (4) |
| *V* (Å$^3$) | 1699.07 (19) |
| *Z* | 4 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 0.80 |
| Crystal size (mm) | 0.32 × 0.21 × 0.05 |
| Density (g/cm$^3$) | 1.405 |
| **Data collection** | |
| Diffractometer | Bruker D8 VENTURE diffractometer |
| Absorption correction | multi-scan |
| $T_{min}$, $T_{max}$ | 0.790, 0.960 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 6574, 6574, 5471 |
| $R_{int}$ | 0.030 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.625 |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.048, 0.109, 1.05 |
| No. of reflections | 6574 |
| No. of parameters | 492 |
| No. of restraints | 193 |
| H-atom treatment | H-atom parameters constrained |

| | |
|---|---|
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.24, -0.27 |
| R-factor (%) | 4.78 |

Computer programs: *SHELXL2013* (Sheldrick, 2013).

A total of 3265 frames were collected. The total exposure time was 20.43 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 6574 reflections to a maximum angle of 74.50° (0.80 Å resolution), of which 6574 were independent (average redundancy 1.000, completeness = 96.6%, Rsig = 4.50%) and 5471 (83.22%) were greater than 2σ(F2). The final cell constants of a = 7.3977(5) Å, b = 11.6656(7) Å, c = 20.3981(13) Å,α = 76.247(3)°,β = 83.564(3)°, γ = 88.301(4)°, volume = 1699.07(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 9585 reflections above 20σ(I) with 4.485° < 2θ< 148.9°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7860 and 0.9610. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 4 for the formula unit, C22H17NO4. The final anisotropic full-matrix least-squares refinement on $F^2$ with 492 variables converged at $R_1$ = 4.78%, for the observed data and $wR_2$ = 10.90% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.235 e-/$Å^3$ and the largest hole was -0.266 e-/$Å^3$ with an RMS deviation of 0.053 e-/Å3. On the basis of the final model, the calculated density was 1.405 g/cm3 and F(000), 752 e-.

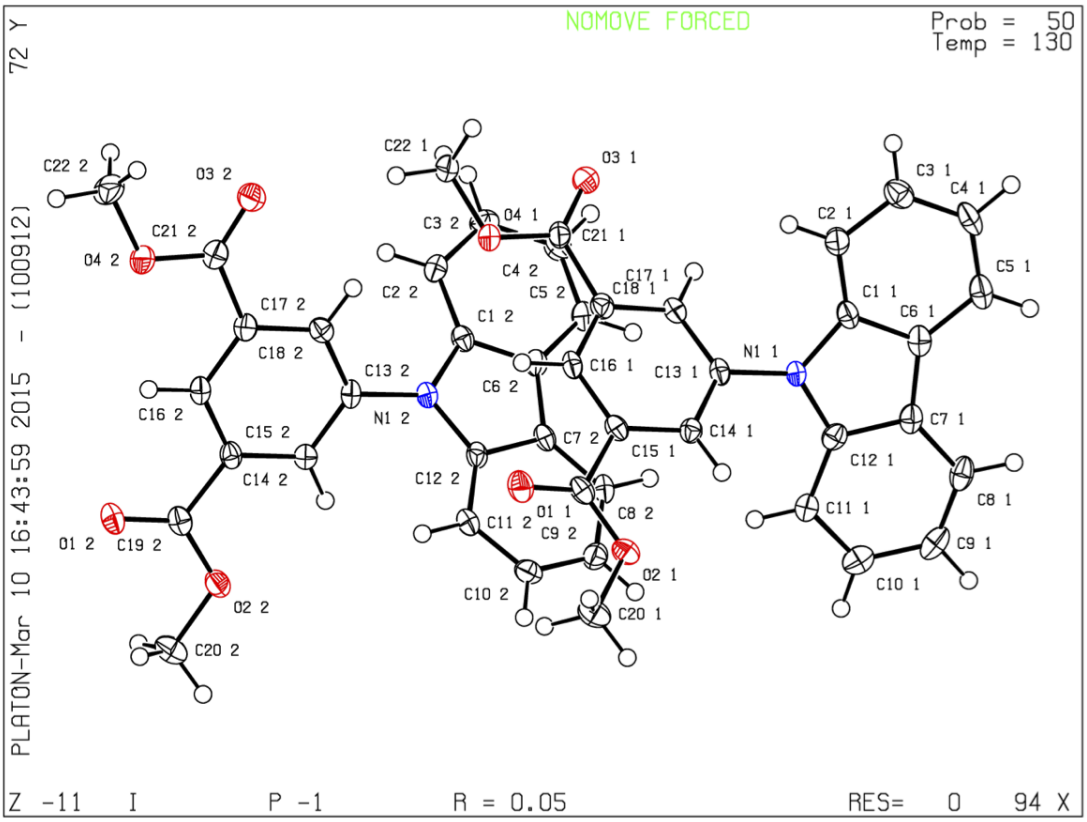



**Figure S5.** Top: ORTEP of **1a** (generated by Platon).

**Table S2.** Crystallographic data for **CuCbz MOF**

| | |
|---|---|
| Chemical formula | $C_{25}H_{20}CuN_2O_5$ |
| $M_r$ | 491.97 |
| Crystal system, space group | Monoclinic, *C*2/*c* |
| Temperature (K) | 299 |
| *a*, *b*, *c* (Å) | 27.7412 (11), 11.1140 (5), 15.0069 (6) |
| α, β, γ (°) | 90, 102.921 (2), 90 |
| *V* (Å$^3$) | 4509.7 (3) |
| *Z* | 8 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 1.70 |
| Crystal size (mm) | 0.14 × 0.10 × 0.08 |
| Density (g/cm$^3$) | 1.449 |
| **Data collection** | |
| Diffractometer | Bruker D8 VENTURE diffractometer |
| Absorption correction | Multi-scan Sheldrick, G. M. (2012). TWINABS v2012/1. Bruker AXS Inc. Madison, WI 53711, USA. |
| $T_{min}$, $T_{max}$ | 0.80, 0.87 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 4492, 4492, 4249 |
| $R_{int}$ | 0.056 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.618 |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.041, 0.112, 1.10 |
| No. of reflections | 4492 |
| No. of parameters | 364 |
| No. of restraints | 116 |
| H-atom treatment | H-atom parameters constrained |

| | |
|---|---|
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.61, -0.29 |
| R-factor (%) | 4.05 |

Computer programs: *APEX2* v2012.10-1 (Bruker-AXS Inc., 2012), *SAINT* v8.35A (Bruker AXS Inc., 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2014), Jmol: an open–source Java viewer for chemical structures in 3D. http://www.jmol.org/, *APEX2* v2012.12 (Bruker, 2011)

A total of 3834 frames were collected. The total exposure time was 22.03 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 4636 reflections to a maximum _ angle of 72.40° (0.81 Å resolution), of which 4636 were independent (average redundancy 1.000, completeness = 93.3%, Rsig = 3.33%) and 4322 (93.23%) were greater than 2_($F^2$). The final cell constants of a = 27.7412(11) Å, b = 11.1140(5) Å, c = 15.0069(6) Å, β = 102.921(2)°, volume = 4509.7(3) Å$^3$, are based upon the refinement of the XYZ-centroids of reflections above 20σ (I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7978 and 0.8702.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/c 1, with Z = 8 for the formula unit, $C_{25}H_{17}CuN_2O_5$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 366 variables converged at $R_1$ = 4.05%, for the observed data and $wR_2$ = 11.20% for all data. The goodness-of-fit was 1.083. The largest peak in the final difference electron density synthesis was 0.597 e-/Å$^3$ and the largest hole was -0.28 e-/Å$^3$ with an RMS deviation of 0.083 e-/Å$^3$. On the basis of the final model, the calculated density was 1.449 g/cm3 and F(000), 2024 e-.

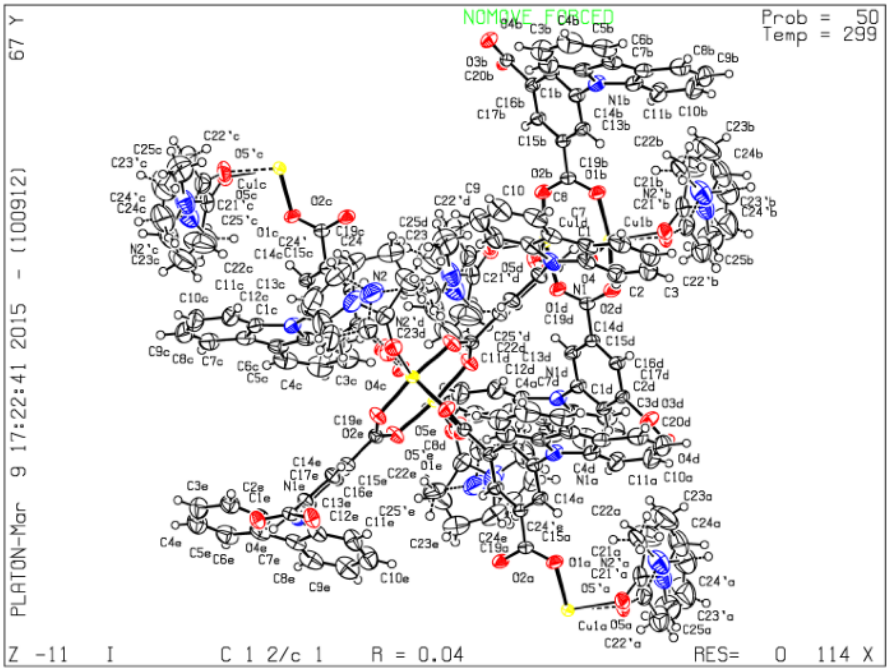



**Figure S6.** ORTEP of CuCbz MOF unit cell (generated by Platon checkcif).

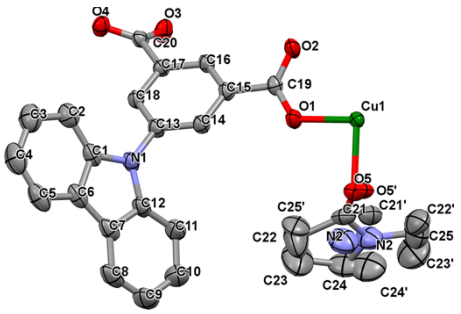



**Figure S7.** ORTEP of CuCbz MOF asymmetric unit (generated by Mercury).

**Table S3.** Crystallographic data for **CoCbz MOF**

| | |
|---|---|
| Chemical formula | $C_{45}H_{35}Co_2N_3O_{11}$•0.663($CH_4O$)•0.337($C_3H_7NO$) |
| $M_r$ | 959.48 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 10.1480 (6), 14.9006 (8), 28.1544 (16) |
| α, β, γ (°) | 90, 92.505 (3), 90 |
| *V* (Å$^3$) | 4253.2 (4) |
| *Z* | 4 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 6.70 |
| Crystal size (mm) | 0.15 × 0.08 × 0.05 |
| Density (g/cm$^3$) | 1.498 |
| **Data collection** | |
| Diffractometer | Bruker D8 VENTURE diffractometer |
| Absorption correction | Multi-scan Sheldrick, G. M. (2014). *SADABS* v2014/5. Bruker AXS Inc. Madison, WI 53711, USA. |
| $T_{min}$, $T_{max}$ | 0.708, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 48714, 7955, 6826 |
| $R_{int}$ | 0.054 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.610 |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.040, 0.093, 1.04 |
| No. of reflections | 7955 |
| No. of parameters | 666 |
| No. of restraints | 74 |
| H-atom treatment | H-atom treated by a mixture of independent and constrained refinement |

| | |
|---|---|
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.51, -0.33 |
| R-factor (%) | 3.95 |

Computer programs: Bruker Instrument Service v3.0.28 (Bruker, 2013), *SAINT* v8.34A (Bruker, 2013), *SHELXS* v2013/1(Sheldrick, 2013), *SHELXL2014/7* (Sheldrick, 2014), *APEX2* v2015.1-rc1 (Bruker, 2015)

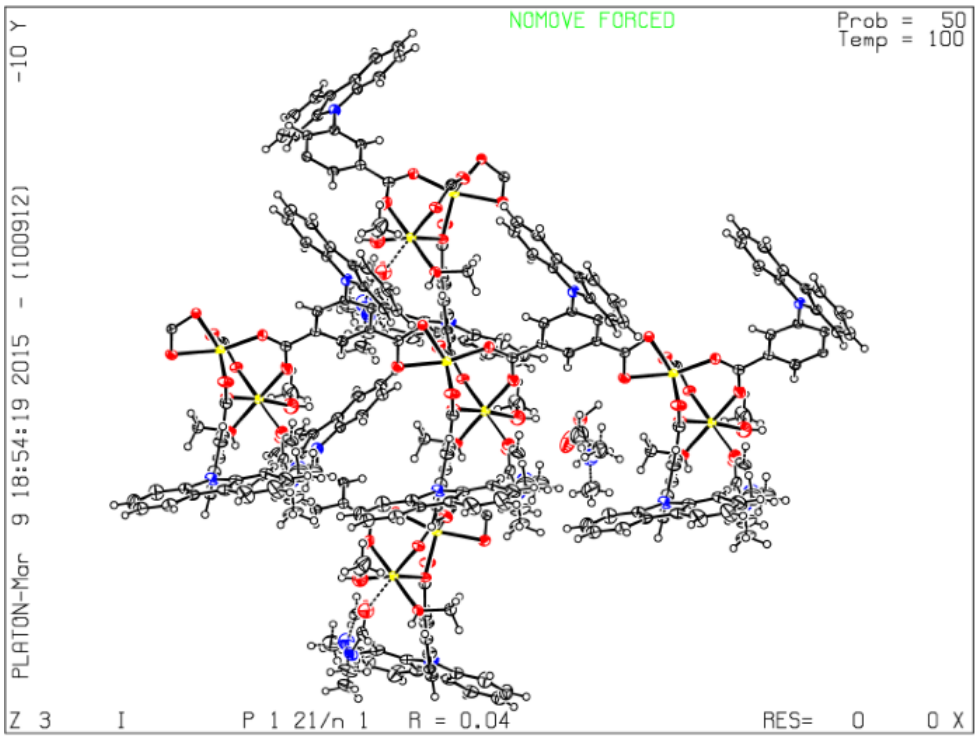



**Figure S8.** ORTEP of CoCbz MOF unit cell (generated by Platon checkcif)

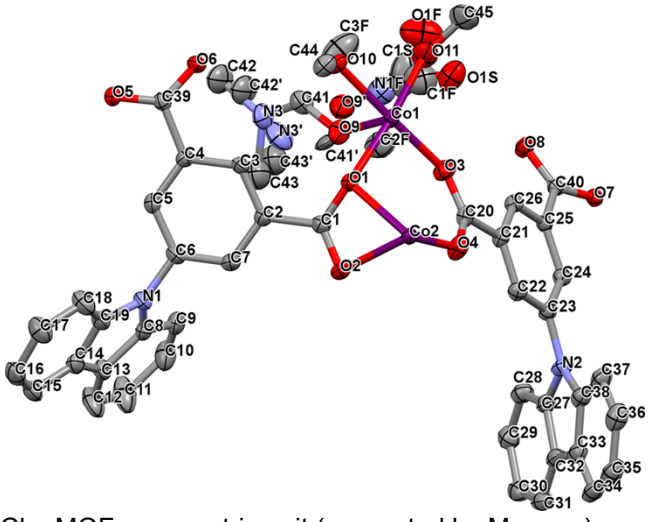



**Figure S9.** ORTEP of CoCbz MOF asymmetric unit (generated by Mercury).

**Table S4.** Single-crystal data for **ZnCbz MOF**

| | |
|---|---|
| Chemical formula | $C_{48}H_{42}Zn_2N_4O_{11}•C_3H_7NO$ |
| $M_r$ | 1054.69 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 10.3375(4), 17.0695(4), 26.9368(7) |
| α, β, γ (°) | 90, 90, 90 |
| *V* (Å$^3$) | 4753.2 (2) |
| *Z* | 4 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 1.827 |
| Crystal size (mm) | 0.19 × 0.14 × 0.11 |
| Density (g/cm$^3$) | 1.474 |
| **Data collection** | |
| Diffractometer | Bruker D8 VENTURE diffractometer |
| Absorption correction | Multi-scan Sheldrick, G. M. (2012). *SADABS* v2012/1. Bruker AXS Inc. Madison, WI 53719, USA. |
| $T_{min}$, $T_{max}$ | 0.772, 0.818 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 36376, 9547, 8472 |
| $R_{int}$ | 0.057 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.603 |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.035, 0.0071, 1.02 |
| No. of reflections | 9547 |
| No. of parameters | 642 |
| No. of restraints | 0 |
| H-atom treatment | H-atom treated by a mixture of independent and |

| | |
|---|---|
| | constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.42, -0.33 |
| R-factor (%) | 3.48 |

Computer programs: Bruker Instrument Service v3.0.30-rc3 (Bruker, 2013), *SAINT* v8.34A (Bruker, 2013), SHELXT (Sheldrick, 2014), *SHELXL2014/7* (Sheldrick, 2014).

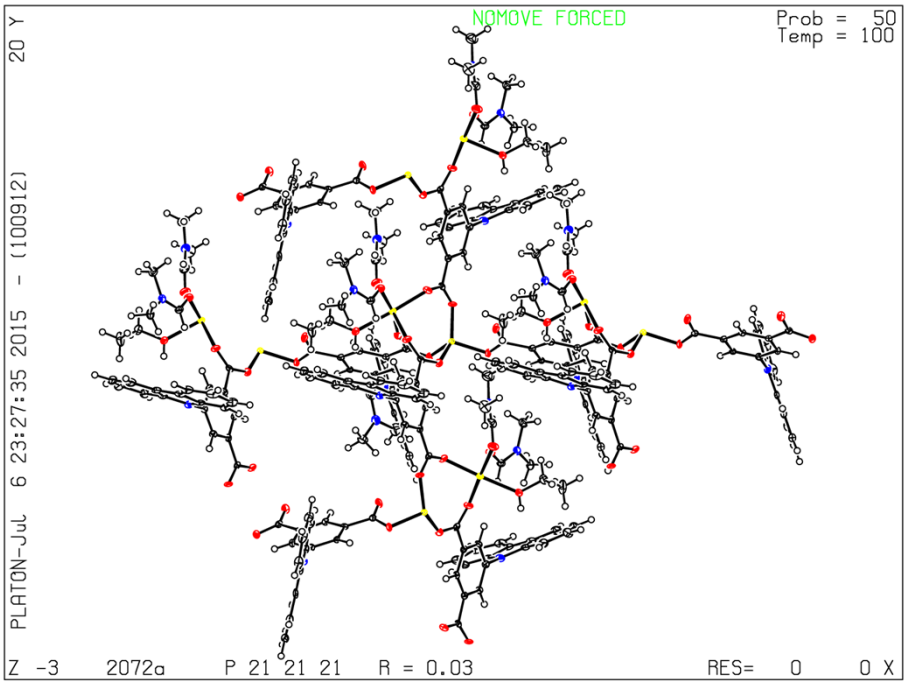



**Figure S10.** ORTEP of ZnCbz MOF unit cell (generated by Platon checkcif).

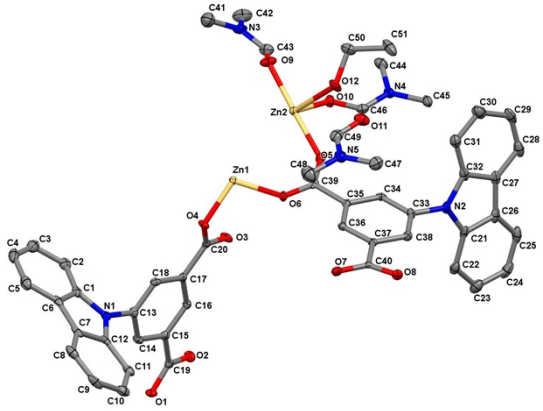


**Figure S11.** ORTEP of ZnCbz MOF asymmetric unit (generated by Mercury).

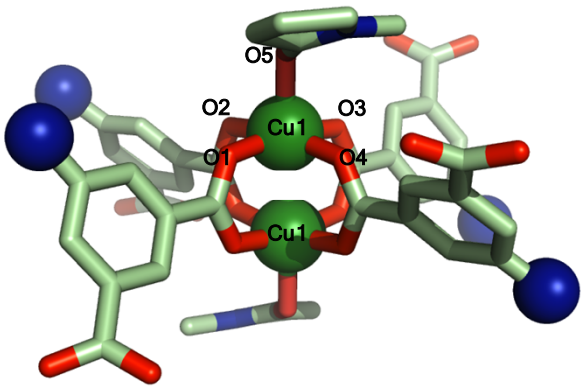



**Figure S12.** Secondary-building unit (SBU) in CuCbz MOF. Carbon = pale green; oxygen = red; nitrogen = blue; copper = forest green. Carbazoles as blue spheres.

**Table S5.** Characteristic distances and angles in CuCbz MOF SBU.[a]

| **Characteristic distances, Å** | | **Characteristic angles, °** | |
|---|---|---|---|
| Cu1 O1 | 1.9519(16) | O1 Cu1 O2 | 87.62(8) |
| Cu1 O2 | 1.9562(17) | O1 Cu1 O4 | 89.59(8) |
| Cu1 O3 | 1.9751(17) | O1 Cu1 O3 | 167.47(7) |
| Cu1 O4 | 1.9699(17) | O1 Cu1 Cu1 | 87.92(5) |
| Cu1 O5 | 2.1500(2) | O1 Cu1 O5 | 100.9(5) |
| Cu1 Cu1 | 2.66 | O2 Cu1 O5 | 90.3(5) |
| | | O2 Cu1 O4 | 167.35(7) |
| | | O2 Cu1 O3 | 88.93(9) |
| | | O2 Cu1 Cu1 | 83.67(5) |
| | | O3 Cu1 O5 | 91.1(5) |
| | | O3 Cu1 Cu1 | 79.73(5) |
| | | O4 Cu1 O5 | 102.3(5) |
| | | O4 Cu1 O3 | 91.16(8) |
| | | O4 Cu1 Cu1 | 83.91(5) |
| | | O5 Cu1 Cu1 | 169.1(5) |

[a] *The numbering scheme in Fig. S12 and Table S5 differs from the atom numbering in the corresponding cif file.*

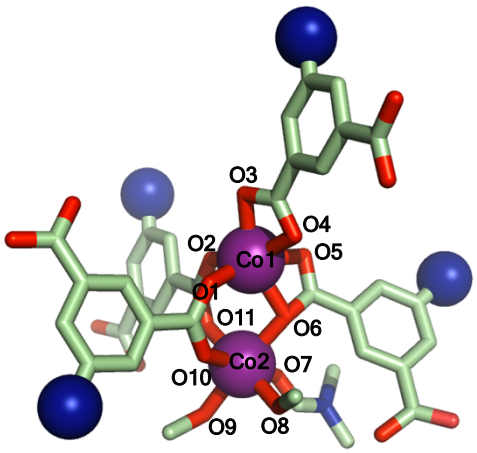



**Figure S13.** Secondary-building unit (SBU) in CoCbz MOF. Carbon = pale green; oxygen = red; nitrogen = blue; cobalt = purple. Carbazoles as blue spheres.

**Table S6.** Characteristic bonds and angles in CoCbz MOF SBU.[a]

| **Characteristic Distances, Å** | | **Characteristic angles, °** | |
|---|---|---|---|
| Co1 O1 | 1.989(4) | O1 Co1 O4 | 90.95(18) |
| Co1 O2 | 1.989(4) | O1 Co1 O6 | 98.99(16) |
| Co1 O3 | 2.147(4) | O1 Co1 O3 | 94.05(16) |
| Co1 O4 | 2.165(4) | O1 Co1 O5 | 159.60(17) |
| Co1 O5 | 2.159(4) | O2 Co1 O1 | 96.70(19) |
| Co1 O6 | 2.147(4) | O2 Co1 O6 | 101.28(17) |
| Co2 O4 | 2.106(4) | O2 Co1 O3 | 100.24(16) |
| Co2 O7 | 2.108(5) | O2 Co1 O5 | 92.67(19) |
| Co2 O8 | 2.100(4) | O2 Co1 O4 | 160.16(17) |
| Co2 O9 | 2.102(5) | O3 Co1 O5 | 102.09(15) |
| Co2 O10 | 2.070(4) | O3 Co1 O4 | 60.84(15) |
| Co2 O11 | 2.049(4) | O5 Co1 O4 | 86.18(18) |
| Co1-Co2 | 3.43 Å | O6 Co1 O3 | 153.27(15) |
| | | O6 Co1 O5 | 61.30(15) |
| | | O6 Co1 O4 | 95.53(16) |
| | | O7 Co2 O6 | 87.35(19) |
| | | O8 Co2 O6 | 88.63(16) |
| | | O8 Co2 O7 | 92.22(19) |
| | | O9 Co2 O7 | 86.3(2) |
| | | O9 Co2 O6 | 173.3(2) |
| | | O9 Co2 O8 | 89.60(19) |
| | | O10 Co2 O8 | 86.75(17) |
| | | O10 Co2 O7 | 177.1(2) |
| | | O10 Co2 O9 | 91.1(2) |
| | | O10 Co2 O6 | 95.29(16) |
| | | O11 Co2 O10 | 93.15(19) |
| | | O11 Co2 O9 | 88.8(2) |
| | | O11 Co2 O8 | 178.36(17) |
| | | O11 Co2 O7 | 87.8(2) |
| | | O11 Co2 O6 | 93.01(17) |

[a] *The numbering scheme in Fig. S13 and Table S6 differs from the atom numbering in the corresponding cif file.*

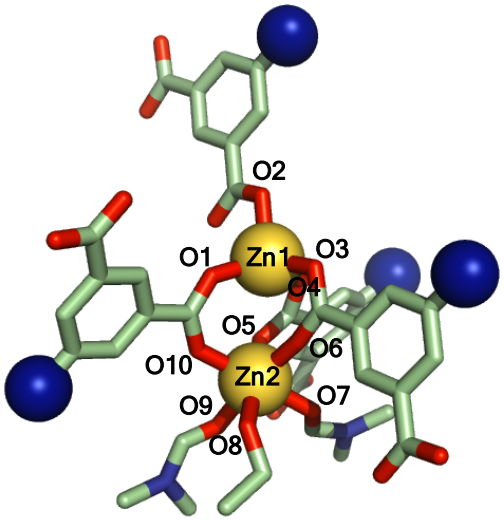



**Figure S14.** Secondary-building unit (SBU) in ZnCbz MOF. *Carbon = pale green; oxygen = red; nitrogen = blue; zinc = yellow. Carbazoles as blue spheres*

**Table S7.** Characteristic bonds and angles in ZnCbz MOF SBU.[a]

| **Characteristic Distances, Å** | | **Characteristic angles, °** | |
|---|---|---|---|
| Zn1 O1 | 1.963(2) | O1 Zn1 O3 | 99.52(11) |
| Zn1 O2 | 1.951(3) | O1 Zn1 O4 | 138.13(10) |
| Zn1 O3 | 2.007(3) | O2 Zn1 O1 | 105.15(11) |
| Zn1 O4 | 1.966(2) | O2 Zn1 O3 | 108.02(10) |
| Zn2 O5 | 2.067(3) | O2 Zn1 O4 | 103.07(11) |
| Zn2 O6 | 2.071(3) | O3 Zn1 O4 | 100.41(11) |
| Zn2 O7 | 2.088(3) | O5 Zn2 O6 | 97.63(10) |
| Zn2 O8 | 2.145(3) | O5 Zn2 O9 | 91.42(11) |
| Zn2 O9 | 2.094(3) | O5 Zn2 O7 | 86.77(12) |
| Zn2 O10 | 2.030(3) | O5 Zn2 O8 | 175.97(11) |
| Zn1-Zn2 | 3.594 | O6 Zn2 O7 | 86.62(11) |
| | | O6 Zn2 O9 | 169.78(12) |
| | | O6 Zn2 O8 | 86.38(11) |
| | | O7 Zn2 O9 | 89.18(11) |
| | | O7 Zn2 O8 | 93.15(12) |
| | | O9 Zn2 O8 | 84.55(11) |
| | | O10 Zn2 O5 | 95.16(11) |
| | | O10 Zn2 O6 | 93.41(11) |
| | | O10 Zn2 O7 | 178.04(13) |
| | | O10 Zn2 O9 | 90.47(10) |
| | | O10 Zn2 O8 | 84.89(12) |

[a] *The numbering scheme in Fig. S14 and Table S7 differs from the atom numbering in the corresponding cif file.*

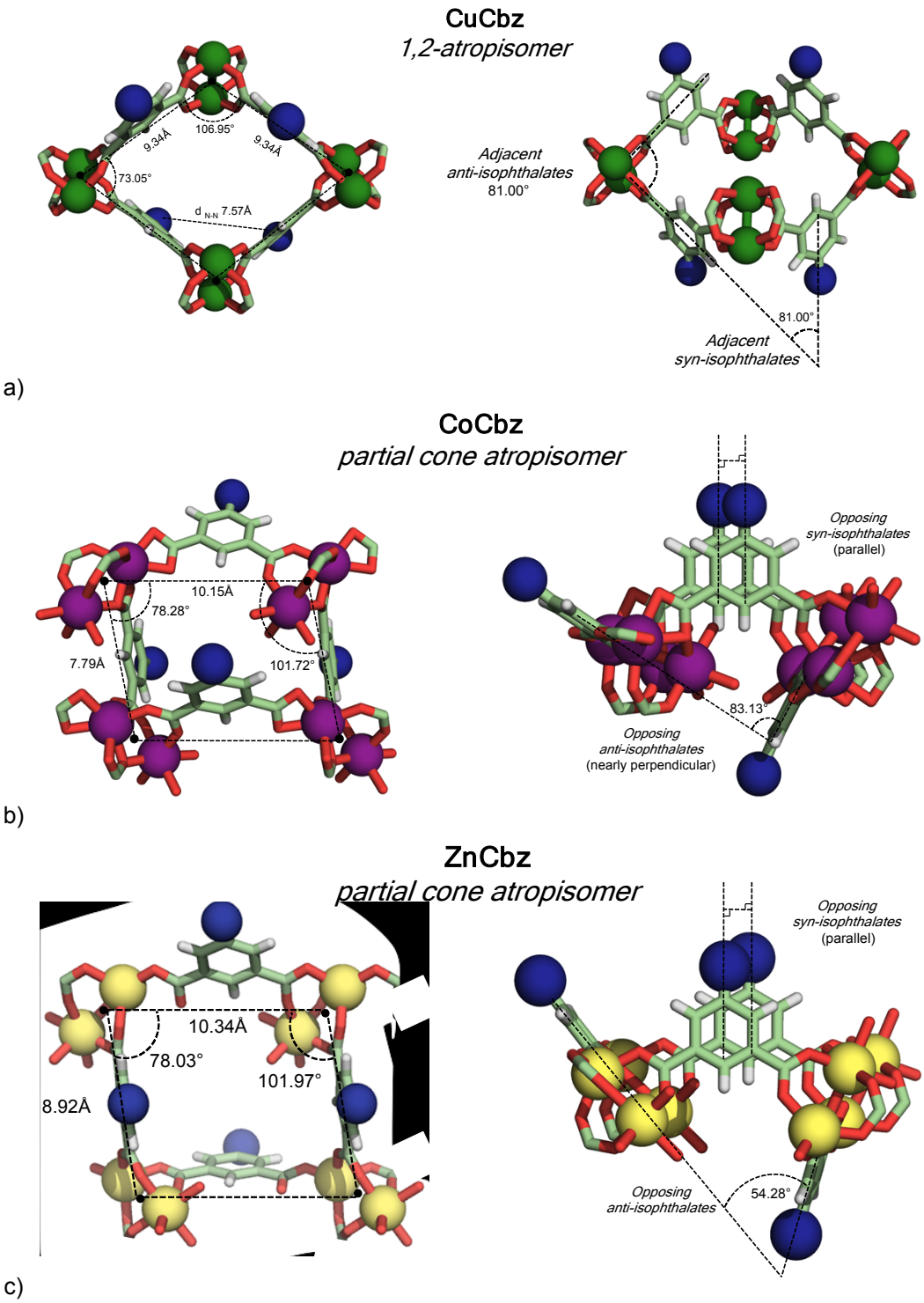



**Figure S15.** *Left:* Bonds and angles of parallelograms formed by SBUs centroids in Cbz MOF structures. *Right:* Dihedral angles between isophthalates of one square unit of the square grids of Cbz MOFs. Carbon = pale green; oxygen = red; copper = green; cobalt = purple; zinc = yellow; carbazoles = blue spheres.

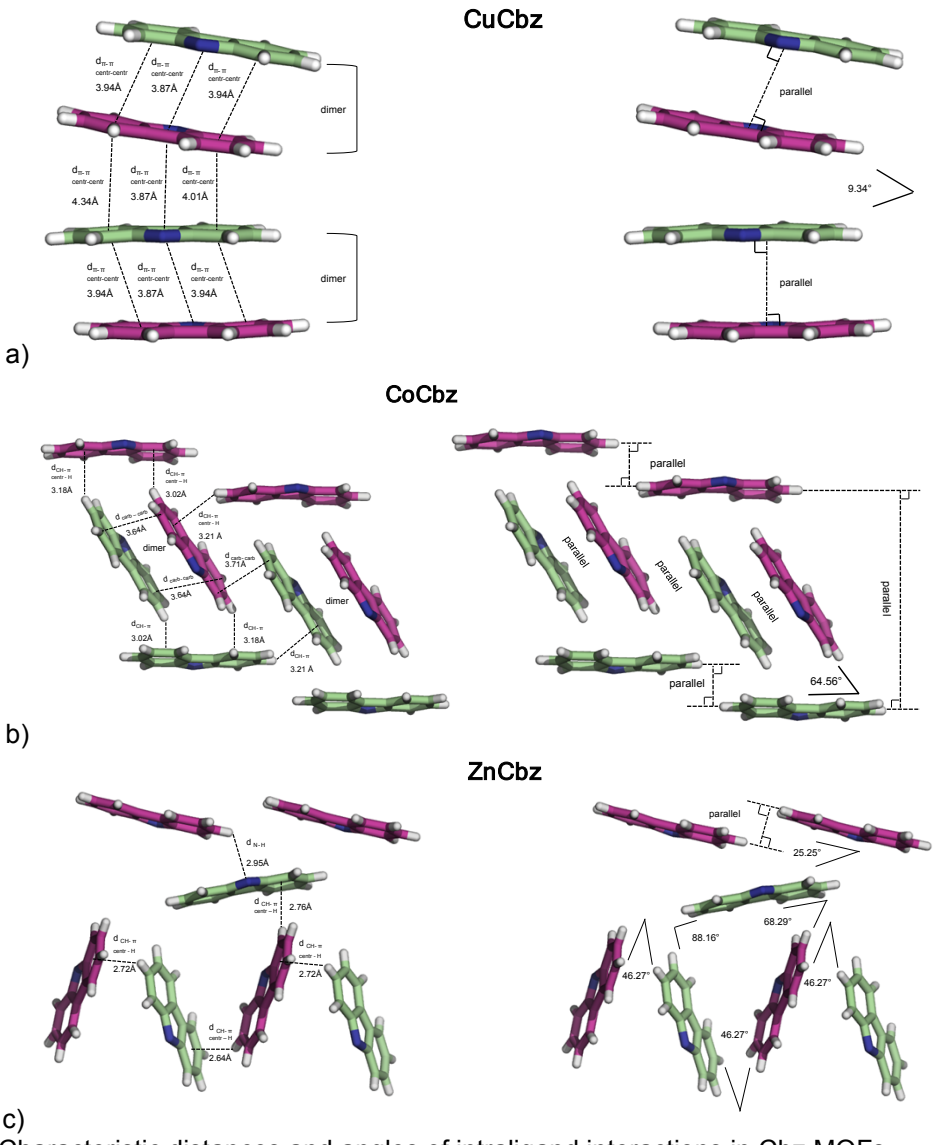



**Figure S16.** Characteristic distances and angles of intraligand interactions in Cbz MOFs.

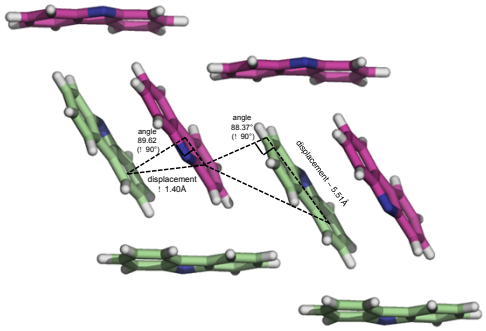



**Figure S17.** Offset of parallel carbazoles in **Co cbz MOF**.

**Table S8.** Summary of closest intraligand interactions

| | π ••• π (Å) | CH ••• π, (Å) |
|---|---|---|
| **Ligand 1a** | 3.45 | - |
| **CuCbz** | 3.87 | - |
| **CoCbz** | 3.56 | 3.02 |
| | | 3.18 |
| | | 3.21 |
| **ZnCbz** | - | 2.64 |
| | | 2.72 |
| | | 2.76 |

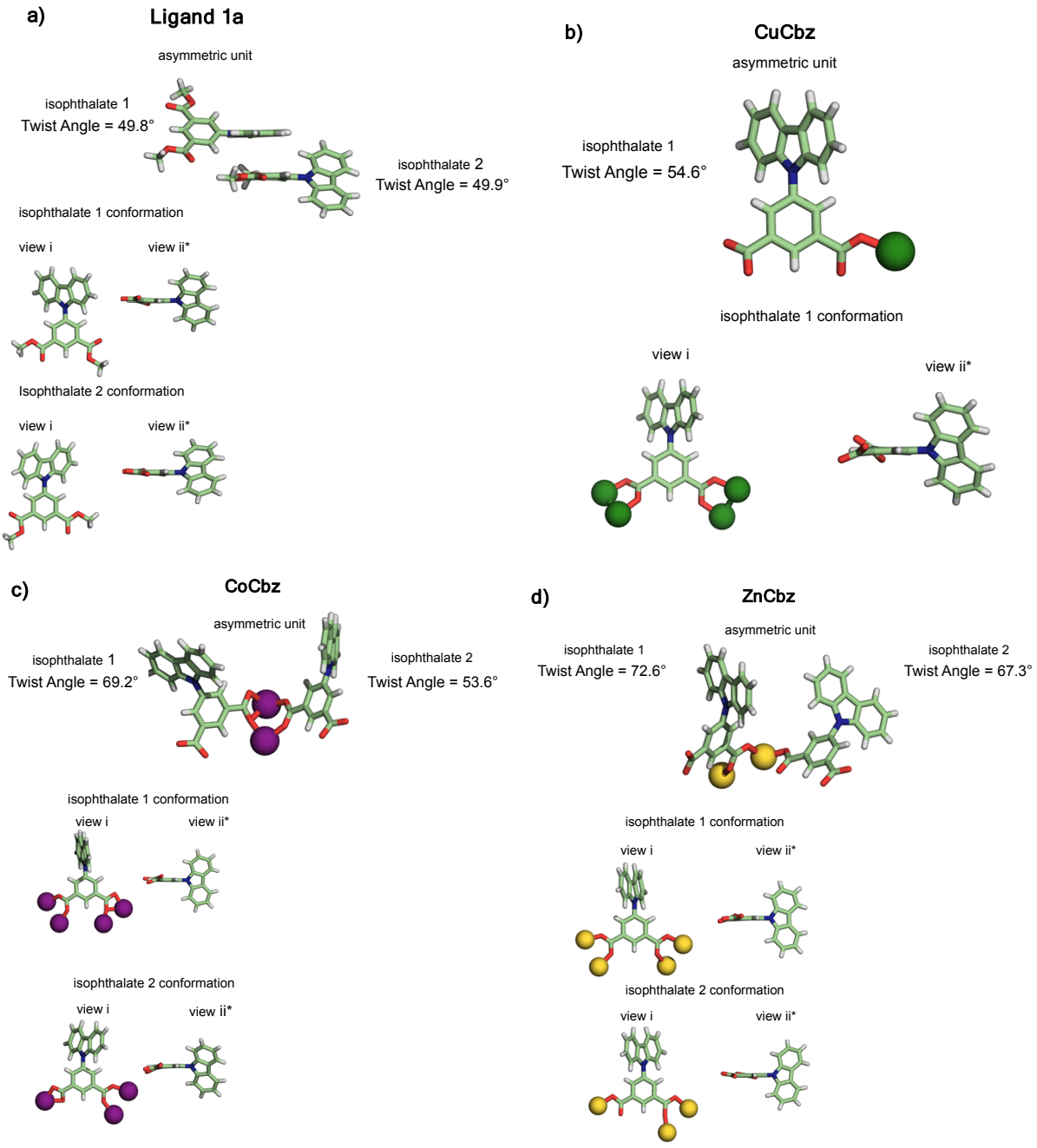



**Figure S18.** Conformations of 5-(9H-carbazol-9-yl) isophlalates in a) **1a** b) **CuCbz** c) **CoCbz** d) **ZnCbz** MOFs. Twist Angle = dihedral angle between carbazole plane and isophthalate plane. Metal ions are omitted in view ii for the sake of clarity.

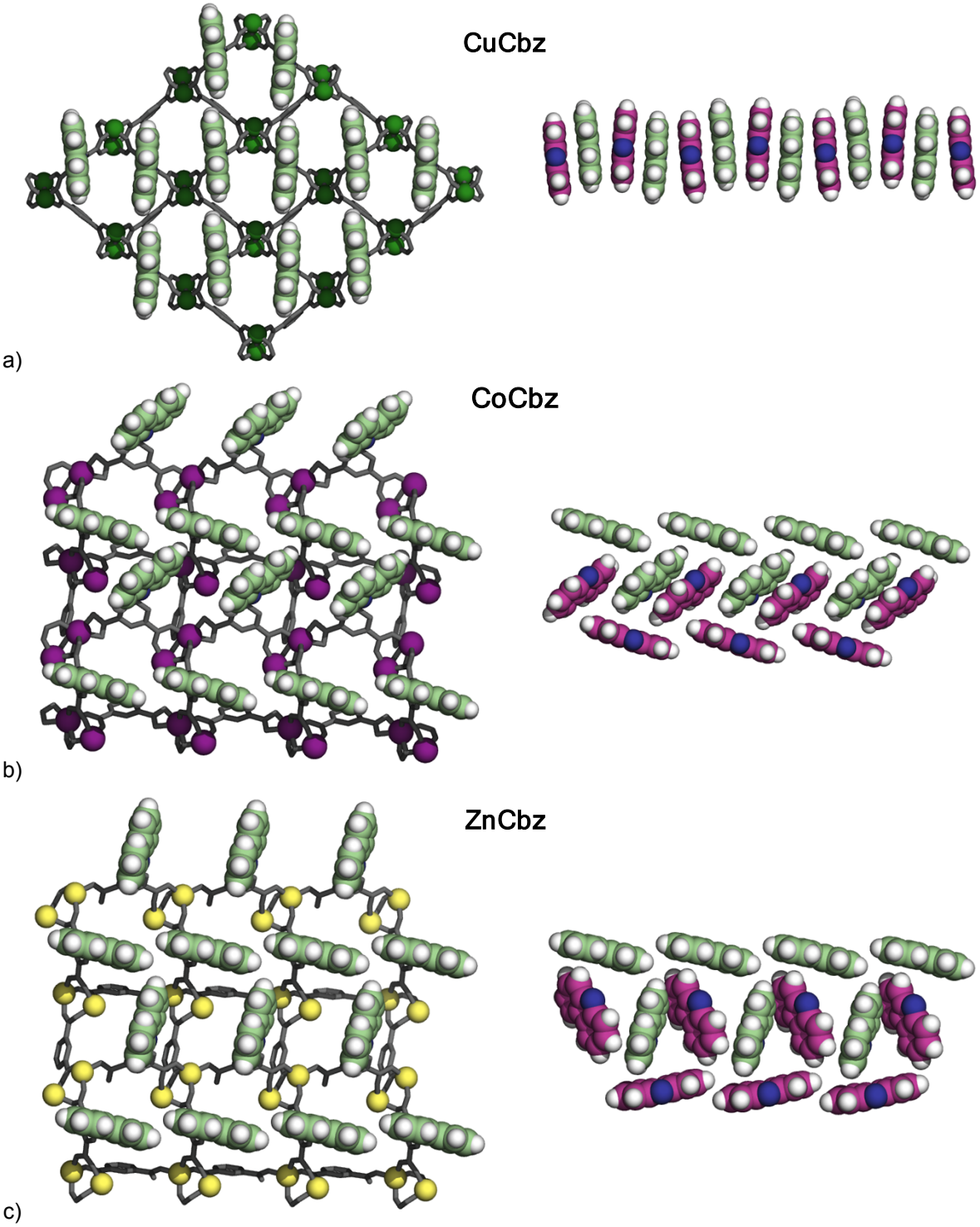



**Figure S19.** 2D Square grids and cleft-like packing motifs found between neighboring layers in a) **Cu Cbz MOF**; b) **CoCbz MOF;** c) **Zn Cbz MOF**. Carbazoles of one layer in green, carbazoles of neighboring layer in magenta.

## 7. Powder X-Ray diffraction patterns

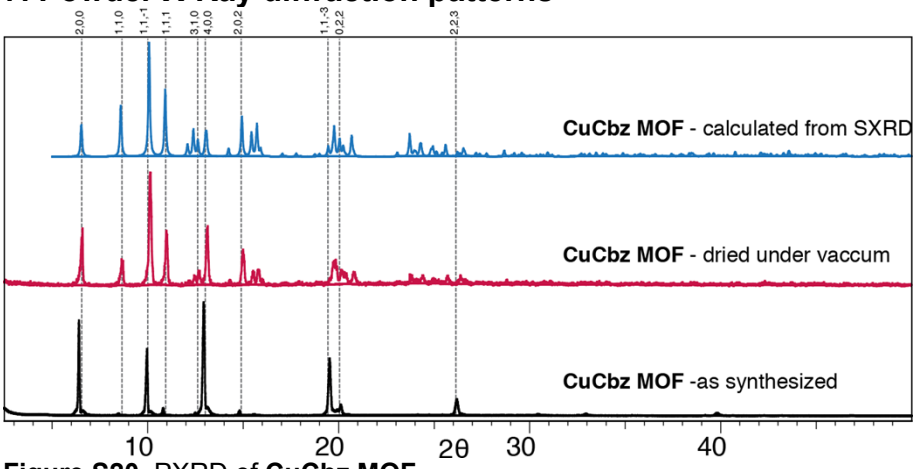



**Figure S20.** PXRD of **CuCbz MOF**.

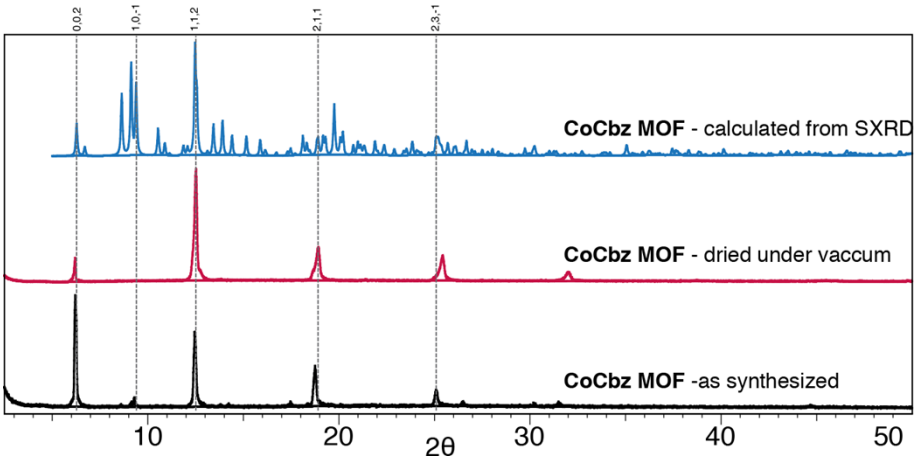



**Figure S21.** PXRD of **CoCbz MOF**.

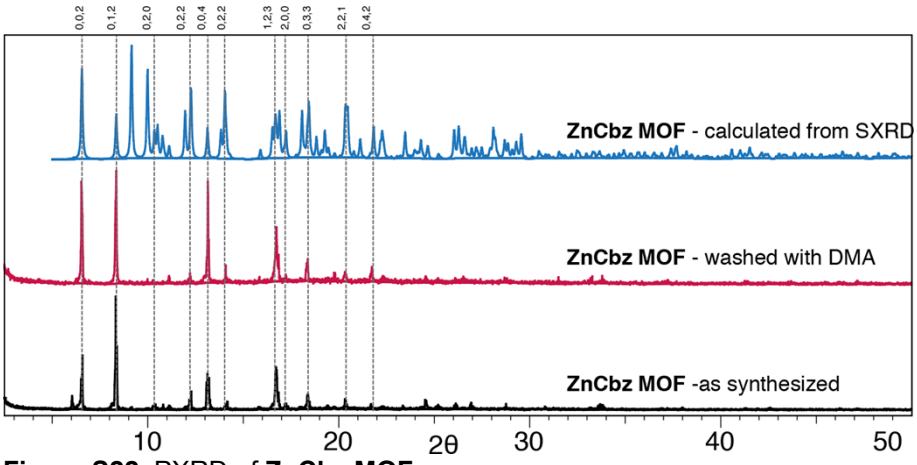



**Figure S22.** PXRD of **ZnCbz MOF**.

**Air Stability of CbzMOFs**

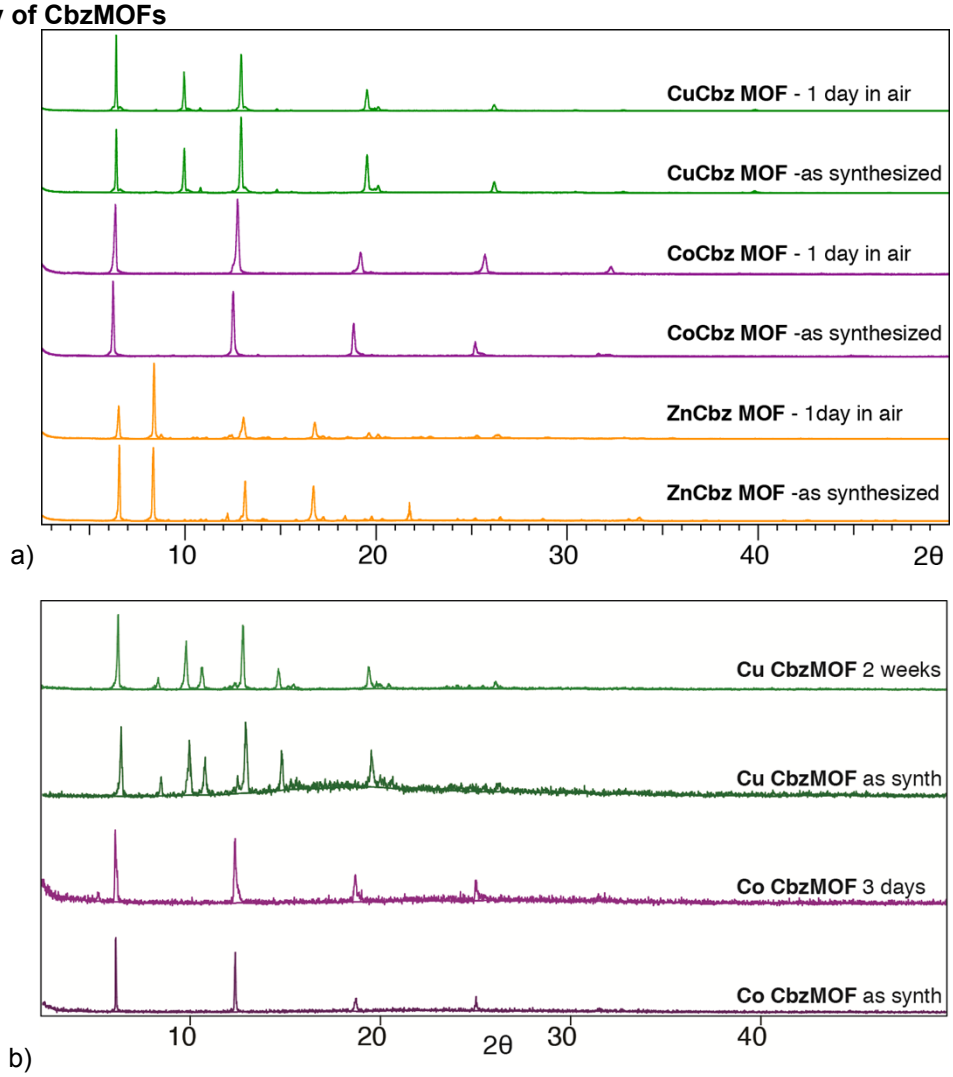



**Figure S23.** Air stability of **Cbz MOF**s. PXRD spectra of as-synthesized MOFs and repeated measurements of the same samples after a) 1 day and b) longer in air under ambient conditions.

**ZnCbz MOF**: no changes observed PXRD for ~2 days if washed with non-volatile solvent (DMA) prior to drying. If washed with volatile solvent (EtOH) and then dried in air, new small peaks appear in the PXRD spectrogram after two days.

## 8. Thermo-gravimetric Analyses (TGA)

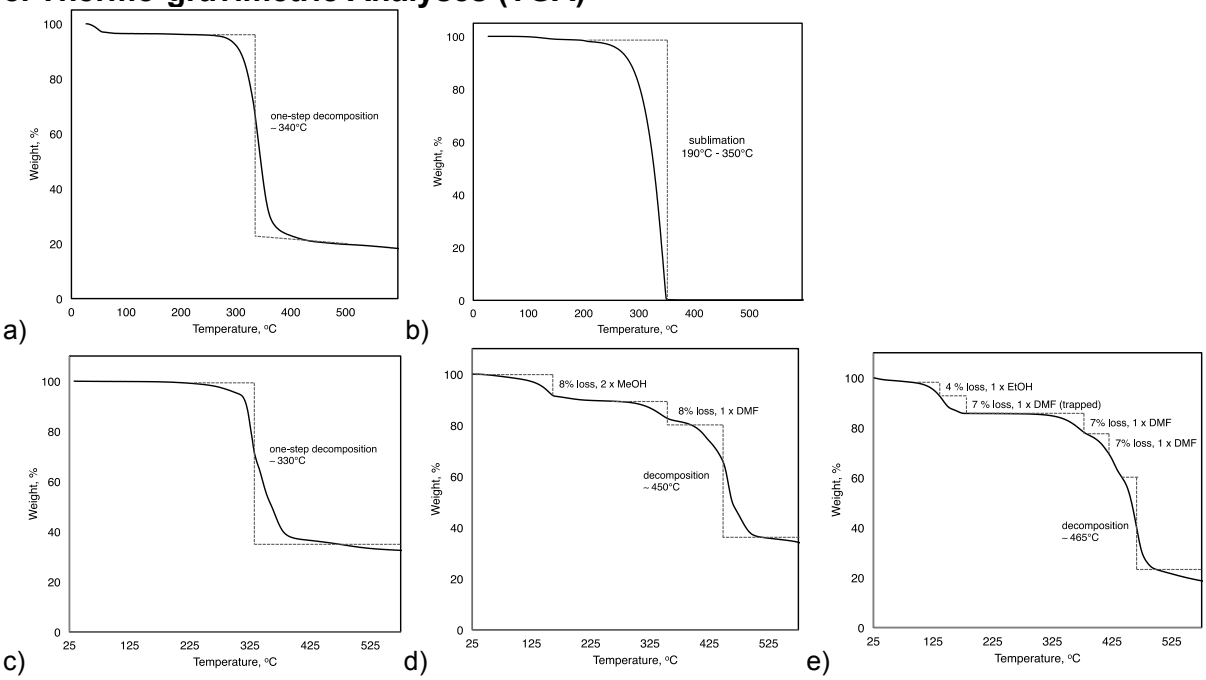



**Figure S24.** TGA profiles for a) **1a**; b) **1b**; c) **CuCbz MOF**; d) **CoCbz MOF** e) **ZnCbz MOF** under $N_2$ flow at 10°C min $^{-1}$ scan rate

## 9. IR Spectra

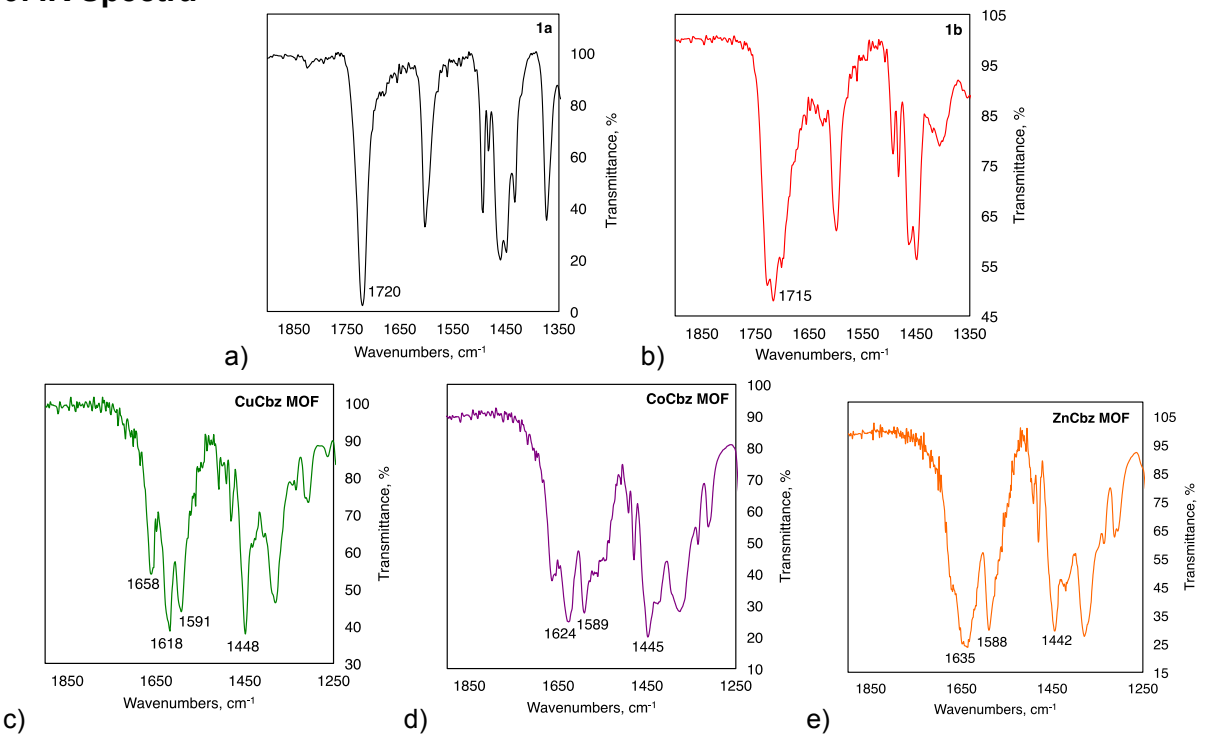



**Figure S25.** Carbonyl regions from the Infrared Spectra of a) **1a**; b) **1b**; c) **CuCbz MOF**; d) **CoCbz MOF**; and e) **ZnCbz MOF.**

## 10. Photophysical measurements

### 10.1 Steady State absorption/reflection and emission

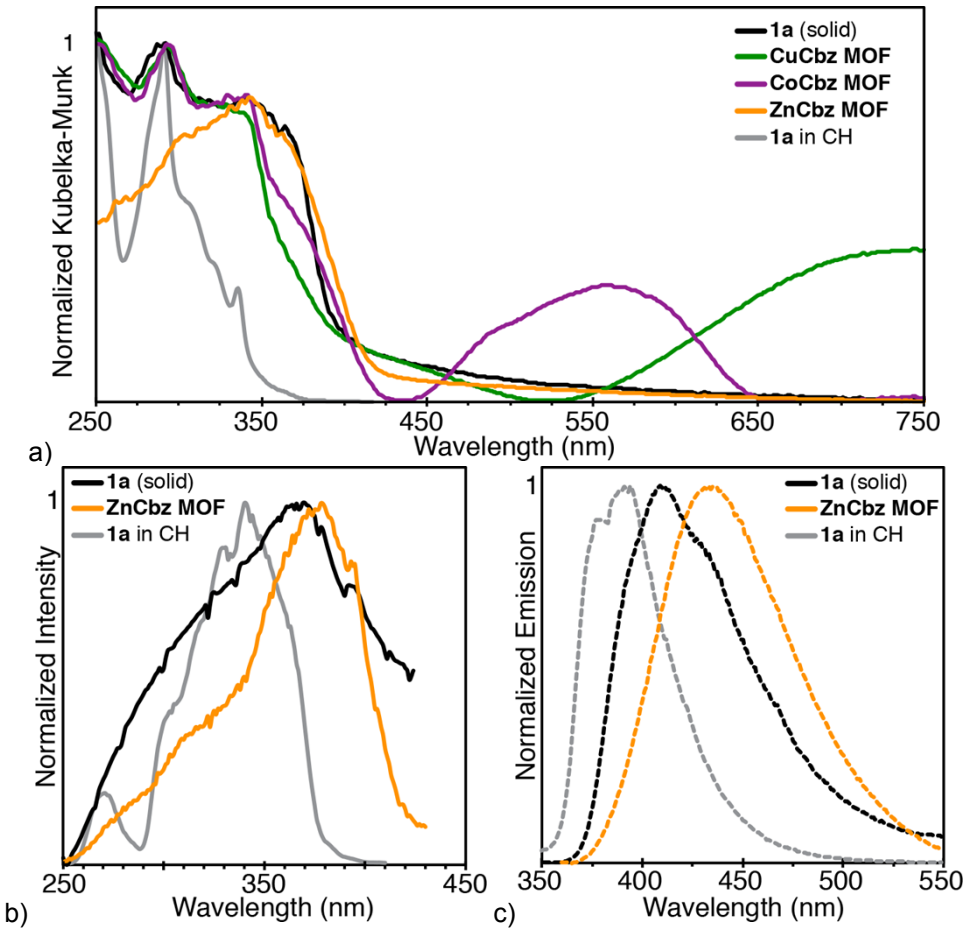



**Figure S26**. (a) Normalized diffuse reflectance spectra of **1a** and **Cbz MOF**s. Normalized solid-state (b) excitation and (c) emission of **1a** and **Zn Cbz MOF**s (reproduced from Figure 2b for ease of comparison). $\lambda_{ex}$ = 290 nm. UV-vis absorption, excitation, and emission traces of **1a** in cyclohexane included for comparison.

The deep green and purple colors of Cu CbzMOF and Co CbzMOF arise from weak, metal centered transitions centered around 740 $cm^{-1}$ and 558 $cm^{-1}$, respectively. These bands appear amplified in diffuse reflection spectrum as strong absorption bands weakly reflect (due to strong absorption of light) whereas bands of weak absorption produce more intense diffuse reflection bands (due to weak light absorption) than in a transmission spectrum. See reference [2].

### 10.2 Time dependent emission decay profiles

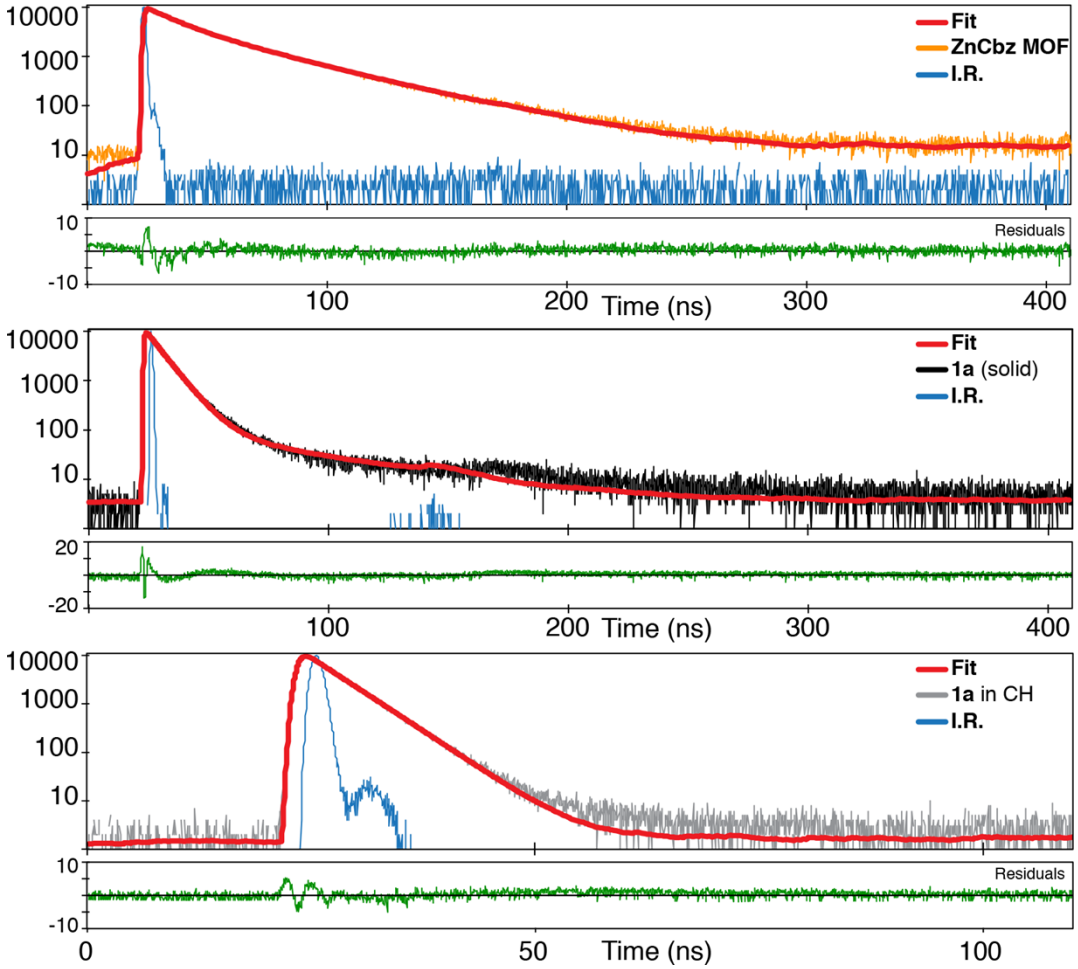



**Figure S27.** Lifetime decay and residual traces for **1a** in cyclohexane ($\lambda_{ex}$ = 340 nm, $\lambda_{em}$ = 390 nm); **1a** (solid) ($\lambda_{ex}$ = 340 nm, $\lambda_{em}$ = 410); and **ZnCbz MOF** ($\lambda_{ex}$ = 340 nm, $\lambda_{em}$ = 450)

**Table S9. Summary of photophysical data***

| | **1a** (CH) | **1a** (solid) | **ZnCbz MOF** | **CoCbz MOF** | **CuCbz MOF** |
|---|---|---|---|---|---|
| $\lambda_{max}$ (abs), nm | 290, 305, 320, 335 | 288, 340 | 300, 340 | 290, 340, 365sh, 558 | 290, 335, 365sh, 740 |
| $\lambda_{em}$, (em), nm | 390 | 410 | 430 | – | – |
| $\Delta\tilde{\nu}$ (cm$^{-1}$) | 0 | 1,250 | 2,385 | | |
| $\tau_1$ ($\alpha_1$), ns | 3.55 | 6.7 (0.9) | 13.1 (0.3) | | |
| $\tau_2$ ($\alpha_2$), ns | | 41.9 (0.1) | 37.1 (0.7) | | |
| $\langle\tau\rangle$[a], ns | 3.55 | 7.31 | 23.9 | | |
| $\chi^2$ | 1.39 | 2.63 | 1.49 | | |
| $\Phi_f$ | 0.04[b] | 0.04[b] | 0.11[b] | | |
| $k_f$[c] (s$^{-1}$) | 1.10 × 10$^8$ | 5.47 × 10$^7$ | 4.76 × 10$^7$ | | |
| $k_{nr}$[d] (s$^{-1}$) | 2.71 × 10$^9$ | 1.31 × 10$^9$ | 3.70 × 10$^8$ | | |

* Data from Table 1 included for ease of comparison. [a] $\langle\tau\rangle = 1/(\alpha_1/\tau_1 + \alpha_2/\tau_2)$; [b] absolute emission QY ± 0.01, [c] $k_f = \Phi_f/\langle\tau\rangle$. [d] $k_{nr} = (1 - \Phi_f)/\langle\tau\rangle$.

## 11 Crystallographic Data Tables

**Table S10.** Crystallographic Bond Distances (Å) and Angles (°) for **1a.**

| | | | |
|---|---|---|---|
| N1_1—C12_1 | 1.391 (3) | N1_2—C12_2 | 1.394 (3) |
| N1_1—C1_1 | 1.401 (3) | N1_2—C1_2 | 1.400 (3) |
| N1_1—C13_1 | 1.423 (3) | N1_2—C13_2 | 1.418 (3) |
| O1_1—C19_1 | 1.209 (3) | O1_2—C19_2 | 1.205 (3) |
| O2_1—C19_1 | 1.339 (3) | O2_2—C19_2 | 1.340 (3) |
| O2_1—C20_1 | 1.445 (3) | O2_2—C20_2 | 1.448 (3) |
| O3_1—C21_1 | 1.203 (3) | O3_2—C21_2 | 1.206 (3) |
| O4_1—C21_1 | 1.341 (3) | O4_2—C21_2 | 1.340 (3) |
| O4_1—C22_1 | 1.447 (3) | O4_2—C22_2 | 1.450 (3) |
| C1_1—C2_1 | 1.392 (3) | C1_2—C2_2 | 1.401 (3) |
| C1_1—C6_1 | 1.408 (3) | C1_2—C6_2 | 1.410 (3) |
| C2_1—C3_1 | 1.385 (3) | C2_2—C3_2 | 1.385 (3) |
| C2_1—H2_1 | 0.95 | C2_2—H2_2 | 0.95 |
| C3_1—C4_1 | 1.397 (4) | C3_2—C4_2 | 1.403 (3) |
| C3_1—H3_1 | 0.95 | C3_2—H3_2 | 0.95 |
| C4_1—C5_1 | 1.375 (4) | C4_2—C5_2 | 1.373 (3) |
| C4_1—H4_1 | 0.95 | C4_2—H4_2 | 0.95 |
| C5_1—C6_1 | 1.402 (3) | C5_2—C6_2 | 1.394 (3) |
| C5_1—H5_1 | 0.95 | C5_2—H5_2 | 0.95 |
| C6_1—C7_1 | 1.441 (3) | C6_2—C7_2 | 1.445 (3) |
| C7_1—C8_1 | 1.400 (3) | C7_2—C8_2 | 1.392 (3) |
| C7_1—C12_1 | 1.403 (3) | C7_2—C12_2 | 1.406 (3) |
| C8_1—C9_1 | 1.372 (4) | C8_2—C9_2 | 1.384 (3) |
| C8_1—H8_1 | 0.95 | C8_2—H8_2 | 0.95 |
| C9_1—C10_1 | 1.398 (4) | C9_2—C10_2 | 1.395 (3) |
| C9_1—H9_1 | 0.95 | C9_2—H9_2 | 0.95 |
| C10_1—C11_1 | 1.389 (3) | C10_2—C11_2 | 1.386 (3) |
| C10_1—H10_1 | 0.95 | C10_2—H10_2 | 0.95 |
| C11_1—C12_1 | 1.400 (3) | C11_2—C12_2 | 1.393 (3) |
| C11_1—H11_1 | 0.95 | C11_2—H11_2 | 0.95 |
| C13_1—C18_1 | 1.385 (3) | C13_2—C18_2 | 1.385 (3) |
| C13_1—C14_1 | 1.394 (3) | C13_2—C14_2 | 1.392 (3) |
| C14_1—C15_1 | 1.389 (3) | C14_2—C15_2 | 1.388 (3) |
| C14_1—H14_1 | 0.95 | C14_2—H14_2 | 0.95 |
| C15_1—C16_1 | 1.394 (3) | C15_2—C16_2 | 1.386 (3) |
| C15_1—C19_1 | 1.489 (3) | C15_2—C19_2 | 1.488 (3) |
| C16_1—C17_1 | 1.382 (3) | C16_2—C17_2 | 1.393 (3) |
| C16_1—H16_1 | 0.95 | C16_2—H16_2 | 0.95 |
| C17_1—C18_1 | 1.390 (3) | C17_2—C18_2 | 1.393 (3) |
| C17_1—C21_1 | 1.493 (3) | C17_2—C21_2 | 1.490 (3) |
| C18_1—H18_1 | 0.95 | C18_2—H18_2 | 0.95 |
| C20_1—H20A_1 | 0.98 | C20_2—H20A_2 | 0.98 |
| C20_1—H20B_1 | 0.98 | C20_2—H20B_2 | 0.98 |
| C20_1—H20C_1 | 0.98 | C20_2—H20C_2 | 0.98 |
| C22_1—H22A_1 | 0.98 | C22_2—H22A_2 | 0.98 |
| C22_1—H22B_1 | 0.98 | C22_2—H22B_2 | 0.98 |

| | | | |
|---|---|---|---|
| C22_1—H22C_1 | 0.98 | C22_2—H22C_2 | 0.98 |
| C12_1—N1_1—C1_1 | 108.47 (19) | C12_2—N1_2—C1_2 | 108.14 (19) |
| C12_1—N1_1—C13_1 | 126.00 (19) | C12_2—N1_2—C13_2 | 125.85 (19) |
| C1_1—N1_1—C13_1 | 125.0 (2) | C1_2—N1_2—C13_2 | 125.77 (19) |
| C19_1—O2_1—C20_1 | 114.56 (19) | C19_2—O2_2—C20_2 | 114.5 (2) |
| C21_1—O4_1—C22_1 | 114.79 (18) | C21_2—O4_2—C22_2 | 114.63 (19) |
| C2_1—C1_1—N1_1 | 130.2 (2) | N1_2—C1_2—C2_2 | 130.0 (2) |
| C2_1—C1_1—C6_1 | 121.4 (2) | N1_2—C1_2—C6_2 | 108.90 (19) |
| N1_1—C1_1—C6_1 | 108.4 (2) | C2_2—C1_2—C6_2 | 121.1 (2) |
| C3_1—C2_1—C1_1 | 117.8 (2) | C3_2—C2_2—C1_2 | 117.8 (2) |
| C3_1—C2_1—H2_1 | 121.1 | C3_2—C2_2—H2_2 | 121.1 |
| C1_1—C2_1—H2_1 | 121.1 | C1_2—C2_2—H2_2 | 121.1 |
| C2_1—C3_1—C4_1 | 121.3 (2) | C2_2—C3_2—C4_2 | 121.0 (2) |
| C2_1—C3_1—H3_1 | 119.4 | C2_2—C3_2—H3_2 | 119.5 |
| C4_1—C3_1—H3_1 | 119.4 | C4_2—C3_2—H3_2 | 119.5 |
| C5_1—C4_1—C3_1 | 121.2 (2) | C5_2—C4_2—C3_2 | 121.3 (2) |
| C5_1—C4_1—H4_1 | 119.4 | C5_2—C4_2—H4_2 | 119.4 |
| C3_1—C4_1—H4_1 | 119.4 | C3_2—C4_2—H4_2 | 119.4 |
| C4_1—C5_1—C6_1 | 118.6 (2) | C4_2—C5_2—C6_2 | 118.9 (2) |
| C4_1—C5_1—H5_1 | 120.7 | C4_2—C5_2—H5_2 | 120.6 |
| C6_1—C5_1—H5_1 | 120.7 | C6_2—C5_2—H5_2 | 120.6 |
| C5_1—C6_1—C1_1 | 119.8 (2) | C5_2—C6_2—C1_2 | 119.9 (2) |
| C5_1—C6_1—C7_1 | 133.2 (2) | C5_2—C6_2—C7_2 | 133.2 (2) |
| C1_1—C6_1—C7_1 | 107.0 (2) | C1_2—C6_2—C7_2 | 106.8 (2) |
| C8_1—C7_1—C12_1 | 119.9 (2) | C8_2—C7_2—C12_2 | 120.0 (2) |
| C8_1—C7_1—C6_1 | 133.0 (2) | C8_2—C7_2—C6_2 | 133.1 (2) |
| C12_1—C7_1—C6_1 | 107.1 (2) | C12_2—C7_2—C6_2 | 106.9 (2) |
| C9_1—C8_1—C7_1 | 118.8 (2) | C9_2—C8_2—C7_2 | 118.9 (2) |
| C9_1—C8_1—H8_1 | 120.6 | C9_2—C8_2—H8_2 | 120.5 |
| C7_1—C8_1—H8_1 | 120.6 | C7_2—C8_2—H8_2 | 120.5 |
| C8_1—C9_1—C10_1 | 121.1 (2) | C8_2—C9_2—C10_2 | 120.3 (2) |
| C8_1—C9_1—H9_1 | 119.4 | C8_2—C9_2—H9_2 | 119.9 |
| C10_1—C9_1—H9_1 | 119.4 | C10_2—C9_2—H9_2 | 119.9 |
| C11_1—C10_1—C9_1 | 121.4 (2) | C11_2—C10_2—C9_2 | 122.1 (2) |
| C11_1—C10_1—H10_1 | 119.3 | C11_2—C10_2—H10_2 | 119.0 |
| C9_1—C10_1—H10_1 | 119.3 | C9_2—C10_2—H10_2 | 119.0 |
| C10_1—C11_1—C12_1 | 117.4 (2) | C10_2—C11_2—C12_2 | 117.1 (2) |
| C10_1—C11_1—H11_1 | 121.3 | C10_2—C11_2—H11_2 | 121.4 |
| C12_1—C11_1—H11_1 | 121.3 | C12_2—C11_2—H11_2 | 121.4 |
| N1_1—C12_1—C11_1 | 129.6 (2) | C11_2—C12_2—N1_2 | 129.1 (2) |
| N1_1—C12_1—C7_1 | 109.0 (2) | C11_2—C12_2—C7_2 | 121.6 (2) |
| C11_1—C12_1—C7_1 | 121.4 (2) | N1_2—C12_2—C7_2 | 109.2 (2) |
| C18_1—C13_1—C14_1 | 120.0 (2) | C18_2—C13_2—C14_2 | 120.0 (2) |
| C18_1—C13_1—N1_1 | 120.0 (2) | C18_2—C13_2—N1_2 | 120.1 (2) |
| C14_1—C13_1—N1_1 | 120.0 (2) | C14_2—C13_2—N1_2 | 119.8 (2) |
| C15_1—C14_1—C13_1 | 119.6 (2) | C15_2—C14_2—C13_2 | 119.5 (2) |
| C15_1—C14_1—H14_1 | 120.2 | C15_2—C14_2—H14_2 | 120.3 |
| C13_1—C14_1—H14_1 | 120.2 | C13_2—C14_2—H14_2 | 120.3 |
| C14_1—C15_1—C16_1 | 120.3 (2) | C16_2—C15_2—C14_2 | 120.9 (2) |

| | | | |
|---|---|---|---|
| C14_1—C15_1—C19_1 | 122.0 (2) | C16_2—C15_2—C19_2 | 117.4 (2) |
| C16_1—C15_1—C19_1 | 117.7 (2) | C14_2—C15_2—C19_2 | 121.7 (2) |
| C17_1—C16_1—C15_1 | 119.6 (2) | C15_2—C16_2—C17_2 | 119.4 (2) |
| C17_1—C16_1—H16_1 | 120.2 | C15_2—C16_2—H16_2 | 120.3 |
| C15_1—C16_1—H16_1 | 120.2 | C17_2—C16_2—H16_2 | 120.3 |
| C16_1—C17_1—C18_1 | 120.4 (2) | C16_2—C17_2—C18_2 | 120.0 (2) |
| C16_1—C17_1—C21_1 | 122.1 (2) | C16_2—C17_2—C21_2 | 122.2 (2) |
| C18_1—C17_1—C21_1 | 117.4 (2) | C18_2—C17_2—C21_2 | 117.8 (2) |
| C13_1—C18_1—C17_1 | 119.9 (2) | C13_2—C18_2—C17_2 | 120.2 (2) |
| C13_1—C18_1—H18_1 | 120.0 | C13_2—C18_2—H18_2 | 119.9 |
| C17_1—C18_1—H18_1 | 120.0 | C17_2—C18_2—H18_2 | 119.9 |
| O1_1—C19_1—O2_1 | 123.5 (2) | O1_2—C19_2—O2_2 | 123.4 (2) |
| O1_1—C19_1—C15_1 | 123.6 (2) | O1_2—C19_2—C15_2 | 124.4 (2) |
| O2_1—C19_1—C15_1 | 112.8 (2) | O2_2—C19_2—C15_2 | 112.2 (2) |
| O2_1—C20_1—H20A_1 | 109.5 | O2_2—C20_2—H20A_2 | 109.5 |
| O2_1—C20_1—H20B_1 | 109.5 | O2_2—C20_2—H20B_2 | 109.5 |
| H20A_1—C20_1—H20B_1 | 109.5 | H20A_2—C20_2—H20B_2 | 109.5 |
| O2_1—C20_1—H20C_1 | 109.5 | O2_2—C20_2—H20C_2 | 109.5 |
| H20A_1—C20_1—H20C_1 | 109.5 | H20A_2—C20_2—H20C_2 | 109.5 |
| H20B_1—C20_1—H20C_1 | 109.5 | H20B_2—C20_2—H20C_2 | 109.5 |
| O3_1—C21_1—O4_1 | 123.5 (2) | O3_2—C21_2—O4_2 | 123.9 (2) |
| O3_1—C21_1—C17_1 | 123.9 (2) | O3_2—C21_2—C17_2 | 124.0 (2) |
| O4_1—C21_1—C17_1 | 112.5 (2) | O4_2—C21_2—C17_2 | 112.1 (2) |
| O4_1—C22_1—H22A_1 | 109.5 | O4_2—C22_2—H22A_2 | 109.5 |
| O4_1—C22_1—H22B_1 | 109.5 | O4_2—C22_2—H22B_2 | 109.5 |
| H22A_1—C22_1—H22B_1 | 109.5 | H22A_2—C22_2—H22B_2 | 109.5 |
| O4_1—C22_1—H22C_1 | 109.5 | O4_2—C22_2—H22C_2 | 109.5 |
| H22A_1—C22_1—H22C_1 | 109.5 | H22A_2—C22_2—H22C_2 | 109.5 |
| H22B_1—C22_1—H22C_1 | 109.5 | H22B_2—C22_2—H22C_2 | 109.5 |

**Table S11.** Crystallographic Bond Distances (Å) and Angles (º) for **CuCbz MOF.**

| | | | |
|---|---|---|---|
| Cu1—O4$^{i}$ | 1.9526 (15) | C14—H14 | 0.93 |
| Cu1—O1 | 1.9548 (16) | C15—C16 | 1.393 (3) |
| Cu1—O2$^{ii}$ | 1.9684 (16) | C15—C19 | 1.498 (3) |
| Cu1—O3$^{iii}$ | 1.9749 (16) | C16—C17 | 1.388 (3) |
| Cu1—O5' | 2.13 (4) | C16—H16 | 0.93 |
| Cu1—O5 | 2.17 (2) | C17—C18 | 1.389 (3) |
| Cu1—Cu1$^{ii}$ | 2.6618 (6) | C17—C20 | 1.500 (3) |
| N1—C1 | 1.389 (3) | C18—H18 | 0.93 |
| N1—C12 | 1.396 (3) | N2—C21 | 1.320 (9) |
| N1—C13 | 1.420 (3) | N2—C24 | 1.439 (12) |
| O1—C19 | 1.258 (3) | N2—C25 | 1.446 (12) |
| O2—C19 | 1.253 (3) | O5—C21 | 1.24 (2) |
| O2—Cu1$^{ii}$ | 1.9684 (16) | C21—C22 | 1.621 (16) |
| O3—C20 | 1.252 (3) | C22—C23 | 1.213 (17) |
| O3—Cu1$^{iv}$ | 1.9749 (16) | C22—H22A | 0.97 |
| O4—C20 | 1.254 (3) | C22—H22B | 0.97 |
| O4—Cu1$^{v}$ | 1.9526 (15) | C23—C24 | 1.495 (12) |
| C1—C2 | 1.395 (4) | C23—H23A | 0.97 |
| C1—C6 | 1.403 (3) | C23—H23B | 0.97 |
| C2—C3 | 1.367 (4) | C24—H24A | 0.97 |
| C2—H2 | 0.93 | C24—H24B | 0.97 |
| C3—C4 | 1.390 (5) | C25—H25A | 0.96 |
| C3—H3 | 0.93 | C25—H25B | 0.96 |
| C4—C5 | 1.367 (5) | C25—H25C | 0.96 |
| C4—H4 | 0.93 | N2'—C21' | 1.346 (18) |
| C5—C6 | 1.395 (4) | N2'—C24' | 1.46 (2) |
| C5—H5 | 0.93 | N2'—C25' | 1.53 (3) |
| C6—C7 | 1.447 (4) | O5'—C21' | 1.18 (4) |
| C7—C8 | 1.398 (4) | C21'—C22' | 1.47 (2) |
| C7—C12 | 1.411 (3) | C22'—C23' | 1.55 (2) |
| C8—C9 | 1.372 (5) | C22'—H22C | 0.97 |
| C8—H8 | 0.93 | C22'—H22D | 0.97 |
| C9—C10 | 1.388 (5) | C23'—C24' | 1.44 (3) |
| C9—H9 | 0.93 | C23'—H23C | 0.97 |
| C10—C11 | 1.380 (4) | C23'—H23D | 0.97 |
| C10—H10 | 0.93 | C24'—H24C | 0.97 |
| C11—C12 | 1.384 (4) | C24'—H24D | 0.97 |
| C11—H11 | 0.93 | C25'—H25D | 0.96 |
| C13—C14 | 1.384 (3) | C25'—H25E | 0.96 |
| C13—C18 | 1.391 (3) | C25'—H25F | 0.96 |
| C14—C15 | 1.391 (3) | | |
| O4$^{i}$—Cu1—O1 | 87.57 (7) | C16—C17—C18 | 120.53 (19) |
| O4$^{i}$—Cu1—O2$^{ii}$ | 89.61 (7) | C16—C17—C20 | 119.57 (19) |
| O1—Cu1—O2$^{ii}$ | 167.31 (7) | C18—C17—C20 | 119.88 (19) |
| O4$^{i}$—Cu1—O3$^{iii}$ | 167.45 (7) | C17—C18—C13 | 119.6 (2) |
| O1—Cu1—O3$^{iii}$ | 89.03 (8) | C17—C18—H18 | 120.2 |
| O2$^{ii}$—Cu1—O3$^{iii}$ | 91.08 (8) | C13—C18—H18 | 120.2 |
| O4$^{i}$—Cu1—O5' | 102.0 (10) | O2—C19—O1 | 126.0 (2) |

| | | | |
|---|---|---|---|
| O1—Cu1—O5' | 96.7 (11) | O2—C19—C15 | 117.86 (19) |
| O2$^{ii}$—Cu1—O5' | 96.0 (11) | O1—C19—C15 | 116.10 (19) |
| O3$^{iii}$—Cu1—O5' | 90.4 (10) | O3—C20—O4 | 126.6 (2) |
| O4$^{i}$—Cu1—O5 | 101.0 (5) | O3—C20—C17 | 116.19 (19) |
| O1—Cu1—O5 | 90.5 (6) | O4—C20—C17 | 117.18 (19) |
| O2$^{ii}$—Cu1—O5 | 102.2 (6) | C21—N2—C24 | 115.1 (9) |
| O3$^{iii}$—Cu1—O5 | 91.1 (5) | C21—N2—C25 | 120.7 (8) |
| O4$^{i}$—Cu1—Cu1$^{ii}$ | 87.93 (5) | C24—N2—C25 | 124.1 (8) |
| O1—Cu1—Cu1$^{ii}$ | 83.64 (5) | C21—O5—Cu1 | 120.8 (14) |
| O2$^{ii}$—Cu1—Cu1$^{ii}$ | 83.89 (5) | O5—C21—N2 | 129.8 (13) |
| O3$^{iii}$—Cu1—Cu1$^{ii}$ | 79.69 (5) | O5—C21—C22 | 131.4 (13) |
| O5'—Cu1—Cu1$^{ii}$ | 170.1 (10) | N2—C21—C22 | 98.4 (8) |
| O5—Cu1—Cu1$^{ii}$ | 169.1 (5) | C23—C22—C21 | 113.5 (13) |
| C1—N1—C12 | 108.62 (19) | C23—C22—H22A | 108.9 |
| C1—N1—C13 | 126.3 (2) | C21—C22—H22A | 108.9 |
| C12—N1—C13 | 125.1 (2) | C23—C22—H22B | 108.9 |
| C19—O1—Cu1 | 123.59 (14) | C21—C22—H22B | 108.9 |
| C19—O2—Cu1$^{ii}$ | 122.72 (14) | H22A—C22—H22B | 107.7 |
| C20—O3—Cu1$^{iv}$ | 127.17 (14) | C22—C23—C24 | 107.7 (10) |
| C20—O4—Cu1$^{v}$ | 118.49 (14) | C22—C23—H23A | 110.2 |
| N1—C1—C2 | 129.3 (2) | C24—C23—H23A | 110.2 |
| N1—C1—C6 | 109.1 (2) | C22—C23—H23B | 110.2 |
| C2—C1—C6 | 121.6 (3) | C24—C23—H23B | 110.2 |
| C3—C2—C1 | 117.4 (3) | H23A—C23—H23B | 108.5 |
| C3—C2—H2 | 121.3 | N2—C24—C23 | 104.3 (7) |
| C1—C2—H2 | 121.3 | N2—C24—H24A | 110.9 |
| C2—C3—C4 | 122.0 (3) | C23—C24—H24A | 110.9 |
| C2—C3—H3 | 119.0 | N2—C24—H24B | 110.9 |
| C4—C3—H3 | 119.0 | C23—C24—H24B | 110.9 |
| C5—C4—C3 | 120.8 (3) | H24A—C24—H24B | 108.9 |
| C5—C4—H4 | 119.6 | N2—C25—H25A | 109.5 |
| C3—C4—H4 | 119.6 | N2—C25—H25B | 109.5 |
| C4—C5—C6 | 119.2 (3) | H25A—C25—H25B | 109.5 |
| C4—C5—H5 | 120.4 | N2—C25—H25C | 109.5 |
| C6—C5—H5 | 120.4 | H25A—C25—H25C | 109.5 |
| C5—C6—C1 | 119.2 (3) | H25B—C25—H25C | 109.5 |
| C5—C6—C7 | 134.0 (3) | C21'—N2'—C24' | 111.4 (16) |
| C1—C6—C7 | 106.8 (2) | C21'—N2'—C25' | 104.9 (12) |
| C8—C7—C12 | 118.7 (3) | C24'—N2'—C25' | 142.7 (14) |
| C8—C7—C6 | 134.4 (3) | C21'—O5'—Cu1 | 123 (3) |
| C12—C7—C6 | 106.8 (2) | O5'—C21'—N2' | 130 (2) |
| C9—C8—C7 | 119.4 (3) | O5'—C21'—C22' | 119 (2) |
| C9—C8—H8 | 120.3 | N2'—C21'—C22' | 111.0 (12) |
| C7—C8—H8 | 120.3 | C21'—C22'—C23' | 102.7 (14) |
| C8—C9—C10 | 120.7 (3) | C21'—C22'—H22C | 111.2 |
| C8—C9—H9 | 119.6 | C23'—C22'—H22C | 111.2 |
| C10—C9—H9 | 119.6 | C21'—C22'—H22D | 111.2 |
| C11—C10—C9 | 121.7 (3) | C23'—C22'—H22D | 111.2 |
| C11—C10—H10 | 119.2 | H22C—C22'—H22D | 109.1 |

| | | | |
|---|---|---|---|
| C9—C10—H10 | 119.2 | C24'—C23'—C22' | 107.3 (14) |
| C10—C11—C12 | 117.5 (3) | C24'—C23'—H23C | 110.2 |
| C10—C11—H11 | 121.2 | C22'—C23'—H23C | 110.2 |
| C12—C11—H11 | 121.2 | C24'—C23'—H23D | 110.2 |
| C11—C12—N1 | 129.5 (2) | C22'—C23'—H23D | 110.2 |
| C11—C12—C7 | 121.9 (2) | H23C—C23'—H23D | 108.5 |
| N1—C12—C7 | 108.6 (2) | C23'—C24'—N2' | 106.4 (15) |
| C14—C13—C18 | 120.0 (2) | C23'—C24'—H24C | 110.4 |
| C14—C13—N1 | 119.96 (19) | N2'—C24'—H24C | 110.4 |
| C18—C13—N1 | 120.0 (2) | C23'—C24'—H24D | 110.4 |
| C13—C14—C15 | 120.4 (2) | N2'—C24'—H24D | 110.4 |
| C13—C14—H14 | 119.8 | H24C—C24'—H24D | 108.6 |
| C15—C14—H14 | 119.8 | N2'—C25'—H25D | 109.5 |
| C14—C15—C16 | 119.81 (19) | N2'—C25'—H25E | 109.5 |
| C14—C15—C19 | 119.94 (19) | H25D—C25'—H25E | 109.5 |
| C16—C15—C19 | 120.23 (19) | N2'—C25'—H25F | 109.5 |
| C17—C16—C15 | 119.57 (19) | H25D—C25'—H25F | 109.5 |
| C17—C16—H16 | 120.2 | H25E—C25'—H25F | 109.5 |
| C15—C16—H16 | 120.2 | | |

Symmetry codes: (i) *x*, −*y*+2, *z*−1/2; (ii) −*x*+1/2, −*y*+3/2, −*z*; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) −*x*+1/2, *y*+1/2, −*z*+1/2; (v) *x*, −*y*+2, *z*+1/2.

**Table S12.** Crystallographic Bond Distances (Å) and Angles (°) for **CoCbz MOF.**

| | | | |
|---|---|---|---|
| Co1—O9' | 2.01 (2) | C24—H24 | 0.95 |
| Co1—O3 | 2.0459 (18) | C25—C26 | 1.392 (3) |
| Co1—O5 | 2.0720 (17) | C25—C40$^{ii}$ | 1.491 (3) |
| Co1—O11 | 2.092 (2) | C26—H26 | 0.95 |
| Co1—O10 | 2.0933 (18) | C27—C28 | 1.386 (4) |
| Co1—O9 | 2.107 (5) | C27—C32 | 1.413 (3) |
| Co1—O1 | 2.1113 (17) | C28—C29 | 1.383 (4) |
| Co2—O6 | 1.9915 (17) | C28—H28 | 0.95 |
| Co2—O4 | 1.9928 (18) | C29—C30 | 1.396 (4) |
| Co2—O1 | 2.1448 (17) | C29—H29 | 0.95 |
| Co2—O7 | 2.1548 (16) | C30—C31 | 1.377 (4) |
| Co2—O2 | 2.1558 (18) | C30—H30 | 0.95 |
| Co2—O8 | 2.1725 (18) | C31—C32 | 1.391 (4) |
| Co2—C1 | 2.472 (3) | C31—H31 | 0.95 |
| Co2—C40 | 2.491 (2) | C32—C33 | 1.445 (4) |
| O1—C1 | 1.284 (3) | C33—C34 | 1.398 (4) |
| O2—C1 | 1.244 (3) | C33—C38 | 1.411 (4) |
| O3—C20 | 1.251 (3) | C34—C35 | 1.381 (4) |
| O4—C20 | 1.257 (3) | C34—H34 | 0.95 |
| O5—C39 | 1.253 (3) | C35—C36 | 1.393 (4) |
| O6—C39 | 1.258 (3) | C35—H35 | 0.95 |
| O7—C40 | 1.272 (3) | C36—C37 | 1.392 (4) |
| O8—C40 | 1.260 (3) | C36—H36 | 0.95 |
| O10—C44 | 1.436 (3) | C37—C38 | 1.383 (4) |

| | | | |
|---|---|---|---|
| O10—H10 | 0.78 (3) | C37—H37 | 0.95 |
| O11—C45 | 1.419 (4) | C39—C4$^{iii}$ | 1.508 (3) |
| O11—H11 | 0.81 (4) | C40—C25$^{iv}$ | 1.491 (3) |
| N1—C19 | 1.394 (3) | O9—C41 | 1.240 (7) |
| N1—C8 | 1.396 (3) | C41—N3 | 1.317 (6) |
| N1—C6 | 1.425 (3) | C41—H41 | 0.95 |
| N2—C38 | 1.399 (3) | N3—C42 | 1.454 (6) |
| N2—C27 | 1.403 (3) | N3—C43 | 1.516 (8) |
| N2—C23 | 1.426 (3) | C42—H42A | 0.98 |
| C1—C2 | 1.494 (4) | C42—H42B | 0.98 |
| C2—C3 | 1.389 (3) | C42—H42C | 0.98 |
| C2—C7 | 1.397 (3) | C43—H43A | 0.98 |
| C3—C4 | 1.390 (4) | C43—H43B | 0.98 |
| C3—H3 | 0.95 | C43—H43C | 0.98 |
| C4—C5 | 1.387 (3) | C44—H44A | 0.98 |
| C4—C39$^{i}$ | 1.508 (3) | C44—H44B | 0.98 |
| C5—C6 | 1.392 (4) | C44—H44C | 0.98 |
| C5—H5 | 0.95 | C45—H45A | 0.98 |
| C6—C7 | 1.388 (4) | C45—H45B | 0.98 |
| C7—H7 | 0.95 | C45—H45C | 0.98 |
| C8—C9 | 1.393 (4) | O9'—C41' | 1.13 (3) |
| C8—C13 | 1.403 (4) | C41'—N3' | 1.42 (4) |
| C9—C10 | 1.377 (4) | C41'—H41' | 0.95 |
| C9—H9 | 0.95 | N3'—C43' | 0.99 (3) |
| C10—C11 | 1.391 (5) | N3'—C42' | 1.43 (3) |
| C10—H10A | 0.95 | C42'—C43' | 2.01 (4) |
| C11—C12 | 1.380 (5) | C42'—H42D | 0.98 |
| C11—H11A | 0.95 | C42'—H42E | 0.98 |
| C12—C13 | 1.391 (4) | C42'—H42F | 0.98 |
| C12—H12 | 0.95 | C43'—H43D | 0.98 |
| C13—C14 | 1.447 (4) | C43'—H43E | 0.98 |
| C14—C15 | 1.392 (4) | C43'—H43F | 0.98 |
| C14—C19 | 1.405 (4) | O1S—C1S | 1.443 (9) |
| C15—C16 | 1.372 (4) | O1S—H1S | 1.07 (6) |
| C15—H15 | 0.95 | C1S—H1S1 | 0.98 |
| C16—C17 | 1.396 (4) | C1S—H1S2 | 0.98 |
| C16—H16 | 0.95 | C1S—H1S3 | 0.98 |
| C17—C18 | 1.382 (4) | O1F—C1F | 1.279 (13) |
| C17—H17 | 0.95 | C1F—N1F | 1.356 (14) |
| C18—C19 | 1.385 (4) | C1F—H1F | 0.95 |
| C18—H18 | 0.95 | N1F—C2F | 1.431 (11) |
| C20—C21 | 1.505 (3) | N1F—C3F | 1.479 (13) |
| C21—C22 | 1.387 (3) | C2F—H2F1 | 0.98 |
| C21—C26 | 1.387 (3) | C2F—H2F2 | 0.98 |
| C22—C23 | 1.390 (3) | C2F—H2F3 | 0.98 |
| C22—H22 | 0.95 | C3F—H3F1 | 0.98 |
| C23—C24 | 1.391 (3) | C3F—H3F2 | 0.98 |
| C24—C25 | 1.389 (3) | C3F—H3F3 | 0.98 |
| O9'—Co1—O3 | 97.3 (5) | C22—C23—N2 | 119.7 (2) |

| | | | |
|---|---|---|---|
| O9'—Co1—O5 | 161.0 (5) | C24—C23—N2 | 120.0 (2) |
| O3—Co1—O5 | 93.40 (8) | C25—C24—C23 | 119.5 (2) |
| O9'—Co1—O11 | 73.6 (5) | C25—C24—H24 | 120.3 |
| O3—Co1—O11 | 88.68 (9) | C23—C24—H24 | 120.3 |
| O5—Co1—O11 | 91.07 (9) | C24—C25—C26 | 120.3 (2) |
| O9'—Co1—O10 | 82.3 (5) | C24—C25—C40$^{ii}$ | 120.6 (2) |
| O3—Co1—O10 | 178.47 (7) | C26—C25—C40$^{ii}$ | 119.1 (2) |
| O5—Co1—O10 | 86.56 (7) | C21—C26—C25 | 120.0 (2) |
| O11—Co1—O10 | 89.79 (9) | C21—C26—H26 | 120.0 |
| O3—Co1—O9 | 86.85 (14) | C25—C26—H26 | 120.0 |
| O5—Co1—O9 | 178.13 (15) | C28—C27—N2 | 129.3 (2) |
| O11—Co1—O9 | 87.08 (16) | C28—C27—C32 | 122.0 (2) |
| O10—Co1—O9 | 93.14 (14) | N2—C27—C32 | 108.7 (2) |
| O9'—Co1—O1 | 100.0 (5) | C29—C28—C27 | 117.3 (2) |
| O3—Co1—O1 | 93.27 (7) | C29—C28—H28 | 121.3 |
| O5—Co1—O1 | 95.01 (7) | C27—C28—H28 | 121.3 |
| O11—Co1—O1 | 173.48 (9) | C28—C29—C30 | 121.5 (3) |
| O10—Co1—O1 | 88.26 (7) | C28—C29—H29 | 119.2 |
| O9—Co1—O1 | 86.82 (15) | C30—C29—H29 | 119.2 |
| O6—Co2—O4 | 96.54 (8) | C31—C30—C29 | 120.8 (3) |
| O6—Co2—O1 | 98.85 (7) | C31—C30—H30 | 119.6 |
| O4—Co2—O1 | 101.47 (7) | C29—C30—H30 | 119.6 |
| O6—Co2—O7 | 94.22 (7) | C30—C31—C32 | 119.1 (3) |
| O4—Co2—O7 | 100.17 (7) | C30—C31—H31 | 120.4 |
| O1—Co2—O7 | 153.18 (6) | C32—C31—H31 | 120.4 |
| O6—Co2—O2 | 159.56 (7) | C31—C32—C27 | 119.2 (3) |
| O4—Co2—O2 | 92.59 (8) | C31—C32—C33 | 133.9 (2) |
| O1—Co2—O2 | 61.31 (6) | C27—C32—C33 | 107.0 (2) |
| O7—Co2—O2 | 102.13 (6) | C34—C33—C38 | 118.9 (3) |
| O6—Co2—O8 | 90.88 (7) | C34—C33—C32 | 133.9 (3) |
| O4—Co2—O8 | 160.36 (7) | C38—C33—C32 | 107.2 (2) |
| O1—Co2—O8 | 95.28 (7) | C35—C34—C33 | 119.0 (3) |
| O7—Co2—O8 | 61.04 (6) | C35—C34—H34 | 120.5 |
| O2—Co2—O8 | 86.47 (7) | C33—C34—H34 | 120.5 |
| O6—Co2—C1 | 129.55 (8) | C34—C35—C36 | 121.2 (3) |
| O4—Co2—C1 | 100.47 (8) | C34—C35—H35 | 119.4 |
| O1—Co2—C1 | 31.27 (7) | C36—C35—H35 | 119.4 |
| O7—Co2—C1 | 128.18 (7) | C37—C36—C35 | 121.1 (3) |
| O2—Co2—C1 | 30.21 (7) | C37—C36—H36 | 119.5 |
| O8—Co2—C1 | 88.54 (8) | C35—C36—H36 | 119.5 |
| O6—Co2—C40 | 94.01 (7) | C38—C37—C36 | 117.5 (3) |
| O4—Co2—C40 | 130.48 (8) | C38—C37—H37 | 121.2 |
| O1—Co2—C40 | 124.39 (7) | C36—C37—H37 | 121.2 |
| O7—Co2—C40 | 30.70 (7) | C37—C38—N2 | 129.0 (2) |
| O2—Co2—C40 | 93.88 (7) | C37—C38—C33 | 122.2 (2) |
| O8—Co2—C40 | 30.38 (7) | N2—C38—C33 | 108.7 (2) |
| C1—Co2—C40 | 109.23 (8) | O5—C39—O6 | 127.3 (2) |
| C1—O1—Co1 | 138.36 (16) | O5—C39—C4$^{iii}$ | 118.0 (2) |
| C1—O1—Co2 | 88.58 (14) | O6—C39—C4$^{iii}$ | 114.7 (2) |

| | | | |
|---|---|---|---|
| Co1—O1—Co2 | 107.40 (7) | O8—C40—O7 | 120.4 (2) |
| C1—O2—Co2 | 89.10 (15) | O8—C40—C25$^{iv}$ | 119.3 (2) |
| C20—O3—Co1 | 139.89 (17) | O7—C40—C25$^{iv}$ | 120.2 (2) |
| C20—O4—Co2 | 127.52 (17) | O8—C40—Co2 | 60.67 (12) |
| C39—O5—Co1 | 132.76 (16) | O7—C40—Co2 | 59.86 (12) |
| C39—O6—Co2 | 130.78 (17) | C25$^{iv}$—C40—Co2 | 175.44 (17) |
| C40—O7—Co2 | 89.44 (14) | C41—O9—Co1 | 127.1 (3) |
| C40—O8—Co2 | 88.95 (14) | O9—C41—N3 | 126.0 (4) |
| C44—O10—Co1 | 122.68 (15) | O9—C41—H41 | 117.0 |
| C44—O10—H10 | 109 (2) | N3—C41—H41 | 117.0 |
| Co1—O10—H10 | 127 (2) | C41—N3—C42 | 122.2 (5) |
| C45—O11—Co1 | 125.2 (2) | C41—N3—C43 | 121.3 (5) |
| C45—O11—H11 | 100 (3) | C42—N3—C43 | 116.1 (4) |
| Co1—O11—H11 | 125 (3) | N3—C42—H42A | 109.5 |
| C19—N1—C8 | 108.9 (2) | N3—C42—H42B | 109.5 |
| C19—N1—C6 | 125.5 (2) | H42A—C42—H42B | 109.5 |
| C8—N1—C6 | 125.4 (2) | N3—C42—H42C | 109.5 |
| C38—N2—C27 | 108.4 (2) | H42A—C42—H42C | 109.5 |
| C38—N2—C23 | 124.8 (2) | H42B—C42—H42C | 109.5 |
| C27—N2—C23 | 124.5 (2) | N3—C43—H43A | 109.5 |
| O2—C1—O1 | 120.3 (2) | N3—C43—H43B | 109.5 |
| O2—C1—C2 | 120.2 (2) | H43A—C43—H43B | 109.5 |
| O1—C1—C2 | 119.2 (2) | N3—C43—H43C | 109.5 |
| O2—C1—Co2 | 60.68 (13) | H43A—C43—H43C | 109.5 |
| O1—C1—Co2 | 60.15 (12) | H43B—C43—H43C | 109.5 |
| C2—C1—Co2 | 167.81 (19) | O10—C44—H44A | 109.5 |
| C3—C2—C7 | 119.9 (2) | O10—C44—H44B | 109.5 |
| C3—C2—C1 | 119.5 (2) | H44A—C44—H44B | 109.5 |
| C7—C2—C1 | 120.3 (2) | O10—C44—H44C | 109.5 |
| C2—C3—C4 | 120.5 (2) | H44A—C44—H44C | 109.5 |
| C2—C3—H3 | 119.7 | H44B—C44—H44C | 109.5 |
| C4—C3—H3 | 119.7 | O11—C45—H45A | 109.5 |
| C5—C4—C3 | 119.8 (2) | O11—C45—H45B | 109.5 |
| C5—C4—C39$^{i}$ | 122.6 (2) | H45A—C45—H45B | 109.5 |
| C3—C4—C39$^{i}$ | 117.6 (2) | O11—C45—H45C | 109.5 |
| C4—C5—C6 | 119.7 (2) | H45A—C45—H45C | 109.5 |
| C4—C5—H5 | 120.2 | H45B—C45—H45C | 109.5 |
| C6—C5—H5 | 120.2 | C41'—O9'—Co1 | 121.9 (16) |
| C7—C6—C5 | 120.8 (2) | O9'—C41'—N3' | 120 (2) |
| C7—C6—N1 | 119.4 (2) | O9'—C41'—H41' | 119.8 |
| C5—C6—N1 | 119.7 (2) | N3'—C41'—H41' | 119.8 |
| C6—C7—C2 | 119.3 (2) | C43'—N3'—C41' | 119 (3) |
| C6—C7—H7 | 120.4 | C43'—N3'—C42' | 111 (3) |
| C2—C7—H7 | 120.4 | C41'—N3'—C42' | 128 (2) |
| C9—C8—N1 | 129.2 (2) | N3'—C42'—C43' | 27.5 (14) |
| C9—C8—C13 | 122.2 (3) | N3'—C42'—H42D | 109.5 |
| N1—C8—C13 | 108.5 (2) | C43'—C42'—H42D | 102.7 |
| C10—C9—C8 | 117.4 (3) | N3'—C42'—H42E | 109.5 |
| C10—C9—H9 | 121.3 | C43'—C42'—H42E | 134.8 |

| | | | |
|---|---|---|---|
| C8—C9—H9 | 121.3 | H42D—C42'—H42E | 109.5 |
| C9—C10—C11 | 121.5 (3) | N3'—C42'—H42F | 109.5 |
| C9—C10—H10A | 119.3 | C43'—C42'—H42F | 87.8 |
| C11—C10—H10A | 119.3 | H42D—C42'—H42F | 109.5 |
| C12—C11—C10 | 120.7 (3) | H42E—C42'—H42F | 109.5 |
| C12—C11—H11A | 119.6 | N3'—C43'—C42' | 42 (2) |
| C10—C11—H11A | 119.6 | N3'—C43'—H43D | 109.5 |
| C11—C12—C13 | 119.4 (3) | C42'—C43'—H43D | 89.7 |
| C11—C12—H12 | 120.3 | N3'—C43'—H43E | 109.5 |
| C13—C12—H12 | 120.3 | C42'—C43'—H43E | 83.1 |
| C12—C13—C8 | 118.7 (3) | H43D—C43'—H43E | 109.5 |
| C12—C13—C14 | 134.0 (3) | N3'—C43'—H43F | 109.5 |
| C8—C13—C14 | 107.2 (2) | C42'—C43'—H43F | 150.7 |
| C15—C14—C19 | 119.1 (3) | H43D—C43'—H43F | 109.5 |
| C15—C14—C13 | 134.0 (3) | H43E—C43'—H43F | 109.5 |
| C19—C14—C13 | 106.9 (2) | C1S—O1S—H1S | 103 (3) |
| C16—C15—C14 | 119.3 (3) | O1S—C1S—H1S1 | 109.5 |
| C16—C15—H15 | 120.3 | O1S—C1S—H1S2 | 109.5 |
| C14—C15—H15 | 120.3 | H1S1—C1S—H1S2 | 109.5 |
| C15—C16—C17 | 120.9 (3) | O1S—C1S—H1S3 | 109.5 |
| C15—C16—H16 | 119.6 | H1S1—C1S—H1S3 | 109.5 |
| C17—C16—H16 | 119.6 | H1S2—C1S—H1S3 | 109.5 |
| C18—C17—C16 | 121.2 (3) | O1F—C1F—N1F | 121.6 (15) |
| C18—C17—H17 | 119.4 | O1F—C1F—H1F | 119.2 |
| C16—C17—H17 | 119.4 | N1F—C1F—H1F | 119.2 |
| C17—C18—C19 | 117.6 (3) | C1F—N1F—C2F | 119.7 (10) |
| C17—C18—H18 | 121.2 | C1F—N1F—C3F | 120.7 (11) |
| C19—C18—H18 | 121.2 | C2F—N1F—C3F | 119.6 (10) |
| C18—C19—N1 | 129.5 (2) | N1F—C2F—H2F1 | 109.5 |
| C18—C19—C14 | 121.9 (2) | N1F—C2F—H2F2 | 109.5 |
| N1—C19—C14 | 108.6 (2) | H2F1—C2F—H2F2 | 109.5 |
| O3—C20—O4 | 126.7 (2) | N1F—C2F—H2F3 | 109.5 |
| O3—C20—C21 | 117.0 (2) | H2F1—C2F—H2F3 | 109.5 |
| O4—C20—C21 | 116.3 (2) | H2F2—C2F—H2F3 | 109.5 |
| C22—C21—C26 | 119.9 (2) | N1F—C3F—H3F1 | 109.5 |
| C22—C21—C20 | 120.5 (2) | N1F—C3F—H3F2 | 109.5 |
| C26—C21—C20 | 119.5 (2) | H3F1—C3F—H3F2 | 109.5 |
| C21—C22—C23 | 120.1 (2) | N1F—C3F—H3F3 | 109.5 |
| C21—C22—H22 | 120.0 | H3F1—C3F—H3F3 | 109.5 |
| C23—C22—H22 | 120.0 | H3F2—C3F—H3F3 | 109.5 |
| C22—C23—C24 | 120.3 (2) | | |

Symmetry codes: (i) −*x*+3/2, *y*−1/2, −*z*+1/2; (ii) *x*+1, *y*, *z*; (iii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iv) *x*−1, *y*, *z*.

**Table S13.** Crystallographic Bond Distances (Å) and Angles (º) for **ZnCbz MOF.**

| | | | |
|---|---|---|---|
| Zn1—O4 | 1.951 (3) | C28—C29 | 1.376 (7) |
| Zn1—O6 | 1.963 (2) | C28—H28 | 0.9500 |
| Zn1—O8$^{i}$ | 1.966 (2) | C29—C30 | 1.407 (6) |
| Zn1—O1$^{ii}$ | 2.007 (3) | C29—H29 | 0.9500 |
| Zn2—O5 | 2.030 (3) | C30—C31 | 1.387 (6) |
| Zn2—O7$^{i}$ | 2.067 (3) | C30—H30 | 0.9500 |
| Zn2—O2$^{ii}$ | 2.071 (3) | C31—C32 | 1.394 (6) |
| Zn2—O9 | 2.088 (3) | C31—H31 | 0.9500 |
| Zn2—O10 | 2.094 (3) | C33—C34 | 1.385 (5) |
| Zn2—O12 | 2.145 (3) | C33—C38 | 1.389 (5) |
| N1—C1 | 1.396 (5) | C34—C35 | 1.387 (5) |
| N1—C12 | 1.401 (5) | C34—H34 | 0.9500 |
| N1—C13 | 1.431 (4) | C35—C36 | 1.385 (5) |
| C1—C2 | 1.391 (5) | C35—C39 | 1.516 (5) |
| C1—C6 | 1.410 (5) | C36—C37 | 1.384 (5) |
| C2—C3 | 1.393 (6) | C36—H36 | 0.9500 |
| C2—H2 | 0.9500 | C37—C38 | 1.398 (5) |
| C3—C4 | 1.394 (6) | C37—C40 | 1.508 (5) |
| C3—H3 | 0.9500 | C38—H38 | 0.9500 |
| C4—C5 | 1.380 (6) | C39—O5 | 1.251 (4) |
| C4—H4 | 0.9500 | C39—O6 | 1.260 (4) |
| C5—C6 | 1.401 (6) | C40—O7 | 1.249 (4) |
| C5—H5 | 0.9500 | C40—O8 | 1.266 (4) |
| C6—C7 | 1.441 (6) | O7—Zn2$^{iv}$ | 2.067 (3) |
| C7—C8 | 1.402 (5) | O8—Zn1$^{iv}$ | 1.966 (2) |
| C7—C12 | 1.416 (5) | N3—C43 | 1.314 (5) |
| C8—C9 | 1.375 (6) | N3—C41 | 1.444 (5) |
| C8—H8 | 0.9500 | N3—C42 | 1.469 (5) |
| C9—C10 | 1.402 (6) | C41—H41A | 0.9800 |
| C9—H9 | 0.9500 | C41—H41B | 0.9800 |
| C10—C11 | 1.386 (6) | C41—H41C | 0.9800 |
| C10—H10 | 0.9500 | C42—H42A | 0.9800 |
| C11—C12 | 1.384 (6) | C42—H42B | 0.9800 |
| C11—H11 | 0.9500 | C42—H42C | 0.9800 |
| C13—C18 | 1.380 (5) | C43—O9 | 1.238 (5) |
| C13—C14 | 1.386 (5) | C43—H43 | 0.9500 |
| C14—C15 | 1.393 (5) | N4—C46 | 1.315 (5) |
| C14—H14 | 0.9500 | N4—C44 | 1.459 (5) |
| C15—C16 | 1.394 (5) | N4—C45 | 1.465 (5) |
| C15—C19 | 1.504 (5) | C44—H44A | 0.9800 |
| C16—C17 | 1.391 (5) | C44—H44B | 0.9800 |
| C16—H16 | 0.9500 | C44—H44C | 0.9800 |
| C17—C18 | 1.397 (5) | C45—H45A | 0.9800 |
| C17—C20 | 1.505 (5) | C45—H45B | 0.9800 |
| C18—H18 | 0.9500 | C45—H45C | 0.9800 |
| C19—O2 | 1.258 (4) | C46—O10 | 1.242 (4) |
| C19—O1 | 1.258 (5) | C46—H46 | 0.9500 |
| O1—Zn1$^{iii}$ | 2.007 (3) | O12—C50 | 1.427 (5) |

| | | | |
|---|---|---|---|
| O2—Zn2$^{iii}$ | 2.071 (3) | O12—H12 | 0.80 (5) |
| C20—O3 | 1.237 (4) | C50—C51 | 1.513 (6) |
| C20—O4 | 1.284 (4) | C50—H50A | 0.9900 |
| N2—C21 | 1.388 (5) | C50—H50B | 0.9900 |
| N2—C32 | 1.392 (5) | C51—H51A | 0.9800 |
| N2—C33 | 1.432 (5) | C51—H51B | 0.9800 |
| C21—C22 | 1.383 (6) | C51—H51C | 0.9800 |
| C21—C26 | 1.415 (5) | O11—C49 | 1.247 (5) |
| C22—C23 | 1.389 (6) | N5—C49 | 1.322 (5) |
| C22—H22 | 0.9500 | N5—C47 | 1.452 (5) |
| C23—C24 | 1.397 (6) | N5—C48 | 1.461 (5) |
| C23—H23 | 0.9500 | C47—H47A | 0.9800 |
| C24—C25 | 1.382 (7) | C47—H47B | 0.9800 |
| C24—H24 | 0.9500 | C47—H47C | 0.9800 |
| C25—C26 | 1.398 (6) | C48—H48A | 0.9800 |
| C25—H25 | 0.9500 | C48—H48B | 0.9800 |
| C26—C27 | 1.442 (6) | C48—H48C | 0.9800 |
| C27—C28 | 1.395 (6) | C49—H49 | 0.9500 |
| C27—C32 | 1.415 (5) | | |

| | | | |
|---|---|---|---|
| O4—Zn1—O6 | 105.15 (11) | C27—C28—H28 | 120.3 |
| O4—Zn1—O8$^{i}$ | 103.07 (11) | C28—C29—C30 | 121.0 (4) |
| O6—Zn1—O8$^{i}$ | 138.13 (10) | C28—C29—H29 | 119.5 |
| O4—Zn1—O1$^{ii}$ | 108.02 (10) | C30—C29—H29 | 119.5 |
| O6—Zn1—O1$^{ii}$ | 99.52 (11) | C31—C30—C29 | 121.0 (5) |
| O8$^{i}$—Zn1—O1$^{ii}$ | 100.41 (11) | C31—C30—H30 | 119.5 |
| O5—Zn2—O7$^{i}$ | 95.16 (11) | C29—C30—H30 | 119.5 |
| O5—Zn2—O2$^{ii}$ | 93.41 (11) | C30—C31—C32 | 117.5 (4) |
| O7$^{i}$—Zn2—O2$^{ii}$ | 97.63 (10) | C30—C31—H31 | 121.3 |
| O5—Zn2—O9 | 178.04 (13) | C32—C31—H31 | 121.3 |
| O7$^{i}$—Zn2—O9 | 86.77 (12) | N2—C32—C31 | 129.2 (4) |
| O2$^{ii}$—Zn2—O9 | 86.62 (11) | N2—C32—C27 | 108.7 (4) |
| O5—Zn2—O10 | 90.47 (10) | C31—C32—C27 | 122.1 (4) |
| O7$^{i}$—Zn2—O10 | 91.42 (11) | C34—C33—C38 | 120.4 (3) |
| O2$^{ii}$—Zn2—O10 | 169.78 (12) | C34—C33—N2 | 119.2 (3) |
| O9—Zn2—O10 | 89.18 (11) | C38—C33—N2 | 120.4 (3) |
| O5—Zn2—O12 | 84.89 (12) | C33—C34—C35 | 120.1 (3) |
| O7$^{i}$—Zn2—O12 | 175.97 (11) | C33—C34—H34 | 119.9 |
| O2$^{ii}$—Zn2—O12 | 86.38 (11) | C35—C34—H34 | 119.9 |
| O9—Zn2—O12 | 93.15 (12) | C36—C35—C34 | 119.8 (3) |
| O10—Zn2—O12 | 84.55 (11) | C36—C35—C39 | 120.6 (3) |
| C1—N1—C12 | 108.7 (3) | C34—C35—C39 | 119.6 (3) |
| C1—N1—C13 | 125.0 (3) | C37—C36—C35 | 120.4 (3) |
| C12—N1—C13 | 125.8 (3) | C37—C36—H36 | 119.8 |
| C2—C1—N1 | 128.8 (4) | C35—C36—H36 | 119.8 |
| C2—C1—C6 | 122.5 (4) | C36—C37—C38 | 120.0 (3) |
| N1—C1—C6 | 108.6 (3) | C36—C37—C40 | 119.9 (3) |
| C1—C2—C3 | 116.6 (4) | C38—C37—C40 | 120.1 (3) |
| C1—C2—H2 | 121.7 | C33—C38—C37 | 119.3 (3) |

| | | | |
|---|---|---|---|
| C3—C2—H2 | 121.7 | C33—C38—H38 | 120.4 |
| C2—C3—C4 | 122.0 (4) | C37—C38—H38 | 120.4 |
| C2—C3—H3 | 119.0 | O5—C39—O6 | 127.3 (3) |
| C4—C3—H3 | 119.0 | O5—C39—C35 | 116.5 (3) |
| C5—C4—C3 | 120.7 (4) | O6—C39—C35 | 116.2 (3) |
| C5—C4—H4 | 119.7 | C39—O5—Zn2 | 133.4 (2) |
| C3—C4—H4 | 119.7 | C39—O6—Zn1 | 133.7 (2) |
| C4—C5—C6 | 119.2 (4) | O7—C40—O8 | 125.7 (3) |
| C4—C5—H5 | 120.4 | O7—C40—C37 | 117.9 (3) |
| C6—C5—H5 | 120.4 | O8—C40—C37 | 116.3 (3) |
| C5—C6—C1 | 119.0 (4) | C40—O7—Zn2$^{iv}$ | 128.2 (2) |
| C5—C6—C7 | 133.6 (4) | C40—O8—Zn1$^{iv}$ | 121.5 (2) |
| C1—C6—C7 | 107.3 (3) | C43—N3—C41 | 124.0 (4) |
| C8—C7—C12 | 118.5 (4) | C43—N3—C42 | 118.9 (4) |
| C8—C7—C6 | 134.5 (4) | C41—N3—C42 | 117.1 (4) |
| C12—C7—C6 | 106.9 (3) | N3—C41—H41A | 109.5 |
| C9—C8—C7 | 119.4 (4) | N3—C41—H41B | 109.5 |
| C9—C8—H8 | 120.3 | H41A—C41—H41B | 109.5 |
| C7—C8—H8 | 120.3 | N3—C41—H41C | 109.5 |
| C8—C9—C10 | 121.2 (4) | H41A—C41—H41C | 109.5 |
| C8—C9—H9 | 119.4 | H41B—C41—H41C | 109.5 |
| C10—C9—H9 | 119.4 | N3—C42—H42A | 109.5 |
| C11—C10—C9 | 120.8 (4) | N3—C42—H42B | 109.5 |
| C11—C10—H10 | 119.6 | H42A—C42—H42B | 109.5 |
| C9—C10—H10 | 119.6 | N3—C42—H42C | 109.5 |
| C12—C11—C10 | 118.0 (4) | H42A—C42—H42C | 109.5 |
| C12—C11—H11 | 121.0 | H42B—C42—H42C | 109.5 |
| C10—C11—H11 | 121.0 | O9—C43—N3 | 124.5 (4) |
| C11—C12—N1 | 129.5 (4) | O9—C43—H43 | 117.7 |
| C11—C12—C7 | 122.1 (4) | N3—C43—H43 | 117.7 |
| N1—C12—C7 | 108.4 (3) | C43—O9—Zn2 | 120.7 (3) |
| C18—C13—C14 | 121.0 (3) | C46—N4—C44 | 120.0 (3) |
| C18—C13—N1 | 118.8 (4) | C46—N4—C45 | 121.9 (3) |
| C14—C13—N1 | 120.2 (4) | C44—N4—C45 | 118.0 (3) |
| C13—C14—C15 | 119.3 (4) | N4—C44—H44A | 109.5 |
| C13—C14—H14 | 120.3 | N4—C44—H44B | 109.5 |
| C15—C14—H14 | 120.3 | H44A—C44—H44B | 109.5 |
| C14—C15—C16 | 119.7 (4) | N4—C44—H44C | 109.5 |
| C14—C15—C19 | 119.8 (4) | H44A—C44—H44C | 109.5 |
| C16—C15—C19 | 120.4 (3) | H44B—C44—H44C | 109.5 |
| C17—C16—C15 | 120.9 (3) | N4—C45—H45A | 109.5 |
| C17—C16—H16 | 119.6 | N4—C45—H45B | 109.5 |
| C15—C16—H16 | 119.6 | H45A—C45—H45B | 109.5 |
| C16—C17—C18 | 118.8 (4) | N4—C45—H45C | 109.5 |
| C16—C17—C20 | 121.4 (3) | H45A—C45—H45C | 109.5 |
| C18—C17—C20 | 119.8 (4) | H45B—C45—H45C | 109.5 |
| C13—C18—C17 | 120.3 (4) | O10—C46—N4 | 123.8 (4) |
| C13—C18—H18 | 119.8 | O10—C46—H46 | 118.1 |
| C17—C18—H18 | 119.8 | N4—C46—H46 | 118.1 |

| | | | |
|---|---|---|---|
| O2—C19—O1 | 124.4 (4) | C46—O10—Zn2 | 118.1 (2) |
| O2—C19—C15 | 117.5 (3) | C50—O12—Zn2 | 128.1 (2) |
| O1—C19—C15 | 118.0 (3) | C50—O12—H12 | 111 (4) |
| C19—O1—Zn1$^{iii}$ | 109.1 (2) | Zn2—O12—H12 | 120 (4) |
| C19—O2—Zn2$^{iii}$ | 168.6 (3) | O12—C50—C51 | 111.7 (4) |
| O3—C20—O4 | 124.8 (4) | O12—C50—H50A | 109.3 |
| O3—C20—C17 | 120.0 (3) | C51—C50—H50A | 109.3 |
| O4—C20—C17 | 115.2 (3) | O12—C50—H50B | 109.3 |
| C20—O4—Zn1 | 110.3 (2) | C51—C50—H50B | 109.3 |
| C21—N2—C32 | 108.9 (3) | H50A—C50—H50B | 107.9 |
| C21—N2—C33 | 124.5 (3) | C50—C51—H51A | 109.5 |
| C32—N2—C33 | 125.6 (3) | C50—C51—H51B | 109.5 |
| C22—C21—N2 | 128.9 (4) | H51A—C51—H51B | 109.5 |
| C22—C21—C26 | 122.3 (4) | C50—C51—H51C | 109.5 |
| N2—C21—C26 | 108.7 (4) | H51A—C51—H51C | 109.5 |
| C21—C22—C23 | 117.6 (4) | H51B—C51—H51C | 109.5 |
| C21—C22—H22 | 121.2 | C49—N5—C47 | 121.2 (4) |
| C23—C22—H22 | 121.2 | C49—N5—C48 | 120.4 (4) |
| C22—C23—C24 | 121.6 (5) | C47—N5—C48 | 118.4 (4) |
| C22—C23—H23 | 119.2 | N5—C47—H47A | 109.5 |
| C24—C23—H23 | 119.2 | N5—C47—H47B | 109.5 |
| C25—C24—C23 | 120.1 (4) | H47A—C47—H47B | 109.5 |
| C25—C24—H24 | 120.0 | N5—C47—H47C | 109.5 |
| C23—C24—H24 | 120.0 | H47A—C47—H47C | 109.5 |
| C24—C25—C26 | 120.1 (4) | H47B—C47—H47C | 109.5 |
| C24—C25—H25 | 120.0 | N5—C48—H48A | 109.5 |
| C26—C25—H25 | 120.0 | N5—C48—H48B | 109.5 |
| C25—C26—C21 | 118.3 (4) | H48A—C48—H48B | 109.5 |
| C25—C26—C27 | 134.7 (4) | N5—C48—H48C | 109.5 |
| C21—C26—C27 | 106.9 (4) | H48A—C48—H48C | 109.5 |
| C28—C27—C32 | 118.9 (4) | H48B—C48—H48C | 109.5 |
| C28—C27—C26 | 134.3 (4) | O11—C49—N5 | 125.4 (4) |
| C32—C27—C26 | 106.8 (4) | O11—C49—H49 | 117.3 |
| C29—C28—C27 | 119.4 (4) | N5—C49—H49 | 117.3 |
| C29—C28—H28 | 120.3 | | |

Symmetry codes: (iv) −*x*+1, *y*−1/2, −*z*+3/2; (v) −*x*, *y*+1/2, −*z*+3/2; (vi) −*x*+3/2, −*y*+2, *z*+1/2.

## 11. References


[1] Huang, X.; Anderson, K.; Zim, D.; Jiang, L.; Buchwald, S. *J. Amer. Chem. Soc.,* **2003,** *125,* 6653-6655.

[2] D. J. Dahm, *Interpreting diffuse reflectance and transmittance: a theoretical introduction to absorption spectroscopy of scattering materials*, NIR Publications, Chichester, U.K, 2007.