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Aromatic Substituent Effects on the Flexibility of Metal−Organic Frameworks

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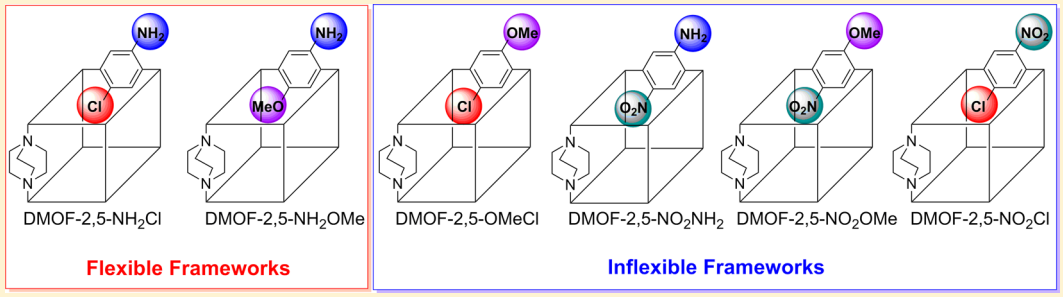
Supporting Information



ABSTRACT: The flexibility (or breathing behavior) of zinc-based metal−organic frameworks (MOFs) has been manipulated by regioisomeric and positional control of organic functionalities. Ten new regioisomeric BDC (ortho- or para-disubstituted benzene-1,4-dicarboxylic acid) ligands have been synthesized and applied to a DMOF (dabco MOF) system, which has a zinc(II) paddle-wheel SBU (secondary building unit). Among the new regioisomeric MOFs, the NH_2−OMe combination showed significant flexibility (breathing behavior) changes by simply altering the functional group positions (from 2,3 to 2,5). The electronic density of the benzene ring was considered to be a major factor in the flexibility changes in the regioisomeric MOF system.

1. INTRODUCTION

Metal−organic frameworks (MOFs) are hybrid three-dimensional porous materials consisting of metal clusters (or ions) and organic linker molecules.[1] During the past decade, MOFs have been widely examined in both fundamental synthetic studies and various applications such as gas adsorption, molecular separation and storage, and catalysis.[2−5] A major advantage of MOFs is the relative ease of functionalization in comparison to other porous materials (e.g., activated carbons, mesoporous silicas, zeolites, etc.), where generally organic moieties can be installed on the linker molecules as substituents. A variety of functional groups such as amines, amides, alcohols, azides, and halides have been introduced into MOF structures through direct synthesis and postsynthetic methods.[6] Postsynthetic modification (PSM) is a late-stage, solid-state functionalization method of MOFs with existing chemical tags and has been widely utilized in MOFs for specific applications.[6]

To introduce more than two functionalities, mixed-ligand syntheses have been explored.[7] A maximum of eight different organic functional group containing ligands were successfully introduced into a single MOF through the multivariate (MTV) concept,[8] and four functional groups were incorporated into MOF pores using a combination of the mixed-ligand strategy and two serial PSMs.[9] Additionally, two different organic functional groups have been installed on a single benzene-1,4-dicarboxylic acid (BDC) molecules in a regioisomeric fashion. Both an amino group and a halide group were placed in either ortho or para positions on the benzene ring.[10] Using these two ligand regioisomers, the synthesis of regioisomeric MOFs was attempted, and a series of Zr(IV)-based UiO-66 (UiO = University of Oslo) frameworks and a series of zinc(II)-based DMOFs (DMOF = dabco MOF, dabco = 1,4-diazabicyclo[2.2.2]octane) were obtained and characterized. UiO-66 has a $Zr_6O_4(OH)_4(BDC)_6$ cluster as the SBU (secondary building unit) and demonstrates high stability to chemicals and moisture.[11] In contrast, DMOFs have dimeric paddle-wheel type SBUs, and the BDC/dabco combination together forms a three-dimensional framework.[12] DMOFs are known to display network flexibility, also called "breathing". Flexible MOFs have the ability to transform between two or more crystal phases trigged by stimuli.[13] In the DMOF system, structural transformations between a large pore (lp) and narrow pore (np) form have been studied, and the functional groups on the BDC ligand can affect flexibility.[14,15] In a previous study, ortho-substituted 2,3-NH_2X and para-substituted 2,5-NH_2X regioisomers displayed significantly different behavior with respect to the flexibility of the DMOF structure. While 2,3-NH_2X substituted DMOFs (i.e., DMOF-2,3-NH_2Cl and DMOF-2,3-NH_2Br) showed a rigid structure and permanent porosity, the regioisomeric 2,5-NH_2X-substituted DMOFs (i.e., DMOF-2,5-NH_2Cl, DMOF-2,5-NH_2Br, and DMOF-2,5-NH_2I) displayed flexible structures, as evidenced by N_2 adsorption

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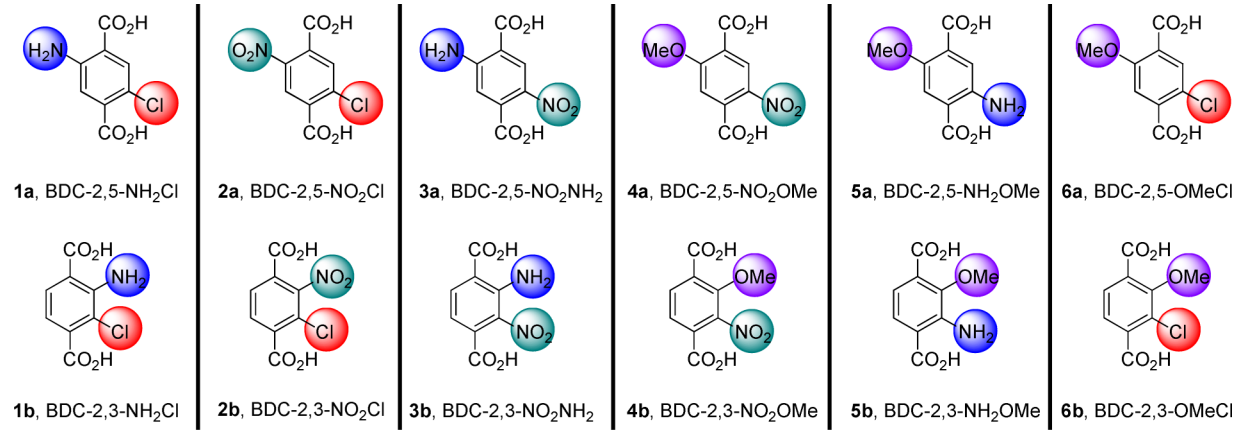

Figure 1. Series of regioisomeric BDC pairs for DMOF synthesis.

experiments and powder X-ray diffraction (PXRD) data.[10] In another study, controlled flexibility of MOFs was achieved using a disubstituted BDC ligand with chloro groups or alkoxy chains.[16−19] Fischer et al. showed that the flexibility was controlled by the length and polarity of the alkoxy chain on the BDC ligands. While ethoxy, *n*-propoxy, isopropoxy, *n*-butoxy, allyloxy, and prop-2-ynyloxy group disubstituted 2,5-BDCs formed flexible DMOF frameworks, *n*-pentoxy group substituted BDC exhibited a less flexible DMOF structure. Additionally, in the case of 2-methoxyethoxy-substituted BDC, the 2,5-disubstituted MOF showed flexibility while the 2,3-disubstituted MOF framework exhibited less flexibility. Fischer's work revealed that the steric issues and interaction between functional groups play a substantial role in the flexibility of MOFs that are capable of "breathing".[17] In this contribution, we have synthesized five new combinations of bifunctional, regioisomeric BDC ligands and utilized them in the synthesis of DMOF derivatives to examine the effect of functional group and isomerism on the degree of flexibility (Figure 1).

2. RESULTS AND DISCUSSION

2.1. Ligand Synthesis. First, the amino group was replaced with the nitro group via oxidation (Scheme S1 in the Supporting Information). All functionalization was performed on the carboxylic methyl ester form (BDCE = benzene-1,4-dicarboxylic acid methyl ester) for ease of purification. The chlorination was performed on dimethyl 2-aminobenzene-1,4-dicarboxylate (BDCE-NH_2) to obtain BDCE-2,5-NH_2Cl and BDCE-2,3-NH_2Cl. The two isomers were separated by flash column chromatography, and each ligand was then oxidized to BDCE-2,5-NO_2Cl and BDCE-2,3-NO_2Cl using trifluoroacetic anhydride and hydrogen peroxide. The target ligands BDC-2,5-NO_2Cl (**2a**) and BDC-2,3-NO_2Cl (**2b**) were obtained by hydrolysis of BDCE-2,5-NO_2Cl and BDCE-2,3-NO_2Cl (Scheme S1). For the next NO_2−NH_2 combination, a nitration was performed on BDCE-NH_2. It was found that using the amide-protected BDCE-NHAc provided a better yield for the nitration in comparison to the free aniline. Two isomeric mixtures of BDCE-2,5-NO_2NHAc and BDCE-2,3-NO_2NHAc were separated by column chromatography, and hydrolysis formed the desired BDC-2,5-NO_2NH_2 (**3a**) and BDC-2,3-NO_2NH_2 (**3b**) (Scheme S2 in the Supporting Information).

The free phenol group could interrupt DMOF formation; thus, the methyl ether was selected to study the alkoxy group effect on the benzene ring of MOF ligands. The major starting material, BDCE-OH, was prepared by a Sandmeyer reaction from BDCE-NH_2. A nitration was performed on BDCE-OH. Two regioisomers (BDCE-2,5-NO_2OH and BDCE-2,3-NO_2OH) were separated by column chromatography, and followed by methylation. Each ligand then hydrolyzed with an aqueous KOH solution to obtain the desired ligands BDC-2,5-NO_2OMe (**4a**) and BDC-2,3-NO_2OMe (**4b**) (Scheme S3 in the Supporting Information). The combination of NH_2 and OMe was easily synthesized by an additional reduction, as shown in Scheme S3. BDCE-2,5-NO_2OMe and BDCE-2,3-NO_2OMe were each converted to the corresponding BDCE-2,5-NH_2OMe and BDCE-2,3-NH_2OMe using a Pd/C hydrogenation. The targeted BDC-2,5-NH_2OMe (**5a**) and BDC-2,3-NH_2OMe (**5b**) were obtained after hydrolysis (Scheme S4 in the Supporting Information). Finally, the last combination of MeO and Cl was synthesized by a Sandmeyer reaction. BDCE-2,5-NH_2OMe and BDCE-2,3-NH_2OMe were converted to BDCE-2,5-OMeCl and BDCE-2,3-OMeCl, and the desired BDC-2,5-OMeCl (**6a**) and BDC-2,3-OMeCl (**6b**) were obtained by hydrolysis (Scheme S5). All new ligands and intermediates were confirmed by ^{1}H NMR, ^{13}C NMR, FTIR, and HR-MS (see the Supporting Information for details).

2.2. Synthesis of MOF Regioisomers and Characterizations. Using these 10 new regioisomeric ligands (**2a**−**6b**, Figure 1), the syntheses of DMOF frameworks were performed. Although the detailed synthetic conditions varied slightly on the basis of the ligand used, the overall reaction conditions were similar. DMOFs were generally synthesized using a zinc nitrate hexahydrate salt, the desired BDC ligand, dabco, and DMF (*N*,*N*-dimethylformamide) as solvent under solvothermal conditions (Figure 2; see also the Supporting Information for detailed synthetic procedures). The 2,5-disubstituted DMOF series was obtained after 24 h of heating, while the 2,3-disubstituted DMOF series were produced after 48 h of solvothermal syntheses. The resulting crystals were shown to possess the same structure as the parent DMOF material, as evidenced by PXRD (Figure 2), and ^{1}H NMR spectra, after acid digestion, confirmed that the desired ligands were successfully incorporated into the DMOF structures. Additionally, the ratio between the disubstituted BDCs and dabco was verified to be the expected 2:1 by ^{1}H NMR spectra (Figure S1 in the Supporting Information). Thermogravimetric analysis (TGA) of fully activated samples (e.g., samples after gas adsorption experiments) showed that these obtained

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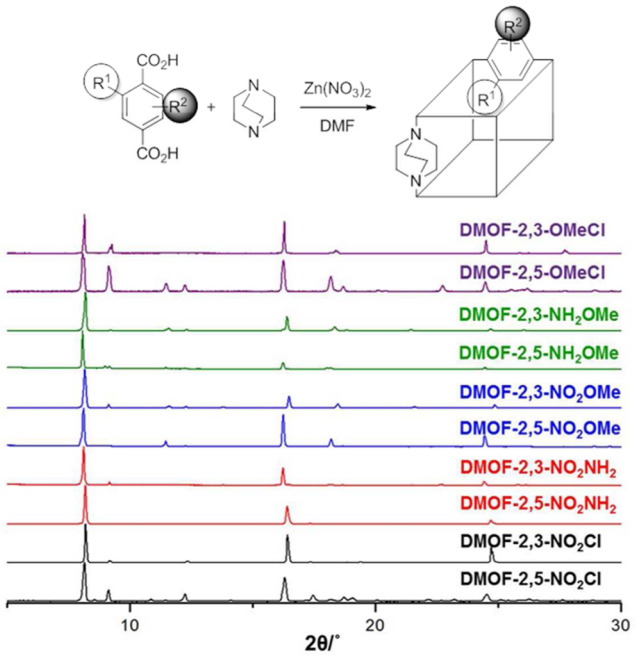

Figure 2. General synthesis of regioisomeric DMOFs and their PXRD patterns, indicating isostructural materials.

regioisomeric MOFs are thermally stable with decomposition temperatures of ~400 °C (Figure S2 in the Supporting Information).

Gas adsorption experiments using N_2 revealed the flexibility of regioisomeric DMOFs. In a previous study, DMOF-2,5-NH_2Cl showed almost no adsorption of N_2 gas, and the BET (Brunauer–Emmett–Teller) surface area was calculated to be ~6 m^2/g. In contrast, DMOF-2,3-NH_2Cl showed markedly higher porosity with a BET surface area of 1169 m^2/g. It was speculated that the framework flexibility was altered because of the functional group isomerism.[10] All newly synthesized DMOFs using regioisomeric ligands (**2a–4b**, **5b**, and **6a**,**b**) exhibited high porosity for N_2 adsorption with BET surface area values ranging between 982 and 1238 m^2/g, except for DMOF-2,5-NH_2OMe (from **5a**), which displayed 114 m^2/g for its BET surface area. However, there was one exception (Figure 3, Figures S3–S7 in the Supporting Information, and Table 1); DMOF-2,5-NH_2OMe remained nonporous to N_2 regardless of the activation method (Figure 3 and Figure S6). In other words, the combination of NH_2 and OMe (**5a**,**b**) produces a second contrasting set of DMOFs that display regioisomeric control over flexibility. DMOF-2,5-NH_2OMe has a BET surface area of 114 m^2/g, while DMOF-2,3-NH_2OMe has a BET surface area of 1205 m^2/g (averaged from at least two independent measurements). Other combinations, using NO_2 and Cl (**2a**,**b**), NH_2 and NO_2 (**3a**,**b**), NO_2 and OMe (**4a**,**b**), and OMe and Cl (**6a**,**b**) formed inflexible, porous DMOFs in all cases (Figure 3 and Figures S3–S7). To date, the NH_2–X and NH_2–OMe combinations are the only isomeric sets that display flexibility control in their corresponding DMOFs.

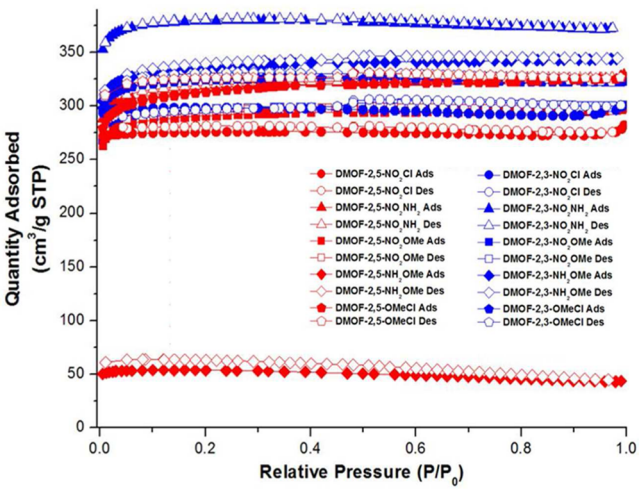

Figure 3. Full dinitrogen sorption isotherms (77 K) of regioisomeric DMOFs.

Carbon dioxide uptake experiments verified the flexibility of regioisomeric DMOFs. While N_2 adsorption completely changed by the organic functional group position in the case of DMOF-2,5-NH_2OMe and DMOF-2,3-NH_2OMe, the CO_2 adsorption capacities were not significantly altered. DMOF-2,5-NH_2OMe absorbed 2.98 mmol/g of CO_2 (1 atm), and DMOF-2,3-NH_2OMe absorbed 3.38 mmol/g of CO_2 (Figure 4 and Figure S8 in the Supporting Information). Selective CO_2 absorption to N_2 gas has been studied in several cases,[18] and this finding strongly supports that the DMOF-2,5-NH_2OMe indeed has a flexible framework, and the pores of the MOFs can be opened by strong interactions such as introduction of CO_2 into the system. Other regioisomeric DMOFs have been tested for their CO_2 adsorption and displayed 2.55–3.45 mmol/g at 1 atm as adsorption amounts (Figure 4 and Figures S9–S13 and Table S1 in the Supporting Information).

2.3. Flexibility (Breathing Behavior) Controls of Functional Groups in DMOFs. Our findings prove that the NH_2–Cl and NH_2–OMe combinations have unique flexibility (breathing behavior) changes on MOFs when they are compared among NH_2, NO_2, Cl, and OMe. Since all four components could partake in hydrogen bonding, we gave more attention to intramolecular differences than to intermolecular differences to explain the flexibility changes. To estimate the electronic environments of six different combinations (**1–6**), the σ value for the substituent constant from a Hammett plot was applied to the ligands[20] and displayed good correlation between electronic environment and flexibility changes (Table 1). Since the nitro group has very strong electron-withdrawing effects, the nitro-containing ligands (**2–4**) have relatively electron-deficient benzene rings and displayed inflexible DMOFs. BDC-2,5-NH_2Cl (**1a**) has a negative value as the sum of the σ values, meaning that there is a relatively negative benzene (i.e., electron rich) ring for DMOF-2,5-NH_2Cl. In addition, the 2,5-NH_2OMe ligand has an electronically rich character in the benzene ring. Finally, ligand **6a** has an almost neutral electronic environment in the benzene ring. Experimental N_2 adsorption data and the Hammett plot matched well to explain the breathing behavior changes in DMOFs. From several computational studies, it was reported that the substituents on the benzene ring and the electron density could affect both the geometry and bond lengths of the functional group on the ligand.[21–23] For example, in the case of para-substituted fluorobenzenes, electron-withdrawing substituents decrease the bond length of the benzene ring–fluoro group while electron-donating substituents increase the bond length of C–F.[23] In the present regioisomeric DMOF and BDC ligand system, the NH_2–Cl and NH_2–OMe combinations in para positions provide electronically rich environments from the two

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Table 1. Substituent Constant (σ_p) from a Hammett Plot and Flexibility of DMOFs

	ligand in synthesis					
	1a,b (R^1 = NH_2, R^2 = Cl)	**2a,b** (R^1 = NO_2, R^2 = Cl)	**3a,b** (R^1 = NH_2, R^2 = NO_2)	**4a,b** (R^1 = NO_2, R^2 = OMe)	**5a,b** (R^1 = NH_2, R^2 = OMe	**6a,b** (R^1 = OMe, R^2 = Cl)
σ_p for R1	−0.66	0.78	−0.66	0.78	−0.66	−0.27
σ_p for R2	0.23	0.23	0.78	−0.27	−0.27	0.23
$\sigma_{p1} + \sigma_{p2}$	−0.43	1.01	0.12	0.51	−0.93	−0.04
flexibility	flexible	inflexible	inflexible	inflexible	flexible	inflexible
BET for DMOF-2,5-R^1R^2 (m^2/g)	6[a]	1098	1095	1111	114	1238
BET for DMOF-2,3-R^1R^2 (m^2/g)	1169[a]	1167	1215	982	1205	1190

[a]Reported BET value in ref 10.

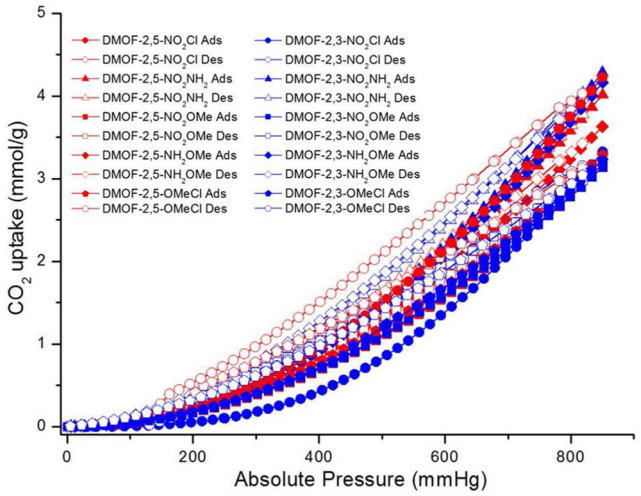

Figure 4. CO_2 isotherm (298 K) of regioisomeric DMOFs.

electron-donating groups and have suitable geometry and bond length to accommodate or induce the breathing behavior changes.

3. CONCLUSIONS

In conclusion, we have synthesized 10 new regioisomeric BDC ligands using 4 different chemical tags such as amino, chloro, methoxy, and nitro groups. All new ligands were successfully incorporated into DMOF frameworks, and the 10 new DMOFs were fully characterized. Interestingly, the NH_2−OMe combination showed flexibility (breathing behavior) changes within its DMOF seemingly by regioisomeric and positional control. The other combinations displayed inflexible but porous structures during N_2 adsorption. The more flexible DMOF-2,5-NH_2OMe could selectively adsorb CO_2 gas with good capacity. The flexibility (breathing behavior) changes in regioisomeric DMOFs were obtained from the functional group combinations of NH_2/halogens and NH_2/OMe, and we speculated that the electronic environment of the BDC ring could affect the flexibility of the DMOFs on the basis of the Hammett substituent constant. This study suggests that the electronic environment of the ligand is important for MOF properties including flexibility and breathing behavior.

4. EXPERIMENTAL SECTION

4.1. General Method. The concentration of solutions was performed using a rotary evaporator, followed by vacuum drying at 0.1−1 Torr. All commercial compounds and organic solvents were used without additional purification unless otherwise stated. ^{1}H and ^{13}C NMR (nuclear magnetic resonance) spectra were recorded on a FT AM 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or FT AM 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) instrument. Parts per million (ppm) units were applied to quoted chemical shift (δ) and the appropriate parent solvent peak or 0 ppm for tetramethylsilane (TMS) was used as a reference peak for calibration. The peak patterns were assigned using following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. ^{13}C NMR was fully decoupled by broad-band decoupling. A triplet at 77.0 ppm of chloroform-*d* (or a septet at 39.52 ppm of DMSO-d_6) was employed as a reference peak for ^{13}C NMR.

4.2. MOF Synthesis. The DMOF series was prepared and activated using a method modified from what has been previously described.[24]

4.2.1. DMOF-2,5-NO_2Cl. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **2a** (0.5 mmol, 123 mg) were dissolved in DMF (12.5 mL). Ligand dabco (0.8 mmol, 90 mg) was added to this solution mixture. When a colorless solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 100 °C in a programmed oven (increasing temperature rate: 2.5 °C/min from room temperature). The temperature was held for 24 h at 100 °C and then reduced to room temperature (decreasing temperature rate: 2.5 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.2. DMOF-2,3-NO_2Cl. Zinc nitrate hexahydrate (0.4 mmol, 119 mg) and ligand **2b** (0.4 mmol, 98 mg) were dissolved in DMF (10 mL). Ligand dabco (0.64 mmol, 72 mg) was added to this solution mixture. When a yellow solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 120 °C in a programmed oven (increasing temperature rate: 1.0 °C/min from room temperature). The temperature was held for 48 h at 120 °C and then reduced to room temperature (decreasing temperature rate: 1.0 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.3. DMOF-2,5-NH_2NO_2. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **3a** (0.5 mmol, 113 mg) were dissolved in DMF (12.5 mL). Ligand dapco (0.8 mmol, 90 mg)

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was added to this solution mixture. When a yellow solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 120 °C in a programmed oven (increasing temperature rate: 2.5 °C/min from room temperature). The temperature was held for 24 h at 120 °C and then reduced to room temperature (decreasing temperature rate: 2.5 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.4. DMOF-2,3-NH_2NO_2. Zinc nitrate hexahydrate (0.4 mmol, 119 mg) and ligand **3b** (0.4 mmol, 90 mg) were dissolved in DMF (10.0 mL). Ligand dapco (0.64 mmol, 72 mg) was added to this solution mixture. When a yellow solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 120 °C in a programmed oven (increasing temperature rate: 1.0 °C/min from room temperature). The temperature was held for 48 h at 120 °C and then reduced to room temperature (decreasing temperature rate: 1.0 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.5. DMOF-2,5-NO_2OMe. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **4a** (0.5 mmol, 120 mg) were dissolved in DMF (12.5 mL). Ligand dapco (0.8 mmol, 90 mg) was added to this solution mixture. When a colorless solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 100 °C in a programmed oven (increasing temperature rate: 2.5 °C/min from room temperature). The temperature was held for 24 h at 100 °C and then reduced to room temperature (decreasing temperature rate: 2.5 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.6. DMOF-2,3-NO_2OMe. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **4b** (0.5 mmol, 120 mg) were dissolved in DMF (12.5 mL). Ligand dapco (0.8 mmol, 90 mg) was added to this solution mixture. When a colorless solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 100 °C in a programmed oven (increasing temperature rate: 1.0 °C/min from room temperature). The temperature was held for 48 h at 100 °C and then reduced to room temperature (decreasing temperature rate: 1.0 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.7. DMOF-2,5-NH_2OMe. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **5a** (0.5 mmol, 106 mg) were dissolved in DMF (12.5 mL). Ligand dapco (0.8 mmol, 90 mg) was added to this solution mixture. When a yellow solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 85 °C in a programmed oven (increasing temperature rate: 2.5 °C/min from room temperature). The temperature was held for 24 h at 100 °C and then reduced to room temperature (decreasing temperature rate: 2.5 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.8. DMOF-2,3-NH_2OMe. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **5b** (0.5 mmol, 106 mg) were dissolved in DMF (12.5 mL). Ligand dapco (0.8 mmol, 90 mg) was added to this solution mixture. When a yellow solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 100 °C in a programmed oven (increasing temperature rate: 1.0 °C/min from room temperature). The temperature was held for 24 h at 100 °C and then reduced to room temperature (decreasing temperature rate: 1.0 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.9. DMOF-2,5-OMeCl. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **6a** (0.5 mmol, 115 mg) were dissolved in DMF (12.5 mL). Ligand dapco (0.8 mmol, 90 mg) was added to this solution mixture. When a colorless solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 100 °C in a programmed oven (increasing temperature rate: 2.5 °C/min from room temperature). The temperature was held for 24 h at 100 °C and then reduced to room temperature (decreasing temperature rate: 2.5 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.2.10. DMOF-2,3-OMeCl. Zinc nitrate hexahydrate (0.5 mmol, 149 mg) and ligand **6b** (0.5 mmol, 115 mg) were dissolved in DMF (12.5 mL). Ligand dapco (0.8 mmol, 90 mg) was added to this solution mixture. When a colorless solid formed, this precipitate was filtered using a fine-porosity fritted-disk filter. Then the solution mixture was moved to a scintillation vial and heated at 100 °C in a programmed oven (increasing temperature rate: 1.0 °C/min from room temperature). The temperature was held for 48 h at 100 °C, and then cooled to room temperature (decreasing temperature rate: 1.0 °C/min). The resulting DMOF crystals were washed with DMF (5 mL × 3). The solvent was exchanged with $CHCl_3$ (5 mL), replacing $CHCl_3$ with fresh $CHCl_3$ every 24 h for three times.

4.3. MOF Characterization. *4.3.1. Acid Digestion of DMOF Series for ^{1}H NMR Analysis.* A fully dried (under vacuum) DMOF sample (approximately ∼10 mg) was mixed with 590 μL of DMSO-d_6 and 10 μL of DCl. The mixture was sonicated until a clear solution was obtained.

4.3.2. Thermal Analysis. A fully dried (under vacuum) 10 mg DMOF sample (e.g., after BET analysis) was used for TGA measurements. A stream of N_2 was employed, and the running temperature range was room temperature to 800 °C (scan rate of 10 °C/min).

4.3.3. Powder X-ray Diffraction. A DMOF sample (approximately 10 mg) was air-dried for 1 min prior to PXRD analysis. PXRD data were collected on a Bruker D8 Discover instrument at ambient temperature (with a scan speed of 1 s/step, a step size of 0.02° in 2θ, and a 2θ range of 5−55°).

4.3.4. BET Surface Area Analysis. A DMOF sample (approximately 20−50 mg) was dried on a vacuum line at

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room temperature (less than 1 min). Then the sample was transferred to a sample tube and degassed until the outgas rate was <5 μmHg/min at 100 °C (on a Micromeritics ASAP 2020 Adsorption Analyzer). BET surface area (m^2/g) measurements were performed at 77 K under dinitrogen using the volumetric technique.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00983.

Overall schemes for ligand synthesis, detailed procedures for ligand synthesis, figures and a table as described in the text, and ^1H and ^{13}C NMR and IR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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