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The Influence of Nitro Groups on the Topology and Gas Sorption Property of Extended Zn(II)-paddlewheel MOFs

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Supplementary Information

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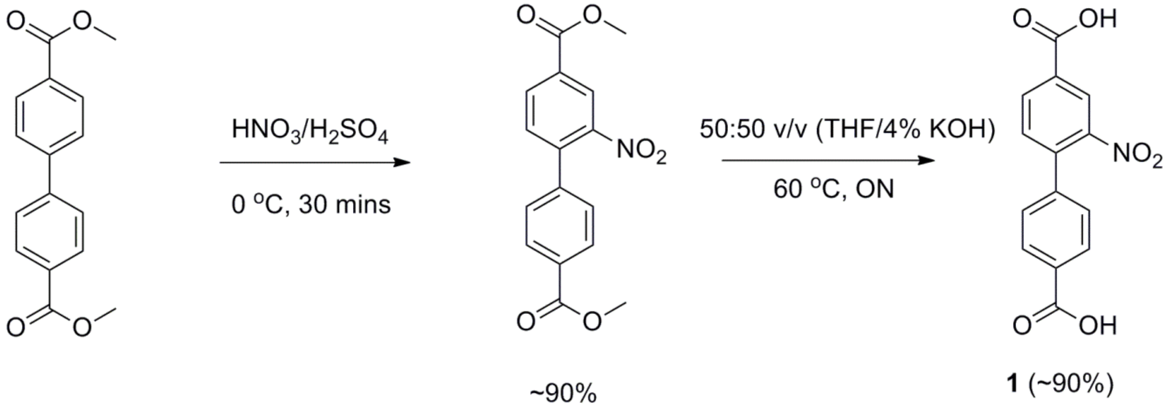
General Methods for Metal-Organic Frameworks Experiments

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Electrospray ionization mass spectrometry (ESI-MS) was performed using a ThermoFinnigan LCQ-DECA mass spectrometer and the data was analyzed using the Xcalibur software suite. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded by a Varian FT-NMR spectrometer (400 MHz). Chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J*, are reported in Hertz unit (Hz). Column chromatography was performed using a CombiFlash automated chromatography system.

Ligand Synthesis

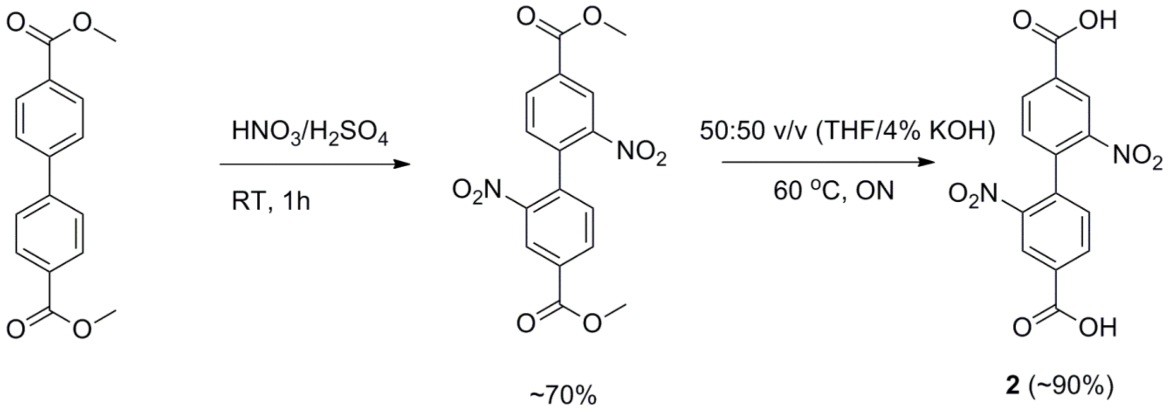


Scheme S1. Synthesis of bpdc-NO_2 (**1**).

Dimethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate. Dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate (2.00 g, 7.4 mmol) were added into a solution of concentrated H_2SO_4 (10 mL). The mixture was cooled down to 0 °C using an ice bath. Nitric acid (485 μL) was then added into concentrated H_2SO_4 (3 mL). This solution was added dropwise into the mixture at 0 °C over a period of ~10 min. The mixture was stirred at 0 °C for 20 min and then poured into ice to yield a white solid. The white solid was collected via vacuum filtration and washed with water to obtain the desired product (~90 %, 2.10 g, 6.7 mmol). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.56 ppm (s, 1H), 8.30 (d, *J*

= 12 Hz, 1H), 8.12 (d, *J* = 8 Hz, 2H), 7.50 (d, J = 12 Hz, 1H), 7.40 (d, *J* = 8 Hz, 2H), 4.00 (s, 3H), 3.95 (s, 3H). Cald [M]: 315.28, found $[M+H]^+$: 316.21.

*Bpdc-NO₂ (**1**).* Dimethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate (2.10 g, 6.7 mmol) was dissolved in tetrahydrofuran (THF, 50 mL) and 4% KOH (50 mL). The mixture was heated to 60 °C and allowed to react overnight. Upon cooling, the aqueous layer was separated and acidified with concentrated HCl to yield a white solid. The white solid was collected via vacuum filtration and washed with water to obtain the desired product (~90%, 1.72 g, 6.0 mmol). ^{1}H NMR (400 MHz, DMSO-*d₆*): *δ* 8.47 ppm (s, 1H), 8.28 (d, *J* = 8 Hz, 1H), 8.03 (d, *J* = 8Hz, 2H), 7.74 (d, *J* = 8 Hz, 1H), 7.53 (d, *J* = 8 Hz, 2H). Cald [M]: 287.22, found $[M-H]^-$: 286.13.



Scheme S2. Synthesis of BPDC-$[NO_2]_2$ (**2**).

Dimethyl 2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate. Dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate (5.00 g, 18.5 mmol) was added into a concentrated H_2SO_4 solution (50 mL). The mixture was stirred at room temperature for ~ 5 min. Nitric acid (3 mL) was added into a concentrated H_2SO_4 (6 mL). This solution was added dropwise into the first mixture at room temperature over a period of ~ 15 min. The mixture was stirred at room temperature for 1.5 h and then poured into ice to yield a beige solid. The beige solid was collected via vacuum filtration and washed with water to obtain the desired product (~70%, 4.67 g, 13.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.90 ppm (s, 2 H), 8.38 (d, J =12 Hz, 2 H), 7.40 (d, J =8 Hz, 2 H), 4.02 (s, 6 H). Cald [M] 360.28, Found $[M-H]^-$ 359.19.

Bpdc-[NO_2]$_2$ **(2)**. Dimethyl 2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate (2.00 g, 5.6 mmol) was dissolved in THF (50 mL) and 4% KOH (50 mL). The mixture was heated to 60 ^{o}C and allowed to react overnight. After cooling, the aqueous layer was separated and acidified with concentrated HCl to yield white solid as product. The white solid was collected via vacuum filtration and washed with water to obtain the desired product (~90%, 1.66 g, 5.0 mmol). Cald. [M]: 332.22, found $[M\text{-}H]^-$: 330.97.

MOFs Synthesis.

DMOF-1-bpdc and BMOF-1-bpdc were synthesized followed the literature.[1]

DMOF-1-bpdc-NO_2. **1** (57 mg, 0.2 mmol) and $Zn(NO_3)_2$•$6H_2O$ (76 mg, 0.4 mmol) were dissolved in *N,N'*-dimethylforamide (DMF, 15 mL) in a 20 mL scintillation vial. 1,4-Diazabicyclo[2.2.2]octane (dabco, 34 mg, 0.3 mmol) was added into the solution. A white precipitate was formed immediately and filtered off using a fine glass frit. The clear solution was heated at a rate of 2.5 ^{o}C/min from 35 ^{o}C to 100 ^{o}C. The temperature was held at 100 ^{o}C for 18 h and then cooled to 35 ^{o}C at a rate of 2.5 ^{o}C/min. Clear yellow crystals were obtained and washed with DMF (3 × 10 mL). The solvent was then exchanged with ethyl acetate (EtOAc, 3×10 mL), where the crystals were left for 3 days, replacing the solution with fresh EtOAc every 24 h.

BMOF-1-bpdc-NO_2. **1** (57 mg, 0.2 mmol), $Zn(NO_3)_2$•$6H_2O$ (76 mg, 0.4 mmol), and 4,4'-bipyridine (4,4'-bpy, 31 mg, 0.2 mmol) were dissolved in DMF (15 mL) in a 20 mL scintillation vial. The clear solution was heated at a rate of 2.5 ^{o}C/min from 35 ^{o}C to 100 ^{o}C. The temperature was held at 100 ^{o}C for 18 h and then cooled to 35 ^{o}C at a rate of 2.5 ^{o}C/min. Clear yellow crystals were obtained after 1 day and washed with DMF (3×10 mL). The solvent was then exchanged with EtOAc (3×10 mL), where the crystals were left for 3 days, replacing the solution with fresh EtOAc every 24 h.

DMOF-1-bpdc-[NO$_2$]$_2$. **2** (66 mg, 0.2 mmol) and $Zn(NO_3)_2•6H_2O$ (76 mg, 0.4 mmol) were dissolved in DMF (15 mL) in a 20 mL scintillation vial. Dabco (34 mg, 0.3 mmol) was added into the solution. A white precipitate was formed immediately and filtered off using a fine glass frit. The clear solution was heated at a rate of 2.5 ^{o}C/min from 35 ^{o}C to 100 ^{o}C. The temperature was held at 100 ^{o}C for 18 h and then cooled to 35 ^{o}C at a rate of 2.5 ^{o}C/min. Clear yellow crystals were obtained and washed with DMF (3×10 mL). The solvent was then exchanged with EtOAc (3×10 mL), where the crystals were left for 3 days, replacing the solution with fresh EtOAc every 24 h.

BMOF-1-bpdc-[NO$_2$]$_2$. **2** (66 mg, 0.2 mmol), $Zn(NO_3)_2•6H_2O$ (76 mg, 0.4 mmol), and 4,4'-bpy (31 mg, 0.2 mmol) were dissolved in DMF (15 mL) in a 20 mL scintillation vial. The clear solution was heated at a rate of 2.5 ^{o}C/min from 35 ^{o}C to 100 ^{o}C. The temperature was held at 100 ^{o}C for 18 h and then cooled to 35 ^{o}C at a rate of 2.5 ^{o}C/min. Clear red crystals were obtained and washed with DMF (3×10 mL). The solvent was then exchanged with EtOAc (3×10 mL), where the crystals were left for 3 days, replacing the solution with fresh EtOAc every 24 h.

MOFs Characterization.

Powder X-ray Diffraction. Approximately 20-30 mg of MOF material was dried in air for ~1 min prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer using a LynxEye detector at 40 kV, 40 mA for Cu Kα (λ= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02^{o}, 2θ range of 5-45^{o}.

BET Surface Area and Gas Sorption Analysis. ~30-100 mg of MOF material was evacuated under vacuum for ~1 min at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 105 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg/min. The sample tube was re-weighed to obtain a consistent mass for the degassed MOF. Brunauer-Emmett-Teller (BET) surface area

(m^2 g^{-1}) measurements were collected at 77 K with N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique. The samples were then manually degassed for at least 2 h at 105 °C prior to N_2 isotherms at 77 K or CO_2 isotherms at 196 K.

Single Crystal X-ray Diffraction. Single crystals of MOFs taken from EtOAc were mounted on nylon loops with paratone oil and placed under a dinitrogen cold stream (250 K). Data was collected on a Bruker Apex diffractometer using Cu Kα (λ= 1.5418 Å) or Mo Kα (λ= 0.71073 Å) radiation controlled using the APEX 2010 software package. The structures were collected at high temperature (250 K) because the crystals were unstable at low temperature.

A multi-scan method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using the SHELXTL software suite.[2] Structures of MOFs were treated with the "SQUEEZE" protocol in PLATON[3] to account for partially occupied or disordered solvent (e.g. DMF, EtOAc) within the porous framework.

Each nitro group of bpdc-$[NO_2]_2$ in the structure of $(Zn(bpdc\text{-}[NO_2]_2)(dabco)_{0.5}(DMF))_n$ are disordered over two positions and were refined using PART 2, PART 1, PART 0, and FVAR parameters. Despite the severe disorder, the intermolecular interactions between the nitro groups can be clearly observed in the structure. The unreasonably close distance between the nitro groups obtained from the structure (1.75 Å, less than the sum of the van der Waals radii ~3.10 Å) is likely a result of the disorder observed in these nitro groups (Fig. S2).

The diffraction pattern of BMOF-1-bpdc-$[NO_2]_2$ show no split diffraction peaks and the quality of the data was good. However, the structure cannot be refined under different crystal systems and space groups. Thus, the structure of BMOF-1-bpdc-$[NO_2]_2$ was refined using a twinning law due to the potential merohedral twins. The structure was solved and refined using orthorhombic unit cell (F*mmm*). Despite the acceptable $R_{all\ data}$, the structure still contained several severely distorted benzene rings of the BPDC-$[NO_2]_2$, and we have added comments about this disorder in the CIF file. Even though the quality of structure is not good, the structure is sufficient to confirm the overall topology of the framework.

Thermalgravimetric Analysis. Approximately 10-15 mg of MOF materials were used for thermogravimetric analysis (TGA) measurements, immediately after collection of gas sorption data (i.e. activated samples). Samples were analyzed under a stream of N_2 (100 mL/min) using a TA Instrument Q600 SDT running from room temperature to 600 °C with a ramping rate of 5 °C/min.

Digestion and Analysis by ^{1}H NMR. Approximately 10 mg of MOF materials were dried under a vacuum at 100 °C overnight and digested with sonication in 580 μL of DMSO-d_6 and 40 μL of DCl (35% aqueous solution).

Modeling the intermolecular interaction of the nitro groups in BMOF-1-bpdc-$[NO_2]_2$ structure. The intermolecular interaction of the nitro groups between the interpenetrated nets of BMOF-1-bpdc-$[NO_2]_2$ was modeled using Materials Studio Modeling v.4.0.0.0 (Accelrys Software Inc.). Due to the poor quality of the BMOF-1-bpdc-$[NO_2]_2$ structure, the nitro groups could only be refined on bpdc-$[NO_2]_2$ ligands lying along the crystallographic *b*-axis (the nitro groups lying along the crystallographic *c*-axis can be located; however, the refinement is unstable for the nitro groups). The twinning disorder of one part of the structure was removed, and the remaining nitro groups on the bpdc-$[NO_2]_2$ along crystallographic *c*-axis in the structure were added using the sketch function of Materials Studio. As the nitro groups of bpdc-$[NO_2]_2$ along crystallographic *b*-axis in the structure are fixed at the certain positions on the ligand, there can only be two possibilities for the location of the nitro groups of bpdc-$[NO_2]_2$ along crystallographic *c*-axis. Both of the possibilities display similar intermolecular interactions between nitro groups of the two nets ($N^{\delta+}\cdots O^{\delta-}$ = ~ <2.8 Å, Fig. 6).

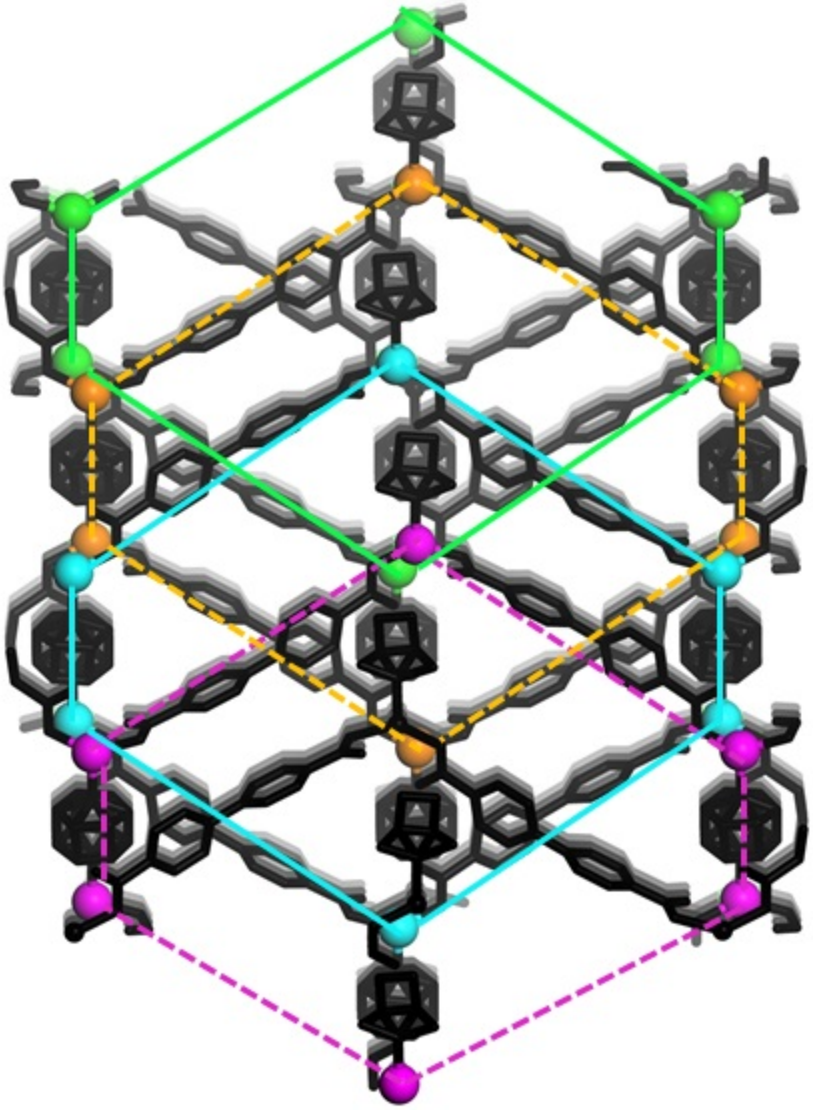


Figure S1. ABCD stacking pattern of (Zn(bpdc-[NO_2]$_2$)(dabco)$_{0.5}$(DMF))$_n$. The zinc atoms of A, B, C, and D layer are displayed as magenta, cyan, orange, and green spheres, respectively. Other atoms are displayed as black stick. A, B, C, and D layers are highlighted with dotted magenta line, solid cyan line, dotted orange line, and solid green line, respectively.

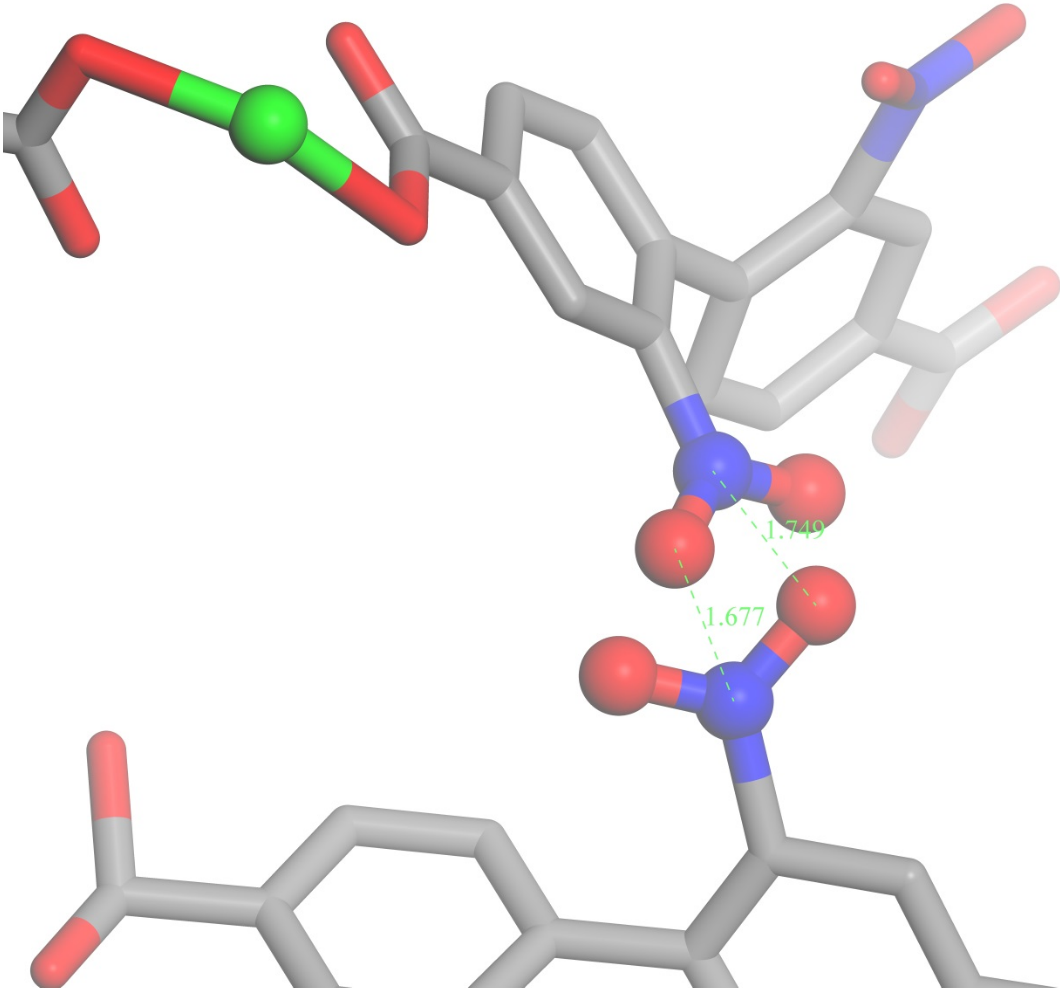


Figure S2. Intermolecular interaction between nitro groups of two different bpdc-$[NO_2]_2$ from two different layers of $(Zn(bpdc\text{-}[NO_2]_2)(dabco)_{0.5}(DMF))_n$. Hydrogen atoms and the disordered nitro groups are omitted for clarity. Carbon (grey), nitrogen (blue), and zinc (green spheres).

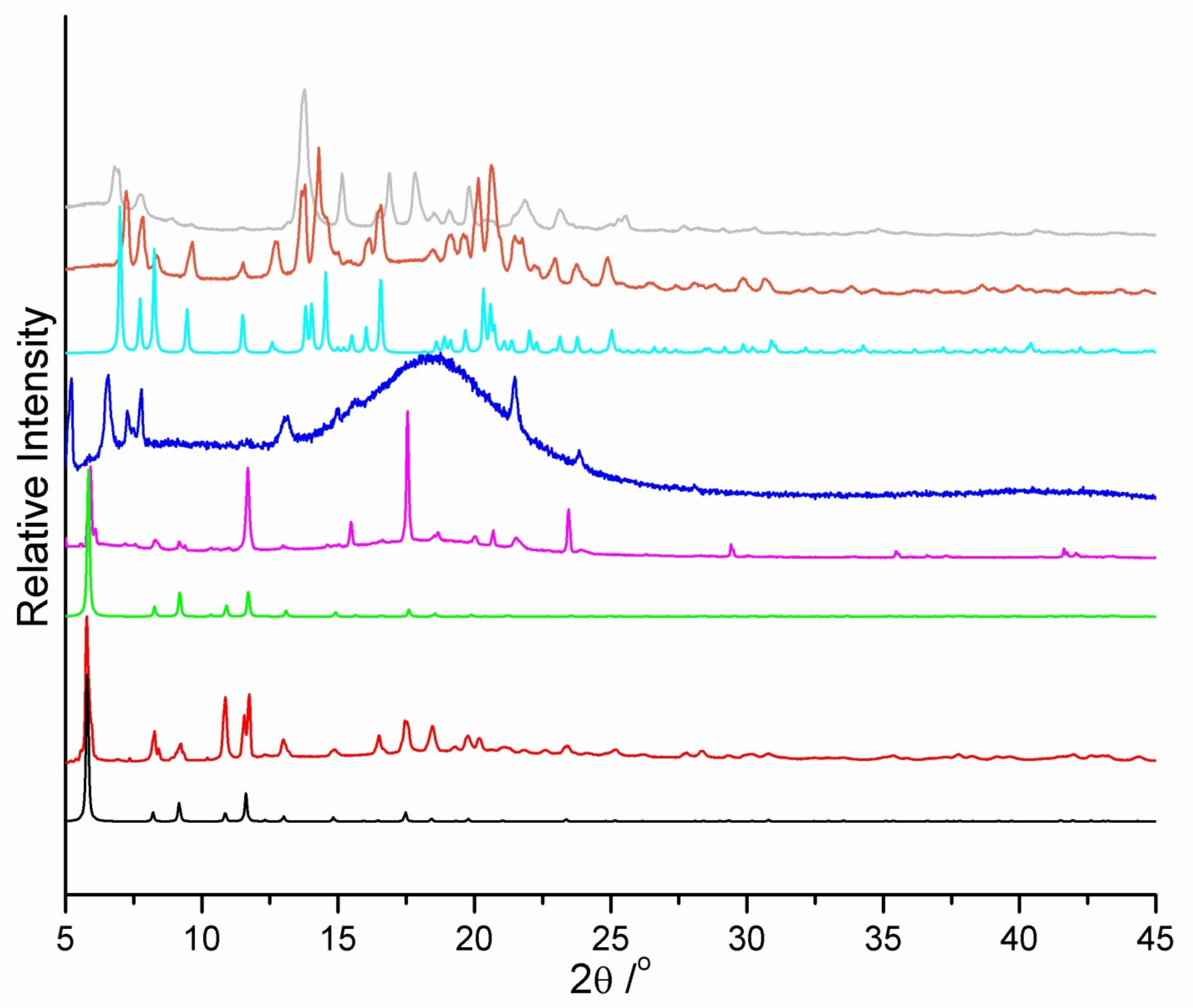


Figure S3. PXRD of simulated DMOF-1-bpdc (black), as synthesized DMOF-1-bpdc, simulated DMOF-1-bpdc-NO_2 (green), as synthesized DMOF-1-bpdc-NO_2, dried DMOF-1-bpdc-NO_2, simulated (Zn(bpdc-[NO_2]$_2$)(dabco)$_{0.5}$(DMF))$_n$ (cyan), as synthesized (Zn(bpdc-[NO_2]$_2$)(dabco)$_{0.5}$(DMF))$_n$ (orange), and dried (Zn(bpdc-[NO_2]$_2$)(dabco)$_{0.5}$(DMF))$_n$ (grey). The difference in the PXRD patterns of the as synthesized and dried MOF materials are due to the flexibility of the framework.

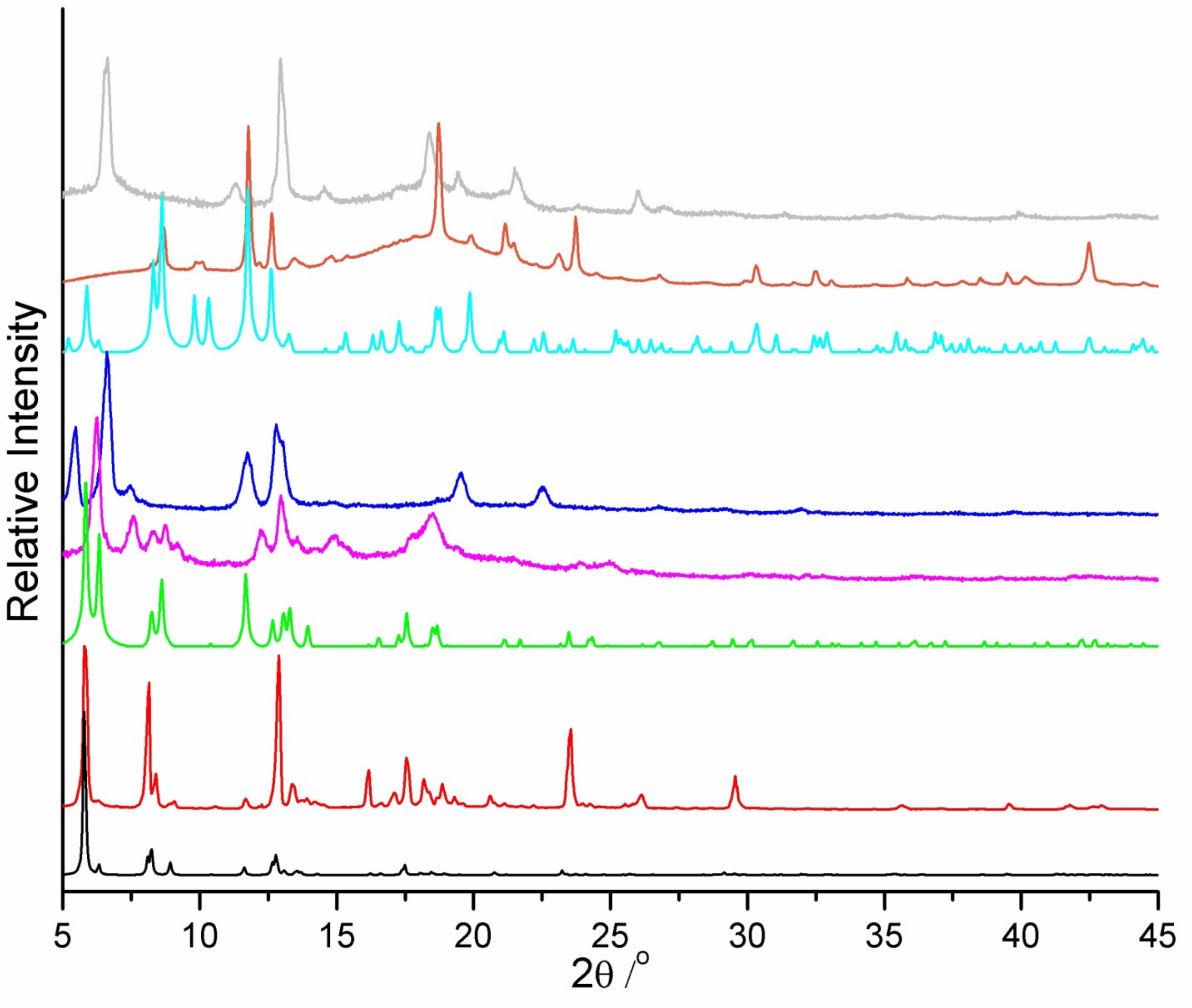


Figure S4. PXRD of simulated BMOF-1-bpdc (black), as synthesized BMOF-1-bpdc, simulated BMOF-1-bpdc-NO_2 (green), as synthesized BMOF-1-bpdc-NO_2, dried BMOF-1-bpdc-NO_2, simulated BMOF-1-bpdc-$[NO_2]_2$ (cyan), as synthesized BMOF-1-bpdc-$[NO_2]_2$ (orange), and dried BMOF-1-bpdc-$[NO_2]_2$ (grey). The difference in the PXRD patterns of the as synthesized and dried MOF materials are due to the flexibility of the framework.

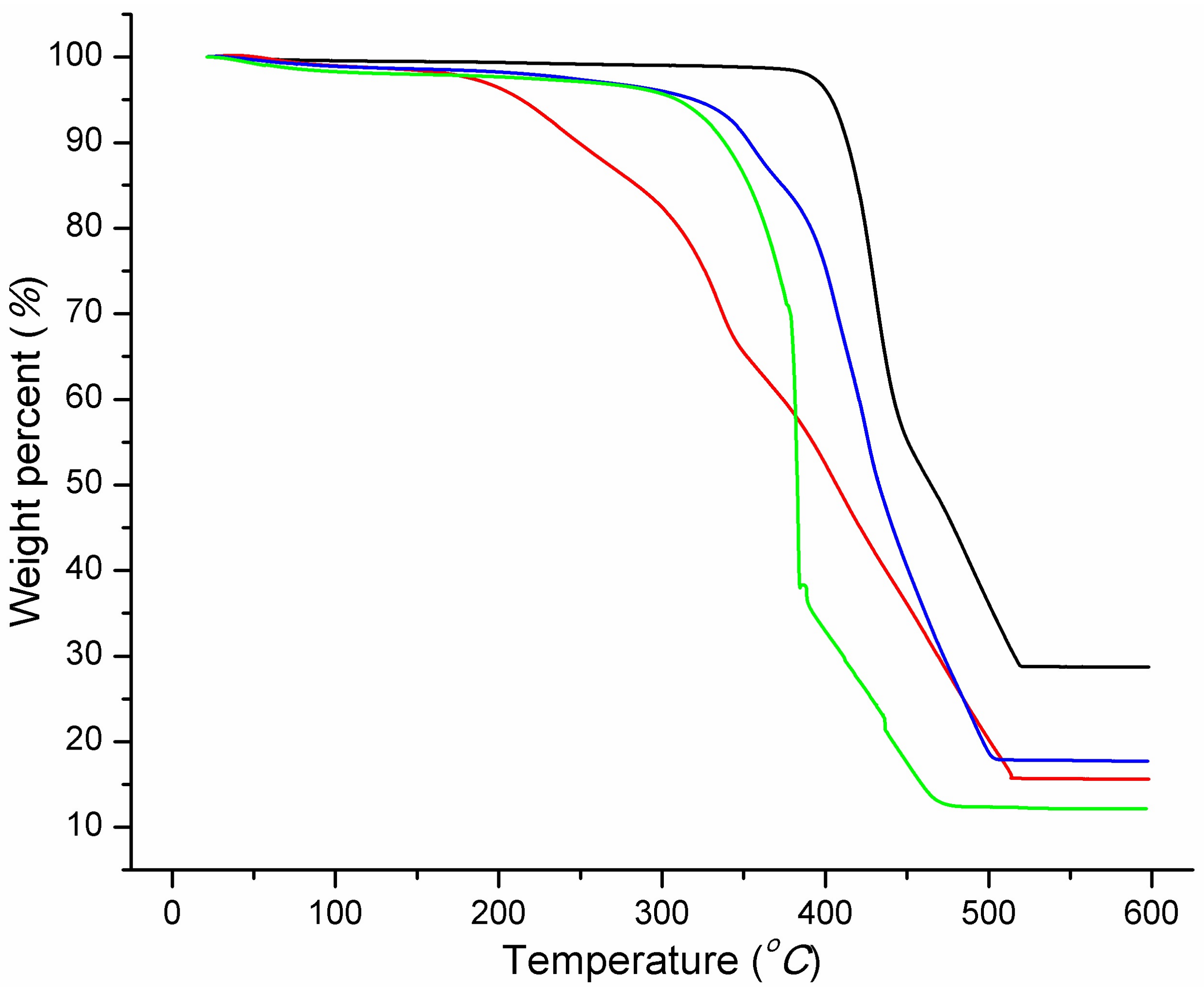


Figure S5. TGA of DMOF-1-bpdc-NO$_2$ (black), (Zn(bpdc-[NO$_2$]$_2$)(dabco)$_{0.5}$(DMF))$_n$ (red), BMOF-1-bpdc-NO2 (blue), and BMOF-1-bpdc-[NO$_2$]$_2$ (green).

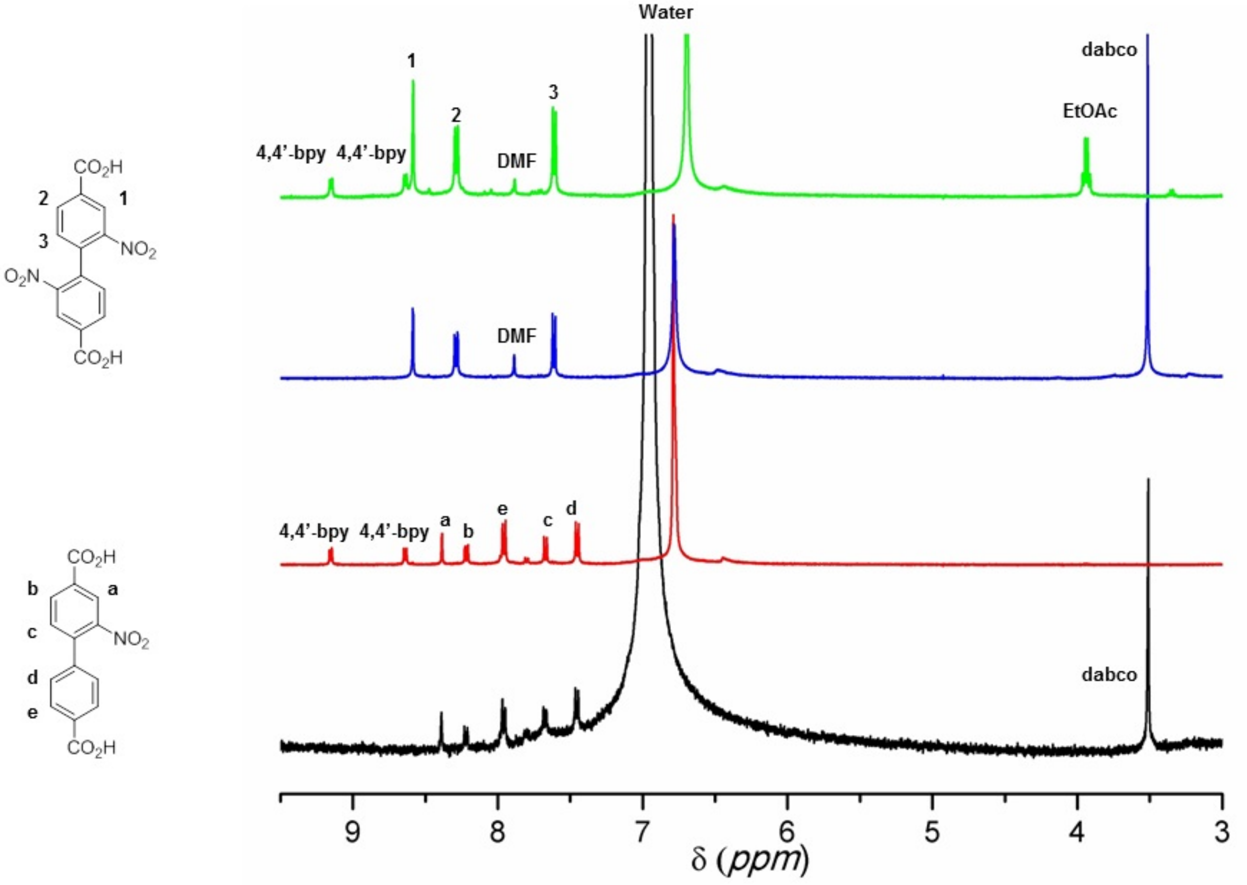


Figure S6. ^{1}H NMR digestions of DMOF-1-bpdc-NO$_2$ (black), BMOF-1-bpdc-NO$_2$ (red), (Zn(bpdc-[NO$_2$]$_2$)(dabco)$_{0.5}$(DMF))$_n$ (blue), and BMOF-1-bpdc-[NO$_2$]$_2$ (green).

Table S1. BET surface areas of MOFs and the (Zn(bpdc-[NO_2]$_2$)(dabco)$_{0.5}$(DMF))$_n$.

	BET surface area (m^2 g^{-1})[1]
DMOF-1-bpdc	185 ± 31[1]
DMOF-1-bpdc-NO_2	708 ± 54
(Zn(bpdc-[NO_2])(dabco)$_{0.5}$(DMF))$_n$	9 ± 3
BMOF-1-bpdc	60 ± 26[1]
BMOF-1-bpdc-NO_2	139 ± 52
BMOF-1-bpdc-[NO_2]$_2$	10 ± 7

[1] The average and standard deviation were calculated based on the measurements of 3 independent samples.

Table 2. Crystal data and structure refinement for DMOF-1-bpdc-NO_2.

Identification code	DMOF-1-bpdc-NO_2
Empirical formula	C_{36} N_2 O_8 Zn_2
Formula weight	719.12
Temperature	250(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I4/ *m c m*
Unit cell dimensions	a = b = 21.355(2) Å α = β = γ = 90° c = 19.211(2) Å
Volume	8760.5(17) $Å^3$
Z	4
Density (calculated)	0.556 mg/m^3
Absorption coefficient	0.568 mm^{-1}
F(000)	1472
Crystal size	0.10 × 0.10 × 0.40 mm^3
Theta range for data collection	2.38 to 26.86°.
Index ranges	-26<=h<=25, -22<=k<=21, -24<=l<=16
Reflections collected	14536
Independent reflections	2500 [$R_{(int)}$ = 0.0464]
Completeness to theta = 26.86°	98.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2500 / 0 / 60
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R_1 = 0.0647, wR_2 = 0.2214
R indices (all data)	R_1 = 0.1058, wR_2 = 0.2398
Largest diff. peak and hole	0.805 and -1.138 e.$Å^{-3}$

Table S3. Crystal data and structure refinement for BMOF-1-bpdc-NO_2.

Identification code	BMOF-1-bpdc-NO_2
Empirical formula	$C_{38} H_8 N_6 O_8 Zn_2$
Formula weight	807.24
Temperature	250(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*C c c m*
Unit cell dimensions	a = 21.3799(18) Å $\alpha = 90^{o}$ b = 21.4597(18) Å $\beta = 90^{o}$ c = 27.944(2) Å $\gamma = 90^{o}$
Volume	12821.1(18) $Å^3$
Z	4
Density (calculated)	0.418 mg/m^3
Absorption coefficient	0.391 mm^{-1}
F(000)	1608
Crystal size	0.05 × 0.10 × 0.10 mm^3
Theta range for data collection	1.53 to 26.07°.
Index ranges	-21<=h<=22, -26<=k<=25, -34<=l<=32
Reflections collected	40438
Independent reflections	5833 [$R_{(int)}$ = 0.0519]
Completeness to theta = 26.07°	89.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5833 / 0 / 170
Goodness-of-fit on F^2	0.993
Final R indices [I>2sigma(I)]	$R_1 = 0.0466$, $wR_2 = 0.1265$
R indices (all data)	$R_1 = 0.0886$, $wR_2 = 0.1379$
Largest diff. peak and hole	0.534 and -0.262 e.$Å^{-3}$

Table S4. Crystal data and structure refinement for (Zn(bpdc-[NO_2]$_2$)(dabco)$_{0.5}$(DMF))$_n$.

Identification code	(Zn(bpdc-[NO_2]$_2$)(dabco)$_{0.5}$(DMF))$_n$
Empirical formula	$C_{20} H_{10} N_4 O_9 Zn$
Formula weight	515.69
Temperature	250(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2/*c*
Unit cell dimensions	a = 13.7580(11) Å α = γ = 90° b = 25.2156(18) Å β = 111.399 (4)° c = 14.9205(11) Å
Volume	4819.3(6) Å^3
Z	8
Density (calculated)	1.421 mg/m^3
Absorption coefficient	1.913 mm^{-1}
F(000)	2080
Crystal size	0.10 × 0.10 × 0.20 mm^3
Theta range for data collection	3.51 to 50.31°.
Index ranges	-13<=h<=8, -25<=k<=25, -14<=l<=14
Reflections collected	8945
Independent reflections	2463 [$R_{(int)}$ = 0.0322]
Completeness to theta = 50.31°	98.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2463 / 0 / 403
Goodness-of-fit on F^2	1.118
Final R indices [I>2sigma(I)]	R_1 = 0.0645, wR_2 = 0.1942
R indices (all data)	R_1 = 0.0704, wR_2 = 0.2009
Largest diff. peak and hole	0.630 and -0.253 e.Å^{-3}

Table S5. Crystal data and structure refinement for BMOF-1-bpdc-[NO$_2$]$_2$.

Identification code	BMOF-1-bpdc-[NO$_2$]$_2$
Empirical formula	$C_{48} N_8 O_{17} Zn_2$
Formula weight	1091.30
Temperature	250(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	F *m m m*
Unit cell dimensions	a = 28.0614(11) Å α = 90° b = 30.0942(19) Å β = 90° c = 30.0947(12) Å γ = 90°
Volume	25415(2) Å^3
Z	16
Density (calculated)	1.141 Mg/m^3
Absorption coefficient	1.476 mm^{-1}
F(000)	8640
Crystal size	0.40 × 0.60 × 0.60 mm^3
Theta range for data collection	2.61 to 82.01°.
Index ranges	-35<=h<=36, -35<=k<=34, -33<=l<=28
Reflections collected	36215
Independent reflections	6067 [$R_{(int)}$ = 0.0380]
Completeness to theta = 82.01°	81.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6067 / 4 / 283
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R_1 = 0.1579, wR_2 = 0.5586
R indices (all data)	R_1 = 0.1671, wR_2 = 0.5968
Largest diff. peak and hole	3.301 and -0.852 e.Å^{-3}

References

1. P. V. Dau, M. Kim, S. J. Garibay, F. H. L. Muench, C. E. Moore and S. M. Cohen, *Inorg. Chem.*, 2012, **51**, 5671-5676.

2. G. M. Sheldrick, *Acta Cryst.* , 2008, **A64**, 122.

3. A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.