Electronic Supplementary Information for:

Post-Synthetic Tuning of Hydrophilicity in Pyrazolate MOFs to Modulate Water Adsorption Properties

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Experimental

Experimental Section

General Considerations. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (TCI), 3,5-dimethylpyrazole (Aldrich), 2 M ethylamine/THF (Alfa Aesar), sodium ethanethiolate (Fluka), $Zn(NO_3)_2 \cdot xH_2O$ (Alfa Aesar) , *N,N*-dimethylformamide (DMF, 99.8%, VWR), and dimethylsulfoxide (DMSO, Aldrich) were used as received unless otherwise noted. 2-amino-3,5-dimethylpyrazole,[1] 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic dianhydride,[2] and dimethyldioxirane (~0.09M in acetone)[3] were prepared according to literature procedures. Powder X-ray diffraction patterns were collected on a Bruker Advance D8 diffractometer using Nickel-filtered Cu-K_α radiation (λ = 1.5418 Å). Powder X-ray diffraction samples were prepared by placing a thin layer of sample on a zero-background silicon plate. IR spectra were collected using a Bruker Tensor 37 FTIR spectrometer equipped with a Pike Ge ATR accessory. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 2 or 4 °C/min under a nitrogen gas flow of 90 mL/min. Elemental analyses were performed at Complete Analysis Laboratories, Inc (Parsippany, NJ).

Gas sorption measurements. A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure N_2 and H_2O adsorption isotherms. Oven-dried sample tubes equipped with TranSeals™ (Micrometrics) were evacuated and tared. Samples (100-200 mg) were transferred to the sample tube, which was then capped by a TranSeal™. Samples were heated to the appropriate temperatures and held at those temperatures until the outgas rate was less than 2 mTorr/minute. The evacuated sample tubes were weighed again, and the sample mass was determined by subtracting the mass of the previously tared tubes. N_2 isotherms were measured using a liquid nitrogen bath

(77 K). H_2O isotherms were measured at 293 K using a circulating water bath with temperature control provided by a Neslab LT-50DD refrigerated circulating bath. Ultra high purity grade (99.999% purity) N_2 and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

Simulation of PXRD pattern from Zn(NDI-H) model structure. A model structure of Zn(NDI-H) was constructed starting from the reported X-ray crystal structure of Co(bdpb) (bdpb^{2-} = 1,4-bis[(3,5-dimethyl)pyrazol-4-yl]benzene).[4] The bdpb^{2-} organic linker was replaced with [NDI-H]$^{2-}$ using Discovery Studio and the unit cell lengths *a* and *b* were increased to 24.5 Å to accommodate the extended linker while the *c* axis length (7.16 Å) and cell angles ($\alpha = \beta = \gamma = 90^\circ$) were left unchanged. The powder X-ray diffraction pattern of the structure was dynamically simulated as a function of breathing angle (θ), defined as the angle made between ligands connected by the metallic vertex, using the original fitting routine MOF-FIT that allows determination of breathing angles and other translational MOF deformations by visually matching powder experimental powder X-ray diffraction patterns with ones predicted by manual modulation of unit cell parameters, and implemented in MATLAB. This script, along with detailed instructions for its use, are provided as additional Electronic Supplementary Information and are also available at http://web.mit.edu/dincalab/.) Using the dynamic modeling function, a structure with a breathing angle of $\theta = 77^\circ$ was found to provide the best visual fit of the experimental pattern of Zn(NDI-H) (Figure S11). The unit cell parameters of the final structure were a = 22 Å, b = 27 Å, c = 7 Å and $\alpha = \beta = \gamma = 90^\circ$. The final powder X-ray diffraction pattern of the model structure was simulated using Mercury 2.4.5. The

Cartesian (XYZ) and fractional coordinates for the model structures with θ = 77˚ and θ = 90˚ are provided in Table 1 and Table 2, respectively.

Synthesis of H_2NDI-H. A dry 100 mL Schlenk flask was charged with 1,4,5,8-Naphthalenetetracarboxylic dianhydride (0.86 g, 3.2 mmol), 3,5-dimethylpyrazole (0.75 g, 6.8 mmol), and anhydrous DMF (50 mL) under a nitrogen atmosphere. The reaction mixture was heated at 150 °C with rapid stirring for 8 hrs. The flask was cooled to room temperature and the dark brown DMF solution was poured into stirring diethyl ether (150 mL). The precipitated yellow solid was separated by filtration and recrystallized from DMF/diethyl ether (10 mL : 20 mL). The product was filtered and dried *in vacuo* at 70 °C to afford 1.2 g (82 %) of light yellow powder. ^{1}H NMR (399.43 MHz; dmso-d_6): δ 1.97 (s, 6H, pyrazole-*CH*$_3$), 2.06 (s, 6H, pyrazole-*CH*$_3$), 8.74 (s, 4H, naph-*CH*), 12.51 (s, 2H, pyrazole-*NH*). ^{13}C NMR (399.43 MHz; dmso-d_6): δ 9.00, 11.38, 111.98, 126.73, 130.82, 136.16, 144.52, 162.28. Elemental analysis calcd. for $C_{24}H_{18}N_6O_4$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.38; H, 3.81; N 18.58.

Synthesis of H_2NDI-Br. A dry 100 mL Schlenk flask was charged with 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic dianhydride (1.0 g), 3,5-dimethylpyrazole (0.44 g, 4.6 mmol), and acetic acid (50 mL). The reaction mixture was heated to reflux with rapid stirring for 8 hrs. The flask was cooled to room temperature, and the precipitated yellow solid was separated by filtration and washed with water (3 × 10 mL) and hot methanol (3 × 100 mL). The product was dried *in vacuo* at 70 °C to afford 0.65 g (53 %) of yellow-orange powder that was used without further purification. ^{1}H NMR (399.43 MHz; dmso-d_6): δ 2.02 (s, 12H, pyrazole-*CH*$_3$), 8.79 (s, 2H, naph-*CH*), 12.47 (s, 2H, pyrazole-*NH*).

Synthesis of H_2NDI-NHEt. A 20 mL scintillation vial was charged with H_2NDI-Br (0.65 g, 1.06 mmol), DMSO (10 mL), and 2 M ethylamine/THF (6.0 mL, 12 mmol). The vial was sealed, and the mixture was heated at 70 °C with rapid stirring for 24 hrs. The vial was allowed to cool to room temperature, and the reaction mixture was poured into stirring water (100 mL). The precipitated blue/purple solid was separated by filtration and washed with water (3 × 10 mL) and methanol (3 × 5 mL). The product was purified by multiple recrystallizations from hot dichloromethane/methanol (15 mL : 45 mL) to afford 0.240 g (42%) of H_2NDI-NHEt as a blue-purple microcrystalline solid. ^{1}H NMR (399.43 MHz; dmso-d_6): δ 1.31 (t, 6H, NH-CH_2-CH_3, $^3J_{H\text{-}H}$ = 7.2 Hz), 1.93 (s, 6H, pyrazole-CH_3), 2.02 (s, 6H, pyrazole-CH_3), 3.53 (m, 4H, NH-CH_2-CH_3), 8.09 (s, 2H, naph-*CH*), 9.19 (s, 2H, *NH*-CH_2-CH_3), 12.45 (s, 2H, pyrazole-*NH*). ^{13}C NMR (399.43 MHz; dmso-d_6): δ 8.94 (pyrazole-CH_3), 11.23 (pyrazole-CH_3), 14.43 (-$NHCH_2CH_3$), 37.07 (-$NHCH_2CH_3$), 101.25, 112.23, 118.2, 121.19, 125.90, 148.53, 161.96, 165.16. Elemental analysis calcd. for ($C_{28}H_{28}N_8O_4$): C, 62.21; H, 5.22; N, 20.73. Found: C, 61.43; H, 5.15; N 20.4.

Synthesis of H_2NDI-SEt. A dry 50 mL Schlenk flask was charged with H_2NDI-Br (0.64 g, 1.04 mmol), sodium ethanethiolate (0.35 g, 3.57 mmol), and DMSO (10 mL). The reaction mixture was heated at 70 °C with rapid stirring for 24 hrs. The flask was cooled to room temperature and the reaction mixture was poured into stirring water (100 mL). The precipitated orange-red solid was separated by filtration and washed with water (3 × 10 mL) and methanol (3 × 5 mL). The product was purified by multiple recrystallizations from hot dichloromethane/methanol (45 mL : 15 mL) to afford 0.40 g (66%) of H_2NDI-SEt as an orange microcrystalline solid. ^{1}H NMR (399.43 MHz; dmso-d_6): δ 1.41 (t, 6H, S-CH_2-CH_3, $^3J_{H\text{-}H}$ = 7.34 Hz), 2.00 (s, 6H, pyrazole-CH_3), 3.26 (q, 4H, S-CH_2-CH_3, $^3J_{H\text{-}H}$

= 7.34 Hz), 8.62 (s, 2H, naph-*CH*), 12.45 (br s, 2H, pyrazole-*NH*). ^{13}C NMR (399.43 MHz; dmso-d_6): δ 9.05, 11.29, 12.84, 25.25, 111.94, 119.22, 124.18, 125.29, 127.53, 147.28, 161.60, 162.38. Elemental analysis calcd. for $C_3H_7NO)_{0.5}$: C, 58.52; H, 4.56; N, 14.62. Found: C, 58.57; H, 4.63; N, 14.61.

Synthesis of Zn(NDI-X) (X = H, NHEt, SEt). A dry 100 mL Schlenk flask was charged with H_2NDI-H (0.64 g, 1.4 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.46 g, 1.5 mmol), and DMF (160 mL) under a nitrogen atmosphere. The reaction mixture was heated at 130 °C for 24 hrs. After allowing the reaction to cool to room temperature, the precipitated yellow solid was separated by filtration, washed with DMF (3 × 5 mL), and air dried to afford 0.97 g of Zn(NDI-H)·*x*DMF as light yellow powder. Zn(NDI-NHEt) and Zn(NDI-SEt) were prepared analogously. Samples for combustion elemental analysis (C, H, N) activated by heating to 140-160 °C under high vacuum (< 10^{-4} torr) for at least 24 h. Zn(NDI-H): Elemental analysis calcd. for ($ZnC_{24}H_{16}N_6O_4$): C, 55.67; H, 3.11; N, 16.23. Found: C, 54.55; H, 3.15; N 16.37. Zn(NDI-NHEt): Elemental analysis calcd. for ($ZnC_{28}H_{26}N_8O_4$): C, 55.68; H, 4.34; N, 18.55. Found: C, 53.44; H, 4.07; N 18.46. Zn(NDI-SEt): Elemental analysis calcd. for ($ZnC_{28}H_{24}N_6O_4S_2$): C, 52.71; H, 3.79; N, 13.17. Found: C, 52.56; H, 3.63; N 13.15.

Postsynthetic oxidation of Zn(NDI-SEt) with DMDO. A solution of dimethyldioxirane (5.3 mL, 0.09 M in acetone) was added over 30 min to a stirring suspension of Zn(NDI-SEt) (0.15 g) in acetone (20 mL) at -20 °C. The mixture was allowed to warm to room temperature and stirred for 12 hrs. The solid was separated by filtration, washed with acetone (5 × 10 mL), and air-dried to afford 0.12 g of yellow powder. The extent of oxidation of the sulfide groups was determined by measuring the IR spectrum of the

recovered solid (Figure S6) and the ^{1}H NMR spectrum of a sample (~15 mg) digested with a dmso-d_6 (0.6 mL) and DCl/D_2O (12 M, 0.05 mL) solvent mixture (Figure S9).

Synthesis of Zn(NDI-SO_2Et). A solution of dimethyldioxirane (20 mL, 0.09 M in acetone) was slowly added over 30 min to a stirring suspension of Zn(NDI-SEt) (0.15 g) in acetone (20 mL) at -20 °C. The mixture was allowed to warm to room temperature and stirred for 12 hrs. The solid was separated by filtration, washed with acetone (5 × 10 mL), and air-dried to afford 0.12 g of yellow powder. Oxidation of the sulfide was confirmed by IR and measuring the ^{1}H NMR spectrum of a sample of the product (~15 mg) after digestion in dmso-d_6 (0.6 mL) and DCl/D_2O (12 M, 0.05 mL).

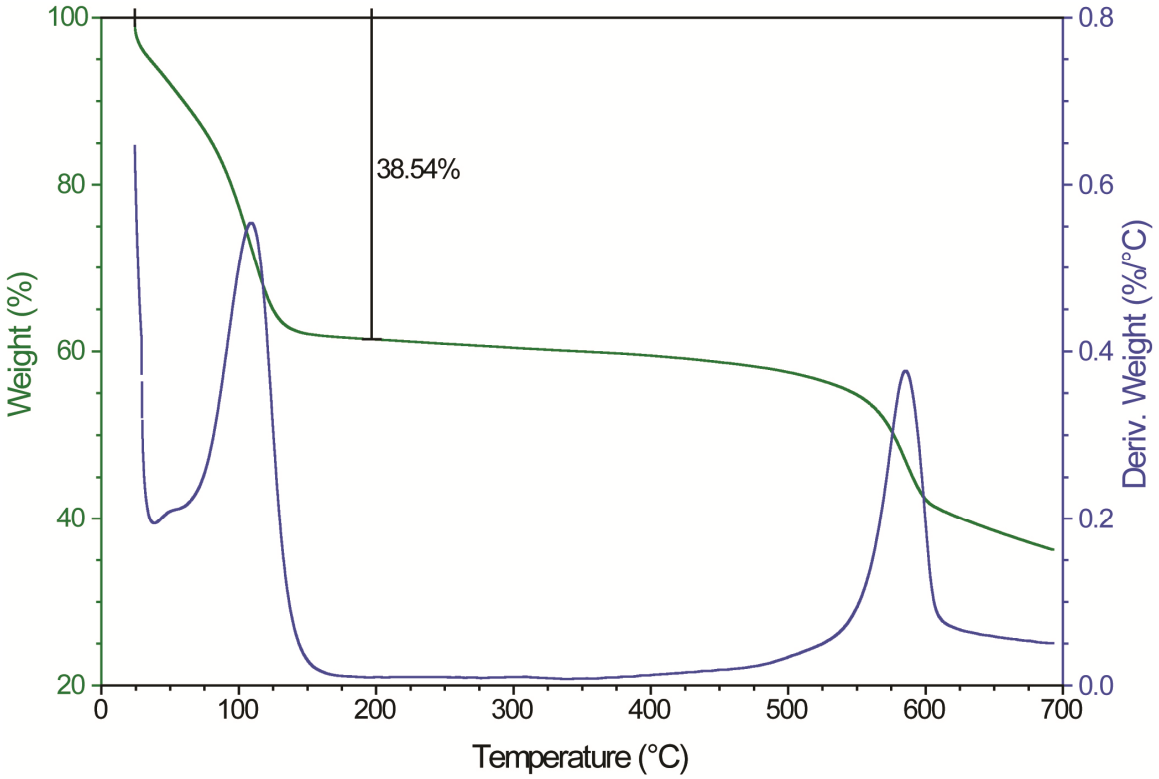

Figure S1. TGA data for Zn(NDI-NHEt) measured using a ramp rate of 4.0 ˚C/min.

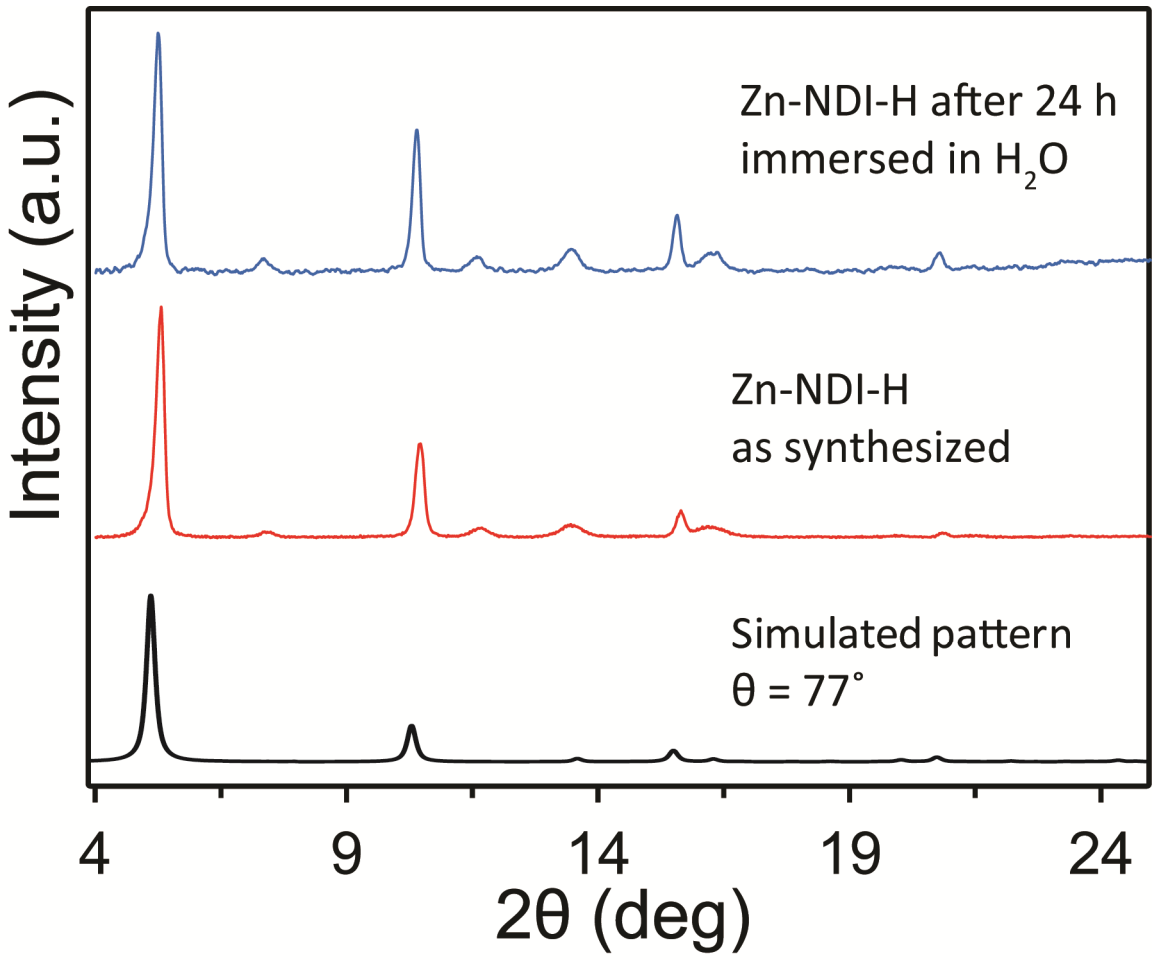

Figure S2. Powder X-ray diffraction patterns of an as-synthesized sample of Zn(NDI-H) and a sample immersed in H_2O for 24 h.

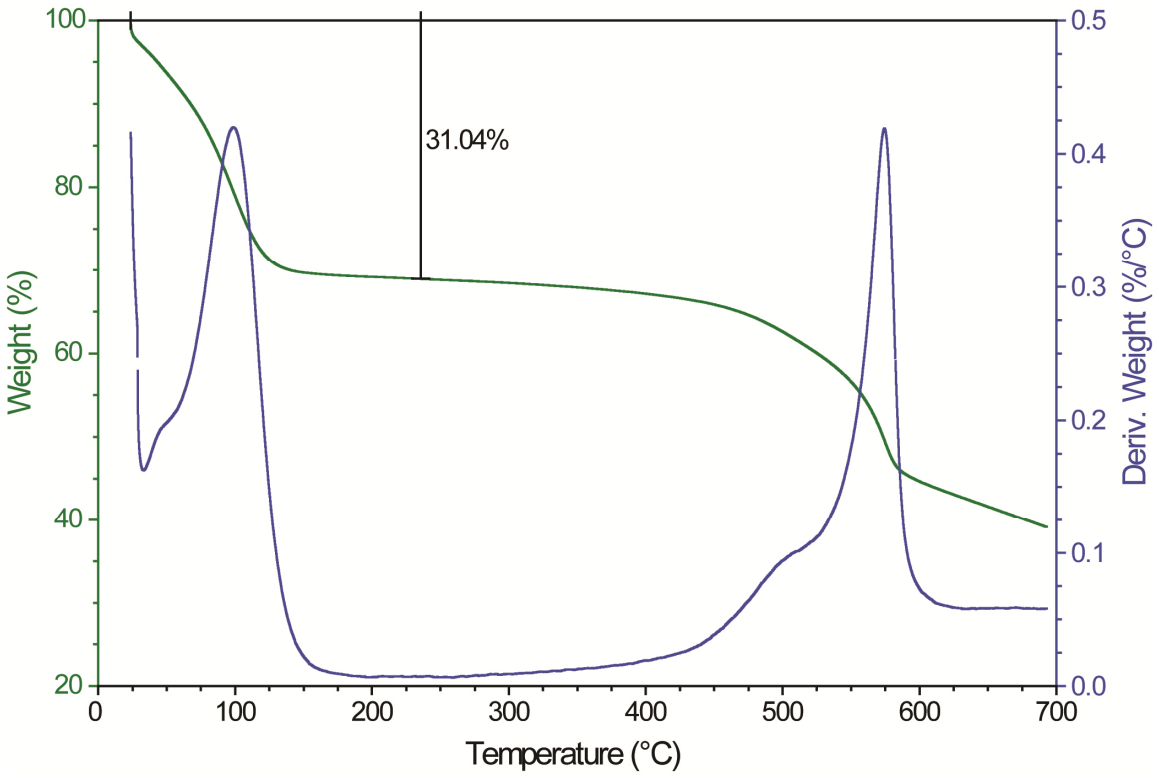

Figure S3. TGA data for Zn(NDI-NHEt) measured using a ramp rate of 4.0 ˚C/min.

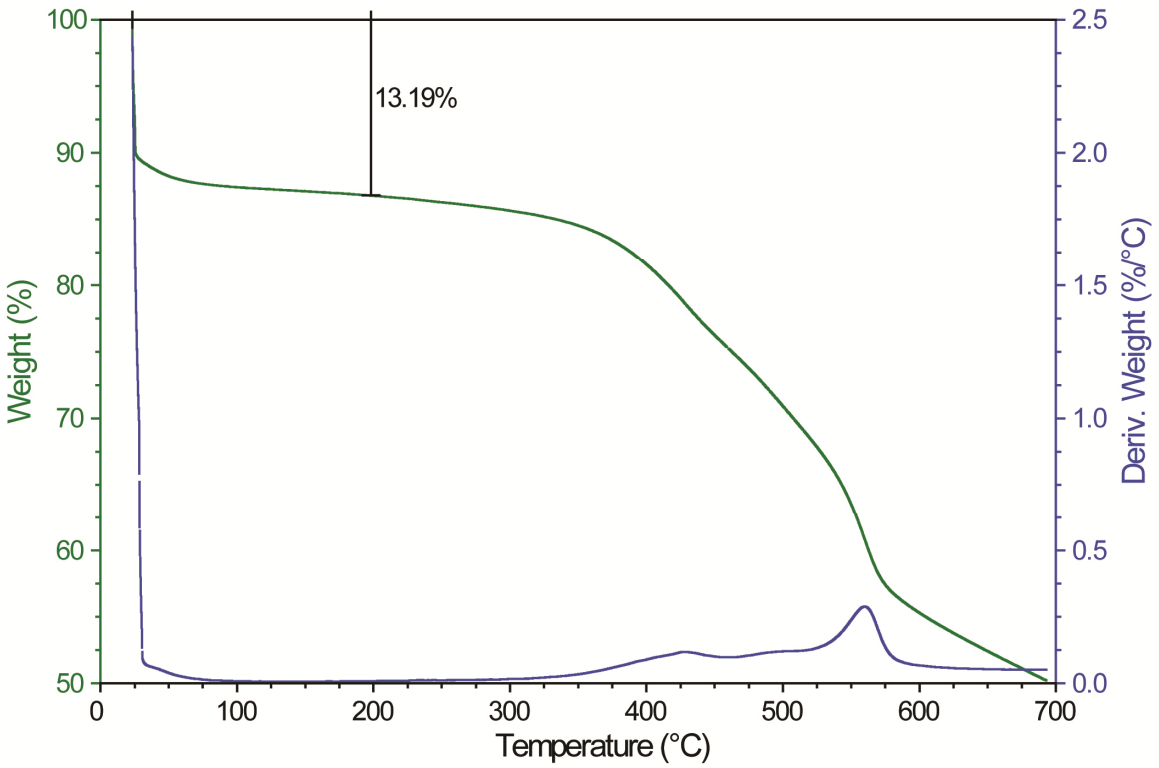

Figure S4. TGA data for Zn(NDI-SEt) measured using a ramp rate of 4.0 ˚C/min.

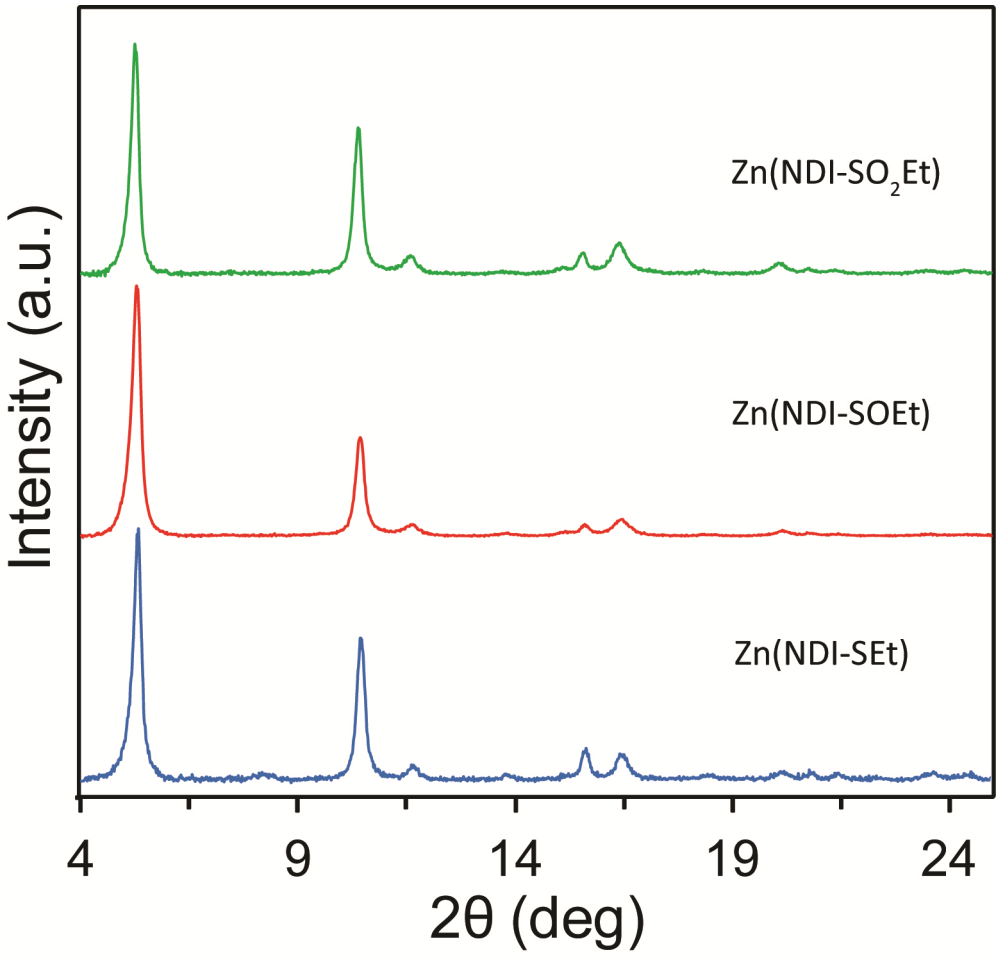

Figure S5. Powder X-ray diffraction patterns of Zn(NDI-SOEt) and Zn(NDI-SO_2Et). FT-IR spectra of Zn(NDI-SOEt) and Zn(NDI-SO_2Et).

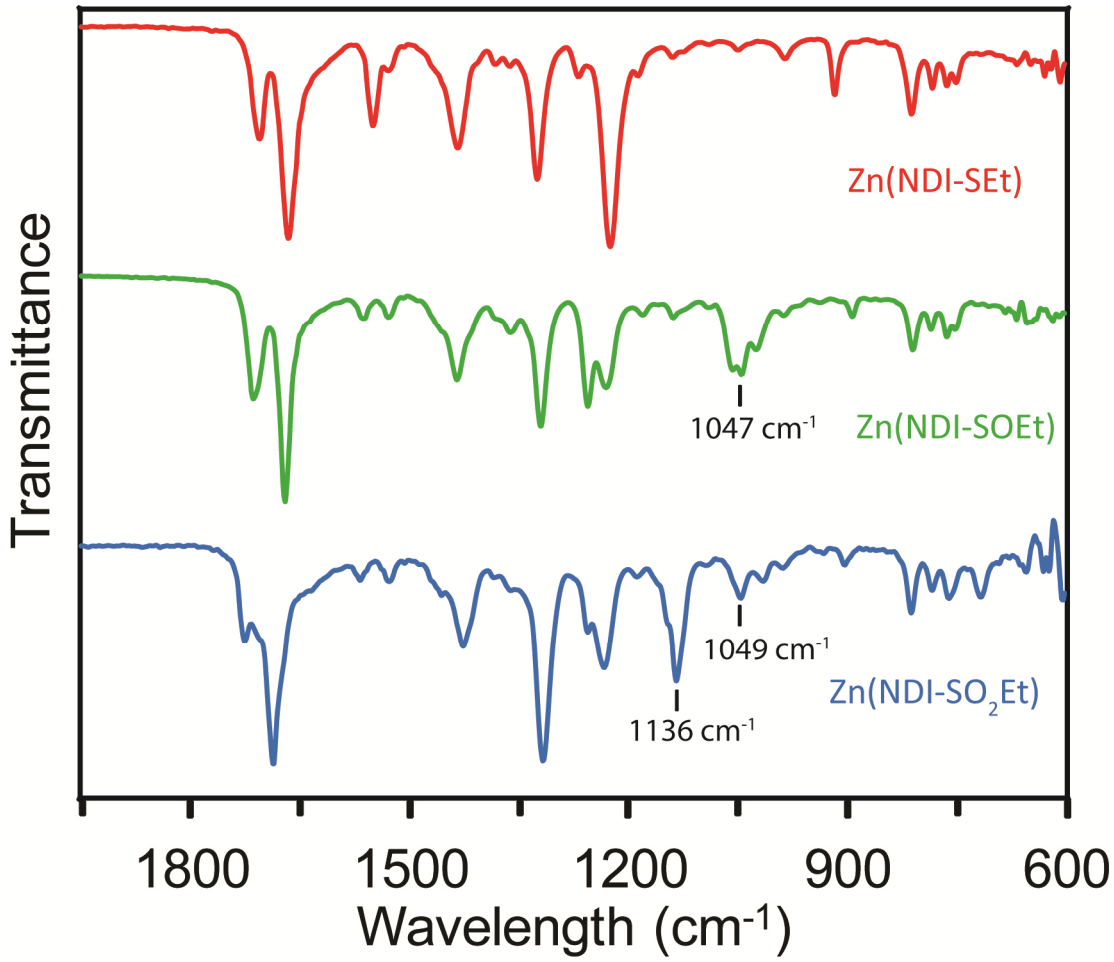

Figure S6. FT-IR spectra of Zn(NDI-SOEt) and Zn(NDI-SO_2Et).

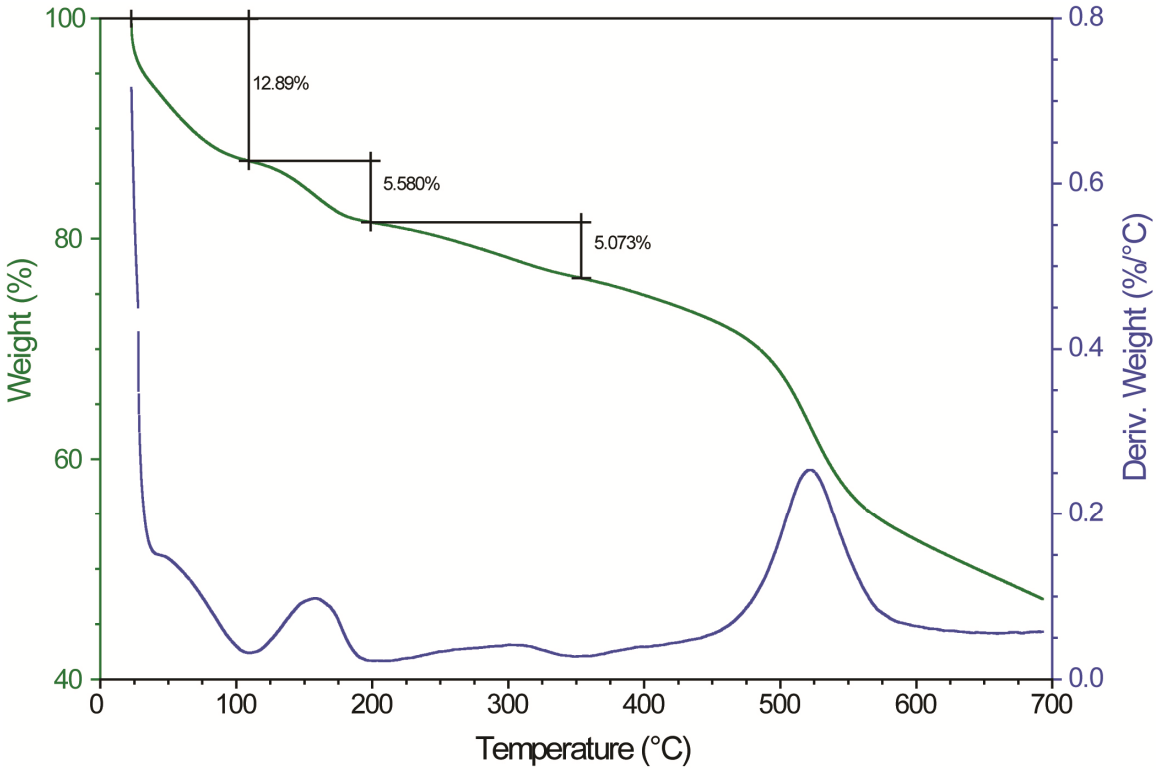

Figure S7. TGA data for Zn(NDI-SOEt) measured using a ramp rate of 4.0 ˚C/min.

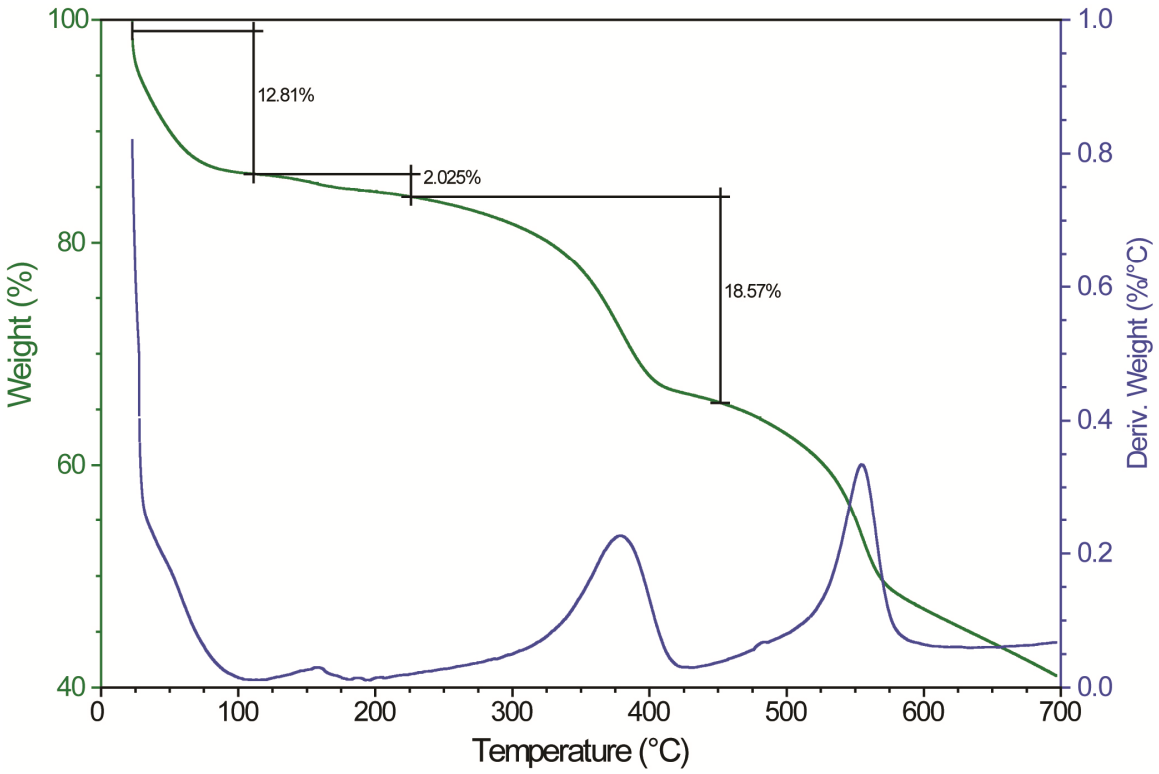

Figure S8. TGA data for Zn(NDI-SO_2Et) measured using a ramp rate of 4.0 ˚C/min.

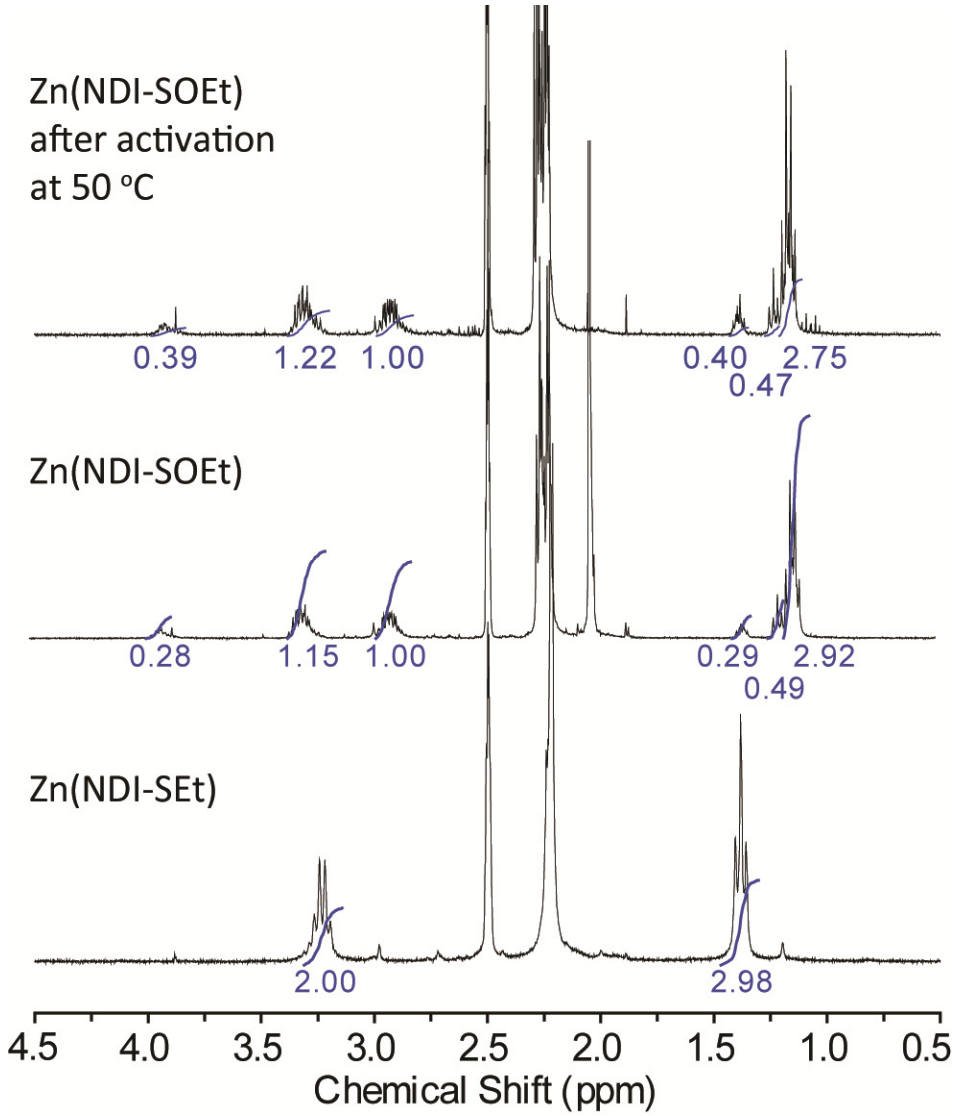

Figure S9. ^{1}H NMR spectra of digested samples of Zn(NDI-SOEt) before and after activation at 50°C.

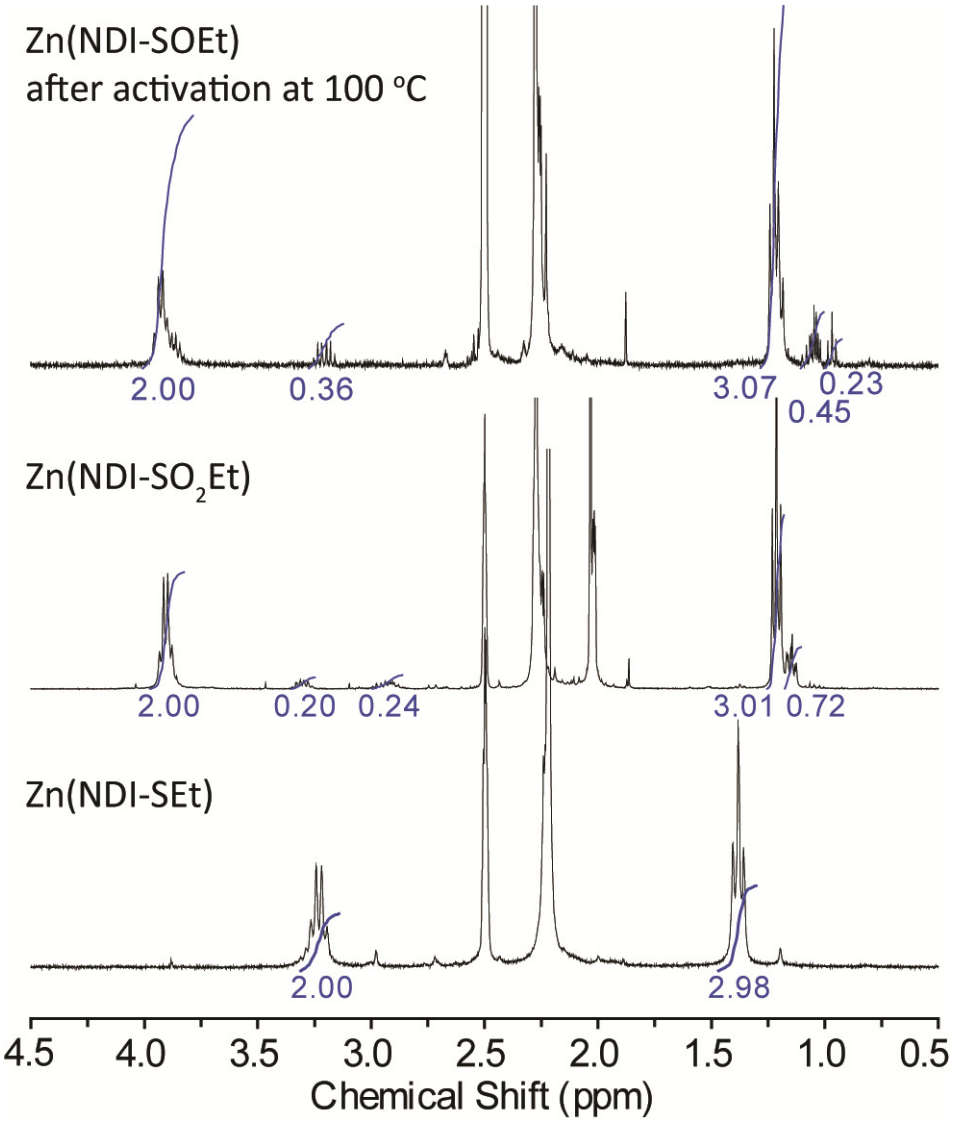

Figure S10. ^{1}H NMR spectra of digested samples of Zn(NDI-SO_2Et) before and after activation at 100°C.

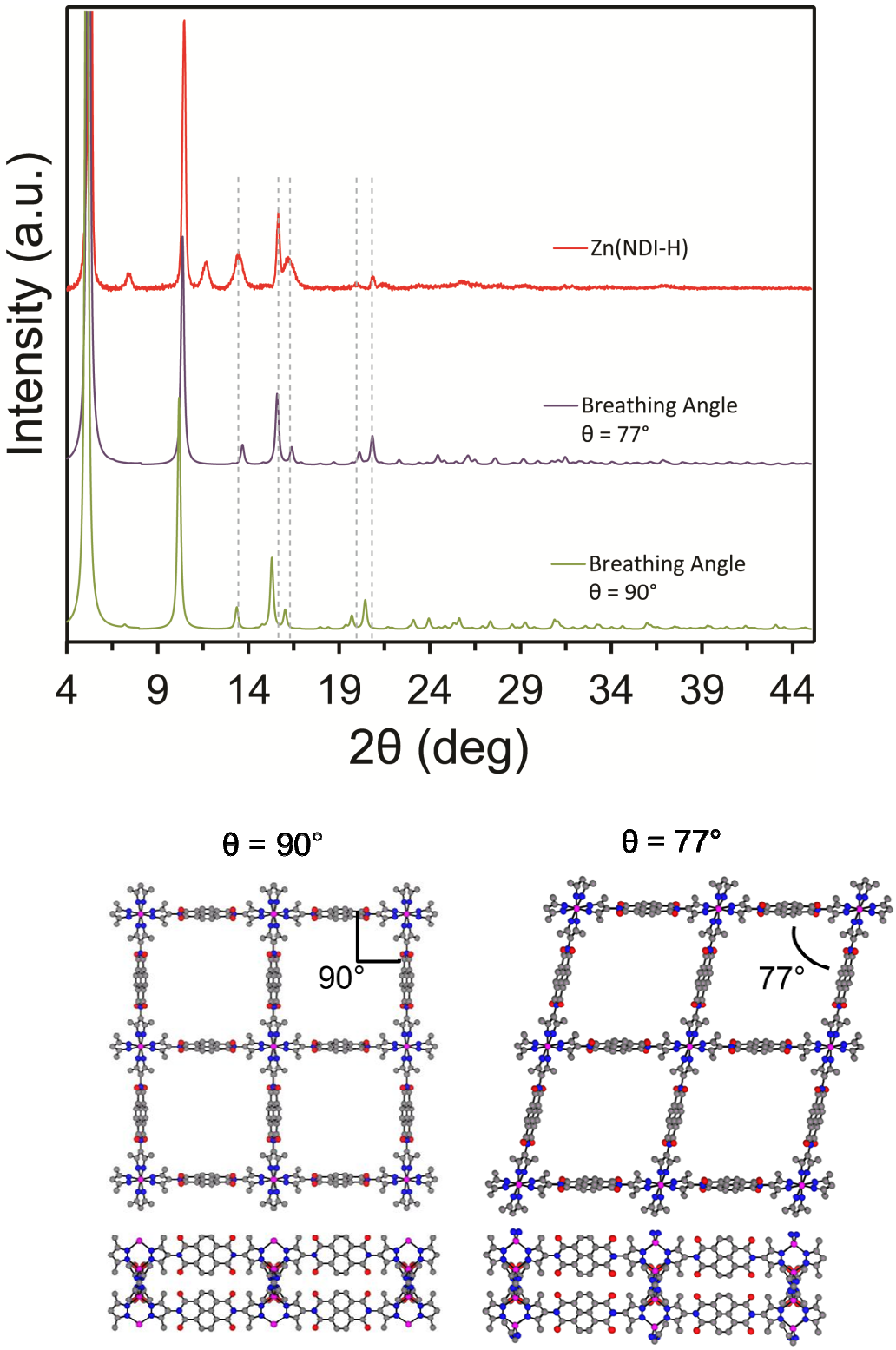

Figure S11. Powder X-ray diffraction patterns of an as-synthesized sample of Zn(NDI-H) and patterns simulated with θ = 77˚ and θ = 90˚.

References

(1) Govor, E. V; Lysenko, A. B.; Quiñonero, D.; Rusanov, E. B.; Chernega, A. N.; Moellmer, J.; Staudt, R.; Krautscheid, H.; Frontera, A.; Domasevitch, K. V *Chem. Commun.* **2011**, *47*, 1764–6.

(2) Chaignon, F.; Falkenström, M.; Karlsson, S.; Blart, E.; Odobel, F.; Hammarström, L. *Chem. Commun.* **2007**, 64–6.

(3) Adam, W.; Chan, Y. Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800–2803.

(4) Tonigold, M.; Lu, Y.; Mavrandonakis, A.; Puls, A.; Staudt, R.; Möllmer, J.; Sauer, J.; Volkmer, D. *Chem. Eur. J.* **2011**, *17*, 8671–95.

Table 1. Coordinates for simulated structure of Zn(NDI-H) with breathing angle θ = 77˚.

Breathing angle θ = 77 ˚

a = 22 Å, b = 27 Å, c = 7 Å; α = β = γ = 90˚

	Fractional Coordinates			Cartesian Coordinates		
Atom	x	y	z	x	y	z
Zn	0.75	0.25	0.25	16.5	6.75	1.75
N	0.6953	0.2852	0.4162	15.2966	7.7004	2.9134
C	0.6195	0.3017	0.1951	13.629	8.1459	1.3657
C	0.6531	0.3162	0.3684	14.3682	8.5374	2.5788
C	0.6439	0.3561	0.5	14.1658	9.6147	3.5
N	0.6012	0.3988	0.5	13.2264	10.7676	3.5
C	0.5711	0.4116	0.6599	12.5642	11.1132	4.6193
C	0.5175	0.4825	0.5	11.385	13.0275	3.5
C	0.5272	0.4523	0.6569	11.5984	12.2121	4.5983
C	0.4999	0.4647	0.8199	10.9978	12.5469	5.7393
O	0.5828	0.3876	0.8046	12.8216	10.4652	5.6322
Zn	0.25	0.75	0.25	5.5	20.25	1.75
N	0.1953	0.7148	0.0838	4.2966	19.2996	0.5866
C	0.1195	0.6983	0.3049	2.629	18.8541	2.1343
C	0.1531	0.6838	0.1316	3.3682	18.4626	0.9212
C	0.1439	0.6439	0	3.1658	17.3853	0
N	0.1012	0.6012	0	2.2264	16.2324	0
C	0.0711	0.5884	-0.1599	1.5642	15.8868	-1.1193
C	0.0175	0.5175	0	0.385	13.9725	0
C	0.0272	0.5477	-0.1569	0.5984	14.7879	-1.0983
C	-0.0001	0.5353	-0.3199	-0.0022	14.4531	-2.2393
O	0.0828	0.6124	-0.3046	1.8216	16.5348	-2.1322
N	0.8047	0.2148	0.4162	17.7034	5.7996	2.9134
C	0.8805	0.1983	0.1951	19.371	5.3541	1.3657
C	0.8469	0.1838	0.3684	18.6318	4.9626	2.5788
C	0.8561	0.1439	0.5	18.8342	3.8853	3.5
N	0.8988	0.1012	0.5	19.7736	2.7324	3.5
C	0.9289	0.0884	0.6599	20.4358	2.3868	4.6193
C	0.9825	0.0175	0.5	21.615	0.4725	3.5
C	0.9728	0.0477	0.6569	21.4016	1.2879	4.5983
C	1.0001	0.0353	0.8199	22.0022	0.9531	5.7393
O	0.9172	0.1124	0.8046	20.1784	3.0348	5.6322
N	0.3047	-0.2148	0.0838	6.7034	-5.7996	0.5866
C	0.3805	-0.1983	0.3049	8.371	-5.3541	2.1343
C	0.3469	-0.1838	0.1316	7.6318	-4.9626	0.9212

C	0.3561	-0.1439	0	7.8342	-3.8853	0
N	0.3988	-0.1012	0	8.7736	-2.7324	0
C	0.4289	-0.0884	-0.1599	9.4358	-2.3868	-1.1193
C	0.4825	-0.0175	0	10.615	-0.4725	0
C	0.4728	-0.0477	-0.1569	10.4016	-1.2879	-1.0983
C	0.5001	-0.0353	-0.3199	11.0022	-0.9531	-2.2393
O	0.4172	-0.1124	-0.3046	9.1784	-3.0348	-2.1322
Zn	0.75	0.25	0.75	16.5	6.75	5.25
N	0.7852	0.1953	0.5838	17.2744	5.2731	4.0866
C	0.8017	0.1195	0.8049	17.6374	3.2265	5.6343
C	0.8162	0.1531	0.6316	17.9564	4.1337	4.4212
C	0.9116	0.0711	0.3401	20.0552	1.9197	2.3807
C	0.9523	0.0272	0.3431	20.9506	0.7344	2.4017
C	0.9647	-0.0001	0.1801	21.2234	-0.0027	1.2607
O	0.8876	0.0828	0.1954	19.5272	2.2356	1.3678
Zn	0.25	0.75	0.75	5.5	20.25	5.25
N	0.2852	-0.1953	-0.0838	6.2744	-5.2731	-0.5866
C	0.3017	-0.1195	-0.3049	6.6374	-3.2265	-2.1343
C	0.3162	-0.1531	-0.1316	6.9564	-4.1337	-0.9212
C	0.4116	-0.0711	0.1599	9.0552	-1.9197	1.1193
C	0.4523	-0.0272	0.1569	9.9506	-0.7344	1.0983
C	0.4647	0.0001	0.3199	10.2234	0.0027	2.2393
O	0.3876	-0.0828	0.3046	8.5272	-2.2356	2.1322
N	0.2148	0.6953	-0.0838	4.7256	18.7731	-0.5866
C	0.1983	0.6195	-0.3049	4.3626	16.7265	-2.1343
C	0.1838	0.6531	-0.1316	4.0436	17.6337	-0.9212
C	0.0884	0.5711	0.1599	1.9448	15.4197	1.1193
C	0.0477	0.5272	0.1569	1.0494	14.2344	1.0983
C	0.0353	0.4999	0.3199	0.7766	13.4973	2.2393
O	0.1124	0.5828	0.3046	2.4728	15.7356	2.1322
N	0.7148	0.3047	0.5838	15.7256	8.2269	4.0866
C	0.6983	0.3805	0.8049	15.3626	10.2735	5.6343
C	0.6838	0.3469	0.6316	15.0436	9.3663	4.4212
C	0.5884	0.4289	0.3401	12.9448	11.5803	2.3807
C	0.5477	0.4728	0.3431	12.0494	12.7656	2.4017
C	0.5353	0.5001	0.1801	11.7766	13.5027	1.2607
O	0.6124	0.4172	0.1954	13.4728	11.2644	1.3678
N	0.3047	0.7148	0.5838	6.7034	19.2996	4.0866
C	0.3805	0.6983	0.8049	8.371	18.8541	5.6343
C	0.3469	0.6838	0.6316	7.6318	18.4626	4.4212
C	0.3561	0.6439	0.5	7.8342	17.3853	3.5

N	0.3988	0.6012	0.5	8.7736	16.2324	3.5
C	0.4289	0.5884	0.3401	9.4358	15.8868	2.3807
C	0.4825	0.5175	0.5	10.615	13.9725	3.5
C	0.4728	0.5477	0.3431	10.4016	14.7879	2.4017
C	0.5001	0.5353	0.1801	11.0022	14.4531	1.2607
O	0.4172	0.6124	0.1954	9.1784	16.5348	1.3678
N	-0.1953	0.2852	-0.0838	-4.2966	7.7004	-0.5866
C	-0.1195	0.3017	-0.3049	-2.629	8.1459	-2.1343
C	-0.1531	0.3162	-0.1316	-3.3682	8.5374	-0.9212
C	-0.1439	0.3561	0	-3.1658	9.6147	0
N	-0.1012	0.3988	0	-2.2264	10.7676	0
C	-0.0711	0.4116	0.1599	-1.5642	11.1132	1.1193
C	-0.0175	0.4825	0	-0.385	13.0275	0
C	-0.0272	0.4523	0.1569	-0.5984	12.2121	1.0983
C	0.0001	0.4647	0.3199	0.0022	12.5469	2.2393
O	-0.0828	0.3876	0.3046	-1.8216	10.4652	2.1322
N	1.1953	-0.2148	0.5838	26.2966	-5.7996	4.0866
C	1.1195	-0.1983	0.8049	24.629	-5.3541	5.6343
C	1.1531	-0.1838	0.6316	25.3682	-4.9626	4.4212
C	1.1439	-0.1439	0.5	25.1658	-3.8853	3.5
N	1.1012	-0.1012	0.5	24.2264	-2.7324	3.5
C	1.0711	-0.0884	0.3401	23.5642	-2.3868	2.3807
C	1.0175	-0.0175	0.5	22.385	-0.4725	3.5
C	1.0272	-0.0477	0.3431	22.5984	-1.2879	2.4017
C	0.9999	-0.0353	0.1801	21.9978	-0.9531	1.2607
O	1.0828	-0.1124	0.1954	23.8216	-3.0348	1.3678
N	0.6953	0.2148	-0.0838	15.2966	5.7996	-0.5866
C	0.6195	0.1983	-0.3049	13.629	5.3541	-2.1343
C	0.6531	0.1838	-0.1316	14.3682	4.9626	-0.9212
C	0.6439	0.1439	0	14.1658	3.8853	0
N	0.6012	0.1012	0	13.2264	2.7324	0
C	0.5711	0.0884	0.1599	12.5642	2.3868	1.1193
C	0.5175	0.0175	0	11.385	0.4725	0
C	0.5272	0.0477	0.1569	11.5984	1.2879	1.0983
C	0.4999	0.0353	0.3199	10.9978	0.9531	2.2393
O	0.5828	0.1124	0.3046	12.8216	3.0348	2.1322
N	1.2148	-0.1953	0.4162	26.7256	-5.2731	2.9134
C	1.1983	-0.1195	0.1951	26.3626	-3.2265	1.3657
C	1.1838	-0.1531	0.3684	26.0436	-4.1337	2.5788
C	1.0884	-0.0711	0.6599	23.9448	-1.9197	4.6193
C	1.0477	-0.0272	0.6569	23.0494	-0.7344	4.5983

C	1.0353	0.0001	0.8199	22.7766	0.0027	5.7393
O	1.1124	-0.0828	0.8046	24.4728	-2.2356	5.6322
N	0.7148	0.1953	0.0838	15.7256	5.2731	0.5866
C	0.6983	0.1195	0.3049	15.3626	3.2265	2.1343
C	0.6838	0.1531	0.1316	15.0436	4.1337	0.9212
C	0.5884	0.0711	-0.1599	12.9448	1.9197	-1.1193
C	0.5477	0.0272	-0.1569	12.0494	0.7344	-1.0983
C	0.5353	-0.0001	-0.3199	11.7766	-0.0027	-2.2393
O	0.6124	0.0828	-0.3046	13.4728	2.2356	-2.1322
N	-0.2148	0.3047	0.0838	-4.7256	8.2269	0.5866
C	-0.1983	0.3805	0.3049	-4.3626	10.2735	2.1343
C	-0.1838	0.3469	0.1316	-4.0436	9.3663	0.9212
C	-0.0884	0.4289	-0.1599	-1.9448	11.5803	-1.1193
C	-0.0477	0.4728	-0.1569	-1.0494	12.7656	-1.0983
C	-0.0353	0.5001	-0.3199	-0.7766	13.5027	-2.2393
O	-0.1124	0.4172	-0.3046	-2.4728	11.2644	-2.1322
N	0.2852	0.6953	0.4162	6.2744	18.7731	2.9134
C	0.3017	0.6195	0.1951	6.6374	16.7265	1.3657
C	0.3162	0.6531	0.3684	6.9564	17.6337	2.5788
C	0.4116	0.5711	0.6599	9.0552	15.4197	4.6193
C	0.4523	0.5272	0.6569	9.9506	14.2344	4.5983
C	0.4647	0.4999	0.8199	10.2234	13.4973	5.7393
O	0.3876	0.5828	0.8046	8.5272	15.7356	5.6322
Zn	-0.25	0.25	0.25	-5.5	6.75	1.75
Zn	0.25	-0.25	0.25	5.5	-6.75	1.75
Zn	1.25	-0.25	0.25	27.5	-6.75	1.75
N	0.3047	0.7852	0.0838	6.7034	21.2004	0.5866
Zn	-0.25	0.25	-0.25	-5.5	6.75	-1.75
Zn	0.75	0.25	-0.25	16.5	6.75	-1.75
Zn	0.25	-0.25	-0.25	5.5	-6.75	-1.75
Zn	0.25	0.75	-0.25	5.5	20.25	-1.75
Zn	1.25	-0.25	0.75	27.5	-6.75	5.25
N	0.2852	0.8047	0.9162	6.2744	21.7269	6.4134
N	0.2148	0.6953	0.9162	4.7256	18.7731	6.4134
N	0.8047	0.2852	0.9162	17.7034	7.7004	6.4134
N	0.1953	0.7852	0.5838	4.2966	21.2004	4.0866
N	0.6953	0.2148	0.9162	15.2966	5.7996	6.4134
N	0.2148	0.8047	0.4162	4.7256	21.7269	2.9134
N	0.7852	0.3047	0.0838	17.2744	8.2269	0.5866

Table 2. Coordinates for simulated structure of Zn(NDI-H) with breathing angle θ = 90˚.

Breathing angle θ = 90 ˚

a = 24.5 Å, b = 24.5 Å, c = 7.16 Å; α = β = γ = 90˚

	Fractional Coordinates			Cartesian Coordinates		
Atom	x	y	z	x	y	z
Zn	0.75	0.25	0.25	18.42045	6.14015	1.790875
Zn	0.25	0.75	0.75	6.14015	18.42045	5.372625
Zn	0.25	0.75	0.25	6.14015	18.42045	1.790875
Zn	0.75	0.25	0.75	18.42045	6.14015	5.372625
N	0.6953	0.2852	0.4162	17.076985	7.004683	2.981449
N	0.3047	0.7148	0.5838	7.483615	17.555917	4.182051
N	0.8047	0.2148	0.4162	19.763915	5.275617	2.981449
N	0.1953	0.7852	0.5838	29.357285	-5.275617	4.182051
N	0.2148	0.6953	0.9162	5.275617	17.076985	-0.600301
N	0.7852	0.3047	0.0838	-5.275617	7.483615	0.600301
N	0.2852	0.8047	0.9162	7.004683	-4.796685	-0.600301
N	0.7148	0.1953	0.0838	17.555917	4.796685	0.600301
N	0.3047	0.7852	0.0838	7.483615	-5.275617	0.600301
N	0.6953	0.2148	0.9162	17.076985	5.275617	-0.600301
N	0.1953	0.7148	0.0838	4.796685	17.555917	0.600301
N	0.8047	0.2852	0.9162	-4.796685	7.004683	-0.600301
N	0.7852	0.1953	0.5838	19.284983	4.796685	4.182051
N	0.2148	0.8047	0.4162	29.836217	-4.796685	2.981449
N	0.7148	0.3047	0.5838	17.555917	7.483615	4.182051
N	0.2852	0.6953	0.4162	7.004683	17.076985	2.981449
C	0.6195	0.3017	0.1951	15.215292	7.409933	1.397599
C	0.3805	0.6983	0.8049	9.345308	17.150667	5.765901
C	0.8805	0.1983	0.1951	21.625608	4.870367	1.397599
C	0.1195	0.8017	0.8049	27.495592	-4.870367	5.765901
C	0.1983	0.6195	0.6951	4.870367	15.215292	-2.184151
C	0.8017	0.3805	0.3049	-4.870367	9.345308	2.184151
C	0.3017	0.8805	0.6951	7.409933	-2.934992	-2.184151
C	0.6983	0.1195	0.3049	17.150667	2.934992	2.184151
C	0.3805	0.8017	0.3049	9.345308	-4.870367	2.184151
C	0.6195	0.1983	0.6951	15.215292	4.870367	-2.184151
C	0.1195	0.6983	0.3049	2.934992	17.150667	2.184151
C	0.8805	0.3017	0.6951	-2.934992	7.409933	-2.184151

C	0.8017	0.1195	0.8049	19.690233	2.934992	5.765901
C	0.1983	0.8805	0.1951	29.430967	-2.934992	1.397599
C	0.6983	0.3805	0.8049	17.150667	9.345308	5.765901
C	0.3017	0.6195	0.1951	7.409933	15.215292	1.397599
C	0.6531	0.3162	0.3684	16.040528	7.766062	2.639033
C	0.3469	0.6838	0.6316	8.520072	16.794538	4.524467
C	0.8469	0.1838	0.3684	20.800372	4.514238	2.639033
C	0.1531	0.8162	0.6316	28.320828	-4.514238	4.524467
C	0.1838	0.6531	0.8684	4.514238	16.040528	-0.942717
C	0.8162	0.3469	0.1316	-4.514238	8.520072	0.942717
C	0.3162	0.8469	0.8684	7.766062	-3.760228	-0.942717
C	0.6838	0.1531	0.1316	16.794538	3.760228	0.942717
C	0.3469	0.8162	0.1316	8.520072	-4.514238	0.942717
C	0.6531	0.1838	0.8684	16.040528	4.514238	-0.942717
C	0.1531	0.6838	0.1316	3.760228	16.794538	0.942717
C	0.8469	0.3162	0.8684	-3.760228	7.766062	-0.942717
C	0.8162	0.1531	0.6316	20.046362	3.760228	4.524467
C	0.1838	0.8469	0.3684	29.074838	-3.760228	2.639033
C	0.6838	0.3469	0.6316	16.794538	8.520072	4.524467
C	0.3162	0.6531	0.3684	7.766062	16.040528	2.639033
C	0.6439	0.3561	0.5	15.81457	8.74603	3.58175
C	0.3561	0.6439	0.5	8.74603	15.81457	3.58175
C	0.8561	0.1439	0.5	21.02633	3.53427	3.58175
C	0.1439	0.8561	0.5	28.09487	-3.53427	3.58175
C	0.1439	0.6439	0	3.53427	15.81457	0
C	0.8561	0.3561	0	-3.53427	8.74603	0
C	0.3561	0.8561	0	8.74603	-3.53427	0
C	0.6439	0.1439	0	15.81457	3.53427	0
N	0.6012	0.3988	0.5	14.765833	9.794767	3.58175
N	0.3988	0.6012	0.5	9.794767	14.765833	3.58175
N	0.8988	0.1012	0.5	22.075067	2.485533	3.58175
N	0.1012	0.8988	0.5	27.046133	-2.485533	3.58175
N	0.1012	0.6012	0	2.485533	14.765833	0
N	0.8988	0.3988	0	-2.485533	9.794767	0
N	0.3988	0.8988	0	9.794767	-2.485533	0
N	0.6012	0.1012	0	14.765833	2.485533	0
C	0.5711	0.4116	0.6599	14.026559	10.109143	4.727194
C	0.4289	0.5884	0.3401	10.534041	14.451457	2.436306
C	0.9289	0.0884	0.6599	22.814341	2.171157	4.727194
C	0.0711	0.9116	0.3401	26.306859	-2.171157	2.436306
C	0.0884	0.5711	0.1599	2.171157	14.026559	1.145444

C	0.9116	0.4289	0.8401	-2.171157	10.534041	-1.145444
C	0.4116	0.9289	0.1599	10.109143	-1.746259	1.145444
C	0.5884	0.0711	0.8401	14.451457	1.746259	-1.145444
C	0.4289	0.9116	0.8401	10.534041	-2.171157	-1.145444
C	0.5711	0.0884	0.1599	14.026559	2.171157	1.145444
C	0.0711	0.5884	0.8401	1.746259	14.451457	-1.145444
C	0.9289	0.4116	0.1599	-1.746259	10.109143	1.145444
C	0.9116	0.0711	0.3401	22.389443	1.746259	2.436306
C	0.0884	0.9289	0.6599	26.731757	-1.746259	4.727194
C	0.5884	0.4289	0.3401	14.451457	10.534041	2.436306
C	0.4116	0.5711	0.6599	10.109143	14.026559	4.727194
C	0.5175	0.4825	0.5	12.71011	11.85049	3.58175
C	0.4825	0.5175	0.5	11.85049	12.71011	3.58175
C	0.9825	0.0175	0.5	24.13079	0.429811	3.58175
C	0.0175	0.9825	0.5	24.990411	-0.42981	3.58175
C	0.0175	0.5175	0	0.429811	12.71011	0
C	0.9825	0.4825	0	-0.42981	11.85049	0
C	0.4825	0.9825	0	11.85049	-0.42981	0
C	0.5175	0.0175	0	12.71011	0.429811	0
C	0.5272	0.4523	0.6569	12.948348	11.108759	4.705703
C	0.4728	0.5477	0.3431	11.612252	13.451841	2.457797
C	0.9728	0.0477	0.6569	23.892552	1.171541	4.705703
C	0.0272	0.9523	0.3431	25.228648	-1.171541	2.457797
C	0.0477	0.5272	0.1569	1.171541	12.948348	1.123953
C	0.9523	0.4728	0.8431	-1.171541	11.612252	-1.123953
C	0.4523	0.9728	0.1569	11.108759	-0.668048	1.123953
C	0.5477	0.0272	0.8431	13.451841	0.668048	-1.123953
C	0.4728	0.9523	0.8431	11.612252	-1.171541	-1.123953
C	0.5272	0.0477	0.1569	12.948348	1.171541	1.123953
C	0.0272	0.5477	0.8431	0.668048	13.451841	-1.123953
C	0.9728	0.4523	0.1569	-0.668048	11.108759	1.123953
C	0.9523	0.0272	0.3431	23.389059	0.668048	2.457797
C	0.0477	0.9728	0.6569	25.732141	-0.668048	4.705703
C	0.5477	0.4728	0.3431	13.451841	11.612252	2.457797
C	0.4523	0.5272	0.6569	11.108759	12.948348	4.705703
C	0.4999	0.4647	0.8199	12.277844	11.413311	5.873354
C	0.5001	0.5353	0.1801	12.282756	13.147289	1.290146
C	0.0001	0.0353	0.8199	24.563056	0.866989	5.873354
C	0.9999	0.9647	0.1801	24.558144	-0.866989	1.290146
C	0.0353	0.4999	0.3199	0.866989	12.277844	2.291604
C	0.9647	0.5001	0.6801	-0.866989	12.282756	-2.291604

C	0.4647	0.0001	0.3199	11.413311	0.002456	2.291604
C	0.5353	0.9999	0.6801	13.147289	-0.002456	-2.291604
C	0.5001	0.9647	0.6801	12.282756	-0.866989	-2.291604
C	0.4999	0.0353	0.3199	12.277844	0.866989	2.291604
C	0.9999	0.5353	0.6801	-0.002456	13.147289	-2.291604
C	0.0001	0.4647	0.3199	0.002456	11.413311	2.291604
C	0.9647	0.9999	0.1801	23.693611	-0.002456	1.290146
C	0.0353	0.0001	0.8199	25.427589	0.002456	5.873354
C	0.5353	0.5001	0.1801	13.147289	12.282756	1.290146
C	0.4647	0.4999	0.8199	11.413311	12.277844	5.873354
O	0.5828	0.3876	0.8046	14.313918	9.519689	5.763752
O	0.4172	0.6124	0.1954	10.246682	15.040911	1.399748
O	0.9172	0.1124	0.8046	22.526982	2.760611	5.763752
O	0.0828	0.8876	0.1954	26.594218	-2.760611	1.399748
O	0.1124	0.5828	0.3046	2.760611	14.313918	2.182002
O	0.8876	0.4172	0.6954	-2.760611	10.246682	-2.182002
O	0.3876	0.9172	0.3046	9.519689	-2.033618	2.182002
O	0.6124	0.0828	0.6954	15.040911	2.033618	-2.182002
O	0.4172	0.8876	0.6954	10.246682	-2.760611	-2.182002
O	0.5828	0.1124	0.3046	14.313918	2.760611	2.182002
O	0.0828	0.6124	0.6954	2.033618	15.040911	-2.182002
O	0.9172	0.3876	0.3046	-2.033618	9.519689	2.182002
O	0.8876	0.0828	0.1954	21.799989	2.033618	1.399748
O	0.1124	0.9172	0.8046	27.321211	-2.033618	5.763752
O	0.6124	0.4172	0.1954	15.040911	10.246682	1.399748
O	0.3876	0.5828	0.8046	9.519689	14.313918	5.763752