

Loop-containing One-dimensional Metal-Organic Frameworks from Flexible Betaine Linkers and Zinc Salts by Controlled Synthesis

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Three new metal-organic frameworks based on Zn^{2+} and 1,4-diazoniabicyclo[2.2.2]octane-1,4-diacetate (**L**) were synthesized and fully characterized by single-crystal X-ray diffraction and other methods. The linker **L** provides both positively charged quaternary ammonium centers and a flexible methylene chain, which brings conformational diversity to the system. The same reactants, and the same preparation procedures were used for the syntheses of $ZnLCl_2$ (**1**), $ZnL_2(NO_3)(OH)\cdot(DMF)\cdot(H_2O)$ (**2**) and $ZnL_3(NO_3)_2(H_2O)$ (**3**), to study the role of solvents and anions during the synthesis. All three MOFs show one-dimensional networks with different topologies. Closed loops with different ring sizes could be found in **2** and **3** along the chain. Rings with 22 atoms were found in **2**, while the smallest loop in **3** contains 44 atoms, including four linkers and four zinc atoms. Clearly, the solvent, stoichiometries of the reactants, and the anions had an impact on the formation of the three distinct network structures.

Key words: Metal-Organic Frameworks, Loop Motif, Solvothermal Synthesis, Double Betaine, Solvent Effects

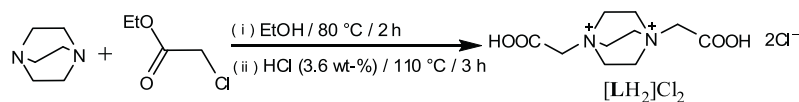
Introduction

Metal-organic frameworks (MOFs) [1–4] are crystalline materials constructed from organic and inorganic building units [1, 5]. Rigid organic linkers tend to form robust frameworks with high symmetries [6, 7], while the MOF structures from flexible linkers show more structural diversity [8–19], partially because of conformational variations of the ligands. Solvents play a big role in the syntheses [8, 20–24] affecting the resulting framework structure. In addition, counterions can compete with the linkers and coordinate to the metal centers [25]. Derivatives of betaines [26–31] could be an ideal ligand model to study the relationship between solvents, counter ions, and linker conformation in MOF synthesis since they provide both positively charged quaternary ammonium centers and flexible chains of methylene groups. In this study, we synthesized a double betaine (1,4-diazoniabicyclo[2.2.2]octane-1,4-diacetate) equipped with carboxylic acid groups at both ends as

the organic linkers for MOF synthesis [26, 32–39]. Three new MOF structures, **1**, **2**, and **3**, were constructed from this linker, together with Zn ions. The reaction conditions were carefully controlled to study the role of solvents, stoichiometry, and anions in this system. Three different modes of topology were shown to form chains and ladders [40]. Despite the one-dimensional nature of the structures, closed loops [41–43] with different ring sizes could be found in **2** and **3**. The conformations of the flexible ligand in the three MOFs were affected by the solvent in the system, and the dimensions of the resulting networks were also influenced by the interactions between anions and metal cations.

Experimental Section

All purchased chemicals were used without further purifications. IR spectra were recorded on an IR Prestige-21 spectrophotometer from KBr pellets between 4000 and 450 cm^{-1} . Thermal analysis (TG) was carried out under N_2

Scheme 1. Synthetic route to $[\text{LH}_2]\text{Cl}_2$.

atmosphere using a TA Q600 analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker AXS D8 Advance diffractometer operated with 1600 W power (40 kV, 40 mA) using $\text{CuK}\alpha_1$ radiation. Simulated PXRD patterns were calculated from the corresponding single-crystal structural data using MERCURY 3.0.

Ligand synthesis

The salt $[\text{LH}_2]\text{Cl}_2$ (Scheme 1) was prepared according to the literature [37]. 1,4-Diazabicyclo[2.2.2]octane (2.26 g, 20.2 mmol) and ethyl chloroacetate (6.0 mL, 69.4 mmol) were added to EtOH (30.0 mL) in a 100 mL round-bottom flask. The mixture was stirred for 2 h at 80 °C. After cooling to room temperature, the solvent was removed *in vacuo* to afford a colorless powder. HCl (20 mL, 3.6 wt-%) was added to the powder, and the mixture was stirred for 3 h at 110 °C. After solvent removal, the product was further dried at 100 °C in an isothermal oven for 12 h, followed by recrystallization from water to afford the product.

Synthesis of **1**, **2** and **3**

ZnLCl_2 (**1**)

$[\text{LH}_2]\text{Cl}_2$ (10.5 mg, 0.035 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50.0 mg, 0.17 mmol) were mixed with *N,N*-diethylformamide (DEF, 0.8 mL), EtOH (0.8 mL), and H_2O (0.4 mL) in a 5-mL vial. After being sonicated for 10 min. at r. t., the vial was capped and placed in an isothermal oven at 85 °C for 24 h. The vial was then removed from the oven and allowed to cool to room temperature naturally. Colorless block-shaped crystals were collected. Yield: 53% based on $[\text{LH}_2]\text{Cl}_2$. – Analysis: calcd. N 7.41, C 32.77, H 4.55; found N 7.68, C 32.92, H 4.39. – IR data (KBr): $\nu = 3436(\text{w})$, 2992(w), 2359(w), 1669(vs), 1456(w), 1378(s), 1352(w), 1346(w), 1287(s), 1127(w), 843(m), 695(w), 468(w) cm^{-1} . Compound **1** can be obtained when the molar ratio of $[\text{LH}_2]\text{Cl}_2$ to $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was between 1 : 4 and 1 : 7.

$\text{ZnL}_2(\text{NO}_3)(\text{OH}) \cdot (\text{DMF}) \cdot (\text{H}_2\text{O})$ (**2**)

$[\text{LH}_2]\text{Cl}_2$ (5.0 mg, 0.017 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (200.5 mg, 0.67 mmol) were mixed with *N,N*-dimethylformamide (DMF, 2.0 mL) in a 5-mL vial. The same procedure as that used to prepare **1** was followed

afterwards. The vial was sonicated very briefly (about 1 second) to make the crystals disconnected from the wall before they were collected and rinsed with fresh DMF. Yield: 88% based on $[\text{LH}_2]\text{Cl}_2$. – Analysis: calcd. N 11.19, C 39.25, H 5.09; found N 11.23, C 39.64, H 5.18. – IR data (KBr): $\nu = 3438(\text{s})$, 3031(w), 1642(s), 1467(w), 1384(vs), 1288(w), 1126(w), 872(w), 698(w) cm^{-1} . The amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ can be reduced to as low as 50.0 mg, and complex **2** is still obtained, albeit with lower yields.

$\text{ZnL}_3(\text{NO}_3)_2(\text{H}_2\text{O})$ (**3**)

The same solid mixture and reaction procedure as for **2** were used in the synthesis of **3**, and DEF (2 mL) was added to the mixture as the solvent instead. Colorless block-shaped crystals were collected after sonication and rinsed with fresh DMF. Yield: 46% based on $[\text{LH}_2]\text{Cl}_2$. – Analysis: calcd. N 12.22, C 31.43, H 4.36; found N 12.38, C 31.12, H 4.37. – IR data (KBr): $\nu = 3444(\text{m})$, 3035(s), 2364(w), 1654(s), 1476(w), 1380(vs), 1279(w), 1132(w), 871(w), 848(w), 704(w) cm^{-1} .

Crystal structure determinations

Crystals of **1**, **2** and **3** coated with Paratone oil on a cryo-loop pin were mounted on a Bruker SMART Apex (II) single-crystal X-ray diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 [44] system of programs. For structure determination of **2**, the disordered solvents were refined using restraints. Details are contained in the corresponding CIF file. A summary of the crystal data and numbers pertinent to data collection and structure refinement is given in Table 1.

CCDC 913382–913384 contain the crystallographic data for these structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Syntheses

The ligand precursor $[\text{LH}_2]\text{Cl}_2$ served as source of the di-topic linker in the construction of three metal-

	1	2	3
Formula	C ₁₀ H ₁₆ Cl ₂ N ₂ O ₄ Zn	C ₄₅ H ₇₀ N ₁₁ O ₃₀ Zn ₂	C ₃₀ H ₅₀ N ₁₀ O ₂₉ Zn ₂
<i>M_r</i>	364.52	1375.86	1145.54
Crystal size, mm ³	0.46 × 0.385 × 0.32	0.20 × 0.15 × 0.12	0.25 × 0.15 × 0.10
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	7.089(3)	17.160(7)	15.533(2)
<i>b</i> , Å	10.267(4)	15.030(6)	15.439(2)
<i>c</i> , Å	18.145(7)	12.796(5)	19.361(3)
β, deg	90.00	105.274(4)	107.353(2)
<i>V</i> , Å ³	1320.7(9)	3184(2)	4431.8(11)
<i>Z</i>	4	2	4
<i>D</i> _{calcd.} , g cm ⁻³	1.83	1.44	1.72
μ (MoKα), mm ⁻¹	2.3	0.8	1.2
<i>F</i> (000), e	744	1434	2368
<i>hkl</i> range	-8 ≤ <i>h</i> ≤ 8 -12 ≤ <i>k</i> ≤ 6 -20 ≤ <i>l</i> ≤ 21	-18 ≤ <i>h</i> ≤ 20 -17 ≤ <i>k</i> ≤ 14 -14 ≤ <i>l</i> ≤ 15	-18 ≤ <i>h</i> ≤ 18 -18 ≤ <i>k</i> ≤ 18 -22 ≤ <i>l</i> ≤ 16
((sin θ)/λ) _{max} , Å ⁻¹	0.6022	0.5948	0.5948
Refl. total / unique / <i>R</i> _{int}	6481 / 2410 / 0.092	7487 / 2773 / 0.024	20643 / 7761 / 0.042
Param. refined	172	247	639
<i>R</i> (<i>F</i>) / <i>wR</i> (<i>F</i> ²) (all data)	0.0618 / 0.0742	0.0781 / 0.2469	0.0651 / 0.1438
<i>x</i> (Flack)	-0.01(2)	–	–
GoF (<i>F</i> ²)	0.790	1.058	1.036
Δρ _{fin} (max / min), e Å ⁻³	0.40 / -0.40	0.62 / -0.44	1.17 / -0.80

Table 1. Crystal structure data for **1–3**.

organic frameworks. Together with small ions, such as Cl⁻ and NO₃⁻, three new one-dimensional structures were obtained.

The stoichiometry proved to be a crucial factor in the synthesis of the three complexes. We put in substantial effort to study the role of reactant ratios for these reactions. Complex **1** can be obtained if the molar ratio of [LH₂]Cl₂ and Zn(NO₃)₂·6H₂O was within the range of 1 : 4 and 1 : 7. Complex **2** can be obtained in a wider stoichiometry range, with the molar ratio of ligand and metal ion as low as 1 : 4 and as high as 1 : 40. Complex **3**, being the most difficult one to synthesize, could only be synthesized when excess Zn(NO₃)₂·6H₂O was used. The stoichiometry of the reactants differs by a factor of 10 compared to **1**. We suspect that the excess amount of Zn(NO₃)₂·6H₂O changes not only the concentration of the reactants, but also the system properties, such as the acidity, making the condition suitable for single-crystal growth of complex **3**.

Crystal and molecular structures

In the molecular structure of **1** (Fig. 1a), the zinc ion is tetrahedrally coordinated to two oxygen atoms from carboxylate groups of two **L**. The other two positions are occupied by two chloride ions originating from the

[LH₂]Cl₂ salt. A zig-zag chain is constructed along the crystallographic *c* axis, with a distance between two zinc atoms near 13.3 Å along the chain. The angle defined by three neighboring zinc atoms (Figs. 1b, 2a) in the chain is 86.3°, which is smaller than the ideal tetrahedral angle (109.47°). This can be explained by two types of groups coordinating to the same Zn²⁺, and the bent carboxylate linker.

By using a different solvent, we obtained compound **2** (Fig. 1c), in which four oxygen atoms from four linkers **L** connect to one Zn²⁺. This cationic framework is charge-balanced by NO₃⁻ and OH⁻ in cavities. The relatively empty space in the structure also allows solvent DMF co-crystallization in the network. Interestingly, due to the different conformations of the flexible -CH₂COO groups, two linkers connect two Zn²⁺ as a pair, forming a small loop (Fig. 1d). These loops are further assembled into a one-dimensional network by sharing Zn atoms. The smallest macrocycle contains 22 atoms (two Zn, four O, four N, and twelve C). The ligands are much more bent than in the structure of **1**, resulting in a distance between the two neighboring zinc atoms of only 10.3 Å along the chain. Two methylene groups in the linker **L** allow it to be accommodated in different conformations, depending on the conditions. In the structure of **2**, two planes defined by two N-CH₂-C groups are almost coplanar, with CH₂-

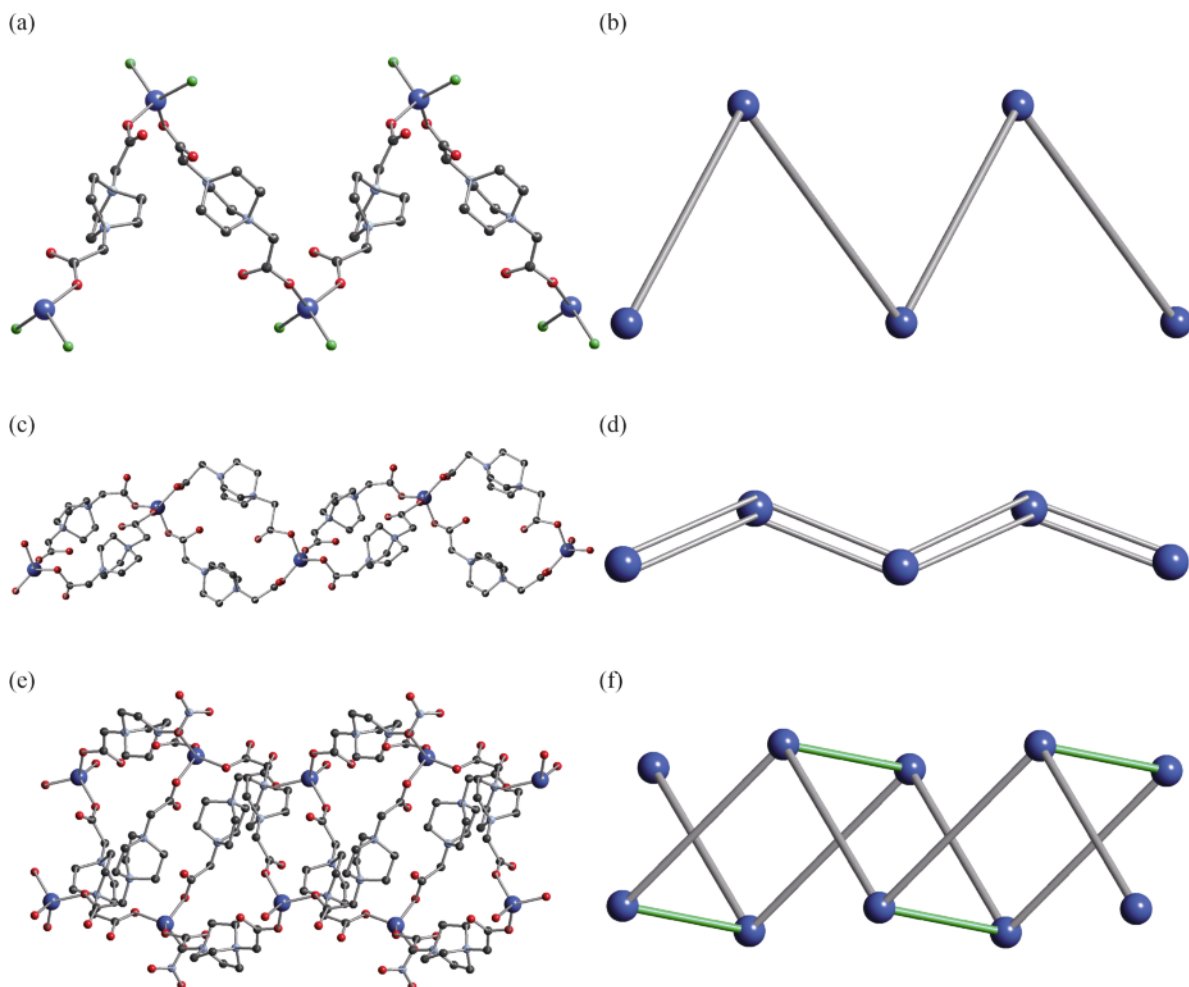


Fig. 1 (color online). One-dimensional structures of **1** (a), **2** (c), and **3** (e), and the corresponding connectivity scheme (b, d, and f) by replacing linkers with rods. Free solvent molecules and anions were omitted for clarity. Color Scheme: Zn, blue; O, red; C, black; Cl, green.

C bonds in *cis*-conformation (Fig. 2b). This observation is in agreement with the shorter Zn–Zn distance compared to that in the structure of **1**.

The simple conformational change of **L** in the network due to different solvent interactions has intrigued us to explore the role of the solvent in the MOF synthesis. By simply replacing DMF with DEF, a new structure, here termed **3** (Fig. 1e), was obtained. Two zinc atoms exist in the asymmetric unit, with each zinc atom coordinating to three carboxylate units from three **L**. The fourth positions are occupied by one oxygen atom from either NO_3^- or H_2O . Zig-zag chains, comprised of zinc atoms and two series of linkers connect-

ing them, can be observed, an assembly similar to the one observed in the structure of **1**. A third dicarboxylate linker (highlighted in green in Fig. 1f) connects two neighboring zig-zag chains, forming a ladder-type structure. Each square loop (Fig. 2c) is formed by four zinc atoms and four linkers, and has an average edge length of 11.8 Å. The smallest closed ring along the loop has 44 atoms.

PXRD, thermal stability studies and IR spectra

PXRD is an important tool to differentiate structures obtained from the same reactants, and determine the

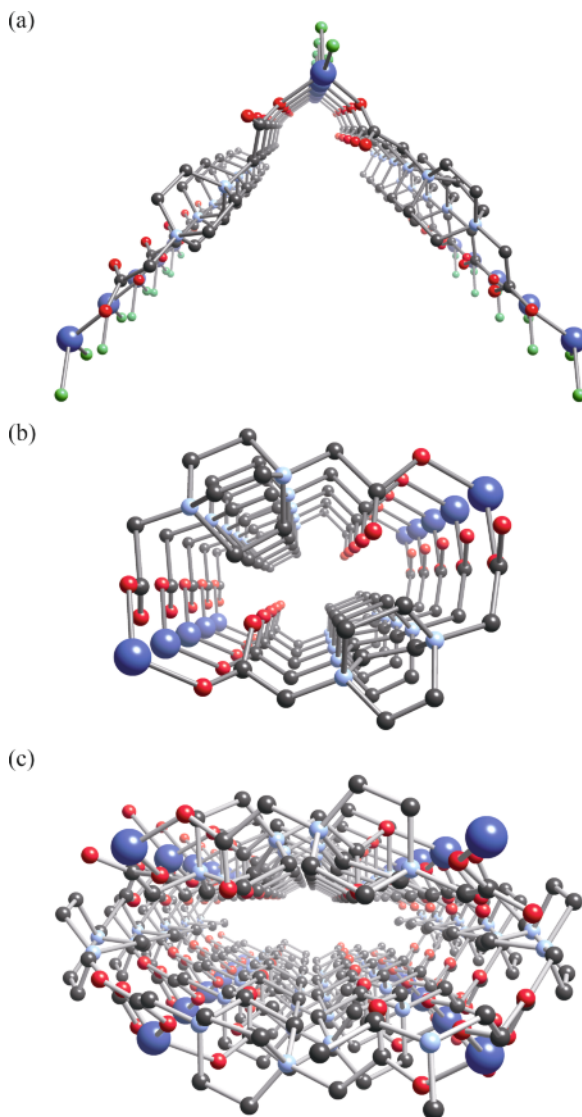


Fig. 2 (color online). Packing mode in the structures of **1** (a), **2** (b), and **3** (c). Loops with 22 atoms and 44 atoms are shown for **2** and **3**.

bulk purity of these materials. As shown in Figs. 3a–c, the PXRD of the three MOFs obtained from various solvents (DMF, DEF, and co-solvents) were completely distinct in terms of diffraction peak positions. Furthermore, the peak positions of the PXRD patterns of the bulk material **1**, **2**, and **3** match fairly well the simulated pattern generated from their single-crystal structures. The differences may be caused by the fact that some of the samples were not finely ground due to experimental difficulties.

The thermal stability of the three MOFs was evaluated by TG analysis (Fig. 3d). For **2** and **3**, clear weight losses at 250 °C were observed. However, the weight-loss pattern for **1** revealed that this MOF is decomposed at approximately 400 °C. Due to the formation of loops in **2** and **3**, the linker is more constrained, and far away from the most stable conformation, thus affecting the thermal stability of these two MOFs.

In the IR spectrum of compound **1**, the bands at 2992, 1669, and 1378 cm^{-1} are assigned to $\nu(-\text{CH}_2-)$, $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$, respectively. In the spectra of compounds **2** and **3**, the bands of $\nu(-\text{CH}_2-)$, $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ also appear. Nitrates commonly show asymmetrical stretching with a strong absorption in the 1660–1625 cm^{-1} region; the symmetrical vibration absorbs strongly near 1300–1255 cm^{-1} . However, in compounds **2** and **3**, these values overlap with $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ bands. The $\Delta\nu$ values ($\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) of **1**, **2** and **3** are 291, 258 and 274 cm^{-1} , respectively. These values suggest a unidentate coordination mode of the carboxylate groups of the ligand [45], in accordance with that determined from the single crystal data.

Conclusion

We have described the synthesis of three new structures using a double betaine and a zinc ion as building units. The zinc atoms are coordinated to the dicarboxylates of a double betaine; terminal anions were introduced to compensate the positively charged quaternary ammonium centers. In structure **1**, no loop was found along the zig-zag chain, while in structures of **2** and **3**, minimum loops with 22 and 44 atoms were observed, respectively.

In the syntheses of the three structures, in addition to the substantial differences in the stoichiometries of the reactants as described above, the effect of the differences in the solvents should be noted. Commonly used solvents for MOF synthesis, such as DMF and DEF, not only play a role as media making the reaction mixtures more homogeneous, but their decomposition under heating may also provide trace amounts of amine that facilitate the deprotonation of the carboxylic acids [46–50]. Mixed solvents, such as DEF-H₂O-EtOH, allow the reactions in a much more complicated system, with solvent-solid, solute-solvent, solvent-solvent interactions [51–55]. This makes the preparation of new structures possi-

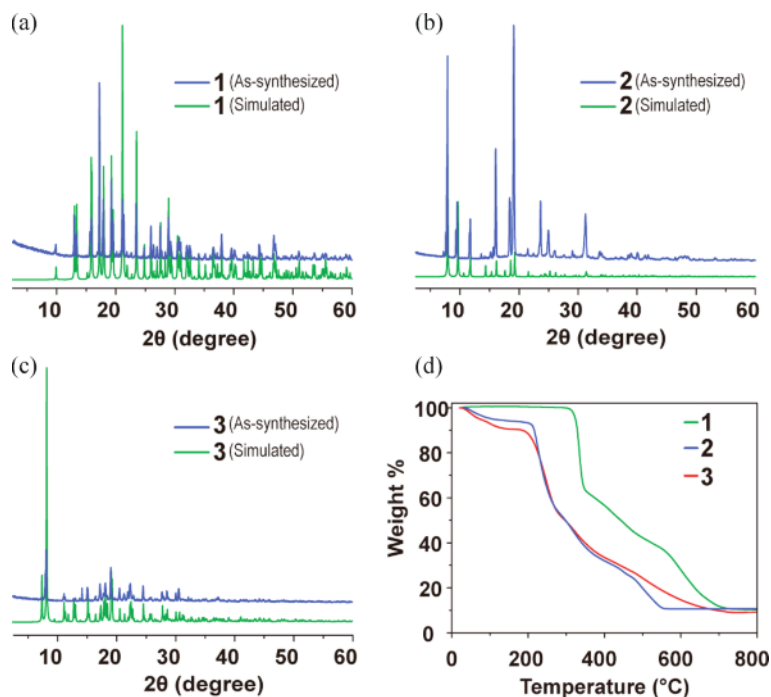


Fig. 3 (color online). Characterization of three MOFs. Both the experimental and simulated data of PXRD are shown for **1** (a), **2** (b), and **3** (c). TG analyses of the three MOFs are shown in (d).

ble that cannot be obtained in a single solvent system. The three different structures reported here clearly demonstrate the role of different solvents in MOF synthesis.

The different structures also demonstrate the role of the anions in MOF synthesis. The ligand was introduced in the quaternary ammonium chloride form. The anion Cl^- , together with NO_3^- from the metal salt, may either coordinate to the metal atom in the MOFs, or simply stay in the cavities to balance the charge of

the cationic framework. In **1**, two chlorine atoms are bonded to each zinc atom, making the one-dimensional chain neutral. However, in both **2** and **3**, anions were found in the cavities to compensate the cationic nature of the main framework.

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