How Structure-Directing Cations Tune the Fluorescence of Metal–Organic Frameworks

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Carlos Ordonez,† Marina Fonar,†,§ Jennifer Lindline,‡ Qiang Wei,*† and Tatiana Timofeeva*†

†Department of Biology and Chemistry and ‡Department of Natural Resources Management, New Mexico Highlands University, Las Vegas, New Mexico 87701, United States
§Institute of Applied Physics Academy of Sciences of Moldova, Academy str., 5 MD2028, Chisinau, Moldova

Supporting Information

ABSTRACT: A series of metal-organic frameworks (MOFs), [Zn-BTC]{cations}, which contain anionic Zn-BTC coordination polymers, is reported here. It was observed that cations with different hydrogen-bond forming abilities could significantly affect the coordination of Zn-BTC structures in the frameworks. The 13 Zn-BTC MOFs reported herein showed solid-state fluorescent emission in the visible spectrum, and the fluorescence of the frameworks was tunable by adjusting the interactions of the cations with the anionic Zn-BTC structure in the MOFs.

INTRODUCTION

Synthesizing and controlling the functionality of highly structurally engineered materials are always a fascinating target in both the industrial side of applications and the academic side of research.† Metal–organic frameworks (MOFs) are among such structurally engineered materials that possess a wide array of potential and realized applications, including drug delivery, gas storage, light emitting materials, chemical separation, and as light emitting and semiconductor materials.‡ During the past two decades, scientists have not only synthesized thousands of MOFs with highly accessible porous structures but also learned how to predict and control the topology of the frameworks§ and their resultant functionality.†−ª MOFs with luminescent functionality have attracted much effort in materials chemistry aimed toward applications in light-emitting and display devices, sensors for environmental or physical stimulations, and biomedical engineering.‡ MOFs with tunable fluorescenceª have attracted great interest in the research field due to their multiple applications and facile tenability. We report a study of a series of anionic MOFs with tunable fluorescence controlled by the included counterions. MOFs with anionic frameworks were constructed from Zn(II) with 1,3,5-benzenetricarboxylate (BTC) organic anions. We examined the influence of various counterions such as NH4+, MeNH3+, Me2NH2+, Et3NH+, and n-Bu4N+ to observe the structural changes of the anionic Zn-BTC connectivity within the frameworks and the fluorescence of the corresponding MOFs. For instance, utilization of the NH4+ cation resulted in a one-dimensional layer of Zn-BTC in the crystal. Cations such as Me4NH2+, Et4NH+, and n-Bu4N+, which have two or less hydrogen bonding sites, can generate three-dimensional framework structures. Correspondingly, the MOF incorporating NH4+ as the counterion emitted light in the violet region of the visible spectrum, while incorporating n-Bu4N+ as the counterion shifted the resulting emitted light wavelength to the blue region. Furthermore, frameworks with 1-butyl-3-methylimidazolium (BMIM) cations can emit light in the green region. Our study developed an understanding of the MOFs’ structure–property relationship in fluorescent tenability, where the key criteria are the differences in interactions (electrostatic and/or hydrogen bonding) between the cations with an anionic Zn-BTC backbone in their framework. All compounds utilized in this study are shown in Scheme 1.

EXPERIMENTAL SECTION

Materials and Measurements. All of the solvents and reagents for synthesis were commercially available and used as received. Powder X-ray diffraction (PXRD) spectra were recorded on a GBC Mini Materials Analyzer powder X-ray diffractometer operating at 35 kV and 30 mA using Cu Kα radiation (λ = 1.5418 Å). The 2θ angles were recorded from 5° to 40°. Solid-state fluorescence spectra were performed on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp light source at ambient temperature.

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Synthesis

Method 1: Decomposition of Formamides.

A mixture of Zn(NO$_3$)$_2$·6H$_2$O (1.5 g, 5.1 mmol), 1,3,5-benzenetricarboxylic acid, H$_3$BTC (1.05 g, 5.0 mmol), and dimethylformamide (50 mL) was dissolved in a beaker. The solution was transferred to a 125 mL Teflon-lined acid digestion vessel. The vessel was placed in an oven set at 150 °C for 3 days. After 3 days the oven was turned off, and the acid digestion vessel was allowed to cool slowly overnight. The crystals were collected, washed with fresh dimethylformamide, and sonicated for 2 min to remove any remaining unreacted starting materials. Washing and sonication were performed twice to ensure the purity of

Table 1. Summary of Reaction Conditions for Method 1

<table>
<thead>
<tr>
<th>cation</th>
<th>Zn(NO$_3$)$_2$·6H$_2$O (g, mmol)</th>
<th>H$_3$BTC (g, mmol)</th>
<th>formamide 1 (mL)</th>
<th>solvent 2 (mL)</th>
<th>yield (%)</th>
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<td>NH$_4^+$</td>
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<td>ethanol, 5</td>
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<td>MeNH$_3^+$</td>
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<td>1.05, 5.0</td>
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<tr>
<td>Me$_2$NH$_2^+$</td>
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<td>1.05, 5.0</td>
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<td>ethanol, 5</td>
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<tr>
<td>Et$_2$NH$_2^+$</td>
<td>0.3, 1.0</td>
<td>0.21, 1.0</td>
<td>N,N-diethylformamide, 5</td>
<td>ethanol, 5</td>
<td>57</td>
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<tr>
<td>n-Bu$_2$NH$_2^+$</td>
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<td>0.105, 0.5</td>
<td>N,N-dibutylformamide, 5</td>
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Table 2. Summary of Reaction Conditions for Method 2

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<th>Zn(NO$_3$)$_2$·6H$_2$O (g, mmol)</th>
<th>H$_3$BTC (g, mmol)</th>
<th>base (g, mmol)</th>
<th>solvent (mL)</th>
<th>yield (%)</th>
</tr>
</thead>
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<td>n-Bu$_2$NH$_2^+$</td>
<td>0.343, 1.15</td>
<td>0.244, 1.16</td>
<td>dibutylamine 0.142, 1.10</td>
<td>NMP, 10</td>
<td>11</td>
</tr>
<tr>
<td>Et$_3$NH$^+$</td>
<td>1.5, 5.1</td>
<td>1.05, 5.0</td>
<td>triethylamine 25 mL</td>
<td>ethanol, 25</td>
<td>35</td>
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<tr>
<td>imidazole</td>
<td>0.05, 0.5</td>
<td>0.105, 0.5</td>
<td>imidazole 0.034, 0.5</td>
<td>NMP, 15</td>
<td>10</td>
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<tr>
<td>imidazole</td>
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<td>imidazole 0.34, 5</td>
<td>NMP, 50</td>
<td>26</td>
</tr>
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</table>
the sample. The resulting crystals were plate shaped and clear (% yield = 77%). The conditions of synthesis of the MOFs by method 1 are listed in Table 1.

Method 2: Addition of Base. A mixture of Zn(NO₃)₂·6H₂O (0.343 g, 1.15 mmol), H₂BTC (0.244g, 1.16 mmol), dibutylamine base (0.142 g, 1.10 mmol), and N-methylpyrrolidone (NMP, 10 mL) was prepared in a capped vial. The solution was transferred to a 23 mL Teflon-lined acid digestion vessel and placed in the oven at 150 °C for 4 days. The produced crystals were collected in a vial, washed with fresh NMP, and sonicated to remove impurities from the crystals. The resulting crystals were plate shaped and yellow (% yield = 11%). The conditions of synthesis of the MOFs by method 2 are listed in Table 2.

Method 3: Direct Addition of Cations. A mixture of Zn(NO₃)₂·6H₂O (3.61 g, 12.1 mmol), H₂BTC (2.55 g, 12.1 mmol), tetrabutylammonium nitrate (3.70 g, 12.2 mmol), and NMP (50 mL) was dissolved in a beaker. The solution was sonicated, placed in a 125 mL Teflon-lined acid digestion vessel, and heated for 3 days at 150 °C. The resulting crystals were large, plate-shaped, yellow crystals (% yield = 21%). The amount of compounds used for the synthesis of each MOF, the solvents used, and the yields obtained are outlined in Table 3.

X-ray Crystallography. Single crystals of each compound were selected using a cross-polarized light microscope. Each crystal data set was collected by a Bruker APEX-II CCD diffractometer using the SHELXTL program package. The function minimized was Σ[w(|F|² - |F|=)|²] with reflection weights w = 1 = [σ²] F|=² + (gP)² + (gP)² where P = [max |F|=² + 2|F|=²]/3. Crystallographic data for all of the compounds reported in the study are displayed in Table 4.

### RESULTS AND DISCUSSION

**Introduction of Cations in the Synthesis.** Anionic MOFs with cations residing in the voids of the frameworks are relatively rare as compared to neutral or cationic MOFs. The reaction of divalent metal ions, such as Zn²⁺, with trivalent BTC ligands is one of the easiest ways to form anionic frameworks where counterions reside in the void spaces. In this study, Zn(NO₃)₂·6H₂O salt and the neutral H₂BTC ligand were dissolved in organic solvents, and the system was heated with corresponding cations under solvothermal conditions to form crystals. Three methods were utilized to introduce the cations needed in the frameworks. Method 1 was in situ generation of cations from the decomposition of formamides. For example, NH₄⁺, MeNH₄⁺, and Me₂NH₂⁺ were generated from formamide, N-methylformamide and N,N-dimethylformamide, respectively. The second method utilized amine bases to generate corresponding organic ammonium cations, such as in the case of Et₃NH⁺ and n-Bu₂NH₂⁺ cations. The third method was directly adding cations, such as quaternary ammonium n-Bu₂N⁺ and Me₂N⁺ in the reaction. The synthetic conditions for introducing different cations are summarized in Tables 1, 2, and 3.

When applying the first method to introduce the cations, the corresponding formamides could be utilized directly as solvents. However, when using the second or third methods to introduce the cations, NMP or a mixture of NMP with EtOH were used as the solvents. In some cases, EtOH was mixed with the formamides in method 1 in order to generate better quality crystals. Imidazole (IM) was planned to be introduced as a base to the reaction system with the aim to generate the imidazolium cations; however, the results revealed a neutral framework with imidazole acting as a coordinating ligand to the Zn(II) in the frameworks. In this study, the reaction system was typically heated at 150 °C for 3 days and allowed to cool to room temperature naturally in the oven. A longer reaction time in method 3 was required to achieve better crystalline samples for single-crystal X-ray crystallography analysis.

**Influence of Cations on the Crystal Structural Changes.** With the exception of imidazole, the MOFs formed in this study all contained anionic Zn-BTC coordination polymers with cations in their structures. It was observed that the dimensionality of the anionic Zn-BTC coordination polymer was strongly related with the hydrogen-bond forming ability of the used cations. It was found that if the cations have four H-bonding sites, the anionic Zn-BTC formed a one-dimensional chain structure; if the cations can form three H-bondings, Zn-BTC formed a 2D layer structure; and when the cations have two or less H-bonding sites, the 3D frameworks of anionic Zn-BTC were formed. The synthetic conditions for introducing different cations are summarized in Tables 1, 2, and 3.

**One-Dimensional Chain Anionic Structure for Cation with Four H-bonding Capability.** In the case of MOF {Zn-BTC}{NH₄⁺}, BTC ligands are connected through only two carboxylate groups from BTC in a linear manner. The cations are coordinated by two carboxylate groups from BTC in a trans-d books.
Table 4. Crystallographic Data and Structure Refinement Details for MOF{Zn-BTC}{cations}

<table>
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<tr>
<th>MOFs</th>
<th>[Zn-BTC][NH4]+</th>
<th>[Zn-BTC][MeNH3]+</th>
<th>[Zn-BTC][Me2NH2]+</th>
<th>[Zn-BTC][Et2NH2]+</th>
<th>[Zn-BTC][n-Bu2NH2]+</th>
<th>[Zn-BTC][n-Bu4N+]</th>
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</thead>
<tbody>
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<td>C10H9NO6Zn</td>
<td>C14H18N2O7Zn</td>
<td>C14.25H17.75N1.25O6.25Zn</td>
<td>C17H23NO6Zn</td>
<td>C28.50H71N5O35Zn</td>
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<td>391.67</td>
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<td>monoclinic</td>
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<td>P1̅</td>
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<td>P21/n</td>
<td>P21/c</td>
<td>C2/c</td>
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<td>7.791(3)</td>
<td>9.429(13)</td>
<td>9.509(3)</td>
<td>9.488(6)</td>
<td>10.284(5)</td>
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<td>b (Å)</td>
<td>9.780(4)</td>
<td>8.989(4)</td>
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<th>[Zn-BTC][Me₄N⁺]</th>
<th>[Zn-BTC][n-Bu₄N⁺]</th>
<th>[Zn-BTC][((PhCH₂)Me₃N⁺]</th>
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Table 4. continued

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<tr>
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<th>(Zn-BTC)[Me4N+]</th>
<th>(Zn-BTC)[n-Bu4N+]</th>
<th>(Zn-BTC)[(PhCH2)Me3N+]</th>
<th>(Zn-BTC)[BMIM]</th>
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<td>1.015</td>
<td>1.181</td>
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<table>
<thead>
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<td>P2₁/n</td>
<td>C2/m</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.366(2)</td>
<td>26.656(15)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.439(3)</td>
<td>24.838(14)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>26.969(5)</td>
<td>10.191(6)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>95.463(3)</td>
<td>110.667(7)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>4461.5(15)</td>
<td>6313(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Dcal (g cm⁻³)</td>
<td>1.454</td>
<td>1.085</td>
</tr>
<tr>
<td>μ(Mo Kα) (mm⁻¹)</td>
<td>1.668</td>
<td>1.182</td>
</tr>
<tr>
<td>F(000)</td>
<td>1994</td>
<td>2100</td>
</tr>
<tr>
<td>total reflections</td>
<td>27980</td>
<td>20708</td>
</tr>
<tr>
<td>unique reflections</td>
<td>6328</td>
<td>4622</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.0472</td>
<td>0.0738</td>
</tr>
<tr>
<td>R₁ [I &gt; 2σ(I)]</td>
<td>0.0946</td>
<td>0.0993</td>
</tr>
<tr>
<td>wR² [I &gt; 2σ(I)]</td>
<td>0.2630</td>
<td>0.2622</td>
</tr>
<tr>
<td>R₁ (all data)</td>
<td>0.1098</td>
<td>0.1162</td>
</tr>
<tr>
<td>wR₂ (all data)</td>
<td>0.2772</td>
<td>0.2720</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.017</td>
<td>1.166</td>
</tr>
</tbody>
</table>
BTC}{NH₄⁺}, MOF {Zn-BTC}{MeNH₃⁺} contains [Zn₂(μ-OOC)₂] dimers in the frameworks, and those dimers are connected through BTC ligands to form a double-layer anionic framework (Figure 2). Each [Zn₂(μ-OOC)₂] is surrounded by six BTC ligands, which are parallel to each other. Each Zn(II) is still in a tetrahedral coordination with the four carboxylate groups of BTC, and each BTC ligand uses one carboxylate group to bridge two Zn atoms to form the [Zn₂(μ-OOC)₂] dimer structure and uses the remaining two carboxylate groups to connect the surrounding Zn₂ dimers to form the double-layer structure. The methyl groups of the MeNH₃⁺ cations are located inside the double layers, while the -NH₃ parts approach out of the layers to form hydrogen bonds with nearby layers in a closed packing structure.

**Three-Dimensional Framework Anionic Structure for Cation with Two or Less H-Bonding Capability.** It was found that when cations have two or fewer hydrogen-bond forming abilities, the 3D framework structures of anionic Zn-BTC formed. In this catalog, the size and shape of the cations can influence the 3D framework structures. However, among those 3D frameworks, the most common anionic Zn-BTC structure observed was in MOF {Zn-BTC}{Me₂NH₂⁺}. In this structure, [Zn₂(μ-OOC)₂] motifs were also formed, and each motif was surrounded by six BTC ligands. However, contrary to those in MOF {Zn-BTC}{MeNH₃⁺}, four BTC ligands were now located in the same plane, while two of the BTC ligands were found in the near perpendicular planes. Such a connection of [Zn₂(μ-OOC)₂] motifs results in the X-shaped chains cross-linked with each other to form a channeled Zn-BTC anionic framework (Figure 3).

If the [Zn₂(μ-OOC)₂] structure motif and BTC are seen as second building units (SBUs), then the Zn-BTC framework can be seen as a (3,6)-connected net; i.e., one BTC ligand connects three Zn₂ units, and each Zn₂ unit connects six BTC ligands. The Zn-BTC anionic framework in MOF {Zn-BTC}{Me₂NH₂⁺} therefore has the same topology as rutile, TiO₂. The topologic similarity between TiO₂ and MOF {Zn-BTC}{Me₂NH₂⁺} is shown in Figure 4.

---

**Figure 1.** (a) One-dimensional structure of anionic Zn-BTC. (b) Packing diagram of chains in MOF {Zn-BTC}{NH₄⁺}. Zn = green, N = blue, O = red, and C = gray. Molecules of formamide are omitted for clarity.

**Figure 2.** (a) The [Zn₂(μ-OOC)₂] dimer with coordinated six BTC ligands. (b) The double-layer structure of Zn-BTC. (c) The packing of the double layers viewed along the a axis.
Cations of Et$_2$NH$_2$\textsuperscript{+}, n-Bu$_2$NH$_2$\textsuperscript{+}, Et$_3$NH\textsuperscript{+}, (PhCH$_2$)Me$_3$N\textsuperscript{+}, and BMIM all gave the same anionic Zn-BTC framework as in MOF (Zn-BTC)\{Me$_2$NH$_2$\textsuperscript{+}\}. However, differences in the size and shape, as well as in the interactions of cations with frameworks result in a different cation packing in the channels, and correspondingly different channels size within the frameworks, as shown in Figure 5 and Table 5.

Except the electrostatic interactions, additional hydrogen bonding interactions exist between the cations and the anionic Zn-BTC frameworks in MOFs with cations of Me$_2$NH$_2$\textsuperscript{+}, Et$_2$NH$_2$\textsuperscript{+}, n-Bu$_2$NH$_2$\textsuperscript{+}, and Et$_3$NH\textsuperscript{+}. The small size of Me$_2$NH$_2$\textsuperscript{+} cations allows DMF solvents to coexist in the channels (Figure 5a).

The relatively larger size of Et$_2$NH$_2$\textsuperscript{+}, n-Bu$_2$NH$_2$\textsuperscript{+}, and Et$_3$NH\textsuperscript{+} excludes the extra solvent molecules and permits them to be incorporated into the channels by approaching the linear alkyl groups through the wall of the channels. The linear shape of (PhCH$_2$)Me$_3$N\textsuperscript{+} and BMIM cations facilitates their accommodation in the centers of the channels, and in both cases only electrostatic interactions exist between the cations and Zn-BTC anionic frameworks. It was noted that in the case of (PhCH$_2$)Me$_3$N\textsuperscript{+}, the closest distance between the centroids of the nearby situated benzene rings of the cations was about 4.5 Å, which did not support ideal $\pi-\pi$ interactions between them.
The geometry and the template cations’ interaction preferences led to the variance of the channel structures in those isoreticular MOFs (as seen in Figure 5 and Table 5). For example, the length of the cross-section of the channels can extend from 10.97 to 12.40 Å in order to adapt cations from smaller Me₂NH₂⁺ to larger n-Bu₂NH₂⁺, and the width also changes from cation to cation. The separation between the nearby cations along the channel direction in those MOFs does not change very much. Only ∼3% relative changes were observed compared with the ∼13% changes of the length of the cross-section size.

However, when nonlinear quaternary ammonium cations such as n-Bu₄N⁺ and Me₄N⁺ were used, two new 3D anionic Zn-BTC frameworks were obtained. The size of the cations clearly affects the Zn-BTC coordinations in the new frameworks. The bulky n-Bu₄N⁺ cations force the Zn-BTC frameworks to incorporate them inside the channels on one same layers and leave the other channels on the alternative layers open for solvents, as shown in Figure 6. In this new

Figure 5. Cations packing position in the isoreticular Zn-BTC anionic frameworks viewed along the channels direction (a) Me₂NH₂⁺, (b) Et₂NH₂⁺, (c) n-Bu₂NH₂⁺, (d) Et₃NH⁺, (e) (PhCH₂)Me₃N⁺, and (f) BMIM. Light blue dash lines represent H-bonding.
Table 5. Structural Parameters of the Channels in the Isoreticular {Zn-BTC}{cation} MOFs

<table>
<thead>
<tr>
<th>Cation</th>
<th>$L$</th>
<th>$W$</th>
<th>(L\text{-Zn} distance in the [Zn}_2(\mu\text{-OOC})_2) (Å)</th>
<th>(N\text{--O} distance in the N\text{--H--O} bonding (Å))</th>
<th>(distance of N\text{--N} of the nearby organic cations along the channels (Å))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_2$NH$_2^+$</td>
<td>10.97</td>
<td>7.31</td>
<td>3.8529(4)</td>
<td>2.722(2)</td>
<td>9.43</td>
</tr>
<tr>
<td>Et$_2$NH$_2^+$</td>
<td>11.37</td>
<td>7.28</td>
<td>3.8816(8)</td>
<td>2.722(3) and 2.748(3)</td>
<td>9.51</td>
</tr>
<tr>
<td>$n$-Bu$_2$NH$_2^{&quot;}\text{a}&quot;$</td>
<td>12.40</td>
<td>6.80</td>
<td>3.975(2)</td>
<td>2.753(6) and 2.683(6)</td>
<td>9.49</td>
</tr>
<tr>
<td>Et$_3$NH$^+$</td>
<td>11.61</td>
<td>7.59</td>
<td>3.972(5)</td>
<td>2.724(6)</td>
<td>9.46</td>
</tr>
<tr>
<td>(PhCH$_2$)$_3$N$^+$</td>
<td>11.55</td>
<td>8.55</td>
<td>4.037(1)</td>
<td>/</td>
<td>9.57</td>
</tr>
<tr>
<td>BMIM</td>
<td>11.60</td>
<td>6.95</td>
<td>4.1142(9)</td>
<td>/</td>
<td>9.30</td>
</tr>
</tbody>
</table>

\(^{"}\text{This MOF is synthesized by method 1.}\)

Figure 6. Crystal structure of {Zn-BTC}{[n-Bu$_4$N$^+$]}. (a) [Zn$_2(\mu\text{-OOC})_2$] dimer with coordinated five BTC ligands. (b) Cation locations in the Zn-BTC anionic framework viewed along the $b$ axis.

Figure 7. Crystal structure of {Zn-BTC}{Me$_4$N$^+$}. (a) The coordination environments of single tetrahedral Zn(II) ions and the [Zn(\mu-OOC)$_2$]$_2$ dimer. (b) Zn-BTC anionic frameworks with and without Me$_4$N$^+$ cations viewed along the $a$ axis, NMP solvent molecules are omitted for clarity.
Figure 8. MOF \([\text{Zn-BTC}\{n-\text{Bu}_2\text{NH}_2\}^\text{-M2}}\): (a) The Zn\(_2\) dimer and Zn\(_4\) cluster coordination environment. (b) The packing diagrams of the Zn-BTC anionic framework viewed along the \(a\) and \(c\) axes, respectively. Disordered NMP solvents are omitted for clarity.

Figure 9. (a) MOF \([\text{Zn-BTC-IM}}\): the conjunction of two different dimeric units, and the 3D Zn-BTC framework structure viewed along the \(c\) axis. IM and NMP are omitted for clarity. (b) MOF \([\text{Zn-BTC-2IM}}\): the fragment of 1D polymeric chain and the hydrogen bonding association between chains viewed along the \(c\)-axis. Individual chains are shown in different colors for clarity.
MOF, \{Zn-BTC\}\(n\)-Bu\(_4\)N\(^+\), the Zn\(_2\) dimer is in the \([Zn\_2(\mu-OOC)\_3]\) configuration being surrounded by five BTC ligands. The BTC ligand uses the two-carboxylate groups to form the Zn\(_2\) dimers in bridging binding mode and uses the other carboxylate in monodentate or chelate binding mode to connect the dimers into a channeled framework.

Me\(_4\)N\(^+\) cations, even smaller in size compared to (PhCH\(_2\))\(-\)Me\(_3\)N\(^+\), generated a Zn-BTC anionic framework that differed from the previously discussed MOF \{Zn-BTC\}\{Me\(_2\)NH\(_2\)\}\(^+\), as shown in Figure 7.

In MOF \{Zn-BTC\}\{Me\(_2\)N\(^+\)\}, two different coordination connectors of the Zn(II) exist. One is the isolated single Zn(II) which is tetrahedrally coordinated by four BTC ligands, and another is the \([Zn\_2(\mu-OOC)\_2]\) dimer as seen in the MOF \{Zn-BTC\}\{Me\(_2\)NH\(_2\)\}\(^+\). The anionic Zn-BTC frameworks are surrounded by the Me\(_4\)N\(^+\) cations, and NMP solvent molecules occupy the remaining void space in the framework.

In this study, it was also observed that different methods for introducing the same cation could lead to different final framework structures. For example, when N\(_2\)N-dibutylamine was used to form n-Bu\(_2\)NH\(^+\) cations (method 2) instead of their in situ generation from decomposition of N\(_2\)N-dibutylformamide (method 1), a new crystalline sample, MOF \{Zn-BTC\}\{n-Bu\(_2\)NH\(_2\)\}\(-\)M2, was obtained. In contrast to the MOFs generated from method 1, the new MOF \{Zn-BTC\}\{n-Bu\(_2\)NH\(_2\)\}\(-\)M2 contains two different Zn-BTC coordination motifs. One is the \([Zn\_2(\mu-OOC)\_3]\) dimer, and another is the \([Zn\_4(O)(\mu-OOC)\_7]\) cluster. The Zn-BTC framework shows an alternative cage and channel structures connected between those Zn\(_2\) and Zn\(_4\) clusters by BTC ligands, as shown in Figure 8.

When imidazole (IM) was used as a base to generate imidazolium cations in the same Zn-BTC reaction system, the reaction failed. The introduced IM acted as an additional coordination ligand to Zn(II) ions resulting only in neutral frameworks. Two reaction composites of Zn(II):BTC:IM with a molar ratio of 1:1:1 and 1:1:2 resulted in two different Zn-BTC neutral MOFs, \{Zn-BTC-IM\} and \{Zn-BTC-2IM\}, respectively. MOF \{Zn-BTC-IM\} represents a 3D grid-like framework. It has two types of Zn(II)-BTC connection environments: one is the \([Zn\_2(\mu-OOC)\_3]\) dimer, and another is the paddle-wheel \([Zn\_2(\mu-OOC)\_4]\) dimer (Figure 9a). The Zn(II) ions of the dimers are also coordinated by NMP solvent molecules or IM ligands. However, MOF \{Zn-BTC-2IM\} shows an entirely different structure, where only \([Zn\_2(\mu-OOC)\_4]\) dimers exist, and those dimers are connected with single Zn(II) ions through the BTC ligands to form a 1D chain (Figure 9b). Those single Zn(II) ions are coordinated by two
The frameworks include the isolated single Zn(II) ions and the framework contains. In this study, the Zn-nodes existing in changes have a close relationship with what type of Zn-nodes of the crystal structures. More specifically, it is noticed those changes have a close relationship with what type of Zn-nodes, and the chains are interconnected through the hydrogen bindings between those IM ligands to form a 3D network.

**Effect of Cations on Fluorescence Changes.** All of the formed Zn-BTC frameworks in this study show fluorescence emission in the visible spectrum at the solid state. The fluorescent spectra of maximum emission of each MOFs are shown in Figures 10 and 11. A summary of the cations H-bond forming ability, the corresponding Zn-BTC structure, the Zn coordination motif, and the fluorescent emission wavelength at maximum intensity are listed in Table 6.

As organized in Tables 5 and 6 and Figures 10 and 11, two interesting conclusions can be drawn for the anionic Zn-BTC structures: (1) When the Zn-BTC anionic structure is changed from 1D chain to 2D layer, and finally to 3D framework, the emission wavelength shifts from violet (e.g., 405 nm) to blue (e.g., 455 nm) and even to the green light (e.g., 515 nm) region. Those wavelength shifts from violet (e.g., 405 nm) to blue (e.g., 455 nm) and even to the green light (e.g., 515 nm) region. Those changes are considered to be related clearly with dimensionality of the crystal structures. More specifically, it is noticed those changes have a close relationship with what type of Zn-nodes, and the chains are interconnected through the hydrogen bindings between those IM ligands to form a 3D network.

Table 6. A Summary of the Cations H-Bond Forming Ability, the Corresponding Zn-BTC Structure, the Zn Coordination Motif, and the Fluorescent Emission Wavelength at Maximum Intensity

<table>
<thead>
<tr>
<th>MOF</th>
<th>cation</th>
<th>number of H-bonding sites</th>
<th>dimensionality of Zn-BTC framework</th>
<th>number of (μ-OOC) involved in Zn cluster motif</th>
<th>FL emission @ maximum intensity (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Zn-BTC){NH₄⁺}</td>
<td>NH₄⁺</td>
<td>4</td>
<td>1D</td>
<td>[Zn₂(μ-OOC)₃] n = 0</td>
<td>405</td>
</tr>
<tr>
<td>(Zn-BTC){MeNH₂⁺}</td>
<td>MeNH₂⁺</td>
<td>3</td>
<td>2D</td>
<td>[Zn₂(μ-OOC)₂], n = 2</td>
<td>440⁺</td>
</tr>
<tr>
<td>(Zn-BTC){Me₂NH₂⁺}</td>
<td>Me₂NH₂⁺</td>
<td>2</td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂]</td>
<td>434</td>
</tr>
<tr>
<td>(Zn-BTC){EtNH₂⁺}</td>
<td>EtNH₂⁺</td>
<td>2</td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂]</td>
<td>455</td>
</tr>
<tr>
<td>(Zn-BTC){n-Bu₂NH₂⁺}·M₁</td>
<td>n-Bu₂NH₂⁺ from formamide</td>
<td></td>
<td></td>
<td>[Zn₂(μ-OOC)₂]</td>
<td>476</td>
</tr>
<tr>
<td>(Zn-BTC){Et₂NH⁺}</td>
<td>Et₂NH⁺</td>
<td>1</td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂]</td>
<td>438</td>
</tr>
<tr>
<td>(Zn-BTC){Ph₂NH₂⁺}</td>
<td>(Ph₂NH₂⁺)Ph₂NH₂⁺</td>
<td>0</td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂]</td>
<td>445</td>
</tr>
<tr>
<td>(Zn-BTC){BMM}</td>
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<td>0</td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂]</td>
<td>520</td>
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<tr>
<td>(Zn-BTC){Me₂N⁺}</td>
<td>Me₂N⁺</td>
<td>0</td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂] + Zn(II)</td>
<td>450</td>
</tr>
<tr>
<td>(Zn-BTC){n-Bu₂N⁺}</td>
<td>n-Bu₂N⁺</td>
<td>0</td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂] + Zn(II)</td>
<td>450</td>
</tr>
<tr>
<td>(Zn-BTC){n-Bu₂NH₂⁺}·M₂</td>
<td>n-Bu₂NH₂⁺ from amine</td>
<td></td>
<td></td>
<td>[Zn₂(μ-OOC)₂] + [Zn₂(μ-OOC)₂], n = 7</td>
<td>470</td>
</tr>
<tr>
<td>[Zn-BTC-IM]</td>
<td>IM as coordination ligand</td>
<td></td>
<td>3D</td>
<td>[Zn₂(μ-OOC)₂] + [Zn₂(μ-OOC)₂]</td>
<td>515</td>
</tr>
<tr>
<td>[Zn-BTC-2IM]</td>
<td>IM as coordination ligand</td>
<td></td>
<td>1D</td>
<td>[Zn₂(μ-OOC)₂] + Zn(II)</td>
<td>470</td>
</tr>
</tbody>
</table>

“*The highest emission is at 370 nm when it is excited at 340 nm. *⁺M₁ and M₂ indicate the cation’s introduction method 1 and method 2, respectively.

extra IM ligands and form a tetrahedral N₅O₅ set. Each chain therefore has eight IM branches approaching out, and the chains are interconnected through the hydrogen bindings between those IM ligands to form a 3D network.

MeNH₂⁺ is used, the framework has a 2D layer structure with [Zn₂(μ-OOC)₂] dimers as the connection nodes, and as we can see in Figure 10, the indigo emission at 440 nm is observed. Moreover, this framework releases an emission peak at 370 nm under an excitation wavelength of 340 nm, which can be assigned to the BTC ligand-centered charge transitions. When the cations are changed to less than two hydrogen-bond forming cations, such as n-Bu₂N⁺, where 3D frameworks are obtained and [Zn₂(μ-OOC)₂] acts as connection node, the emission shifts to the blue light region at 470 nm. However, when it is in the Me₂N⁺ case, the framework uses both [Zn₂(μ-OOC)₂] and single Zn(II) as connection nodes in the structure. Because fewer (μ-OOC) used in those Zn-nodes, the emission wavelength shifts toward the violet direction and gives an emission at 450 nm, compared to the n-Bu₂N⁺ case. When the 3D frameworks contain both [Zn₂(μ-OOC)₂] and [Zn₂(μ-OOC)₂] clusters as nodes, as in the case of MOF [Zn-BTC]{n-Bu₂NH₂⁺}·M₂, the emission wavelength shifts to 515 nm, producing a green light. (2) Frameworks, which have the same Zn-BTC anionic structure as shown in Figure 5, provided us good examples for understanding how the differences in the inclusive cations influence the fluorescence of the frameworks. It is suggested that the fewer the interactions between the cations and anionic frameworks in the MOFs, the longer wavelength of emission the MOFs can have. For example, as listed in Table 5, for cations that can form additional hydrogen bonding with the frameworks, i.e., Me₂NH₂⁺, Et₂NH₂⁺, Et₃NH⁺, and n-Bu₂NH₂⁺, the pKₐ of the corresponding amines increases (pKₐ for Me₂NH = 10.64, Et₂NH = 10.65, Et₃NH = 10.98, and (n-Bu₂NH)NH = 11.25), which suggests the strength of hydrogen bonding N–H···O can decrease in the same order. For the similar ammonium cations R₃NH⁺, from Me- to Et-, and further to Bu-substituted ones, one might conclude that the interaction between cations and framework becomes weaker and weaker in the same order, and as it was observed, the emission changed...
from indigo light at 434 nm to 455 nm and finally to blue light at 476 nm, respectively. When we compare the BMIM and (PhCH$_2$)$_2$Me$_2$N$^+$ cations which cannot have hydrogen bonding with the frameworks, the imidazolium cation gave a green emission at 520 nm, while (PhCH$_2$)$_2$Me$_2$N$^+$ gave an indigo emission at 445 nm. This could also result from the BMIM emission at 445 nm as the Me$_2$NH$_2$ [$\text{Zn-BTC-IM}$] has a 3D framework and contains both $\{\text{Zn}_2(\mu$-$\text{OOC})_3\}$ and $\{\text{Zn}_2(\mu$-$\text{OOC})_4\}$ clusters as connection nodes, while MOF $\{\text{Zn-BTC-2IM}\}$ has 1D chain structures that are cross-linked through hydrogen bonding to form a framework and contains the cluster $\{\text{Zn}_2(\mu$-$\text{OOC})_4\}$ and single $\text{Zn(II)}$ ions as the connection nodes. As deduced from conclusion 1, MOF $\{\text{Zn-BTC-IM}\}$ should give a longer wavelength emission than MOF $\{\text{Zn-BTC-2IM}\}$. As observed in this study, MOF $\{\text{Zn-BTC-IM}\}$ gave a yellow emission at 543 nm, and MOF $\{\text{Zn-BTC-2IM}\}$ gave a blue emission at 470 nm. The overall longer emission wavelength of both Zn-BTC-IM frameworks compared to the anionic Zn-BTC frameworks may arise from the electron contribution of the coordinated IM ligands, which is also consistent with conclusion 2.

**CONCLUSION**

In summary, a series of anionic Zn-BTC frameworks with NH$_4^+$ or organic cations residing in the voids of the frameworks were analyzed via single-crystal X-ray crystallography, and the corresponding fluorescence of the frameworks was studied. It was observed that cations acting as structure-directing agents affect the coordination structure of the Zn-BTC anionic frameworks. Most of the frameworks contain (μ-OOC) bridged Zn(II)-clusters as connecting nodes, such as $\{\text{Zn}_2(\mu$-$\text{OOC})_3\}$, $\{\text{Zn}_2(\mu$-$\text{OOC})_4\}$, $\{\text{Zn}_2(\mu$-$\text{OOC})_5\}$, and $\{\text{Zn}_4(\mu$-$\text{OOC})_3\}$.

All of the Zn-BTC anionic frameworks reported herein showed fluorescent emission in the visible spectrum region. The fluorescent emissions are closely related to the (μ-OOC) bridged Zn(II)-clusters. The more the Zn(II) and (μ-OOC) bridging BTC contributed to the cluster, the longer the observed emission wavelength. In the same isoreticular Zn-BTC anionic frameworks, the strength of interactions between the inclusive cations and framework influences the emission as well. Lesser interactions result in emission shifts to the longer wavelength direction.

**ASSOCIATED CONTENT**

Supporting Information

PXRD patterns as well as X-ray crystallographic files (CIF) are available for all compounds. These materials are available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Authors

*(Q.W.) Current address: Department of Biology and Chemistry, New Mexico Highlands University, NM 87701, USA. E-mail: qwei@nmhu.edu.

*(T.T.) Current address: Department of Biology and Chemistry, New Mexico Highlands University, NM 87701, USA. E-mail: tvtimofoeeva@nmhu.edu.

Notes

The authors declare the following competing interest(s): The MOFs reported in this manuscript have been filed in a provisional application for patent.

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