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A self-catenated rob-type porous coordination polymer constructed from triazole and carboxylate ligands: fluorescent response to the reversible phase transformation

Mingli Deng,a Shijun Tai,b Weiquan Zhang,a Yongchen Wang,a Jiaxing Zhu,a Jinsheng Zhang,b Yun Ling*a and Yaming Zhoua

A flexible structure of \([\text{[Zn}_2(\text{dmtrz})_2(L1)] \cdot 6\text{H}_2\text{O}]\) (MAC-11) (Hdmtrz = 3,5-dimethyl-1H,1,2,4-triazole, H2L1 = (E)-4,4'-stilbenedicarboxylic acid), which is a self-catenated rob-type net built of two-dimensional \([\text{[Zn}(\text{dmtrz})]\) layers pillared by L1 ligands, has been solvothermally synthesized. It shows interesting thermo/water-induced reversible phase transformation accompanied by a photoluminescent response from 418 nm to 453 nm. Based on an iso-framework of \([\text{[Zn}_2(\text{trz})_2(L2)] \cdot 4\text{H}_2\text{O}]\) (MAC-13, Htrz = 1H, 1,2,4-triazole), a pcu-type framework of \([\text{[Zn}(\text{trz})_2(L1)] \cdot 4\text{H}_2\text{O}]\), (MAC-14, Htrz = 1H, 1,2,4-triazole), a layer structure of \([\text{[Zn}(\text{dmtrz})(\text{HCOO})]\), a possible mechanism of the photoluminescent response to the reversible phase transformation for MAC-11 was also proposed.

Introduction

Flexible coordination polymers are of great interesting crystalline materials, especially those showing external stimuli-induced reversible structural changes accompanied by photoluminescent responses.1-6 The intrinsic structural flexibility make them more promising in molecular recognition and sensing.7-9 For examples, adsorption of CO2 can be converted into detectable photoluminescent signals by incorporation of a fluorescent reporter distyrylbenzene (DSB) into a flexible structure of \([\text{[Zn}_2(\text{bdc})(\text{dabco})]\);10 aromatics can be well decoded by an interpenetrated dynamic frameworks because of distinct photoluminescent responses,11 even high efficient sensing O2 can be directly achieved by a flexible \([\text{[Cu}(\text{tez})]\).12

Up to now, several types of structures showing framework flexibility has been studied,13-19 in which most of them are exclusively connected via metal-carboxylate coordination bonds. However, it has been argued due to its easy cleavage by H2O.20 Furthermore, even if these flexible frameworks are strong enough, there is still one challenge that is the distinguishable photoluminescent response to a phase transformation.21-22 Generally, most of the phase transformation of MOFs are caused by the adjustment of metal-carboxylate coordination angles.23 This change could not lead to a sufficient change of energy state because coordinated carboxylate groups are separated with organic emitters by \(\sigma\) bonds (Scheme 1a).

Polyazoheterocycles, such as pyrazoles, imidazoles, triazoles, and tetrazoles, are promising ligands to construct robust coordination polymers because of the strong metal-nitrogen coordination bonds.24-26 Taking the Zn4O-based MOFs for an example, when the extendable group changes from carboxylate to azolate ligands, the framework stability in air and moisture condition can be greatly improved,27,28 even the defect chemistry of the framework can be well-investigated in water.27 Furthermore, azolate ligands can serve as an efficient superexchange pathway and/or capacity for spin electrons, because the r-conjugated azolates are directly coordinated to metal ions. This characteristic has no doubt endue the energy

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state of metal-alazoles more sensitive to the external stimuli-induced structural changes (Scheme 1b).

Recently, we have reported a series of porous coordination polymers constructed from triazole and carboxylate ligands. Encouraged by our previous works and taking the above mentioned issues in consideration, we propose to construct flexible porous structures in which the structural flexibility are originated from metal-alazoles. In this paper, by combining photoluminescent 2D metal-triazole with photoluminescent stilbenedicarboxylic acid, a flexible and robust structure of \( \{[Zn_2(dmtrz)_2(L1)] \cdot 6H_2O\}_n \) (MAC-11) (Hdmtrz = 3,5-dimethyl-1H,1,2,4-triazole, \( L_1 = (E)-4,4'-\text{stilbenedicarboxylic acid} \)) has been successfully isolated, which is a self-catenated rob-type net built of 2D \([Zn(dmtrz)]\) layers pillared by L1 ligands. It can retain its framework integrity in water, and shows thermo/water induced reversible phase transformation accompanied by photoluminescence response from purple to blue. Furthermore, based on the isostructur of \( \{[Zn(dmtrz)_2(L2)] \cdot 4H_2O\}_n \) (MAC-13, \( H_2L_2 = (E)-\text{azobenzene-4,4'-dicarboxylic acid} \)), a pcu-type framework of \( \{[Zn( trz)_2(L1)] \cdot 4H_2O\}_n \) (MAC-14, \( \text{Htrz} = 1H, 1,2,4-\text{triazole} \)), a layer structure of \( [Zn(dmtrz)[HCOO]] \) and the \( H_2L_1 \) ligand, the possible mechanism of photoluminescence response to the reversible phase transformation was proposed for MAC-11.

### Experimental

#### Materials and General characterization

All of the chemicals were obtained from commercial sources and were used without further purification, except Hdmtrz, \( H_2L_2 \) ligands, which were synthesized according to previous literatures. FT-IR spectra were recorded on a Nicolet 470 FT-IR spectrometer in the range of 400–4000 cm\(^{-1}\) on KBr pellets. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 powder diffractometer with Cu Ka radiation (\( \lambda = 1.5406 \) Å). Thermogravimetric analyses (TGA) were carried out on a TGA/SDTA 851 in the temperature range 30–800 °C under N\(_2\). Thermogravimetric analysis (TGA) was used without further purification, except Hdmtrz, \( H_2L_2 \) ligands.

#### Crystal Data Collection and Refinement

Data collection for MAC-11, MAC-13 and MAC-14 was carried out on a Bruker Apex Duo diffractometer with graphite monochromated Mo Ka radiation (\( \lambda = 0.71073 \) Å) at 293(2) K, respectively. Data reduction was performed with SAINT, and empirical absorption corrections were applied by SADABAS program. Structures were solved by direct method using SHELLXS program and refined with SHEXL program. Heavy atoms and other non-hydrogen atoms were directly obtained from difference Fourier map. Final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on \( F^2 \). C-bonded H atoms were placed geometrically and refined as riding modes. H atoms of lattice water were positioned from difference Fourier maps and then refined with rigid mode. Crystallographic data are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MAC-11</th>
<th>MAC-13</th>
<th>MAC-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>( \text{C}<em>{24} \text{H}</em>{32} \text{N}<em>8 \text{O}</em>{28} \text{Zn}_2 )</td>
<td>( \text{C}<em>{24} \text{H}</em>{32} \text{N}<em>8 \text{O}</em>{28} \text{Zn}_2 )</td>
<td>( \text{C}<em>{24} \text{H}</em>{32} \text{N}<em>8 \text{O}</em>{28} \text{Zn}_2 )</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>C2/c</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td>α(Å)</td>
<td>39.356(13)</td>
<td>38.503(5)</td>
<td>38.088(10)</td>
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<tr>
<td>β(Å)</td>
<td>9.332(3)</td>
<td>9.451(12)</td>
<td>9.647(3)</td>
</tr>
<tr>
<td>γ(Å)</td>
<td>9.842(3)</td>
<td>9.8023(13)</td>
<td>9.871(3)</td>
</tr>
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<td>D, /g cm(^{-3})</td>
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<td>1.241</td>
<td>1.120</td>
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<td>μ/(mm(^{-1}))</td>
<td>1.409</td>
<td>1.415</td>
<td>1.375</td>
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<tr>
<td>F(000)</td>
<td>1440</td>
<td>1328</td>
<td>1232</td>
</tr>
<tr>
<td>Total collected</td>
<td>8550</td>
<td>10436</td>
<td>12625</td>
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<tr>
<td>Unique data, R(int)</td>
<td>3168, 0.021</td>
<td>3144, 0.059</td>
<td>4053, 0.042</td>
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<tr>
<td>Observed data</td>
<td>2811</td>
<td>2249</td>
<td>3017</td>
</tr>
<tr>
<td>Rgo on F(^2)</td>
<td>1.10</td>
<td>1.12</td>
<td>1.15</td>
</tr>
<tr>
<td>R(I &gt; 2σ(I))</td>
<td>0.0554, 0.1747</td>
<td>0.0618, 0.0845</td>
<td>0.0753</td>
</tr>
<tr>
<td>Peak and hole / Å(^3)</td>
<td>-0.94, 1.13</td>
<td>-0.84, 1.38</td>
<td>-0.76, 1.36</td>
</tr>
</tbody>
</table>

#### Synthesis of \( \{[Zn_2(dmtrz)_2(L1)] \cdot 6H_2O\}_n \) (MAC-11)

Zn(NO\(_3\))\(_2\)·6H\(_2\)O (0.3 mmol, 0.089 g) and Hdmtrz (0.2 mmol, 0.028 g) and \( H_2L_1 \) (0.1 mmol, 0.0271 g) were dissolved in 2 mL DMF. The mixture was stirred at room temperature for 10 min. HNO\(_2\) (0.2 mL) and HBF\(_4\) (0.06 mL) was added to the solution and stirred for another 30 min. The mixture was then transferred into 15 mL Teflon-lined stainless steel vessel, sealed and heated at 140 °C for 3 days under autogenous pressure. Light-yellow sheet crystals of MAC-11 were collected by filtration, washed with acetone for three times, and air-dried (Yield: 62 % based on Zn(II)). Anal. Calcd for \( \text{C}_{24} \text{H}_{32} \text{N}_8 \text{O}_{28} \text{Zn}_2 \): C, 41.34; H, 4.91; N, 12.05. Found: C, 41.21; H, 5.08; N, 12.01. FT-IR (KBr pellets cm\(^{-1}\)): 3480, 3280, 2940, 2860, 1670, 1620, 1560, 1520, 1420, 1380, 1340, 1260, 1180, 1140, 1090, 1010, 856, 787, 708, 650.

#### Synthesis of \( \{[Zn_2(dmtrz)_2(L2)] \cdot 4H_2O\}_n \) (MAC-13)

The synthesis procedure is analogous to that of MAC-11, except that \( H_2L_1 \) was replaced by \( H_2L_2 \). Orange sheet crystals of MAC-13 were isolated in yield of 56% (based on Zn(II)). Anal. Calcd for \( \text{C}_{24} \text{H}_{32} \text{N}_8 \text{O}_{28} \text{Zn}_2 \): C, 39.84; H, 4.26; N, 16.89. Found: C, 39.76; H, 4.35; N, 16.81. FT-IR (KBr pellets cm\(^{-1}\)): 3490, 2930, 2850, 1670, 1620, 1570, 1520, 1500, 1410, 1370, 1340, 1220, 1140, 1090, 1010, 877, 858, 793, 708, 644.
channels along into a three-dimensional (3D) lamella structure with 1D layers are further connected together by L1 ligands, resulting in a self-catenated hopf links (Fig. 1d). Similar to that of MAC-11, MAC-14 is also built of two-dimensional Zn-triazolate layers and pillared by L1 ligands (Fig. 1 and Fig. S6). Interestingly, considering the \([\text{Zn}(_{2}\text{trz})_{2}])\) dimer as a 6-connected node, MAC-14 is a \(\text{pcu}\)–type net rather than a self-catenated \(\text{rob}\) net. Furthermore, their porous structures are confirmed by N\(_2\) sorption isothermal at 77K, giving a BET (Langmuir) surface area of 722 (763), 719 (755) and 677 (831) m\(^2\)/g for MAC-11, MAC-13 and MAC-14, respectively (Fig. S5a). The pore size is of 5.9, 7.8 and 6.8 Å for MAC-11, MAC-13 and MAC-14 by H-K method \(^{30}\).

**Crystal phase transformation**

The PXRD pattern of MAC-11 matches well with the simulated one, confirming the pure crystal phase (Fig.2). It can retain its framework integrity in different solvents, especially in water for at least two days (Fig. S7), confirming its structural stability. We ascribe the robust framework to its unique lamella structure, in which the layer is formed exclusively by Zn(II) ions in trz and dmtrz ligands (Fig. 1). Considering the \([\text{Zn}(_{2}\text{trz})_{2}])\) dimer as a 6-connected node and the L1 ligand as the linear linker, MAC-11 can be considered as a 6-connected framework with a vertex symbol of \(4.6.8\), which is a self-catenated \(\text{rob}\) net with catenated hopf links (Fig. 1d). Similar to that of MAC-11, MAC-14 can be recovered to its original phase after being soaked in water, demonstrating a reversible phase transformation. Similarly, thermo-induced phase transformation is also observed for MAC-13 (Fig. S9). However, there is no obvious phase transformation for MAC-14 (Fig. S10).
Photoluminescent response

Upon excitation at $\lambda_{ex} = 369$ nm (Fig. 3 and Fig. S11), MAC-11 gives a broad emission with a maximum peak at $\lambda_{em} = 418$ nm (two shoulder emissions at 393 and 440 nm). Increasing the temperature to 60 °C, there is no obvious shift but a slight decay in its intensity (Fig. 3b). Further increasing the temperature to 90 °C, an obvious shift is observed, which gives a maximum peak at $\lambda_{em} = 453$ nm (with two shoulder emissions at 386 and 410 nm). The observable red-shift (35 nm) of the photoluminescent emission indicates a response to the structural transformation.

The mechanism study of MAC-11

MAC-11 is constructed by 2D layer of photoluminescent [Zn(dmtrz)(COO)]$_n$ (ligand-to-metal charge transfer, LMCT) pillared by photoluminescent stilbenedicarboxylate (Fig. 4). To explore the possible mechanism, the photoluminescent properties of H$_2$L1 and the 2D layer of [Zn(dmtrz)(HCOO)]$_{in}$ was studied respectively (Fig. 3d, Fig. S12). The emission spectrum of H$_2$L1 is located in the blue region (440—485 nm) with a maximum peak at 466 nm (a shoulder at 441 nm) upon excited at 369 nm. This emission could be ascribed to the $^\pi\pi$ transition of ligand. For the layer structure of [Zn(dmtrz)(HCOO)]$_n$, the photoluminescent emission is located in the purple region (380—440 nm) with a maximum peak at 416 nm. This emission could be ascribed to the ligand-to-metal charge transition (LMCT). No obvious shift of the photoluminescent emission has been observed for both of them after they were treated at 90 °C for 30 min (Fig. S12a and b). The mechanical mixture of H$_2$L1 and [Zn(dmtrz)(HCOO)]$_n$ (in a mole ratio of 1 : 2) have also been explored, which gives an emission like H$_2$L1 with a maximum peak at 464 nm (two shoulders at 408 and 443 nm). No obvious shift of the emission has been detected after the mixture was heated at 90 °C for 30 min (Fig. S12c).

Since there is no obvious photoluminescent shifts for MAC-14, the photoluminescent response to phase transformation of MAC-11 is structural related. Two possible approaches are proposed here: (i) the configurational adjustment of ligands in MAC-11 since it has two different configurations, trans- and cis-forms; (ii) the rearrangement of the 2D layer of [Zn(dmtrz)] to a more planar one. For the case (i), it is well known that the thermal process can only trigger the transformation of L1 from cis- to trans-form rather than trans- to cis-form. Besides, the trans-form has a larger $\pi$-electron conjugation effect than the cis-one, this kind of transformation can only lead to a blue- rather than a red-shift of photoluminescent emission. Therefore, case (i) should be excluded. For the case (ii), the 2D [Zn(dmtrz)] layer is required to be flexible, and then a thermo-induced phase transformation gives a more planar 2D layer. This rearrangement of 2D layer could be accompanied by a slight red-shift of photoluminescent emission owing to an enhanced effect of $\pi$-electron conjugation. It has been confirmed that the
layered metal-triazolate structure is flexible enough to twist from being markedly corrugated to virtually planar one, and parameters of \( \omega, \phi, \) and \( d \) are used to assess the state of 2D layer (Fig. 4a,b). The smaller of the parameters are, a more planar 2D layer will be. From Table 2, we can see that the 2D layer \([\text{Zn(dmtrz)}]\) in MAC-11 has similar state with that of \([\text{Zn(dmtrz)(HCOO)}], [\text{Zn(dmtrz)}]\) and \([\text{Cd(dmtrz)}]\). These compounds have similar emission spectra with peaks around 410 nm. These results suggest that the emission spectra of MAC-11 may originated from the 2D layer of \([\text{Zn(dmtrz)}]\). While, the photoluminescent contribution of pillar L1 ligands could not be excluded because of its slight broadening of the emission spectra. After a thermo-induced phase transformation from MAC-11 to MAC-11', this photoluminescence emission turns quite similar to that of MAC-14. We assume that a thermo-treatment of MAC-11 leads to a decrease of the parameters, resulting a more planar 2D layer of \([\text{Zn(dmtrz)}]\). Therefore, a slight red-shift of the emission spectrum is observed. On the other hand, the vibration band at 1675 cm\(^{-1}\) was disappeared from the FT-IR spectra when the phase turns from MAC-11 to MAC-11'. This disappearance indicates an change of the coordinated carboxylate from mono-bridge \( (\mu_1) \) to chelating \( (\eta_{1,2}) \) mode (Fig. S13), suggesting an enhanced interaction of L1 ligands to Zn centres. Therefore, the red-shift emission of 2D layer might further be overlaid with that of photoluminescence spectra of stilbenedicarboxylate ligand, giving a maximum emission peak at 453 nm. Taking the structural differences of MAC-11 and MAC-14 in consideration (Fig. 4c,d), the inclination state of the pillared L1 ligands and the flexible 2D layers make it possible for a thermo-induced phase transformation accompanied by photoluminescent response for MAC-11.

![Fig. 4](image)

**Table 2.** A short summary of structural parameters with the photoluminescent properties for the related metal-triazolate compounds as well as the structures reported here.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compounds</th>
<th>Structure</th>
<th>( \omega^\circ )</th>
<th>( d/\text{Å} )</th>
<th>( \phi^\circ )</th>
<th>( \lambda_{\text{max}}/\text{nm} )</th>
<th>Possible Origin</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>([\text{Zn(dmtrz)}])</td>
<td>2D</td>
<td>79.8</td>
<td>2.85</td>
<td>97.4</td>
<td>410</td>
<td>([\text{LMCT}])</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Cd(dtrz)}])</td>
<td>2D</td>
<td>74.8</td>
<td>2.82</td>
<td>109.7</td>
<td>410</td>
<td>([\text{LMCT}])</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>([\text{Cu(trz)}])</td>
<td>2D</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>468</td>
<td>([\text{MLCT}])</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>([\text{Ag(trz)}])</td>
<td>2D</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>508</td>
<td>([\text{LMCT}])</td>
<td>43</td>
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<tr>
<td>5</td>
<td>([\text{Zn(dmtrz)(HCOO)}])</td>
<td>2D</td>
<td>88.1</td>
<td>2.82</td>
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<td>416</td>
<td>([\text{LMCT}])</td>
<td>40</td>
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<tr>
<td>6</td>
<td>MAC-11</td>
<td>3D/rob</td>
<td>82.8</td>
<td>2.76</td>
<td>96.1</td>
<td>418±453</td>
<td>([\text{LMCT}], [\text{n}^*\text{-n}])</td>
<td>this work</td>
</tr>
<tr>
<td>7</td>
<td>MAC-13</td>
<td>3D/rob</td>
<td>81.9</td>
<td>2.73</td>
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<td>this work</td>
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<td>68.1</td>
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<td>9</td>
<td>H_2L1</td>
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<td>N.A.</td>
<td>N.A.</td>
<td>No</td>
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<td>10</td>
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<td>No</td>
<td>466</td>
<td>([\text{LMCT}], [\text{n}^*\text{-n}])</td>
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\( ^a\text{TIPT = thermo-induced phase transformation} \)

**Conclusions**

In this paper, a flexible porous Zinc-coordination polymer of MAC-11 showing a self-catenated rob-type net has been successfully synthesized, and an interesting photoluminescent response to a thermo-induced phase transformation has been observed and studied. The robust feature of MAC-11 could be ascribed to its unique layered structure, in which the layer is formed exclusively by Zn-triazolates. Since the \( \pi \)-conjugated triazolate are directly coordinated to metal ions, the thermo-induced phase transformation of 2D Zn-triazolate layer to a more planar one could induce to a sufficient change of the energy state, resulting into a red-shift of the emission spectra. On the other hand, no obvious crystal phase as well as photoluminescent transformation has been observed for the
case of pcu-type MAC-14, although it is built of similar photoluminescent modules. So, our studies here not only gives an example of flexible coordination polymer showing thermo/water induced reversible structural-photoluminescent response, but also demonstrates that the framework type also plays a crucial role in affecting the structure-photoluminescent properties.

Acknowledgements
We gratefully acknowledge the financial support from NSFC (Nos. 21201039, 21203032, 21471035), the Shanghai Leading Academic Discipline Project (B108).

Notes and references
§ CCDC number 1063268-1063270 for MAC-11, MAC-13 and MAC-14 respectively.

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