Electronic supporting Information:

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

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**Fig. S1.** the PXRD patterns obtained for synthesis pure phase of MA-11. (*Case 1*: 0.02 mL HAC, *Case 2*: 0.06 HNO$_3$, *Case 3*: 0.06 mL HBF$_4$, *Case 4*: HNO$_3$ (0.2 mL) and HBF$_4$ (0.06 mL), *Case 5*: 0.12 mL HNO$_3$, *Case 6*: 0.06 mL HNO$_3$ and 0.06 mLHBF$_4$)
Fig. S2. the crystal structure of the side product obtained without additional acid. (a) the structure motif (A: 2/3-x, 4/3-y, 1/3-z; B: -x+y, 1-x, z; C: 1-y, 1+x-y, z; D: 2/3+x-y, 1/3+x, 1/3-z; E: -1/3+y, 1/3-x+y, 1/3-z; F: 2/3-x, 1/3-y, 1/3-z); (b) the two-dimensional layer structure; (c) the packing structure
Fig. S3. (a) the structural motif of MAC-11 with atomic label (symmetry codes: A: 0.5-x, 0.5-y, -z; B: 0.5-x, 0.5+y, 0.5-z; C: x, -y, -0.5+z; D: -x, -y, -z); (b) the three-dimensional structure of MAC-11 showing 1D channel along c axis (the green: Connolly with probe atom radii of 1.4 Å, cell: 1 × 4 × 4); (c) the two-dimensional layer formed exclusively by Zn2(dmtrz)2 dimers (α: the dihedral angle); (d) the rob (48.66.8) net of 1 after considering of Zn2(dmtrz)2 as 6-connected node (the pink and red ring show the self-catenated hopf links).
Fig. S4. (a) the structure motif of MAC-13 (symmetry codes: A: 0.5-x, 0.5-y, -z; B: 0.5-x, -0.5+y, 0.5-z; C: x, 1-y, -0.5+z); (b) the two-dimensional (4,4) layer with the dihedral angle of 82.84°, which is slightly smaller than that in 1; (c) the three-dimensional structure of 2 showing the accessible porous structure along c axis (the green surface: calculated by Connolly method with the probe atomic radii settled to be 1.4 Å).
**Fig. S5.** N$_2$ sorption isothermal of MAC-11, MAC-13 and MAC-14 at 77 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore size (H-K, Å)</th>
<th>Pore Volume (micropore, Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET</td>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td>MAC-11</td>
<td>722</td>
<td>763</td>
<td>5.9</td>
</tr>
<tr>
<td>MAC-13</td>
<td>719</td>
<td>755</td>
<td>7.8</td>
</tr>
<tr>
<td>MAC-14</td>
<td>677</td>
<td>831</td>
<td>6.9</td>
</tr>
</tbody>
</table>
Fig. S6. (a) the structure motif of **MAC-14** (symmetry codes: A: 0.5-x, 0.5-y, 1-z; B: x, -y, -0.5+z; C: 0.5-x, 0.5+y, 1.5-z; D: 1-x, y, 0.5-z); (b) the three-dimensional structure of MAC-14 showing the accessible porous structure along $c$ axis (the green surface: calculated by Connolly method with the probe atomic radii settled to be 1.4 Å); (c) considering the Zn-dmtrz dimer as a 6-connected node, **MAC-14** can be regarded as 6-connected $pcu$-type framework.
Fig. S7. The PXRD patterns of MAC-11 in common solvent.
Fig. S8. (a) the TGA data of as-made MAC-11 and MAC-13 (the first step weigh loss of MAC-11 agrees well with the weight loss of lattice water theoretically calculated from molecular weight, while MAC-13 is not. It could be ascribed to the severe disorder of the lattice water in MAC-13 that causes the difference between the TGA data and the molecular weight); (b) the TGA data of activated MAC-11 and MAC-13.
Fig. S9 the temperature-dependent PXRD patterns of MAC-13 (phase transformation: $2\theta = \sim 4.6^\circ$ shifts to $\sim 5.9^\circ$ and then shifts back to $5.3^\circ$ in water solution after 1 h)
Fig. S10. the temperature-dependent PXRD patterns of MAC-14 (the diffraction peak at $2\theta = \sim 4.6^\circ$ slightly shifts to $2\theta = \sim 4.9^\circ$. The shift is much smaller than that of MAC-11)
Fig. S11. The excitation and emission spectra of MAC-11

\[ \lambda_{\text{ex}} = 369 \text{ nm} \]

\[ \lambda_{\text{em}} = 418 \text{ nm} \]
Fig. S12. The emission spectra of 2D layer [Zn(dmtrz)(HCOO)] (a), H2L1 (b), their mixture (c) and MAC-14 before and after heated at 90 °C ($\lambda_{ex} = 369$ nm)
**Fig. S13.** (a) The FT-IR spectra of MAC-11 and MAC-11’ showing the disappearance of the vibration band at 1675 cm\(^{-1}\); (b) the FT-IR spectra of MAC-13 and MAC-13’ showing the similar change of the carboxylate groups as that of MAC-11 on the vibration band; (c) the FT-IR spectra of MAC-14 and MAC-14’, indicating that there is no obvious change on the vibration band of carboxylate group.