Supporting Information

Guest-Dependent Thermal Response of the Flexible MOF Zn₂(BDC)₂(DABCO)

Yonghwi Kim, a Ritesh Haldar, a Hyunuk Kim, d Jaehyoung Koo, a,b and Kimoon Kim*a,b,c

* To whom correspondence should be addressed. E–mail: kkim@postech.ac.kr

aCenter for Self-assembly and Complexity (CSC), Institute for Basic Science (IBS), bDepartment of Chemistry, and cDivision of Advanced Materials Science, Pohang University of Science and Technology, Pohang, 790-784 (Republic of Korea), dEnergy Materials Laboratory, Korea Institute of Energy Research, Daejeon, 305-343, Republic of Korea
Figure S1. Crystal structure of Zn$_2$(BDC)$_2$(DABCO) (1) at 298K. Ellipsoids are drawn at a 50% probability level and H atoms have been omitted for clarity.
Figure S2. Crystal Structure of 1·4DMF at 298K. Green and organe colored thick bonds in (b) are presenting the BDC linkers at different layers along the c-axis.
Figure S3. Crystal Structures of 1·4DMF at 298K (a, c, e), and 100K (b, d, f). Green and blue dashed lines indicate the CH⋯O interactions of DMF with DABCO and BDC, respectively.
**Table S1.** List of CH···O distances between DMF, and DABCO and BDC in 1·4DMF.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>CH···O distance between DABCO and DMF (Å)</th>
<th>CH···O distance between BDC and DMF (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>2.806</td>
<td>3.101</td>
</tr>
<tr>
<td>250K</td>
<td>2.784</td>
<td>3.073</td>
</tr>
<tr>
<td>200K</td>
<td>2.540</td>
<td>2.953</td>
</tr>
<tr>
<td>150K</td>
<td>2.552</td>
<td>2.921</td>
</tr>
<tr>
<td>100K</td>
<td>2.552</td>
<td>2.885</td>
</tr>
</tbody>
</table>

**Figure S4.** Framework structures of 1 and 1·3benzene at 298K.
Figure S5. Interatomic distances for selected atoms in the Zn$_2$ paddle wheel unit in 1 at different temperatures.

Figure S6. Zn$_2$ paddle wheel structures of Zn$_2$(BDC)$_2$(DABCO) at 298K (a) and 100K (b,c,d), respectively. The arrows are representing the directions of thermal responses upon cooling.
Figure S7. Three major vibration motions, contributing to the transverse vibration in Zn$_2$(BDC)$_2$(DABCO): libration (red arrows) and translation (green arrow) of the aromatic ring, and twisting of the paddle wheel unit (blue arrows).

Figure S8. Interatomic distances for selected carbon atoms at the aromatic ring of BDC in 1.
Figure S9. Crystal Structures of Zn₂(BDC)₂(DABCO) at 298K (a and c), and 100K (b and d). Blue arrows indicate the rotational direction of BDC ligands. Ellipsoids are drawn at a 50% probability level and H atoms have been omitted for clarity.
**Figure S10.** The Zn$_2$ paddle wheel structures of Zn$_2$(BDC)$_2$(DABCO) at 100K. The tilting angles of BDC are indicated for the aromatic rings (a) and carboxylates (b), respectively.

**Figure S11.** The local structures around the paddle wheel unit of [Zn$_2$(BDC)$_2$(DABCO)]·4DMF at 298 (a) and 100K (b), respectively.
Figure S12. The local structures around the paddle wheel unit of [Zn₂(BDC)₂(DABCO)]·3benzene at 298 (left) and 100K (right), respectively.

Figure S13. The tilting angle profile of BDC from the paddle wheel unit at different temperature.
Figure S14. The structures of $[\text{Zn}_2(\text{BDC})_2(\text{DABCO})] \cdot 3\text{benzene}$ at 298K (a) and 100K (b). Blue dash lines represent $\text{CH} \cdots \pi$ interactions between BDC and benzene.

Figure S15. The structures of $[\text{Zn}_2(\text{BDC})_2(\text{DABCO})] \cdot 3\text{benzene}$ at 298K. Guest benzene molecules are highlighted in green and blue.
**Figure S16.** The structural changes of $[\text{Zn}_2(\text{BDC})_3(\text{DABCO})] \cdot 3\text{benzene}$ upon cooling from RT to 100K.