Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Guest-Dependent Thermal Response of the Flexible MOF $Zn_2(BDC)_2(DABCO)$

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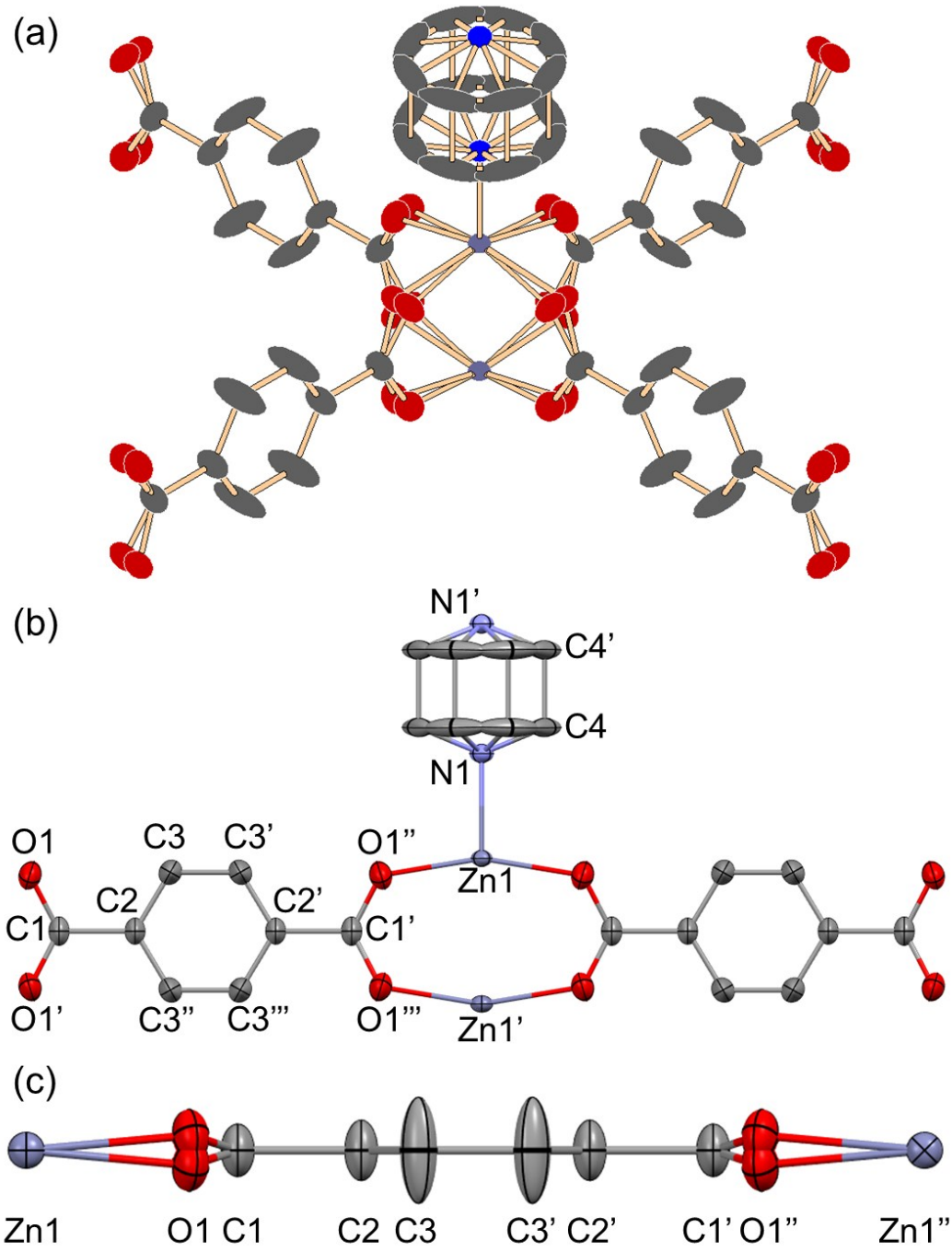

Figure S1. Crystal structure of $Zn_2(BDC)_2(DABCO)$ (**1**) at 298K. Ellipsoids are drawn at a 50% probability level and H atoms have been omitted for clarity.

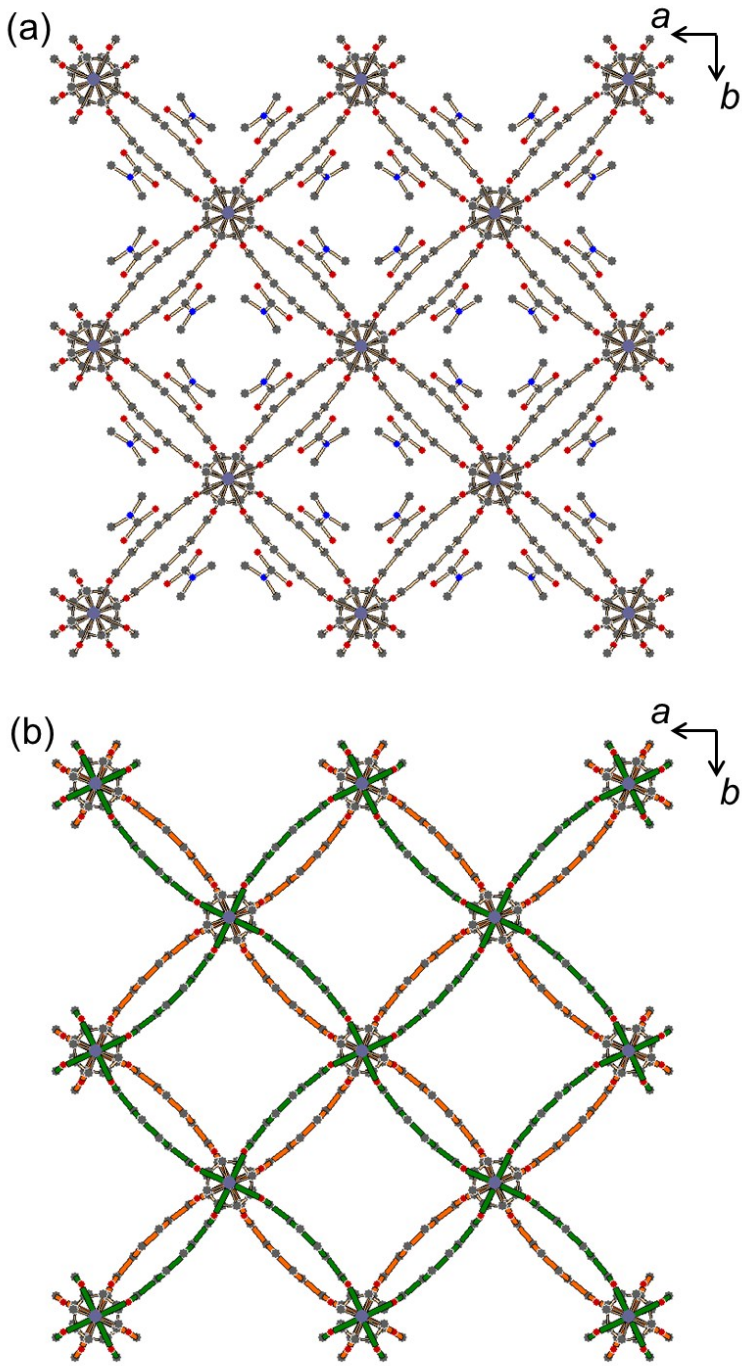

Figure S2. Crystal Structure of **1**·4DMF at 298K. Green and organe colored thick bonds in (b) are presenting the BDC linkers at different layers along the *c*-axis.

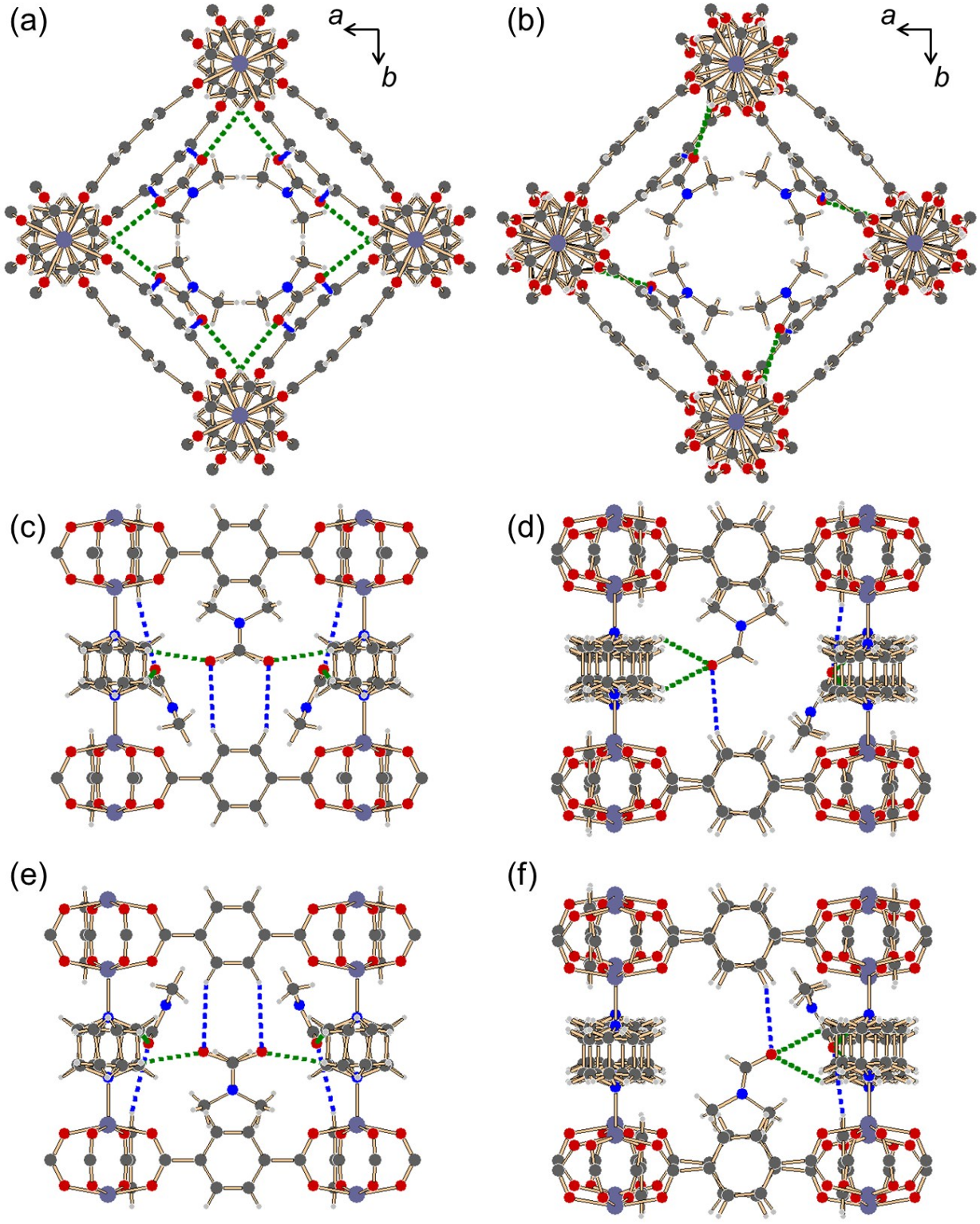

Figure S3. Crystal Structures of **1**·4DMF at 298K (a, c, e), and 100K (b, d, f). Green and blue dashed lines indicate the CH···O interactions of DMF with DABCO and BDC, respectively.

Table S1. List of CH···O distances between DMF, and DABCO and BDC in **1**·4DMF.

Temperature	CH···O distance between DABCO and DMF (Å)	CH···O distance between BDC and DMF (Å)
RT	2.806	3.101
250K	2.784	3.073
200K	2.540	2.953
150K	2.552	2.921
100K	2.552	2.885

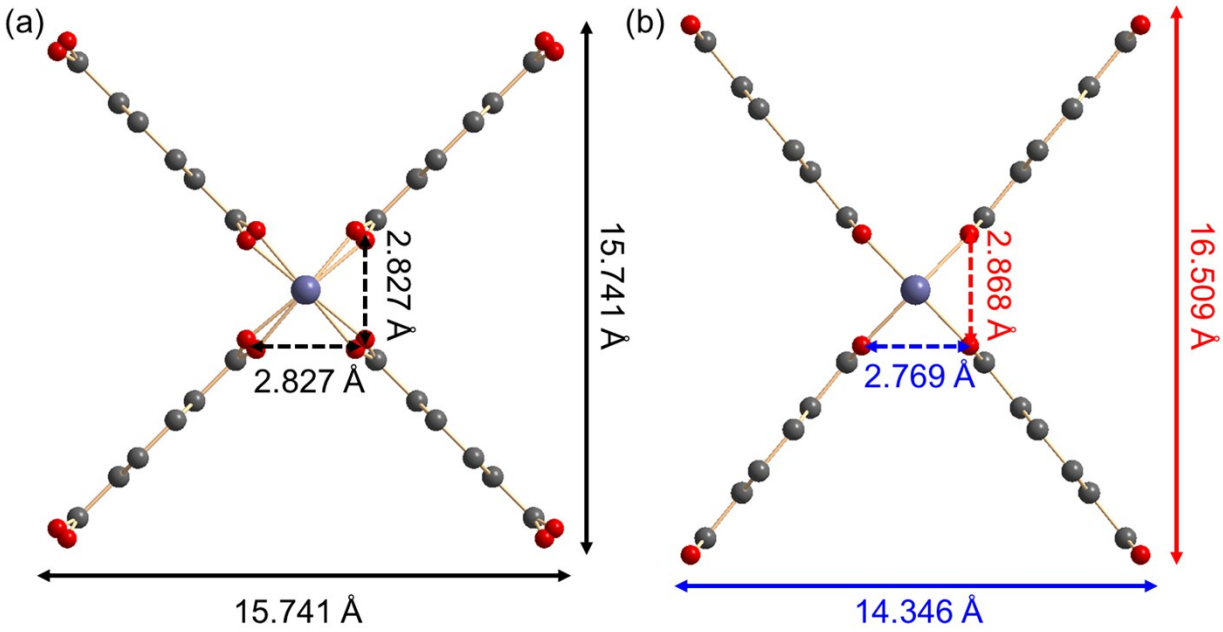

Figure S4. Framework structures of **1** and **1**·3benzene at 298K.

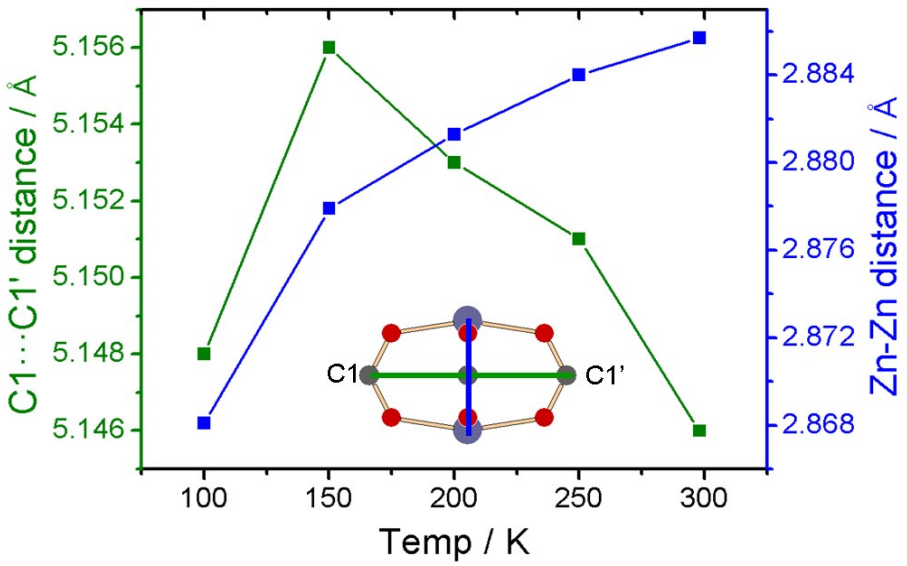

Figure S5. Interatomic distances for selected atoms in the Zn_2 paddle wheel unit in **1** at different temperatures.

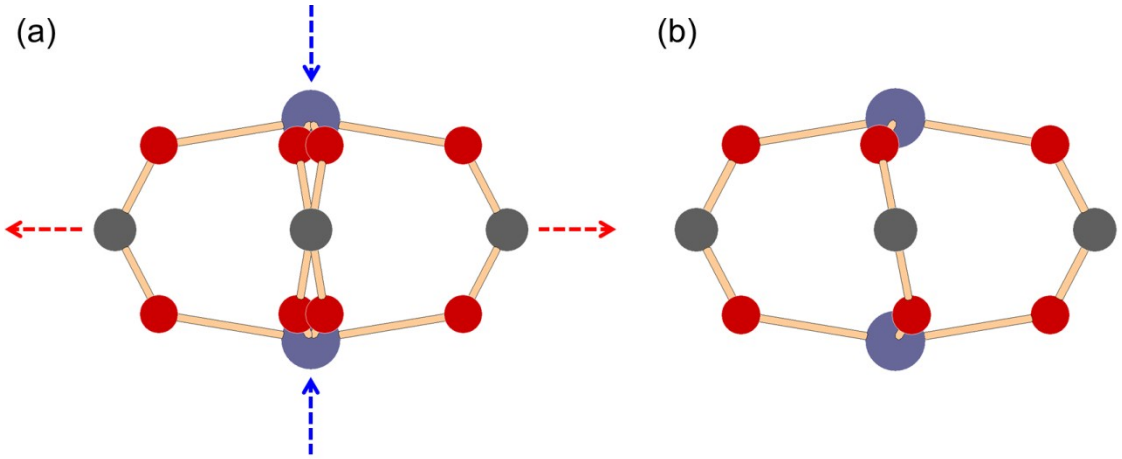

Figure S6. Zn_2 paddle wheel structures of $Zn_2(BDC)_2(DABCO)$ at 298K (a) and 100K (b,c,d), respectively. The arrows are representing the directions of thermal responses upon cooling.

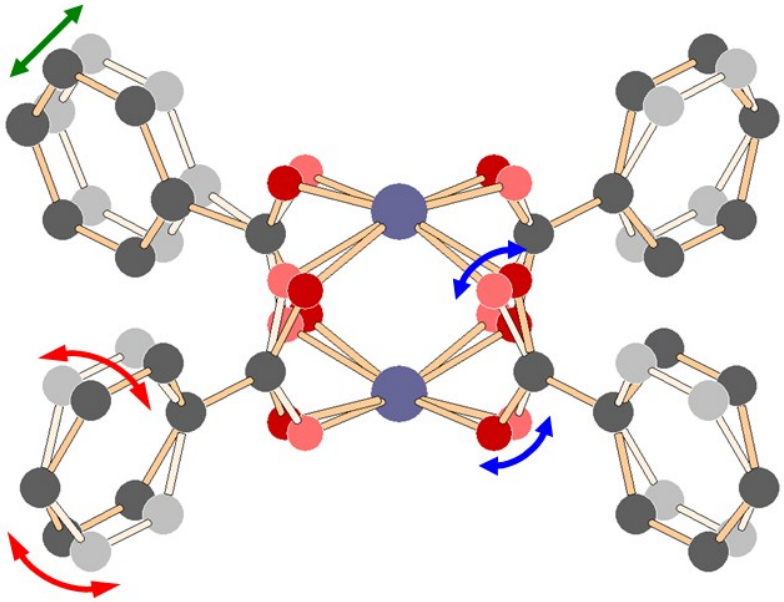

Figure S7. Three major vibration motions, contributing to the transverse vibration in $Zn_2(BDC)_2(DABCO)$: libration (red arrows) and translation (green arrow) of the aromatic ring, and twisting of the paddle wheel unit (blue arrows).

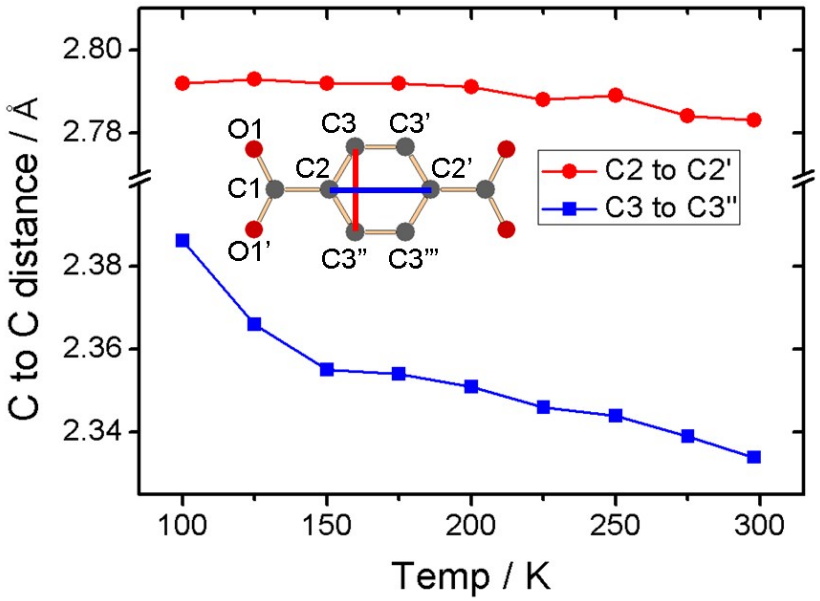

Figure S8. Interatomic distances for selected carbon atoms at the aromatic ring of BDC in **1**.

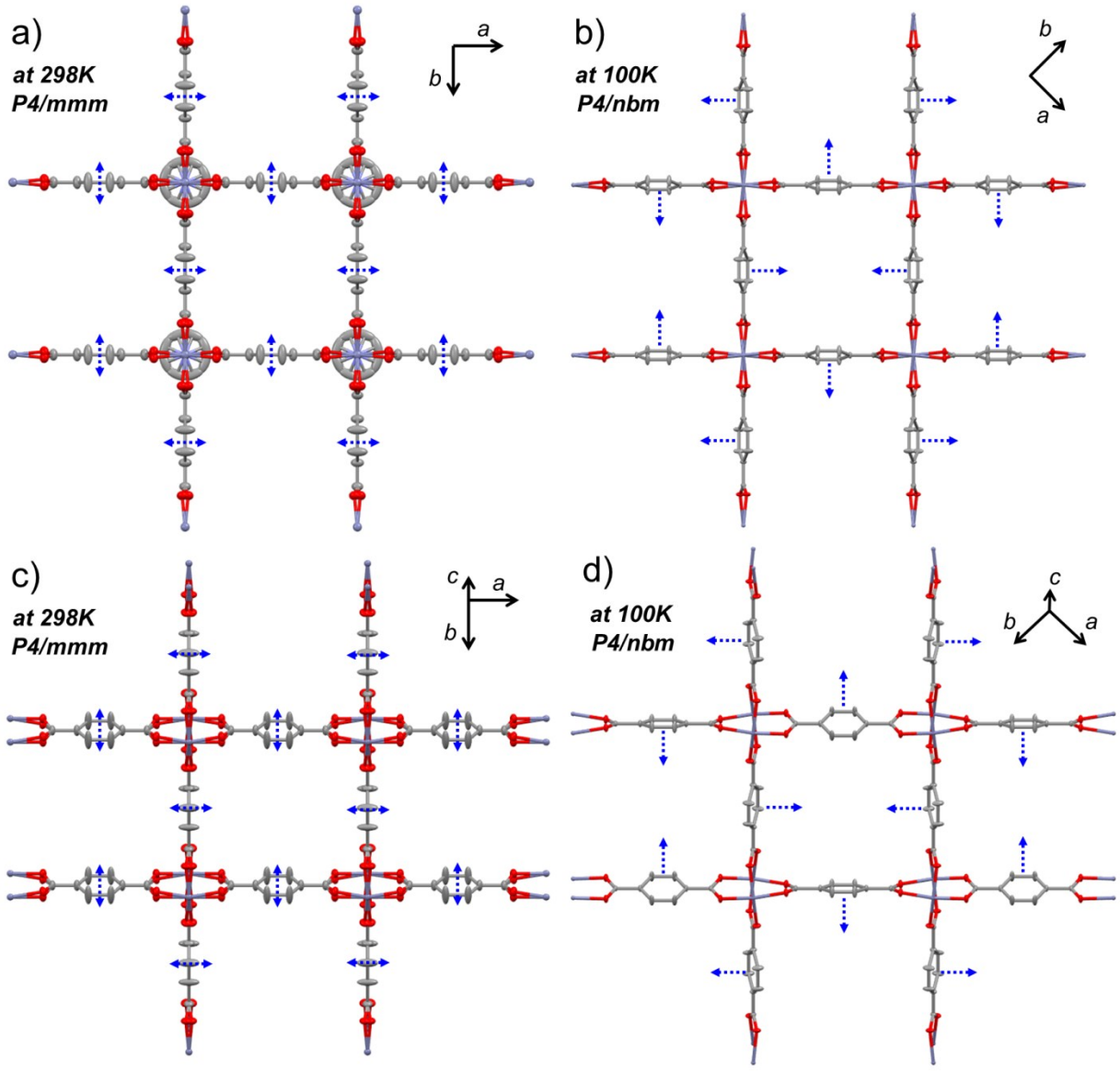

Figure S9. Crystal Structures of $Zn_2(BDC)_2(DABCO)$ at 298K (a and c), and 100K (b and d). Blue arrows indicate the rotational direction of BDC ligands. Ellipsoids are drawn at a 50% probability level and H atoms have been omitted for clarity.

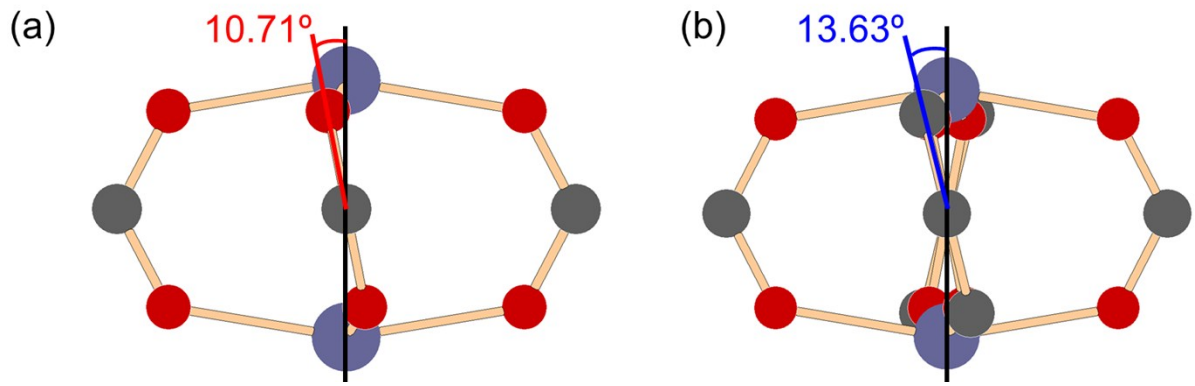

Figure S10. The Zn_2 paddle wheel structures of $Zn_2(BDC)_2(DABCO)$ at 100K. The tilting angles of BDC are indicated for the aromatic rings (a) and carboxylates (b), respectively.

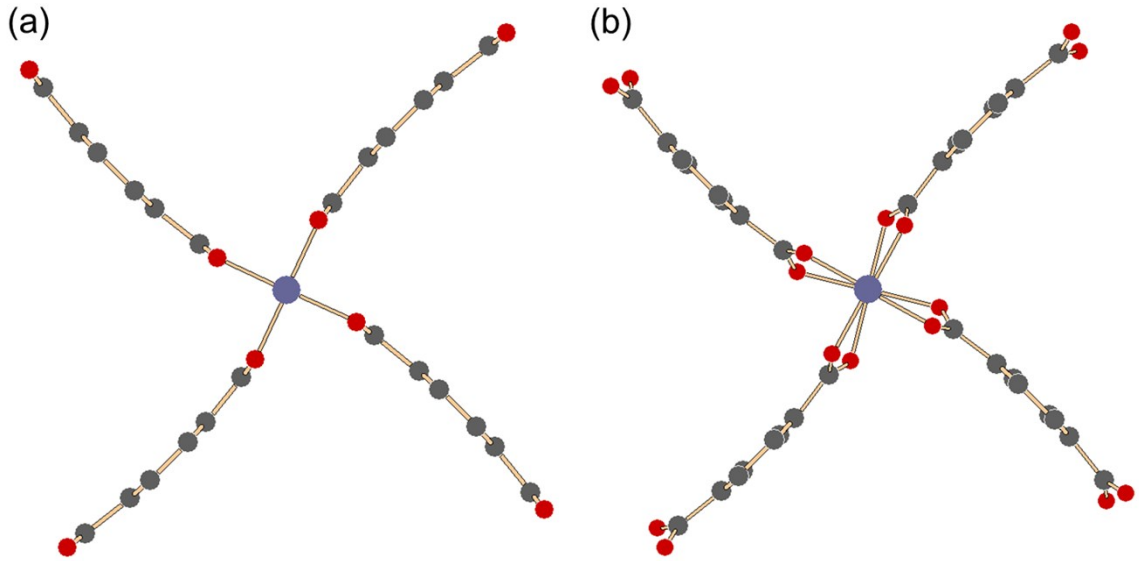

Figure S11. The local structures around the paddle wheel unit of $[Zn_2(BDC)_2(DABCO)]\cdot 4DMF$ at 298 (a) and 100K (b), respectively.

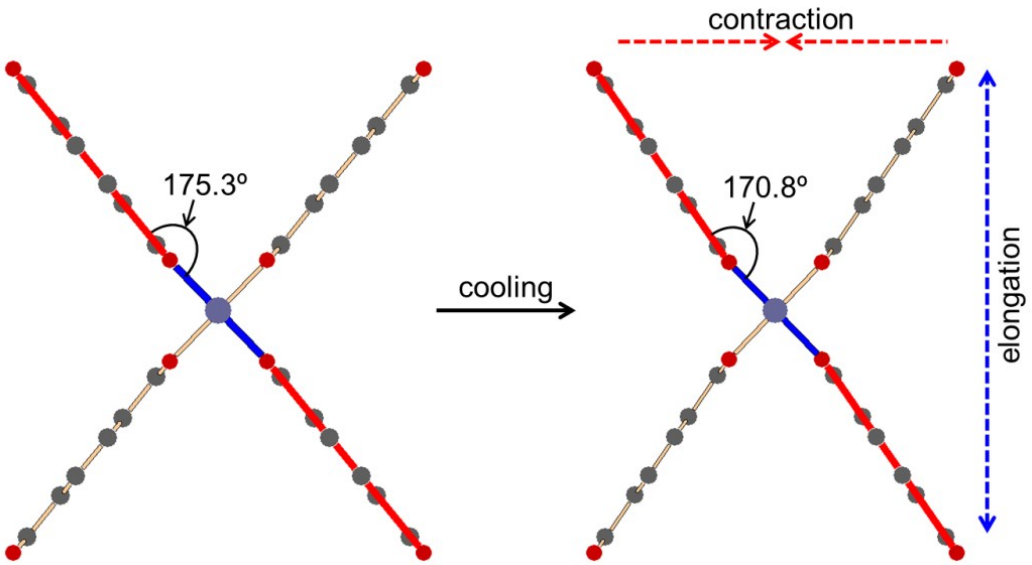

Figure S12. The local structures around the paddle wheel unit of $[Zn_2(BDC)_2(DABCO)]\cdot 3benzene$ at 298 (left) and 100K (right), respectively.

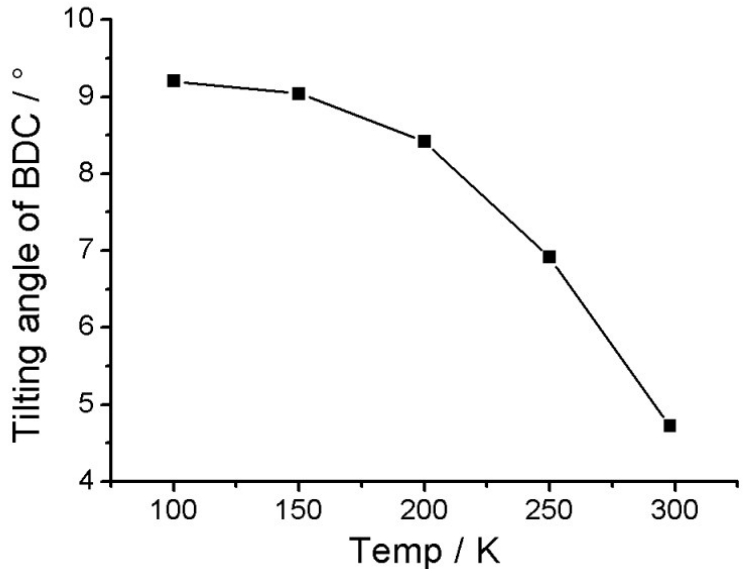

Figure S13. The tilting angle profile of BDC from the paddle wheel unit at different temperature.

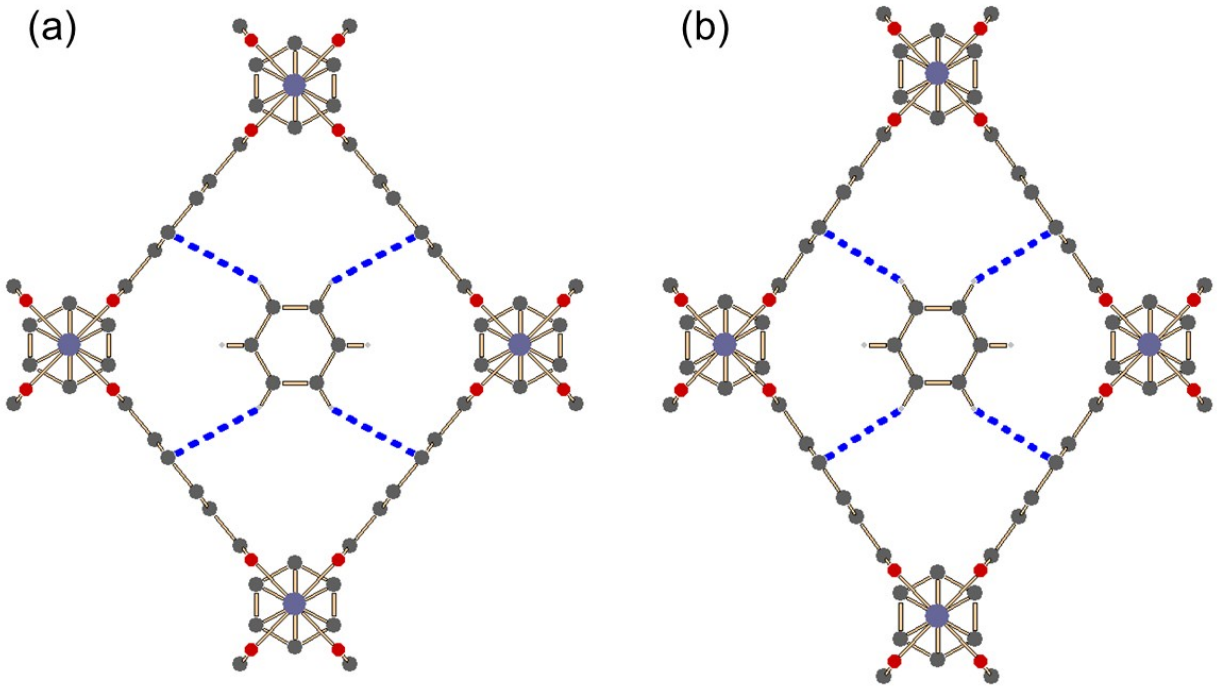

Figure S14. The structures of $[Zn_2(BDC)_2(DABCO)]\cdot 3$benzene at 298K (a) and 100K (b). Blue dash lines represent CH···π interactions between BDC and benzene.

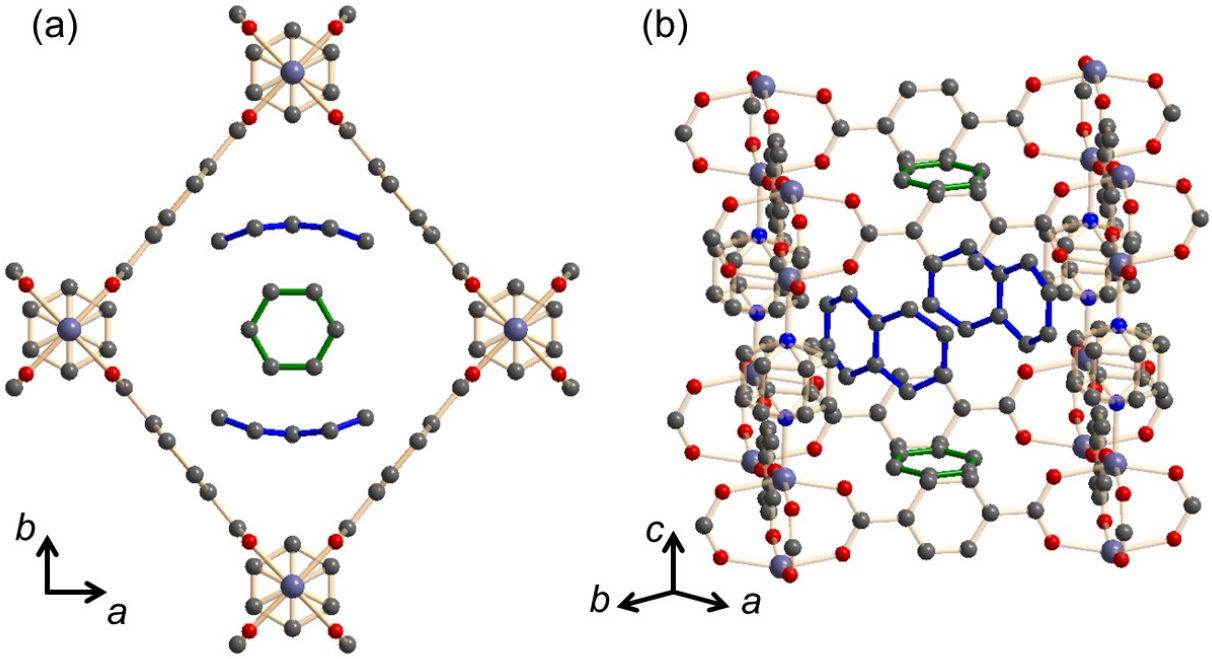

Figure S15. The structures of $[Zn_2(BDC)_2(DABCO)]\cdot 3$benzene at 298K. Guest benzene molecules are highlighted in green and blue.

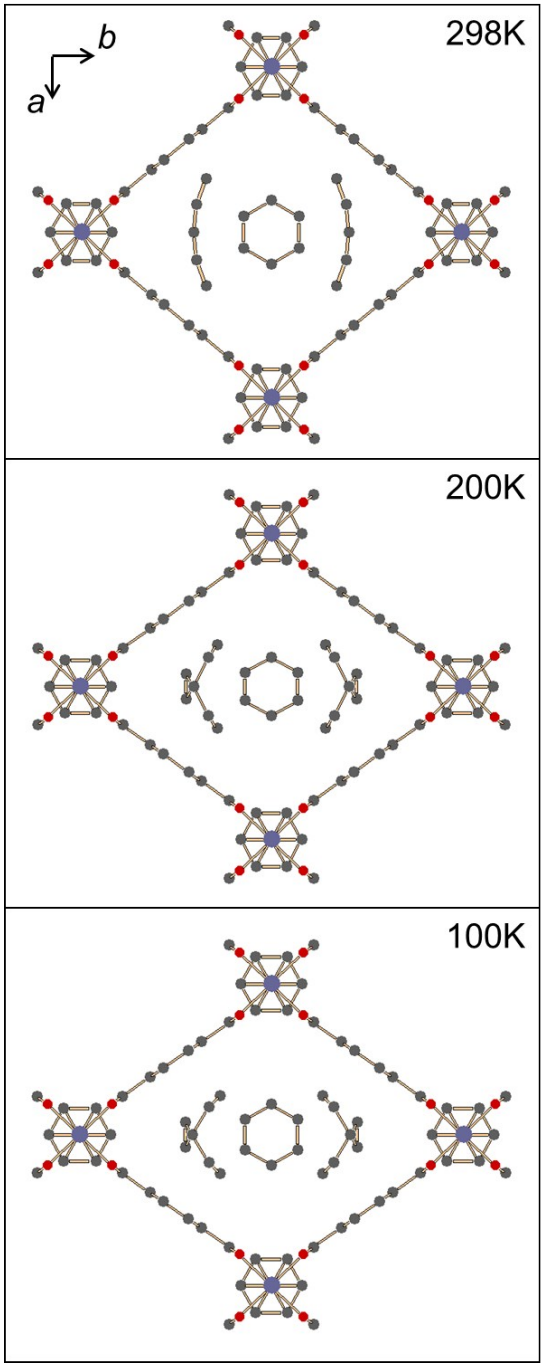

Figure S16. The structural changes of $[Zn_2(BDC)_2(DABCO)]\cdot 3$benzene upon cooling from RT to 100K.