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# Distinct interpenetrated metal–organic frameworks constructed from crown ether-based strut analogue†

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**Rigid struts containing crown ether units (benzo-12-crown-4 and benzo-15-crown-5) coordinate with $Zn_4O(CO_2)_6$ clusters, affording two different interpenetrated metal–organic frameworks (MOFs), *i.e.*, benzo-12-crown-4-based MOF presents a "close contact" interpenetration mode, while the benzo-15-crown-5-based one has a "body center" interpenetration mode.**

Since the first report on cyclic polyethers by Charles Pedersen in 1967,[1] these macrocyclic molecules and their analogs have attracted increasing attentions on account of their abilities to serve as host platforms for binding with organic and inorganic guests, making them widely useful in various areas such as supramolecular chemistry, biological science, materials science, and nanoscience.[2] As such, the design and synthesis of novel crown ether derivatives with superior properties and proper applications continue to be an important research area.

In the wake of the emergence and development of metal–organic frameworks (MOFs),[3] there is considerable interest in incorporating crown ether derivatives into porous metal–organic frameworks for potential applications. Some research groups have fabricated[4] such types of MOFs using struts consisting of the crown ether units or crown ether based mechanically interlocked molecules such as rotaxanes and catenanes. For example, Valente *et al.* recently described the synthesis of a linear organic strut possessing a bisparaphenylene[34]crown-10 recognition site and its subsequent incorporation into MOFs.[5] Such novel types of struts still present the intrinsic properties of the crown ether units, allowing the incorporation of specific features and functions into MOFs. The introduction of the crown ether units into MOFs has led to a new type of porous domain—the active domain—wherein an ordered distribution of guests within MOFs is maintained by highly specific supramolecular recognition in addition to the size and shape selectivity provided by the MOF itself.[6] It is well known that benzo-12-crown-4 and benzo-15-crown-5 have relatively small cavities, which are suitable for forming stable complexes[2n] with $Li^+$ ($k = 1.05 \times 10^3\ M^{-1}$ in dimethyl sulfoxide (DMSO)) and $Na^+$ ($k = 7.41 \times 10^2\ M^{-1}$ in DMSO), respectively, for a wide range of applications. In order to further explore the emerging research area, simple rigid struts consisting of such crown ethers were to be used for the preparation of MOFs.

Herein, we report the design and synthesis of the rigid struts (BC-4 and BC-5) containing benzo-12-crown-4 and benzo-15-crown-5 units and their incorporation into MOFs (MOF–BC-4 and MOF–BC-5), respectively. The synthesis of the struts BC-4 and BC-5 is outlined in Scheme 1. The intermediate **5** was prepared from commercially available 1,2-dihydroxybenzene in five steps (see the ESI†) according to a modified procedure.[7] Cyclization of **5** with either 1,2-bis(2-chloroethoxy)ethane or bis[2-(2-chloroethoxy)ethyl]ether afforded the macrocyclic intermediate **6a** or **6b** in a moderate yield on account of the template-assisted ring closure approach. Chemoselective Suzuki–Miyaura cross coupling of **6a** or **6b** with 4-(methoxycarbonyl)phenylboronic acid pinacol ester, followed by saponification, led to the diacid BC-4 or BC-5.‡

Direct evidence for the formation of the struts BC-4 and BC-5 was obtained in the single crystal forms by slow evaporation of BC-4 and BC-5 solutions in *N*,*N*-dimethylformamide (DMF) and DMSO, respectively. The crystal data and experimental and refinement parameters for the two crystals are listed in Tables S1 and S2 (see ESI†). $^1H$ NMR, UV-Vis and mass spectra (MS) were recorded (Fig. S10–S15 in the ESI†) for investigating the complexation between BC-4 and LiCl and between BC-5 and NaCl at different ratios. The downfield shifts, approximately 0.49 for BC-4 with $Li^+$ and 0.46 ppm for BC-5 with $Na^+$, of H resonances corresponding to the protons in crown ether rings are indicative of the inclusion complex formation. In addition, absorption and MS studies clearly demonstrate the complexation of BC-4 with $Li^+$ and BC-5 with $Na^+$. As shown in Fig. S12 and S13 (ESI†), the absorption intensities of BC-4 and BC-5 in DMF decrease upon the addition of

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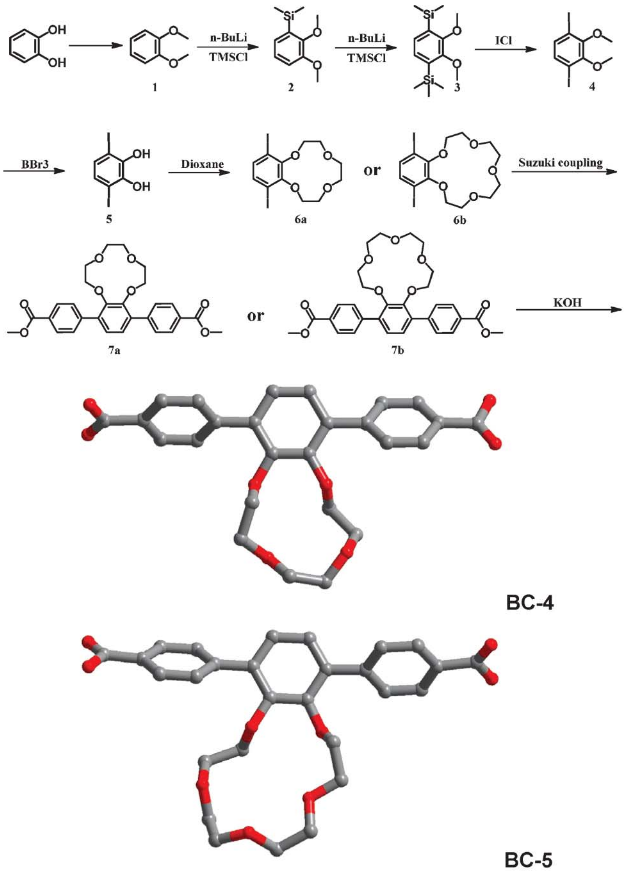
† Electronic supplementary information (ESI) available: Synthesis and characterization data, and CCDC 883383–883386. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26401c



**Scheme 1** Synthetic route leading to the production of dicarboxylic acid-terminated struts BC-4 and BC-5, and their X-ray single crystal structures. C, grey; O, red. Hydrogen atoms are omitted for clarity.

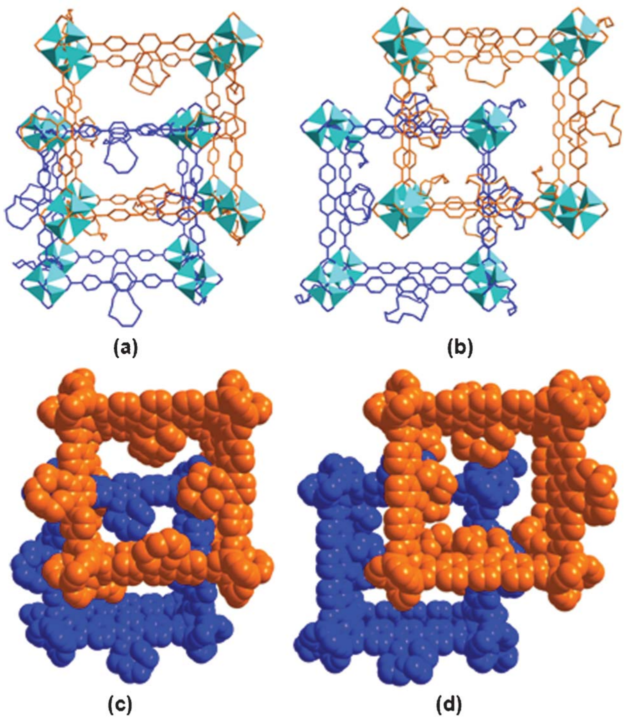


**Fig. 1** Crystal superstructures of (a) MOF–BC-4 and (b) MOF–BC-5. Hydrogen atoms and solvent molecules are omitted for the sake of clarity. Crown ether units with polyether chains and hydroquinone rings are colored dark blue/brown, and the metal joints are colored pale blue. The space filling representations for the crystal superstructures of (c) MOF–BC-4 and (d) MOF–BC-5. Atoms in the metal joints and the rigid backbones of the struts were located by single X-ray diffraction, and the crown ether units in both structures were modeled by Materials Studio.

$Li^+$ and $Na^+$ in the range of 250–330 nm, leading to high binding constants of $1.67 \times 10^4$ and $9.94 \times 10^5$ $M^{-1}$, respectively. Moreover, the absorption bands of the crown ether units around 280 nm are slightly shifted after the coordination with the metal cations. These spectral changes indicate the complex formation of BC-4 with $Li^+$ and BC-5 with $Na^+$, according to previous reports.[8] The ESI/MS signals at 471.23 and 531.17 (*m*/*z*) corresponding to $[BC\text{-}4{\cdot}Li]^+$ and $[BC\text{-}5{\cdot}Na]^+$ were detected for the samples of BC-4 with 1.0 equiv. of $Li^+$ and BC-5 with 1.0 equiv. of $Na^+$, respectively, further supporting the complex formation.

MOF–BC-4 $[Zn_4O(C_{26}H_{22}O_8)_3]$ and MOF–BC-5 $[Zn_4O(C_{28}H_{26}O_9)_3]$ were successfully prepared using a solvothermal approach. Either BC-4 or BC-5 in DMF in the presence of $Zn(NO_3)_2{\cdot}6H_2O$ was heated up in a programmable oven with a temperature increase step of 10 °C $h^{-1}$ to 70 °C, and the reaction mixture was then kept at this temperature for 48 h. Colorless crystals of MOF–BC-4 and MOF–BC-5 were analyzed by X-ray crystallography at low temperature, revealing the superstructures (Fig. 1) isoreticular with IRMOF-15, a MOF prepared from the triphenyl rigid strut without the crown ether unit.[9] Rigid struts emanate from each secondary building unit (SBU)—$Zn_4O(CO_2)_6$ cluster—in an octahedral array to form a framework with the $P4_2/ncm$ space group for MOF–BC-4 and a framework with the $Im\bar{3}m$ space group for MOF–BC-5, both in *pcu* topology.[10] The crown ethers were found to be highly disordered, thus cannot be located precisely. Nonetheless, the positions of all the atoms in the inorganic SBUs and the rigid backbone of the struts are unambiguous.

The side length of the cube defined by eight SBUs and twelve struts is 21.5 Å for both MOF–BC-4 and MOF–BC-5. It is not surprising that the slender nature of the struts brings interpenetration to the frameworks. Similar to IRMOF-15, both SBU and BC-5 in MOF–BC-5 were disordered over two sites with an equal probability. The SBUs from the second framework (Fig. 2) occupy the body center of the first framework cube in MOF–BC-5. In MOF–BC-4, however, the SBUs in the second framework are away from the body center of the first framework by 6.5 Å in the *c* direction (Fig. 2). Analysis by TOPOS[11] indicates that the interpenetration of MOF–BC-4 belongs to class IIa, while the interpenetration of MOF–BC-5 belongs to class Ia (the two interpenetrated networks are generated by translation). A closer examination of MOF–BC-4 reveals that the closest distance between two struts from two frameworks is 3.8 Å, which suggests a π–π stacking interaction between two central phenyl rings of the two struts along the *c* direction perpendicular to each other (Fig. 2). Two types of the strut conformations were observed in

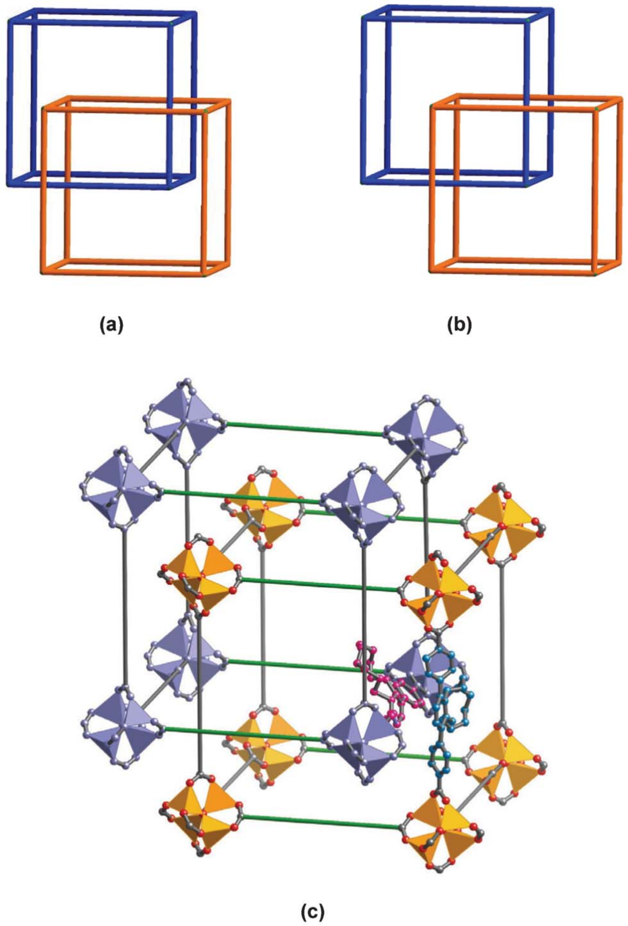


**Fig. 2** Representation of different interpenetration modes for (a) MOF–BC-4 and (b) MOF–BC-5. (c) The π–π stacking interaction between two central phenyl rings of the two struts (in blue and pink) in MOF–BC-4. Struts with coplanar carboxylates are colored green, and struts with perpendicular carboxylates are colored grey.

MOF–BC-4. For each SBU, there are two struts with coplanar carboxylates at the ends along the *c* axis, and the other four struts connect neighboring SBUs with carboxylates perpendicular to each other (in which crown ether units could be fully located by single crystal X-ray diffraction, see Fig. S17 in the ESI†). The resulting reduction in symmetry, along with the π–π stacking interaction, makes the doubly interpenetrated "close-contact" fashion favorable for MOF–BC-4. Compared to MOF–BC-5, the smaller crown ether ring size in MOF–BC-4 enables the crown ether units to be less bulky and flexible, thus the struts are easier to accommodate in the confined geometry and conformation.

The calculated densities of MOF–BC-4 and MOF–BC-5 are 0.60 and 0.56 g $cm^{-3}$, respectively, and they are in the same range with other highly porous MOFs, such as MOF-5 (0.59 g $cm^{-3}$).[12] In comparison, the densities of BC-4 and BC-5 crystals obtained are 1.32 and 1.35 g $cm^{-3}$ (including crystallized solvent molecules). After the activation of the MOFs through solvent exchange method from DMF to EtOH (or to $CHCl_3$) followed by vacuum drying at room temperature, low surface areas (103.8 $m^2$ $g^{-1}$ for MOF–BC-4 and 80.1 $m^2$ $g^{-1}$ for MOF–BC-5) were determined from the $N_2$ adsorption isotherms measured at 77 K. Both activated MOF–BC-4 and MOF–BC-5 present relatively low metal ion sorption capacity towards $Li^+$ (0.08 wt%) and $Na^+$ (0.06 wt%), respectively, when immersing the MOF crystals into the corresponding metal ion solution (1 mM) in DMF/$H_2O$ (v/v = 100 : 1) overnight at room temperature followed by the ICP-MS (inductively coupled plasma mass spectrometry) analysis. Powder X-ray diffraction (PXRD) measurements showed that bulky crystalline samples of as-synthesized MOF–BC-4 and MOF–BC-5 have good phase purities (Fig. S19 in the ESI†). PXRD of the samples after activation shows lower quality of patterns with broader peak width, even though the main diffraction peaks remain (Fig. S20 in the ESI†).

Thermal gravimetric analysis was performed (Fig. S23 and S24 in the ESI†) in order to evaluate the thermal stabilities of MOF–BC-4 and MOF–BC-5. The percentage weight-loss patterns of both as-synthesized MOF–BC-4 and MOF–BC-5 reveal nearly identical decomposition temperatures at approximately 350 °C. The stepwise weight-loss patterns between 350–550 °C for MOF–BC-4 and MOF–BC-5 are attributed to the subsequent decomposition of the organic struts, since BC-4 and BC-5 show similar decomposition profiles.

In summary, we have successfully incorporated the struts containing benzo-12-crown-4 and benzo-15-crown-5 units into the three-dimensional frameworks, MOF–BC-4 and MOF–BC-5, respectively, through the coordination with $Zn(NO_3)_2 \cdot 6H_2O$. The single crystal superstructures reveal that both MOF–BC-4 and MOF–BC-5 adopt doubly interpenetrated frameworks, but with significantly different interpenetration modes. Their supramolecular recognitions towards alkali metal ions were further investigated. The expected binding ability in the solid–solution interface was hindered on account of framework collapse after vacuum activation, together with increased rigidity of the crown ethers after their incorporations into the interpenetrated MOFs with restrained pore environments. The present work sheds light on the introduction of macrocyclic molecules into three-dimensional frameworks for the construction of novel functional materials.

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‡ MOF synthesis: in a one-pot reaction, $Zn(NO_3)_2 \cdot 6H_2O$ (0.3 mmol) was added to a DMF solution (8 mL) of either BC-4 or BC-5 (0.06 mmol), leading to a clear and colorless solution after stirring for 10 min. Then, the resulted homogeneous solution was placed in a programmable oven, with a temperature increase step of 10 °C $h^{-1}$ to 70 °C, and was kept at this temperature for 48 h. The reaction mixture was cooled down to room temperature, and the colorless crystals were collected for single crystal

X-ray diffraction analysis. Crystal data for MOF–BC-4: $C_{70}H_{48}O_{21}Zn_4$, $M_r$ = 1486.64, tetragonal, space group $P4_2/ncm$, $T$ = 143(2) K, $a$ = 21.4901(11) Å, $c$ = 42.883(4) Å, $V$ = 19805(2) Å$^3$, $\lambda$ = 0.71073 Å, $Z$ = 4, independent reflections 6856, $R_{int}$ = 0.1495, $R_1$ [$I > 2\sigma(I)$] = 0.0767, w$R_2$ (all data) = 0.2301, GOF = 0.945. Crystal data for MOF–BC-5: $C_{60}H_{24}O_{13}Zn_4$, $M_r$ = 1214.27, cubic, space group $Im\bar{3}m$, $T$ = 153(2) K, $a$ = 21.4744(13) Å, $V$ = 9902.9(10) Å$^3$, $\lambda$ = 0.71073 Å, $Z$ = 2, independent reflections 907, $R_{int}$ = 0.1062, $R_1$ [$I > 2\sigma(I)$] = 0.0921, w$R_2$ (all data) = 0.3150, GOF = 1.105. The MOF crystals were weakly diffracting and the structures were extensively disordered, thus partial bismethylenedixoy units and solvent molecules cannot be located. Full structure formulas for MOF–BC-4 and MOF–BC-5 are $[Zn_4O(C_{26}H_{22}O_8)_3]\cdot 8.5(C_7H_7NO)$ and ($[Zn_4O(C_{28}H_{26}O_9)_3]\cdot 9.5(C_7H_7NO)$, respectively, estimated by PLATON/SQUEEZE. Crystal data for BC-4: $C_{35}H_{45}N_3O_{11}$, $M_r$ = 683.74, triclinic, space group $P\bar{1}$, $T$ = 103(2) K, $a$ = 9.2812(5) Å, $b$ = 10.8141(7) Å, $c$ = 17.5421(12) Å, $V$ = 1722.44(19) Å$^3$, $\alpha$ = 90.146(4)°, $\beta$ = 96.815(4)°, $\gamma$ = 99.763(3)°, $\lambda$ = 0.71073 Å, $Z$ = 2, independent reflections 6776, $R_{int}$ = 0.0766, $R_1$ [$I > 2\sigma(I)$] = 0.0761, w$R_2$ (all data) = 0.1942, GOF = 1.130. Crystal data for BC-5: $C_{32}H_{40}O_{11}S_2$, $M_r$ = 664.76, triclinic, space group $P\bar{1}$, $T$ = 103(2) K, $a$ = 9.5432(16) Å, $b$ = 10.5250(19) Å, $c$ = 17.1192(31) Å, $V$ = 1641.6(5) Å$^3$, $\alpha$ = 105.358(8)°, $\beta$ = 93.281(9)°, $\gamma$ = 96.235(9)°, $\lambda$ = 0.71073 Å, $Z$ = 2, independent reflections 5704, $R_{int}$ = 0.0998, $R_1$ [$I > 2\sigma(I)$] = 0.0587, w$R_2$ (all data) = 0.1827, GOF = 1.006.

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