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Stabilization of a highly porous metal–organic framework utilizing a carborane-based linker†

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The first tritopic carborane-based linker, H_3BCA ($C_{15}B_{24}O_6H_{30}$), based on *closo*-1,10-$C_2B_8H_{10}$, has been synthesized and incorporated into a metal–organic framework (MOF), NU-700 ($Cu_3(BCA)_2$). In contrast to the analogous MOF-143, NU-700 can be activated with retention of porosity, yielding a BET surface area of 1870 $m^2\ g^{-1}$.

Metal–organic frameworks (MOFs) are a class of porous crystalline materials with tailorable pore volumes and high surface areas. The chemical diversity of MOFs has led to extensive studies of their potential applications in areas including ion exchange,[1,2] catalysis,[3–6] separation,[7–10] sensing,[11–13] and gas storage.[14–19] Of particular interest are applications in gas storage, where high surface areas play a critical role in the gas sorption properties of MOFs. Two notable examples of high surface area MOFs, MOF-177 and MOF-200, are synthesized using Zn^{2+} in combination with tritopic linkers.[20] Key to achieving this high surface area is the process of activation, which removes residual solvents and excess reagents from the pores. Activation is typically achieved by applying vacuum after solvent exchange or by CO_2 supercritical drying after solvent exchange.[21,22] In contrast to Zn^{2+} MOFs, there are few examples of Cu^{2+}-based MOFs that contain tritopic linkers that can be fully activated, as activation generally results in structural collapse and loss of porosity. One exception to this is HKUST-1, which contains the prototypical tritopic linker trimesic acid, and when activated yields a surface area of 1240 $m^2\ g^{-1}$ (Fig. 1a). Expansion of the trimesic acid linker with a phenyl spacer gives the crystalline framework, MOF-143 ($Cu_3(BTB)_2$) [BTB = 1,3,5-benzenetrisbenzoate] (Fig. 1b). Surprisingly, upon activation, the MOF-143 framework collapses, resulting in loss of crystallinity and very low surface area.

Carboranes are a fascinating family of compounds with high chemical and thermal robustness, unique geometry, rigidity, and synthetic versatility.[23] Recently, we have shown that the incorporation of icosahedral carboranes ($C_2B_{10}H_{12}$) and their derivatives into MOFs engenders many desirable properties, including, enhanced thermal stability,[24–26] increased *volumetric* surface area,[27] and the formation of unusual topologies.[28] Therefore we sought to couple these concepts—the use of tritopic ligands and carboranes—to synthesize a stable and highly porous MOF. Herein, we have used a tritopic linker, based on the 10-vertex carborane *closo*-1,10-$C_2B_8H_{10}$, to synthesize **NU-700**, an analogue of the previously reported organic-based MOF-143, (Fig. 1b and c). **NU-700** was successfully activated, and reversible gas sorption measurements revealed a surface area of 1870 $m^2\ g^{-1}$. This is in stark contrast to MOF-143, which cannot be activated.

The tritopic carborane linker, H_3BCA, was obtained *via* a three-step synthesis starting from *closo*-1,10-$C_2B_8H_{10}$ (Scheme 1).[29,30] Detailed experimental procedures are presented in the ESI.† Briefly, 1,3,5-tribromobenzene and 1-Cu-*closo*-1,10-$C_2B_8H_9$ were stirred in THF for 12 h at 70 °C to produce 1,3,5-tris(1′-$C_2B_8H_9$)benzene. Subsequent treatment with *n*-BuLi and ethyl chloroformate produced the tri-ester, which was saponified to give linker H_3BCA in 48% overall yield (Scheme 1).

NU-700 ($Cu_3(BCA)_2(H_2O)_3$) was synthesized *via* the solvothermal reaction between linker H_3BCA and $Cu(NO_3)_2{\cdot}2.5H_2O$ in a 1:1 mixture of DMF/NMP at 90 °C for 48 h. Single-crystal X-ray diffraction was used to determine the structure of **NU-700**, which revealed that **NU-700** crystallizes in the $Pm\bar{3}n$ (no. 223) space group. The experimental unit cell dimensions are a = 28.973(2) Å, and the solvent-accessible void space is 79% as calculated *via* PLATON.[31] The tritopic linkers are connected *via* bis-copper paddlewheel nodes to give a structure with the **pto** topology. Thus, **NU-700** is an isoreticular analogue of MOF-143, which contains the tritopic H_3BTB linker (Fig. 1b). Because the C···C distances across the

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† Electronic supplementary information (ESI) available: General procedures, materials, and instrumentation; synthesis, characterization (^1H, ^{13}C, ^{11}B NMR, HR-MS, elemental analysis) for **1**, **2** and **H_3BCA**. Synthesis, characterization and crystallographic information files (CIF) for **NU-700**; PXRD, adsorption excess isotherms, and TGA analysis. Crystallographic data for compound **1** and **NU-700** in cif format. CCDC 1016255 and 1016256. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc09212k

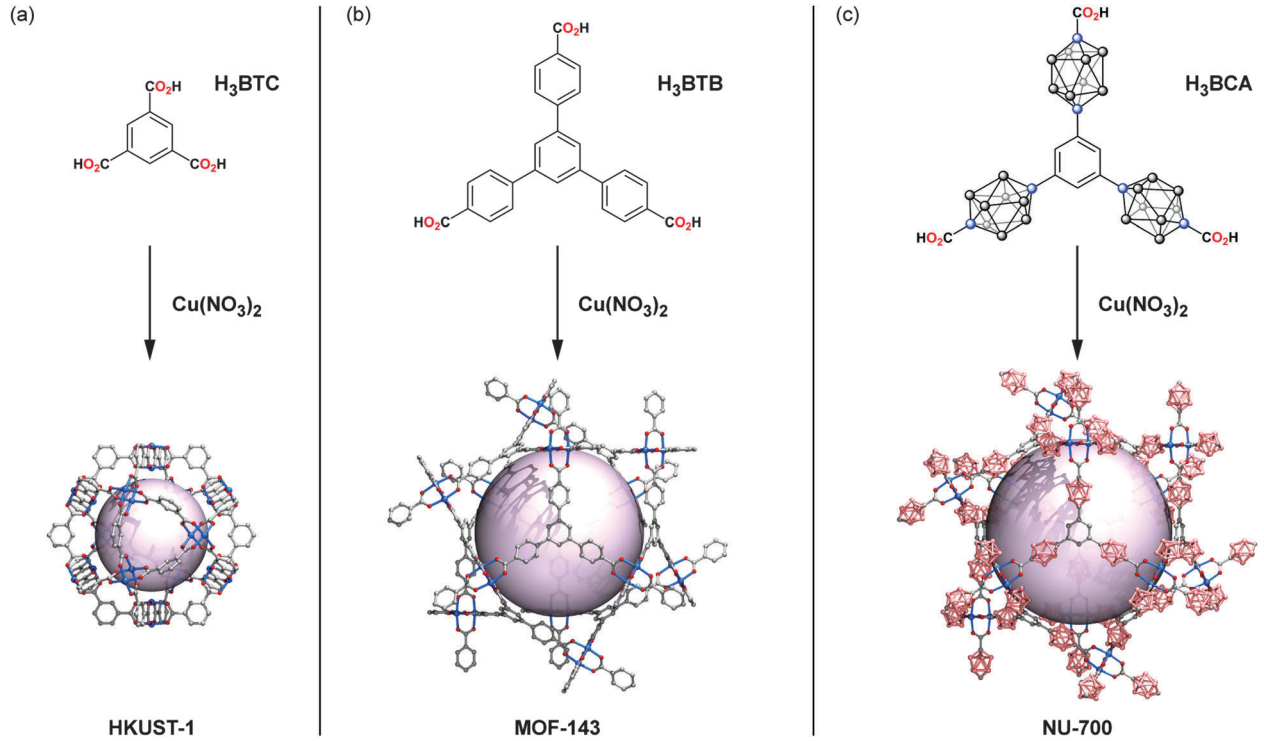
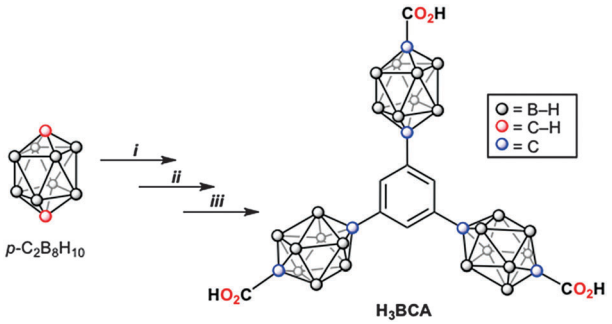


Fig. 1 Detail of pores, viewed along the [111] axis of (a) HKUST-1; (b) MOF-143; (c) **NU-700**. Lilac spheres indicate the largest sphere-shaped voids that can be found within the evacuated MOF as defined by the internal van der Waals surface of the material. Hydrogen atoms removed for clarity.



Scheme 1 Reaction conditions: (i) *n*-BuLi, THF; CuCl, THF −40 to 70 °C; 1,3,5-tribromobenzene, $PdCl_2(PPh_3)_2$, 70 °C, 12 h (79%). (ii) *n*-BuLi, THF; ethyl chloroformate −78 °C to rt, 12 h (68%); (iii) LiOH, THF/EtOH/H_2O 3 : 2 : 1, rt, 12 h; H_3O^+ (90%).

closo-1,10-$C_2B_8H_8$ moieties (3.35 Å) in linker H_3BCA are greater than the corresponding distances across the *para*-phenylene units (*ca.* 2.77 Å) of H_3BTB, the unit cell dimensions of **NU-700** are 1.5 Å longer than those of MOF-143. The enlarged linker of **NU-700** also increases the absolute pore volume of **NU-700** when compared to that of MOF-143. But due to the globular nature of the carboranes, the calculated void fraction of **NU-700** is 7% lower than that of MOF-143.

The activation of **NU-700** was achieved using a multi-step procedure: upon completion of the solvothermal reaction, the mother liquor was decanted and exchanged for ethanol once a day for three days. Guest solvent molecules were then removed *via* supercritical CO_2 (see ESI† for details), and coordinated solvent molecules were removed *via* subsequent heating at 120 °C for 12 h under dynamic vacuum.

Upon complete activation of **NU-700**, the porosity was measured using nitrogen adsorption at 77 K. The experimental Brunauer–Emmet–Teller (BET)[32] surface area was determined to be 1870 $m^2\ g^{-1}$ (Fig. 2), which is approximately 40% of the calculated surface area of **NU-700**.[33] The improved stability of **NU-700** over MOF-143 is attributed to the unique properties of the constituent carboranyl moieties. As mentioned above,

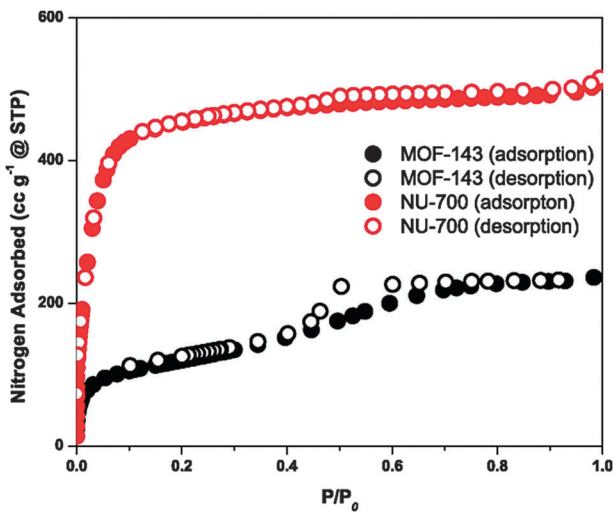


Fig. 2 Nitrogen adsorption and desorption isotherms of **NU-700** (red) and MOF-143 (black) at 77 K.

closo-dicarbaboranes have exceptional thermodynamic and kinetic stability, and it has been shown that MOFs constructed from carborane moieties also exhibit high stability.[24] The surface of the carborane is composed of radially oriented, hydridic B–H units, and exhibits a highly symmetric and uniform charge density that potentially prevents strong interactions with solvent molecules. The difference in porosity observed in these two MOFs therefore is hypothesized to be a result of how each framework interacts with solvents during the activation process. Importantly, in comparison to the phenylene units traditionally used to synthesize MOF linkers, the three-dimensional *closo*-1,10-$C_2B_8H_8$ moiety is considerably more sterically demanding. It is hypothesized that these steric effects rigidify the framework, leading to enhanced stability, as the collapse of the framework during activation would require the linkers to flex and rotate.

In summary, we have demonstrated the first synthesis of a MOF (**NU-700**) that contains a tritopic linker that is based on a carborane unit (*closo*-1,10-$C_2B_8H_{10}$). In contrast to MOF-143, which contains a phenylene-based ligand, **NU-700** can be activated revealing a surface area of 1870 $m^2\ g^{-1}$. This work demonstrates a potentially general platform for stabilization of difficult to activate MOFs, whereby simple replacement of phenyl spacers with carboranes does not affect the underlying structure.

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33 The theoretical maximum surface areas in the solvent free frameworks were calculated to be 4725 $m^2\ g^{-1}$ and 4740 $m^2\ g^{-1}$ for **NU-700** and MOF-143, respectively.