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Controlling phase in low-nuclearity calixarene-capped porous coordination cages with ligand functionalization

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Porosity in low-nuclearity coordination cages is relatively rare as cages with larger pore sizes are usually targeted as a way to increase gas adsorption capabilities in this promising class of molecular adsorbents. This work presents the design, synthesis, and characterization of a series of carbazole dicarboxylic acid bridged calixarene capped cages that exhibit significant porosity to N_2 and CO_2 given their limited size, presenting with Braun-Emmett-Teller (BET) surface areas in excess of 450 m^2/g and 350 m^2/g, respectively. Furthermore, we report, to the best of our knowledge, the first class of calixarene capped cages bridged by a ligand with a 90° bridging angle in addition to the first permanently porous calixarene cage to utilize Mn^{2+} cations.

As reports of permanent porosity in coordination cages have increased over the past decade[1], so too have investigations into tuning the properties of these materials.[2,3,4] The packing of cages in the solid state and their amenability to solution-based characterization and modification strategies can be controlled through choice of the metal cations that comprise these cages or functionalization of their organic ligands.[5,6] The former approach is particularly important for porous coordination cages containing metal cations with coordinatively-unsaturated sites.[7,8] For many cages, particularly cluster-capped structures, ligand functionalization is the primary route to tune these highly promising materials where judiciously placed organic groups can be installed to give a measure of control over surface area,[9] adsorption selectivity,[10] solubility,[11] and even phase.[12]

A particular challenge for the modification of specific permanently porous coordination cages, however, is that ligand placement is often not necessarily compatible with the installation of functional groups. Calixarene-capped coordination cages are a particularly compelling example of this. These polyhedral structures, which are often referred to as Metal-Organic Super Container (MOSC) or Changchun Institute of Applied Chemistry (CIAC) families of materials, feature thiacalix[4]arene (TC4A) or sulfonylcalix[4]arene (SC4A) capping units at their vertices and di- or tri-carboxylate ligands at their edges or faces. MOSCs, which utilize SC4A as its capping unit, have been categorized by "type" depending on the carboxylic acid based bridging ligand used in the synthesis (Figure 1).[13,14,15,16] While the calixarene capping units of these cages are functionalizable, only cages that use terephthalic acid or isophthalic acid ligands have been shown to incorporate functionality via functionalized bridging ligands[15,17] Although additional structure types have been reported using thiophene or benzoate derivatives (Figure 1).[18,19] We targeted carbazole-based ligands in this work for the purpose of synthesizing low-nuclearity calixarene-capped cages that resemble the geometry observed in type IV calixarene cages while employing bridging ligands with a significantly lesser binding angle than those previously reported.[16] The use of carbazole based ligands also allows for an easier route for functional group incorporation that is not as straight forward when using dibenzoate derivatives.

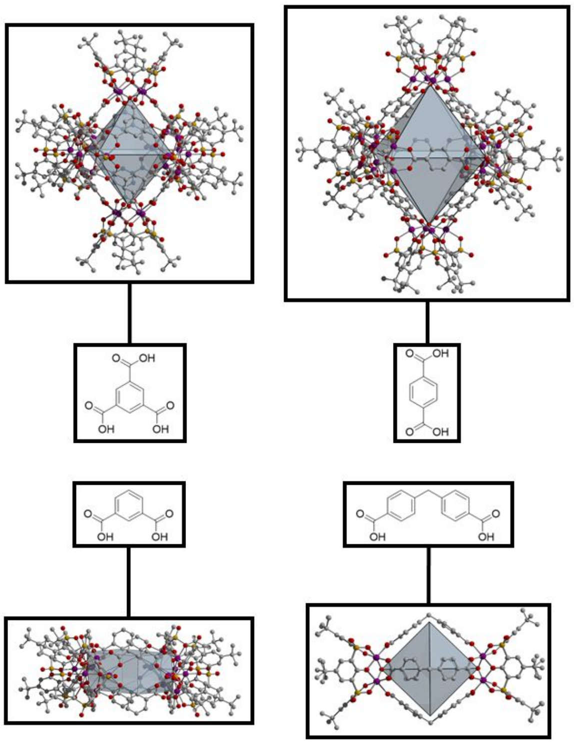

Fig. 1 Multicarboxylate-based ligands and the cages they form when used in tandem with SC4A. Cages based on triangular (Type I) (top left), linear (Type II) (top right), bent (Type III) (bottom left), and extended bent (Type IV) (bottom right) linkers have been reported.

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The 9-position of carbazoledicarboxylate has been shown to be of significant importance when incorporating this ligand into porous materials. Linking two of these molecules via Sonogashira coupling yields a tetracarboxylic acid molecule that is observed in the MOF PCN-81.[20] Additionally, our group has previously shown that the same 9-position of carbazoledicarboxylate is of importance for modification of the in order to install a variety of functional groups into coordination cages.[21,22] This ligand, which features a 90° angle between carboxylate groups on its 3,6 positions has been shown to be easily incorporated into discrete coordination cages, reliably forming $M_{12}L_{12}$ type cages when reacted with a variety of divalent transition metal cations that are prone to adopting paddlewheel configurations, including Cr^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mo^{2+}, and $Ru^{2+/3+}$.[7,21,23] When 9-position functionalized, the organic groups installed onto the bridging ligand exhibit on the exterior surface of these octahedral structures and have shown to have a tremendous impact on a variety of cage properties, including solid-state packing, surface area, solubility, and thermal stability. The amenability of this ligand toward straightforward modification routes makes it a promising target for the synthesis of novel porous coordination cages, however, investigations into incorporating this ligand into alternative cage geometries have not been documented.

Although calixarene-capped cages have been prepared from a wide range of dicarboxylate ligands,[24,25] the use of a ligand with 90° between carboxylate groups to bridge metal/calixarene tetranuclear clusters has yet to be reported. Our initial attempts to isolate cages upon reactions of various metal salts with 9-functionalized carbazoledicarboxylic acid ligands proved unsuccessful regardless of reaction conditions or the nature of the installed functional group, which included alkyl, aryl, and benzyl groups. The reaction of 9-^{t}Bu-benzyl-carbazoledicarboxylic acid with nickel did, however, afford a crystalline cage-like material that illustrates the issue with this approach. The carboxylate groups in this structure are coplanar with the carbazole unit, therefore causing the orientation of the carbazole ligand to inhibit the formation of an enclosed cage. Rather the observed product appears as a portion of a cage containing the expected calixarene capping ligands but with just two dicarboxylate ligands and trinickel rather than tetranickel clusters (Figure 2). Metal-bound DMF completes the coordination sphere for two of the three nickel(II) cations in the structure.

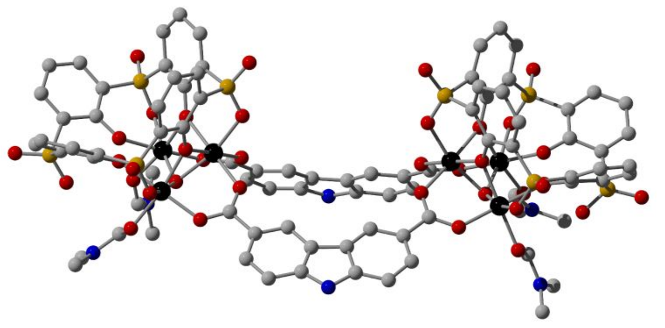

Fig. 2 The reaction of nickel(II) with functionalized carbazole ligand affords a partial cage structure featuring trinickel clusters and nickel-bound DMF molecules. ^{t}Bu groups on the calixarene caps and carbazole functional groups are omitted for clarity. The carboxylate groups and aromatic system are coplanar in this molecule. Black, red, yellow, gray, and blue spheres represent nickel, oxygen, sulfur, carbon, and nitrogen atoms, respectively. Hydrogen atoms have been omitted.

In order to address this, we turned to functionalization of adjacent carbazole positions as a means to force the desired torsion of carboxylate groups that would allow for complete cage formation, therefore tuning the nuclearity and phase of resulting structures. By performing an acylation addition at the 3- and 6-positions of 9-phenyl-2,7-dibromocarbazole, followed by oxidation of the acyl groups to carboxylic acid and subsequent esterification affords methyl-ester functionalized ligand in high yield. After straightforward coupling reactions to install 2,7-positioned phenyl rings and base catalysed hydrolysis of the ester groups affords the targeted tri-phenyl functionalized ligand in high yield. Although this approach is widely compatible with the presence of a variety of functional groups on the 9-position of the ligand, we found that the 9-phenyl congener offered optimized scalability and produced a highly soluble ligand, which generally aids in synthetic efforts toward isolation of functionalized cages.

Calixarene-capped coordination cages have previously been reported for a wide variety of metal ions, including Mg, Fe, Co, Ni, and Zn.[2,26,27,28,29] With this in mind, we targeted the synthesis of a large family of isostructural species based on these metal cations. Despite our best efforts, and our prior success in isolating iron(II)-based cages with these capping ligands,[2] we were unable to isolate an Fe^{2+} cage and typically produced partially metalated cap with no carboxylic acid ligand. However, reaction of 2,7,9-triphenylcarbazole-3,6-dicarboxylic acid (H_2tpcd) with $MgCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, or $Ni(NO_3) \cdot 6H_2O$ and *p-tert*-butylsulfonylcalix[4]arene in amide/alcohol mixtures affords the targeted $[(M_4X(SC4A))_2(tpcd)_4]^{2-}$ (M = Mg^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}; X = OH^- or OMe^-; hereafter referred to as M-TriPhenyl-cdc) cages in high yield. While the μ_4 species present in the metal cation clusters that comprise these cages can vary[2,28,30] the cages isolated here feature either methoxide or hydroxide ions in these positions. As a result, the cages present as 2^- anions. As is typically the case for these types of cages, and related ionic cages featuring significant extra-cage pore space in their solid-state structures, we were unable to crystallographically resolve the cationic species in the structures with the exception of the magnesium congener. In this case, the cage was isolated as a dimethylammonium salt, $[H_2NMe_2]_2[(Mg_4OH(SC4A))_2(tpcd)_4]$ as is common for anionic cages isolated from solvent mixtures containing dimethylformamide, which readily decomposes to afford dimethylamine over the course of cage syntheses.

The capping ligand in these cages, p-tert-butylsulfonylcalix[4]arene, offers a large degree of structural flexibility and is compatible with a range of transition metal cations. As a result, we are able to report isoreticular cages containing four unique metals in slightly different coordination geometries. The internal lengths of each cage, measured between the oxygen in each μ_4 species change only slightly as a function of metal cation with distances of 10.160(6), 10.09(1), 9.80(1), and 9.93(2) Å for magnesium, manganese, cobalt and nickel cages, respectively. This is expected as the cap-to-cap distance in the cage is largely governed by the carbazole-based bridging ligand. Notable deviations from a perfect octahedral geometry, however, are observed to different extents for each metal cation. For example, the angle between the metal ion, sulfonyl oxygen, and the μ_4 species or "strained angle", varies significantly depending on what metal is present while the two angles in equatorial plane of the octahedron remain relatively close to 180°. The extremes of this case lie in the Co^{2+} and Mn^{2+} cages with angles of 169.3° and 162.0°.

In order to assess the porosity of these materials, crystals were collected after vapor diffusion of an antisolvent into each respective reaction mixture and solvent exchanged three times with methanol at 24 hour intervals in order to remove less volatile DMF molecules that may be trapped in the pores of each cage. The materials were then dried under vacuum in an air free environment before being transferred to sample tubes for further activation and gas adsorption analysis. Complete solvent exchange and removal was confirmed by infrared spectroscopy. Prior to adsorption measurements, each material was activated under flowing N_2 at 50 °C for 48 hours. Nitrogen adsorption isotherms were collected for all materials at 77 K which where fit to afford apparent Langmuir (BET) surface areas of 485 (455), 399, 596 (503), and 619 (464) m^2/g for Mg-, Mn-, Co-, and Ni-TriPhenyl-cdc, respectively. In addition, CO_2 adsorption isotherms for Mg-, Mn-, and Co-TriPhenyl-cdc afforded Langmuir (BET) surface areas of 744 (387), 593 (397), and 663 (406) m^2/g.

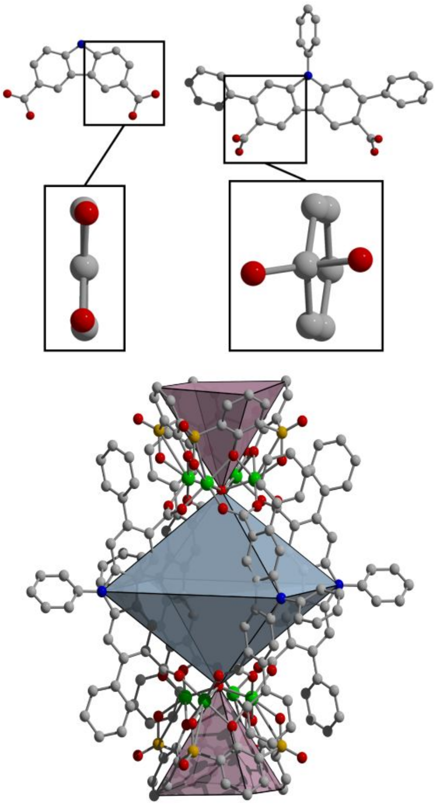

Fig. 3 (Top) 3,6-functionalization of carbazole enforces rotation of the carboxylate groups of the ligand. (Bottom) Structure of $[NH_2Me_2]_2[(Mg_4OHSC4A)_2(tpcd)_4]$ as determined by single-crystal X-ray diffraction ^{t}Bu groups and hydrogen atoms have been omitted for clarity.

Although these surface areas are modest as compared to those reported for high surface area network solids, they are notable given the low nuclearity of these cages[1] and are significantly greater than the previously reported uptakes in other ligand-modified Type IV calixarene containing cage materials. As previously reported for analogous cages with calixarene molecules as capping units, the bowl-like voidspace formed by the p-tert-butyl phenol units cap proves significant void space for gas adsorption (Fig. 3).[31,32] In addition to this, the ^{t}Bu-^{t}Bu interactions between cages typically endows these types of cages with moderate thermal stability and form regular extra-cage space that is accessible to adsorbate molecules.[26] The closest ^{t}Bu-^{t}Bu interactions that is observed between cages is in the case of Co-TriPhenyl-cdc where caps present in a staggered orientation. The top two ^{t}Bu groups of one cage will interact with the bottom two ^{t}Bu groups of another cage at distances of 4.7732(6) and 4.6286(6) Å respectively (Figure S40). Similarly, the same type of cap-cap orientation is observed in the case of Mn and Ni systems where the distances between ^{t}Bu groups in each case is 4.7487 and 4.7487 Å for the former and 4.8892(4) and 4.8892(4) Å for the latter (Figure S38 and S40). In the case of Mg-TriPhenyl-cdc, the orientation of the caps interacting between cages presents in a less staggered orientation than the other three systems. In this case, each ^{t}Bu group of one cage is interacting with its corresponding ^{t}Bu group in the other cage meaning to say that there are now four points of interaction between each calixarene cap rather than two. In the Mg-TriPhenyl-cdc system we observe 5.5867(3), 5.4049(3), 5.5867(3), and 5.4049(3) Å between the four ^{t}Bu interactions present (Figure S36).

Although it has previously been shown that these ^{t}Bu-^{t}Bu interactions dominate cage-cage contacts,[33] the carbazole functional groups used in this work play a vital role in cage packing. Several examples of face-to-edge pi-pi stacking are present across all four cage materials in the solid state. Single crystal X-ray diffraction (scxrd) shows that in the case of Mg-TriPhenyl-cdc, two examples of this pi-pi stacking confirmation can clearly be seen between the ligands of two cages at distances of 4.9868(2), 4.2409(2), and 4.9439(3) Å. Similarly, in the case of Co-TriPhenyl-cdc and Ni-TriPhenyl-cdc, one can see similar T-shaped pi-pi confirmation between two ligands of any given cages. The distances at which these interactions occur when examining Co-TriPhenyl-cdc are 4.6245(5), 4.6784(5), and 5.4462(5) Å, and when examining Ni-TriPhenyl-cdc these distances are 4.7075(3), 4.6627(3) and 5.0057(3) Å. While the pi-pi interaction in the Mg, Co, and Ni analogs of these cages are clearly identifiable as T-shaped pi-pi stacking as the acute angle between the planes of each ring (γ) is close to 90°. Mn-TriPhenyl-cdc displays a smaller angle between the two rings interacting between cages (Figure 4). The distances here (4.6782(2) and 4.3545(3) Å) are consistent with those observed in the other three materials.

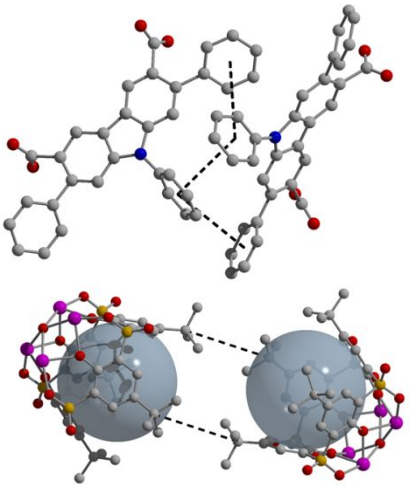

Fig. 4 (Top) Pi-Pi interactions observed between ligands of neighbouring cages in Ni-TriPhenyl-cdc, (Bottom) ^{t}Bu- ^{t}Bu interactions between Mn-TriPhenyl-cdc cages.

These results show that construction of calixarene capped, functionalized carbazole containing cages of Type IV structure types are isolable given judicious ligand functionalization. The incorporation of phenyl rings at the 2-, and 7- positions not only allow for the torsion of the carboxylic acid groups that facilitates cage growth, but also plays a key role in increasing inter-cage interactions that allow for increased porosity in this class of materials. The isoreticular materials presented here show tunability for incorporation of a variety of transition metal cations. As a result of the highly functionalizable nature of the carbazole bridging ligand, we expect that further modification of the carbazole group, particularly at the 9-position, can be leveraged to further tune surface area, solubility, and gas adsorption properties. Future work in our group will expand on this and elucidate the structure/function relationships upon functional group incorporation.

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