Engineering Solid-State Porosity of Synthetic Supercontainers via Modification of *Exo*-Cavities

Li-Ji Cheng,^[a,b] Xin-Xia Fan,^[a,b] Yi-Peng Li,^[a,b] Qiao-Hua Wei,^{*,[a,b]} Feng-Rong Dai,^{*,[b]} Zhong-Ning Chen,^[b] and Zhenqiang Wang^[c]

ABSTRACT: Two new coordination supercontainers have been successfully isolated from the self-assembly reactions of the container precursor *p*-phenylsulfonylcalix[4]arene, Ni(II) or Co(II) ion, and diphenylmethane-4,4'-dicarboxylic acid. Crystal structure analysis revealed that these two coordination supercontainers possess a similar endo cavity and two deeper exo cavities compared to the related supercontainers based on *p*-*tert*-butylsulfonylcalix[4]arene. Gas and vapor adsorption studies indicated that the new compounds are permanently porous and show much better CO₂/O₂ and CO₂/N₂ selectivity and higher vapor adsorption than the *tert*-butyl analogues.

Keywords: coordination container, sulfonylcalix[4]arene, supramolecular chemistry, gas separation, vapor adsorption

Molecular containers possessing hollow space have received considerable attention in view of their promising applications in a wide array of areas, including stabilization of highly reactive species, transportation of small molecules, gas storage and separation, sensing, supramolecular catalysis and molecular recognition.[1-6] Because of the relatively robust and reversible nature of coordination bonding between metal and ligand, coordination-driven self-assembly affords an excellent means to construct elegant supramolecular architectures containing hollow structures.[7-13] We have focused on the construction of coordination containers featuring unique multiple binding cavities within a single host structure by incorporating sulfonylcalix[4]arenes[14] as container precursors. A new family of coordination containers, namely, metal-organic supercontainers (MOSCs), have been obtained from the assembly of sulfonylcalix[4]arenes, divalent metal ions and carboxylate linkers of trigonal, linear, angular-planar, or angular-nonplanar shape.[15-18] The lower rim of sulfonylcalix[4]arenes was bridged by the carboxylate linkers via both binding to the same metal ions to generate four prototypes of MOSCs that possess a characteristic multi-pore architecture, i.e., an *endo* cavity and multiple *exo* cavities. Related

supercontainer structures derived from thiacalix[4]arenes, in place of sulfonycalix[4]arenes, have also been recently investigated by the research groups of Liao and Hong [19, 20]. While it has been shown that the geometry of the *endo* cavity can range from *face*-directed octahedron (type I MOSCs)[15], *edge*-directed octahedron (type II MOSCs)[16], barrel-shaped box (type III MOSCs)[17], to cylindrical structure (type IV MOSCs)[18], depending on the type of carboxylate linker chosen, we anticipate that the *exo* cavities can be precisely controlled by the cup-shape configuration[14] of the sulfonycalix[4]arene units locked in by the metal coordination. Therefore, chemically modifying the *para* position of the sulfonycalix[4]arene precursor provides a fruitful strategy to manipulate the *exo* porosity of the MOSCs [15-19]. Herein, we demonstrate that replacing *p-tert*-butylsulfonycalix[4]arene (TBSC) used in our previous studies with *p*-phenylsulfonycalix[4]arene (PSC) [21] in the modification of type IV MOSCs proves effective in engineering their solid-state porosity and gas/vapor adsorption properties. In particular, we show that incorporating extended phenyl groups at the upper rim of the *exo* cavities not only produces a deeper, π -electron rich cavity but also allows more substantial π - π stacking that contribute to maintaining the solid-state packing and structural ordering of the discrete container crystals.

Scheme 1. Assembly of *p*-phenyl-sulfonycalix[4]arene based coordination supercontainer. The yellow sphere serves to guide the eyes.

The new supercontainer **1** was isolated as green crystals upon the reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with diphenylmethane-4,4'-dicarboxylic acid (**H₂DPMDC**) and *p*-phenylsulfonycalix[4]arene (**H₄PSC**) in DMF at 100°C (Scheme 1).[22] The compound was fully characterized by single-crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Fourier transform IR spectroscopy (FTIR), and UV–Vis spectroscopy. The PXRD patterns confirmed the crystallinity and phase purity of the as-synthesis material (Figure 1a). The TGA revealed that compound **1** has a thermal stability similar to that of the TBSC-derived MOSCs, featuring a de-composition temperature of above 400 °C under the nitrogen atmosphere (Figure 1b).[18] The ca. 25% weight loss before 200 °C is attributed to the release of solvent molecules (i.e., *N,N*-dimethylformamide, DMF, estimated to be 14 molecules, vide infra) entrapped within the coordination capsule.

Figure 1. a) Powder X-ray diffraction patterns of **1**; b) TGA of as-synthesized and activated sample of **1**.

SCXRD studies showed that compound **1** crystallized in the tetragonal crystal system and $P4/mnc$ space group.[23] The molecular structure of compound **1** resembles a cylindrical shape similar to the *tert*-butyl MOSCs, although it should be noted that **1** crystallized in a space group with a much higher symmetry (i.e., $P4/mnc$ vs. $P-1$). As shown in Figure 1, two tetranuclear units, each containing a μ_4 -oxygen species from a presumably neutral water molecule, were bridged by four DPMDC linkers, which adopted the V-shaped geometry with a dihedral angles of 107.8° between the two benzene rings. **1** exhibits an *endo* cavity similar to that observed in the TBSC analogue, which is defined by the lower rim of PSC and DPMDC ligands and features a longitudinal diameter of ca. $10 \text{ \AA}$ and pore openings of ca. $4.6 \text{ \AA} \times 10 \text{ \AA}$; however, comparing to the TBSC analogue, **1** possesses two much wider (with an opening of $13 \text{ \AA} \times 13 \text{ \AA}$) and deeper (with a depth of ca. $8 \text{ \AA}$) cup-shaped *exo* cavities, defined by the upper rim of PSC. Multiple face-to-face π - π interactions are found between the aromatic rings of PSC: each PSC formed eight visible π - π interactions (with a centroid-centroid distance of $3.463 \text{ \AA}$) with four adjacent PSC ligands. As a result, compound **1** adopts a less efficient packing mode, namely, pseudo body-centered cubic (bcc) packing, in solid state, with a total potential solvent-accessible volume of ca. 44.7% calculated using the PLATON program.[24] The free volume, which includes the enclosed *exo* and *endo* cavities and the interstitial space, is presumably occupied with the solvent molecules (i.e. DMF); unfortunately, they are highly disordered and not able to be located by the X-ray crystallography. However, according to the crystallographic analysis, SQUEEZE results, and TG analysis, the empirical formula of compound **1** is estimated to be $[\text{Ni}_4(\mu_4\text{-H}_2\text{O})\text{PSC}]_2(\text{DPMDC})_4 \cdot 14\text{DMF}$. Furthermore, an isomorphous crystal of cobalt analogue, namely, compound **2**, was also successfully isolated under similar reaction conditions by simply replacing the Ni^{2+} with Co^{2+} , indicating that the formation of such coordination supercontainers is highly predictable and reliable.

Figure 2. a) Face-to-face π - π stacking interactions between the aromatic rings from adjacent PSC; b) The 3D packing of **1** through π - π interactions. The hydrogen atoms and solvent molecules are not included.

Preliminary gas/vapor adsorption studies of **1** were investigated using the activated sample. Its N_2 sorption at 77 K gave a “pseudo” type I adsorption isotherm which features a small but visible adsorption/desorption hysteresis. It confirmed that compound **1** adsorbs up to $284 \text{ cm}^3/\text{g}$ at 77 K and 1 atm, and has a Brunauer-Emmett-Teller (BET) surface area estimated at $835 \text{ cm}^2/\text{g}$. This finding is particularly remarkable when compared to the TBSC analogue, which exhibited essentially negligible N_2 uptake at 77 K and 1 atm ($\sim 10 \text{ cm}^3/\text{g STP}$) and thus nonporous to N_2 [18]. This result highlights the profound impact of replacing t-butyl units with the more extended phenyl groups on retaining the crystal packing and solid-state porosity of compound **1** even after the removal of its lattice solvents. Additional adsorption studies involving O_2 and H_2 at 77 K, CO_2 at 196 K were also carried out, which revealed that compound **1** has a persistently higher adsorption capacity than that of the TBSC-based analogue. The apparent CO_2/O_2 and CO_2/N_2 adsorption selectivity of compound **1** at ambient temperature was further established by the examining its affinity with CO_2 , N_2 , and O_2 at 293 K (Figure 3d). The result indicated its potentially relevant applications in carbon dioxide separation/capture. Moreover, vapor adsorption experiments showed significant uptake of MeOH ($\sim 203 \text{ cm}^3/\text{g STP}$ or ~ 30 molecules per container) and benzene ($\sim 113 \text{ cm}^3/\text{g STP}$ or ~ 17 molecules per container) at 293 K by compound **1** (Figure 3), both of which double the corresponding adsorption capacity of the TBSC analogue.

Figure 3. a) N_2 (77 K); b) Benzene (293 K); c) MeOH (293 K), and d) N_2 (293 K), O_2 (293 K) and CO_2 (293 K) sorption isotherms of **1** by comparing to the TBSC analogue.

In conclusion, two new coordination supercontainers derived from *p*-phenylsulfonylcalix[4]arene have been successfully obtained from the self-assembly reaction. Incorporating the phenyl groups to these new structures represents an effective approach to modifying their *exo* cavities and overall solid-state porosity. Compared to the *p*-*tert*-butylsulfonylcalix[4]arene based analogue, these new supercontainers possess a similar endo cavity but exhibited deeper *exo* cavities sustained by extended phenyl groups and more extensive π - π interactions. Thanks to these substantial π - π interactions, the new supercontainers have a less efficient but more robust crystal packing, giving rise to higher overall porosity and gas/vapor adsorption capacity. Most importantly, these characteristics have led to higher CO_2/O_2 and CO_2/N_2 adsorption selectivity, indicating the potential applications of these new materials for gas separation.

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Appendix A. Supplementary data

Structural, spectroscopic, and additional characterizations of the new compounds. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.xxxx>.

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- [22] **1**: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (145.5 mg, 0.50 mmol), H_2DPMDC (56.4 mg, 0.22 mmol) and H_4PSC (84.9 mg, 0.10 mmol) were dissolved in 12 mL of DMF. The solution was then divided into ten dram vials (4 mL capacity). The vial was placed in a sand bath, which was transferred to a programmable oven and heated at a rate of 0.5 °C/min from 35 to 100 °C. The temperature was held at 100 °C for 24 h before the oven was cooled at a rate of 0.2 °C/min to a final temperature of 35 °C. Green crystals of **1** were isolated by washing with methanol and dried in the air to give 50.2 mg of the as-synthesized material. **2**: The preparation of compound **2** was similar to that of **1** except that $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used instead of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.
- [23] Crystal data for **1**: $\text{C}_{156}\text{H}_{100}\text{Ni}_8\text{O}_{42}\text{S}_8$, $M_r = 3372.51$, Tetragonal, $P4/mnc$, $a = 15.4910(10) \text{ \AA}$, $b = 15.4910(10) \text{ \AA}$, $c = 42.256(5) \text{ \AA}$, $V = 10140.3(18) \text{ \AA}^3$, $Z = 2$, $D_c = 1.105 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.869 \text{ mm}^{-1}$, $F(000) = 3448$, $GOOF = 1.099$. A total of 35812 reflections were collected, 1458 of which were unique ($R_{\text{int}} = 0.0626$). $R_1/wR_2 = 0.0740/0.2181$ for 244 parameters and 1458 reflections ($I > 2\sigma(I)$). Crystal data for **2**: $\text{C}_{156}\text{H}_{100}\text{Co}_8\text{O}_{42}\text{S}_8$, $M_r = 3374.27$, Tetragonal, $P4/mnc$, $a = 15.4705(9) \text{ \AA}$, $b = 15.4705(9) \text{ \AA}$, $c = 42.773(5) \text{ \AA}$, $V = 10237.3(17) \text{ \AA}^3$, $Z = 2$, $D_c = 1.095 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.773 \text{ mm}^{-1}$, $F(000) = 3432$, $GOOF = 1.089$. A total of 39648 reflections were collected, 1657 of which were unique ($R_{\text{int}} = 0.0523$). $R_1/wR_2 = 0.0862/0.2448$ for 217 parameters and 1657 reflections ($I > 2\sigma(I)$). X-ray single-crystal diffraction data were collected at 100 K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker CCD APEXII diffractometer. The collected frames were processed with the software SAINT. The data were corrected for absorption using the SADABS program. The structure was solved by the Direct methods (SHELX97) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2 . Hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were refined

anisotropically. The electron count due to disordering solvents in the void space was calculated using the program SQUEEZE in PLATON software package.

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