Functional Frameworks

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Extending Rectangular Metal–Organic Frameworks to the Third Dimension: Discrete Organometallic Boxes for Reversible Trapping of Halocarbons Occurring with Conservation of the Lattice**

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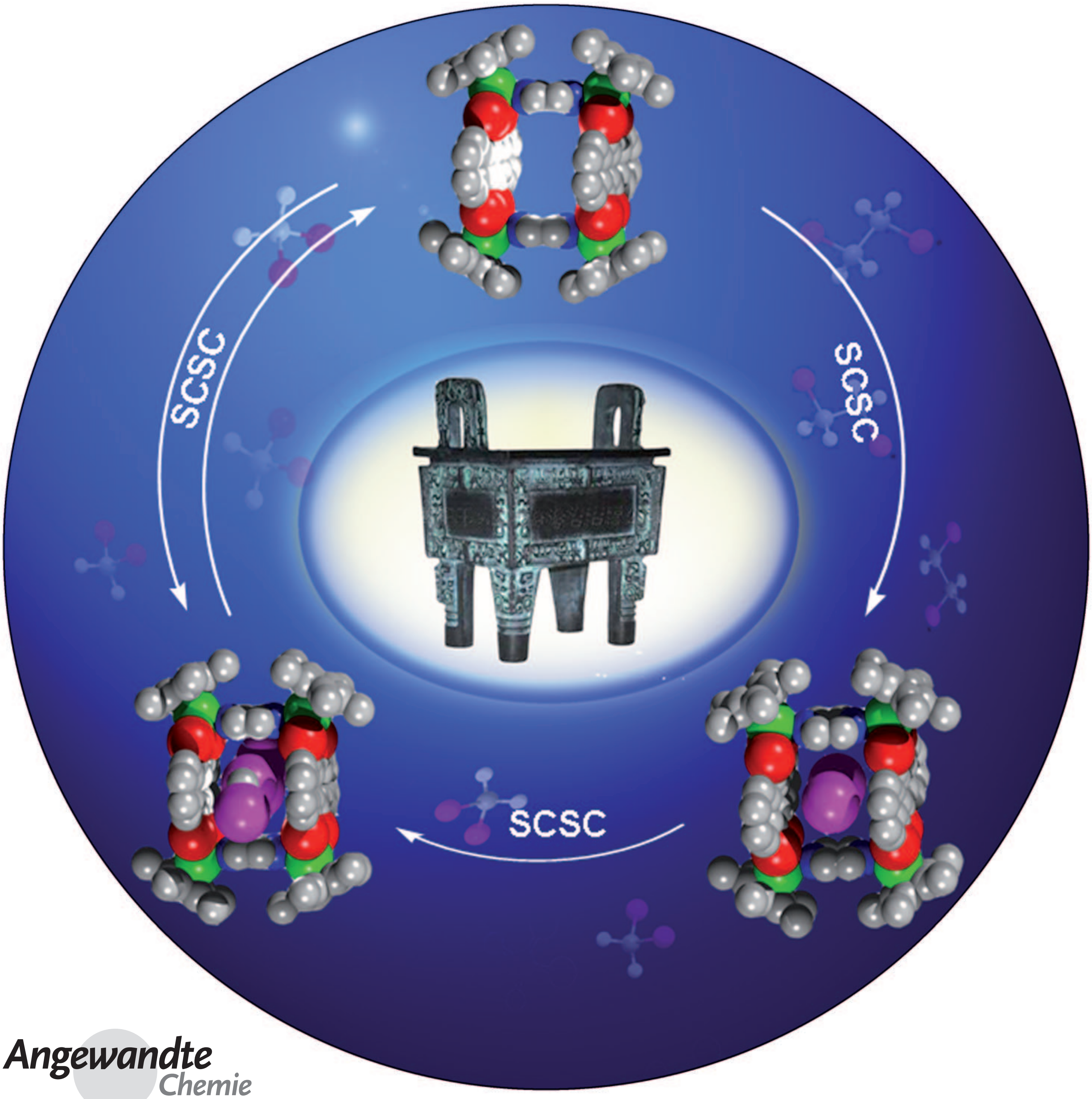
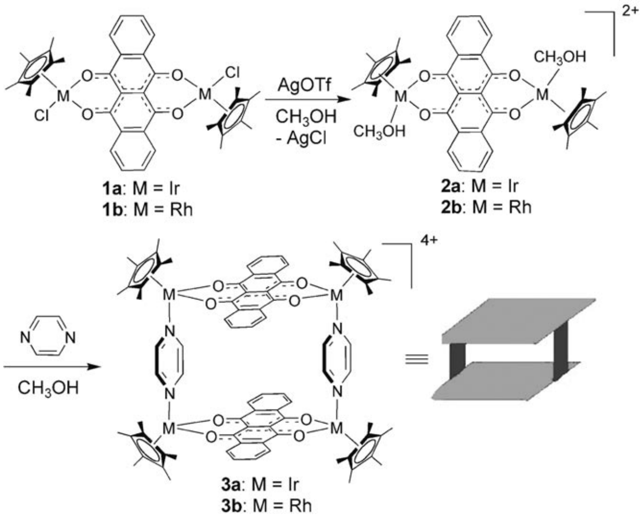


During the last decade, significant progress has been made in the rational design of functional metallasupramolecular architectures with triangles, squares, and other polygons as basic units and, furthermore, the construction of three-dimensional cages and polyhedra. Owing to their capability of encapsulating guest moieties within cavities of different sizes and shapes, metallasupramolecules have demonstrated great potential in the applications of separation processes, catalysis, selective recognition, and sensor technologies.[1] Among the reported host–guest systems, the metallacycles exhibit high shape and size selectivity.[2] Metal–organic frameworks also belong to this class of materials and, even though they are normally highly rigid, they retain their structures upon various stresses, such as temperature changes, chemical reactions, guest exchanges, or other physical stimuli.[3] Related studies for packing molecular cyclic arrangements to form cavities and pores are quite rare.[4] The design and synthesis of such host frameworks that can interact with certain guest molecules have implications for the generation of advanced materials, because they have many characteristic features, including the confinement of guest molecules in the cavity with a deep, van der Waals-type, potential energy well. The high selectivity recognition, accommodation, and separation of the target molecules depends on the relationship between the size of the cavity and the molecular dimensions of the guest molecules.[5] However, the monomer host frameworks can be used to build up higher dimensional structures by supramolecular interactions, such as π–π stacking interactions, C–H···π interactions, and C–H···X (X = F, Cl, Br, I) interactions.[5g,6]

Planar molecular rectangles with metal centers at the corners and two pairs of differing opposite ligand "edges" can be assembled from a binuclear complex possessing a tightly binding rigid spacer and coordination sites to connect two such molecules by a second type of linear building unit.[1] We recently reported that oxalato and chloranilate bridged dinuclear species are suitable units not only for rectangles, but also for prisms and cages by the aforementioned construction principles.[7] We wondered if we could tune such molecular rectangles by extending the spacers of the rectangular structure into the third dimension to form large cavities, thus simulating the caging properties of metal–organic frameworks (MOFs) for soluble compounds. Based on 6,11-dihydroxy-5,12-naphthacenedione (H_2dhnq) and pyrazine spacing ligands, and half-sandwich iridium corners, we built up a molecular organometallic box, which exhibited selective and reversible CH_2Cl_2 adsorption properties while retaining single crystallinity. This rare example of C–H···Cl interactions between layers of the monomeric complex was studied and indicated that the charged guests served as a template for the creation of intercalated supramolecular arrays.

Tetranuclear complexes $[Cp^*_4M_4(\mu\text{-pyrazine})_2(\mu\text{-L})_2](OTf)_4$ (M = Ir (**3a**), Rh (**3b**); L = dhnq^{2-}) were obtained in high yields by direct reactions of **1a** or **1b**, respectively, with pyrazine in the presence of AgOTf (Tf = O_2SCF_3; Scheme 1 and the Supporting Information). The methanol-coordinating cationic intermediates **2a** and **2b** were confirmed by NMR spectroscopy and single-crystal structure analyses. In the solid state structures of **2a** and **2b**, it was found that π–π stacking between the planar dhnq^{2-} ligands and the nearby Cp* rings (3.45 Å) arranged two molecules through a somewhat displaced face-to-face interaction (see the Supporting Information, Figures S1 and S2). Organometallic rectangles **3a** and **3b** were characterized by solution NMR spectroscopy and single-crystal X-ray diffraction. The ^{1}H NMR spectrum of the iridium complex **3a** in CD_3OD showed two singlets at 1.66 and 8.77 ppm (15:2 integration ratio), attributable to Cp* and pyrazine, respectively, which indicated a highly symmetric structure. Two distinct signals at approximately 7.88 and 8.57 ppm were detected for the aromatic protons of the dhnq^{2-} ligands.



Scheme 1. Stepwise formation of **3a** and **3b**.

The overall shape of the organometallic molecules, as derived from the X-ray crystal structure of **3a** and **3b**, is characterized best as a splint with two connected large plates "protecting" a cavity (Figure 1). The complex cation indeed adopts a rectangular structure with nonbonding Ir–Ir distances of 8.4 and 6.9 Å and a diagonal distance between the dhnq^{2-} bridging ligands of 9.8 Å. Somewhat displaced face-to-face π–π interactions between the planes of adjacent dhnq^{2-} ligands (3.78 Å) generate one-dimensional (1D) coordination frameworks (Figure 4, left). Two H_2O molecules are located near to the corresponding triflates anions, but outside of the

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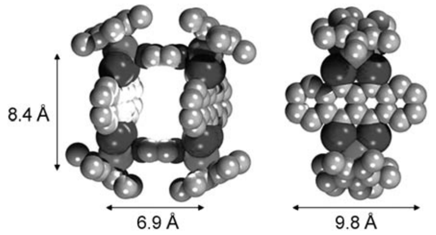

Figure 1. Two views of the cation of **3a**. Compounds **3a** and **3b** are isostructural. H atoms have been omitted for clarity.

framework, with an O–O distance of 2.97 Å (see the Supporting Information, Figure S3).

Interesting, a complex of the formula $[Cp^*_4Ir_4(\mu\text{-pyrazine})_2(\mu\text{-L})_2](OTf)_4{\cdot}2\,CH_2Cl_2{\cdot}4\,H_2O$ (**4**) was readily obtained by slow diffusion of Et_2O into a CH_3OH/CH_2Cl_2 mixed-solvent solution of **3a**, in which two CH_2Cl_2 guest molecules are positioned at the walls of the cavity and interact with the "splint" with π–π (3.7 Å; half the distance between face-to-face $dhnq^{2-}$ units) and C–H···π (2.96 Å) interactions (Figure 2). Two of four H_2O molecules are located near to the corresponding triflate anions with an O–O distance of 2.73 Å, whereas the other two are unrestricted. The crystal structure revealed that the two unrestricted H_2O molecules in **4** were easily lost, while retaining the morphology and the single crystallinity, to produce the transparent crystal **5**. In addition, **5** could be readily obtained by exposure of **3a** to CH_2Cl_2 vapor for three days at room temperature (Figure 3). It is especially interesting to note that the structural transformation of **3a** to **5** is reversible. When a single crystal of **5** was allowed to stand in air for two weeks at room temperature or at low pressure (circa 13.3–133 Pa), the two CH_2Cl_2 guests could be released and the structure of **3a** was regenerated. The corresponding structures were verified by single-crystal X-ray diffraction studies, although the change in the unit cell parameters is unremarkable.[8] In the solid state, the molecular splints stack along the *b* axis to form rectangular channels, as a result of the interactions between the independent molecules (see the Supporting Information, Figure S5). It provides a channel for the guest molecules to travel within the crystal, thus allowing the absorption and desorption of CH_2Cl_2.

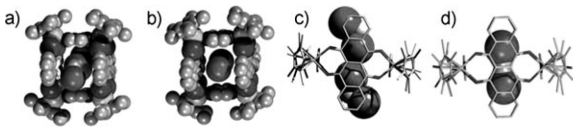

Figure 2. Side views of the cations of **4** or **5** (a) and **6** (b) in space-filling mode. Top views of the cations of **4** or **5** (c) and **6** (d) in stick mode. H atoms have been omitted for clarity.

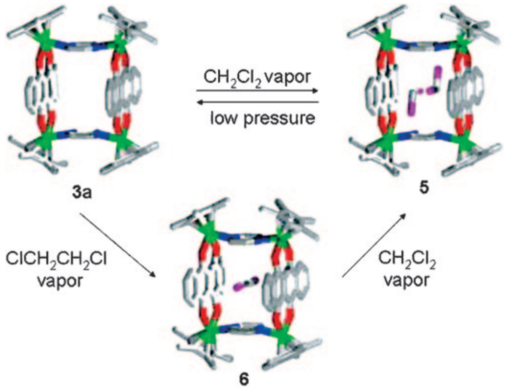

Figure 3. Stick representation of the single-crystal to single-crystal transformation processes of chlorocarbon uptake and release between **3a**, **5**, and **6** (C gray, Cl pink, Ir green, N blue, O red). H atoms have been omitted for clarity.

Exposure of a single crystal of **3a** to $ClCH_2CH_2Cl$ vapor for about 3 days led to the filling of empty cavities by one $ClCH_2CH_2Cl$ molecule, generating a new host–guest system of the formula $[Cp^*_4Ir_4(\mu\text{-pyrazine})_2(\mu\text{-L})_2](OTf)_4{\cdot}ClCH_2CH_2Cl{\cdot}4\,H_2O$ (**6**). In this case, one $ClCH_2CH_2Cl$ molecule is accommodated in the middle of the cavity which is stabilized by the π–π stacking interactions with the opposite $dhnq^{2-}$ ligands (Figure 2). In addition, when a single crystal of **6** was exposed to CH_2Cl_2 vapor for seven days, the $ClCH_2CH_2Cl$ guest in **6** was replaced by CH_2Cl_2 molecules and the structure of **5** was obtained. When crystals of **3a** were exposed to mixed $CH_2Cl_2/ClCH_2CH_2Cl$ or $CH_2Cl_2/CHCl_3$ vapor in 1:1 molar ratio for three days, only CH_2Cl_2 molecules were selectively adsorbed, as determined by single-crystal structure analysis. The adsorption properties of the crystalline host **4** with different guests were studied in greater detail. The lack of absorptivity by the crystal for larger molecules such as $CHCl_3$ and also aromatic molecules suggested size-selective molecular-sieve-like behavior for guest molecules based on the cavity size.[5] After submerging a single crystal of **4** into benzene or decahydronaphthalene for three days, no detectable change occurred in the morphology, size, or transparency of the crystal, but crystal-structure determinations revealed that the unrestricted H_2O molecules of **4** escaped and the occupancy of CH_2Cl_2 in **5** gradually decreased over time (see the Supporting Information). As the solvent-exchange processes were carried out in the vapor phase, rendering formation of homogeneous solutions quite improbable, it is plausible to assume that the solvent exchange occurred without structural change in a single-crystal to single-crystal (SCSC) process through the channels of the crystals (Figure 3). The phase purities of the bulk samples were established by comparison of their experimental and simulated powder X-ray diffraction (PXRD) patterns and thermogravimetric analyses (see the Supporting Information, Figure S6 and S7).

When a single crystal of **3a** was allowed to stand in $Cl_2C{=}CCl_2$ vapor for three days at room temperature, single-crystal X-ray diffraction analysis indicated that compound **7** was produced (Figure 4).[9] The $Cl_2C{=}CCl_2$ guests were shown to effect the transformation of the 1D assemblies to a two-dimensional (2D) framework through C–H···Cl interactions (3.7 Å). The 1D rows were perfectly aligned to form the 2D framework, in which the displaced face-to-face π–π interactions between the planes of the monomeric complexes are

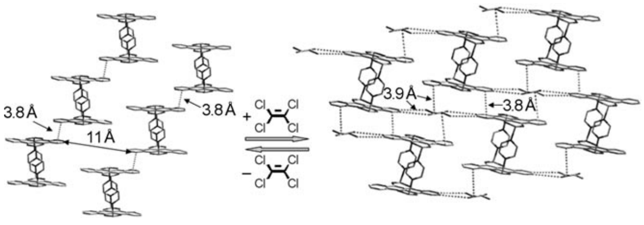

Figure 4. Extended structure of the cations of **3a**, demonstrating displaced face-to-face π–π interactions (left), and of the cations of **7** with C−H···Cl interactions between the monomeric complexes (right). Cp* groups and H atoms have been omitted for clarity.

retained. Complex **7** also retains its single crystallinity after removal of the guest $Cl_2C{=}CCl_2$ molecules by heating the crystal at 80 °C for about 5 h under a N_2 atmosphere, indicating that the transformation is completely reversible.

Intrigued by this finding, we pursued the assembly of even larger such molecular “splints” utilizing longer rigid spacers, $[Cp^*_4M_4(\mu\text{-bpy})_2(\mu\text{-L})_2](OTf)_4$ (M = Ir (**8a**), Rh (**8b**); bpy = 4,4′-dipyridyl) and $[Cp^*_4M_4(\mu\text{-bpe})_2(\mu\text{-L})_2](OTf)_4$ (M = Ir (**9a**), Rh (**9b**); bpe = 1,2-bis(4-pyridyl)ethylene). The complex cations incorporated a rectangular cavity with dimensions of 8.5 × 9.8 × 11.2 Å for **8a**, and of 8.5 × 9.8 × 13.6 Å for **9a**. When viewed down the *a* axis, rhombohedrally distorted rectangular channels were evident in **8a** (see the Supporting Information, Figure S8). Although the small molecules were not found in the cavities, the encapsulation of slightly bigger molecules, such as benzene, also left much to be desired.

In summary, we successfully designed and constructed a series of open-channel structures, comprised of organometallic rectangular building blocks, tuned by the size and nature of the bridging spacers. As summarized in Figure 3, **3a** selectively recognized CH_2Cl_2 and $ClCH_2CH_2Cl$ molecules while retaining of single crystallinity. These complexes also underwent interesting reversible SCSC structural transformations that were induced by solvent exchange. The 1D coordination assemblies, which were formed as a result of face-to-face π–π interactions between monomeric complexes, underwent a reversible SCSC structural transformation to a novel 2D framework, induced by C−H···Cl interactions. Further efforts to explore new splint-like hosts and their applications are underway.

Experimental Section

For experimental and X-ray single-crystal diffraction data details please see the Supporting Information. CCDC 712011, 712012, 712013, 712014, 712015, 712016, 712017, 712018, 712019, 712020, 712021, 712022, 712023, 712024, and 712025 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[8] Crystal data: **3a**: Triclinic; space group $P\bar{1}$; $a = 13.073(4)$, $b = 13.532(4)$, $c = 16.805(5)$ Å; $\alpha = 66.754(4)$, $\beta = 76.431(4)$, $\gamma = 75.778(4)°$; $V = 2615.9(14)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.726\ \mathrm{g\,cm^{-3}}$; R_1 $(I > 2\sigma(I)) = 0.0465$; wR_2 $(I > 2\sigma(I)) = 0.1162$. **5**: Triclinic; space group $P\bar{1}$; $a = 13.029(7)$, $b = 13.493(7)$, $c = 16.841(9)$ Å; $\alpha = 67.018(7)$, $\beta = 75.898(7)$, $\gamma = 75.815(8)°$; $V = 2606(2))$ Å^3; $Z = 1$; $\rho_{calcd} = 1.761\ \mathrm{g\,cm^{-3}}$; R_1 $(I > 2\sigma(I)) = 0.0523$; wR_2 $(I > 2\sigma(I)) = 0.1060$. **6**: Triclinic; space group $P\bar{1}$; $a = 13.152(8)$, $b = 13.407(8)$, $c = 16.853(10)$ Å; $\alpha = 66.946(9)$, $\beta = 76.942(9)$, $\gamma = 76.621(9)°$; $V = 2630(3)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.746\ \mathrm{g\,cm^{-3}}$; R_1 $(I > 2\sigma(I)) = 0.0594$; wR_2 $(I > 2\sigma(I)) = 0.1294$.

[9] Crystal data: **7**: Triclinic, space group $P\bar{1}$; $a = 13.080(4)$, $b = 13.384(5)$, $c = 16.779(6)$ Å; $\alpha = 66.954(4)$, $\beta = 77.049(5)$, $\gamma = 76.504(5)°$; $V = 2599.1(15)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.764\ \mathrm{g\,cm^{-3}}$; R_1 $(I > 2\sigma(I)) = 0.0436$; wR_2 $(I > 2\sigma(I)) = 0.1012$.