Compressed Corannulene in a Molecular Cage

Bernd M. Schmidt, Takafumi Osuga, Tomohisa Sawada, Manabu Hoshino, and Makoto Fujita*

Abstract: Self-assembled coordination cages can be employed as a molecular press, where the bowl-shaped guest corannulene ($C_{20}H_{10}$) is significantly flattened upon inclusion within the hydrophobic cavity. This is demonstrated by the pairwise inclusion of corannulene with naphthalene diimide as well as by the dimer inclusion of bromocorannulene inside the box-like host. The compressed corannulene structures are unambiguously revealed by single-crystal X-ray analysis.

Self-assembled coordination cages are often employed to design tailor-made arrays of molecules[1] or metal ions within their cavities.[2] The size and shape of the cavity are particularly important to bind substrates in a predicted array or aggregation manner. Box-shaped, pillared cages, such as **1**, show strong binding abilities towards flat organic molecules or metal complexes in programmed stacking modes.[1] Herein, we show that corannulenes (**2**), bowl-shaped non-planar aromatic compounds,[3] adapt their shape to fit into the box-shaped cavity of pillared cage **1** (Figure 1).
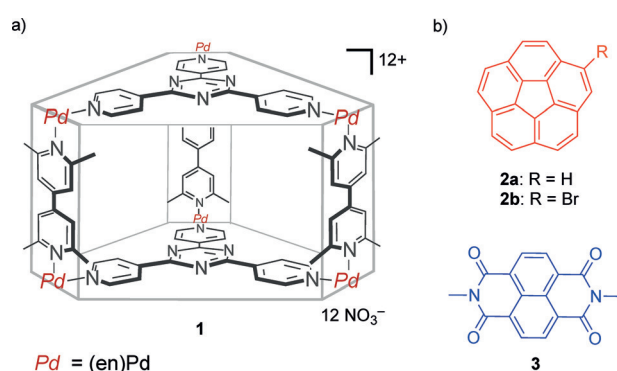

Figure 1. a) Self-assembled box-shaped cage **1**; b) structure of the studied guests corannulenes **2** and naphthalene diimide **3**.

To efficiently fill the cavity, corannulene **2a** was bound pairwise with an electron-deficient naphthalene diimide **3**, whereas bromocorannulene[3] **2b** was encapsulated by the formation of a homo-dimer. In both cases, corannulenes **2** were compressed in the box-shaped cavity and considerably flattened. Recently, Siegel and Stoddart reported the signifi-

cant reduction of the energy barrier for the concave-convex inversion of corannulene **2a** by inclusion in their box-shaped macrocycle. However, planarization of **2a** was insignificant.[4]

Attempts using only corannulene (**2a**) as a template for the multicomponent self-assembly of **1** resulted in formation of a mixture of products.[5] Therefore, we turned our attention to pairwise encapsulation, which we found previously as a highly effective way for accommodating an aromatic donor–acceptor pair in the cavity.[6] Accordingly, an excess amount of water-insoluble guests (**2a** and **3**, 20 μmol) were suspended in an aqueous solution containing tris(4-pyridyl)-2,4,6-triazine (**4**, 20 μmol), 2,2′,6,6′-tetramethyl-4,4′-bipyridine (**5**, 30 μmol), and (en)Pd(NO₃)₂ (**6**, 60 μmol) and stirred at 100°C for 2 h.

After removal of excess guests by filtration, a set of signals assignable as inclusion complex **1·(2a·3)** was observed in the ¹H NMR spectrum (Figure 2). Guest signals are shifted
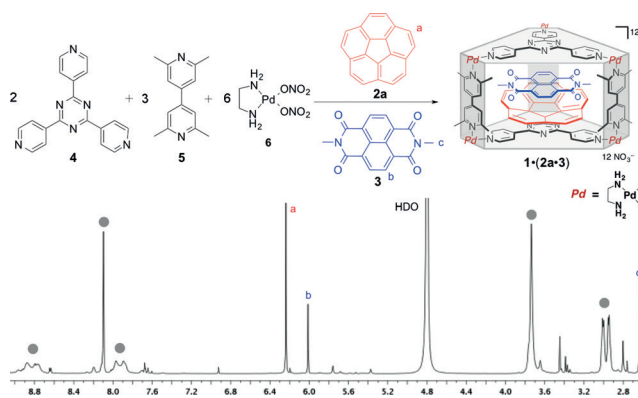

Figure 2. a) Formation of the inclusion complex **1·(2a·3)** at 100°C for 2 h in H₂O solvent; b) ¹H NMR spectrum (500 MHz, 27°C) of **1·(2a·3)** in D₂O. Signals originating from the cage itself are denoted with a gray dot.

significantly upfield owing to the shielding by the panel-like ligands and by the co-enclathrated guest: for **2a**, $\delta = 6.24$ ($\Delta\delta = -1.02$); for **3**, $\delta = 6.01$ ($\Delta\delta = -2.74$) ppm.[7] The host-guest ratios were determined as 1:2 by the integral ratio in the ¹H NMR spectrum. Diffusion-ordered NMR spectroscopy (DOSY) supported the formation of a single host–guest assembly, as all of the observed proton resonances showed the same diffusion coefficient ($D = 1.6 \times 10^{-10}$ m² s⁻¹; Supporting Information, Figure S2).

Single crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution of **1·(2a·3)** at room temperature. Both Mo K_α and Cu K_α radiations were examined, and it was found that Cu K_α radiation at 100 K gave much better resolution for the encapsulated **2a**. In the crystallographic refinement of **2a**, standard restraints for the atomic displacement parameters (DELU) were applied on all

[*] Dr. B. M. Schmidt, Dr. T. Osuga, Dr. T. Sawada, Dr. M. Hoshino, Prof. Dr. M. Fujita
Department of Applied Chemistry, School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113–8656 (Japan)
E-mail: mfujita@appchem.t.u-tokyo.ac.jp

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the framework carbons but no geometrical restraints (such as DFIX and DANG) were applied except for SADI on the peripheral carbon atoms (Supporting Information, Figure S6). Considering that **2a** is a non-covalently trapped guest in the host cavity, the accuracy of the guest geometry is sufficient to discuss the geometry of encapsulated **2a**.

A striking feature displayed in the X-ray structure is the significant compression of the bowl-shaped guest **2a** to induce a better fit into the box-shaped cavity of **1** (Figure 3). The
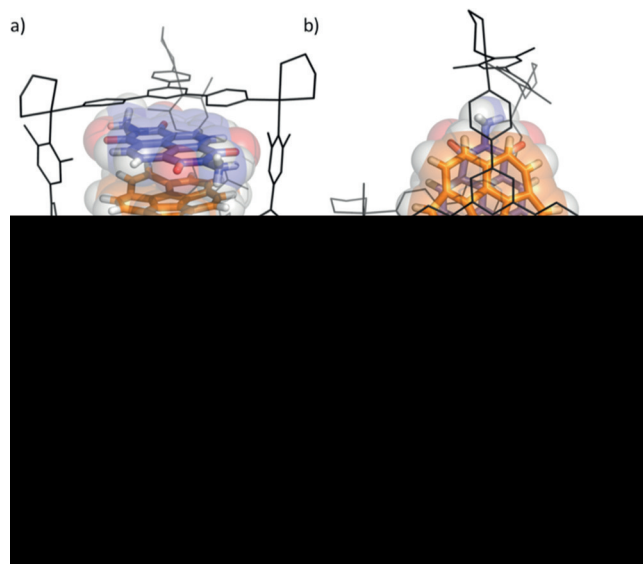

2a in **1a·(2·3)**   free **2a**

BD: 0.56(10) Å   BD: 0.87 Å

Figure 4. Calculated POAV and bowl depth (BD) obtained for **2a** (uncomplexed and complexed forms) from the corresponding X-ray crystal structures. X-ray data for free **2a** was obtained from a previously published data set.[10] The BD is defined as the distance between the centroid of the 5 interior carbon atoms and that of the 10 carbon atoms on the rim.

Figure 3. Structure of **1·(2a·3)** obtained from single-crystal X-ray analysis: a) side view and b) top view of **1·(2a·3)**; c), d) close-up view of the ORTEP (ellipsoids set at 30% probability) of the c) **2a·3** part and d) **2a** part. Space-filling depictions of the stacked guests are shown in the background. Hydrogen atoms of the host, solvent molecules (H₂O) and counteranions (NO₃⁻) are omitted for clarity.

Figure 5. Excerpt of the structure **1·(2a·3)** as obtained from single-crystal X-ray analysis, showing the contact of the convex side of **2a** (orange, top) to the electron deficient triazine ligand **4** (black, bottom). Closest contact is 3.11 Å.

convex surface of **2a** is stacked on the triazine ligand **4** rather than the donor–acceptor counterpart **3** in the box. Presumably, the metal-coordinated ligand **4** is a better electron acceptor than **3**, resulting in pronounced stacking interactions.

The overall bowl-depth (BD) of **2a** is reduced from 0.87 Å[8] to 0.56(10) Å upon encapsulation, concomitant with a slight distortion of the bowl-shaped framework. The curvature increases slightly at the edge of the cavity. Overall, the slightly taller cage allows non-planar guest **2a** to retain a certain amount of curvature. To gain more insight into the local curvature, π-orbital axis vectors (POAVs)[9] were calculated and compared with the unbound free **2a** (Figure 4). The POAV is defined as a vector that makes equal angles ($\theta_{\sigma\pi}$) to the three bonds at a conjugated carbon atom. As evident from the POAV values, local curvature decreases by up to 47% inside the cavity for **1·(2a·3)**.

At the convex face, corannulene is stacked on triazine ligand **4** not at the central five-membered ring but at two of the peripheral fused benzene rings to gain maximum contact area (Figure 5). As a result, the center of corannulene is slightly out of the C_3 axis of cage **1**.
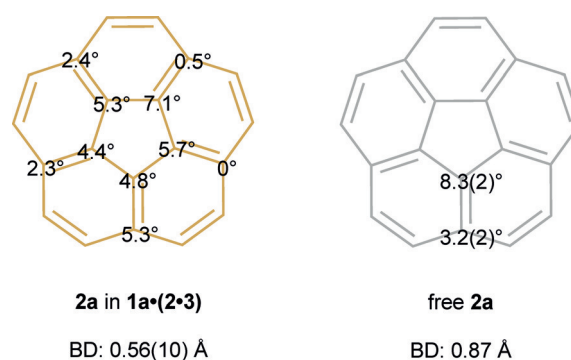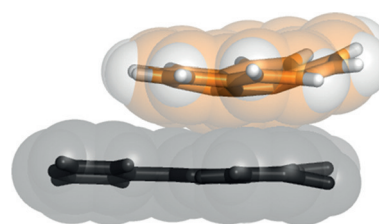
Corannulene dimer inclusion in cage **1** was also successfully observed when bromo-derivative **2b** was examined as a templating guest. A slight excess of guest **2b** was suspended in an aqueous solution of the component mixture (**4** + **5** + **6**) to induce the formation of a dimer inclusion complex **1·(2b)₂**. ¹H NMR spectrum of the filtered solution showed good conversion into the **1·(2b)₂** inclusion complex, in which broad signals of C_1-symmetric **2b** from 5–6.5 ppm were observed (Supporting Information, Figures S3–S5). Interestingly, efficient homo-dimer inclusion did not occur in the case of guest **2a**. This is probably because strongly polarized **2b** cancels its dipole moment by forming a stacked dimer.[11] This stabilization effect does not occur in the dimeric structure (**2a**)₂, which is rather destabilized by the charge repulsion between electron-rich π-systems (see the Supporting Information for DFT calculations and electrostatic potential maps for **2a** and **2b**, Figure S12).

Again, single crystals for X-ray analysis were obtained for the dimer inclusion complex **1·(2b)₂**. In the crystallographic analysis, host framework **1** was reasonably refined, but unfortunately, guest **2b** was disordered owing to its sliding and spinning motions in the cavity. Two sets of disordered structures (65%:35% and 57%:43%) were modeled and refined, but residual electron density peaks attributable to bromine atoms still remain near the periphery of encapsulated **2b**. Presumably, there are some more disordered

structures in small populations. The guest framework had to be refined with geometrical restraints (SADI) over the framework, making the detailed geometrical discussion invalid. However, the effective cavity height (the distance between the surfaces of the two triazine rings) is estimated to be 7.0 Å, which is much smaller than twice the heights of **2b** molecule ($4.3 \times 2 = 8.6$ Å; Supporting Information, Figure S9). This observation indicates the considerable flattening of the corannulene core by ca. 0.8 Å (from 4.3 to 3.5 Å).

For the bowl depth of 0.56 Å, an activation energy required for complete planarization of **2a** is estimated to be 6.22 kcal mol^{-1} by DFT calculation (B3LYP 6-31G + (d,p); see the Supporting Information for additional computational details of all compounds, Table S1), which is considerably smaller than 9.41 kcal mol^{-1} for free **2a** (BD: 0.87 Å). The inversion barriers for **2a** in **1·(2a·3)** and **2b** in **1·(2b)**$_2$ are, therefore, considerably reduced.[4, 12]

Owing to the considerable flattening, the inversion of **2b** in **1·(2b)**$_2$ should be very fast at room temperature (BD: 0.17 Å, around 1 kcal mol^{-1} barrier) and unfortunately cannot be measured by NMR spectroscopy. The bowl inversion is indirect competition to the fast exchange (as indicated by the broad coalesced NMR signals of the cage **1**; Supporting Information, Figure S5) and rotation of the guests inside the cage even at room temperature.

In case of **1·(2a·3)**, inclusion of the unsymmetrical donor–acceptor pair does not break the symmetry of the cage, which is indicative of both rapid interchanging guests[6, 13] and intramolecular bowl-flipping.

The overall crystal packing for the obtained structures of **1·(2a·3)** reveals infinite columnar stacks within the close distance of 3.31 Å, where the host–guest array is recognized within each column, leading to electronically favorable unidirectional strands in the both cases (Supporting Information, Figure S10).

In conclusion, we showed that encapsulation of corannulene with a synthetic receptor lead to dramatic compression of the guest molecule. It is anticipated that such a cushion-like nature of corannulene results in efficient aromatic stacks with fine-tuned donor–acceptor interactions. The stacking components, namely corannulene,[14] naphthalene diimides,[15] and the host material itself,[16] have been independently reported to be excellent materials for electron conductivity purposes. We may propose the potential applicability of the programmed stack of these components, both discretely in the cage and infinitely in a crystalline state, for tailor-made conducting materials.

Experimental Section

Preparation of inclusion complex **1·(2a·3)** and **1·(2b)**$_2$: Corannulene **2a** (5.01 mg, 0.020 mmol) and naphthalenediimide **3** (5.89 mg, 0.020 mmol), or monobromocorannulene **2b** (8.23 mg, 0.025 mmol), triazine panel ligand **4** (tris(4-pyridyl)-2,4,6-triazine, 6.25 mg, 0.020 mmol), pillared ligand **5** (2,2′,6,6′-tetramethyl-4,4′-bipyridine, 6.36 mg, 0.030 mmol), and (en)Pd(NO$_3$)$_2$ **6** (17.40 mg, 0.060 mmol; en = ethylenediamine) were mixed in water (1.0 mL) at 100 °C for 2 h. After filtration of the bright orange **1·(2a·3)** or yellow **1·(2b)**$_2$ solution, the ^{1}H NMR spectrum revealed the quantitative formation of complex **1·(2a·3)** and **1·(2b)**$_2$, respectively. See the Supporting

Information for the complete characterization of the complexes. The crystals of **1·(2a·3)** and **1·(2b)**$_2$ scattered weakly owing to severe disorder of the cage framework. Crystal data of **1·(2a·3)**: Monoclinic space group $P2_1/c$, $T = 100(2)$ K, $a = 18.705(4)$, $b = 37.303(8)$, $c = 27.809(6)$ Å, $\beta = 98.28(3)$, $V = 19201(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.340$ Mg m^{-3}, $F(000) = 7948$, reflections collected/unique 115113/39689 ($R_{int} = 0.0494$). The structure was solved by direct methods (SHELXS-2013)[17] and refined by full-matrix least-squares methods (SHELXL-2014)[18] on F^2 with 2130 parameters. $R_1 = 0.1278$ ($I > 2\sigma$-(I)), w$R_2 = 0.4342$. GOF 1.177. Crystal data of **1·(2b)**$_2$: Monoclinic space group $P2_1/c$, $T = 100(2)$ K, $a = 19.3300(3)$, $b = 37.4023(4)$, $c = 27.2068(3)$ Å, $\beta = 101.228(1)$, $V = 19293.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.330$ Mg m^{-3}, $F(000) = 7776$, reflections collected/unique 106246/39619 ($R_{int} = 0.0399$). The structure was solved by direct methods (SHELXT-2014)[19] and refined by full-matrix least-squares methods (SHELXL-2014) on F^2 with 2284 parameters. $R_1 = 0.1249$ ($I > 2\sigma(I)$), w$R_2 = 0.3818$. GOF 1.351. CCDC 1433284 and 1433285 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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