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VIP Host–Guest Systems

Porphine Dimeric Assemblies in Organic-Pillared Coordination Cages**

*Kosuke Ono, Michito Yoshizawa, Tatsuhisa Kato, Kentaro Watanabe, and Makoto Fujita**

The π-stacked structure of porphyrin dimers and oligomers attracts considerable interest in many areas such as biomimetic and bioinspired chemistry and material science.[1,2] The property of such assemblies is significantly affected by their spatial arrangement. Cofacially stacked porphyrin dimers have been previously prepared by linking the two porphyrin molecules by 1) covalent spacer(s),[3,4] 2) hydrogen bonding,[5] or 3) electrostatic interactions.[6] However, the synthesis and the functionalization of porphyrin dimers are still limited because all of these methods need precise and sometimes complicated modification on the porphyrin ring to form the dimers. Another promising method, which we focus on here, is to utilize host–guest π-stacking interactions, where any direct modifications on the porphine core are not required. Herein, we report the assembly of porphine dimers in the box-shaped cavity of organic-pillared cages. Depending on the cavity size, two porphine molecules are stacked directly (**A**; Figure 1) or layered with an aromatic spacer (**B**). They exhibit unique UV/Vis absorption and ESR spectra (when the porphine guest contains Cu^{II}), depending on the manner of stacking in the cavity.

We recently reported the self-assembly of organic-pillared coordination cages **1** and **2** from two panel-like ligands, three pillar-like ligands, and six *cis*-protected Pd complexes (Figure 1).[7] The cavities of the box-shaped hosts are large and well-fitting enough to accommodate two or three molecules of large planar aromatics by π-stacking interactions. Therefore, we employed these hosts to mediate the formation of the porphine dimers. To our knowledge, there are no reports on synthetic hosts that can fully encapsulate two or more porphine or porphyrin molecules in the cavity.[8]

The complexation of **1** with porphine **3a** was examined (Figure 2a). When a purple-red powder of water-insoluble **3a** (40.0 μmol) was suspended in a colorless solution of **1** (10.0 μmol) in D_2O (1.0 mL) for 12 h at room temperature,

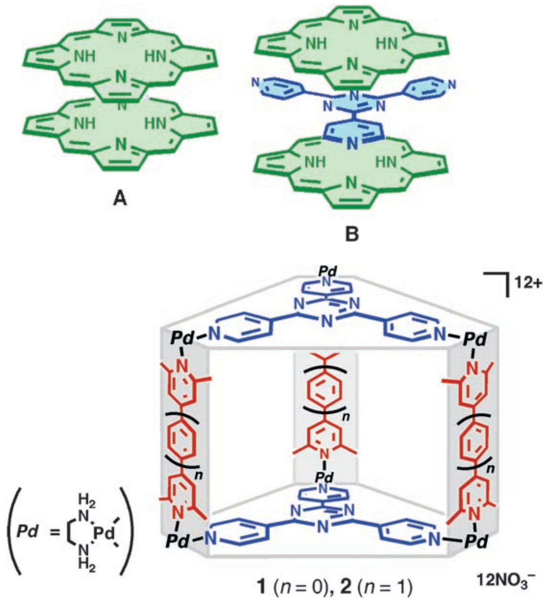

Figure 1. The two types of cofacial porphine dimers **A** and **B** and the chemical structures of organic-pillared coordination cages **1** ($n=0$) and **2** ($n=1$).

a clear red solution of $\mathbf{1}\supset(\mathbf{3a})_2$ was obtained. After filtration of suspended **3a**, the ^{1}H NMR spectrum of the D_2O solution showed two singlet signals derived form **3a** at $\delta = 7.63$ and 7.46 ppm with pronounced shifting upfield owing to inclusion of **1** in the cavity (Figure 2c). Aromatic protons H_a and H_b of panel-like ligand **1** were also remarkably shifted upfield because of shielding by the accommodated porphine rings. Upon evaporation, $\mathbf{1}\supset(\mathbf{3a})_2$ was isolated in 89% yield. The integral ratio of **1** and **3a** in ^{1}H NMR spectra as well as by mass spectrometric analysis (CSI-MS) confirmed the formation of the 1:2 host–guest complex $\mathbf{1}\supset(\mathbf{3a})_2$.[11]

The orientation of the two porphine guests in **1** was revealed by X-ray crystallographic analysis (Figure 3).[9] In the crystal structure, two molecules of **3a** are stacked one on top of the other with an interplane distance of approximately 3.4 Å. The porphine guests are also stacked with respect to ligand **1** (interplane distance ca. 3.3 Å). The two panel-like ligands at the top and the bottom of **1** are twisted by about 20° owing to efficient π stacking among the host and the two guests. Note that the box-shaped host **1** can fully encapsulate two molecules of porphine, whose diameter is as large as 10.4 Å.

When coordination cage **2**, which contains extended pillar **5**, was employed, we observed the formation of the inclusion complex $\mathbf{2}\supset(\mathbf{3a}\cdot\mathbf{4}\cdot\mathbf{3a})$ in which two molecules of porphine **3a** sandwich the free ligand **4** in the cavity of **2** (Figure 4a). The

[*] K. Ono, Dr. M. Yoshizawa, Prof. M. Fujita
Department of Applied Chemistry
School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-7257
E-mail: mfujita@appchem.t.u-tokyo.ac.jp

Prof. T. Kato, K. Watanabe
Faculty of Science, Josai University
1-1 Keyakidai, Sakado, Saitama 350-0295 (Japan)

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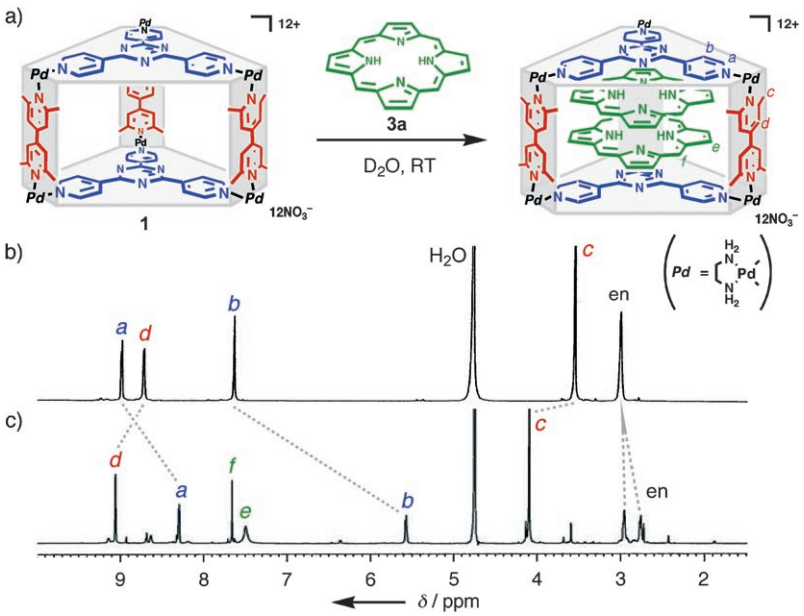

Figure 2. a) Schematic representation of the encapsulation of **3a** by **1**. b, c) ^{1}H NMR spectra (500 MHz, D_2O, RT) of **1** and **1**⊃(**3a**)$_2$. en = 1,2-ethylenediamine.

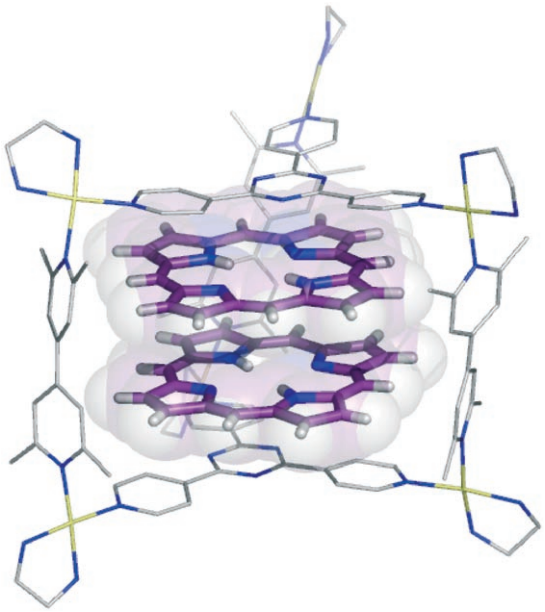

Figure 3. X-ray crystal structure of **1**⊃(**3a**)$_2$ (wire representation (**1**): Pd yellow, N blue, C gray; stick representation (**3a**): N blue, C purple, H white).

yield determined by NMR spectroscopy was quantitative when the components were combined in such a ratio that they constitute a **2**⊃(**3a**·**4**·**3a**) complex without excess of any components except for guest **4** (twofold excess employed). Namely, [(en)Pd(NO_3)$_2$] (30.0 μmol), panel-like ligand **4** (15.0 μmol), pillar-like ligand **5** (15.0 μmol), and **3a** (20.0 μmol) were combined in D_2O (0.5 mL), and the suspended solution was stirred at 100 °C for 2 h to give a red solution of **2**⊃(**3a**·**4**·**3a**) in high yield. After excess **4** was filtered out, the ^{1}H NMR spectrum showed the selective formation of **2**⊃(**3a**·**4**·**3a**) (Figure 4b). For the host framework **2**, six signals (*a*–*e* and en protons) were observed appropriately. For the guests, upfield-shifted signals of encapsulated **3a** (at $\delta = 8.12$ and 7.53 ppm) and **4** (at $\delta = 6.74$ and 3.20 ppm) were observed. The composition of **2**⊃(**3a**·**4**·**3a**) was confirmed by the integral ratio. Upon evaporation, **2**⊃(**3a**·**4**·**3a**) was isolated in 79 % yield.

The D_{3h} symmetry observed in the ^{1}H NMR spectra indicated that, in the whole structure, the five aromatic molecules adopt A-D-A-D-A (A = electron acceptor: ligated or free **4**; D = electron donor: **3a**) alternate stacking without disorder of the guests. A NOESY study also supported the D-A-D order of the guests (**3a**·**4**·**3a**): correlation signals were observed between **4** (H_h and H_i) and the middle portion of the pillar ligand **2** (H_d and H_e). Surprisingly, the unique quintuple stacking structure **2**⊃(**3a**·**4**·**3a**) was stable even under CSI-MS conditions. In the CSI-MS analysis, intense peaks for [**2**⊃(**3a**·**4**·**3a**) $- m\,NO_3^- + n\,DMF]^{m+}$ were observed: for example, m/z 831.5 ($m = 5$, $n = 4$) and 681.9 ($m = 6$, $n = 4$).

UV/Vis absorption spectra of **1**⊃(**3a**)$_2$ and **2**⊃(**3a**·**4**·**3a**) complexes are quite characteristic of the stacking manner of the guests (Figure 5). For the **1**⊃(**3a**)$_2$ complex, the Soret band appears at $\lambda_{max} = 380$ nm ($\varepsilon = 5.4 \times 10^5$ cm^{-1}M^{-1}), which is relatively broadened and remarkably blue-shifted ($\Delta\lambda =$ 21 nm) in comparison with that of free **3a** ($\lambda_{max} = 401$ nm ($\varepsilon = 8.5 \times 10^5$ cm^{-1}M^{-1})). This observation is interpreted as exciton coupling between cofacial porphine nuclei and, hence, is consistent with the face-to-face orientation of the porphine dimer.[10] In contrast, the Soret band of the **2**⊃(**3a**·**4**·**3a**) complex ($\lambda_{max} = 396$ nm ($\varepsilon = 6.1 \times 10^5$ cm^{-1}M^{-1})) was less broadened and hardly blue-shifted, indicating a very weak interaction between the separated porphine molecules.

The cavity-directed stacking of porphine molecules was also applied to metal-incorporating derivatives. We expected that the stacking of Cu^{II}-porphine molecules **3b** would induce intermolecular spin–spin exchange interactions. Accordingly, inclusion complexes **1**⊃(**3b**)$_2$ and **2**⊃(**3b**·**4**·**3b**) were prepared and characterized by CSI-MS and UV/Vis spectroscopic analyses.[11] The ESR spectrum of the **1**⊃(**3b**)$_2$ complex in H_2O (2.0 mM) at 103 K gave rise to a broadened signal around 310 mT and a seven-line $\Delta m_s = 2$ signal around 155 mT, indicating the spin–spin exchange interaction (triplet state, $S = 1$) of dimer **3b** (Figure 6a). In contrast, the ESR spectrum of the **2**⊃(**3b**·**4**·**3b**) complex showed the typical feature for doublet monomeric **3b** around 310 mT under the same conditions (Figure 6b), while the $\Delta m_s = 2$ region is silent. This result demonstrates that the free ligand **4** strongly suppresses the spin–spin exchange interaction between two molecules of **3b** in the cavity of **2** and that there is no guest disorder and disproportion. The spectra were consistent with simulated ones (Figure 6, blue lines).[11]

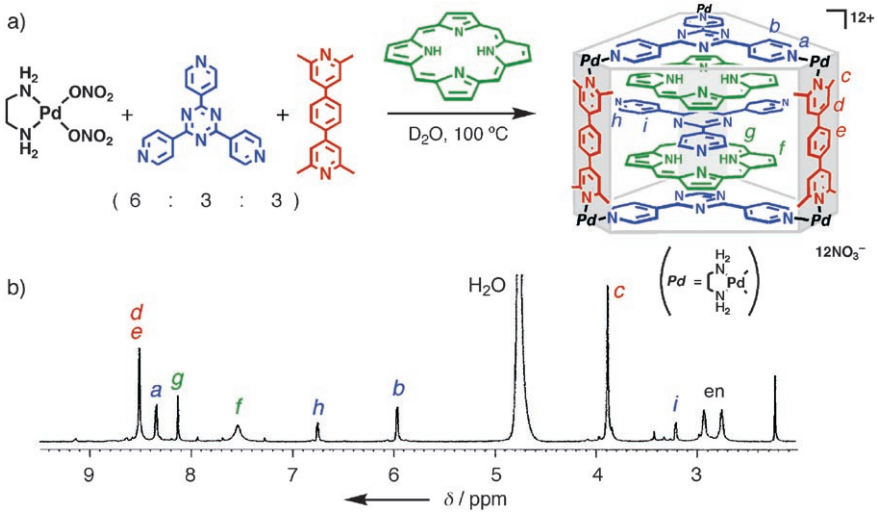

Figure 4. a) Schematic representation of the formation of **2**⊃(**3a**·**4**·**3a**) and b) its ^{1}H NMR spectrum (500 MHz, D_2O, RT).

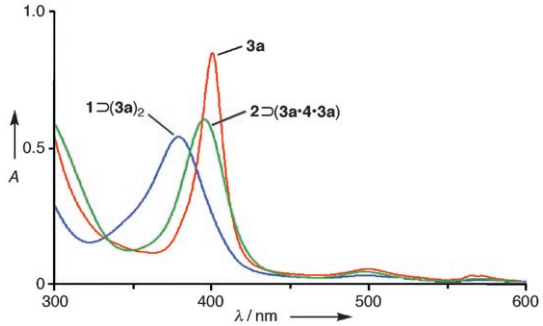

Figure 5. UV/Vis spectra (RT, 0.01 mM) of **1**⊃(**3a**)$_2$ and **2**⊃(**3a**·**4**·**3a**) in H_2O, and **3a** in $CHCl_3$.

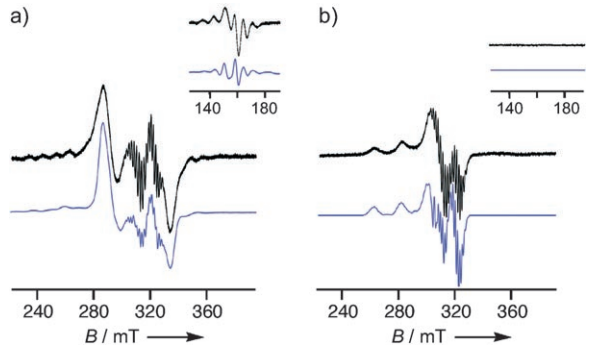

Figure 6. ESR spectra (2.0 mM in H_2O, 103 K) of a) **1**⊃(**3b**)$_2$ and b) **2**⊃(**3b**·**4**·**3b**) (black line: observed spectra; blue line: calculated spectra). The insets show the corresponding $\Delta m_s = 2$ regions.

In summary, two porphine molecules were efficiently assembled in the cavity of box-shaped cages **1** and **2**. While the two guests form a stacked dimer in **1**, they sandwich a free ligand in the larger cavity of **2**. The results also demonstrate the potential ability of **1** and **2** to induce the discrete stacking of planer molecules and metal complexes, which may be hardly soluble in water, even in a heterotopic fashion (such as the **3a**·**4**·**3a** assembly in **2**).[12] Developing new properties from such discrete stacking is currently a major interest in our group.

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[9] X-ray crystal data of **1**⊃(**3a**)$_2$: $C_{130}H_{148}N_{47}O_{54.5}Pd_6$, $M_r = 3879.35$, crystal dimensions $0.20 \times 0.10 \times 0.10$ mm^3, monoclinic space group $P2_1/n$, $a = 21.347(3)$ Å, $b = 31.526(4)$ Å, $c = 26.240(3)$ Å, $\beta = 111.237(2)°$, $V = 16460(4)$ Å^3, $Z = 4$, $r_{calcd} = 1.565$ g cm^{-3}, $F(000) = 7876$, radiation, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 80(2)$ K, reflections collected/unique 123791/37792 ($R_{int} = 0.2067$). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1818

parameters. $R_1 = 0.1296$ ($I > 2\sigma(I)$), $wR_2 = 0.3224$, GOF 1.019; max/min residual density 3.052/−2.565 e Å^{-3}. CCDC 622300 contains 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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[11] Detailed ESR measurement of the **1**⊃(**3b**)$_2$ complex around liquid-helium temperature (1.5–8 K) suggested two molecules of **3b** in **1** are in a triplet state closely lying with singlet state within a few cm^{-1} (see the Supporting Information).

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