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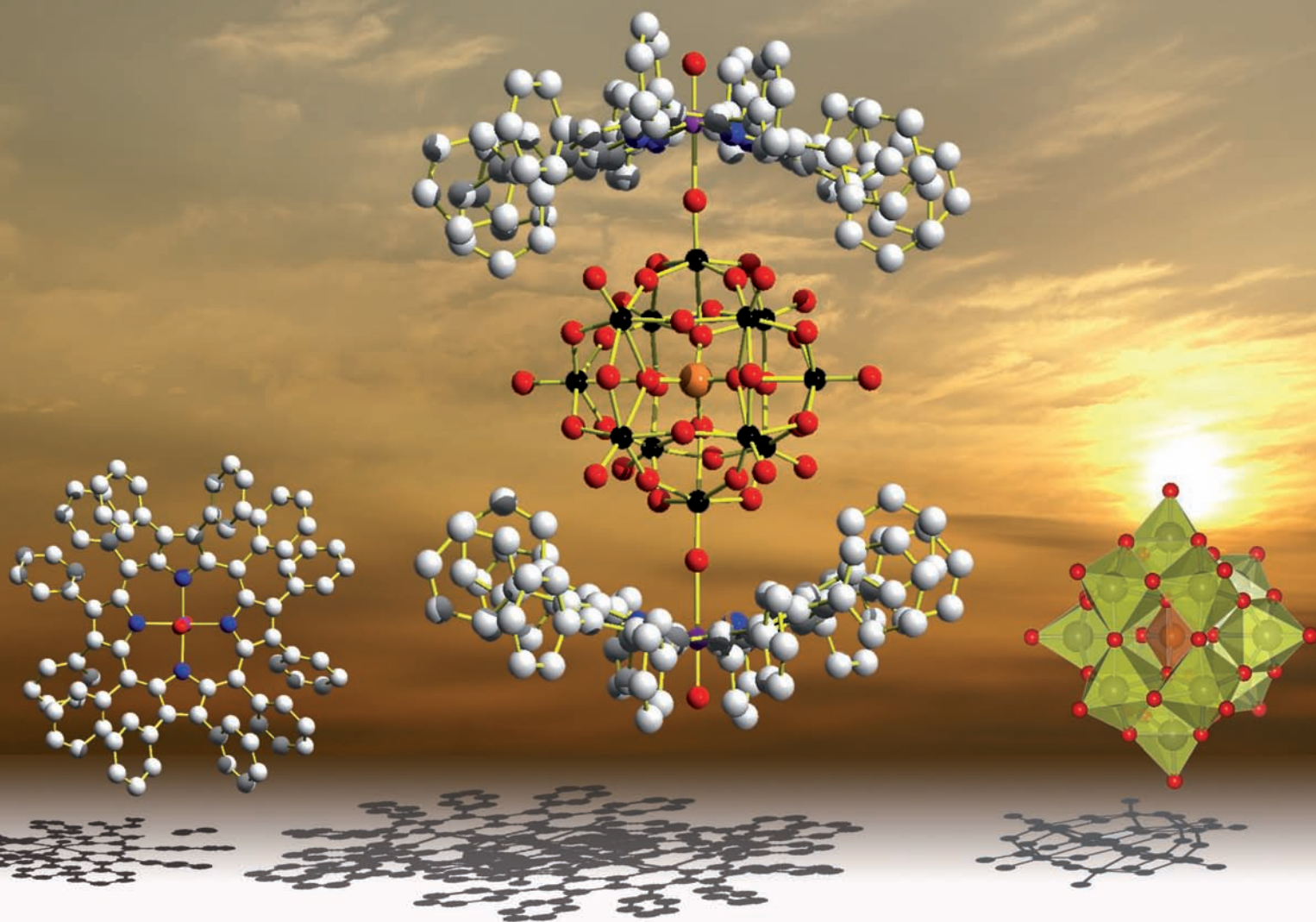
COMMUNICATION
Takahiko Kojima *et al.*
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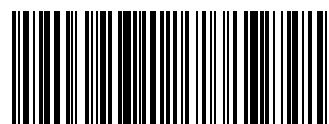
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A discrete conglomerate of a distorted Mo(V)-porphyrin with a directly coordinated keggin-type polyoxometalate†

Atsutoshi Yokoyama, Takahiko Kojima,* Kei Ohkubo and Shunichi Fukuzumi*

The reaction of a saddle-distorted Mo(V)-dodecaphenyl-porphyrin complex and a Keggin-type polyoxometalate gives a discrete and nanosized molecule, [{Mo(DPP)(O)}$_2$(H$_2$SiW$_{12}$O$_{40}$)], which involves direct coordination between the Mo(V) centers and terminal oxo groups of the polyoxometalate and exhibits excellent stability in solution to show reversible multi-redox processes.

Metalloporphyrins have been utilized to construct supramolecular structures by self-assembly. Those structures have been given by virtue of intermolecular interactions, including hydrogen bonding,[1] π–π interactions,[2] and coordination.[3] As for metalloporphyrin assemblies containing coordination bonds, they can be formed by axial coordination to the metal ions in the porphyrin complexes[4] and coordination of functional groups attached to the peripheral substituents of porphyrins to other metal complexes as linkers.[5] The benefits of using metalloporphyrins as building blocks for supramolecules are their photochemical excitations[6] and rich redox chemistry.[7]

On the other hand, polyoxometalates (POM) have been known to undergo photoexcitation to perform energy transfer from ^{3}LMCT,[8] exhibiting multistep redox processes.[9] Those properties have been utilized catalytic oxidation reactions,[10] and other applications including photochemical response and optoelectronics.[11] Combination of POM with metalloporphyrins has been reported to form ion pairs in the crystals by hydrothermal synthesis, in which those two components have not been directly related.[12] Inclusion of Zn-porphyrins has been reported into a cavity of a gigantic circular POM, molybdenum-blue, to form a large supramolecule, which has been observed by STM.[13] Thus, the ensembles of two photofunctional components, metalloporphyrins and POM, have begun to gain much attention for constructing functional materials.

We have recently reported on the formation of a porphyrin nanotube composed of saddle-distorted [Mo(DPP)(O)(H$_2$O)]$^+$ (H$_2$DPP = dodecaphenylporphyrin) (**1**), including tetranuclear Mo(VI)-oxo clusters which are in the category of POM.[14] As for the porphyrin nanotube, the supramolecule was formed by chance and accompanied by the decomposition of **1**. Thus, in order to regulate the structure of the supramolecular conglomerates derived from self-assembly of **1** and POM, we examined the reaction of **1** with a rigid and well-known Keggin-type POM ([(n-C$_4$H$_9$)$_4$N]$_4$[SiW$_{12}$O$_{40}$] (**2**)) into the inner space derived from self-assembly of the saddle-distorted complex **1**.

We report herein the isolation and crystal structure of an unprecedented metalloporphyrin-POM conglomerate forming a discrete large molecule, formulated as [{Mo(DPP)(O)}$_2$(H$_2$SiW$_{12}$O$_{40}$)] (**3**). In the molecule, two [Mo(DPP)(O)]$^+$ units were coordinated by two terminal oxo groups of the Keggin-type POM.

We first established the synthetic procedure of **1** as a perchlorate salt. A precursor complex, [Mo(DPP)(O)(OCH$_3$)] was treated with 2% HClO$_4$ in CH$_2$Cl$_2$[15] and the crude product was recrystallized from a solution of CH$_2$Cl$_2$–hexane to give pure **1** in 92% yield.[16]

The reaction of **1** with **2** was made in ethyl acetate–acetonitrile (3 : 1 v/v) and vapour diffusion with hexanes gave brown crystals of **3**. The crystal structure of **3** was determined by X-ray crystallography.‡ The molecular structure of **3** is depicted in Fig. 1. From its shape, we named this compound as a *Porphyrin Hamburger*. In the crystal structure, the POM is disclosed to coordinate directly to the Mo^V centers of two [Mo(DPP)(O)]$^+$ ions to form a discrete and nano-sized molecule (1.82 nm for the distance between the two oxo ligands of the [Mo(DPP)(O)]$^+$ units). Thus, the ligand substitution reaction occurred from the aqua ligand to the POM in the course of crystallization. This direct coordination should be ascribed to strong Lewis acidity of the Mo(V) center in the distorted DPP^{2-} and the close proximity causes steric hindrance between the DPP^{2-} ligands and [H$_2$SiW$_{12}$O$_{40}$]$^{2-}$. The distortion of the DPP^{2-} ligands is changed
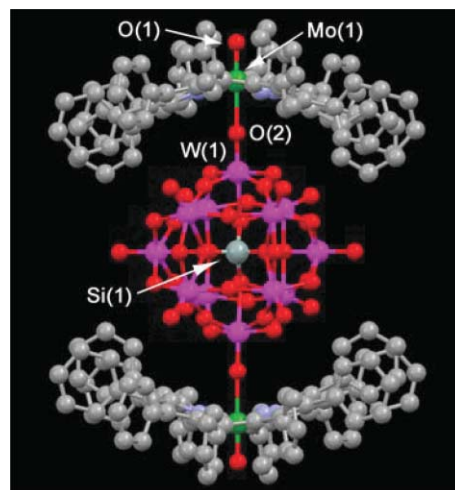

Fig. 1 Crystal structure of **3**. Gray, carbon; blue, nitrogen; red, oxygen; green, molybdenum; pink, tungsten; dark gray, silicon.

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† Electronic supplementary information (ESI) available: displacement of each atom of DPP, disordering of the Keggin moiety, TG-MS analysis, XPS, ESR, MALDI-TOF-MS, CV data. See DOI: 10.1039/b704994c

from saddle-distortion to ruffling with saddle distortion. The displacement of atoms of the porphyrin core in **3** is much smaller than that in **1** (see ESI Fig. S1†).

The $Mo^V{=}O$ bond in the $[Mo(DPP)(O)]^+$ unit is 1.682(12) Å (Mo(1)–O(1)) and the Mo–O bond with the Keggin-type POM is 2.260(11) Å (Mo(1)–O(2)), which is shorter than that of $Mo^V{-}OH_2$ (2.340(2) Å)[14] in **1**. Concerning the bridging moiety, the bond angle of Mo(1)–O(2)–W(1) is 169.14(9)°. As for the Keggin part of **3**, the structure was revealed to be an α-isomer. We encountered its directional disorder to give two different structures (see ESI Fig. S2†). Therefore, each atom of the Keggin moiety was refined isotropically.

In the crystal, molecules of **3** interact with each other in the *ac* plane *via* intermolecular π–π interactions between peripheral phenyl groups at distances of 3.34(2), 3.485(17) and 3.47 (2) Å for adjacent independent molecules to form a two-dimensional sheet as shown in Fig. 2(a). In the direction of the crystallographic *b* axis, the sheets stack together due to intermolecular π–π interactions in an edge-to-edge manner between peripheral phenyl groups and CH···O hydrogen bonding between the Mo=O moiety and two β-phenyl groups of neighbouring molecules at a distances of 3.256(19) Å. The stacking of the 2D sheets results in a layered structure in the crystal as shown in Fig. 2(b). In addition, the 2D sheet of **3** in the *ac* plane affords two channels running in the [1 0 0] and [0 0 1] directions of the crystal. TG-MS analysis of **3** indicated that large amounts of H_2O and CH_3CN molecules are included in the channels, engaging the thermodynamic stability of the crystals of **3** up to *ca*. 300 °C to support its robustness as a solid material (see ESI Fig. S3†).[17]
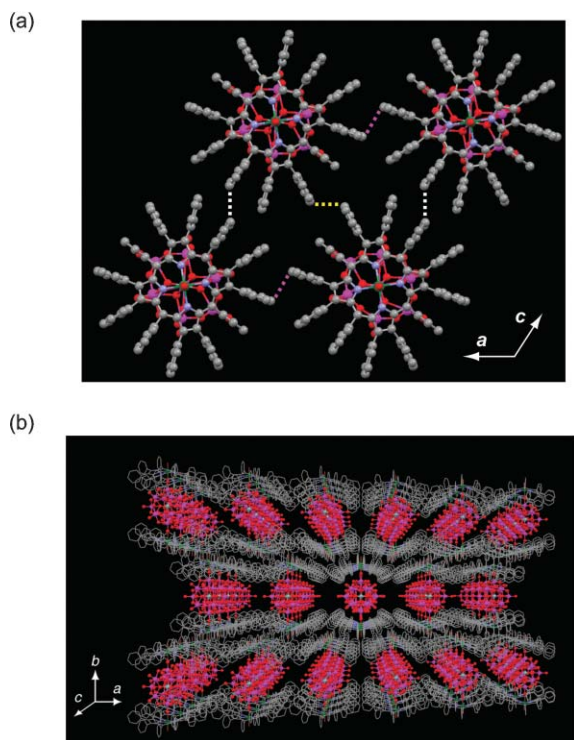

(a)

(b)

Fig. 2 Crystal packing of **3**: (a) *ac* plane; (b) three-dimensional description. In (a), atomic distances for intermolecular π–π interactions were as follows: 3.34(2) Å (yellow dotted line), 3.485(17) Å (white dotted line), and 3.47(2) Å (pink dotted line).

The XPS spectrum of **3** in the solid state exhibited two peaks at 235.5 ($Mo\ 3d_{3/2}$) and 232.4 ($Mo\ 3d_{5/2}$) eV for binding energies, which were consistent with those of **1**. This indicates that the Mo ions in **3** are in the Mo^V oxidation state.[18] In the XPS spectrum, peaks were observed at 36.72 ($W\ 4f_{5/2}$) and 34.51 ($W\ 4f_{7/2}$) eV;[19] These are comparable to those observed for **2** (37.23 and 35.05 eV), suggesting the oxidation state of W ions involved in **3** are all intact to be +6 in the course of the formation of **3**. Curve-fitting for the W part of the XPS spectrum of **3** supports that no contamination by W^V ions occurs (see ESI Fig. S4†). In addition, successive chemical reduction of **3** by tetramethylsemiquinone radical anion diminished and eliminated the ESR signals derived from the Mo^V-DPP moieties without any residual signal (see ESI Fig. S5†). Thus, no unpaired electron exists in the Keggin part of **3**,[20] supporting the oxidation state of W^{VI}.

Based on the charge balance with the $[Mo(DPP)(O)]^+$ moieties, the Keggin part should have the negative charge 2−, rather than the original charge of 4−. As described below, the Keggin part is doubly protonated to be $[H_2SiW_{12}O_{40}]^{2-}$. Probably, this protonation to the Keggin moiety occurs randomly to cause the disorder.

The MALDI-TOF-MS spectrum of **3** in CH_2Cl_2 (negative mode) exhibits a molecular ion peak cluster at 5542.126, which is consistent with the calculated mass number, but the isotropic pattern is unclear in the observed spectrum (see ESI Fig. S6†). This indicates that the complex **3** maintains its structure in solutions as in the solid state.

UV-vis spectroscopic titration in benzonitrile with triethylamine (NEt_3) allowed us to confirm the existence of two protons in one molecule. As shown in Fig. 3, we could observe spectral change with three isosbestic points at 510, 556 and 635 nm upon addition of NEt_3 up to 2 eq. and no change for more than 2 eq. (inset of Fig. 3). This observation lends credence to the existence of two protons per unit.

The ESR spectrum of **3** was measured in CH_2Cl_2 at room temperature (see ESI Fig. S7†). The ESR signal is assigned to a Mo(v) center at $g = 1.963$ with superhyperfine coupling ($a_N = 0.220$ mT) with four nitrogen atoms of the porphyrin ligand. This superhyperfine coupling constant a_N is smaller than that ($a_N = 0.25$ mT) of a planar $[Mo^V(TPP)(O)(OCH_3)]$.[21] This indicates weaker interactions of the porphyrin ligand with the Mo^V center to
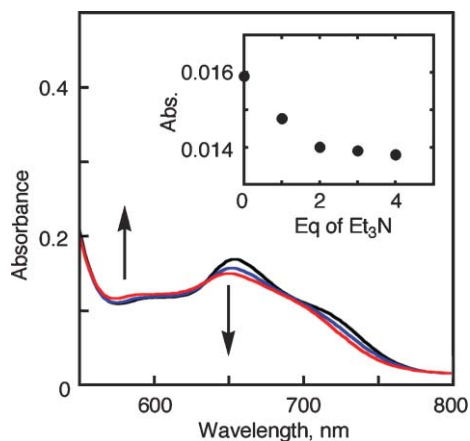

Fig. 3 UV-vis spectral change upon addition of triethylamine in benzonitrile in the range from 550 to 800 nm. Inset: Change of absorbance at 653 nm upon addition of NEt_3.
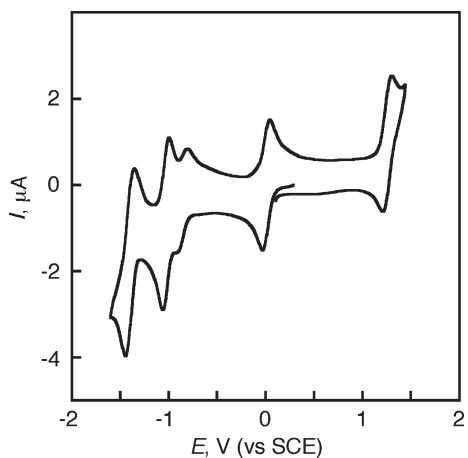
Fig. 4 Cyclic voltammogram of **3** in benzonitrile at room temperature under Ar in the presence of 0.1 M TBAPF$_6$ as an electrolyte.

make it more Lewis-acidic than those in planar Mo^V porphyrin complexes. This strong Lewis acidity derived from the distortion can allow the direct coordination of the Keggin ligand to the Mo^V centers.

Electrochemical measurements for **3** in benzonitrile at room temperature in the presence of TBAPF$_6$ (0.1 M) were performed to investigate its redox properties. The cyclic voltammogram of **3** exhibits five reversible redox waves as shown in Fig. 4. By comparison of the voltammogram with that of **1** (see ESI Fig. S8(a)†), redox waves observed for **3** at −1.41 and −1.04 V are assigned to two-electron and one-electron reduction of the DPP^{2-} ligand, respectively.[22,23] The redox processes observed at −0.00 and +1.26 V are ascribed to the Mo^V/Mo^{IV} redox couple and one-electron oxidation of the DPP^{2-} ligand in **3**, respectively.[24] A reversible redox couple observed at −0.87 V exhibits a half peak current as compared with other redox waves and we assigned this to the one-electron reduction of the trapped Keggin anion. This is in contrast to the CV of **2** showing two reversible redox waves at −0.77 and −1.24 V in CH$_3$CN (see ESI Fig. S8(b)†). These observations indicate that two [Mo(DPP)-(O)]$^+$ units attach to one Keggin anion and the characteristics of the Keggin anion in **3** should be different from those of **2**.[23]

In summary, the saddle-distorted Mo(v)-DPP complex can react with a polyoxometalate to form a unique and discrete nano-sized molecule, [{Mo(DPP)(O)}$_2$(H$_2$SiW$_{12}$O$_{40}$)], including unusual coordination of terminal W=O moieties. It behaves as a discrete nano-sized molecule in the crystal and even in solution. POM in the *Porphyrin Hamburger* showed an unusual oxidation state as observed in electrochemical measurements. This suggests that the inner space surrounded by DPP can induce and stabilize an unusual electronic structure of an encapsulated entity. The strategy described herein allows us to construct a new category of supramolecules derived from ensembles of metalloporphyrins and polyoxometalates toward developments of novel functional molecules and materials.

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