Polyoxomolybdates

A Molybdenum Crown Cluster Forms Discrete Inorganic–Organic Nanocomposites with Metalloporphyrins**

Akihiko Tsuda, Eri Hirahara, Yeong-Sang Kim, Hiroyuki Tanaka, Tomoji Kawai,* and Takuzo Aida**

Molybdenum blue (MB), formed by partial reduction of Mo^{VI} in an acidic aqueous solution, is a striking inorganic material due to its vivid blue color. It is a mixture of polyoxomolybdate (POM) clusters consisting of mixed-valent Mo^{V} and Mo^{VI} centers.[1–3] Although the initial exploration was made more than 200 years ago,[4] the first success in structural analysis of POM clusters was only reported in 1995, when Müller and co-workers isolated a crown-shaped POM cluster and obtained its crystal structure.[5] To date, they have also succeeded in structural determination of large POM clusters with hollow and spherical shapes.[6,7] Despite their interesting potentials in materials sciences, no examples have yet been reported of the utilization of such inorganic nano-objects for the fabrication of discrete inorganic/organic nanocomposite materials. Herein we report that the crown-shaped POM (molybdenum crown cluster; MC), upon mixing with metalloporphyrins having meso-aminophenyl substituents, forms discrete inclusion complexes, where the inorganic cavity of MC can accommodate up to three molecules of the guest compounds, to give spatially isolated metalloporphyrin molecules (Scheme 1).

$$Na_{(32-n)}[(MoO_3)_{176}(H_2O)_{63}(MeOH)_{17}H_n]\cdot$$
$$\approx 600\,H_2O\cdot \approx 30\,MeOH \quad \textbf{MC}$$

MC has a large cavity with a diameter of approximately 2.3 nm.[7] We expected that this cavity can incorporate proton acceptors through a hydrogen-bonding interaction, since a

---

[*] Dr. A. Tsuda, E. Hirahara, Dr. Y.-S. Kim, Prof. Dr. T. Aida
Department of Chemistry and Biotechnology
School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-7310
E-mail: tsuda@macro.t.u-tokyo.ac.jp
aida@macro.t.u-tokyo.ac.jp

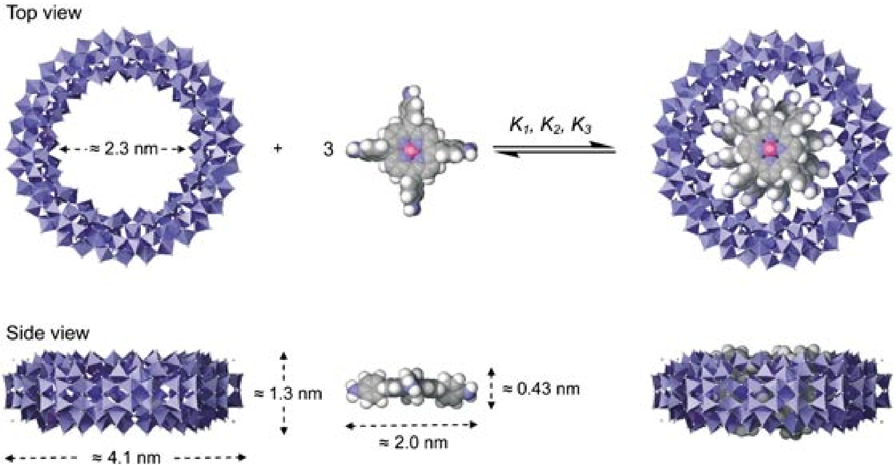
Dr. H. Tanaka,[+] Prof. Dr. T. Kawai
The Institute of Scientific and Industrial Research
Osaka University
8-1 Mihogaoka, Ibaraki, Osaka 567-0047 (Japan)
E-mail: kawai@sanken.osaka-u.ac.jp

[+] Responsible for scanning tunneling microscopy.

[**] The present work was supported by a Grants-in-Aid for Scientific Research (No. 15350128) and Encouragement of Young Scientists (No. 15750028) from the Ministry of Education, Science, Sports, and Culture, Japan. A.T. thanks the Kurata Memorial Hitachi Science and Technology Foundation, and the Tokuyama Science Foundation.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200460990

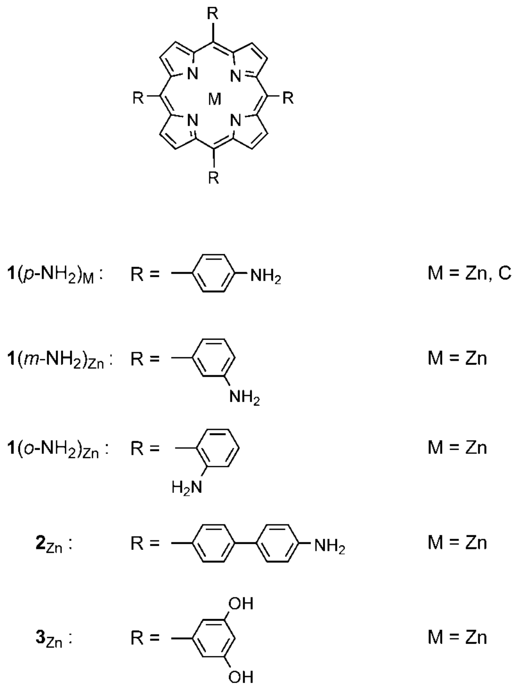


Scheme 1. Schematic representations of the complexation of molybdenum crown cluster (MC; blue polyhedra) with zinc 5,10,15,20-*tetrakis*(4-aminophenyl)porphyrin ($\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$; space-filling model: pink Zn, blue N, gray C, white H). Molecular models of MC and $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$ are based on X-ray crystallography (see ref. [7]) and MM2 calculation, respectively.

great number of proton-donating μ_3-O···H species are concentrated in its inner surface.

MC was prepared according to a literature method,[7] and characterized by means of MALDI-TOF mass spectrometry and scanning tunneling microscopy (STM), along with UV/Vis and IR spectroscopy.[8] The MC, thus obtained, was highly soluble in MeCN to give a clear blue solution, which showed characteristic broad absorption bands at 730 and 1058 nm (Figure 1 a). For the complexation studies with MC, we chose as potential guest molecules zinc complexes of 5,10,15,20-*tetrakis*(aminophenyl)porphyrins, such as $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$, $\mathbf{1}(m\text{-NH}_2)_{\mathrm{Zn}}$, and $\mathbf{1}(o\text{-NH}_2)_{\mathrm{Zn}}$, and $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}$, a copper analogue of $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$. Compounds $\mathbf{2}_{\mathrm{Zn}}$ having 4-aminobiphenyl groups and $\mathbf{3}_{\mathrm{Zn}}$ bearing 3,5-dihydroxyphenyl groups at the meso-positions were used as references. According to molecular models, $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$, $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}$, $\mathbf{1}(m\text{-NH}_2)_{\mathrm{Zn}}$, $\mathbf{1}(o\text{-NH}_2)_{\mathrm{Zn}}$, and $\mathbf{3}_{\mathrm{Zn}}$ are 2.0, 2.0, 1.8, 1.6, and 1.8 nm in diameter (longer molecular axis), respectively,[9] and smaller than the cavity of MC, whereas compound $\mathbf{2}_{\mathrm{Zn}}$ is much larger (2.8 nm). Compound $\mathbf{3}_{\mathrm{Zn}}$ is different from these complexes, in that it has Brønsted acidic OH functionalities in place of the amino functionalities.

Electronic absorption spectroscopy in MeCN with the five zinc porphyrin complexes indicated that $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$ and $\mathbf{1}(m\text{-NH}_2)_{\mathrm{Zn}}$ interact with MC. For example, upon titration of $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$ which has 4-aminophenyl groups with MC, the Soret-band at 430 nm decreased in intensity with a small blue shift to 427 nm, while a red-shifted shoulder appeared at 440 nm (Figure 1 b). Compound $\mathbf{1}(m\text{-NH}_2)_{\mathrm{Zn}}$ which has 3-aminophenyl groups also showed a spectral change upon titration with MC, a considerable broadening of the Soret band in the longer wavelength region took place.[8] In contrast, $\mathbf{1}(o\text{-NH}_2)_{\mathrm{Zn}}$ bearing amino groups directed towards the porphyrin unit (Figure 1 c) and the larger sized $\mathbf{2}_{\mathrm{Zn}}$[8] hardly showed spectral changes under similar titration conditions. Likewise, the absorption spectrum of $\mathbf{3}_{\mathrm{Zn}}$ having phenolic OH functionalities was virtually unchanged upon addition of MC. These contrasting observations indicate that the complexation of the zinc porphyrins with MC is chemo-,



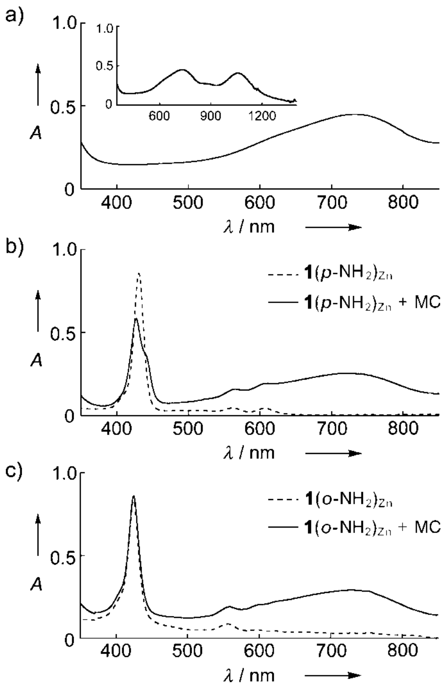


Figure 1. Absorption spectra (350–850 nm) of a) MC (2.2×10^{-6} M)[10] (inset: 350–1400 nm), and zinc porphyrins, b) $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Zn}}$ (2.4×10^{-6} M), and c) $\mathbf{1}(o\text{-NH}_2)_{\mathrm{Zn}}$ (2.5×10^{-6} M) in the absence and presence of MC (0.5 equiv) in MeCN at 20 °C.

regio-, and size-selective. Namely, the peripheral amino groups are crucial for the complexation with MC, but they should be oriented away from the porphyrin ring, and such guest molecules should be smaller than the MC cavity. Therefore, MC accommodates $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ and $\mathbf{1}(m\text{-NH}_2)_{\text{Zn}}$ inside the cavity through the formation of multiple hydrogen bonds (e.g., μ_3-O···H···N), to give inclusion complexes $[\text{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]$, and $[\text{MC}\supset\mathbf{1}(m\text{-NH}_2)_{\text{Zn}}]$, respectively. Copper complex $\mathbf{1}(p\text{-NH}_2)_{\text{Cu}}$, upon titration with MC, also showed an essentially identical spectral change profile to that of $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$.[8]

To determine the stoichiometry of the complexation, spectroscopic titration of MC with $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ was conducted in MeCN (Figure 2a), where MC showed stepwise spectral changes in response to $[\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]/[\text{MC}]$ at 0–2, 2–4 , and 4–10 (Figure 2b–d),[10] with isosbestic points at 1121, 1138, and 1143 nm, respectively. This observation indicates the stepwise formation of 1:1, 1:2, and 1:3 complexes between MC and $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$.[11] Slow evaporation of a concentrated MeCN solution of a 1:3 mixture of MC and $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ allowed the isolation of $[\text{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]$ as a green precipitate, which was subjected to inductively coupled plasma atomic emission spectroscopy (ICP-AES) to give a Mo/Zn ratio of 61.9. This value is in good agreement with that calculated for the 1:3 inclusion complex between MC and $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ (58.7). According to the crystal structure,[7] the cavity of MC is 1.3 nm deep and large enough to accommodate up to three molecules of $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ when they are stacked face to face (Scheme 1). Thus, the spectral changes observed for the complexation of $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ (Figure 1b) and $\mathbf{1}(m\text{-NH}_2)_{\text{Zn}}$[8] with MC are considered to reflect such a stacking association of these guest molecules in the MC cavity, as well as the proton-donation from their peripheral amino groups.

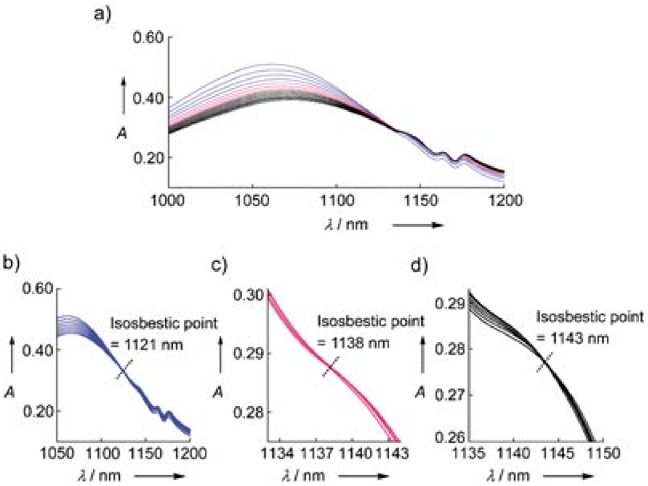


Figure 2. Spectroscopic titration of MC (2.5×10^{-6} M)[10] with $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ in MeCN at 20°C. $[\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]$ = a) 0–2.1×10^{-5} M (overall spectral change), b) 0–0.5×10^{-5} M, c) 0.6×10^{-5}–1.0×10^{-5} M, and d) 1.2×10^{-5}–2.1×10^{-5} M.

Ultrahigh-vacuum scanning tunneling microscopy (UHV-STM)[12] (Figure 3) demonstrated that the product upon complexation of MC with $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ is indeed an inclusion complex $[\text{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]$. Thus, a dilute aqueous solution of a mixture of MC and $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ (1:3)[10] was sprayed by the pulse injection technique onto a clear flat Cu(111) surface. The UHV-STM image showed the presence of numerous doughnut-like discrete nano-objects with a diameter of 4–5 nm (Figure 3b), which is consistent with the reported dimension of crystallographically defined MC.[7] Some of these nano-objects in the STM image (Figure 3c) appear to have a filled cavity.[13] By means of scanning tunneling spectroscopy (STS)[14] on one of these filled objects, correlations between differential conductance (dI/dV) and sample bias voltage (V_s) were measured separately for the shell and core parts.[8] As shown in Figure 3, these two parts exhibit different dI/dV–V_s profiles. Although the shell part, as with intact MC, displays a gradual increase in dI/dV with either decreasing or increasing V_s, the core part, in contrast, shows two bands at −0.7 and +1.6 V, which are assignable to resonant tunneling currents through the HOMO and LUMO of the guest compound.[15] Since the energy gap of 2.3 eV, thus observed, is consistent with the optical HOMO–LUMO energy gap of $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ (2.1 eV), it is clear that the object with a filled cavity (Figure 3c) is $[\text{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]$.

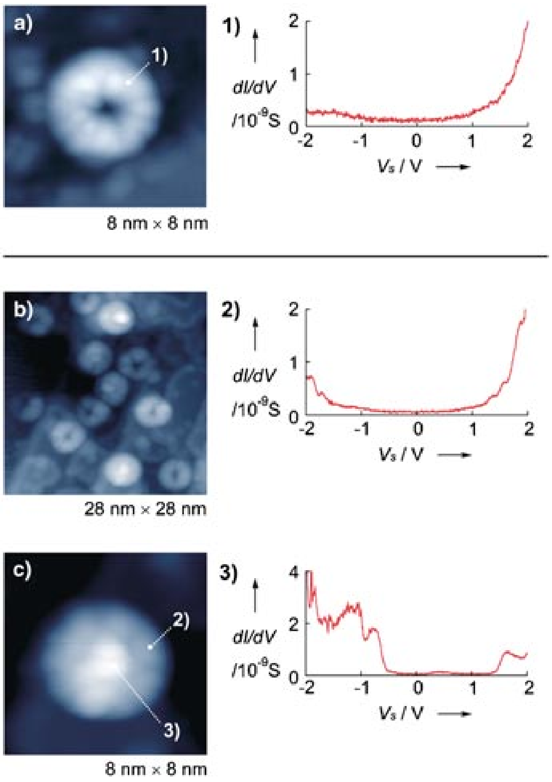


Figure 3. Left: ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) images and right: scanning tunneling spectroscopy (STS) data on Cu(111) surfaces at 80 K. UHV-STM of a) intact MC (imaging conditions: $I=2.0$ pA, $V_s=1.0$ V), b) a 1:3 mixture of MC and $\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}$ ($I=2.0$ pA, $V_s=3.0$ V), and c) $[\text{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]$ ($I=2.0$ pA, $V_s=1.0$ V). STS differential conductance (dI/dV)–sample bias voltage (V_s) correlations of area (1) an intact MC observed in (a), and areas (2) the shell and (3) the core of $[\text{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\text{Zn}}]$ observed in (c).

We also conducted an electron paramagnetic resonance (EPR) study on the inclusion complex of MC with copper porphyrin $\mathbf{1}(p\text{-NH}_2)_{\text{Cu}}$ ($[\text{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\text{Cu}}]$). MC is diamagnetic at the ground state, while copper porphyrins are paramagnetic ($S = 1/2$) and generally show anisotropic EPR spectra with two distinct $g_\parallel$ and $g_\perp$ values and hyperfine splittings induced by copper ($I = 3/2$) and nitrogen ($I = 1$) nuclei.[16] In contrast, $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}$ alone in MeCN at 103 K displayed an isotropic EPR pattern possibly arising from an irregular aggregation caused by hydrogen-bonding interactions at the peripheral amino groups (Figure 4). On the other hand, when $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}$ was mixed with MC at a 1:3 molar ratio,[10] the resulting inclusion complex $[\mathrm{MC}\supset\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}]$ showed in its EPR spectrum an anisotropic pattern with $g_\parallel$ and $g_\perp$ values of 2.187 and 2.085, respectively, along with sharp hyperfine arising from the copper ($a_\parallel = 19.3$ mT) and nitrogen nuclei. Thus, $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}$ is freed from its hydrogen-bonded irregular assembly and incorporated into the MC cavity to form a uniform assembly in the confined nanospace.

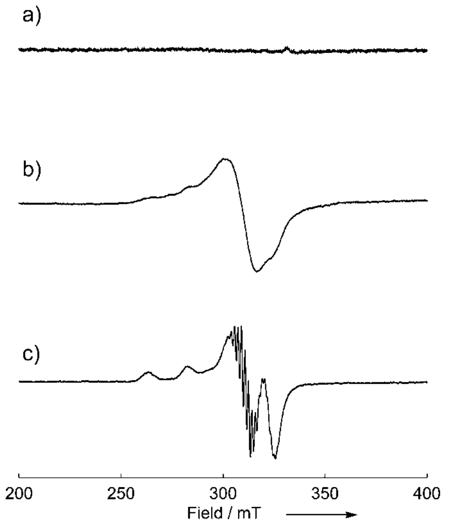


Figure 4. EPR spectra at 103 K in MeCN. a) MC (3.0×10^{-5} M), b) $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}$ (3.0×10^{-5} M), c) a mixture of $\mathbf{1}(p\text{-NH}_2)_{\mathrm{Cu}}$ (3.0×10^{-5} M) and MC (1.0×10^{-5} M).[10]

In conclusion, we have demonstrated the first example of organic functionalization of doughnut-like molybdenum crown cluster (MC). In its nanocavity MC can accommodate metal complexes of aminophenyl-substituted porphyrins, such as $\mathbf{1}(p\text{-NH}_2)_{\mathrm{M}}$ (M = Zn, Cu) and $\mathbf{1}(m\text{-NH}_2)_{\mathrm{Zn}}$ as a result of hydrogen-bonding interactions, to form discrete inorganic/organic nanocomposite materials. The results indicate a new potential for MC as an inorganic host in supramolecular chemistry and also as an building block for nanoscopic materials science.

Experimental Section

MC, $\mathbf{1}(m\text{-NH}_2)_{\mathrm{Zn}}$, and $\mathbf{1}(o\text{-NH}_2)_{\mathrm{Zn}}$ were synthesized according to literature methods,[7,17] while 5,10,15,20-*tetrakis*(4-aminophenyl)-21*H*,23*H*-porphine $\mathbf{1}(p\text{-NH}_2)_{\mathrm{H}}$ and 5,10,15,20-*tetrakis*(3,5-dihydroxyphenyl)-21*H*,23*H*-porphine $\mathbf{3}_{\mathrm{H}}$ were obtained from commercial sources. Column chromatography was carried out with Wakogel C-400 or alumina (Merck Ltd.). ^{1}H NMR spectra were recorded in CDCl$_3$ on a JEOL model α-500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane (TMS) as internal standard. Electronic absorption spectra were recorded on a JASCO model V-570 spectrometer equipped with a temperature controller. IR spectra were recorded on a JASCO model FT/IR-610 spectrometer. MALDI-TOF mass spectrometry was performed on a Perceptive Biosystems model Voyager-DE spectrometer with 9-nitroanthracene as matrix. ICP-AES was performed on a Seiko Instruments Inc. model SPS4000 inductively coupled plasma atomic emission analyzer. Ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) was performed on a Unisoku Japan model USM-1200.

Metalation of porphyrins**:** Typically, a saturated MeOH solution of Zn(OAc)$_2$ or Cu(OAc)$_2$ was added to a CHCl$_3$ solution of a free-base porphyrin, and the resulting mixture was heated under reflux for 1–2 h. After the complete metalation was confirmed by thin layer chromatography (TLC) or MALDI-TOF MS, the mixture was poured into water and extracted with CHCl$_3$. The combined organic extract was washed with water and brine, dried over anhydrous Na$_2$SO$_4$, and then evaporated to dryness. Recrystallization of the residue from THF/hexane gave the corresponding metalloporphyrin in an analytically pure form.

$\mathbf{2}_{\mathrm{Zn}}$: (1,1′-Biphenyl)-4-nitro-4′-carboxaldehyde (786 mg, 3.5 mmol) and pyrrole (232 mg, 3.5 mmol) were heated in refluxing propionic acid (25 mL) for 3 h. A crystalline precipitate, obtained from the reaction mixture on cooling, was isolated by filtration and washed with water and MeOH. The precipitate (70 mg) and anhydrous SnCl$_2$ (250 mg, 1.1 mmol) were dissolved in concentrated aq.HCl/THF (2:1; 15 mL), and the resulting solution was stirred for 24 h at 50 °C. Aqueous KOH was added to the mixture until it turned basic, and the mixture was extracted with CH$_2$Cl$_2$ (4 × 50 mL). The combined organic extract was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel with CHCl$_3$:MeOH (95:5) as eluent, and a reddish purple fraction isolated was stirred with excess Zn(OAc)$_2$ in CHCl$_3$ for 1 h. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was extracted with CHCl$_3$/water. The combined organic extract was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. Recrystallization of the residue from THF/hexane gave $\mathbf{2}_{\mathrm{Zn}}$ (5 mg, 4.7 μmol) as purple powdery substance. MALDI-TOF MS *m*/*z* 1040, calcd for $C_{68}H_{48}N_8Zn$ 1040; UV/Vis (CHCl$_3$): $\lambda_{\max} = 427$, 522, 559, and 600 nm; ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): $\delta = 4.61$ (s, 8H, NH$_2$), 6.72 (d, $J = 10.0$ Hz, 8H, bipheny), 7.62 (d, $J = 10.0$ Hz, 8H, bipheny), 7.87 (d, $J = 10.0$ Hz, 8H, bipheny), 8.14 (d, $J = 10.0$ Hz, 8H, bipheny), and 8.88 ppm (s, 8H, pyrrole-β).

Received: June 16, 2004

Keywords: inorganic/organic nanocomposites · polyoxomolybdates · porphyrinoids · scanning probe microscopy · supramolecular chemistry

---

[1] J. J. Berzelius, *Poggendorff's Ann. Phys.* **1826**, *6*, 369–392.
[2] F. B. Schrmer, Jr., L. F. Aurieth, S. T. Gross, D. S. McClellan, L. J. Seppi, *J. Am. Chem. Soc.* **1942**, *64*, 2543–2545.
[3] a) R. I. Buckely, R. J. H. Clark, *Coord. Chem. Rev.* **1985**, *65*, 167–218; b) H. K. Chae, W. G. Marquart, *Coord. Chem. Rev.* **1993**, *128*, 209–224.
[4] C. W. Scheele in *Sämtliche Physische und Chemische Werke, Vol. 1* (Ed.: D. S. F. Hermbstädt), Martin Sändig oHG: Niederwalluf/Wiesbaden, **1971**, pp. 185–200 (reprint: original 1793).
[5] A. Müller, E. Krickermeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem.* **1995**, *107*, 2293–2295; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2122–2124.
[6] Recent reviews: a) A. Müller, C. Serain, *Acc. Chem. Res.* **2000**, *33*, 2–10; b) A. Müller, P. Kögerler, A. W. M. Dress, *Coord. Chem. Rev.* **2001**, *222*, 193–218; c) A. Müller, S. Roy, *Coord. Chem. Rev.* **2003**, *245*, 153–166.

[7] A. Müller, M. Koop, H. Bögge, M. Schmidtmann, C. Beugholt, *Chem. Commun.* **1998**, 1501 – 1502.

[8] See Supporting Information.

[9] Molecular models of metalloporphyrins were obtained using a MM2 force field.

[10] Concentrations of MC are estimated to include, at most, 18% deviations arising from its loosely bound crystal water.

[11] K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, H. Chiba, *Nature* **2002**, *415*, 509 – 511.

[12] a) H. Tanaka, T. Kawai, *J. Vac. Sci. Technol. B* **1997**, *15*, 602 – 604; b) H. Tanaka, T. Kawai, *Surf. Sci.* **2003**, *539*, 531 – 536.

[13] Some of the inclusion complexes presumably lost the guest molecule in the injection process.

[14] a) M. Pomerantz, A. Aviram, R. A. McCorkle, L. Li, A. G. Schrott, *Science* **1992**, *255*, 1115 – 1118; b) P. Guaino, A. A. Cafolla, O. McDonald, D. Carty, G. Sheerin, G. Hughes, *J. Phys. Condens. Matter* **2003**, *15*, 2693 – 2698.

[15] Similar spectral patterns have been reported for thin films of metalloporphyrins on an Au(111) surface, see: L. Scudiero, D. E. Barlow, K. W. Hipps, *J. Phys. Chem. B* **2002**, *106*, 996 – 1003.

[16] a) S. S. Eaton, G. R. Eaton, C. K. Chang, *J. Am. Chem. Soc.* **1985**, *107*, 3177 – 3184; b) M. C. Feiters, M. C. T. Fyfe, M.-V. Martínez-Díaz, S. Menzer, R. J. M. Nolte, J. F. Stoddart, P. J. M. V. Kan, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 8119 – 8120.

[17] a) M. Momenteau, J. Mispelter, B. Loock, J.-M. Lhoste, *J. Chem. Soc. Perkin Trans. 1* **1985**, 221 – 231; b) B. C. Bookser, T. C. Bruice, *J. Am. Chem. Soc.* **1991**, *113*, 4208 – 4218.