Molecular Capsules

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An M_2L_4 Molecular Capsule with a Redox Switchable Polyradical Shell

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Abstract: *Preparation of molecular nanostructures with polyradical frameworks remains a significant challenge because of the limited synthetic accessibility which is entirely different from that of neutral and ionic ones. Herein we report the quantitative formation of a new M_2L_4 molecular capsule from metal ions and dihydrophenazine-based ligands. The capsule has a spherical nanocavity (ca. 1 nm in diameter) enclosed by eight redox-active, dihydrophenazine panels. Electrochemical oxidation of the capsule leads to the generation of multiple radical cations on the shell framework. Moreover, a stable tetra(radical cation) capsule can be reversibly obtained by chemical as well as electrochemical oxidation.*

Considerable attention has been drawn to the preparation of confined molecular nanospaces, because molecules encapsulated in the space often exhibit intriguing physical properties and chemical reactivities through enhanced host–guest interactions.[1,2] A huge number of supramolecular cages and capsules with well-designed nanocavities have been constructed using neutral, cationic, or anionic organic frameworks. On the other hand, preparation of similar supramolecules with polyradical frameworks remains rare and has been limited to the use of stable verdazyl radicals[3] or highly reactive TTF-based radicals.[4] Thus, stimuli-responsive switching between nonradical and stable polyradical states of the cage frameworks has not been demonstrated to date. To address this issue, we focused on M_2L_4 molecular capsules with spherical polyaromatic shells, which have an isolated cavity with a diameter of around 1 nm, displaying strong fluorescent emissions ($M = Zn^{II}$ and Cu^{II}) and wide-ranging host capabilities ($M = Pd^{II}$ and Pt^{II}).[5,6] These capsules are quantitatively formed by mixing metal ions and bispyridine ligands with redox-inactive anthracene panels.[7] In keeping the simple structural motif,[8] Herein we designed an M_2L_4 molecular capsule (**1**) bearing redox-active panels by the replacement of the anthracene rings with dihydrophenazine rings (Figure 1), for the development of a new class of functional nanospaces encircled by polyradical frameworks.

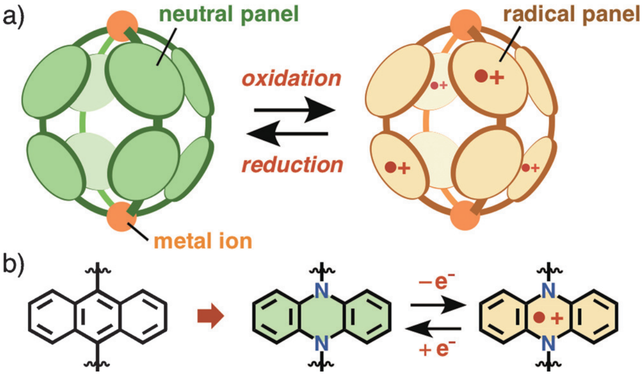

Figure 1. a) Schematic representation of an M_2L_4 molecular capsule (**1**) with switchable neutral/radical panels. b) A redox-inactive anthracene panel and a redox-active dihydrophenazine panel employed in this work.

Dihydrophenazine derivatives generate relatively stable radical cation (●+) species by single-electron oxidation under ambient conditions (Figure 1 b, right)[9] and are widely employed in electro-, photo-, and magnetochemical compounds.[10] However, to our knowledge, their utilities in the organic frameworks of (supra)molecular cages, capsules, and tubes have yet to be revealed.[1,2] Herein we report the quantitative assembly of new M_2L_4 molecular capsule **1** from metal ions and redox-active ligands **2** which contain two pyridine and two dihydrophenazine rings (Figure 2 a). In contrast to the analogous M_2L_4 capsules with anthracene panels[5,6] and the previous radical cages,[3,4] the present capsule can reversibly convert into a stable tetra(radical cation) capsule, without a configurational change, by electrochemical and chemical oxidation.

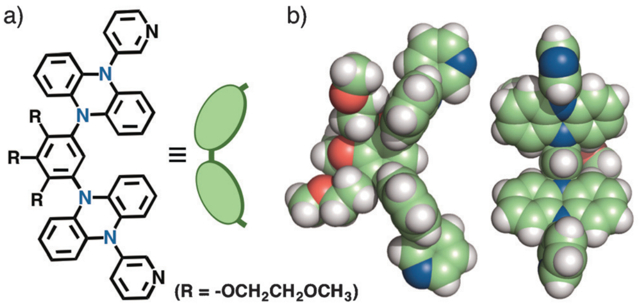

Figure 2. a) Ligand **2** with two dihydrophenazine rings and b) its X-ray crystal structure (side and front views).

Redox-active ligand **2** was synthesized in two steps. Treatment of commercially available phenazine with 3-pyridyllithium gave rise to air-sensitive 5-(3-pyridyl)-5,10-dihydrophenazine. The crude product was applied to the palladium-catalyzed cross-coupling reaction with 1,5-

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dibromo-2,3,4-tri(2-methoxyethoxy)benzene to afford ligand **2**.[11,12] The bent conformation of **2** bearing two planar dihydrophenazine rings was confirmed by X-ray crystallographic analysis (Figure 2b).

When neutral ligand **2** (12.3 μmol) and $Pd(NO_3)_2$ (7.4 μmol), prepared in situ from $PdCl_2(DMSO)_2$ and $AgNO_3$, were mixed in $[D_6]$DMSO (0.5 mL), M_2L_4 molecular capsule **1** was quantitatively formed at room temperature within 30 min (Figure 3a). The structure obtained is stable under ambient conditions and can be fully characterized by NMR spectroscopy, MS, and X-ray crystallographic analyses (Figure 3). In the ^1H NMR spectrum, the shifts of pyridyl signals $H_{a–d}$ suggest the metal–ligand interactions and the huge upfield shifts of *m*-phenylene signal H_i ($\Delta\delta = -0.66$ ppm) and dihydrophenazine signal H_e ($\Delta\delta = -0.47$ ppm) indicate the formation of a capsular structure (Figure 3b,c). The M_2L_4 composition of the product was revealed by the ESI-TOF MS spectrum, where signals at *m*/*z* 867.9, 1177.9, and 1797.7 were assigned to $[\mathbf{1}-n\cdot NO_3^-]^{n+}$ ions ($n = 4$, 3, and 2, respectively; Figure 3d). Each of the isotope patterns is in accord with the calculated ones. Although suitable crystals of capsule **1** were not obtained under various conditions, the assembly of a spherical M_2L_4 capsule was unambiguously determined by the X-ray crystallographic analysis of **1′**, which is an analogue of **1** with shorter side chains (R = -OCH_3) and BF_4^- counterions.[11,13] In the crystal structure, the inside cavity of the capsule provides a Pd$\cdots$Pd distance of 1.28 nm and a volume of approximately 760 Å^3,[14] fully surrounded by eight dihydrophenazine panels (Figure 3e). The dihydrophenazine rings slightly bent away toward the outside with dihedral angles of about 160°. The molecular size and shape of **1′** are quite similar to those of other M_2L_4 capsules with anthracene panels.[5,6] In addition, capsule **1** also displayed host capability toward hydrophobic guests, such as triphenylene (**3a**) and *p*-cyclophane (**3b**) in aqueous solutions.[15]

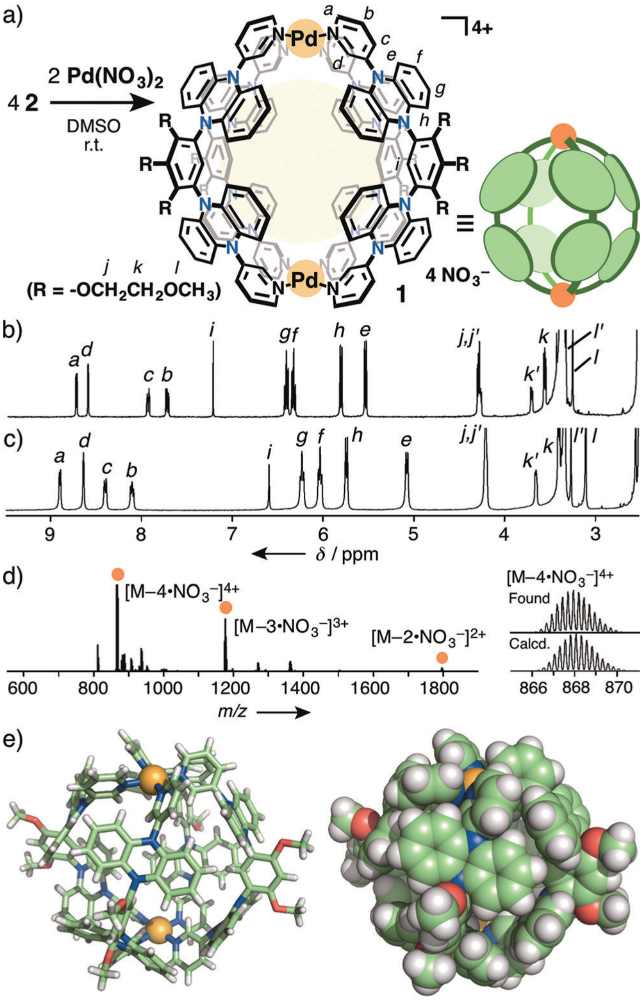

Figure 3. a) Schematic representation of the formation of M_2L_4 molecular capsule **1**. ^1H NMR spectra (400 MHz, $[D_6]$DMSO, RT) of b) ligand **2** and c) capsule **1**. d) ESI-TOF MS spectrum (CH_3CN) of capsule **1** and the expansion and simulation of the $[\mathbf{1}-4\,NO_3^-]^{4+}$ signals. e) X-ray crystal structure of **1′**: ball-and-stick (left) and space-filling (right) representations.[13]

Electrochemical studies elucidated the unique redox properties of dihydrophenazine-shelled capsule **1**. Cyclic voltammograms (CV) were measured for acetonitrile solutions of **2** and **1** containing tetra(*n*-butyl)ammonium hexafluorophosphate (NBu_4PF_6) at a scan rate of 100 mV s^{-1} under a N_2 atmosphere. Free-ligand **2** showed reversible two redox waves around −100 mV (vs. Fc/Fc$^+$; Fc = $[(C_5H_5)_2Fe]$; Figure 4a), indicating the generation of mono- and di(radical cation) species ($\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{2(\bullet+)}$, respectively; Figure 4d).[11] In sharp contrast, under the same conditions, two prominent oxidation waves were irreversibly observed for capsule **1** at the peak potentials of 55 and 725 mV (Figure 4b), which are presumably attributed to the formation of tetra(radical cation) capsule $\mathbf{1}^{4(\bullet+)}$ and octa(radical cation) capsule $\mathbf{1}^{8(\bullet+)}$,

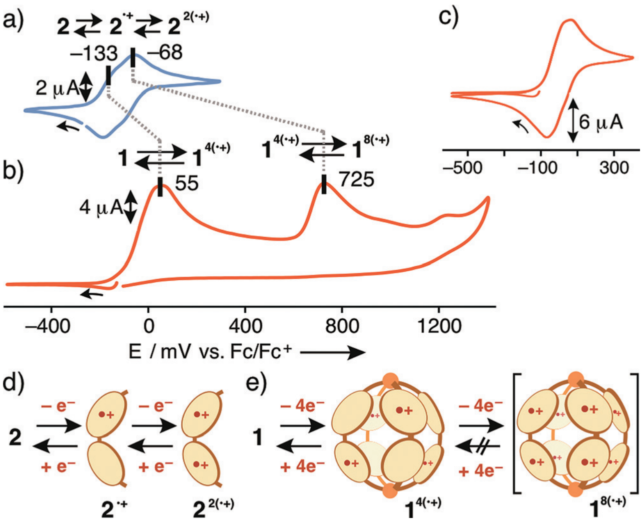

Figure 4. Cyclic voltammograms (0.1 M NBu_4PF_6 in CH_3CN, RT, scan rate 100 mV s^{-1}) of a) ligand **2** in the range of −495 to 305 mV, and b) capsule **1** in the range of −590 to 1410 mV and c) capsule **1** in the range of −590 to 410 mV (the first three cycles). Proposed transformations of d) ligand **2** and e) capsule **1** by the sequential oxidation/reduction processes.

respectively.[16] The areas of the two oxidation waves are comparable and each of the areas is approximately two-times larger than that of the $\mathbf{2}/\mathbf{2}^{2(\bullet+)}$ oxidation (two-electron oxidation process), as indicated by the differential pulse voltammogram (Figure S23b).[17] The potential of the former oxidation wave of capsule **1** is positively shifted ($\Delta E = +188$ mV) as compared with that of the ligand $\mathbf{2}/\mathbf{2}^{\bullet+}$ oxidation, due to the polycationic nature (4+) of the Pd$^{\text{II}}$-linked capsule framework.[18] The four-electron redox process of **1** occurred reversibly in the range of −590 to 410 mV (Figure 4c,e). This behavior indicates the adequate stability of $\mathbf{1}^{4(\bullet+)}$ as well as the absence of ligand dissociation during the redox process. On the other hand, further oxidation of $\mathbf{1}^{4(\bullet+)}$ at a much higher oxidation potential ($\Delta E = +793$ mV based on the $\mathbf{2}^{\bullet+}/\mathbf{2}^{2(\bullet+)}$ oxidation) gave rise to a highly reactive species most probably assigned to $\mathbf{1}^{8(\bullet+)}$, in which all of the dihydrophenazine rings of **1** are mono-oxidized. These findings suggest that tetra(radical cation) capsule $\mathbf{1}^{4(\bullet+)}$ consists of four monoradical and four neutral panels arranged alternately to form a spherical shell in such a way that each of the radical panels avoids each other (Figure 4e).[19]

Reversible generation of tetra(radical cation) capsule $\mathbf{1}^{4(\bullet+)}$ was also confirmed by in situ electronic absorption spectroscopy. When an CH_3CN solution of **1** (with BF_4^- counterions) was oxidized at a constant voltage of 200 mV, which is below the $\mathbf{1}^{4(\bullet+)}/\mathbf{1}^{8(\bullet+)}$ oxidation potential, new absorption bands were observed around 475 and 570–820 nm at room temperature (Figure 5a, step *i*). These broad bands are characteristic of a mono(radical cation) state of the dihydrophenazine ring.[11] Subsequent reduction of the solution at −200 mV led to the disappearance of the absorption bands (Figure 5a, step *ii*). In situ oxidation of ligand **2** in CH_3CN at 200 mV also showed absorption bands around 475 and 540–820 nm, which disappeared upon reduction at −200 mV (Figure 5b, steps *i* and *ii*).

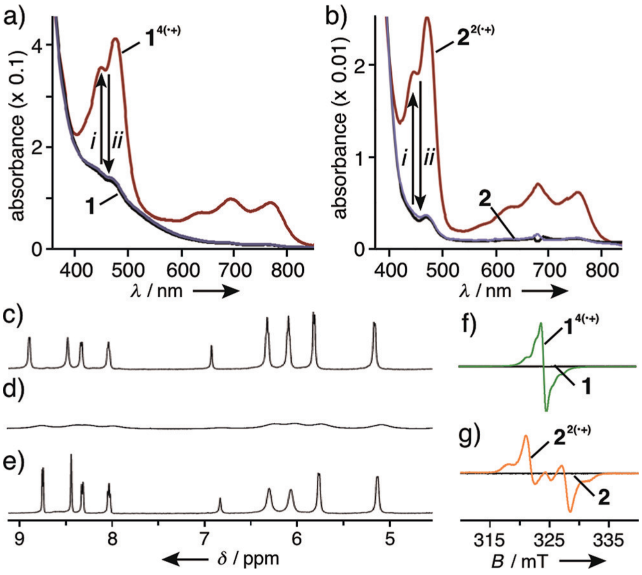

Figure 5. In situ electronic absorption spectra (0.1 M NBu_4PF_6 in CH_3CN, room temperature) of a) capsule **1** being oxidized at *i*) 200 mV for 2 h and then being reduced at *ii*) −50 to −200 mV for 15 h and b) ligand **2** being oxidized at *i*) 200 mV for 4 min and then being reduced at *ii*) −200 mV for 6 min. ^{1}H NMR spectra (400 MHz, room temperature) of a CD_3CN solution of capsule **1** c) before and d) after heating at 100 °C for 1 h in the presence of $AgNO_3$, and then e) after the subsequent addition of an aqueous $NaHSO_3$ solution at room temperature. ESR spectra (DMSO glass, 77 K) of f) capsule **1** and g) ligand **2** before and after the chemical oxidation.

Furthermore, interconversion between the nonradical and polyradical capsules was demonstrated by chemical stimuli and was confirmed by ^{1}H NMR spectroscopy, ESI-TOF MS, and electronic absorption spectroscopy.[11,20] When oxidizing reagent $AgNO_3$ (ca. 10 equiv) was added to an acetonitrile solution of capsule **1** and the mixture was stirred for 1 h at an elevated temperature (e.g., 100 °C), the capsule was converted into radical species $\mathbf{1}^{4(\bullet+)}$. The ^{1}H NMR spectrum of the product showed significantly broadened aromatic signals caused by the generation of radical species on the dihydrophenazine panels (Figure 5c,d). The UV/Vis spectrum displayed new absorption bands around 480 and 570–820 nm (Figure S25), which are quite similar to those of $\mathbf{1}^{4(\bullet+)}$ generated by the electrochemical oxidation (Figure 5a). Note that the generated polyradical capsule is remarkably stable and the absorption bands remain intact for a few days even at room temperature under air.[21] Moreover, the existence of poly(radical cation) species on the capsule shell was confirmed by the ESR analysis of the product. The observed prominent ESR peak around 325 mT with hyperfine splittings indicates long-distance spin-spin interactions between the dihydrophenazine radicals within the capsule (Figure 5 f).[11,19] In contrast, di(radical cation) ligand $\mathbf{2}^{2(\bullet+)}$ showed short-distance spin–spin interactions between the two radicals within the ligand (Figure 5g). Notably, addition of an aqueous $NaHSO_3$ solution, a reducing reagent, to the acetonitrile solution of the poly(radical cation) capsule $\mathbf{1}^{4(\bullet+)}$ led to the regeneration of nonradical capsule **1**, as confirmed by NMR (Figure 5e) and UV/Vis spectroscopic analyses (Figure S25).

Finally, we preliminary revealed that capsule **1** provides host capability in not only the neutral state[15] but also the polyradical state. For instance, chemical oxidation of triphenylene (**3a**)-encapsulated capsule $\mathbf{1}\supset(\mathbf{3a})_2$ by $AgNO_3$ in an aqueous solution gave rise to $\mathbf{1}^{n(\bullet+)}\supset(\mathbf{3a})_2$ species, as indicated by ^{1}H NMR spectroscopy and ESI-TOF MS (Figure S37,38). In addition, radical host–guest complex $\mathbf{1}^{4(\bullet+)}\supset(\mathbf{3a})_2$ could be reversibly generated by the electrochemical oxidation of $\mathbf{1}\supset(\mathbf{3a})_2$. In the cyclic voltammogram (Figure S39), the first oxidation wave was observed at the peak potential of 246 mV, which is positively shifted ($\Delta E \approx 160$ mV) as compared with that of empty **1** under the same conditions.

In summary, incorporation of dihydrophenazine rings into a simple M_2L_4 structural motif resulted in the formation of a new supramolecular capsule. The capsule obtained has a spherical approximately 1 nm-sized cavity surrounded by eight redox-active, dihydrophenazine panels. Electrochemical oxidation of the capsule led to the generation of multiple radical cations on the shell framework. Moreover, a stable tetra(radical cation) capsule could be reversibly generated by the controlled, chemical oxidation. By combining the host capability, the exploration of unique host–guest interactions in the present polyradical nanospace is our next project.

Acknowledgements

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[11] See the Supporting Information.

[12] No stereoisomers of **2** were observed in the NMR spectrum (Figure 3b), indicating that the pyridyl–dihydrophenazyl bonds rotate freely at room temperature.

[13] The dark-red single crystals suitable for X-ray crystallographic analysis were obtained by layering diffusion of 2-ocatanol into an acetonitrile solution of capsule **1′** at room temperature and leaving for two weeks.

[14] The cavity volume was calculated by Materials Studio (version 5.5.3).

[15] In a manner similar to the Pd^{II}-linked capsule with anthracene panels,[6a,b] capsule **1** quantitatively encapsulated two molecules of triphenylene (**3a**) or one molecule of *p*-cyclophane (**3b**) in a 10:1 D_2O/CD_3CN solution at 70 °C.[11] The structures of host–guest complexes $\mathbf{1}\supset(\mathbf{3a})_2$ and $\mathbf{1}\supset\mathbf{3b}$ were characterized by NMR spectroscopy and ESI-TOF MS analyses (Figure S28–S36).

[16] Cyclic voltammogram of capsule **1** in the range of −590 to 910 mV also showed the irreversible second oxidation wave. The preliminary theoretical calculation (PM6 level) also indicated that the repulsion energy of capsule $\mathbf{1}^{8(\bullet+)}$ is much higher ($> 300\ \text{kcal mol}^{-1}$) than that of capsule $\mathbf{1}^{4(\bullet+)}$.

[17] DOSY NMR spectroscopic analysis indicated that the diffusion coefficients of ligand **2** and capsule **1** are 1.0×10^{-9} and $1.3\times10^{-9}\ \text{m}^2\,\text{s}^{-1}$, respectively, under the same conditions.

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[19] Before chemical oxidations, capsule **1** and ligand **2** are ESR silent (black lines in Figure 5 f,g). In the ESR spectrum of $\mathbf{1}^{4(\bullet+)}$, the observed signals with small splitting of $D = 3.1$ mT are most probably attributed to the spin–spin interactions between distant dihydrophenazine radicals (average spin–spin distance $(r) = 9.7$ Å; Figure S27b,d) on the adjacent ligands of $\mathbf{1}^{4(\bullet+)}$. In contrast, the ESR spectrum of $\mathbf{2}^{2(\bullet+)}$ showed signals with large splitting of $D = 7.1$ mT arising from the intramolecular spin–spin interaction ($r = 7.3$ Å; Figure S27a,c). The theoretical calculation (B3LYP/LanL2DZ// PM6 (CPCM, CH_2Cl_2) level) of $\mathbf{1}^{4(\bullet+)}$ also suggested the proposed arrangement of the tetra(radical cation) centers on the framework (Figure S40).

[20] The ESI-TOF MS spectrum of the product exhibited several multivalent ion peaks assignable to the poly(radical cation) capsule at e.g., *m/z* 1240.0 ($[\mathbf{1}^{3(\bullet+)}]^{3+}$) and 1260.6 ($[\mathbf{1}^{4(\bullet+)} + NO_3^-]^{3+}$).

[21] Intensity of the absorption bands of $\mathbf{1}^{4(\bullet+)}$ in CH_3CN decreased only by about 15 % in one week under ambient conditions (Figure S25).

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