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Ferromagnetic Spin Coupling between Endohedral Metallofullerene La@C$_{82}$ and a Cyclodimeric Copper Porphyrin upon Inclusion

Fatin Hajjaj,[†,‡] Kentaro Tashiro,[*,§] Hidefumi Nikawa,[||] Naomi Mizorogi,[||] Takeshi Akasaka,[||] Shigeru Nagase,[⊥] Ko Furukawa,[⊥] Tatsuhisa Kato,[#] and Takuzo Aida[*,†,‡]

[†]School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[‡]Responsive Matter Chemistry & Engineering Research Group, Advanced Science Institute, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

[§]National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

[||]Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

[⊥]Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan

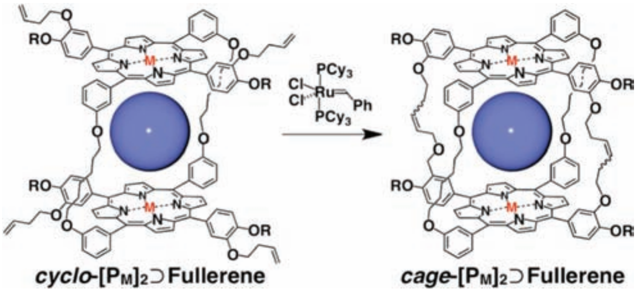
[#]Institute for the Promotion of Excellence in Higher Education, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

S *Supporting Information*

ABSTRACT: The cyclic host *cyclo*-$[\mathrm{P_{Cu}}]_2$ carrying two covalently connected Cu(II) porphyrin units can accommodate La@C$_{82}$, a paramagnetic endohedral metallofullerene, in its cavity to form the inclusion complex *cyclo*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$, which can be transformed into the caged complex *cage*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ by ring-closing olefin metathesis of its side-chain olefinic termini. On the basis of electron spin resonance (ESR) and electron spin transient nutation (ESTN) studies, *cyclo*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ is the first ferromagnetically coupled inclusion complex featuring La@C$_{82}$, whereas *cage*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ is ferrimagnetic.

As a first step toward the realization of ultrahigh-density memory devices,[1] ordered clustering of spin-active molecules by means of well-defined host/guest chemistry might give a clue to the yet-unaddressed issue of how one can rationally design ferromagnetic spin coupling.[2] However, successful examples of supramolecular approaches are still very rare,[3] and new molecular motifs have been awaited. Although endohedral metallofullerenes with paramagnetic character[4] are quite attractive motifs, only internal spin coupling within their carbon cages has been studied to date.[4c] In the present work, we took notice of La@C$_{82}$, which is considered to be a potential motif for supramolecular spin coupling because its paramagnetic character originates from a carbon radical delocalized over the spherical network of C$_{82}$.[5] Here we report that the cyclodimeric copper(II) porphyrin *cyclo*-$[\mathrm{P_{Cu}}]_2$ (Scheme 1) is the first host molecule that can be ferromagnetically coupled with La@C$_{82}$. The research strategy made use of our well-established inclusion chemistry of fullerenes with cyclic dimers of metalloporphyrins.[6−9] *cyclo*-$[\mathrm{P_{Cu}}]_2$, which was newly designed to host La@C$_{82}$, is paramagnetic. Furthermore, it bears alkyl side chains with olefinic termini and thus can be transformed into its caged analogue *cage*-$[\mathrm{P_{Cu}}]_2$ by intramolecular ring-closing olefin metathesis (Scheme 1). This "convertible" molecular design was inspired by our curiosity about how the mode of host/guest spin coupling is affected by geometry. From our previous experiences with higher fullerenes[9a] and short-spaced cyclodimeric metalloporphyrin hosts,[9b] we assumed that upon inclusion of La@C$_{82}$, *cyclo*-$[\mathrm{P_{Cu}}]_2$ would not allow such a large fullerene to be located in the geometrical center of its cavity. In contrast, *cage*-$[\mathrm{P_{Cu}}]_2$ might force La@C$_{82}$ to stay within its tetrapodal cage. As highlighted in the present communication, these two inclusion complexes displayed spin-coupling profiles that were quite different from one another.

Scheme 1. Schematic Illustration of the Structures of *cyclo*-$[\mathrm{P_M}]_2\supset$Fullerene and *cage*-$[\mathrm{P_M}]_2\supset$Fullerene [R = C$_{12}$H$_{25}$; M = 2H, Cu, Zn; Fullerene (blue-colored sphere) = La@C$_{82}$, C$_{82}$] and Their Transformation by Ring-Closing Metathesis



For the synthesis of *cyclo*-$[\mathrm{P_{Cu}}]_2$, we first prepared the zinc complex *cyclo*-$[\mathrm{P_{Zn}}]_2$ (Scheme 1) by fluoride-mediated coupling of the corresponding zinc porphyrin precursors bearing bromoalkyl side chains and silylated phenolic groups, and this complex was unambiguously characterized by MALDI−TOF mass spectrometry and ^{1}H NMR spectroscopy (Figures S2 and S7 in the Supporting Information).[10] Next, *cyclo*-$[\mathrm{P_{Zn}}]_2$ was transformed quantitatively into *cyclo*-$[\mathrm{P_{Cu}}]_2$ by demetalation under acidic conditions followed by metalation with Cu(OAc)$_2$. Upon titration with La@C$_{82}$ in toluene at 25 °C, the Soret absorption band of *cyclo*-$[\mathrm{P_{Cu}}]_2$ displayed a bathochromic red shift from 418 to 425 nm (Figure S13),[10] just like analogous inclusion complexes reported to date.[6−9] From this spectral change profile, the association constant (K_{assoc}) of *cyclo*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$

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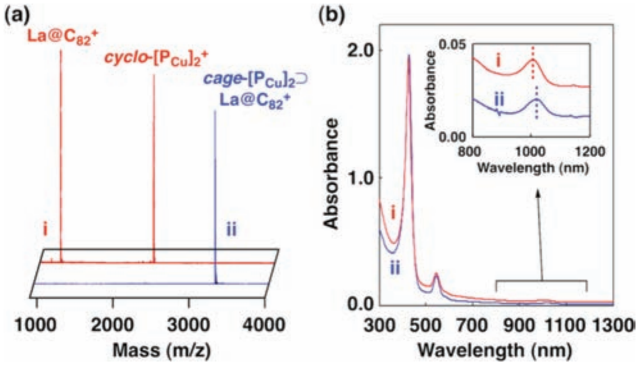


Figure 1. (a) MALDI−TOF mass and (b) absorption (toluene, 25 °C) spectral profiles of (i) *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$ and (ii) *cage*-$[P_{Cu}]_2{\supset}La@C_{82}$.

was evaluated as $1.5 \times 10^6\ M^{-1}$ (Figure S13).[10] Next, *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$ was subjected to ring-closing olefin metathesis (Scheme 1). However, because of concomitant liberation of the guest $La@C_{82}$, *cage*-$[P_{Cu}]_2{\supset}La@C_{82}$ was obtained in only 20% yield. We later found that the free-base form of *cyclo*-$[P_{Cu}]_2$ (*cyclo*-$[P_{2H}]_2$) in the presence of $La@C_{82}$ can be metathesized to give a better yield (40%) of its cage product, *cage*-$[P_{2H}]_2{\supset}La@C_{82}$. Accordingly, the K_{assoc} value ($1.5 \times 10^7\ M^{-1}$) of *cyclo*-$[P_{2H}]_2{\supset}La@C_{82}$ (Figure S12)[8,10] was 1 order of magnitude greater than that of *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$. The resultant complex *cage*-$[P_{2H}]_2{\supset}La@C_{82}$ was quantitatively converted into *cage*-$[P_{Cu}]_2{\supset}La@C_{82}$ by metalation with $Cu(OAc)_2$. MALDI−TOF mass spectrometry of the product showed only a single peak due to the host/guest complex [Figure 1a(ii)]. In sharp contrast, like other fullerene-included noncaged cyclodimeric metalloporphyrins reported to date,[6−9] *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$ underwent complete dissociation during MALDI−TOF mass spectrometry, affording the molecular-ion peaks of *cyclo*-$[P_{Cu}]_2$ and $La@C_{82}$ [Figure 1a(i)]. Hence, $La@C_{82}$ is indeed caged by *cage*-$[P_{Cu}]_2$ and not allowed to escape from its tetrapodal cavity. Because of the presence of the guest $La@C_{82}$, both inclusion complexes showed a red-shifted NIR absorption band at ~1000 nm (Figure 1b inset). However, the red shift for the caged version (ii) was more explicit than that for the noncaged one (i).

In order to explore the possibility of ferromagnetic spin coupling, we measured electron spin resonance (ESR) and electron spin transient nutation (ESTN)[11] spectra of the above inclusion complexes and their components in frozen chlorobenzene (Figure 2). ESTN spectroscopy is a pulsed ESR method that allows the investigation of the spin states of diluted analytes in frozen solvents. As shown in Figure 2a(i), *cyclo*-$[P_{Cu}]_2$ at −150 °C displayed just an ordinary ESR spectral feature analogous to that of its monomeric copper(II) porphyrin precursor (Figure S15).[10] Furthermore, the spin ground state of *cyclo*-$[P_{Cu}]_2$, as determined by ESTN spectroscopy at −268 °C, was a doublet [$S = {}^1/_2$; Figure 2b(i)]. Therefore, in *cyclo*-$[P_{Cu}]_2$, the two copper-centered spins hardly interact with one another. This is also the case for its caged analogue (*cage*-$[P_{Cu}]_2$), whose ESR and ESTN spectral features [Figure 2a(iii),b(iii)] are similar to those of *cyclo*-$[P_{Cu}]_2$. Meanwhile, when *cyclo*-$[P_{Cu}]_2$ was allowed to include $La@C_{82}$, a featureless ESR signal centered at 320 mT resulted [Figure 2a(ii)]. This spectral profile is essentially different from those of guest-free *cyclo*- and *cage*-$[P_{Cu}]_2$ [see above; Figure 2a(i,iii)] as well as that of $La@C_{82}$ [Figure 2a(v)]. Of particular interest, ESTN spectroscopy clearly showed that the spin ground state of *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$ is a quartet [$S = {}^3/_2$; Figure 2b(ii)]. For reference, when diamagnetic C_{82} (the C_2-symmetric isomer)[12] was incorporated into the cavity of *cyclo*-$[P_{Cu}]_2$ in place of $La@C_{82}$ ($K_{assoc} = 2.1 \times 10^7\ M^{-1}$; Figure S14),[10] neither the ESR nor the ESTN profile changed (Figure S15).[10] Therefore, it is clear that $La@C_{82}$ in *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$ is ferromagnetically coupled with the copper(II) porphyrin units of the host component (Figure 3a). In sharp contrast, *cage*-$[P_{Cu}]_2{\supset}La@C_{82}$, as determined by ESTN spectroscopy, was a doublet in its spin ground state [$S = {}^1/_2$; Figure 2b(iv)]. However, in view of the fact that its ESR spectrum [Figure 2a(iv)] was substantially different from those of the precursors *cage*-$[P_{Cu}]_2$ [Figure 2a(iii)] and $La@C_{82}$ [Figure 2a(v)], the host and guest spins indeed interact with one another. Hence, from the doublet character of *cage*-$[P_{Cu}]_2{\supset}La@C_{82}$ in its spin ground state, the host/guest spin coupling is most likely ferrimagnetic (Figure 3b).

A density functional theory (DFT) study[10] of a simplified model of *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$ suggested that its two Cu(II) porphyrin units are not oriented parallel to one another and that the geometrical center of the included $La@C_{82}$ does not lie on the Cu−Cu axis of the host component (Figure 3a).[13] Such a noncentrosymmetric geometry is reasonable considering the bulkiness of $La@C_{82}$.[9b] In contrast, in the optimized structure of *cage*-$[P_{Cu}]_2{\supset}La@C_{82}$, $La@C_{82}$ is in the geometrical center and the two copper(II) porphyrin units are aligned parallel to one another (Figure 3b).[13] When the energy profile of *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$ as

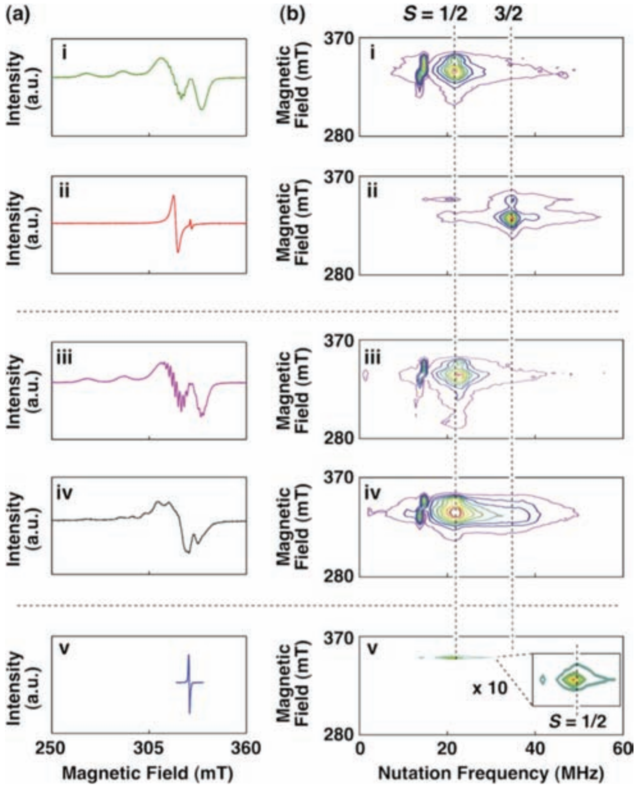
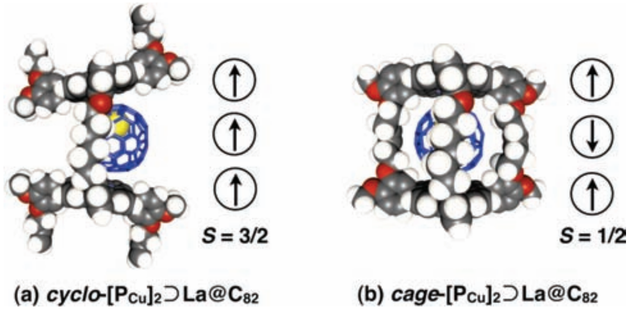


Figure 2. (a) ESR and (b) ESTN spectra at −150 and −268 °C, respectively, of (i) *cyclo*-$[P_{Cu}]_2$, (ii) *cyclo*-$[P_{Cu}]_2{\supset}La@C_{82}$, (iii) *cage*-$[P_{Cu}]_2$, (iv) *cage*-$[P_{Cu}]_2{\supset}La@C_{82}$, and (v) $La@C_{82}$ (inset: magnified) in frozen chlorobenzene.



(a) *cyclo*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ (b) *cage*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$

Figure 3. Geometry-optimized molecular models of (a) *cyclo*- and (b) *cage*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ and their spin ground states, calculated using DFT at the BLYP level.[10]

a function of spin state was analyzed by DFT calculations using its optimized geometry (Figure 3a) as the initial state, the quartet spin state was slightly but definitely more stable than the doublet spin state (Table S1),[10] in conformity with our experimental result [Figure 2b(ii)]. In contrast, for the optimized structure of *cage*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$, the doublet spin state was calculated to have a lower energy than the quartet spin state (Table S1).[10] These theoretical considerations suggest the interesting possibility that the mode of coupling among the clustering spins can be changed by altering the cluster geometry.

In summary, through studies of the inclusion complexation of paramagnetic *cyclo*-$[\mathrm{P_{Cu}}]_2$ and *cage*-$[\mathrm{P_{Cu}}]_2$ with La@$\mathrm{C_{82}}$, we have demonstrated that the former compound is the first host molecule that can be ferromagnetically coupled with paramagnetic La@$\mathrm{C_{82}}$. Also noteworthy is the result that this ferromagnetic nature turns ferrimagnetic when *cyclo*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ is transformed into its caged analogue (*cage*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$). As shown by DFT calculations, this transformation is likely accompanied by a change in the geometry of the host/guest complex. Thus, a host molecule with the ability to change its conformaton in response to physical stimuli might lead to the development of stimuli-responsive memory devices based on endohedral metallofullerenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis and characterization of *cyclo*- and *cage*-$[\mathrm{P_{M}}]_2$ and their complexes with La@$\mathrm{C_{82}}$ and $\mathrm{C_{82}}$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

TASHIRO.Kentaro@nims.go.jp; aida@macro.t.u-tokyo.ac.jp

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(13) The optimized model of *cyclo*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ adopted a Cu−La−Cu angle and Cu−La distances of 144.5° and 5.691 and 9.415 Å, respectively, while the corresponding angle and distances in the model of *cage*-$[\mathrm{P_{Cu}}]_2\supset\mathrm{La@C_{82}}$ after optimization were 175.1° and 5.368 and 8.977 Å, respectively.