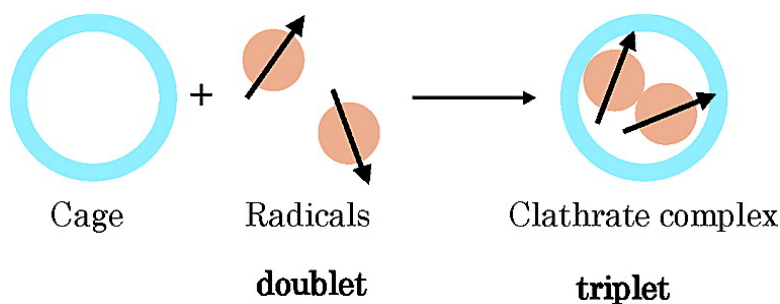Communication

Cavity-Induced Spin–Spin Interaction between Organic Radicals within a Self-Assembled Coordination Cage

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Cage + Radicals → Clathrate complex

doublet   triplet

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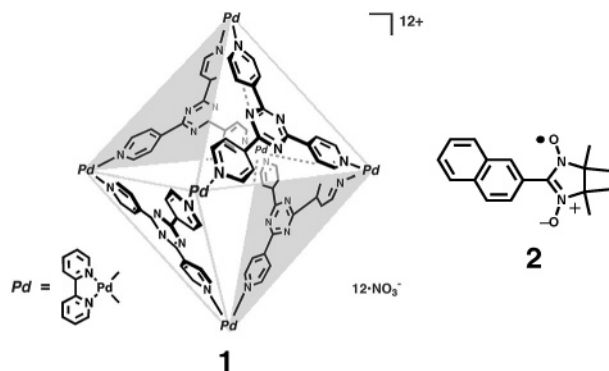# Cavity-Induced Spin−Spin Interaction between Organic Radicals within a Self-Assembled Coordination Cage

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Control over spins at molecular levels is a fundamental, yet difficult task in designing magnetic functional materials. Since the discovery in 1989 of a stable organic radical that exhibits ferromagnetism, numerous studies have been accumulated on organic radicals because they are promising to the development of molecular-scale magnetic devices that can be designed and synthesized at will.[1] Whereas spin−spin interaction via covalent or coordination bonds has been well studied, through-space interaction between organic radicals has been seldom controlled because radical centers, whose interaction is proportional to $1/r^3$ (r = spin−spin distance), have to be located in very short distances. We report here that organic radical **2**,[2] which has no particular intermolecular interaction in solution, is accommodated by self-assembled cage **1** to give a stable 1:2 host−guest complex in solution. The two radical centers of the guests are enforced to be close to each other within the cavity of **1**. As a result, the through-space interaction between the two organic radicals is observed in solution. Since the geometry of the radicals is fixed only by weak hydrophobic host−guest interaction, the spin−spin interaction is sensitive to thermal stimuli and suppressed at elevated temperature. We note that the dimeric aggregate of **2** shows the same behavior both in solution and in solid state because, once enclathrated in the cavity of **1**, the guest does not feel the environment of the cage. Organic enclathration, catalytic reaction, stereoselective transformations, and stabilization of labile species within host compounds have been previously reported.[3,4]

An excess of powdered **2** was suspended in an aqueous solution of **1** at 20 °C for 1 h to give, after filtration of surplus **2**, clathrate compound **1·(2)₂**.[5] The 1:2 host−guest stoichiometry was confirmed by the elemental analysis of a crystalline sample, which was obtained by evaporating water from the solution.[6] In addition, 2 molar equiv of **2** to cage **1** was recovered by extraction with chloroform, being consistent with the 1:2 complexation.

The remarkable feature of the clathrate complex **1·(2)₂** is that the enclathration induces intermolecular spin−spin interaction between two guests, which is clearly observed by ESR.[7] The ESR
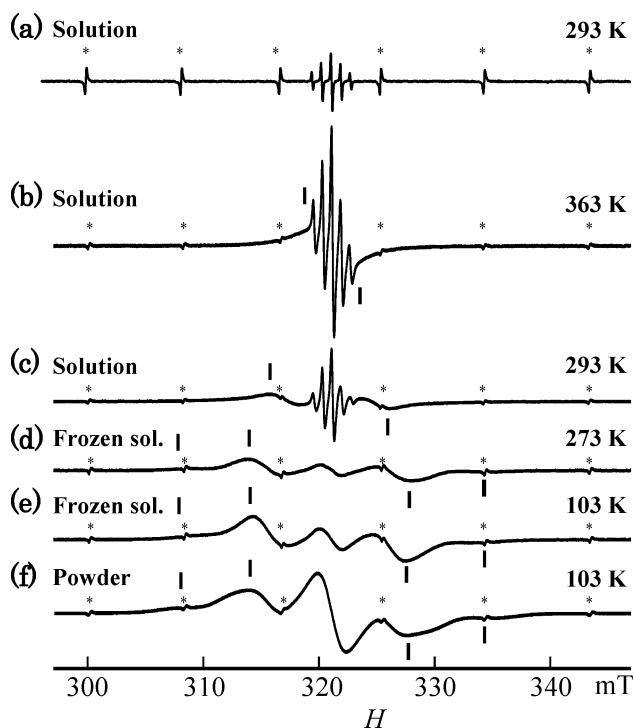
Figure 1. ESR spectra of (a) radical **2** (saturated) and (b−e) clathrate complex **1·(2)₂** (5 mM) in water at various temperatures. (f) Powder ESR spectra of clathrate complex **1·(2)₂** at 103 K. Signals with an asterisk are of a Mn²⁺ external reference.

spectrum of radical **2** shows a sharp signal at 320 mT, which is split into a 1:2:3:2:1 quintet due to coupling with two nucleus spins of nitrogen atoms ($I = 1$) (Figure 1a). The spectrum of **1·(2)₂** in solution at 293 K showed, however, an additional broad signal (indicated by blue bar) besides the sharp signal of **2** in a doublet state (Figure 1c). Powdered **1·(2)₂** complex also gave a similar (but broadened) spectrum (Figure 1f). We assigned the new broad signal to a dimeric aggregate of radical **2** in a triplet state that stems from intermolecular spin−spin interaction. The fine structure constant (D') of 14 mT was obtained from the powder ESR spectrum (Figure 2a). The observation of both doublet and triplet states of **2** suggests that two guest molecules adopt spin−spin-interacted and noninteracted orientations in the cavity. In contrast to covalently linked radical centers,[8] the two radicals in the cavity are weakly associated only by hydrophobic forces, and thus the spin−spin interaction is sensitive to a thermal molecular motion. Figure 1b−d indicates that a split width between the broad signals was decreasing when the solution was warmed. At 363 K, the triplet species was hardly observed. The spectral feature of the frozen solution in spectra d and e of Figure 1 is similar to that of a powder spectrum in Figure 2a. The signal intensity at 103 K is enhanced compared to that at
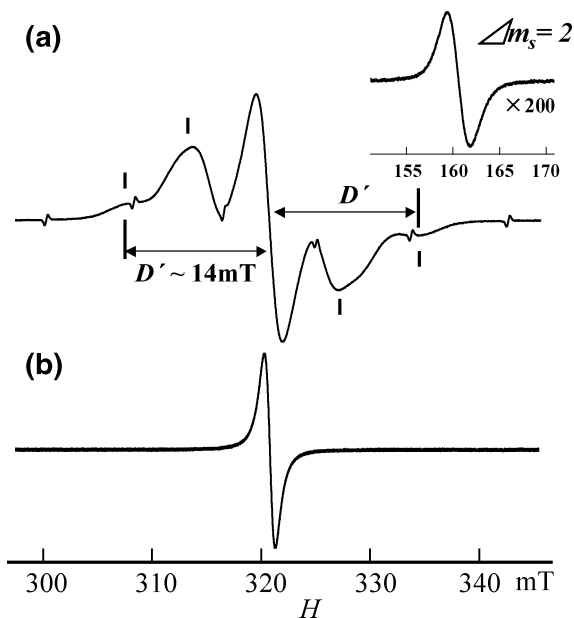
Figure 2. Powder ESR spectra of (a) clathrate complex $\mathbf{1}\cdot(\mathbf{2})_2$ and (b) radical $\mathbf{2}$ at 103 K. The inset in (a) shows forbidden transition of $\mathbf{1}\cdot(\mathbf{2})_2$.
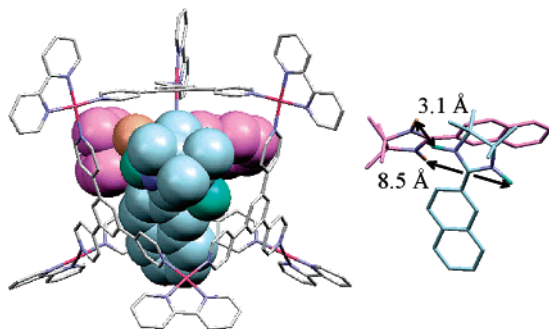

Figure 3. Crystal structure of clathrate complex $\mathbf{1}\cdot(\mathbf{2})_2$ (left) and configuration of the radicals within the cage (right).

273 K, according to Curie's law. The central doublet signal drastically became broader below 273 K because the molecular motion was frozen.

A reliable evidence for the intermolecular spin−spin interaction comes from the clear observation of a forbidden transition, $\Delta m_s = 2$, at half the magnetic field of $\Delta m_s = 1$ (160 mT) that reveals the presence of a triplet species (Figure 2a, inset). Particularly interesting is that radical $\mathbf{2}$ itself does not show a $\Delta m_s = 2$ transition even in solid state because the steric demand of methyl groups between radicals leads to the antiparallel packing of $\mathbf{2}$ in crystal, where radical centers are apart from each other (see the crystal structure of $\mathbf{2}$ in Figure S2 of the Supporting Information). We therefore speculate that the two radical centers of $\mathbf{2}$ in the $\mathbf{1}\cdot(\mathbf{2})_2$ complex are very close to each other because of tight enclathration of the two guests within the restricted cavity of $\mathbf{1}$.

The postulated guest orientation was clearly evidenced by the X-ray crystallographic analysis of the $\mathbf{1}\cdot(\mathbf{2})_2$ complex.[9] A single crystal of $\mathbf{1}\cdot(\mathbf{2})_2$ suitable for X-ray diffraction was obtained by slow evaporation of H_2O at room temperature for 3 days. Although radical $\mathbf{2}$ was considerably disordered in the cavity, the refinement of the disordered structure revealed the close contact of two radicals

of $\mathbf{2}$ (occupancy factor, 50%) in the cage of $\mathbf{1}$. In this structure, the shortest and furthest intermolecular distances between the radical centers are 3.1 and 8.5 Å, respectively; the former is close to the sum of van der Waals radii of the two nitronyl oxygen atoms. From these distances, the fine structure constant of D' was estimated to be 14.3 mT by a point dipole approximation, in good agreement with the observed value (14 mT).[10]

To our knowledge, our study first reveals that even nonassociative stable organic radicals can be interacted through space if they are forced to be in contact with each other by accommodation in a restricted cavity. Sustained only by weak hydrophobic forces, the spin−spin interaction should be quite sensitive to external stimuli. Doublet/triplet switching in the cavity by, for example, photochemical or electrochemical stimuli is currently under investigation in due course.

Supporting Information Available: Experimental details, UV−vis spectra of $\mathbf{1}\cdot(\mathbf{2})_2$, and a thermal ellipsoid plot of the molecular structure of $\mathbf{1}\cdot(\mathbf{2})_2$. The crystallographic details are described in the cif file deposited in CCSD 249974. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Awaga, K.; Maruyama, Y. *J. Chem. Phys.* **1989**, *91*, 2743−2747. (b) Chiarell, R.; Novak, A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, *363*, 147−149. (c) Nakatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161−2174. (d) Yoshioka, N.; Irisawa, M.; Mochizuki, Y.; Kato, T.; Inoue, H.; Ohba, S. *Chem. Lett.* **1997**, *3*, 251−252. (e) Matuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 8309−8310. (f) Hosokoshi, Y.; Katoh, K.; Nakazawa, Y.; Nakano, H.; Inoue, K. *J. Am. Chem. Soc.* **2001**, *123*, 7921−7922. (g) Doi, K.; Ishida, T.; Nogami, T. *Chem. Lett.* **2003**, *32*, 544−545.
(2) 2-Naphthyl nitronyl nitroxide used as the guest radical was prepared by the improved Ullman's procedure described in the following reference: Hirel, C.; Vostrikova, K. E.; Pecaut, J.; Ovcharenko, V. I.; Rey, P. *Chem.−Eur. J.* **2001**, *7*, 2007−2014.
(3) (a) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975−982. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. (c) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509−518. (d) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759−771. (e) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 3674−3675. (f) Yoshizawa, M.; Tamura, M.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 6846−6847.
(4) (a) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488−1508. (b) Lee, W. J.; Samal, S.; Selvapalam, N.; Kim, H. J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621−630. (c) Corbellini, F.; Costanzo, L. D.; Crego-Calama, M.; Geremia, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2003**, *125*, 9946−9947. (d) Ziganshina, A. Y.; Ko, Y. H.; Jeon, W. S.; Kim, K. *Chem. Commun.* **2004**, 806−807.
(5) The UV−vis spectra are available in Supporting Information (Figure S1).
(6) Elemental Anal. Calcd for $C_{166}H_{134}N_{52}O_{40}Pd_6\cdot21H_2O$: C, 44.17; H, 3.93; N, 16.14. Found: C, 44.49; H, 4.06; N, 15.75.
(7) With a value of $g = 2.007 \pm 0.001$ in all spectra.
(8) These signal profiles resemble those of triarylmethyl-based diradicals reported in the following reference, in which the two radical centers are connected with a covalent bond: Rajca, A.; Rajca, S. *J. Am. Chem. Soc.* **1996**, *118*, 8121−8126.
(9) Crystal data for $\mathbf{1}\cdot(\mathbf{2})_2$: $C_{149}H_{96}N_{48}O_{76}Pd_6$, $M = 4413.14$, tetragonal, $P4_32_12$, $a = b = 29.162(3)$ Å, $c = 30.451(6)$ Å, $V = 25\ 896(7)$ Å^3, $Z = 4$, $T = 80(2)$ K, $D_c = 1.132$ g cm^{-3}, λ (Mo Kα) = 0.71073 Å, 295 168 reflections measured, 31 871 unique ($R_{int} = 0.2379$), which were used in all calculations. The structure was solved by direct method (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1048 parameters. R1 = 0.1504 ($I > 2\sigma(I)$) and wR2 = 0.3338, GOF 1.045; max/min residual density 2.171/−0.899 e Å^{-3}. The detail of the refinement is described in a cif file.
(10) $D' = {}^3\!/_2(\mu_0 g \beta)/(4\pi r^3)$, where $\mu_0 = 4\pi \times 10^{-7}$ H m^{-1}, $g = 2.007$, $\beta = 9.274 \times 10^{-24}$ J T^{-1}, and the average spin−spin distance, $r = 5.8$ Å, between radicals within the cage.

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