Host–Guest Systems

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pH-Switchable Through-Space Interaction of Organic Radicals within a Self-Assembled Coordination Cage

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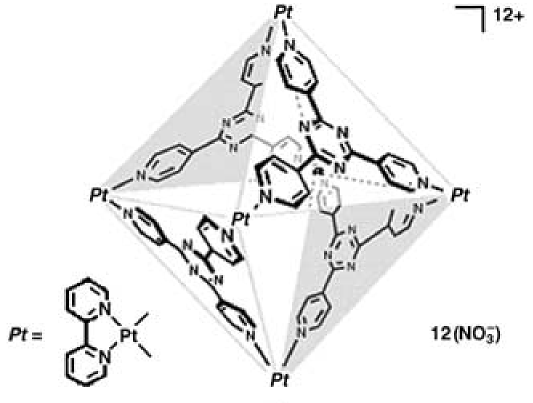
Whereas the control of the through-space interaction of organic radicals by external stimuli promises the development of a variety of molecular scale magnetic devices, it has been achieved only in the solid state and never in solution.[1] We recently reported the through-space interaction of non-associative stable organic radicals in aqueous solution by accommodating two organic radicals in a self-assembled coordination cage **1**.[2] Owing to restriction by the cage, two organic radicals are fixed in the cavity such that the two radical centers are in close proximity. If such a through-space interaction could be switched by a slight change in the environment, molecular magnetic devices that are responsive



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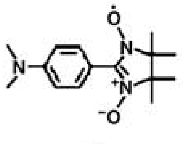

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to external stimuli in solution could be prepared. Accordingly, we demonstrate herein the pH-responsive switching of spin–spin interactions between stable organic radicals.[3] Radical **2**[4] has an amine group that may be protonated, and upon doing so the affinity of radical **2** for the host should be significantly lowered as a result of cationic repulsion.[5] We show that the pH response of the through-space magnetic interaction between accommodated **2** is quite sensitive and digitalized.[6]

An excess of powdered **2** (4.1 mg, 15×10^{-3} mmol) was suspended in a solution of **1** (20.5 mg, 5.0×10^{-3} mmol) in H_2O (1.0 mL) at 80 °C for 1 h. After filtration of surplus **2**, a solution of the clathrate compound $\mathbf{1}\cdot(\mathbf{2})_2$ (5 mM) remained.[7] The solution of the clathrate was diluted with H_2O (9 mL) and used for ESR and UV/Vis spectroscopy measurements. A single crystal of $\mathbf{1}\cdot(\mathbf{2})_2$ suitable for X-ray diffraction was obtained by slow evaporation of H_2O from the solution at room temperature for 2 days. The crystal structure of $\mathbf{1}\cdot(\mathbf{2})_2$ is shown in Figure 1.

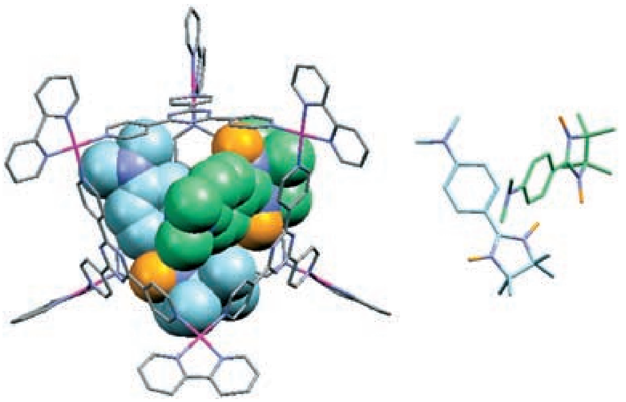
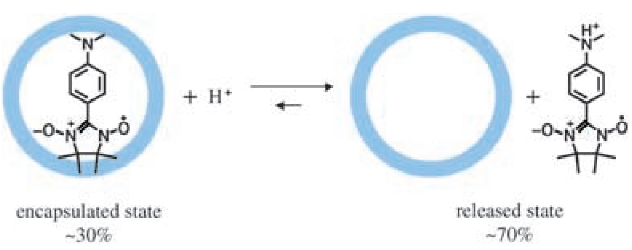


Figure 1. Molecular structure of the clathrate complex $\mathbf{1}\cdot(\mathbf{2})_2$ (left). Host **1**: stick representation (Pt magenta, N dark blue, C gray); guest **2**: space-filled representation (O yellow, N dark blue, C green/pale blue). The configuration of the radicals within the cage is shown more clearly by the stick representation on the right.

An advantage of using a discrete host is that the array of the guests is fixed regardless of whether they are in solution or in the solid state. Namely, the orientation of the guest depends upon the nature of the cavity in the host rather than the guest or the environment. In crystalline $\mathbf{1}\cdot(\mathbf{2})_2$, the guests are suitably oriented so that two spin centers[8] are in close proximity for efficient spin–spin interaction. The average distance between the spin centers is approximately 6.3 Å,[9] and we suggest that this orientation is fixed even in solution.

As expected from the X-ray diffraction study, the encapsulated guests in the cage showed intermolecular triplet-state spin–spin interactions. An intriguing feature of this clathrate complex is that the spin–spin interaction can be switched by pH.[10] As illustrated in Scheme 1, we observed the reversible process of release and reencapsulation of **2** in the pH range of 1.3 to 6.5 by ESR spectroscopy. Around pH 7, the ESR spectrum of the aqueous solution (frozen) of $\mathbf{1}\cdot(\mathbf{2})_2$ at 103 K[11] showed a split allowed transition ($\Delta m_s = 1$) at 321 mT and a forbidden transition ($\Delta m_s = 2$) at 160 mT; the observation of the latter is a proof of a triplet state that is derived from two interacting radicals in the cage (Figure 2a). When the solution was acidified to pH ≈ 1.3 with HNO_3, the triplet signal was completely suppressed and only a doublet signal with a hyperfine structure (due to coupling with the nitrogen nucleus) was observed. This observation strongly suggests that the protonated radical, $\mathbf{2}H^+$, was released from the cage (Figure 2b). The profile of the doublet signal agreed with that of the signal of $\mathbf{2}H^+$ in the absence of **1**.[12] The decapsulation of **2** from **1** is probably caused by a decreased hydrophobic interaction as well as coulombic repulsion between the host and the guest. When the solution was treated with K_2CO_3 to pH ≈ 6.5, the released guest returned to the cavity of **1** and the triplet signals reappeared (Figure 2c).



Scheme 1. Equilibrium in the acidified solution of host and guest, $\mathbf{1}\cdot(\mathbf{2})_2$.

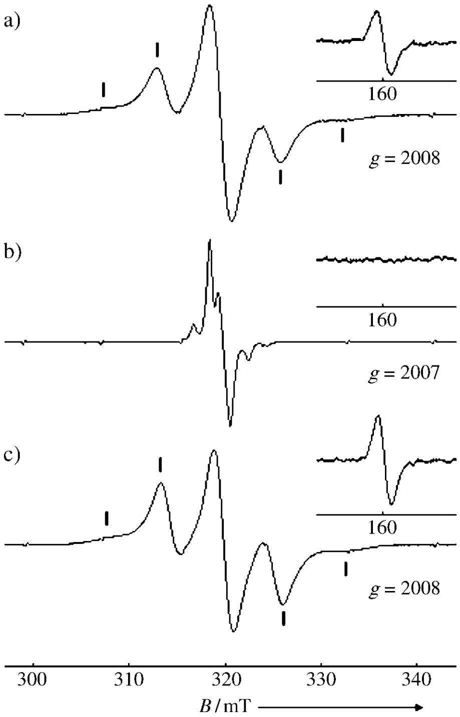


Figure 2. ESR spectra of clathrate compound $\mathbf{1}\cdot(\mathbf{2})_2$ (0.5 mM, 103 K): a) the initial solution (pH ≈ 6.5), b) the acidified solution (pH ≈ 1.3; with HNO_3), and c) the neutralized solution (pH ≈ 6.5; with K_2CO_3). The insets show forbidden transition; vertical bars indicate the signals derived from a triplet state. g = splitting factor.

The pH-dependent UV/Vis absorption spectra of **1**·(**2**)$_2$ also supported the pH-switchable encapsulation of **2**. Radicals **2** and **2**H$^+$ showed absorption bands ascribed to an n–π* transition at 650 nm and 560 nm, respectively (Figure 3a).

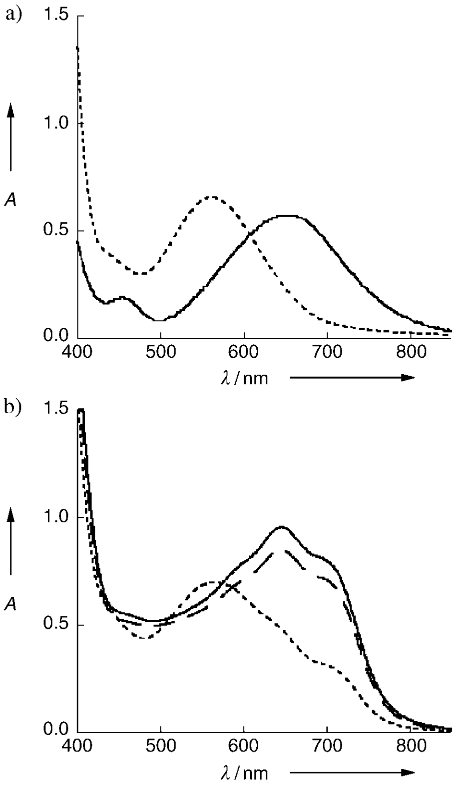


Figure 3. a) UV/Vis spectra of radical **2** (——, saturated solution, pH 6.5) and the protonated radical **2**H$^+$ (-----, saturated solution, pH 1.3) at 293 K. b) UV/Vis spectra of clathrate compound **1**·(**2**)$_2$ (0.5 mM) at 293 K. ——: the initial solution at pH ≈ 6.5; -----: the acidified solution at pH ≈ 1.3 (HNO_3); – – –: the neutralized solution at pH ≈ 6.5 (K_2CO_3).

Under neutral conditions, **1**·(**2**)$_2$ showed an absorption band at 650 nm accompanied by a vibronic coupling derived from **2**. The presence of the vibronic coupling indicated that **2** remained in the hydrophobic environment (Figure 3b). The acidified solution of **1**·(**2**)$_2$ showed absorption bands at both 560 nm and 650 nm, which suggests that **2**H$^+$ (out of the hydrophobic pocket of **1**) and **2** (encapsulated in **1**) were in equilibrium (Scheme 1). Deconvolution analysis of the spectrum of **1**·(**2**)$_2$ in acidified solution clarified that the ratio of the released and encapsulated guests was 7:3. When treated with K_2CO_3 (pH ≈ 6.5), the solution showed a similar spectrum to that observed initially, confirming that the released guest was reencapsulated in **1**.

In conclusion, we have demonstrated the pH-controlled doublet–triplet switching of organic radicals accommodated in a self-assembled coordination host. The facile solution-state control of the spin interaction is ascribed to the encapsulation effect of the cage: radicals are fixed in the host under neutral conditions, whereas they are expelled under acidic conditions. By applying such an encapsulation effect of a cage, new molecular magnetic materials that are responsive to other stimuli (particularly light) may be developed.

Experimental Section

1·(**2**)$_2$: An excess of powdered **2** (4.1 mg, 15×10^{-3} mmol, $M_w = 276.35$) was suspended in a solution of **1** (20.5 mg, 5.0×10^{-3} mmol, 5 mM) in H_2O (1.0 mL) at 80 °C for 1 h to give a solution of the clathrate compound (5 mM) after filtration of surplus **2**.[7] The solution of the clathrate was diluted tenfold with H_2O (9 mL) and was used for ESR and UV/Vis spectroscopy. A single crystal of **1**·(**2**)$_2$ suitable for X-ray diffraction studies was obtained by slow evaporation of H_2O from an aqueous solution of the clathrate at room temperature for 2 days. Elemental analysis (%): calcd for $C_{162}H_{182}N_{54}O_{61}Pt_6\cdot 21\,H_2O$: C 38.67, H 3.65, N 15.03; found: C 38.95, H 3.81, N 14.66. Crystal data for **1**·(**2**)$_2$: $C_{162}H_{140}N_{50.50}O_{80.75}Pt_6$, $M_r = 5256.79$, tetragonal, $P4_12_12$, $a = b = 29.0831(9)$ Å, $c = 30.773(2)$ Å, $V = 26029(2)$ Å^3, $Z = 4$, $T = 90.0(1)$ K, $\rho_{calcd} = 1.341$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å; 404871 reflections were measured of which 40114 were unique ($R_{int} = 0.1341$) and were used in all calculations. The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1520 parameters. $R_1 = 0.0716$ ($I > 2\sigma(I)$) and $wR_2 = 0.1774$, GOF = 1.011, max./min. residual density 1.155/−0.831 e Å^{-3}.

Crystal data for **2**: $C_{15}H_{22}N_3O_2$, $M_r = 276.36$, monoclinic, $P2_1/n$, $a = 13.018(2)$ Å, $b = 9.434(1)$ Å, $c = 13.505(2)$ Å, $\alpha = \gamma = 90$, $\beta = 116.840(2)$°, $V = 1479.9(3)$ Å^3, $Z = 4$, $T = 90.0(1)$ K, $\rho_{calcd} = 1.258$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å; 5418 reflections were measured of which 3305 were unique ($R_{int} = 0.0919$) and 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 187 parameters. $R_1 = 0.0968$ ($I > 2\sigma(I)$) and $wR_2 = 0.2418$, GOF = 1.146; max./min. residual density 0.870/−0.494 e Å^{-3}. All the diffraction data were measured on a Siemens SMART/CCD diffractometer ($Mo_{K\alpha}$ radiation: $\lambda = 0.71073$ Å). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. CCDC-271224 (**2**) and CCDC-271223 (**1**·(**2**)$_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[7] Evaporation of a solution obtained by the same procedure gave a green powder whose elemental analysis agreed with complex **1**·(**2**)$_2$ (see Experimental Section), which suggests the quantitative formation of the 1:2 host–guest complex by this procedure.

[8] The spin center was defined as the oxygen atoms of the nitronyl nitroxides.

[9] From this distance (6.3 Å), the fine-structure constant of D was estimated to be 11.2 mT by a point-dipole approximation, in near-complete agreement with the observed value (12 mT). $D' = 3/2(\mu_0 g\beta)/(4\pi r^3)$, where $\mu_0 = 4\pi \times 10^{-7}\,\mathrm{H\,m^{-1}}$, $g = 2.008$, $\beta = 9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}}$, and $r = 6.3$ Å, the average spin–spin distance between radicals within the cage.

[10] Both the acidified and neutral solutions of another stable radical that lacks an amino group gave identical ESR spectra (see Supporting Information).

[11] See Supporting Information for the ESR spectrum of an aqueous solution of **1**·(**2**)$_2$ at 293 K.

[12] See Supporting Information.