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# A Supramolecular Oscillator Composed of Carbon Nanocluster $C_{120}$ and a Rhodium(III) Porphyrin Cyclic Dimer

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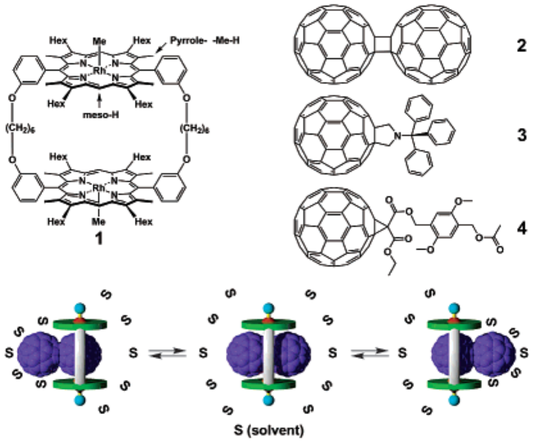
Received April 6, 2002

Oscillating motion is applicable to sensing, imaging, and switching. For example, by a change in oscillation frequency of quartz crystal microbalances,[1] one can sense chemical and physical phenomena gravimetrically. In noncontacting atomic force microscopy,[2] cantilever oscillation provides ultrahigh-resolution images of samples. More recently, molecular-level oscillators have attracted great attention for molecular electronics. An interesting example is a single-$C_{60}$ transistor, where the oscillation of single $C_{60}$ couples with single-electron hopping between electrodes.[3] Rotaxane-based molecular shuttles[4] are also promising candidates for molecular electronics and machinery.[5] Herein we report that a rhodium(III) porphyrin cyclic dimer (**1**, Chart 1)[6] forms a supramolecular oscillator with carbon nanocluster $C_{120}$ (**2**).[7]

Recently, we have reported that **1** binds fullerenes such as $C_{60}$ and $C_{70}$ to form highly stable supramolecular inclusion complexes, where the association constants ($K_{\mathrm{assoc}}$) exceed $10^7$ $M^{-1}$.[6b] This observation prompted us to investigate how **1** recognizes the $\pi$-electronic surface of **2**. Considering the extremely low dissociation activities of $\mathbf{1}\supset C_{60}$ and $\mathbf{1}\supset C_{70}$,[6b] we initially thought that **1** may stay on either of the two $C_{60}$ moieties of **2**, but found that included **2** oscillates back and forth within the $\pi$-electronic cavity of **1** (Chart 1).

**Chart 1**



1
2
3
4

Upon mixing **1** and **2** in toluene, the Soret absorption band of **1** shifted bathochromically[8] from 404.5 to 411.0 nm. ESI-MS spectrometry of a $CHCl_3$/MeOH (4/1) solution of a mixture of **2** and an excess amount of **1** showed two sets of isotopic distributions centered at 3612 ($[\mathbf{1}+\mathbf{2}]^+$) and 5782 ($[\mathbf{1}_2+\mathbf{2}]^+$), which correspond to 1:1 and 2:1 complexes of **1** with **2** ($\mathbf{1}\supset\mathbf{2}$ and $\mathbf{1}_2\supset\mathbf{2}$), respectively.[8] Job's plots (404.5 nm) of a toluene solution of **1** with **2** at 20 °C and $^1$H NMR titration in toluene-$d_8$ ($C_6D_5CD_3$) at −40 °C indicated that $\mathbf{1}_2\supset\mathbf{2}$ hardly exists at $[\mathbf{1}]/[\mathbf{2}] \leq 1$.[8] Thus, the 1:1 association constant ($K_{\mathrm{assoc}}$) was evaluated at 20 °C to be $8.4 \times 10^6$ $M^{-1}$ from the spectroscopic titration in a range of $[\mathbf{1}]/[\mathbf{2}]$ below unity, monitored at 404.5 nm.[8] As already reported,[6b] the $^1$H NMR spectrum of **1** in $C_6D_5CD_3$ at 25 °C shows seven inequivalent doublet signals for Me−Rh at $\delta$ −5.54 to −6.24 ppm due to the presence of some conformational isomers. On the other hand, when an equimolar amount of **2** was added to the solution of **1** (1.0 mM), the spectrum was simplified to give only a single Me−Rh signal at $\delta$ −5.58 ppm,[8] as the result of an "induced-fit" conformational change of **1**[6b] upon inclusion of **2**.

Inclusion complex $\mathbf{1}\supset\mathbf{2}$ showed pairs of two singlet signals both for the meso (Figure 1a) and for the pyrrole-$\beta$-methyl protons,[8] due to the protrusion of one of the $C_{60}$ moieties of **2** from the cavity of **1**. Interestingly, upon elevation of the temperature, these two pairs coalesced at 42 and 35 °C, respectively. A line shape analysis, using a program DNMR5,[9] showed that the two inequivalent meso-H signals exchange at a rate from 10 to 1225 $s^{-1}$ upon elevating the temperature from 20 to 70 °C (Figure 2a). Reference inclusion complexes $\mathbf{1}\supset\mathbf{3}$[10] (VT $^1$H NMR; Figure 1b) and $\mathbf{1}\supset\mathbf{4}$[11] in Chart 1 at 25 °C showed similar inequivalent meso-H signals, which however were more difficult to coalesce, displaying much smaller site-exchange rates ($R_{\mathrm{site-exchange}}$; Figure 2b and c) than $\mathbf{1}\supset\mathbf{2}$.[8] The $^1$H NMR site exchange, thus observed, is caused by the dissociation/association dynamics of the inclusion complexes. However, in the case of $\mathbf{1}\supset\mathbf{2}$, the $^1$H NMR site exchange can also be induced by the oscillation of included **2**. Considering that $K_{\mathrm{assoc}}$ of $\mathbf{1}\supset\mathbf{2}$ is 3−4 times larger than those of $\mathbf{1}\supset\mathbf{3}$ ($2.8 \times 10^6$ $M^{-1}$) and $\mathbf{1}\supset\mathbf{4}$ ($2.1 \times 10^6$ $M^{-1}$),[8] the exceptionally large site-exchange activity of $\mathbf{1}\supset\mathbf{2}$ (Figure 2a) suggests that included **2** oscillates much more frequently than it dissociates.[6b] Although these two dynamical events are hardly distinguishable in the VT $^1$H NMR profile of $\mathbf{1}\supset\mathbf{2}$,[12] we found that the dissociation activity of $\mathbf{1}\supset\mathbf{2}$ can be evaluated from the rate-determining step of the guest exchange between $\mathbf{1}\supset\mathbf{2}$ and $\mathbf{1}\supset\mathbf{4}$. $\mathbf{1}\supset\mathbf{2}$ and $\mathbf{1}\supset\mathbf{4}$ at 25 °C showed Me−Rh signals respectively at $\delta$ −5.58 and −5.53 ppm, which coalesced at higher temperatures[8] due to the guest exchange. Because the $K_{\mathrm{assoc}}$

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10.1021/ja0264450 CCC: $22.00 © 2002 American Chemical Society

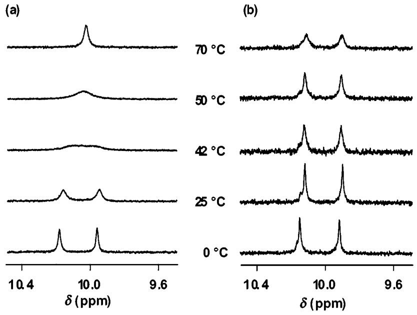

***Figure 1.*** Variable-temperature $^1$H NMR spectral profiles (meso-H region) of (a) $\mathbf{1}\supset\mathbf{2}$ and (b) $\mathbf{1}\supset\mathbf{3}$ in $C_6D_5CD_3$ ([**1**] = 1.0 mM).

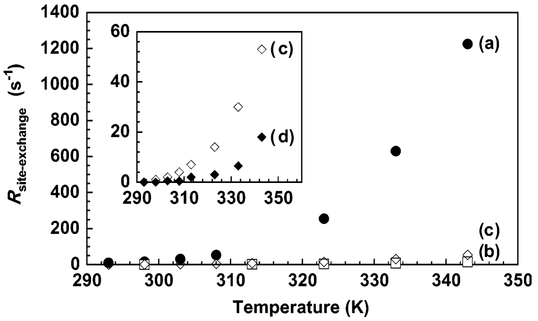

***Figure 2.*** $^1$H NMR site-exchange rates ($R_{site-exchange}$) for (a) meso-H of $\mathbf{1}\supset\mathbf{2}$, (b) meso-H of $\mathbf{1}\supset\mathbf{3}$, (c) meso-H of $\mathbf{1}\supset\mathbf{4}$, and (d) Me−Rh of $\mathbf{1}\supset\mathbf{2}$/$\mathbf{1}\supset\mathbf{4}$ (1:1) in $C_6D_5CD_3$ ([**1**] = 1.0 mM) at 20−70 °C.

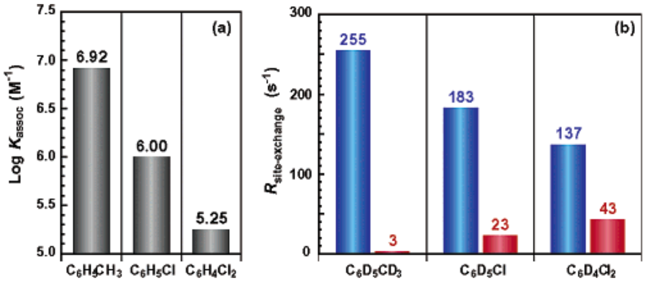

***Figure 3.*** (a) Association constants ($K_{assoc}$) of $\mathbf{1}\supset\mathbf{2}$ at 20 °C in $C_6H_5CH_3$, $C_6H_5Cl$, and $C_6H_4Cl_2$. (b) $^1$H NMR site-exchange rates ($R_{site-exchange}$) for meso-H of $\mathbf{1}\supset\mathbf{2}$ (blue bar) and $CH_3$−Rh of $\mathbf{1}\supset\mathbf{2}$/$\mathbf{1}\supset\mathbf{4}$ (1:1) (red bar) at 50 °C in $C_6D_5CD_3$, $C_6D_5Cl$, and $C_6D_4Cl_2$ ([**1**] = 1.0 mM).

values of the complexes are both very large, the overall guest-exchange rate ($R_{guest-exchange}$) should be determined by the dissociation rate ($R_{dissoc}$) of either of the two complexes. By a $^1$H NMR line shape analysis, we evaluated $R_{guest-exchange}$ values at 20−70 °C (Figure 2d), which are obviously smaller than the aforementioned $R_{dissoc}$ values of $\mathbf{1}\supset\mathbf{4}$ (Figure 2c). Therefore, the dissociation of $\mathbf{1}\supset\mathbf{2}$ is the rate-determining step for the guest exchange,[6b] and we compared the observed $R_{guest-exchange}$, as the first approximation to the $R_{dissoc}$ of $\mathbf{1}\supset\mathbf{2}$, with the $R_{site-exchange}$ of $\mathbf{1}\supset\mathbf{2}$. As shown in Figure 2a and d, a large difference was observed between these two rates, indicating that $\mathbf{1}\supset\mathbf{2}$ hardly dissociates during the oscillation. For example, $\mathbf{1}\supset\mathbf{2}$ at 70 °C is estimated to oscillate 1207 times a second ($R_{site-exchange} - R_{guest-exchange}$), while it dissociates only at a rate of 18 s$^{-1}$.

Of interest, similar experiments in chloro- and 1,2-dichlorobenzenes ($C_6H_5Cl$, $C_6H_4Cl_2$) indicated that the complexation and oscillation events both compete with the solvation of **2**. As shown in Figure 3a, $K_{assoc}$ of $\mathbf{1}\supset\mathbf{2}$[8] was smaller as the affinity of the solvent toward carbon nanoclusters was higher ($C_6H_5CH_3 < C_6H_5Cl < C_6H_4Cl_2$),[13] indicating that the inclusion of **2** into the cavity of **1** requires desolvation of **2**. On the other hand, the $R_{site-exchange}$ of $\mathbf{1}\supset\mathbf{2}$, which reflects the oscillation activity, was smaller as $K_{assoc}$ was smaller (blue bars, Figure 3b).[8] Because VT $^1$H NMR analysis on a 1:1 mixture of $\mathbf{1}\supset\mathbf{2}$ and $\mathbf{1}\supset\mathbf{4}$ in $C_6D_5Cl$ and $C_6D_4Cl_2$ again indicated that the dissociation step of $\mathbf{1}\supset\mathbf{2}$ determines the overall guest-exchange rate (i.e., $R_{guest-exchange}$ [red bars, Figure 3b] < $R_{dissoc}$ of $\mathbf{1}\supset\mathbf{4}$[8]), the observed $R_{guest-exchange}$ values roughly correspond to the $R_{dissoc}$ values of $\mathbf{1}\supset\mathbf{2}$. As shown in Figure 3b, $R_{dissoc}$ of $\mathbf{1}\supset\mathbf{2}$ (∼red bar) is larger as $K_{assoc}$ is smaller, whereas the oscillation rate, as estimated by subtracting the red bar from the blue bar, is obviously smaller. This trend seems strange but is rather reasonable, considering that the oscillation of $\mathbf{1}\supset\mathbf{2}$ also requires desolvation of **2**. In $\mathbf{1}\supset\mathbf{2}$, the protruding $C_{60}$ moiety of included **2** must be solvated. Hence, the transition state for the oscillation requires desolvation of the protruding $C_{60}$ moiety (Chart 1). In $C_6H_4Cl_2$, the $C_{60}$ moiety should be heavily solvated due to the high affinity of $C_6H_4Cl_2$ toward **2**,[13] thereby giving the smallest oscillation frequency among the three solvents (Figure 3b). In conformity with a less solvated transition state model, the $\Delta S^{\ddagger}$ values for the oscillation, as calculated from Eyring plots of the estimated oscillation rates,[8] were all positive,[14] indicating that this is an entropy-driven oscillation.

In summary, we demonstrated that an inclusion complex of a cyclic dimer of rhodium(III) porphyrin (**1**) with $C_{120}$ ($\mathbf{1}\supset\mathbf{2}$) serves as a novel supramolecular oscillator, which can visualize the solvation/desolvation dynamics of carbon nanoclusters. This result shows an interesting potential of the supramolecular chemistry of fullerenes[6,15] for molecular sensing.

**Supporting Information Available:** UV−vis, MS, (VT) $^1$H NMR data for **4** and mixtures of **1** with **2**−**4**, Job's plots of mixtures of **1** with **2**, Eyring plot, and a method for the determination of $K_{assoc}$ values (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Compound **4** was prepared according to a method reported in: Saigo, K.; et al. *Fullerene Sci. Technol.* **2001**, *4*, 467 (see Supporting Information).
(12) Formation of $\mathbf{1}_2\supset\mathbf{2}$ at [**1**] > [**2**] and precipitation of uncomplexed **2** at [**1**] < [**2**] are also essential problems, which hamper evaluation of the dissociation/association dynamics of $\mathbf{1}\supset\mathbf{2}$.
(13) Solubilities of $C_{60}$ in $C_6H_5CH_3$, $C_6H_5Cl$, and $C_6H_4Cl_2$ have been reported to be 2.8, 7.0, and 27.0 mg mL$^{-1}$, respectively: Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379.
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JA0264450