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Dynamic aspects in host–guest complexation by coordination nanotubes†

Masahide Tominaga, Shohei Tashiro, Masaru Aoyagi‡ and Makoto Fujita*
Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo and CREST, Japan Science and Technology Corporation (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.
E-mail: mfujita@appchem.t.u-tokyo.ac.jp

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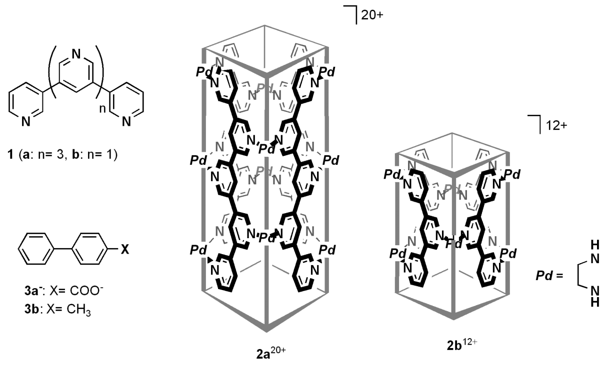
Rod-like guests accommodated in self-assembled coordination nanotubes are shown to stay in the tubes without flipping along its length at room temperature, but rapidly exchange intermolecularly at high temperature.

Oligo(3,5-pyridine) ligands **1** have been shown to self-assemble into coordination nanotubes **2** in the presence of rod-like guests.[1] The previous paper has described that the rod-like guests play an important role in templating the assembly of the tubes and stabilizing the tubular structures. Studies on the dynamic behavior of the guest molecules that are accommodated in the tubes are particularly interesting because the guests are expected to move only in a one-dimensional way within the tubes leading to the novel functions of tubular molecules: *e.g.* shape-selective transportation,[2] site-specific chemical transformation[3] and molecular level data storage.[4] Here we discuss the dynamic aspects of the host–guest complexation within the self-assembled coordination nanotubes.[5] NMR studies show that guests stay in the tubes without flipping along the length at room temperature, but rapidly exchange intermolecularly at high temperature.



To address the guest motion in the tube, unsymmetrical biphenyl derivative **3a**$^-$ was used as a template. Thus, (en)Pd(NO$_3$)$_2$, ligand **1a** and Na·**3a** were combined at a ratio of 10 : 4 : 1 in D$_2$O. After 1 h at 70 °C, NMR revealed the self-assembly of tube **2a·3a**$^{19+}$.§ Guest signals were upfield shifted and observed at δ 5.2–5.5 indicating the efficient accommodation of **3a**$^-$ in nanotube **2a**$^{20+}$.

A significant observation by NMR is the dissymmetrization of the host framework at ambient temperature: *e.g.* H*d* H*d′* and H*e* H*e′* as shown in Fig. 1a. Upon heating, these pairs coalesced at 47 °C (Fig. 1b and c). From T_c, the activation energy was estimated to be 16.0 kcal mol^{-1}.[6] These results evidence the following guest behavior: (i) the guest molecule is trapped in the tube and unable to flip at room temperature on the NMR timescale, dissymmetrizing the host framework; (ii) the guest spins around its long axis because all four units of **1a** in the tube are found equivalent in the NMR spectrum; (iii) at high temperature, the guest is able to escape from the tube, symmetrizing the host environment.

The coalescence temperature T_c (47 °C) markedly changed upon the addition of an excess amount of the guest. For example, when a small amount (0.1 equiv.) of the guest was added to the 1 : 1 host–guest complex, T_c was dramatically dropped to 33 °C as revealed by VT NMR measurement. Further addition of the guest (up to 2.0 equiv.) caused gradual decrease in T_c: at [H] : [G] = 1 : 1.2 and 1 : 1.5, T_c was 29 and 14 °C, respectively. At [H] : [G] = 1 : 2, the dissymmetrization of the ligand framework was not observed even at 5 °C.

The significant change in T_c at [G]/[H] = 1 strongly suggests two possible pathways for guest release. When [G]/[H] < 1, guest molecules must self-dissociate *via* an empty intermediate (S$_N$1-like pathway, Fig. 2a). In the case of [G]/[H] > 1, the guest can be replaced by a second guest *via* an S$_N$2-like pathway (Fig. 2b). Obviously, the latter process requires lower energy and, therefore, the T_c drops significantly at [G]/[H] > 1. Since the S$_N$2-like displacement accelerates with increase in guest concentration, the T_c gradually drops upon the addition of further amounts of the guest.

The activation energy also depends on the tube length: when shorter tube **2b**$^{12+}$ was complexed with **3a**$^-$ (1 equiv.), the activation energy was calculated to be 14.9 kcal mol^{-1}.¶ Thus, the shorter tube can trap the guest less tightly.

The preferential binding of anionic guest **3a**$^-$ over a neutral guest, 4-methylbiphenyl (**3b**), was shown by a guest exchange experiment. Thus, **2a·3b**$^{20+}$ complex was prepared by treating (en)Pd(NO$_3$)$_2$ with ligand **1a** in the presence of **3b** (D$_2$O, 20 h, 70 °C).‖ Again, the dissymmetrization of the host framework was observed showing that this guest was also trapped in the tube at room temperature. Upon the addition of **3a**$^-$ (1.0 equiv.) to this solution, however, guest **3b** was immediately replaced by **3a**$^-$. This result suggested that, in addition to the aromatic

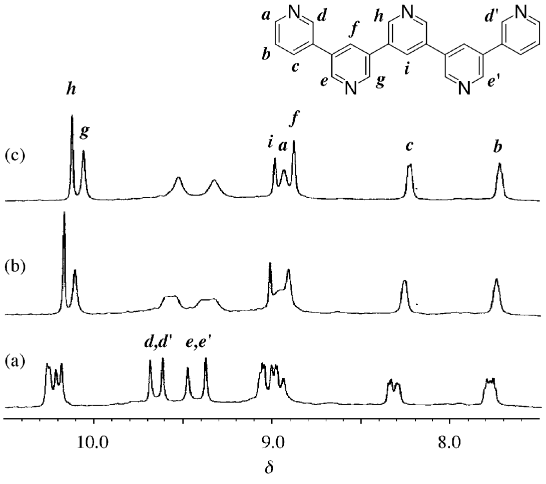


Fig. 1 Variable-temperature ^{1}H NMR spectra recorded in D$_2$O at (a) 27 °C, (b) 47 °C and (c) 60 °C (500 MHz, TMS as an external standard).

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† Electronic supplementary information (ESI) available: Figs. S1–15: ^{1}H, H–H COSY and NOESY NMR spectra for **2a·3a**$^{19+}$, **2a·3b**$^{20+}$ and **2b·3a**$^{11+}$. See http://www.rsc.org/suppdata/cc/b2/b205196f/

‡ Present address: Nanoarchitechtonics Research Center, National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 4-4, 1-1-1 Higashi-Tsukuba, Ibaraki 305-8562, Japan.

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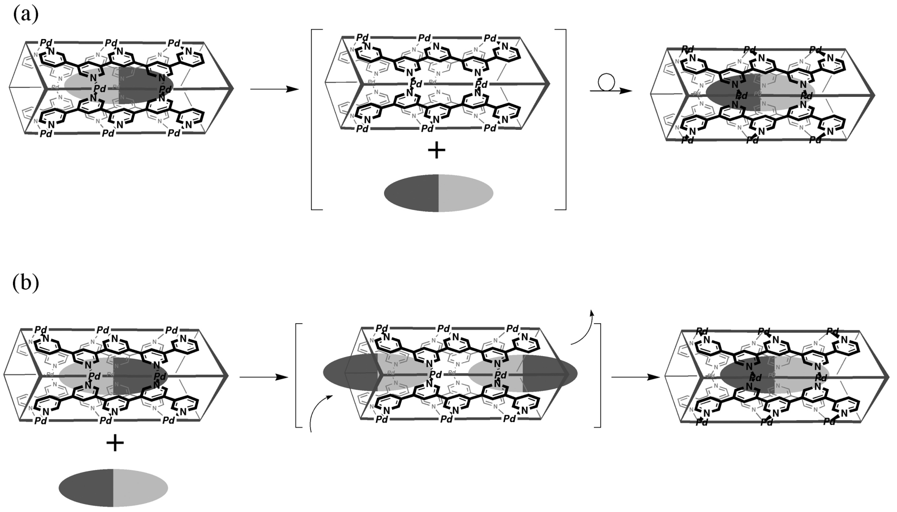

Fig. 2 Illustration for the mechanism of guest exchange at (a) [H] : [G] = 1 : 1 and (b) [H] : [G] = 1 : 2.

interactions, efficient electrostatic interaction between the tube and the template was also particularly important for the host–guest complexation.[1] The weaker host–guest interaction in the **2a·3b**$^{20+}$ complex agreed well with its activation energy (15.6 kcal mol^{-1}) being lower than that of **2a·3a**$^{19+}$ by 0.4 kcal mol^{-1}.

Notes and references

§ Preparation of **2a·3a**$^{19+}$: (en)Pd$(NO_3)_2$ (0.10 mmol) and **1a** (0.04 mmol) were combined in D_2O (2.0 mL) and stirred for 5 h at 70 °C. To this solution, an aqueous solution (0.1 mL) of Na·**3a** (0.01 mmol) was added and the mixture was stirred at 70 °C for 1 h. ^{1}H NMR showed the quantitative formation of **2a·3a**$^{19+}$: see Fig. 1a.

¶ Complex **2b·3a**$^{11+}$: (en)Pd$(NO_3)_2$ (0.15 mmol) and **1b** (0.10 mmol) were combined in D_2O (3.0 mL) and stirred for 1 h at 70 °C. To this solution (0.6 mL), an aqueous solution (0.05 mL) of Na·**3a** (0.005 mmol) was added and the mixture was stirred at 70 °C for 4 h to give **2b·3a**$^{11+}$ quantitatively. ^{1}H NMR (500 MHz, D_2O, 15 °C, TMS) δ 9.73 (br s, 4H, PyH_α), 9.64 (br s, 4H, PyH_α), 9.40 (br s, 4H, PyH_α), 9.32 (br s, 4H, PyH_α), 8.89 (br s, 8H, PyH_α), 8.71 (br s, 4H, PyH_γ), 8.05 (d, J 8.0 Hz, 8H, PyH_γ), 7.52 (dd, J 7.0 Hz, 8H, PyH_β), 5.84–4.80 (9H, **3a**·ArH), 3.0–2.9 (m, 24H, $NH_2CH_2CH_2NH_2$).

‖ Complex **2a·3b**$^{20+}$: ^{1}H NMR (500 MHz, D_2O, 27 °C, TMS) δ 10.11 (br s, 8H, PyH_α), 10.08 (br s, 8H, PyH_α), 9.49 (br s, 8H, PyH_α), 9.35 (br s, 8H, PyH_α), 8.99 (br s, 4H, PyH_γ), 8.94 (d, J 5.2 Hz, 8H, PyH_α), 8.83 (br s, 8H, PyH_γ), 8.21 (d, J 7.4 Hz, 8H, PyH_γ), 7.75 (t, J 6.5 Hz, 8H, PyH_β), 4.94–4.64 (9H, **3b**·ArH), 3.0–2.8 (m, 40H, $NH_2CH_2CH_2NH_2$), −0.49 (s, 3H, **3b**·CH_3).

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