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Spectroscopic and crystallographic studies on the stability of self-assembled coordination nanotubes†

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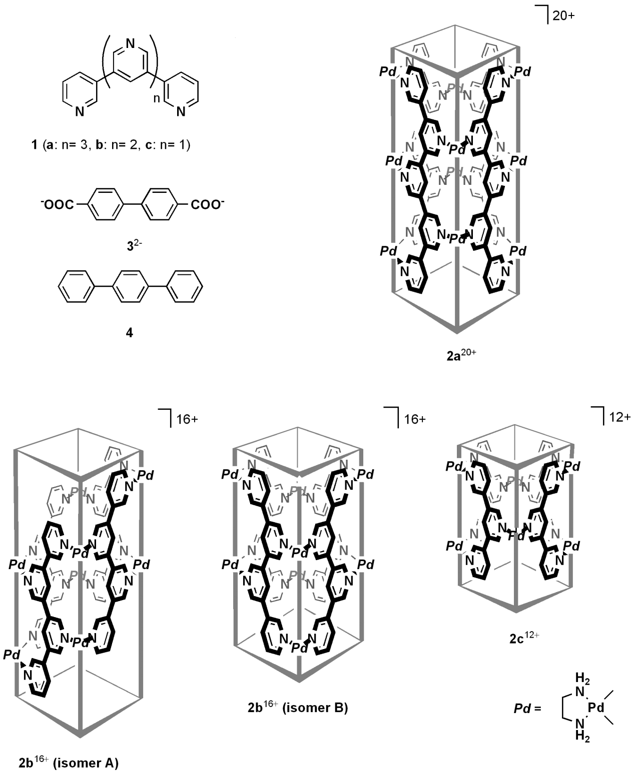
On complexation with (en)Pd(NO$_3$)$_2$, tetrakis(3,5-pyridine) ligand gives two isomeric coordination nanotubes, which are in slow equilibrium despite the presence of sixteen Pd–N bonds in the tube framework.

Tube structures have attracted considerable current interest due to their potential function as molecular level channels for selective transportation of ions and molecules.[1–5] Recently, we have shown that tape-shaped oligo(3,5-pyridine) ligands **1** are efficiently assembled into coordination nanotubes **2** upon complexation with an end-capped Pd(II) component in the presence of rod-like guests as templates.[6,7] The length of the tube can be strictly controlled according to the numbers of pyridine nuclei involved in the component ligand **1**. From **1a** and **1c** that contain odd number of pyridine nuclei, **2a** and **2c** are exclusively assembled, respectively, without the formation of any structural isomers. However, ligand **1b** that contains an even number of pyridine nuclei is anticipated to assemble into the two structural isomers of **2b**: isomers **A** and **B** in Scheme 1, whose symmetries are dictated as C_{2h} and D_{2h}, respectively. Though both isomers of **2b** are sustained by sixteen Pd–pyridine bonds, the labile nature of the coordination bonds may allow the two isomers to interconvert into each other. The study on such an interconversion process is particularly important for elucidating the kinetic stability of the coordination nanotubes. In this paper, we show that a very slow interconversion exists between the isomers **A** and **B** but the tube is substantially stable on a laboratory timescale unless the template molecule is removed. The stability of **2a** and **2b**(isomer **A**), whose structures have been assigned only by spectroscopic methods, is also discussed based on diffraction studies.

We observed the formation of two isomers **A** and **B** for nanotube **2b** in a *ca.* 1 : 1 ratio when tetrakis(3,5-pyridine) ligand **1b** was treated with (en)Pd(NO$_3$)$_2$ in the presence of 4,4′-biphenylenedicarboxylate ($\mathbf{3}^{2-}$) as a template. In isomer **A**, each ligand is placed on a non-C_2-symmetric environment and thus fourteen individual signals are observed for the ligand part in ^{1}H NMR. In isomer **B**, however, each ligand keeps its symmetry on complexation showing only seven protons that correspond to half of the framework (Fig. 1a). Fortunately, isomer **A** accommodating $\mathbf{3}^{2-}$ was isolated as single crystals by slow diffusion of ethanol into the aqueous solution of the 1 : 1 mixture of **A** and **B**. The pure crystals of isomer **A** were carefully dissolved in D_2O at room temperature and subjected to ^{1}H NMR study (Fig. 1b). The signals of isomer **A** are fully assigned by COSY and NOESY NMR spectra.

To examine the stability of the isomers, the solution was allowed to stand at room temperature. Within 1 h, no detectable interconversion of the host framework was observed showing that the nanotube structure has sufficient kinetic stability on the timescale of hours. Within days, however, signals of isomer **B** gradually appeared. Finally, after 2 weeks the two isomers were almost equilibrated (Fig. 1c and d). The framework of $\mathbf{2b}^{16+}$ is



Scheme 1

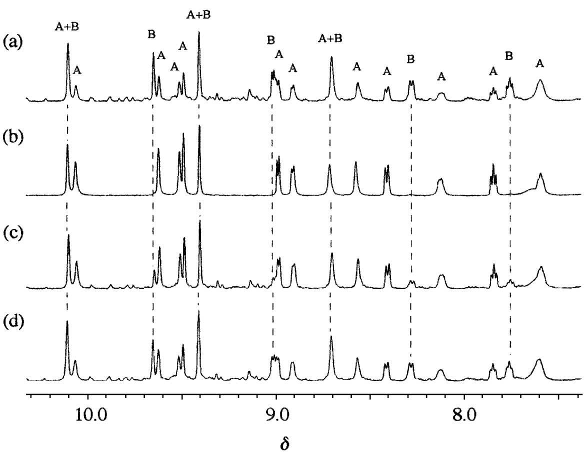


Fig. 1 ^{1}H NMR observation of isomerism of **2b** recorded in D_2O (500 MHz, 25 °C, TMS as an external standard). (a) A crude mixture. (b) The complex isolated as crystals: after 1 h. (c) After 5 d. (d) After 13 d.

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† Electronic supplementary information (ESI) available: Crystallography section; Figs. S1–9: ^{1}H, ^{13}C, H–H and C–H COSY NMR spectra for $\mathbf{2b}\cdot\mathbf{3}^{14+}$(isomer A) and $\mathbf{2a}\cdot\mathbf{4}^{20+}$. See http://www.rsc.org/suppdata/cc/b2/b205194j/

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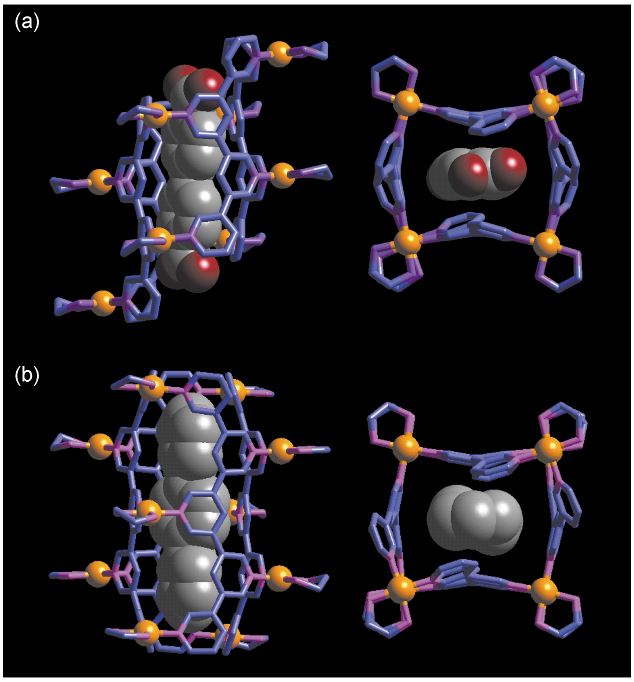

Fig. 2 Crystal structure of (a) **2b**·**3**$^{14+}$ (isomer **A**) and (b) **2a**·**4**$^{20+}$. Left: side view. Right: top view. For clarity, H atoms, water molecules and NO_3^- ions are omitted.

sustained by sixteen Pd–N bonds and at least eight of them must be cleaved at once for the interconversion. Nevertheless, the spectroscopic study revealed the existence of the interconversion process between the isomers.

Nanotube **2a**$^{20+}$ should be more stable than **2b**$^{16+}$ because of the presence of twenty Pd–pyridine bonds. However, **2a**$^{20+}$ immediately collapses when the template molecule is removed.[6] This fact suggests that the stability of the tube is not mainly attributed to the cooperation of the Pd–N bonds but to the non-bonded interactions between the tube and the template.

The non-bonded host–guest interactions required studying in more detail to account for the stability of the tubes. Thus the single crystal of isomer **A** was subjected to a diffraction study.¶ The crystal structure showed the expected linkage connectivity of the isomer **A** (Fig. 2a). The top view of the complex shows strong π–π and CH–π interactions between the biphenyl group of **3**$^{2-}$ and the framework of **2b**$^{16+}$ as previously observed in the complexation of **2c**$^{12+}$ with an anionic guest. The tube length is also suitable to accommodate **3**$^{2-}$. As shown by the side view, the biphenyl moiety is efficiently surrounded by hydrophobic pyridine nuclei while two COO$^-$groups are exposed outwards to have opportunity of hydrophilic and ionic interactions with solvent molecules and Pd^{2+} centers.

Crystallographic study was also carried out for tube **2a**$^{20+}$. To gain a better host–guest interaction, *p*-terphenyl (**4**) is selected as a template. Single crystals were successfully obtained by standing an aqueous solution of **2a**·**4**$^{20+}$ complex at ambient temperature for two weeks.‖ The crystal structure again revealed nice host–guest compatibility both in the width and the length (Fig. 2b). The most interesting feature is that the *p*-terphenyl molecule (14.1 Å in length) is completely insulated within the tube framework of **2a** (19.4 Å in length).

Notes and references

¶ X-Ray crystallographic analysis for isomer **A** of tube **2b**: A mixture of **1b** (23.3 mg, 0.075 mmol), (en)Pd$(NO_3)_2$ (43.6 mg, 0.15 mmol) and Na_2·**3** (10.7 mg, 0.038 mmol) was stirred for 1 h at 70 °C in H_2O and cooled to room temperature. After filtration, ethyl alcohol was slowly diffused into the solution for 3 weeks to give crystals of **2b**·(**3**)$_2^{12+}$. *Crystal data* for isomer **A** of tube **2b**: The asymmetric unit contains two halves of the tube, one full guest and two halves of dibenzoate anion, 12 nitrate anions and 43 water molecules. The hydrogen atoms on the water molecules were not located. $C_{124}H_{218}N_{44}O_{85}Pd_8$, M = 4536.62, triclinic, space group $P1$, a = 17.549(2), b = 20.344(3), c = 29.840(4) Å, α = 107.231(3), β = 91.243(3), γ = 114.438(3)°, V = 9133(2) Å^3 ,T = 153 K, Z = 2, D_C = 1.650 g cm^{-3}, = 0.71073 Å, 48058 reflections measured, 31565 unique (R_{int} = 0.0653) which were used in all calculations. R_1 = 0. 0.1318 and wR_2 = 0.3226.

X-Ray crystallographic analysis for tube **2a**·**4**$^{20+}$: A mixture of **1a** (7.7 mg, 0.020 mmol), (en)Pd$(NO_3)_2$ (14.5 mg, 0.050 mmol), and *p*-terphenyl (**4**) (1.2 mg, 0.005 mmol) was stirred for 3 d at 70 °C in H_2O and cooled to room temperature. After filtration, crystals of complex **2a**·**4**$^{20+}$ were obtained from H_2O solution at ambient temperature for two weeks. *Crystal data* for **2a**·**4**$^{20+}$: $C_{138}H_{218}N_{60}O_{88}Pd_{10}$, M = 5189.72, triclinic, space group $P1$, a = 18.477(2), b = 18.905(2), c = 20.012(3) Å, α = 66.452(2), β = 86.410(2), γ = 61.910(2)°, V = 5584.8(12) Å^3, T = 173 K, Z = 1, D_C = 1.543 g cm^{-3}, λ = 0.71073 Å, 29877 reflections measured, 19432 unique (R_{int} = 0.0710) which were used in all calculations. R_1 = 0.1014 and wR_2 = 0.2467. CCDC reference numbers 142798 and 186880. See http://www.rsc.org/suppdata/cc/b2/b205194j/ for crystallographic data in CIF or other electronic format.

‖ *Physical data* for tube **2a**·**4**$^{20+}$: ^1H NMR (500 MHz, D_2O, 27 °C, TMS) δ 10.31 (br s, 8H, PyH_α), 10.27 (br s, 8H, PyH_α), 9.66 (s, 8H, PyH_α), 9.47 (br s, 8H, PyH_α), 9.22 (br s, 4H, PyH_γ), 9.05 (d, J 5.5 Hz, 8H, PyH_α), 8.88 (br s, 8H, PyH_γ), 8.33 (d, J 6.8 Hz, 8H, PyH_γ), 7.79 (t, J 6.8 Hz, 8H, PyH_β), 5.32 (t, J 7.3 Hz, 2H, **4**·Ar*H*), 5.25 (s, 4H, **4**·Ar*H*), 4.94 (t, J 7.3 Hz, 4H, **4**·Ar*H*), 4.86 (d, J 7.3 Hz, 4H, **4**·Ar*H*), 3.01–2.80 (m, 40H, $NH_2CH_2CH_2NH_2$). ^{13}C NMR (125 MHz, D_2O, 27 °C, TMS) δ 152.85 (Py*C*H), 150.95 (Py*C*H), 150.46 (Py*C*H), 149.95 (Py*C*H), 149.19 (Py*C*H), 139.20 (Py*C*H), 136.34 (C_q), 135.37 (C_q), 134.63 (Py*C*H, C_q), 133.22 (Py*C*H), 132.99 (C_q), 132.29 (C_q), 132.14 (C_q), 127.17 (Py*C*H, **4**·Ar*C*H), 124.15 (**4**·Ar*C*H), 122.29 (**4**·Ar*C*H), 47.30–46.93 ($NH_2CH_2CH_2NH_2$); mp decomp. at 245 °C. Anal. Calc. for $C_{138}H_{162}N_{60}O_{60}Pd_{10}$·$37H_2O$: C, 30.97; H, 4.44; N, 15.70. Found: C, 30.66; H, 4.11; N, 15.37%.

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