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A circular tris[2]catenane from molecular 'figure-of-eight'†

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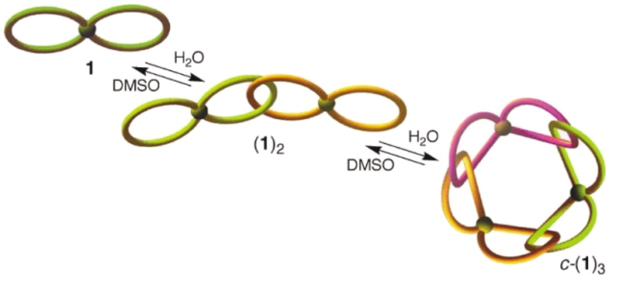
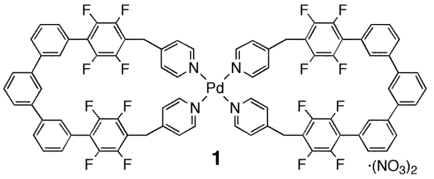
A 'figure-of-eight'-shaped molecule with Pd(II) at the node was self-assembled into an unprecedented circular tris[2]catenane *via* reversible double catenation at both loops of the 'figure-of-eight' molecule.

Whereas recent studies on interlocked molecules[1] are mostly directed towards the development of molecular-based devices and machineries owing to their dynamic and electro- and photo-responsive properties,[2] their inherent unique nature that stems from mechanically linked structures[3] has been less exploited for simply connecting molecular subunits or preparing oligomeric/polymeric materials. In this regard, the reversible catenation of metal-clipped coordination rings, which we have been studying for the last decade,[4] may offer a new class of molecular assemblies. Several groups have prepared poly[2]catenanes by conventional poly-condensation of catenated monomeric units.[5] However, oligo- or polycatenanes that directly form *via* catenation have been less explored partially because of the lack of quantitative catenation reactions. Here we discuss the unique behavior of a 'figure-of-eight'-shaped compound with a Pd(II) ion at the node of the molecule: complex **1**. Related Pd(II) single loop compound **2** has been shown to quantitatively assemble into [2]catenane (**2**)$_2$ in aqueous media.[6] We have found that the 'figure-of-eight' molecule **1** is spontaneously assembled into an unprecedented circular tris[2]catenane *c*-(**1**)$_3$ *via* reversible double catenation at *both* loops of the 'figure-of-eight' structure (Scheme 1). While circular pseudo-rotaxane structures have been reported recently,[7–9] our molecule provides, to our knowledge, the first example of an oligocatenated counterpart.

Monomer **1** was formed spontaneously and quantitatively in DMSO from its components. Typically, bis(4-pyridyl) appended precursor ligand (14.2 mg, 0.02 mmol) and $Pd(NO_3)_2$ (2.3 mg, 0.01 mmol) were combined in DMSO (1 mL) at 60 °C. NMR revealed the formation of a single product (Fig. 1a) whose signals in the aromatic region were qualitatively the same as those of (en)Pd(II)-linked ring **2**.[6] Thus this compound was assigned to monomer **1**, by analogy with the formation of **2**. By adding a large amount of diethyl ether, **1** was isolated as a colorless powder in 95% yield. The elemental analysis of **1** was consistent with the formula of **1**·dmf·H_2O. CSI-MS (cold spray ionization mass spectrometry)[10] also revealed that complex **1** was stable in DMF. For example, prominent peaks were observed at *m/z* 761 $[\mathbf{1} - (NO_3)_2]^{2+}$ and 798 $[\mathbf{1} - (NO_3)_2 + \mathrm{dmf}]^{2+}$. No peaks were observed for any oligomeric species.



Scheme 1



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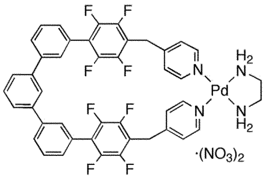

2

The double loop structure of **1** is evidenced by X-ray crystallographic studies (Fig. 2).¶ Single crystals suitable for X-ray studies were obtained by recrystallizing **1** from a DMF–MeOH–diethyl ether solution. As expected, the Pd(II) center adopted a square planar geometry with four pyridyl sites. With respect to a PdN_4 plane, all pyridyl groups are orthogonal while peripheral $-(C_6H_4)_3-$ sites are almost in plane.

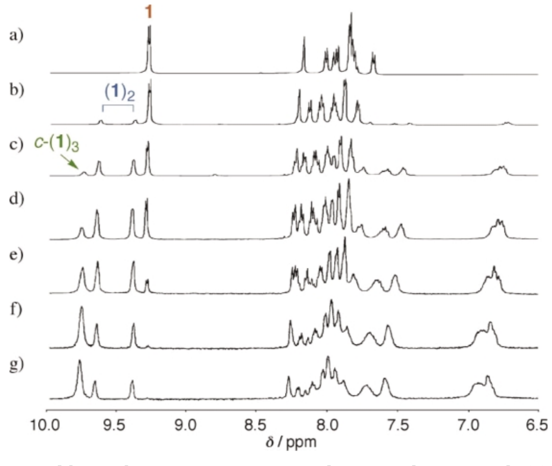

Fig. 1 Equilibrium between monomer **1** and catenated compounds $(\mathbf{1})_n$ (n = 2, 3) shown by ^1H NMR spectroscopy (aromatic region, 500 MHz, 25 °C, 0.5 mM). Spectra were obtained by treating the ligand with $Pd(NO_3)_2$ for 30 min at 60 °C in (a) DMSO-d_6, (b) 1 : 3 D_2O–DMSO-d_6, (c) 1 : 2.5 D_2O–DMSO-d_6, (d) 1 : 2 D_2O–DMSO-d_6, (e) 1 : 1.5 D_2O–DMSO-d_6, (f) 1 : 1 D_2O–DMSO-d_6, and (g) 1 : 0.9 D_2O–DMSO-d_6.

In D_2O–DMSO-d_6 mixed solvents (1 : 3–1 : 0.9), the 'figure-of-eight' monomer **1** was transformed into oligomeric structures by organic stack-driven catenation as revealed by NMR and CSI-MS. Monomer **1** decreased with increasing D_2O content as shown in Fig. 1. The first oligomeric component that appeared in the

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† Electronic supplementary information (ESI) available: physical properties of **1** and CSI-MS data for **1**, (**1**)$_2$, and (**1**)$_3$. See http://www.rsc.org/suppdata/cc/b4/b407108e/

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spectrum was assigned to the simple dimer $(\mathbf{1})_2$. Since the 'figure-of-eight' framework loses its symmetry in dimer $(\mathbf{1})_2$, the two loops become inequivalent and are observed separately: *e.g.*, PyH_α(in) and PyH_α(out) appeared at δ 9.7 and 9.4, respectively. Some aromatic protons of $(\mathbf{1})_2$ were shifted upfield in agreement with the interlocked structure (to around δ 6.5–8.0). In a 1 : 1.5 D_2O–DMSO-d_6 solution at 0.5 mM (Fig. 1e), the proportion of $(\mathbf{1})_2$ was maximized (*ca.* 60%). CSI-MS of a 1.2 : 1 H_2O–DMF solution of the mixture clearly indicated the formation of the dimer: *e.g.*, *m*/*z* 780 $[(\mathbf{1})_2 - (NO_3)_4 + \text{dmf}]^{4+}$, 798 $[(\mathbf{1})_2 - (NO_3)_4 + 2\text{dmf}]^{4+}$, 1036 $[(\mathbf{1})_2 - (NO_3)_3]^{3+}$, 1586 $[(\mathbf{1})_2 - (NO_3)_2]^{2+}$ (Fig. 3).

Under more aqueous conditions, a third component appeared and gradually became dominant (Fig. 1c–g) which was assigned to catenated trimer $(\mathbf{1})_3$ in due course. Unlike dimer $(\mathbf{1})_2$, however, the newly formed component was shown to have a symmetrical 'figure-of-eight' framework. For example, only one signal was observed for the PyH_α protons (δ = 9.8). This spectroscopic observation strongly suggested the formation of circular tris[2]catenane *c*-$(\mathbf{1})_3$ as shown in Fig. 1c because this structure fully agrees with the equivalency of all loops and the absence of a non-catenated terminus. In Fig. 1g, the *c*-$(\mathbf{1})_3$ content was approximately 50%. The CSI-MS spectrum of Fig. 3 also included several signals for 2+ to 6+ charged *c*-$(\mathbf{1})_3$ species: *m*/*z* 786 $[(\mathbf{1})_3 - (NO_3)_6 + 2\text{dmf}]^{6+}$, 955 $[(\mathbf{1})_3 - (NO_3)_5 + 2\text{dmf}]^{5+}$, 1174 $[(\mathbf{1})_3 - (NO_3)_4]^{4+}$, 1192 $[(\mathbf{1})_3 - (NO_3)_4 + \text{dmf}]^{4+}$, 1577 $[(\mathbf{1})_3 - (NO_3)_4 + Cl]^{3+}$, 2397 $[(\mathbf{1})_3 - (NO_3)_2]^{2+}$. The isolation of pure *c*-$(\mathbf{1})_3$ was unsuccessful because further addition of water caused precipitation of the mixture.

The mixture of **1**, $(\mathbf{1})_2$, and *c*-$(\mathbf{1})_3$ in a 1 : 1.5 D_2O–DMSO-d_6 solution was also subjected to a DOSY (diffusion-ordered NMR spectroscopy) study[11,12] to separate the three components spectroscopically (Fig. 4). The spectra of **1** and $(\mathbf{1})_2$ were observed separately at cross sections (a) and (b), respectively. At the cross section (c), the spectrum of *c*-$(\mathbf{1})_3$ was obtained with a smaller diffusion coefficient, though somewhat disturbed by that of $(\mathbf{1})_2$. These observations agree with the order of increasing molecular weight $(\mathbf{1}) < (\mathbf{1})_2 <$ *c*-$(\mathbf{1})_3$. Further oligomers $(\mathbf{1})_n$ ($n \geq 4$) were not observed at smaller diffusion coefficients.

In conclusion, we have shown the self-assembly of the circular tris[2]catenane *via reversible catenation*. Linear polymerization of the 'figure-of-eight' module remains another goal of the present dynamic double catenation.

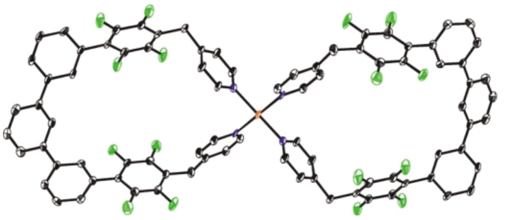

Fig. 2 Crystal structure of **1**: the ORTEP drawing showing 40% probability thermal ellipsoids.

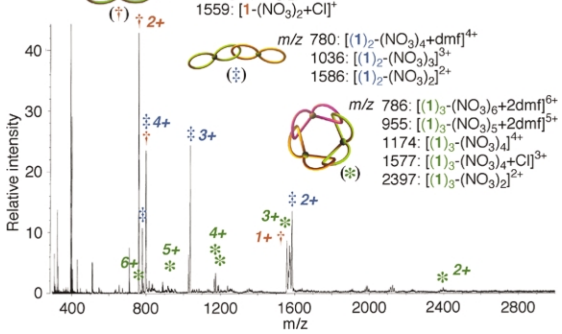

Fig. 3 CSI-MS spectrum of the mixture of **1**, dimer $(\mathbf{1})_2$ and trimer $(\mathbf{1})_3$ in a 1.2 : 1 H_2O–DMF solution.

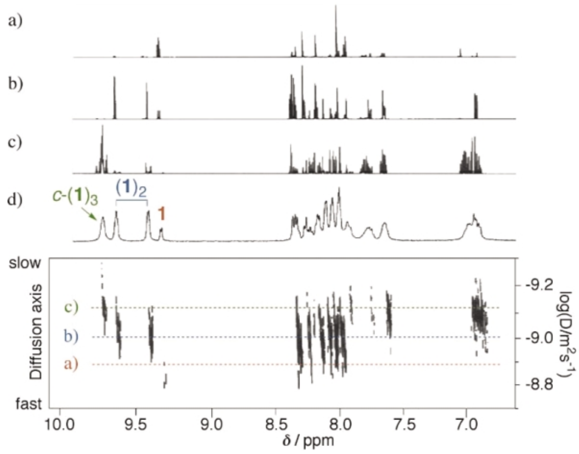

Fig. 4 DOSY spectrum of a solution obtained from the self-assembly of the components **1**, $(\mathbf{1})_2$ and $(\mathbf{1})_3$ showing the slices of the 2D DOSY spectrum at the diffusion coefficients of (a) figure-of-eight **1**, (b) dimer $(\mathbf{1})_2$, (c) trimer $(\mathbf{1})_3$, and (d) complete ^{1}H-NMR spectrum of the mixture. The spectrum was obtained by treating the ligand with $Pd(NO_3)_2$ for 30 min at 60 °C in a 1 : 1.5 D_2O–DMSO-d_6 solution (0.5 mM).

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¶ Crystal data for $\mathbf{1}\cdot 4Et_2O$ ($C_{100}H_{88}F_{16}N_6O_{10}Pd$: M_r = 1944.16): monoclinic, $P2_1/n$, T = 193(2) K, a = 15.485(3), b = 9.562(2), c = 30.234(6) Å, β = 104.052(4)°, V = 4342.7(15) Å^3, D_c = 1.487 g cm^{-3}, Z = 2, $F(000)$ = 2000, λ = 0.71073 Å, μ(Mo–Kα) = 0.315 mm^{-1}. GOF = 0.960, R = 0.0917, Rw = 0.2189. CCDC 238243. See http://www.rsc.org/suppdata/cc/b4/b407108e/ for crystallographic data in .cif or other electronic format.

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