

Selective cross-catenation of Pd(II) and Pt(II) coordination rings

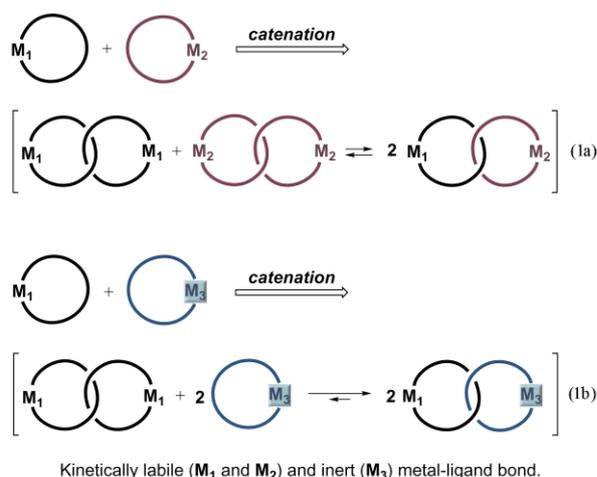
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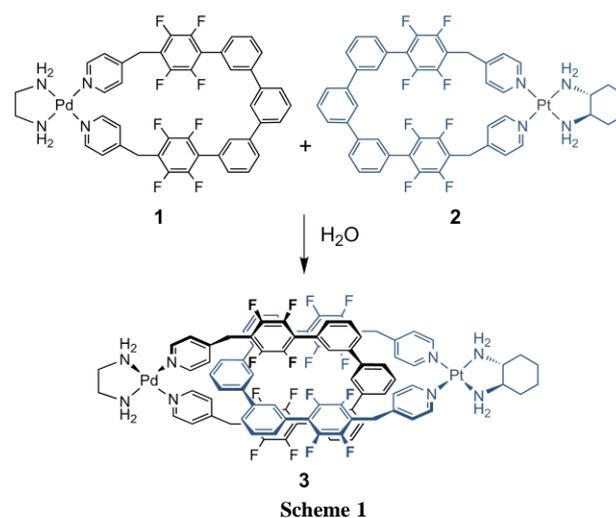
The reversible cross-catenation of two different coordination rings (Pd(II)- and Pt(II)-linked rings) has been achieved by using the labile nature of the Pd–N interaction and efficient hydrophobic contact between the rings.

The labile nature of metal–ligand coordination bonds has been exploited in the self-assembly of metal-linked [2]catenanes^{1,2} where component rings utilize the principle of threading/dethreading on each other *via* ligand dissociation. We have previously reported the reversible catenation of Pd(II)-linked organic rings which are catenated in aqueous conditions but dissociated in organic media due to enhanced/reduced hydrophobic interaction.^{3,4} In this reversible catenation, the structures of two coordination rings should be identical: otherwise, homo- and cross-catenated products will result from two different rings in a statistical ratio (eqn. (1a)). However, if the metal–ligand



bond of one ring is kinetically inert while that of another ring is kinetically labile,⁵ two types of coordination rings are expected to undergo cross-catenation because the equilibration of eqn. (1b) strongly shifts so that all rings will be stabilized by catenation. Based on this idea, we have designed here the cross-catenation of Pd(II)- and Pt(II)-linked rings (1 and 2) as shown in Scheme 1. Such a selective cross-catenation is particularly important to design new molecular switching systems where metal–metal interaction (*e.g.*, magnetic, electronic, *etc*) is observed upon catenation but suppressed upon decatenation.⁶

Rings 1 and 2, prepared independently in DMF,⁴ were combined in aqueous conditions to promote the catenation. In 2, chiral 1,2-cyclohexanediamine (*S,S* form unless noted) is attached on Pt center as a chiral probe for monitoring the catenation by circular dichroism (CD) experiments (*vide post*). Thus, D₂O (0.66 ml) was added dropwise into a DMF-*d*₇ (0.33 ml) solution of Pd(II)-linked ring 1 (5.0 mg, 0.005 mmol) and Pt(II)-linked ring 2 (6.4 mg, 0.005 mmol), and the mixture was stirred for 3 h at room temperature. NMR studies showed the

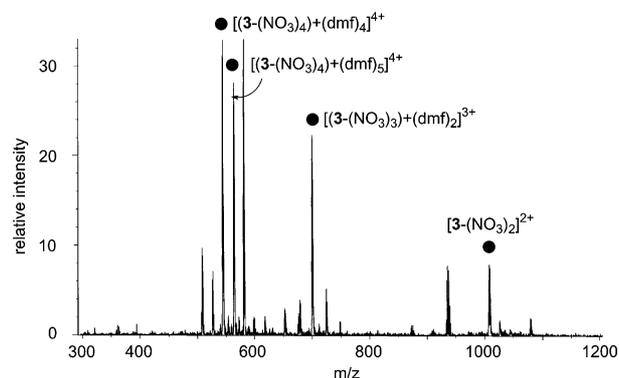


Scheme 1

complete transfer of the monomer rings into catenated species 3 as expected. The spectrum of the product with characteristic upfield shift of some aromatic protons is almost the same to that of homo Pd/Pd catenane 4.⁷

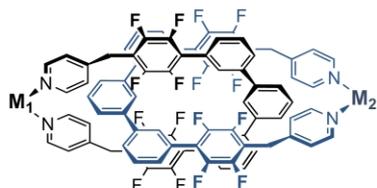
While the detailed characterization of the product by NMR was unsuccessful due to the overlap of signals, CSI-MS (coldspray ionization mass spectrometry)⁸ provided strong support for the selective formation of cross-catenane 3. The direct subjection of the reaction mixture in H₂O–DMF (2:1) solution to CSI-MS measurement clearly indicated the formation of 3. Namely, peaks were observed for [(3–(NO₃)_n) + (dmf)_m]ⁿ⁺; *e.g.*, *m/z* 544.4 [(3–(NO₃)₄) + (dmf)₄]⁴⁺, 700.1 [(3–(NO₃)₃) + (dmf)₂]³⁺, 1008.2 [3–(NO₃)₂]²⁺ (Fig. 1). A more important observation is that neither homo-[2]catenanes (4 and Pt/Pt catenane 5) or monomer rings (1 and 2) were observed suggesting the selective formation of cross-[2]catenane 3.

The cross-catenation was monitored *in situ* by a CD experiment. The principle of the experiment is based on our previous observation that a chiral Pd(II)-linked ring 1* (an analog of 1 with chiral 1,2-cyclohexanediamine end-capped

Fig. 1 CSI-MS spectrum of the catenane 3 in H₂O–DMF (2:1) solution.

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ligand) is CD silent but becomes CD active when catenated.⁴ From achiral Pd ring **1** and chiral Pt ring **2**, induced circular dichroism (ICD) should be observed only if the Pt ring is involved in the catenation (Fig. 2(a)).⁹ Thus the addition of water to a DMF solution of **1** and **2** was immediately followed by CD measurement.¹⁰ As shown in Fig. 2(b), CD was rapidly induced in minutes at room temperature. The reaction follows typical second order kinetics ($k \approx 20 \text{ M}^{-1} \text{ s}^{-1}$). No ICD was observed when only **2** was treated under the same conditions (Fig. 2(b)) because the kinetically inert Pt ring has no opportunity to be catenated.^{5,11} Therefore, the clear ICD monitored from the mixture of **1** and **2** is obviously ascribed to the formation of cross-[2]catenane **3**.¹²



3: $M_1 = (\text{en})\text{Pd}$; $M_2 = (\text{chxn})\text{Pt}$
3*: $M_1 = (\text{chxn})\text{Pd}$; $M_2 = (\text{chxn})\text{Pt}$
4*: $M_1 = M_2 = (\text{chxn})\text{Pd}$
5: $M_1 = M_2 = (\text{chxn})\text{Pt}$

(chxn = 1,2-cyclohexanediamine; S,S form unless noted)

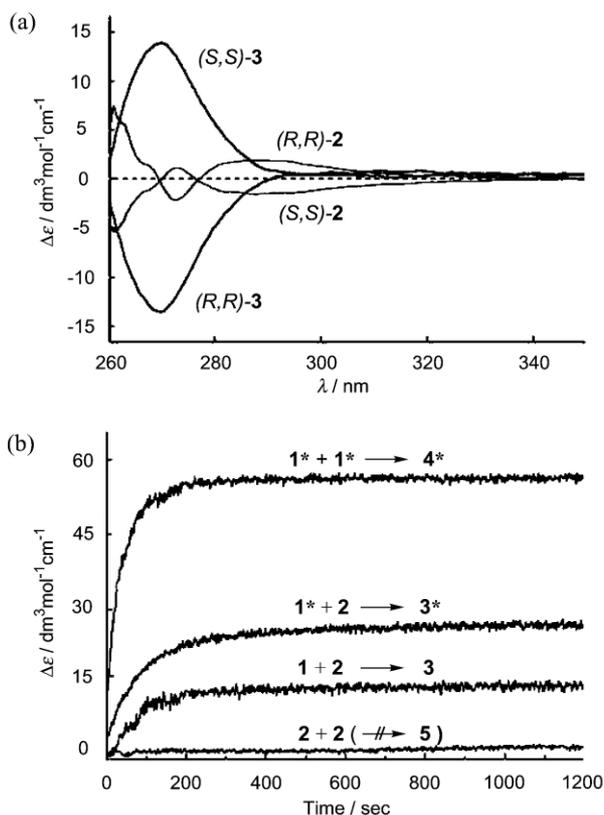
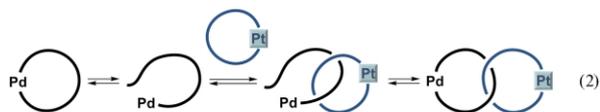


Fig. 2 (a) CD spectra of **2** and **3** in DMF and H₂O–DMF (2:1) solution, respectively; (b) time dependent ICD of the cross-catenation monitored at 270 nm. $\Delta\epsilon$: molar circular dichroism.

The CD experiments also provided a mechanistic insight of the catenation. When chiral Pd ring **1*** was treated under the same conditions, Pd/Pd catenane **4*** was formed at a rate constant of $k \approx 35 \text{ M}^{-1} \text{ s}^{-1}$, which is roughly twice that for the formation of Pd/Pt catenane **3**. This result implies that both homo-[2]catenane **4** and cross-[2]catenane **3** are mainly formed via a dissociation–threading–reconnection pathway (eqn. (2)) rather than a ligand exchange mechanism^{3b} which was previously suggested for the catenation of related Pd(II)-linked rings.



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- Homo-catenane **4**, consisting of two molecules of **1**, has been documented.⁴
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- The CD spectrum of a mixture of Pd(II)-linked ring **1** and Pt(II)-linked ring **2** was measured in H₂O–DMF (2:1) solvent (0.10 mM) at 25 °C.
- The chiral orientation of the catenane was confirmed by X-ray crystallography of a Pd(II) analog.⁴
- The Pt(II)-linked ring has no opportunity to be catenated because of the kinetic inertness of the Pt–N(pyridine) bond around room temperature. However, two Pt(II) rings are quantitatively transformed into Pt(II) catenane **5** by stirring for 1 h in H₂O–DMF (2:1) solvent at 100 °C because the Pt–N(pyridine) bond is kinetically labile around 100 °C. The Pt(II)–catenane **5** shows clear ICD similar to that of Pd(II) containing catenanes.
- The conformation of the Pt(II)-linked ring seems more rigid than that of the Pd(II)-linked ring because of the stronger coordination field of the Pt center. Due to the rigidity of the ring, the intensity of ICD of **3*** is lower than that of **4***.