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Formation of bis- and tris[2]catenanes via the cross-catenation of Pd(II)- and Pt(II)-linked coordination rings

Ken-ichi Yamashita,[a,b] Akiko Hori[a,b,†] and Makoto Fujita[a,b,*]

[a] Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[b] CREST, Japan Science and Technology Agency (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Abstract—We have demonstrated the self-assembly of linear oligo[2]catenanes via selective cross-catenation. A Pd(II)-linked double looped molecule **1** was transformed into the cyclic trimer *c*-(**1**)$_3$ through the catenation. When **1** was treated with a kinetically inert Pt(II)-linked single looped molecule **2a** in aqueous media (1:1.2 DMSO/H_2O) at room temperature, linear oligo[2]catenanes of **2a**–(**1**)$_n$–**2a** (n=1 and 2) were selectively obtained, because the kinetically inert Pt(II)-linked ring **2a** is allowed to thread on only kinetically labile Pd(II)-linked ring of **1**. The distribution of the oligomers depends on the monomer ratio of **1** to **2a**. When the ratio of **1** to **2a** was 1:2, bis[2]catenane **3a** (**2a**–**1**–**2a**) was quantitatively assembled. When the ratio of **1** to **2a** was 1:1, not only **3a** but also tris[2]catenane **4** (**2a**–**1**–**1**–**2a**) was assembled. The ratio of **3a** to **4** was carefully determined to be 1:1 by NMR. The lengths of **3a** and **4** in an extended conformation were estimated by MD/MM2 simulation to be 3.6 and 5.4 nm, respectively.

1. Introduction

Much attention has been paid to non-covalently linked polymers due to their potential unique properties and facile polymerization/degradation processes.[1–5] To connect monomer units non-covalently, both hydrogen[4,6] and coordination[4,7] bonds have been frequently employed. Another type of non-covalent polymers of current interest is interlocked polymers[8] such as polycatenanes[9,10] and polyrotaxanes,[11] which possess mechanically linked structures. Several groups have prepared poly[2]catenanes by the conventional polycondensation of catenated monomer units.[9] However, interlocked polymers, which directly form via catenation have been less explored because of, partly, the lack of quantitative catenation reactions.

Metal-linked coordination rings are often transformed reversibly into [2]catenanes via metal–ligand dissociation.[12] Since the first discovery of the reversible catenation of coordination rings in 1994,[13] we have extended this unique transformation to the construction of a variety of interlocked compounds such as a 3D catenane,[14] a doubly interlocked catenane,[15] a circular dichromism-switchable catenane,[16,17] and a bimetallic cross-catenane.[17,18] An intriguing extension of the reversible catenation, in due course, is the synthesis of interlocked polymers that are formed from preformed coordination rings. Being driven by the organic stack of the ligands, the catenation is quite sensitive to the polarity of solvents. Hence, the polymeric materials obtained by this method should be capable of rapid assembly and degradation depending on the polarity of the media. To develop such polymeric materials, we have previously prepared double looped molecule **1** that undergoes catenation at both loops of **1**.[19] Interestingly, we observed the conversion of **1** into a circular tris[2]catenane *c*-(**1**)$_3$, but could not observe the formation of linear oligomers (Scheme 1a). We have therefore considered that the selective cross-catenation of Pt(II)-linked single loop compound **2a** at both ends of oligomeric (**1**)$_n$ would not allow the formation of *c*-(**1**)$_3$ and alternatively lead to linear oligomers (Scheme 1b). Since kinetically inert Pt(II) ring **2a** is allowed to thread on only kinetically labile Pd(II) rings via the dissociation of Pd(II)–pyridine bonds,[17,18] the ends of (**1**)$_n$ should be always blocked by the Pt(II) rings. Here we demonstrate the simplest cases for this scheme. Namely, the high yield formations of the simplest linear oligomers, bis- and tris[2]catenanes **3a** and **4**, from monomers **1** and **2a** are revealed by NMR and MS analyses. The distribution of the oligomers (**3a** and **4**) depends on the monomer ratio (**1**: **2a**) and the solvent polarity. The full characterization of these linear oligo[2]catenanes provides the first step for the polycatenation

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Keywords: Catenanes; Interlocked polymers; Palladium; Platinum; Self-assembly.

* Corresponding author. Tel.: +81 3 5841 7259; fax: +81 3 5841 7257; e-mail: mfujita@appchem.t.u-tokyo.ac.jp
† Present address: Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Sagamihara, Kanagawa 228-8555, Japan.

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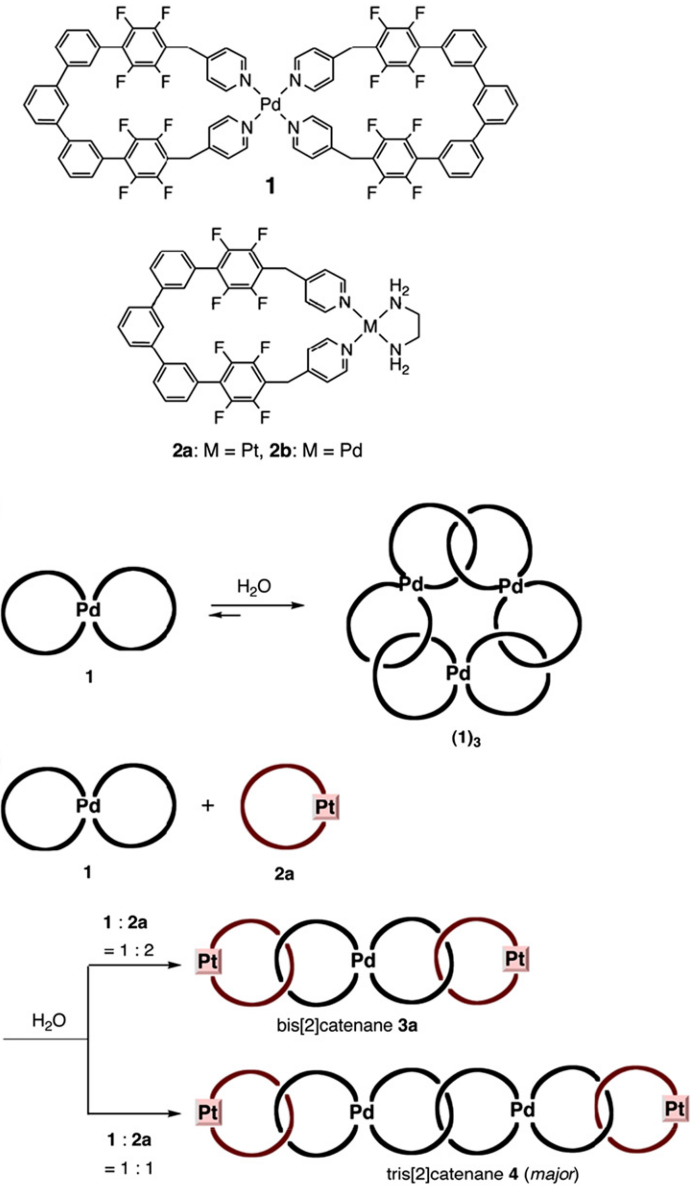


Scheme 1.

of coordination rings into interlocked polymers. We emphasize that our strategy contrasts to previous polycatenane synthesis in which [2]catenane precursors are polymerized by conventional condensation methods.

2. Results and discussion

Components **1** and **2a** (stoichiometry 1:2) were prepared according to the reported procedures.[16–19] When D_2O (1.64 mL) was slowly added into a DMSO-d_6 solution (1.36 mL) of **1** (2.50 mg, 0.0015 mmol) and **2a** (3.30 mg, 0.0030 mmol) at room temperature, these components were quantitatively interlocked to give bis[2]catenane **3a**. This transformation was monitored by NMR and cold spray ionization mass spectrometry (CSI-MS).[20] In NMR observation (Fig. 1a), two components **1** and **2a** disappeared and a new single product appeared, which was reasonably assigned as **3a**. Some of the aromatic protons of **3a** were upfield shifted in good agreement with the interlocked structure (around δ 6.5–8.0). Since bis[2]catenane **3a** consists of two different components, the two loops were inequivalently observed: e.g., PyH_α derived from **1** and **2a** appeared at δ 9.6 and 9.3, respectively. CSI-MS also revealed the formation of **3a** as well as its stability even under MS conditions. Prominent peaks were observed as DMSO adducts. For example, the following peaks were observed for [**3a**$-(NO_3)_n$+(dmso)$_m$]$^{n+}$: *m*/*z* 653.4 [**3a**$-(NO_3^-)_6$+(dmso)$_6$]$^{6+}$, 666.6 [**3a**$-(NO_3^-)_6$+(dmso)$_7$]$^{6+}$, 679.5 [**3a**$-(NO_3^-)_6$+(dmso)$_8$]$^{6+}$, 692.6 [**3a**$-(NO_3^-)_6$+(dmso)$_9$]$^{6+}$, 705.6 [**3a**$-(NO_3^-)_6$+(dmso)$_{10}$]$^{6+}$, 796.4 [**3a**$-(NO_3^-)_5$+(dmso)$_6$]$^{5+}$, 812.0 [**3a**$-(NO_3^-)_5$+(dmso)$_7$]$^{5+}$, 827.8 [**3a**$-(NO_3^-)_5$+(dmso)$_8$]$^{5+}$, 952.4 [**3a**$-(NO_3^-)_4$+(dmso)$_3$]$^{4+}$, 972.2 [**3a**$-(NO_3^-)_4$+(dmso)$_4$]$^{4+}$, 991.5 [**3a**$-(NO_3^-)_4$+(dmso)$_5$]$^{4+}$, 1212.5 [**3a**$-(NO_3^-)_3$]$^{3+}$, 1238.5 [**3a**$-(NO_3^-)_3$+dmso]$^{3+}$, 1264.5 [**3a**$-(NO_3^-)_3$+(dmso)$_2$]$^{3+}$, 1849.5 [**3a**$-(NO_3^-)_2$]$^{2+}$ (Fig. 2a).[21] The fragments, **1**·**2a**, **1**, and **2a**, were also observed in the CSI-MS spectrum.

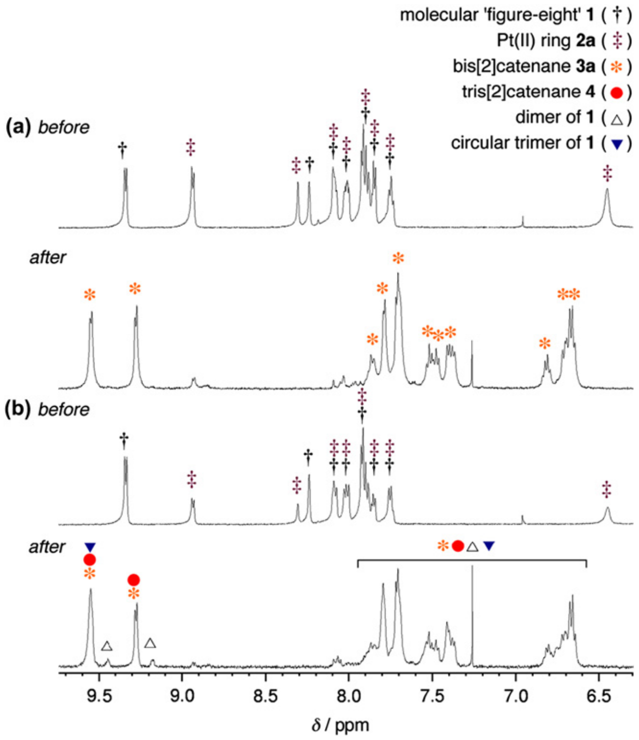
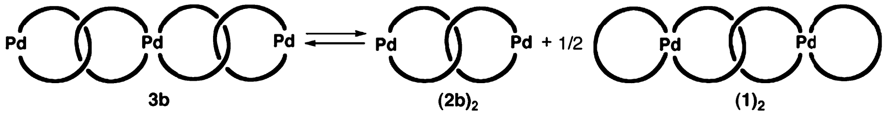


Figure 1. ^{1}H NMR spectra (aromatic region, 500 MHz, 27 °C, 0.5 mM, PyH_α proton of **2a** at δ 8.9 as an internal standard): before (in DMSO-d_6) and after (in 1.2:1 D_2O/DMSO-d_6) catenations of (a) **3a** by treating **1**/**2a**=1:2 and (b) **4** by treating **1**/**2a**=1:1.

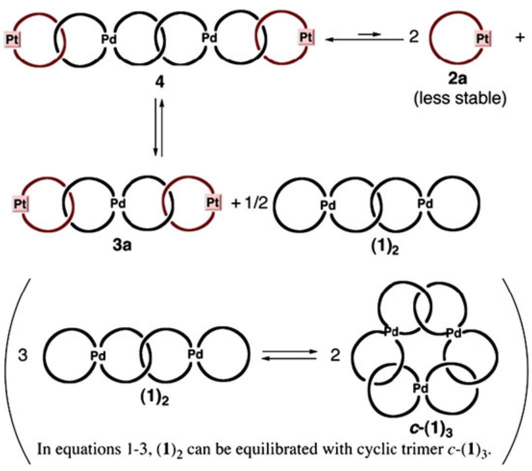
Because of the inert nature of the Pt(II)–pyridine bond, Pt(II)-linked ring can never afford homo-catenanes $(\mathbf{2a})_2$. Homo-dimer $(\mathbf{1})_2$ (or higher oligomers including cyclic homo-trimer c-$(\mathbf{1})_3$) was also not formed because the equilibration in Eq. 1 was pushed toward the left under the conditions. In fact, these homo-catenated products were not detected by either NMR or CSI-MS analysis. As a result, bis[2]catenane **3a** is formed as the sole product. Note that, from kinetically labile Pd(II)-linked rings **2b** and **1**, bis[2]catenane **3b** was not selectively formed because of the equilibration of **3b** with homo-dimers $(\mathbf{2b})_2$ and $(\mathbf{1})_2$ (or c-$(\mathbf{1})_3$) (Eq. 2). Thus, when **1** and **2b** were reacted in a 1:2 ratio under the same conditions (1.2:1 D_2O/DMSO-d_6, rt), homo-catenane $(\mathbf{2b})_2$ was dominantly observed along with a small amount of bis[2]catenane **3b**. The ratio of $(\mathbf{2b})_2$/**3b** was 3.7:1. Under the reaction conditions, homo-oligomers $(\mathbf{1})_n$ (including c-$(\mathbf{1})_3$) were precipitated, pushing the equilibration of Eq. 2 to the right.

(1)

Next, we examined the selective formation of tris[2]-catenane **4** from four components (2×**1**+2×**2a**). As discussed above and in a previous paper,[17,18] the equilibration among the components (Eq. 3) should shift so that kinetically inert Pt(II) ring **2a** is catenated with kinetically labile Pd(II) ring **1**. Therefore, the equilibration in Eq. 3 leads to the selective formation of tris[2]catenane **4**. Thus, upon the slow addition of D_2O (1.64 mL) to a DMSO-d_6 solution (1.36 mL) of **1** (2.50 mg, 0.0015 mmol) and **2a** (1.70 mg, 0.0015 mmol) at room temperature, the formation of **4** was observed. Careful analysis of the NMR spectrum showed that tris[2]catenane **4** was not the sole product but bis[2]catenane **3a** and a small amount of dimer $(\mathbf{1})_2$ were also formed (Fig. 1b). Probably due to entropic disadvantage in the formation of **4**, the equilibration in Eq. 3 was not overwhelmingly pushed to the left. NMR spectra of **3a** and **4** are almost identical except for the integral ratio of the two PyH_α signals, appearing at δ 9.6 and 9.3, which are derived from Pd(II) and Pt(II) rings, respectively. From the integral ratio of these two signals, the ratio **4**/**3a** was estimated to be 1:1. CSI-MS measured in a 1.2:1 H_2O/DMSO solvent clearly showed the formation of **4** as evident from prominent peaks for $[\mathbf{4}-(NO_3)_8+(dmso)_m]^{8+}$ (m=10–12) (Fig. 2b).[21] The CSI-MS spectrum



(2)



In equations 1-3, $(\mathbf{1})_2$ can be equilibrated with cyclic trimer c-$(\mathbf{1})_3$.

(3)

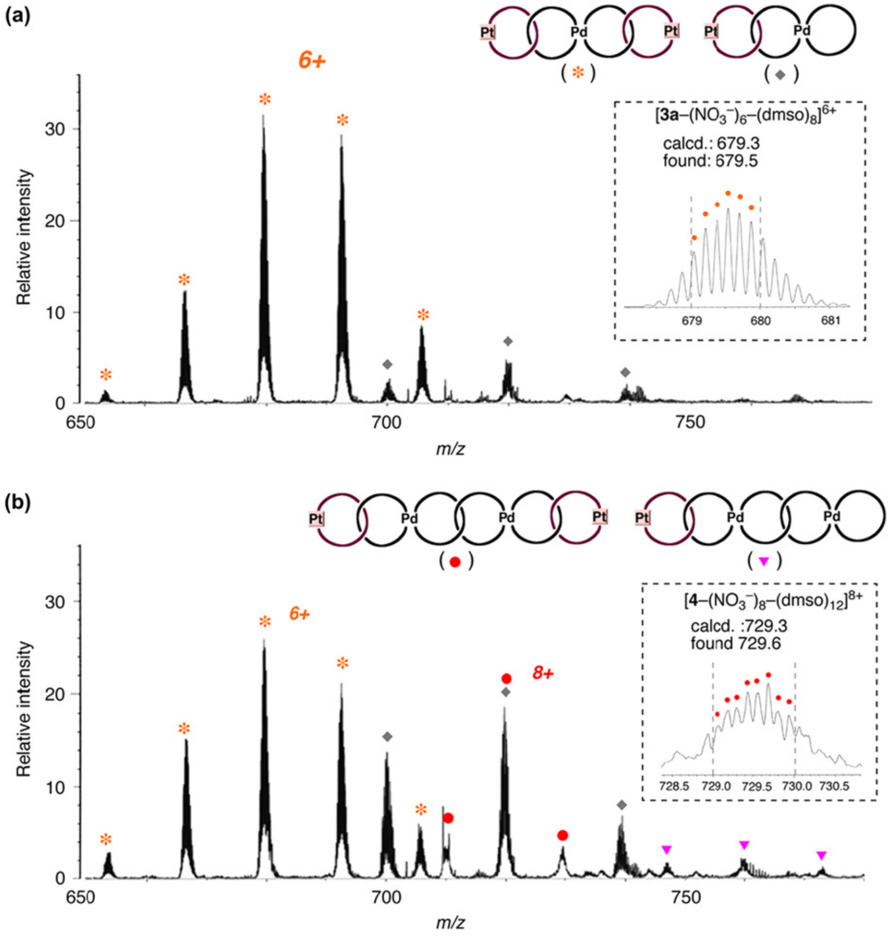
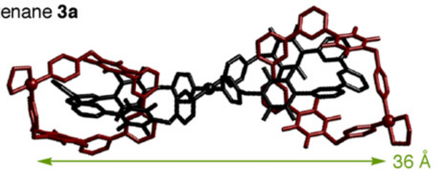


Figure 2. CSI-MS spectra of (a) **3a** and (b) mixture of **3a** and **4** in 1.2:1 H_2O/DMSO solutions ranging from *m/z* 650 to 780. Those measurements were performed under the same conditions.[21]

was quite similar to that of pure **3a**, but new peaks assignable to **4** and its fragments, $(\mathbf{1})_2\cdot\mathbf{2a}$, were also observed (Fig. 2b), for example, *m/z* 729.6 $[\mathbf{4}-(NO_3^-)_8+(dmso)_{12}]^{8+}$. The lengths of **3a** and **4** in an extended conformation were estimated by MD/MM2 to be 3.6 and 5.4 nm, respectively (Fig. 3).[22]

(a) bis[2]catenane **3a**



(b) tris[2]catenane **4**

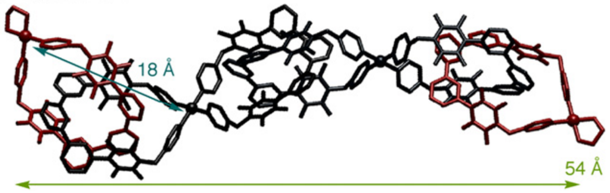


Figure 3. MD/MM2 simulation of structures **3a** and **4**. The black and red rings are **1** and **2a**, respectively. Metal-to-metal distance and ligand orientation were estimated in good accordance of the X-ray crystallographic result of the related single [2]catenane, which was previously reported.[16,17]

3. Conclusions

In conclusion, we have demonstrated the self-assembly of linear oligomeric catenanes via selective cross-catenation. Since these catenanes possess the precise arrangement of Pd(II) and Pt(II) ions, the present results are expected to provide a new method for the integration/segregation of transition metals via the reversible catenation.

4. Experimental section

4.1. General

Complexes **1**, **2a**, and **2b** were prepared according to the previously published procedures.[11–13] All the chemicals were of reagent grades and used without any further purification. All NMR spectral data were recorded on Bruker DRX 500 spectrometer. These data were collected at ambient temperature unless otherwise noted and the chemical shift values reported here are with respect to external TMS standard. CSI-MS data were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with the CSI source.

4.1.1. Preparation of bis[2]catenane 3a. Water (1.64 mL) was slowly added into a DMSO solution (1.36 mL) of **1**

(2.50 mg, 0.0015 mmol) and **2a** (3.30 mg, 0.0030 mM) at room temperature, and bis[2]catenane **3a** was formed quantitatively. ^{1}H NMR (500 MHz, DMSO-d_6/D_2O=1:1.2, TMS): δ=9.54 (d, J=5.5 Hz, 8H), 9.28 (d, J=5.6 Hz, 8H), 7.87 (s, 2H), 7.85 (s, 2H), 7.78 (d, J=5.8 Hz, 8H), 7.72–7.71 (m, 16H), 7.53–7.46 (m, 16H), 7.40 (d, J=6.8 Hz, 4H), 7.37 (d, J=8.0 Hz, 4H), 6.83–6.80 (m, 4H), 6.72–6.65 (m, 16H), 4.18 (s, 8H), 4.13 (s, 8H), 2.97 (s, 8H) ppm. CSI-MS (H_2O/DMSO 1.2:1): m/z=653.4 $[\mathbf{3a}-(NO_3^-)_6+(dmso)_6]^{6+}$, 666.6 $[\mathbf{3a}-(NO_3^-)_6+(dmso)_7]^{6+}$, 679.5 $[\mathbf{3a}-(NO_3^-)_6+(dmso)_8]^{6+}$, 692.6 $[\mathbf{3a}-(NO_3^-)_6+(dmso)_9]^{6+}$, 705.6 $[\mathbf{3a}-(NO_3^-)_6+(dmso)_{10}]^{6+}$, 796.4 $[\mathbf{3a}-(NO_3^-)_5+(dmso)_6]^{5+}$, 812.0 $[\mathbf{3a}-(NO_3^-)_5+(dmso)_7]^{5+}$, 827.8 $[\mathbf{3a}-(NO_3^-)_5+(dmso)_8]^{5+}$, 952.4 $[\mathbf{3a}-(NO_3^-)_4+(dmso)_3]^{4+}$, 972.2 $[\mathbf{3a}-(NO_3^-)_4+(dmso)_4]^{4+}$, 991.5 $[\mathbf{3a}-(NO_3^-)_4+(dmso)_5]^{4+}$, 1212.5 $[\mathbf{3a}-(NO_3^-)_3]^{3+}$, 1238.5 $[\mathbf{3a}-(NO_3^-)_3+dmso]^{3+}$, 1264.5 $[\mathbf{3a}-(NO_3^-)_3+(dmso)_2]^{3+}$, 1849.5 $[\mathbf{3a}-(NO_3^-)_2]^{2+}$.

4.1.2. Preparation of tris[2]catenane 4. Water (1.64 mL) was slowly added into a DMSO solution (1.36 mL) of **1** (2.50 mg, 0.0015 mmol) and **2a** (1.70 mg, 0.0015 mM) at room temperature, and tris[2]catenane **4** was formed along with bis[2]catenane **3a** (**3a**/**4**=1:1). CSI-MS (H_2O/DMSO 1.2:1): m/z=709.9 $[\mathbf{4}-(NO_3^-)_8+(dmso)_{10}]^{8+}$, 729.6 $[\mathbf{4}-(NO_3^-)_8+(dmso)_{12}]^{8+}$, 1079.0 $[\mathbf{4}-(NO_3^-)_5+(dmso)_3]^{5+}$, 1094.5 $[\mathbf{4}-(NO_3^-)_5+(dmso)_4]^{5+}$, 1761.8 $[\mathbf{4}-(NO_3^-)_3]^{3+}$.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.101.

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22. Molecular dynamics calculation and energy minimization were conducted using standard methods implemented in the Cerius^2 3.0 package on a Silicon Graphics Octane Machine.