J|A|C|S
COMMUNICATIONS

Assembly Modulation by Adjusting Countercharges of Heterobimetallic Supramolecular Polymers Composed of Tris(spiroborate) Twin Bowls

Hiroshi Danjo,*,[†] Kadzuya Hirata,[†] Masanori Noda,[‡] Susumu Uchiyama,[‡] Kiichi Fukui,[‡]
Masatoshi Kawahata,[§] Isao Azumaya,[§] Kentaro Yamaguchi,[§] and Toshifumi Miyazawa[†]

Department of Chemistry, Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada-ku, Kobe 658-8501, Japan, Department of Biotechnology, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan, and Kagawa School of Pharmaceutical Sciences, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan

Received September 26, 2010; E-mail: danjo@konan-u.ac.jp

Abstract: Heterobimetallic supramolecular polymers were prepared by treatment of the supramolecular polymers composed of tris(spiroborate) type molecular connecting modules with a potassium cation. On the other hand, the addition of a barium cation led to dissociation of the supramolecular polymer chain. Modulation of polymer formation was realized by the use of small metal cations as a control factor.

The development of metallosupramolecular polymers is recognized as one of the most important approaches for the creation of functionalized nanomaterials because these polymers show potential for charge or electron transfer and other optoelectronic characteristics.[1] Coordination polymers are representatives of this class of compounds.[2] Bifunctional bisterpyridine ligands are employed as coordination sites to transition metal cations, such as iron(II), cobalt(II), nickel(II), copper(II), zinc(II), ruthenium(II), and iridium(III), to construct the metallosupramolecular polymers.[3] Here, the metal centers play key roles in both polymerization and generation of physical properties mainly derived from the metal-to-ligand charge transfer (MLCT) and redox behavior. On the other hand, minimal attention has been paid to the development of metallosupramolecular polymers formed by host−guest interaction.[4] In those polymers, the chemical modification of ligand moieties can be avoided, thus allowing us to employ a wide range of functional metal complexes as monomers.

In our previous report, we demonstrated that back to back twin-bowl-shaped D_3-symmetric tris(spiroborate) cyclophanes $\mathbf{1}^{3-}$ act as molecular connecting modules to form a one-dimensional array of cationic guest molecules owing to electrostatic and CH−π interactions.[5] In this case, we chose $[\mathrm{Ir(tpy)_2}]^{3+}$ (tpy = 2,2′:6′,2″-terpyridine) as a guest because the trianionic twin bowl requires a tricationic guest to balance the total charge of the chain structure. As the next stage of this work, we have moved on to the preparation of heteromultimetallic supramolecular polymers that contain two or more kinds of metals in a single polymer chain, since the introduction of various metals to supramolecular polymers would be advantageous for the creation of new functional materials.[6] Twin bowls $\mathbf{1}^{3-}$ have two kinds of molecular recognition sites: two bowl-shaped cavities and a crown-ether-like cavity that would be able to bind a suitable guest individually. The utilization of these two different recognition modes makes it possible to construct a supramolecular polymer that is composed of three components: the twin bowl, a cationic guest complex (for the bowl-shaped cavities), and a metal cation (for the crown-ether-like cavity) (Figure 1). In this case, the sum of charges of the supramolecular polymer is expected to strongly affect the degree of polymerization, and this allows us to regulate the metallosupramolecular polymer formation by the use of a metal cation as a control factor. Herein we demonstrate the construction of heterobimetallic supramolecular polymers by using tris(spiroborate) cyclophanes as the molecular connecting module in both solution and crystal phases and describe the modulation of their degree of polymerization by adjusting countercharges.

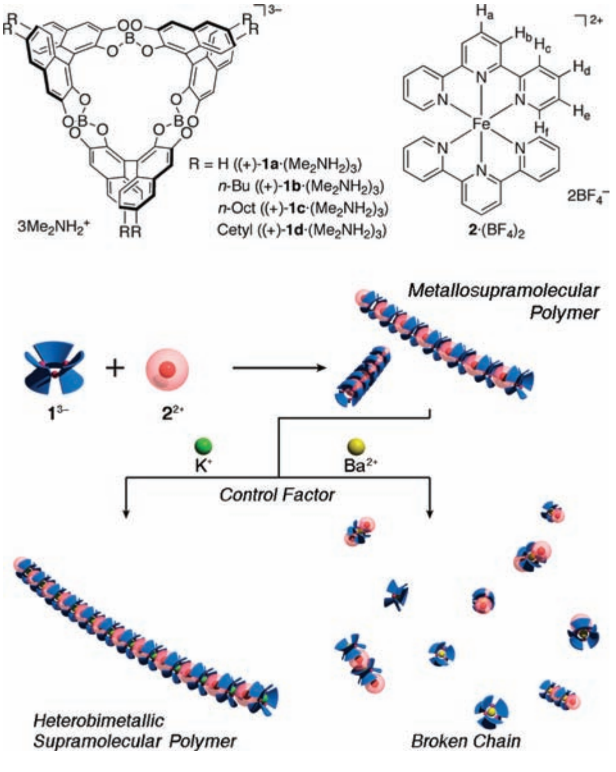

Figure 1. Chemical structures of twin bowls $\mathbf{1}\cdot(\mathrm{Me_2NH_2})_3$ and $\mathbf{2}\cdot(\mathrm{BF_4})_2$ (top), and a schematic representation of the formation or dissociation of the supramolecular polymer chain by the addition of K^+ or Ba^{2+} as a control factor (bottom).

The guest inclusion behavior of the crown-ether-like cavity of $\mathbf{1}^{3-}$ was observed in the crystal state (see the Supporting Information, Figure S1).[7] Treatment of *rac*-$\mathbf{1a}\cdot(\mathrm{Me_2NH_2})_3$ with potassium or barium trifluoromethanesulfonate (KOTf or $\mathrm{Ba(OTf)_2}$) in DMF and subsequent vapor diffusion crystallization

---

[†] Konan University.
[‡] Osaka University.
[§] Tokushima Bunri University.

10.1021/ja1084964

with diethyl ether gave colorless prismatic crystals. In the crystals, potassium and barium cations were incorporated at the center of the crown-ether-like cavity of $\mathbf{1a}^{3-}$ to form complexes $[\mathbf{1a}\cdot\mathrm{K}\cdot(\mathrm{dmf})_2]^{2-}$ and $[\mathbf{1a}\cdot\mathrm{Ba}\cdot(\mathrm{dmf})_4]^{-}$, respectively. Here, the total charge of the molecular connecting module was controlled by choosing the valence of the metal cation added: the addition of the potassium(+) cation gave a total charge of 2− and the addition of the barium(2+) cation gave 1−. These countercharges are expected to strongly affect the polymerization behavior of the molecular connecting module with the cationic guest complexes.

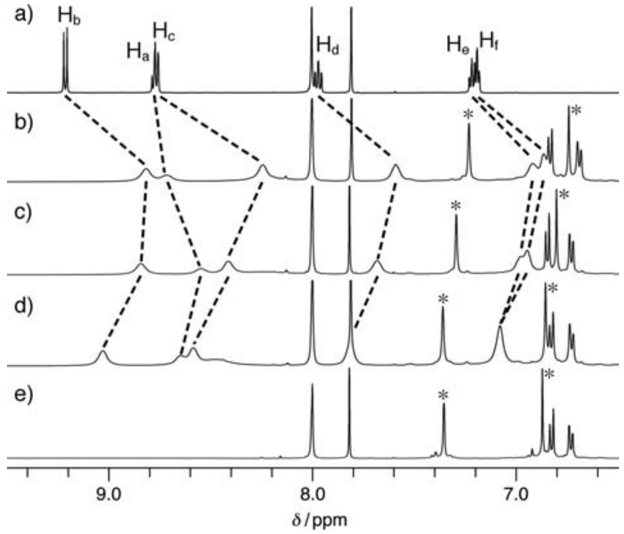

Figure 2. ^{1}H NMR spectra (500 MHz, 25 °C, in DMF-d_7/CDCl$_3$ (1:2), 4.2 mM for each component) of (a) $\mathbf{2}\cdot(\mathrm{BF}_4)_2$; (b) $\mathbf{2}\cdot(\mathrm{BF}_4)_2$ and (+)-$\mathbf{1c}\cdot(\mathrm{Me_2NH_2})_3$; (c) $\mathbf{2}\cdot(\mathrm{BF}_4)_2$, (+)-$\mathbf{1c}\cdot(\mathrm{Me_2NH_2})_3$, and KOTf; (d) $\mathbf{2}\cdot(\mathrm{BF}_4)_2$, (+)-$\mathbf{1c}\cdot(\mathrm{Me_2NH_2})_3$, and Ba(OTf)$_2$; and (e) (+)-$\mathbf{1c}\cdot(\mathrm{Me_2NH_2})_3$.

Then, the formation of the metallosupramolecular polymers was examined by mixing twin bowl (+)-$\mathbf{1c}\cdot(\mathrm{Me_2NH_2})_3$ with $[\mathrm{Fe(tpy)_2}](\mathrm{BF_4})_2$ ($\mathbf{2}\cdot(\mathrm{BF}_4)_2$) in the absence or presence of potassium or barium trifluoromethanesulfonate in DMF-d_7/CDCl$_3$ (1:2). According to ^{1}H NMR measurement, almost all the signals assigned to tpy were shifted upfield in each case, indicating that $\mathbf{2}^{2+}$ was recognized by the bowl-shaped cavities of $\mathbf{1c}^{3-}$ to form the supramolecular chain structure (Figure 2). A difference was noted in the behavior of the signal assigned to H_a (assignment shown in Figure 1) before and after the addition of potassium salt. In the absence of the potassium cation, only a small shift of the H_a signal was observed because this proton was located inside the crown-ether-like cavity where the anisotropic effect of the naphthalene rings was small. In the presence of the potassium cation, the crown-ether-like cavity was occupied and the H_a proton on tpy would be kicked outside of the cavity to result in the upfield shift of the ^{1}H NMR signal. The upfield shift of tpy protons was diminished when barium trifluoromethanesulfonate was added. In this case, each repeating unit has a charge of 1+, and this positive charge is accumulated in the long chain structure to result in the weakened association between the twin bowl and the spherical guest. Moreover, the coordination of DMF-d_7 molecules to the barium center would prevent the host−guest interaction of these monomer units. The association/dissociation behavior of these polymers could also be monitored by the shift of the ^{1}H signals assigned to the 4- and 5-position of the naphthalene ring of $\mathbf{1c}^{3-}$ (marked by an asterisk). Their upfield shift found in Figure 2b, caused by the anistropic effect of tpy, was decreased by the addition of metal cations (in Figure 2c and d), due to the avoidance of a deep association between $\mathbf{1c}^{3-}$ and $\mathbf{2}^{2+}$. The larger decrease of the upfield shift seen in Figure 2d indicated that addition of the barium cation led to the dissociation of the polymer chain.

The sizes of the supramolecular polymers consisting of $\mathbf{1}^{3-}$ and $\mathbf{2}^{2+}$ were compared by means of 2D-DOSY NMR measurement in CDCl$_3$ using the BPPSTE pulse sequence (see the Supporting Information, Figure S2).[8] As the molecular connecting module, (+)-$\mathbf{1d}\cdot(\mathrm{Me_2NH_2})_3$ bearing six cetyl groups at the 6-position of each naphthalene ring was employed because the metallosupramolecular polymers formed by $\mathbf{1d}^{3-}$ exhibit high solubility in CDCl$_3$, in which the polymerization would be advantageous rather than in DMF-d_7 owing to the solvophobic effect on the cationic guest. Thus, the diffusion coefficient (D) of $\mathbf{1d}^{3-}$ in (+)-$\mathbf{1d}\cdot(\mathrm{Me_2NH_2})_3$ was determined to be 1.8×10^{-10} m^2 s^{-1} (the corresponding hydrodynamic radius is ca. 2 nm). The D value of $\mathbf{1d}^{3-}$ was decreased to 0.90×10^{-10} m^2 s^{-1} when the measurement was carried out with $\mathbf{1d}\cdot\mathbf{2}\cdot\mathrm{Me_2NH_2}$, which was obtained by reprecipitation of the mixture of (+)-$\mathbf{1d}\cdot(\mathrm{Me_2NH_2})_3$ and $\mathbf{2}\cdot(\mathrm{BF}_4)_2$ with an excess amount of ethanol. This indicates the formation of a supramolecular polymer structure. It is worthy to note that a smaller D value (0.35×10^{-10} m^2 s^{-1}) was observed with K$^+$-containing metallosupramolecular polymer $[\mathbf{1d}\cdot\mathrm{K}]\cdot\mathbf{2}$, which was obtained from the mixture of (+)-$\mathbf{1d}\cdot(\mathrm{Me_2NH_2})_3$, $\mathbf{2}\cdot(\mathrm{BF}_4)_2$, and KOTf. This implies that the presence of the potassium cation harmonized the charge in the metallosupramolecular polymer to result in polymer elongation. The removal of a dimethylammonium cation would also be advantageous for the growth of the polymer chain. On the other hand, a larger D value (1.5×10^{-10} m^2 s^{-1}) was observed with the product obtained from the mixture of (+)-$\mathbf{1d}\cdot(\mathrm{Me_2NH_2})_3$, $\mathbf{2}\cdot(\mathrm{BF}_4)_2$, and Ba(OTf)$_2$, which was purified according to the same reprecipitation protocol as above.[9] In this case, $[\mathrm{Fe(tpy)_2}]^{2+}$ was partly dissolved into the ethanol layer during the reprecipitation, probably due to destabilization of the polymer structure. DLS measurement in chloroform also indicated that the average particle size of $\mathbf{1d}\cdot\mathbf{2}\cdot\mathrm{Me_2NH_2}$ was smaller than that of the potassium-containing supramolecular polymer and larger than that of the barium-containing one (see the Supporting Information, Figure S3).

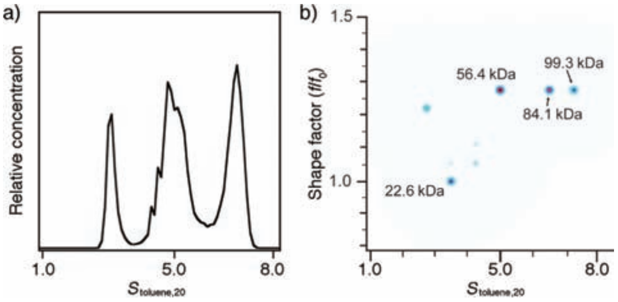

Figure 3. AUC-SV results of $[\mathbf{1d}\cdot\mathrm{K}]\cdot\mathbf{2}$. (a) s-value distribution obtained from $C(s)$ analysis. (b) s-value and shape factor distribution obtained from 2DSA-MC (molecular weight of major discrete species were indicated in the figure).

The polymerization state of $[\mathbf{1d}\cdot\mathrm{K}]\cdot\mathbf{2}$ in solution was examined by analytical ultracentrifugation sedimentation velocity (AUC-SV).[10] Parameters required for data analysis, such as a partial specific volume of the compound, were experimentally determined in this study. As shown in Figure 3, sedimentation coefficient distribution ($C(s)$) analysis apparently showed the formation of polymerized $[\mathbf{1d}\cdot\mathrm{K}]\cdot\mathbf{2}$ with sedimentation coefficient (s-values) 3.1, 4.8, and 6.9 S. The shape factor (f/f_0) obtained from $C(s)$ analysis was 1.26. Consistently, the two-dimensional spectrum analysis with Monte Carlo simulation (2DSA-MC) provided four discrete species, 3.5, 5.0, 6.5, and 7.3 S with their f/f_0 of 1.00, 1.28, 1.28, and 1.28, respectively. Thus, the molecular weight (M_w) estimates using the *s*-values and the corresponding f/f_0 were 22600, 56400, 84100, and 99300, showing the formation of the 8-mer, 20-mer, 29-mer, and 34-mer of [**1d**·K]·**2**. Considering the error of M_w from AUC-SV, these AUC-SV results indicate that [**1d**·K]·**2** forms the 8- to 10-mer supramolecular polymer and this basic polymer further constitutes larger supramolecular polymers in solution.

To determine the precise structure of the heterobimetallic supramolecular polymer, X-ray diffraction analysis of *rac*-[**1b**·K]·**2** was carried out (Figure 4).[7] In its crystal structure, potassium and iron were iteratively positioned to form a heterobimetallic 1D array through nonbonding interaction. The average distance between potassium and iron was estimated to be 7.5 Å, and the length of one repeating unit was determined to be 14.9 Å. When compared with the length of 14.0 Å previously found in the crystal structure of *rac*-**1b**·[Ir(tpy)$_2$], only a small difference was noted between them in spite of the steric hindrance of the potassium cation in [**1b**·K]·**2**. This indicates that charge control upon supramolecular polymerization is effectively achieved by the addition of the potassium cation.

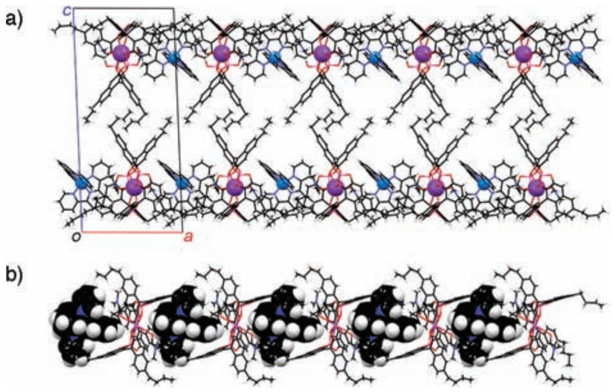

Figure 4. Crystal structure of *rac*-[**1b**·K]·**2**: (a) a view of the crystal packing from *b* axis; (b) the side view of the single polymer chain (almost from *c* axis). K$^+$ and Fe^{2+} ions are shown as purple and sky blue spheres, respectively. Free solvent molecules are omitted for clarity.

In conclusion, heterobimetallic supramolecular polymers were prepared by utilization of the dual molecular recognition modes of tris(spiroborate) molecular connecting module **1**$^{3-}$. From NMR measurements, it was found that the polymerization with **1**$^{3-}$ and **2**$^{2+}$ was enhanced by the addition of a potassium cation, whereas the presence of a barium cation disturbed the association of the monomers. AUC-SV showed that heterobimetallic supramolecular polymers with polymerization units up to 34-mer are formed in solution. X-ray crystallographic analysis revealed the molecular structure of the heterobimetallic supramolecular polymer, in which two kinds of metal centers line up to form an iterative metal array. Studies of the introduction of various metal guests into the metallosupramolecular polymers for the rational design of their physical properties are in progress.

Acknowledgment. We gratefully acknowledge the financial support of Konica Minolta Technology Center Inc. We thank Drs. S. Baba and K. Miura (the Japan Synchrotron Radiation Research Institute (JASRI)) for their valuable help in data collection of X-ray analysis of *rac*-[**1b**·K]·**2**. The synchrotron radiation experiment was performed at the BL38B1 in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2009B1225). We also thank Prof. Dr. Y. Makino and Dr. T. Kurita (Tokushima Bunri University) for their technical guidance in DLS measurement and Prof. Dr. Y. Kobayashi (Osaka University of Pharmaceutical Sciences) and Mr. T. Maruno (Osaka University) for their kind help in density measurement.

Supporting Information Available: Detailed experimental procedures for synthesis and characterization of all new compounds, DOSY and AUC-SV data, and X-ray diffraction data in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Rehahn, M. *Acta Polym.* **1998**, *49*, 201–224. (b) *Supramolecular Polymers*, 2nd ed.; Ciferri, A., Ed.; Taylor & Francis: New York, 2005. (c) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097. (d) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892–2926. (e) Whittell, R.; Manners, I. *Adv. Mater.* **2007**, *19*, 3439–3468. (f) Ariga, K.; Hill, J. P.; Lee, M. V.; Vinu, A.; Charvet, R.; Acharya, S. *Sci. Technol. Adv. Mater.* **2008**, *9*, 014109 (96 pp).

(2) (a) Hofmeier, H.; Schmatloch, S.; Wouters, D.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 2197–2203. (b) Fujigaya, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 14690–14691. (c) Beck, J. B.; Ineman, J. M.; Rowan, S. J. *Macromolecules* **2005**, *38*, 5060–5068. (d) Kurth, D. G.; Higuchi, M. *Soft Matter* **2006**, *2*, 915–927. (e) Fustin, C. A.; Guillet, P.; Schubert, U. S.; Gohy, J. F. *Adv. Mater.* **2007**, *19*, 1665–1673. (f) Chow, C.-F.; Fujii, S.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 5007–5010. (g) Burnworth, M.; Mendez, J. D.; Schroeter, M.; Rowan, S. J.; Weder, C. *Macromolecules* **2008**, *41*, 2157–2163. (h) Matsukizono, H.; Kuroiwa, K.; Kimizuka, N. *J. Am. Chem. Soc.* **2008**, *130*, 5622–5623.

(3) (a) Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1992**, 3467–3475. (b) Dobrawa, R.; Würthner, F. *Chem. Commun.* **2002**, 1878–1879. (c) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1413–1427. (d) Schmatloch, S.; van den Berg, A. M. J.; Alexeev, A. S.; Hofmeier, H.; Schubert, U. S. *Macromolecules* **2003**, *36*, 9943–9949. (e) Hofmeier, H.; Hoogenboom, R.; Wouters, M. E. L.; Schubert, U. S. *J. Am. Chem. Soc.* **2005**, *127*, 2913–2921. (f) Dobrawa, R.; Würthner, F. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4981–4995. (g) Higuchi, M.; Kurth, D. G. *Chem. Rec.* **2007**, *7*, 203–209. (h) Chiper, M.; Meier, M. A. R.; Wouters, D.; Hoeppener, S.; Fustin, C.-A.; Gohy, J.-F.; Schubert, U. S. *Macromolecules* **2008**, *41*, 2771–2777. (i) Chiper, M.; Hoogenboom, R.; Schubert, U. S. *Macromol. Rapid Commun.* **2009**, *30*, 565–578.

(4) Kishimura, A.; Yamashita, T.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 179–183.

(5) Danjo, H.; Hirata, K.; Yoshigai, S.; Azumaya, I.; Yamaguchi, K. *J. Am. Chem. Soc.* **2009**, *131*, 1638–1639.

(6) (a) Higuchi, M.; Kurth, D. G. *Chem. Rec.* **2007**, *7*, 203–209. (b) Gasnier, A.; Royal, G.; Terech, P. *Langmuir* **2009**, *25*, 8751–8762. (c) Kumpfer, J. R.; Jin, J.; Rowan, S. J. *J. Mater. Chem.* **2010**, *20*, 145–151.

(7) CCDC 787174 (*rac*-[**1a**·K·(dmf)$_2$]·(Me$_2$NH$_2$)$_2$), 787175 (*rac*-[**1a**·Ba·(dmf)$_4$]·Me$_2$NH$_2$), and 787176 (*rac*-[**1b**·K]·**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.au.uk/data_request/cif.

(8) (a) Gibbs, S. J.; Johnson, C. S. *J. Magn. Reson.* **1991**, *93*, 395–402. (b) Jerschow, A.; Müller, N. *J. Magn. Reson.* **1997**, *125*, 372–375.

(9) Formula of the product was roughly determined to be [**1d**·Ba]$_2$·**2** by ^{1}H NMR.

(10) (a) Schuck, P. *Biophys. J.* **2000**, *78*, 1606–1619. (b) Tomiyama, T.; Uchiyama, S.; Shinohara, H. *Chem. Phys. Lett.* **1997**, *264*, 143–148.

JA1084964