Canadian Journal of Chemistry
Revue canadienne de chimie

**Structures and Properties of Saturn-Like Complexes
Composed of Oligothiophene Macrocycle with
Methano[60]fullerene and [70]Fullerene**

Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2016-0461.R1
Manuscript Type:	Article
Date Submitted by the Author:	01-Oct-2016
Complete List of Authors:	Iyoda, Masahiko; Tokyo Metropolitan University, Department of Chemistry Shimizu, Hideyuki; Tokyo Metropolitan University Aoyagi, Shinobu; Nagoya Shiritsu Daigaku Okada, Hiroshi; The University of Tokyo Zhou, Biao; Nihon University Matsuo, Yutaka; The University of Tokyo
Keyword:	oligothienylene macrocycles, methanofullerene, [70]fullerene, Saturn-like complexes, crystal structure determination

SCHOLARONE™
Manuscripts

Structures and Properties of Saturn-Like Complexes Composed of Oligothiophene Macrocycle with Methano[60]fullerene and [70]Fullerene

Masahiko Iyoda,*¹ Hideyuki Shimizu,¹ Shinobu Aoyagi,*² Hiroshi Okada,³ Biao Zhou,⁴ and Yutaka Matsuo*^{3,5}

¹ Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

² Department of Information and Basic Science, Nagoya City University, Nagoya 467-8501, Japan

³ Department of Mechanical Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

⁴ Department of Chemistry, College of Humanities and Sciences, Nihon University, Sakurajosui 3-25-40, Setagaya-ku, Tokyo 156-8550, Japan

⁵ Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China

Corresponding authors:

Masahiko Iyoda, e-mail: iyoda@tmu.ac.jp, tel: +81-42-677-2731, fax: +81-42-677-2525

Shinobu Aoyagi, e-mail: aoyagi@nsc.nagoya-cu.ac.jp, tel: +81-52-872-5061, fax: +81-52-872-3495

Yutaka Matsuo, e-mail: matsuo@photon.t.u-tokyo.ac.jp, tel: +81-3-5841-0978

Abstract

π -Expanded oligothiénylene macrocycle with a large inner cavity incorporates fullerenes such as methano[60]fullerene ($C_{61}H_2$) and [70]fullerene (C_{70}) inside to form Saturn-like complexes. Although the oligothiophene macrocycle weakly interacts with fullerenes in solution, it forms stable Saturn-like fullerene complexes in the solid state. X-ray analysis of the Saturn-like complexes exhibited short contacts between the sulfur atoms of the oligothiophene macrocycle and fullerene-carbons, which hinder the rotation of fullerenes. As a result, the non-covalent interaction between the oligothiophene macrocycle and fullerenes was employed in crystal structure determination of fullerenes. UV-vis-NIR spectra of the Saturn-like complexes showed weak donor-acceptor interaction between the oligothiophene macrocycle and fullerenes.

Key words: oligothiénylene macrocycles, methanofullerene, [70]fullerene, Saturn-like complexes, crystal structure determination.

Introduction

Cycloparaphenylenes, cyclo-2,5-thienylenes, and their π -expanded congeners attracted much attention because of the highly symmetric structures and unique electronic properties that arise from their round, infinite π -conjugation modes.¹⁻⁴ These oligophenylene and oligothiophene macrocycles have moderate to large inner cavities and sometimes incorporate small to large molecules to form supramolecular complexes. Among these macrocyclic hosts, oligothiophene macrocycles are a promising candidate as supramolecular hosts which can incorporate alkanes and fullerenes in their cavities.^{5,6} Furthermore, development of new versatile host molecules such as π -expanded oligothiophene macrocycles broadens opportunity for highly attractive structural, optical, and electronic properties of fullerene complexes.⁷

X-ray crystallographic analysis of fullerenes such as fulleroids, metallofullerenes, and higher fullerenes is still one of the powerful characterization tools to obtain precise structural information and properties. Recently, Saturn-like complexes **1** of oligothiophene macrocycles **2** and **3** with [60]fullerene (C_{60}) have been reported (Fig. 1),⁶ and the donor-acceptor properties in the Saturn-like complex **2**⊃ C_{60} have been explored. Interestingly, oligothiophene macrocycle **2** weakly interacts with C_{60} in solution ($K_a = 248 \pm 19 \text{ M}^{-1}$ in toluene- d_8 at 273 K, $\Delta H = -22.8 \text{ kJ mol}^{-1} \text{ K}^{-1}$; $\Delta S = -38.8 \text{ J mol}^{-1} \text{ K}^{-1}$), while **2** forms a stable C_{60} -complex **2**⊃ C_{60} in the solid state. X-ray analysis revealed that the short interatomic S⋯S distances (13.607 and 13.661 Å) in the nearly planar oligothiophene ring are ca. 1% shorter than the sum (13.72 Å) of the van der Waals radii of the sulfur atoms (3.70 Å) and C_{60} (10.02

Å). Consequently, the short contacts between the sulfur atoms of **2** and C_{60} -carbons stop the rotation of C_{60} . Although the known supramolecular C_{60} -complexes are usually stabilized by metal- π coordination or convex-concave π - π interactions, $2 \supset C_{60}$ is stabilized mainly by the van der Waals interaction between the sulfur atoms of the thiophene rings and C_{60} . The non-covalent interaction between **2** and fullerenes can be employed in crystal structure determination of fullerenes without modifying the fullerene skeletons.

Fig. 1. Saturn-like complex **1** and oligothiophene macrocycles **2** and **3**.

1,2-Dihydromethano[60]fullerene ($C_{61}H_2$)^{8,9} and its congeners¹⁰ have been synthesized since 1993, and X-ray analysis revealed the structural properties of methano[60]fullerene derivatives. There are two isomers of $C_{61}H_2$: the 6,5-annulene and the 6,6-cyclopropane isomers, which have been uniquely isolated and characterized. However, the detailed crystal structure of $C_{61}H_2$ was not determined until now, even though this molecule is the simplest methano[60]fullerene. This is owing to rotation mode of $C_{61}H_2$ in the solid state, as known to "plastic crystal" nature, characterized with orientational disorder and well-ordered centers of mass, like C_{60} and $C_{60}O$.¹¹ Because of this behavior, only a few studies by powder X-ray diffraction and computational calculation had been performed to understand

its structure and phase transition.¹² Hence, the X-ray crystallographic analysis with employment of macrocycles host to stop rotation provides important experimental information for the structure of the pristine $C_{61}H_2$. We report herein the successful X-ray analysis of a Saturn-like complex $2 \supset C_{61}H_2$, in which the structure of $C_{61}H_2$ has been crystallographically determined. Furthermore, we elucidated the formation, properties, and crystal structure of a new Saturn-like complex $2 \supset C_{70}$ (Fig. 2).

Fig. 2. Saturn-like complexes $2 \supset C_{61}H_2$ and $2 \supset C_{70}$.

Results and discussion

Formation of Saturn-like complexes $2 \supset C_{61}H_2$ and $2 \supset C_{70}$

Macrocycles with precise shapes and inner cavities form various kinds of C_{60} -containing complexes.^{13–22} Among them, oligothiophene macrocycle **2** is one of the best host molecules to form supramolecular fullerene-complexes. Under room light, **2** exists as an equilibrium mixture of *E,E*- and *Z,Z*-isomers in solution, and only *E,E*-isomer **2** incorporates C_{60} to form a Saturn-like complex $2 \supset C_{60}$ in a pure form (Fig. 3). In solution, **2** exhibited a similar binding behavior with methano[60]fullerene $C_{61}H_2$, affording an inclusion complex with methano[60]fullerene $C_{61}H_2$ (Fig. 3). The 6,6-isomer of $C_{61}H_2$ synthesized with a high yield method⁹ was used in this study. Small but good quality of single

crystals of $2\supset C_{61}H_2$ was obtained by crystallization from cold toluene. The crystal structure of $2\supset C_{61}H_2$ at 100 K was determined by an X-ray diffraction measurement at the large synchrotron radiation facility, SPring-8.

Fig. 3. Formation of the Saturn-like complexes $2\supset C_{60}$, $2\supset C_{61}H_2$ and $2\supset C_{70}$.

Oligothiophene macrocycle **2** interacts with [70]fullerene in solution and the solid state to form $2\supset C_{70}$ (Fig. 3). The binding constant (K_a) was determined by monitoring the 1H NMR signal of the olefin protons in toluene- d_8 . The Job plot indicated the formation of a 1:1 complex, and K_a with C_{70} in toluene- d_8 was determined to be $425 \pm 12 M^{-1}$ at 273 K ($\Delta H = -29.5 kJ mol^{-1} K^{-1}$; $\Delta S = -58.2 J mol^{-1} K^{-1}$). The larger binding constant of **2** with C_{70} as compared to **2** with C_{60} ($K_a = 248 \pm 19 M^{-1}$ at 273 K) reflects the larger molecular size of C_{70} as compared to C_{60} . The smaller ΔH and ΔS values of **2** with C_{70} as compared to **2** with C_{60} are also attributable to the larger molecular size of C_{70} . Single crystals of $2\supset C_{70}$ were obtained by crystallization from benzene. The crystal structure of $2\supset C_{70}$ at 173 K was determined by an X-ray diffraction measurement using Mo $K\alpha$ radiation. A cast film of $2\supset C_{70}$

exhibited a broad charge-transfer absorption in the range of 600-800 nm (Fig. S4). However, this charge-transfer absorption is slightly weaker than that of $2\supset C_{60}$, presumably due to slightly charge-transfer weaker interaction between **2** and C_{70} as compared to that of $2\supset C_{60}$.

Structure of $2\supset C_{61}H_2$

The crystal structure of $2\supset C_{61}H_2$ crystallized with toluene solvent molecules contains two crystallographically independent $2\supset C_{61}H_2$ complex molecules. The two independent $C_{61}H_2$ molecules (**A** and **B**) on the crystal mirror plane show an orientation disorder, while C_{60} molecules in a $2\supset C_{60}$ crystal on the crystal glide plane show no orientation disorder.⁶ The addition of a methylene group induces the orientation disorder of $C_{61}H_2$ molecules in the $2\supset C_{61}H_2$ crystal. C_{60} cages of both of the two independent $C_{61}H_2$ molecules (**A** and **B**) have two orientations with the fractions of 0.5 in the crystal structure. The methylene group of the molecule **A** occupies four positions around the C_{60} cage with the fractions of 0.33, 0.27, 0.20, and 0.20. The methylene group of the molecule **B** occupies four positions around the C_{60} cage with the fractions of 0.25.

The orientation disorder of $C_{61}H_2$ in the $2\supset C_{61}H_2$ crystal is rather suppressed compared to that in a pure $C_{61}H_2$ crystal. The crystal structure of 6,5-isomer of $C_{61}H_2$ had been investigated by the powder X-ray diffraction.^{12a} The methylene group occupies six positions around the C_{60} cage with the fractions of 0.17 in the cubic close packed structure of 6,5-isomer of $C_{61}H_2$. The crystal structure of 6,6-isomer of $C_{61}H_2$ was not reported to date. We have obtained a hexagonal close packed crystal of 6,6-isomer of

$C_{61}H_2$. However, the crystal structure analysis of 6,6-isomer of $C_{61}H_2$ at low temperature was failed by a severe orientation disorder like almost free rotations.

Figure 4a shows the determined structure of a $2\rightarrow C_{61}H_2$ complex molecule (molecule **A**). The disordered structures are omitted in the figure. Only a methylene group with the fraction of 0.33 is shown. The distance from the center of the C_{60} cage to the methylene carbon atom is 4.92(4) Å, which is consistent with the theoretical distance of 4.93 Å.^{12b} The methylene carbon atom (C_m) is attached to two carbon atoms (C_f and C_f') on a C–C bond shared by two hexagons of the C_{60} cage (Fig. 4). Unfortunately, the interatomic distances could not be determined reliably because of the orientation disorder of $C_{61}H_2$ molecules, and the C_m – C_f (C_f') and C_f – C_f' interatomic distances are evaluated to be 1.55(4) and 1.38(2) Å, which are longer and shorter than the theoretical distances of 1.49 and 1.65 Å, respectively. A further suppression of orientation disorder is needed to determine the detailed structure of $C_{61}H_2$.

Geometric relationships among sulfur atoms of **2** and carbon atoms of $C_{61}H_2$ are a key to understand interactions between **2** and $C_{61}H_2$. A $C_{61}H_2$ molecule is coordinated by eight sulfur atoms (S1~S8) of **2** (Fig. 4a). The sulfur atoms lie on a plane perpendicular to a C_2 axis of the C_{60} cage. Four hexagons (H) and four pentagons (P) of the C_{60} cage form a belt on the plane with the manner of PHHP–PHHP–. The four sulfur atoms (S2, S3, S6, and S7) face to the hexagons, while the other four sulfur atoms (S1, S4, S5, and S8) face to the pentagons, as shown in Figs. 4b and 4c. Interatomic

distances between each sulfur atom and carbon atoms on adjacent hexagons or pentagons are listed in Table 1. The sulfur atoms facing to hexagons are close to the centers of the hexagons, while the sulfur atoms facing to pentagons are shifted from the centers of the pentagons. DFT calculations on the Saturn-like complex of unsubstituted **2** with C₆₀ also indicate the similar structure,⁶ and the lone pair p-orbitals of the sulfur atoms are located in between the p-orbitals of C₆₀ to avoid overlap of p-orbitals of the sulfur atoms and C₆₀. Average of the shortest S–C interatomic distances of each sulfur atom in the **2**⊃C₆₁H₂ crystal is 3.73 Å, which is slightly longer than the sum (3.55 Å) of van der Waals radii of sulfur (1.85 Å) and carbon (1.70 Å). The S–C van der Waals interactions and the sulfur on carbon-rings structure restrict the orientation of a C₆₁H₂ molecule. Assuming that the eight sulfur atoms are equivalent, the C₆₀ cage can have four orientations related by 45° rotations about the C₂ axis perpendicular to the sulfur plane. Actually, the C₆₀ cages in the **2**⊃C₆₁H₂ crystal have two orientations because the eight sulfur atoms are not equivalent in the monoclinic structure and not exactly on the same plane.

The geometric relationship between the oligothiophene macrocycle **2** and the C₆₀ cage in the **2**⊃C₆₁H₂ crystal is also found in the **2**⊃C₆₀ crystal.⁶ Average of the shortest S–C interatomic distances of each sulfur atom in the **2**⊃C₆₀ crystal is 3.76 Å, which is comparable to that in the **2**⊃C₆₁H₂ crystal. The C₆₀ cages in the **2**⊃C₆₀ crystal have only one orientation without disorder. The orientation ordering of C₆₀ in the **2**⊃C₆₀ crystal would be caused by intermolecular interactions between **2**⊃C₆₀ complex molecules. The intermolecular interactions are weakened and disturbed by the addition of a

methylene group and hence the $C_{61}H_2$ molecules show the orientation disorder in the $2\text{-}C_{61}H_2$ crystal.

Draft

Fig. 4. Structure of an independent $2\supset\text{C}_{61}\text{H}_2$ complex molecule (molecule **A**) in the $2\supset\text{C}_{61}\text{H}_2$ crystal.

The disordered structures are omitted in the figure. Four hydrogen atoms on two ethylene bonds of the oligothiophene macrocycle could not be clearly observed due to the disordered structure. (a) Molecular structure with the thermal ellipsoids of non-hydrogen atoms at 50% probability level. (b) and (c) Structure around sulfur atoms of **2**. Hexagons and pentagons close to the sulfur atoms are colored in blue in (b) and (c).

Table 1. Interatomic distances between eight sulfur atoms and carbon atoms on adjacent hexagons or pentagons in the $2\text{C}_{61}\text{H}_2$ crystal.

Sulfur	S-C interatomic distance (Å)
S1	3.60, 3.85, 3.86, 4.23, 4.23
S2	3.89, 3.89, 4.04, 4.04, 4.19, 4.19
S3	3.71, 3.77, 3.78, 3.91, 3.93, 3.99
S4	3.67, 3.86, 4.03, 4.31, 4.41
S5	3.80, 3.82, 4.14, 4.33, 4.46
S6	3.91, 3.95, 4.11, 4.18, 4.32, 4.41
S7	3.64, 3.73, 3.80, 3.97, 4.03, 4.11
S8	3.63, 3.68, 4.14, 4.21, 4.47

Structure of 2C_{70}

The triclinic 2C_{70} crystal contains a crystallographically independent 2C_{70} complex molecule.

The C_{70} cage on the inversion center show an orientation disorder with two orientations with the fractions of 0.5. Figure 5a shows the determined structure of a $2\supset C_{70}$ complex molecule. The disordered structures are omitted in the figure. The C_{70} cage with D_{5h} symmetry has an ellipsoidal shape. Interestingly, the long axis with D_5 symmetry and the short axis with C_2 symmetry of the C_{70} cage are both inclined from the axis perpendicular to the sulfur plane of **2**. C_{70} does not have PHHP–PHHP– belts unlike C_{60} . The eight sulfur atoms (S1~S8) in the $2\supset C_{70}$ crystal face to hexagons and pentagons on a PHHH–HHHP– belt of the C_{70} cage, as shown in Figs. 5b and 5c. The shortest S–C interatomic distances for S1~S8 are 3.54, 3.80, 3.63, 3.61, 3.71, 3.63, 3.83, and 3.58 Å, respectively. Average of the shortest S–C interatomic distances is 3.67 Å, which is shorter than those in the $2\supset C_{61}H_2$ and $2\supset C_{60}$ crystals but still longer than the sum (3.55 Å) of van der Waals radii of sulfur and carbon. Therefore, the oligothiophene macrocycle **2** presumably can capture other fullerenes larger than C_{70} .

In summary, we have shown how the Saturn-like complexes composed of oligothiophene macrocycle **2** with fullerenes can be constructed. Despite the weak donor-acceptor interaction between **2** and fullerenes, **2** hinders the rotation of circular fullerenes using non-covalent interactions between **2** and fullerenes to produce single crystals suitable for X-ray analysis. Therefore, **2** can be employed as a potential partner to determine the structures of exotic fullerenes.

Fig. 5. Structure of an independent 2C_{70} complex molecule in the 2C_{70} crystal. The disordered structures are omitted in the figure. (a) Molecular structure with the thermal ellipsoids of non-hydrogen atoms at 50% probability level. (b) and (c) Structure around sulfur atoms of **2**. Hexagons and pentagons close to the sulfur atoms are colored in blue in (b) and (c).

Supplementary material

Supplementary information including characterization data, binding behavior, and crystallographic information file (cif) are available with the article through the journal Web site at <http://...>

Acknowledgements

The work at Tokyo Metropolitan University was supported by the Grants-in-Aid for Scientific Research (26288040), JSPS, Japan and partly performed under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices" (M.I.). The work at The University of Tokyo was supported by the Grants-in-Aid for Scientific Research (16H04187), MEXT, Japan (Y.M.). The synchrotron radiation experiments were performed at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2015A0100).

References

- (1) Reviews of cycloparaphenylenes: (a) Darzi, E. R.; Jasti, R. *Chem. Soc. Rev.* **2015**, *44*, 6401; (b) Lewis, S. E. *Chem. Soc. Rev.* **2015**, *44*, 2221; (c) Yamago, S.; Kayahara, E.; Iwamoto, T. *Chem. Rec.* **2014**, *14*, 84.
- (2) Review of cyclo-2,5-thienylenes: Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141.
- (3) Reviews of cyclic paraphenyleneacetylenes: (a) Kawase, T. *Synlett* **2007**, 2609; (b) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250.
- (4) Reviews of π -expanded oligothiophene macrocycles: (a) Iyoda, M.; Shimizu, H. *Chem. Soc. Rev.* **2015**, *44*, 6401; (b) Iyoda, M. *Pure Appl. Chem.* **2010**, *82*, 831.
- (5) (a) Nakao, K.; Nishimura, M.; Tamachi, T.; Kuwatani, Y.; Miyasaka, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc.* **2006**, *128*, 16740; (b) Iyoda, M.; Tanaka, K.; Shimizu, H.; Hasegawa, M.; Nishinaga, T.; Nishiuchi, T.; Kunugi, Y.; Ishida, T.; Otani, H.; Sato, H.; Inukai, K.; Tahara, K.; Tobe, Y. *J. Am. Chem. Soc.* **2014**, *136*, 2389.

- (6) Shimizu, H.; Cojal Conzález, J. D.; Hasegawa, M.; Nishinaga, T.; Tahmina, H.; Takase, M.; Otani, H.; Rabe, J. P.; Iyoda, M. *J. Am. Chem. Soc.* **2015**, *137*, 3877.
- (7) Iyoda, M.; Yamakawa, J.; Rahman, M. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 10522.
- (8) (a) Smith, A. B. III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J. *J. Am. Chem. Soc.* **1993**, *115*, 5829.
- (9) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 8086.
- (10) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301; (b) Smith, A. B. III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492; (c) Beulen, N. W. J.; Echegoyen, L. *Chem. Commun.* **2000**, 1065; (d) Zhu, Y. H.; Bahnmüller, S.; Chibun, C.; Carpenter, K.; Hosmane, N. S.; Maguire, J. A. *Tetrahedron Lett.* **2003**, *44*, 5473; (e) Tokuyama, H.; Isobe, H.; Nakamura, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 935.
- (11) Meingast, C.; Roth, G.; Pintschovius, L.; Michel, R. H.; Stoermer, C.; Kappes, M. M.; Heiney, P. A.; Brard, L.; Strongin, R. M.; Smith III A. B. *Phys. Rev. B* **1996**, *54*, 124.
- (12) (a) Lommen, A.; Heiney, P. A.; Vaughan, G. B. M.; Strongin, R. M.; Brard, L.; Smith, A. B.; Stephens, P. W.; Liu, D.; Wudl, F.; Suzuki, T.; Li, C.; Khemani, K. C. *Phys. Rev. B* **1994**, *49*, 12572; (b) Curioni, A.; Giannozzi, P.; Hutter, J.; Andreoni, W. *J. Phys. Chem.* **1995**, *99*, 4008.
- (13) (a) Diederich, F.; Effing, J.; Jonas, U.; Jullien, L.; Plesnivý, T.; Ringsdorf, H.; Thilgen, C.; Weinstein, D. *Angew. Chem. Int. Ed.* **1992**, *31*, 1599; (b) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *Chem. Commun.* **1992**, 604; (c) Yoshida, Z.-i.; Takekuma, H.; Takekuma, S.-i.; Matsubara, Y. *Angew. Chem. Int. Ed.* **1994**, *33*, 1597.
- (14) (a) Gil-Ramírez, G.; Karlen, S. D.; Shundo, A.; Porfyrakis, K.; Ito, Y.; Briggs, G. A. D.; Morton, J. L.; Anderson, H. L. *Org. Lett.* **2010**, *12*, 3544; (b) Mulholland, A. R.; Woodward, C. P.; Langford, S. J. *Chem. Commun.* **2011**, *47*, 1494.
- (15) Rahman, M. J.; Shimizu, H.; Araki, Y.; Ikeda, H.; Iyoda, M. *Chem. Commun.* **2013**, *49*, 9251.
- (16) (a) Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 9477; (b) Kieran, A. L.; Pascu, S. I.; Jarroson, T.; Sanders, J. K. M. *Chem. Commun.* **2005**, *41*, 1276; (c) Nobukuni, H.; Shimazaki, Y.; Tani, F.; Naruta, Y. *Angew. Chem. Int. Ed.* **2007**, *46*, 8975; (d) Song, J.; Aratani, N.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2010**, *132*, 16356.
- (17) (a) Wang, M.-X.; Zhang, X.-H.; Zheng, Q.-Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 838; (b) Yamaguchi, Y.; Kobayashi, S.; Amita, N.; Wakamiya, T.; Matsubara, Y.; Sugimoto, K.; Yoshida, Z.-i. *Tetrahedron Lett.* **2002**, *43*, 3277; (f)

- (18) (a) Kawase, T.; Tanaka, K.; Fujiwara, N.; Darabi, H. R.; Oda, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 1624; (b) Kawase, T.; Tanaka, K.; Shiono, N.; Seirai, Y.; Oda, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 1722.
- (19) Isla, H.; Gallego, M.; Pérez, E. M.; Viruela, R.; Ortí, E.; Martín, N. *J. Am. Chem. Soc.* **2010**, *132*, 1772.
- (20) (a) Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 8342; (b) Xia, J.; Bacon, J. W.; Jasti, R. *Chem. Sic.* **2012**, *3*, 3018.
- (21) (a) Isobe, H.; Hitosugi, S.; Yamasaki, T.; Iizuka, R. *Chem. Sic.* **2013**, *4*, 1293; (b) Hitosugi, S.; Iizuka, R.; Yamasaki, T.; Zhang, R.; Murata, Y.; Isobe, H. *Org. Lett.* **2013**, *15*, 3199; (c) Hitosugi, S.; Ohkubo, K.; Iizuka, R.; Kawashima, Y.; Nakamura, K.; Sato, S.; Kono, H.; Fukuzumi, S.; Isobe, H. *Org. Lett.* **2014**, *16*, 3352; (d) Sato, S.; Yamasaki, T.; Isobe, H. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 8374.
- (22) Miki, K.; Matsushita, T.; Inoue, Y.; Senda, Y.; Kowada, T.; Ohe, K. *Chem. Commun.* **2013**, *49*, 9092.