

Synthesis of Sexithiophene-Bridged Cage Compound: A New Class of Three-Dimensionally Expanded Oligothiophenes

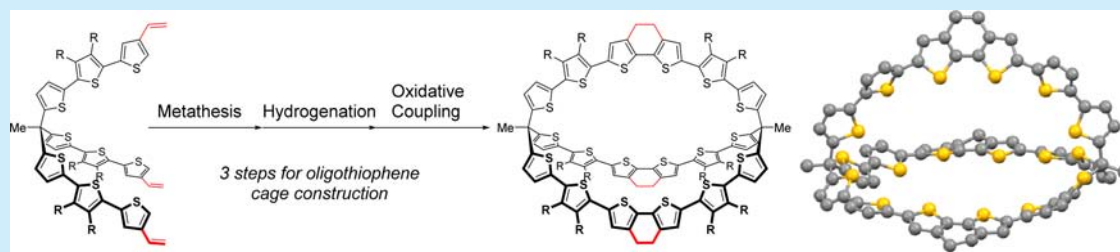
Kazuhiko Adachi,[†] Yasukazu Hirao,[†] Kouzou Matsumoto,[‡] Takashi Kubo,^{*,†} and Hiroyuki Kurata^{*,§}

[†]Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

[‡]Institute of Natural Sciences, Senshu University, Kawasaki, Kanagawa 214-8580, Japan

[§]Department of Environmental and Biological Chemistry, Faculty of Engineering, Fukui University of Technology, Fukui 910-8505, Japan

S Supporting Information



ABSTRACT: A bicyclo-type cage-shaped compound consisting of three sexithiophenes was successfully synthesized and characterized by NMR, HRMS, and X-ray crystallographic analysis. The strained cage architecture was reflected in the blue-shifted absorption spectrum relative to its linear analogue. Intramolecular interaction between three-dimensionally fixed sexithiophenes was suggested by electrochemical analysis.

The design and synthesis of novel functionalized π -conjugated systems have always been among the central issues in the field of organic molecular electronics. One strategy to create such π -conjugated compounds is an expansion of molecular dimensionality.¹ In particular, π -conjugated three-dimensional (3D) compounds are of great interest due to their potential isoelectronic properties and thus facile processability.^{1a} Among them, oligothiophenes have been used as key components because of their outstanding chemical and physical properties in addition to their synthetic availability. Various molecular architectures, such as tetrahedral, dendritic, cruciform, or star-shaped structures, have been employed as 3D oligothiophene platforms.^{1a,b}

We previously reported on the syntheses of bicyclo-type cage-shaped compounds in which two tris(2-thienyl)methanes are bridged by three π -conjugated components such as ethylene or stilbene.² One of the notable features of these compounds is their 3-fold symmetric structure. By utilizing this thiophene-based cage framework, we designed a novel 3D oligothiophene-bridged cage-shaped compound by replacement of the π -bridges only with thiophenes. Although this structural modification could be considered as a 3D expansion of cyclophane-based oligothiophenes, or oligothiophenes fixed by appropriate linkers,³ our newly designed cage will possess sufficient intramolecular interactions because the fixation of three π -bridges attached to a single atom will lead to efficient orbital overlap. The cage will provide a novel class of 3D molecular platforms.

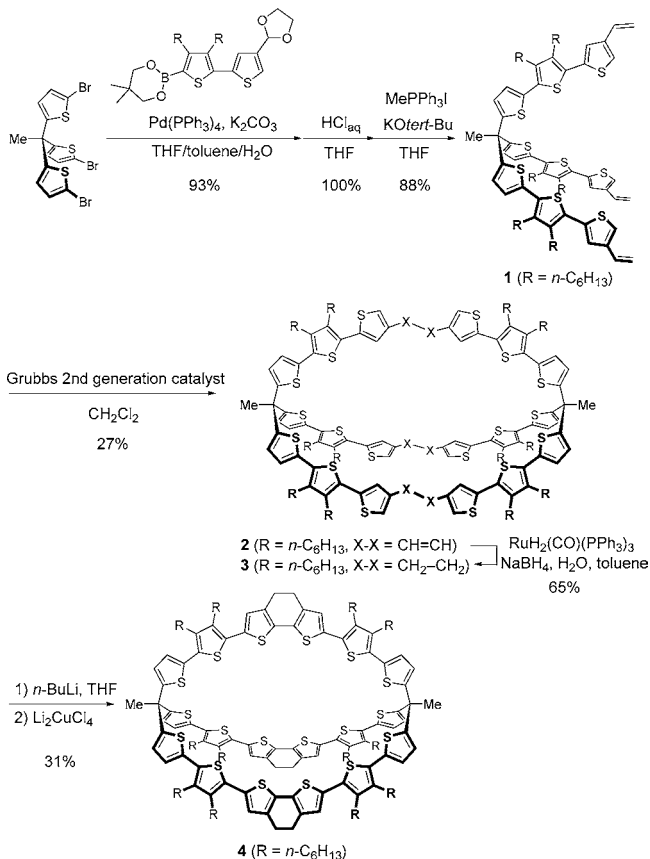
Synthesis of cage-shaped oligothiophenes is challenging because three oligothiophenes must be fixed in the rigid cage scaffold. Itami et al. reported cage-shaped oligo-*p*-phenylenes by applying their cyclo-*p*-phenylene synthesis strategy to a trisubstituted benzene core.⁴ Following this work, Yamago et al. reported octahedral-shaped phenylenes.⁵ However, the synthesis of strained oligothiophene π -systems is still rare, and their structure–property relationships have not been fully explored.⁶ Construction of such a strained oligothiophene was achieved by Bäuerle et al. by involving a Pt(II)–thiophene complex as a precursor for cyclic oligothiophenes.^{6b} However, the use of an equimolar amount of expensive platinum complex is required. Herein, we report the synthesis of a bicyclo-type, cage-shaped compound composed of three sexithiophenes by a new methodology for the construction of a strained macrocyclic oligothiophene. We also present the optical and redox properties of the sexithiophene-bridged cages.

Our synthetic strategy started from tris(terthienyl)methane **1**, in which the terminal thiophene rings bear vinyl groups at the β -positions (Scheme 1). Compound **1** was prepared from 1,1,1-tris(5-bromo-2-thienyl)ethane^{2c} in three steps (see the Supporting Information). By Grubbs olefin metathesis reaction under high dilution conditions (0.5 mM), **1** was transformed into the corresponding vinylene-bridged dimer **2**. After GPC separation, dimer **2** was isolated as the main product. The signal of vinylene protons of **2** is observed at δ 6.90 ppm, whose

Received: September 20, 2014

Published: October 31, 2014

Scheme 1. Synthesis of Cage 4



value is similar to that of (*E*)-1,2-bis(2-thienyl)ethene (7.06 ppm)⁷ rather than those of (*Z*)-1,2-bis(2-thienyl)ethene (6.59 ppm)⁸ or (*Z*)-etheno-bridged tris(2-thienyl)methane cages (6.45–6.54 ppm).² Therefore, the configurations of the three double bonds of compound **2** are indicated to be all (*E*)-form, probably because the thermodynamically favorable conformation was produced as a result of reversible bond formation/dissociation. An attempt to reduce the three ethylene linkers in **2** with H₂ and Pd/C resulted in recovery of **2**. The ruthenium complex, RuH₂(CO)(PPh₃)₃, was found to be a more powerful reduction catalyst for **2** to afford **3** in good yield.⁹ Subsequent Fe(III)-mediated 3-fold intramolecular bond formation failed, which led to the production of an unidentifiable mixture. The key to clean bond formation was to use Li₂CuCl₄ as a THF-soluble stoichiometric oxidant.¹⁰ After lithiation of **3** with an excess amount of *n*-BuLi, the Li₂CuCl₄-mediated oxidative coupling reaction at –78 °C proceeded smoothly to afford the desired three sexithiophene-bridged cage compound **4** as orange crystals.

The characterization of **4** was carried out by high-resolution mass spectrometry and ¹H and ¹³C NMR spectroscopy. In the ¹H NMR spectrum, two sets of doublets and one singlet were observed in the aromatic region, which strongly support the highly symmetric structure of **4** in solution (Figure 1). The formation of **4** was unambiguously confirmed by X-ray crystallographic analysis¹¹ (Figure 2a–c). Although the hexyl chains are disordered, the cage skeleton itself could be clearly seen. In contrast to the solution state, the crystal structure of **4** was deformed since two sexithiophene chains were arranged nearly planar (Figure 2b). Interestingly, only two of the six thiophenes were attached to carbon atoms at the bridgehead

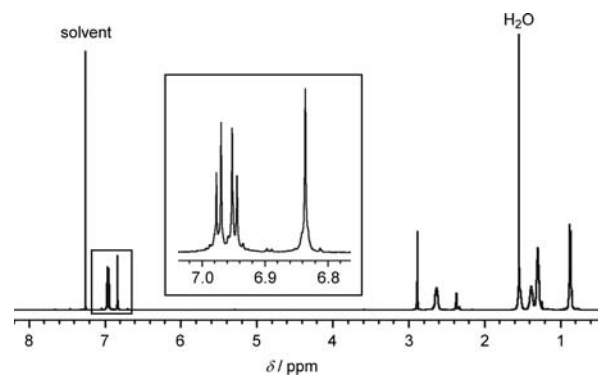


Figure 1. ¹H NMR spectrum of **4** (500 MHz, 30 °C, in CDCl₃). (Inset) Thiophene signals in the aromatic region.

direct S atoms outside of the central cavity. As a result, one of the three sexithiophenes adopts an *all-syn*-conformation, whereas the other two thiophene chains are arranged in a *syn-syn-syn-syn-anti* manner. A similar thiophene inversion could be observed in the crystal structure of cyclic analogue **5** (see Figure 3 and the Supporting Information for details). This fact suggests that the inversion of only two thiophenes observed in **4** is due to not only packing forces but also the molecular structure in which sexithiophenes are bridged between sp³ carbons. The torsion angles of adjacent thiophene units vary over a large range from 5.6° to 58.4°. These values differ greatly from those of linear sexithiophene derivatives as observed in the crystal structure of cyclo[10]thiophene (C10T).^{6d,12} The large difference in torsion angles of **4** is likely caused by the nearly coplanar conformation of the central bithiophene moieties, which demand that the other thiophene–thiophene bonds compensate for the molecular strain. S–S distances are distributed widely (3.13–3.57 Å) except for the inverted thiophenes. These values are smaller than the sum of van der Waals radii (3.6 Å).¹³ Some of the hexyl chains interpenetrate into the central cavities of the adjacent molecules to form a one-dimensional molecular alignment (see Figure 2c and Supporting Information for details). CH–π interactions are observed between the neighboring columns (red dotted lines in Figure 2c).

To reveal the electronic structure of cage **4**, UV–vis absorption measurements were carried out in CH₂Cl₂ (Figure 4a). For comparison, we also synthesized cyclic and linear analogues **5** and **6** by a similar synthetic method (see Figure 3 and the Supporting Information for synthetic details). A notable feature in the UV spectra is the hypsochromic shift of λ_{max} of cage **4** compared to that of linear analogue **6** (418 and 437 nm, respectively). This shift could be ascribed to the fixation of both edges of the sexithiophenes in **6**, which plausibly prohibits the thiophene chains from adopting a coplanar conformation. A similar trend was observed in cyclic analogue **5** (418 nm). It should also be noted that a new absorption band appeared in the short-wavelength region for **4** and **5**. In contrast to the absorption spectra, emission spectra of these three sexithiophene derivatives **4–6** were quite similar. As a result, Stokes shifts of **4** and **5** are larger than **6** (Figure 4b).

A unique electronic interaction in cage **4** was observed in cyclic voltammetry and differential pulse voltammetry measurements (Figure 5). All the sexithiophene derivatives **4–6** exhibit two reversible redox waves, which correspond to monocation and dication formation for each sexithiophene moiety. However, as can be seen in Figure 4a, the first oxidation

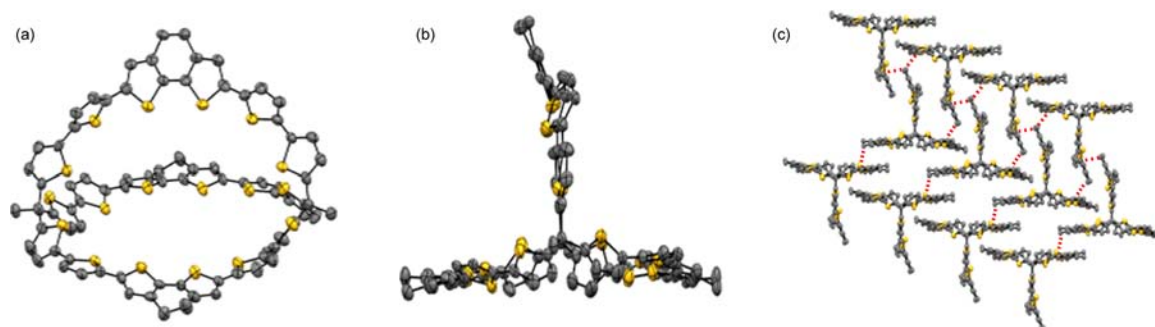


Figure 2. ORTEP drawings of **4** at the 50% probability level [(a) and (b)] and (c) packing structure of **4**. Intermolecular contacts smaller than the sum of van der Waals radii are represented as red dotted lines. Hydrogen atoms and hexyl chains are omitted for clarity.

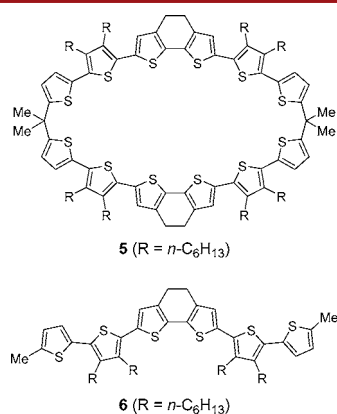


Figure 3. Structure of cyclic analogue **5** and linear analogue **6**.

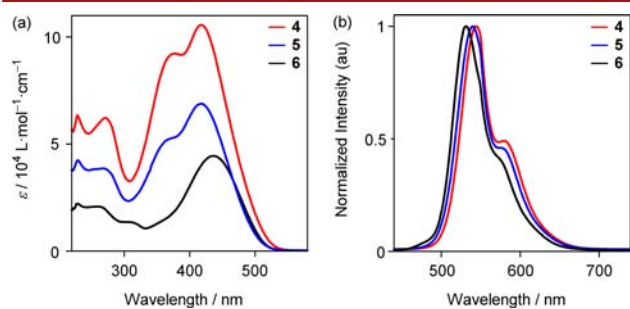


Figure 4. (a) UV-vis and (b) fluorescence spectra of **4–6** (in CH_2Cl_2).

peak of **4** is broadened and a new peak appears as a shoulder. This peak broadening could be ascribed to stepwise oxidation of one electron ($4^{\bullet+}$) followed by two-electron transfer ($4^{3(\bullet+)}$). This redox behavior suggests an intramolecular interaction between three oligothiophenes in the mono(radical cation) species $4^{\bullet+}$. Appearance of the electronic interaction at the mono(radical cation) state is different from that observed in alkylene-bridged cyclophane-type oligothiophenes^{3b} but is similar to those linked by other spacers.^{3c,e} The higher potential of the second oxidation wave of $4^{3(\bullet+)}$ compared to 6^+ is due to increased Coulomb repulsion in the formation of the hexacation species. The first oxidation wave of **5** is also broadened, but the extent of the peak broadening is smaller than that observed in **4**. This indicates that tight fixation and/or incorporation of a larger number of oligothiophene units enhances the electronic communication between the bridged thiophene chains.

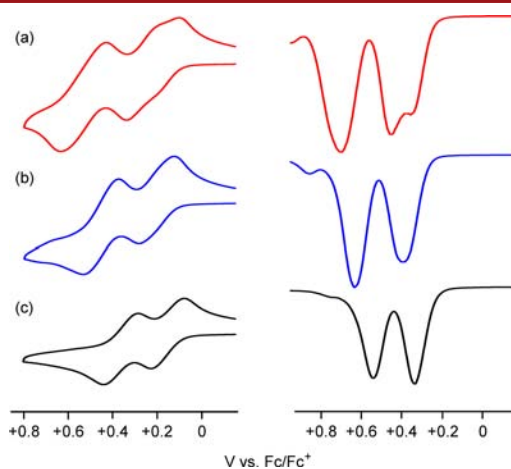


Figure 5. Cyclic voltammograms (left) and differential pulse voltammograms (right) of (a) **4**, (b) **5** and (c) **6** in CH_2Cl_2 solution containing 0.1 M $n\text{-Bu}_4\text{NPF}_6$.

In summary, we successfully synthesized the three sexithiophene-bridged cage-shaped compound **4** by a new synthetic method in which β -alkylene-linked **3** is employed as a key synthetic intermediate. The high efficiency for the specific three-bond formation would make this methodology a promising synthetic tool for not only cage molecular synthesis but also strained oligothiophene construction. The X-ray structure of **4** shows the three sexithiophenes arranged in an unsymmetrical fashion, in which two sexithiophene chains adopt a nearly coplanar conformation. The rigidity of the cage architecture of **4** is reflected in the hypsochromically shifted absorption spectrum compared to linear **6**. Significant intramolecular interactions between bridged thiophene chains in **4** could be confirmed by electrochemical analysis of the one-electron oxidation state $4^{\bullet+}$. Further investigation on electronic communication between bridged thiophenes will be required for a more detailed understanding of the electronic properties of thiophene-based cage architectures, which will provide insight into the design and creation of novel 3D π -conjugated compounds.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures for **1–6**, high-resolution mass spectrum of cage **4**, ^1H and ^{13}C NMR spectra of all new compounds, X-ray crystallographic analysis of **5**, and crystallographic information (CIF) for **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kubo@chem.sci.osaka-u.ac.jp.

*E-mail: kurata@fukui-ut.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. Tomohiko Nishiuchi from the Department of Chemistry, Graduate School of Science, Osaka University, for helpful discussions. This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Reaction Integration" (No. 2105) from MEXT and a Grant-in-Aid for Scientific Research (No. 18550034) from the Japan Society for the Promotion of Science.

REFERENCES

- (1) (a) Roncali, J.; Leriche, P.; Cravino, A. *Adv. Mater.* **2007**, *19*, 2045–2060. (b) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141–1276. (c) Skabara, P. J.; Arlin, J.-B.; Geerts, Y. H. *Adv. Mater.* **2013**, *25*, 1948–1954. (d) Kanibolotsky, A. L.; Perepichka, I. F.; Skabara, P. J. *Chem. Soc. Rev.* **2010**, *39*, 2695–2728. (e) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070–4098.
- (2) (a) Kurata, H.; Nakaminami, H.; Matsumoto, K.; Kawase, T.; Oda, M. *Chem. Commun.* **2001**, 529–530. (b) Kurata, H.; Haruki, K.; Nakaminami, H.; Kawase, T.; Oda, M. *Chem. Lett.* **2003**, *32*, 422–423. (c) Kurata, H.; Haruki, K.; Oda, M. *Chem. Lett.* **2005**, *34*, 484–485. (d) Kurata, H.; Rikitake, N.; Okumura, A.; Oda, M. *Chem. Lett.* **2004**, *33*, 1018–1019.
- (3) (a) Kaikawa, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Org. Lett.* **2000**, *2*, 4197–4199. (b) Sakai, T.; Satou, T.; Kaikawa, T.; Takimiya, K.; Otsubo, T.; Aso, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8082–8089. (c) Knoblock, K. M.; Silvestri, C. J.; Collard, D. M. *J. Am. Chem. Soc.* **2006**, *128*, 13680–13681. (d) Song, C.; Swager, T. M. *Org. Lett.* **2008**, *10*, 3575–3578. (e) Takita, R.; Song, C.; Swager, T. M. *Org. Lett.* **2008**, *10*, 5003–5005. (f) Cornelis, D.; Franz, E.; Asselberghs, I.; Clays, K.; Verbiest, T.; Koeckelberghs, G. *J. Am. Chem. Soc.* **2011**, *133*, 1317–1327. (g) Tsuge, A.; Hara, T.; Moriguchi, T.; Yamaji, M. *Chem. Lett.* **2008**, *37*, 870–871.
- (4) Matsui, K.; Segawa, Y.; Namikawa, T.; Kamada, K.; Itami, K. *Chem. Sci.* **2013**, *4*, 84–88.
- (5) Yamago, S.; Kayahara, E.; Iwamoto, T. *Chem. Rec.* **2014**, *14*, 84–100.
- (6) (a) Krömer, J.; Rios-Carreras, I.; Fuhrmann, G.; Musch, C.; Wunderlin, M.; Debaerdemaeker, T.; Mena-Osteritz, E.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3481–3486. (b) Zhang, F.; Götz, G.; Winkler, H. D. F.; Schalley, C. A.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 6632–6635. (c) Zade, S. S.; Bendikov, M. *J. Org. Chem.* **2006**, *71*, 2972–2981. (d) Zhang, F.; Götz, G.; Mena-Osteritz, E.; Weil, M.; Sarkar, B.; Kaim, W.; Bäuerle, P. *Chem. Sci.* **2011**, *2*, 781–784. (e) Mena-Osteritz, E.; Zhang, F.; Götz, G.; Reinker, P.; Bäuerle, P. *Beilstein J. Nanotechnol.* **2011**, *2*, 720–726. (f) Nakao, K.; Nishimura, M.; Tamachi, T.; Kuwatani, Y.; Miyasaka, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc.* **2006**, *128*, 16740–16747. (g) Iyoda, M.; Yamakawa, J.; Rahman, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 10522–10553.
- (7) (a) Ngwendson, J. N.; Atemnkeng, W. N.; Schultze, C. M.; Banerjee, A. *Org. Lett.* **2006**, *8*, 4085–4088. (b) Diliën, H.; Chambon, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Adriaensens, P. J. *Macromolecules* **2011**, *44*, 4711–4720. (c) Neculqueo, G.; Fuentes, V. R.; López, A.; Matute, R.; Vásquez, S. O.; Martínez, F. *Struct. Chem.* **2012**, *23*, 1751–1760.
- (8) (a) Rahimi, A.; Pápani, I.; Ádám, M.; Gjikaj, M.; Namyslo, J. C.; Schmidt, A. *Eur. J. Org. Chem.* **2012**, 754–763. (b) Fischer, E.; Larsen,

J.; Christensen, J. B.; Fourmigué, M.; Madsen, H. G.; Harrit, N. *J. Org. Chem.* **1996**, *61*, 6997–7005.

(9) Adair, G. R. A.; Kapoor, K. K.; Scolan, A. L. B.; Williams, J. M. J. *Tetrahedron Lett.* **2006**, *47*, 8943–8944.

(10) Tamura, M.; Kochi, J. *Synthesis* **1971**, 303–305.

(11) Crystal data of **4**: triclinic, *P*-1, *a* = 13.3862(17) Å, *b* = 23.118(3) Å, *c* = 26.137(3) Å, *a* = 77.272(3)°, *b* = 88.520(3)°, *g* = 86.926(3)°, *V* = 7877.3(17) Å³, *Z* = 2, *D*_{calc} = 1.105 g/cm³, *R*₁ (*I* > 2σ(*I*)) = 0.0830, *wR*₂ (all data) = 0.2405, refl/param = 10574/1488, *GOF* = 0.829, *T* = 150(2) K. CCDC 1010974.

(12) Nonsubstituted *a*-6T: (a) Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J.-L.; Garnier, F. *Chem. Mater.* **1995**, *7*, 1337–1341. (b) Siegrist, T.; Fleming, R. M.; Haddon, R. C.; Laudise, R. A.; Lovinger, A. J.; Katz, H. E.; Bridenbaugh, P.; Davis, D. D. *J. Mater. Res.* **1995**, *10*, 2170–2173. Six-membered ring fused linear *a*-6T: (c) Nishida, J.; Miyagawa, T.; Yamashita, Y. *Org. Lett.* **2004**, *6*, 2523–2526. 3',4',3''',4''''-Tetraalkyl-substituted linear *a*-6T: (d) Huang, W.; Masuda, G.; Maeda, S.; Tanaka, H.; Ogawa, T. *Chem.—Eur. J.* **2006**, *12*, 607–619. (e) Liao, J.-H.; Benz, M.; LeGoff, E.; Kanatzidis, M. G. *Adv. Mater.* **1994**, *6*, 135–138.

(13) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.