Topochemical Polymerization of Phenylacetylene Macrocycles: A New Strategy for the Preparation of Organic Nanorods

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Ⓢ *Supporting Information*

ABSTRACT: Soluble organic nanorods were prepared from phenylacetylene macrocycles using the topochemical polymerization of butadiyne moieties placed both inside and outside the macrocycles' skeletons. Macrocycles containing amide groups were self-assembled in a columnar fashion through the formation of an organogel in ethyl acetate. Upon irradiation with UV light, the Raman signals associated with butadiyne units completely vanished, indicating the creation of covalently linked nanorods.

T he supramolecular self-assembly of macrocycles is one of the most popular strategies for preparing organic nanotubes with new properties for various applications, including host−guest chemistry,[1] scaffolding,[2] and gas storage.[3] One major drawback of these supramolecular assemblies is their relative kinetic instability. Because they rely on weak interactions such as hydrogen-bonding, $\pi-\pi$, and van der Waals interactions, the conditions under which they can be employed and characterized are very restricted, limiting their use in devices. Thus, strategies to improve their stability have been developed, and one of the most promising ones is covalent attachment of the macrocycles once the supramolecular assembly is formed. This strategy has proven to be successful with many types of macrocycles, such as cyclodextrin,[4] cyclic oligopeptides,[5] and calixarene.[6] Many attempts to prepare nanotubes from phenylacetylene macrocycles (PAMs) in the crystalline state using 1,3-butadiyne topochemical polymerization[7] have been reported, but most of them failed[8] or have led to rapid decomposition to produce undefined, insoluble carbon residues.[9,10]

We recently attempted to use this strategy to make stable organic nanotubes from PAM **1** (Figure 1)[11] by cross-linking the butadiyne moieties through photoinduced topochemical reactions to yield polydiacetylene (PDA)-walled nanotubes. However, we found that only very short PDA oligomers were formed under UV irradiation and that the yield of polymerization was very low, although PDA formation from non-macrocyclic 1,4-diarylbutadiyne derivatives in the gel state proved to be efficient.[12] We hypothesized that the butadiyne moieties were unreactive because of the high rigidity of the macrocycle.[13] One way to drive the topochemical polymerization is to heat the butadiyne-containing materials in the solid state. Shimizu[14] and Lauher[15] independently used this strategy
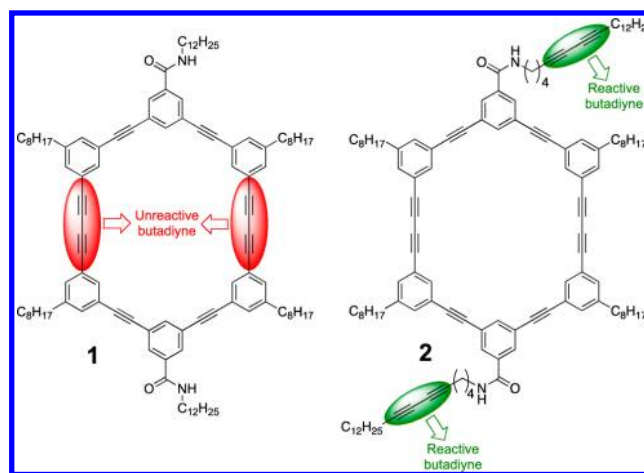

**Figure 1.** Phenylacetylene macrocycles **1** and **2**.

very recently to prepare insoluble, nonprocessable nanotubes from macrocycles with flexible backbones. However, heating PAM **1** in the solid state, which was not crystalline but in a dried gel state, destroyed the hydrogen-bonding network holding the macrocycles in a face-to-face configuration. Therefore, we have designed the new PAM **2** (Figure 1) possessing at each end a cross-linkable butadiyne unit with an alkyl fragment attached, providing a more flexible environment that should enable the topochemical polymerization. The cross-linking of those units at the exterior of the macrocycle should lead to a covalently linked, stable organic nanotube that can be further heated to allow topochemical polymerization of the butadiyne moieties present within the PAM backbone.

Herein we report the synthesis, self-assembly, and topochemical polymerization in the gel state of PAM **2** bearing multiple cross-linkable butadiyne moieties, leading to soluble, one-dimensional (1D) nanorods. It was not possible to confirm whether or not the resulting architectures possess an inner cavity. To the best of our knowledge, this is the first report of a controlled topochemical polymerization involving a six-membered PAM, although many over the years have pursued this goal. The use of rigid, conjugated, carbon-rich macrocycles represents a necessary step toward the preparation of shape-

Scheme 1. Synthesis of PAM 2
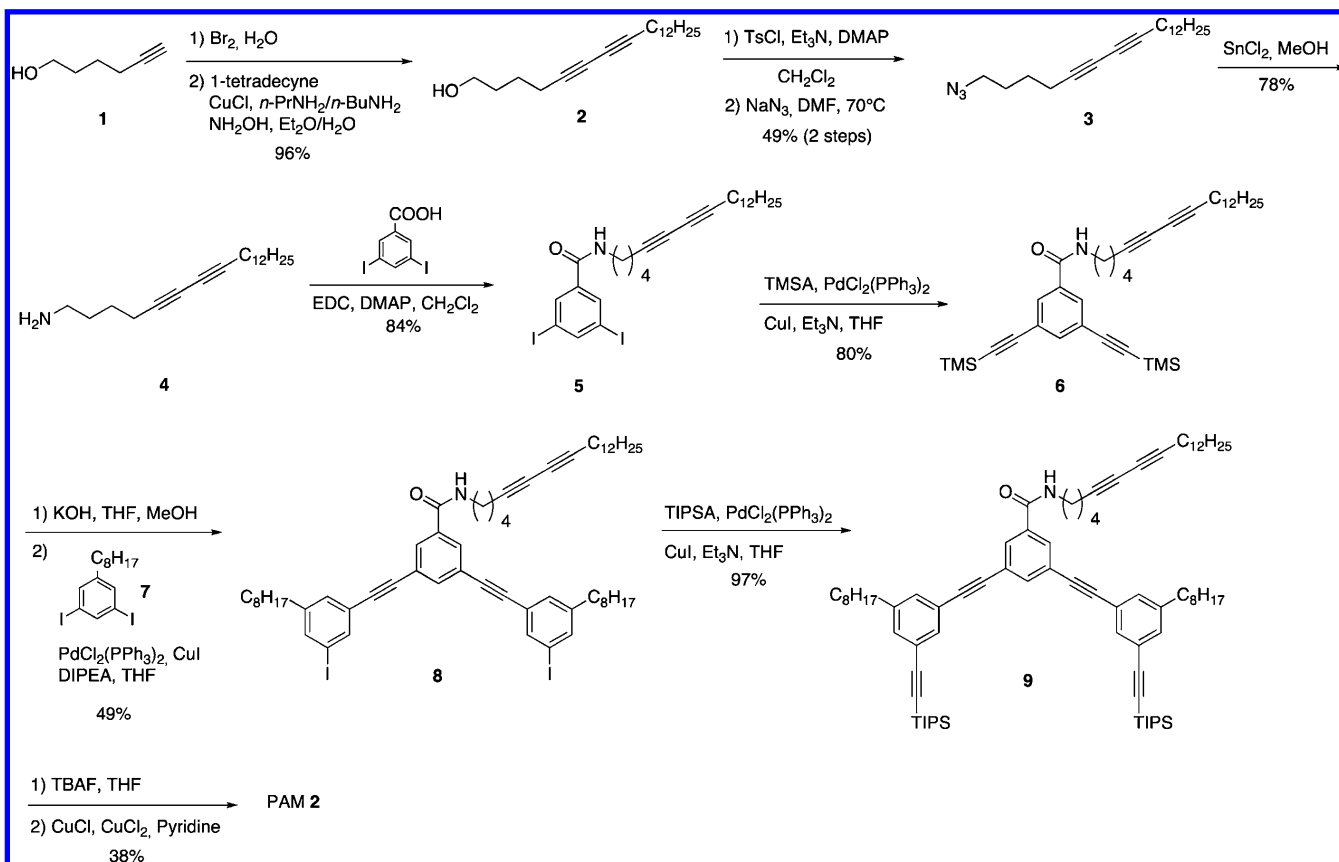
persistent, nongraphitic nanotubes and nanorods with unique semiconducting properties.

We reported the synthesis of PAM **1** previously,[11] and the synthesis of PAM **2** is shown in Scheme 1. Starting from 5-hexyn-1-ol, a bromination reaction on the terminal alkyne was conducted with bromine to yield the corresponding bromoalkyne, which was immediately subjected to a Cadiot–Chodkiewicz[16] coupling reaction with 1-tetradecyne to yield compound **2** in 96% yield over two steps. Next, the hydroxyl group was replaced by an azido group using a tosylate intermediate to give compound **3**. The azido group was then reduced into an amine using tin chloride, and the resulting compound **4** was coupled to 3,5-diiodobenzoic acid[11] using standard Steglich conditions to give compound **5** in 84% yield. Sonogashira coupling was used to install trimethylsilylacetylene (TMSA) at the 3 and 5 positions, and the alkyne groups were then deprotected. The resulting compound was coupled again through Sonogashira coupling to 3,5-diiodo-1-octylbenzene[11] in moderate yield. Another Sonogashira coupling was performed at the iodo-bearing positions with triisopropylsilylacetylene (TIPSA), and the resulting compound **9** was deprotected using tetrabutylammonium fluoride (TBAF) to provide the half-macrocycle. Finally, a ring closure reaction using Eglinton conditions was performed in dilute solution to give PAM **2** in moderate 38% yield. PAM **2** was purified by standard column chromatography and showed moderate to good solubility in common organic solvents.

The gelation properties of PAM **2** were studied in common organic solvents, and the detailed results are presented in Table S1 in the Supporting Information (SI). PAM **2** gelified in several solvents, including benzene, acetone, cyclohexane, and

hexanes. In those solvents, translucent gels were obtained at concentrations as low as 1.0 wt %. In ethyl acetate, however, very stable but opaque gels were obtained at the same concentration, leading to larger crystallites within the organogel (see Figure S19 in the SI). It is worth noticing that further characterization of the ethyl acetate organogel had to be performed quickly since it turned blue very rapidly under ambient conditions, indicating the formation of PDA within the supramolecular assembly.

To gain better insight into the nanoscale morphology of the ethyl acetate organogel, scanning electron microscopy (SEM) analysis was performed (Figure 2). As expected, the organogel
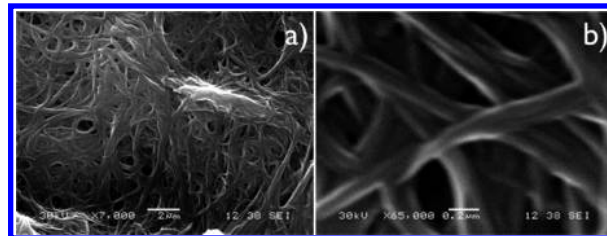

Figure 2. SEM images of a dried ethyl acetate organogel of PAM **2** (10 mg/mL). Scale bars are (a) 2 μm and (b) 0.2 μm.

of PAM **2** was made of micrometers-long fibers with diameters of ca. 200 nm. As we observed previously for PAM **1**, the fibers stacked to form few-micrometers-thick bundles, suggesting strong interfiber interactions.[8,17]

Powder X-ray diffraction (PXRD) analysis on the same dried gel was also performed to obtain information about the intermolecular interactions and the distances within the

supramolecular assembly. The PXRD pattern is rather complex and shows peaks in the small-angle region at $2\theta = 7.0$ and $4.0°$, corresponding to a ratio of $1{:}1/\sqrt{3}$, which can be indexed as the (100) and (110) reflections of a hexagonal lattice (Col$_h$) (Figure S20).[11,18] The other peaks in the small-angle region cannot yet be assigned with certainty but are likely to be due to a columnar phase with different symmetry. The broad peak centered at $2\theta = 20.2°$ (4.39 Å) can be ascribed to the intracolumnar liquidlike order between the alkyl chains. These results suggest that the macrocycles within the organogel phase are in the proper orientation to react with each other through topochemical reactions to give a nanotubular structure.

To connect the macrocycles in order to fix the supramolecular assembly, topochemical polymerization of the external butadiyne units was attempted by irradiating the organogel with UV light (254 nm). Organogels obtained from different solvents, all at a concentration of 10 mg/mL, were tested. Interestingly, only the organogel obtained from ethyl acetate turned blue under UV irradiation for 24 h (Figure S19). After the reaction, the ethyl acetate was removed and chloroform was added, providing an intense blue solution with slight turbidity (Figure S19). This solution was analyzed by size-exclusion chromatography (SEC) after it was filtered on a 0.45 μm filter. It is worth mentioning that an appreciable amount of insoluble blue material was left on the filter (30−50 wt % of the irradiated material). As shown in Figure S23, high-molecular-weight materials were formed upon irradiation, although PAM **2** was still present in rather high concentration. Hence, a semipreparative SEC experiment was performed to isolate the higher-molecular-weight fraction between 6 and 7.5 min. About 3 mg of intense blue material was thus obtained from 20 mg of PAM **2**, resulting in a yield of ca. 15% of soluble, cross-linked material. It is worth mentioning that the nanorods stayed soluble as long as they were not dried, in which case they could be dispersed but not resolubilized. The other fractions (retention time >8 min) were also collected, but no further analysis was performed on them since they appeared as bluish-green materials, suggesting incomplete topochemical polymerization.

The optical properties of the SEC-purified blue material were studied by UV−vis spectroscopy in chloroform solution. A broad absorption band with $\lambda_{max} = 654$ nm appeared upon irradiation, which is characteristic of the PDA backbone (Figure S22). As an empirical proof of the formation of organic nanorods, the thermochromic properties of this material were studied in both solution and the solid state. As expected, no sign of thermochromism in either solution or the solid state was detected under the numerous conditions tested, which indicates that the PDAs were formed in a very rigid environment without the possibility of chain torsion. This result eliminates at some point the possibility of having a covalent polymer chain in which the macrocycles are attached at only one end to each other. In this particular case, one can assume that the resulting PDA would exhibit chromism properties due to the steric hindrance between the macrocycles, which would force the polymer chain to twist, especially when a polar solvent such as dimethyl sulfoxide or *N,N*-dimethylformamide (DMF) is used to break the intramolecular hydrogen-bonding network.

To assess whether all of the external diyne moieties were consumed upon irradiation to form PDA, the purified blue material was analyzed by Raman spectroscopy (Figure 3). The powder spectrum of PAM **2** exhibits a strong band at 2222 cm^{-1} associated with the stretching mode of the diyne moieties.
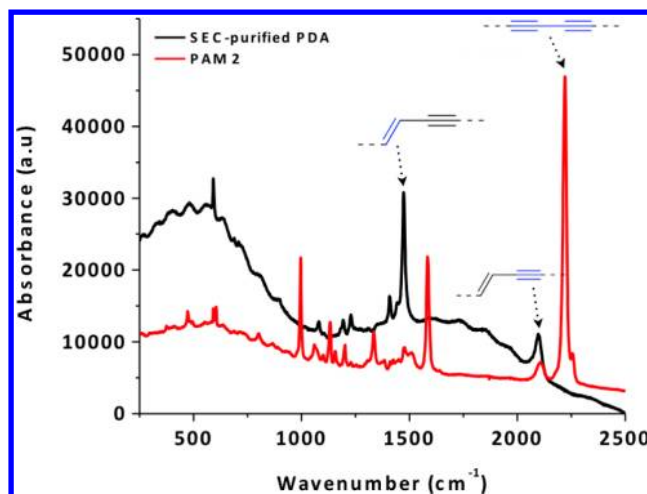

Figure 3. Raman spectra of PAM **2** (red) and the SEC-purified blue material (black).

Unexpectedly, this band disappeared completely upon irradiation for 24 h, suggesting that all of the diyne moieties, even those within the macrocycle skeleton, reacted to give PDA derivatives (Figure S24). This was confirmed by the appearance of new bands at 1473 and 2096 cm^{-1} attributed to the stretching vibration modes of newly formed alkene and alkyne groups, respectively. Although the driving force for the topochemical polymerization of the diyne units inside the macrocycle is not yet understood, we hypothesize that topochemical polymerization reactions occur on the outer part of the macrocycle first, placing the diyne moieties inside the macrocycle into the proper position to undergo the second topochemical polymerization. The lack of diyne signals in the final material eliminates the possibility of having a single-point attachment between two macrocycles. This result is in perfect agreement with the absence of thermochromic properties of the blue material obtained after UV irradiation.

PXRD analysis was performed on the nanorods obtained after SEC purification, and the diffractogram is presented in Figure S21. Interestingly, the broad peak at $2\theta = 20.2°$ (4.39 Å) was still present, indicating that the intramolecular alkyl chain interactions were preserved. Also, a less intense and broad peak appeared at $2\theta = 3.6°$ (24.5 Å), corresponding to the diameter of the nanorods.

High-resolution transmission electron microscopy (HRTEM) measurements were recorded on the purified nanorods (Figure 4). The nanorods formed were several tens
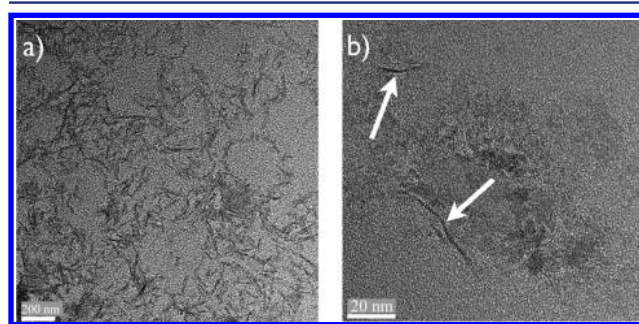

Figure 4. HRTEM images of the nanorods. Scale bars are (a) 200 nm and (b) 20 nm. White arrows indicate the position of individualized nanorods.

of nanometers long and 2−3 nm wide, in perfect agreement with the structural parameters calculated by molecular modeling and the distance measured by PXRD. The length of the nanorods also suggests that topochemical polymerization can be accomplished over a long range (several tens of macrocycles). Although it was not possible to visualize an internal void in the nanorods by HRTEM, the presence of columnar phases and the $\pi-\pi$ stacking between the macrocycles within the organogel phase of PAM **2**, as proven by PXRD, serve as a strong indication that the resulting material is made of covalently linked 1D stacks of macrocycles, probably forming tubular architectures with a calculated internal diameter of ca. 8 Å (Figure 24). In fact, intercolumnar topochemical reactions are unlikely because the formation of PDA is very dependent on the distance between monomers (∼4.9 Å) and the angle between the reacting butadiyne units (45°).[7] For the same reason, cross-linking reactions occurring in amorphous phases (if present) are highly improbable, leaving the formation of 1D nanorods as the only plausible product, as shown in Figure 5.
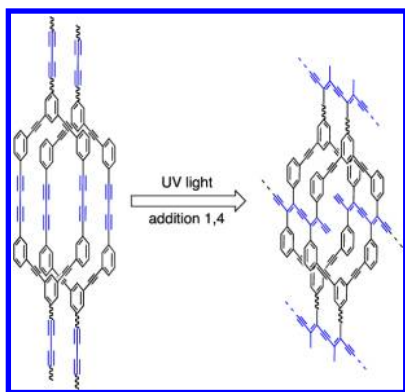

Figure 5. Proposed mechanism for the topochemical polymerization between macrocycles in the dried gel state.

In conclusion, new soluble organic nanorods were prepared from phenylacetylene macrocycles through topochemical reactions of butadiyne units properly located within the macrocycle structure. This finding opens the way for the formation of nongraphitic semiconducting nanorods and nanotubes for electronic applications. Our efforts are now being directed toward the preparation of new macrocycles as building blocks that will lead to nanorods with different diameters. We also plan to investigate the porous properties of these new architectures for gas storage and separation. This study will allow us to assess whether or not the nanorods have a formal internal cavity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data for all new compounds, PXRD patterns, UV−vis spectra, and gelation properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) (a) Prince, R. B.; Okada, T.; Moore, J. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 233. (b) Prince, R. B.; Barnes, S. A.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 2758. (c) Organo, V. G.; Rudkevich, D. M. *Chem. Commun.* **2007**, 3891. (d) Tan, C.; Pinto, M. R.; Kose, M. E.; Ghiviriga, I.; Schanze, K. S. *Adv. Mater.* **2004**, *16*, 1208. (e) Tanatani, A.; Mio, M. J.; Moore, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 1792.

(2) Block, M. A. B.; Kaiser, C.; Khan, A.; Hecht, S. *Top. Curr. Chem.* **2005**, *245*, 89.

(3) Dawn, S.; Dewal, M. B.; Sobransingh, D.; Paderes, M. C.; Wibowo, A. C.; Smith, M. D.; Krause, J. A.; Pellechia, P. J.; Shimizu, L. S. *J. Am. Chem. Soc.* **2011**, *133*, 7025.

(4) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516.

(5) Ghadiri, M. R.; Granja, J. R.; Milligan, R. A.; McRee, D. E.; Khazanovich, N. *Nature* **1993**, *366*, 324.

(6) Ikeda, A.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2375.

(7) (a) Wegner, G. *Z. Naturforsch., B: J. Chem. Sci.* **1969**, *24*, 824. (b) Wegner, G. *Makromol. Chem.* **1972**, *154*, 35.

(8) (a) Hisaki, I.; Sakamoto, Y.; Shigemitsu, H.; Tohnai, N.; Miyata, M. *Cryst. Growth. Des.* **2009**, *9*, 414. (b) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294. (c) Suzuki, M.; Comito, A.; Khan, S. I.; Rubin, Y. *Org. Lett.* **2010**, *12*, 2346. (d) Nishinaga, T.; Nodera, N.; Miyata, Y.; Komatsu, K. *J. Org. Chem.* **2002**, *67*, 6091.

(9) (a) Boese, R.; Matzger, A. J.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2052. (b) Haley, M. M.; Bell, M. L.; English, J. J.; Johnson, C. A.; Weakley, T. J. R. *J. Am. Chem. Soc.* **1997**, *119*, 2956. (c) Nomoto, A.; Sonoda, M.; Yamaguchi, Y.; Ichikawa, T.; Hirose, K.; Tobe, Y. *J. Org. Chem.* **2006**, *71*, 401.

(10) Baldwin, K. P.; Matzger, A. J.; Scheiman, D. A.; Tessier, C. A.; Vollhardt, K. P. C.; Youngs, W. J. *Synlett* **1995**, 1215.

(11) Cantin, K.; Rondeau-Gagné, S.; Néabo, J. R.; Daigle, M.; Morin, J.-F. *Org. Biomol. Chem.* **2011**, *9*, 4440.

(12) Néabo, J. R.; Tohoundjona, K. I. S.; Morin, J.-F. *Org. Lett.* **2011**, *13*, 1358.

(13) During the course of this study, Tamaoki and co-workers reported the formation of nanotubes from flexible, non-phenylacetylene macrocycles using UV irradiation. See: Nagasawa, J.; Yoshida, M.; Tamaoki, N. *Eur. J. Org. Chem.* **2011**, 2247.

(14) Xu, Y.; Smith, M. D.; Geer, M. F.; Pellechia, P. J.; Brown, J. C.; Wibowo, A. C.; Shimizu, L. S. *J. Am. Chem. Soc.* **2010**, *132*, 5334.

(15) Hsu, T.-J.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **2012**, *134*, 142.

(16) Xie, H.; Zhang, S.; Li, H.; Zhang, X.; Zhao, S.; Xu, Z.; Song, X.; Yu, X.; Wang, W. *Chem.—Eur. J.* **2012**, *18*, 2230.

(17) Zhang, P.; Wang, H.; Liu, H.; Li, M. *Langmuir* **2010**, *26*, 10183.

(18) (a) Balakrishnan, K.; Datar, A.; Zhang, W.; Yang, X.; Naddo, T.; Huang, J.; Zuo, J.; Yen, M.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 6576. (b) Shimura, H.; Yoshio, M.; Kato, T. *Org. Biomol. Chem.* **2009**, *7*, 3205.