Nanoscale Morphology of Bis(1-anthraquinoxy)glycols†

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The nanoscale morphologies on a series of new anthraquinone substitutes have been carried out. Among the substitutes, only bis[2-(1-anthraquinonoxy)-ethyl]ether in a mixture of dichloromethane/acetone (1/1) slowly forms uniform nanowires with 80-120 nm diameters. The same compound in a mixture of dichloromethane/tetrahydrofuran (1/1) slowly produces uniform nanobelts with 400-600 nm widths. Thus, both the spacer lengths and the solvent effects of the compounds are important factors for the formation of nanoscale morphologies. The nano patterns seem to be formed by the $\pi-\pi$ interactions between the anthraquinone moieties.

Key Words : 1-Anthraquinone substitutes, Morphology, Nanobelts, Nanowires, $\pi-\pi$ interaction

Introduction

One of main goals in the field of nanomaterials chemistry is the control of shape and dimensionality.[1-7] In particular, the ability to modulate a morphology by means of chemical triggers is of central importance in the recent development of advanced functional nanomaterials.[8-12] Unique morphologies from molecular building blocks promise to provide size- and shape-dependent materials with task-specific properties such as photo-electronic devices, pigments, ion exchangers, desicants, molecular recognizers, drug delivery system, biomimetics, and catalysts.[13-16] Facile methods on the formation of nano-/micro-morphology based on surface tension, capillary effects, electric and magnetic forces, and hydrophilic interactions have been developed and highly desired.[17-21] The low molecular weight organic compounds are interesting since they are tractable nanomaterials.[22,23] The noncovalent weak forces such as hydrogen bondings, $\pi-\pi$ stacking interactions, and van der Waals interactions have been used to form specific nanostructures.[24-28] Among various organic molecules, discotic molecules have been used as building blocks in self-assembled cylindrical shaped fibers.[29-31] The intermolecular noncovalent interactions in some anthraquinone derivatives have been known to be important factors in molecular bulk properties.[32-34] However, their formation of morphologies remains unexplored. Thus, in this paper, we report the morphologic patterns of anthraquinone derivatives dependent on solvents and time without intentional addition of any template. Some quinone substitutes have served as biological modulators, drugs[35] as well as electronically noninnocent ligands.[36]

Experimental

Materials. 1-Chloroanthraquinone was used after recrystallization from a mixture of dichloromethane and hexane. Tetrahydrofuran (THF) was distilled under nitrogen atmosphere from sodium and benzophenone. Other reagents and solvents were used as received. ^{1}H NMR spectra were recorded on a Varian Gemini 300 instrument. Infrared spectra were obtained in 5000-400 cm^{-1} range on a Perkin-Elmer 16F PC FT-IR spectrophotometer with samples prepared as KBr pellets. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed by using a Stanton Red Croft TG 100 with a scanning rate of 10 °C/min. Scanning electron microscope (SEM) images were obtained with a JEM 2011.

Synthesis of Bis[2-(1-anthraquinonoxy)ethyl]ether (1).[37] A solution of the diethylene glycol (10 mmol) in dry THF (10 mL) was added slowly to a suspension of sodium hydride (1 g, 25 mmol; 60% oil dispersion was thoroughly washed with dry THF) in THF (100 mL) under an argon atmosphere, and the mixture was refluxed for 1 h. After the mixture was cooled to room temperature, a solution of 1-chloroanthraquinone (20 mmol) in THF (100 mL) was added, and the mixture was refluxed for 48 h under an argon atmosphere. The solvent was evaporated to afford a solid residue. The residue was extracted with chloroform/water, and the organic phase was successively washed with water (3 × 100 mL). The solid product was dried over anhydrous magnesium sulfate. The yellow solid was purified by column chromatography on silica using dichloromethane/methanol (30:1). Yield. 65%. ^{1}H NMR ($CDCl_3$, $SiMe_4$, ppm): 8.18 (m, 4H, Ar), 7.94 (dd, 2H, Ar), 7.68 (m, 4H, Ar), 7.60 (t, 2H, Ar), 7.38 (dd, 2H, Ar), 4.38 (t, 4H, -OCH_2-), 4.21 (t, 4H, -OCH_2-). ^{13}C NMR ($CDCl_3$, $SiMe_4$, ppm): 183.6, 182.3, 160.0, 135.9, 135.3, 135.1, 134.5, 133.5, 132.8, 127.4, 126.9, 122.2, 120.4, 120.1, 70.4, 70.1. IR (KBr, cm^{-1}): 2872 (m), 1680 (s), 1264 (m).

Bis[2-(1-anthraquinonoxy)ethoxy]ethane (2). This compound was synthesized by above procedure using triethylene glycol instead of diethylene glycol. Yield 54%. ^{1}H NMR ($CDCl_3$, $SiMe_4$, ppm): 8.19 (m, 4H, Ar), 7.92 (dd, 2H, Ar), 7.70 (m, 4H, Ar), 7.63 (t, 2H, Ar), 7.33 (dd, 2H, Ar), 4.33 (t,

†Dedicated to Prof. Sang Chul Shim at Kyungpook National University for his the 65th birthday and his distinguished achievements in organometallic chemistry.

4H, -OCH_2-), 4.06 (t, 4H, -OCH_2-), 3.93 (s, 4H, -OCH_2-). ^{13}C NMR ($CDCl_3$, $SiMe_4$, ppm): 183.6, 182.3, 160.0, 135.9, 135.3, 135.1, 134.5, 133.5, 132.8, 127.4, 126.9, 122.2, 120.4, 120.1, 71.6, 69.9, 69.8. IR (KBr, cm^{-1}): 2874 (m), 1671 (s), 1267 (m).

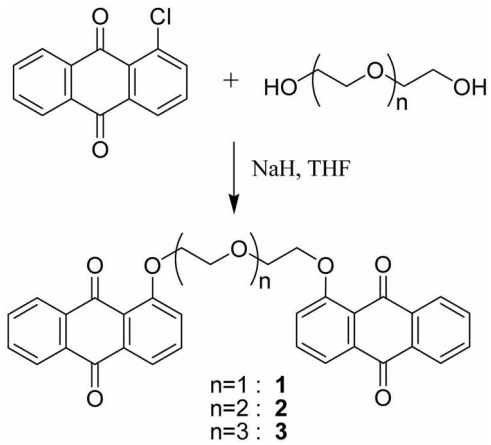
Bis[2-{2-(1-anthraquinonoxy)ethoxy]ethyl]ether (3). This compound was synthesized by above procedure using tetraethylene glycol instead of diethylene glycol. Yellow solid was obtained in 42% yield. ^1H NMR ($CDCl_3$, $SiMe_4$, ppm): δ = 8.20 (m, 4H, Ar), 7.93 (dd, 2H, Ar), 7.70 (m, 4H, Ar), 7.64 (t, 2H, Ar), 7.35 (dd, 2H, Ar), 4.31 (t, 4H, -OCH_2-), 4.02 (t, 4H, -OCH_2-), 3.86 (t, 4H, -OCH_2-), 3.73 (t, 4H, -OCH_2-). ^{13}C NMR ($CDCl_3$, $SiMe_4$, ppm): 183.6, 182.2, 159.9, 135.8, 135.2, 135.0, 134.4, 133.3, 132.7, 127.3, 126.8, 122.2, 120.4, 120.2, 71.4, 70.9, 70.5, 69.7. IR (KBr, cm^{-1}): 2889 (m), 1664 (s), 1260 (m).

2-(1-Anthraquinonoxy)ethoxyethanol (1-OH). This compound was synthesized by using 1-chloroanthraquinone and diethylene glycol in the mole ratio of 1:1. Yellow solid was obtained in 60% yield. ^1H NMR ($CDCl_3$, $SiMe_4$, ppm): 8.28 (m, 2H, Ar), 8.01 (dd, 1H, Ar), 7.79-7.73 (m, 3H, Ar), 7.37 (dd, 1H, Ar), 4.35 (t, 2H, -OCH_2-), 4.09 (t, 2H, -OCH_2-), 3.88-3.82 (m, 4H, -OCH_2-), 3.14 (m, 1H, -OH). ^{13}C NMR ($CDCl_3$, $SiMe_4$, ppm): 183.3, 182.9, 160.0, 136.1, 135.4, 135.1, 134.5, 13375, 132.9, 127.7, 127.0, 122.2, 120.6, 119.7, 72.9, 70.4, 70.1, 69.5. IR (KBr, cm^{-1}): 3495 (br), 2880 (m), 1675 (s), 1264 (m).

Formation of Morphologies. Dichloromethane solution (5 mM) of anthraquinone derivative **1** was prepared. Cosolvent of 1 mL was dropped carefully into the dichloromethane solution of 1 mL. The solutions were kept for 1-7 days. The morphologies were collected by the filtration using a membrane (membrane filter, Advantec MFS Inc.) for further characterization. The precipitation products were carefully dried in vacuum at the room temperature.

Results and Discussion

Reactions of the corresponding glycols with 1-chloroanthaquinone smoothly produce the desired products as depicted in Scheme 1. Their compositions and structures



Scheme 1

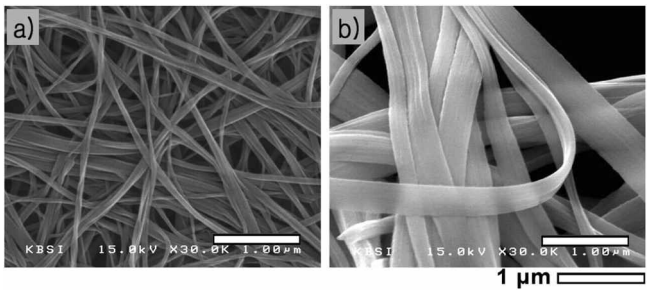


Figure 1. Solvent-dependent SEM images of **1** in CH_2Cl_2/acetone(1/1) (a: nanowires) and CH_2Cl_2/THF(1/1) (b: nanobelts).

were confirmed by chemical analysis, IR, ^1H NMR, and ^{13}C NMR. The pure products were isolated from column chromatography. The solid products are very soluble in N,N-dimethylformamide, dimethylsulfoxide, chloroform, and dichloromethane, but are insoluble in hexane and water. The products are much less soluble in organic solvents such as acetone, tetrahydrofuran, methanol, and ethanol than in N,N-dimethylformamide, dimethylsulfoxide, chloroform, and dichloromethane. All products are consistent with their chemical analysis, and stable even in solutions.

The morphologies of the products were slowly formed from a mixture of solvents, and observed by SEM images as shown in Figure 1. The morphology pattern of each product indicates that the organic spacer length is one of important factors in the formation of morphologies. For **1**, the nanowires with 80-120 nm diameters were self-assembled within 7 days in a mixture of dichloromethane/acetone (1/1). The lengths of nanowires are infinitive. In order to confirm the solvent effects in the formation of the morphology, **1** in a mixture of dichloromethane/tetrahydrofuran (1/1) solution has been accomplished. The compound **1** in the solvent pair slowly gives uniform nanobelts with 400-600 nm width. Thus, the difference as shown in the SEM images shows significant solvent effects on the formation of morphology. A combination of π–π interaction between intermolecular anthraquinone moieties and delicate solvent effects may be a driving force for the formation of the nano morphologiese. The compounds **2** and **3** with long glycol spacers failed to form such nanowires or nanobelts (Supporting Information). Instead, for **2** and **3**, irregular shapes were formed. These results support that the flexibility of the long chain aliphatic spacers is an obstacle to form the π–π interaction. Furthermore, mono substituted analogue, **1**-OH afforded single crystal instead of the nanowires. As expected, the mono substitute is also unfavorable in the intermolecular π–π interaction. These results support that the π–π interaction play an important role in the formation of the nano morphologies.

In order to confirm the formation mechanism of the nanowires, the nanowires were immersed into the same solution for 30 days. As a result, new wires begin to sprout at the end of original nanowires as shown in Figure 2. The nanowire lengths increase as the time goes in the same solution. Of course, the diameter did not increase signifi-

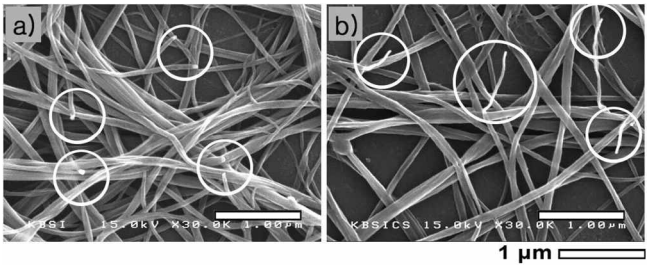


Figure 2. SEM images (CH_2Cl_2/MeOH; 1/1) showing the appearance of new nanowires at the end of original nannowires after 7 days (a) and 30 days (b).

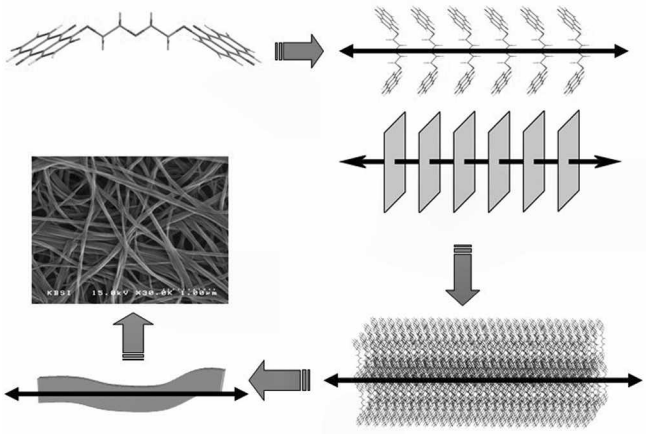


Figure 3. A proposed formation process of nanowires of **1** with the most stable conformations of **1** modeled from Chem3D Ultra (MM2).

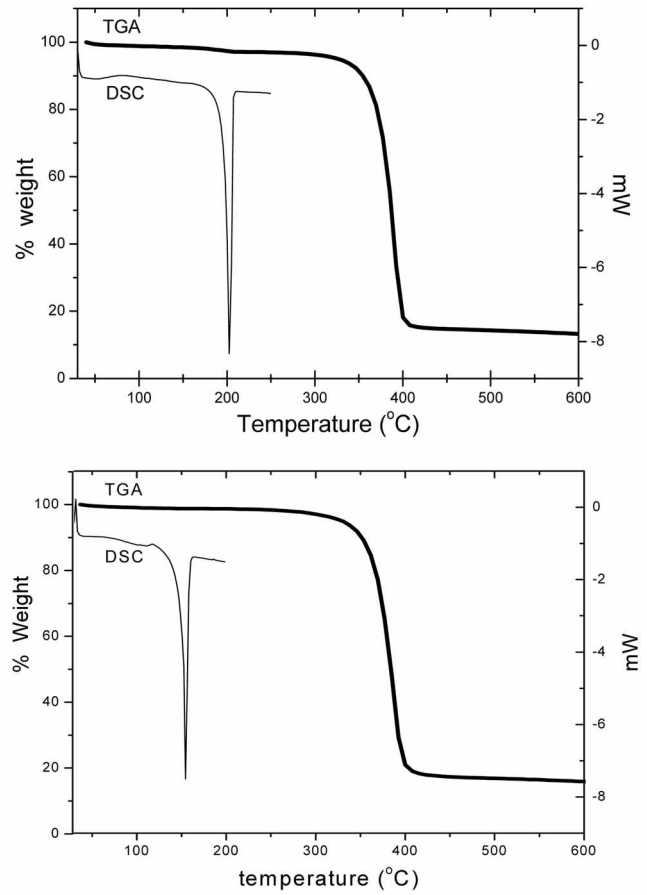


Figure 4. DSC and TGA thermograms of **1** (a) and **3** (b).

cantly. Such a result supports the plausible growing process of the nanowires. That is, the lengths of nanowires grow via the π–π stacking interaction between intermolecular anthraquinone-anthraquinone. For the analogues with long aliphatic spacers (**2**, **3**), the intermolecular π–π interaction seems to be unfavorable owing to the pliable conformation of the long chain.

The thermogravimetric analysis (TGA) shows that the compounds are thermally stable up to 350 °C (Figure 4). According to the differential scanning calorimetry (DSC) curve, melting points are strongly dependent upon the pliable chain lengths. **1** melts at 200 °C while **3** melts at 158 °C. The low melting point of the long chain compound seems to be related to the flexibility of the long chain. This is consistent with the low possibility of the intermolecular π–π interaction. The explainable TGA and DSC curves support that the nanowire is composed of pure compound rather than composite. Remaining quantity (15 wt %) after 400 °C may be attributed to the formation of black tar.

In conclusion, the present results show that the bis-(anthraquinone) derivatives are good tectonics for nanowires or nanobelts presumably *via* the π–π stacking interaction between intermolecular anthraquinone moieties. Uniform nanowires are slowly formed in a mixture of organic solvents without intentional addition of any template, that is, a genuine self-assembly. Self-assembly of the nanomaterials is dependent upon the solvents. Thus, further experiments on the superstructure with hydrophilic surface will provide more useful information on the formation of enormous nano morphology that are useful to weaving materials, drug delivery system, adsorber/desorber, and surface-reformer.

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References

1. Chun, I. S.; Kwon, J. A.; Yoon, H. J.; Bae, M. N.; Hong, J.; Jung, O.-S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4960.
2. Chun, I. S.; Lee, K. S.; Hong, J.; Do, Y.; Jung, O.-S. *Chem. Lett.* **2007**, *36*, 548.
3. Yoon, H. J.; Chun, I. S.; Na, Y. M.; Lee, Y.-A.; Jung, O.-S. *Chem. Commun.* **2007**, 492.
4. Chan, E. M.; Mathies, R. A.; Alivisatos, A. P. *Nano Lett.* **2003**, *3*, 199.
5. Liu, H.; Li, Y.; Jiang, L.; Luo, H.; Xiao, S.; Fang, H.; Li, H.; Zhu, D.; Yu, D.; Xu, J.; Xiang, B. *J. Am. Chem. Soc.* **2002**, *124*, 13370.
6. Jonkheijm, P.; Stutzmann, N.; Chen, Z.; de Leeuw, D. M.; Meijer, E. W.; Schenning, A. P. H. J.; Wurthner, F. *J. Am. Chem. Soc.* **2006**, *128*, 9535.
7. Iwaura, R.; Hoeben, F. J. M.; Masuda, M.; Schenning, A. P. H. J.; Meijer, E. W.; Shimizu, T. *J. Am. Chem. Soc.* **2006**, *128*, 13298.
8. Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353.
9. Liu, B.; Zeng, C. *J. Am. Chem. Soc.* **2004**, *126*, 8124.
10. Colfen, H.; Mann, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 2350.

11. Velikov, K. P.; Christova, C. G.; Dullens, R. P. A.; van Blaaderen, A. *Science* **2002**, *296*, 106.
12. Yu, S.-H.; Cölfen, H. *J. Mater. Chem.* **2004**, *14*, 2124.
13. Sun, X. M.; Li, Y. D. *Chem.-Eur. J.* **2003**, *9*, 2229.
14. Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393.
15. Peng, Q.; Dong, Y. S.; Li, Y. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 3027.
16. Shi, H. T.; Qi, L. M.; Ma, J. M.; Cheng, H. M. *J. Am. Chem. Soc.* **2003**, *125*, 3450.
17. Witesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.
18. Yu, S.-H.; Cölfen, H.; Antonietti, M. *J. Phys. Chem. B* **2003**, *107*, 7396.
19. Busch, S.; Dolhaine, H.; DuChesne, A.; Heinz, S.; Hochrein, O.; Laeri, F.; Podebrad, O.; Vietze, U.; Weiland, T.; Knief, R. *Eur. J. Inorg. Chem.* **1999**, 643.
20. Mann, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3392.
21. Sun, X.; Dong, S.; Wang, E. *J. Am. Chem. Soc.* **2005**, *127*, 13102.
22. Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133.
23. Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237.
24. Palmans, A. R. A.; Vekeman, A. J. M.; Hikmet, R. A.; Fischer, H.; Meijer, E. W. *Adv. Mater.* **1998**, *10*, 873.
25. Chang, J. Y.; Yeon, J. R.; Shin, Y. S.; Han, M. J.; Hong, S.-K. *Chem. Mater.* **2000**, *12*, 1076.
26. Bushey, M. L.; Nguyen, T.-Q.; Zhang, W.; Horoszewski, D.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5546.
27. Sakamoto, A.; Ogata, D.; Shikata, T.; Hanabusa, K. *Macromolecules* **2005**, *38*, 8983.
28. Brunsveld, L.; Schenning, A. P. H. J.; Broeren, M. A. C.; Janssen, H. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Lett.* **2000**, 292.
29. Van Gorp, J. J.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2002**, *124*, 14759.
30. Ishi-i, T.; Yaguma, K.; Kuwahara, R.; Taguri, Y.; Mataka, S. *Org. Lett.* **2006**, *8*, 585.
31. De Feyter, S.; Miura, A.; Yao, S.; Chen, Z.; Wurthner, F.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W.; De Schryver, F. C. *Nano Lett.* **2005**, *5*, 77.
32. Liu, H.; Li, Y.; Xiao, S.; Li, H.; Jiang, L.; Zhu, D.; Xiang, B.; Chen, Y.; Yu, D. *J. Phys. Chem. B* **2004**, *108*, 7744.
33. Walter, D.; Neuhauser, D.; Roi, B. *Chem. Phys.* **2004**, *299*, 139.
34. Shklyarevskiy, I. O.; Jonkheijm, P.; Christianen, P. C. M.; Schenning, A. P. H. J.; Del Guerzo, A.; Desvergne, J.-P.; Meijer, E. W.; Maan, J. C. *Langmuir* **2005**, *21*, 2108.
35. Kogan, N. M.; Rabinowitz, R.; Levi, P.; Gibson, D.; Sandor, P.; Schlesinger, M.; Mechoulam, R. *J. Med. Chem.* **2004**, *47*, 3800.
36. Hui, L.; Cha, M. S.; Lee, Y.-A.; Lee, S. S.; Jung, O.-S. *Inorg. Chem. Commun.* **2006**, *10*, 71.
37. Fang, J. P.; Lu, T.; Kim, H.; Delgado, I.; Geoffroy, P.; Atwood, J. L; Gokel, G. W. *J. Org. Chem.* **1991**, *56*, 7059.