J|A|C|S
ARTICLES

Formation of Water-Dispersible Nanotubular Graphitic Assembly Decorated with Isothiouronium Ion Groups and Its Supramolecular Functionalization

Guanxin Zhang,† Wusong Jin,† Takanori Fukushima,*,†,‡ Atsuko Kosaka,†
Noriyuki Ishii,§ and Takuzo Aida*,†,‡

Contribution from the ERATO-SORST Nanospace Project, Japan Science and Technology Agency (JST), National Museum of Emerging Science and Innovation, 2-41 Aomi, Koto-ku, Tokyo 135-0064, Japan, Department of Chemistry and Biotechnology, School of Engineering, and Center for NanoBio Integration, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Biological Information Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central-6, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8566, Japan

Received October 5, 2006; E-mail: fukushima@nanospace.miraikan.jst.go.jp; aida@macro.t.u-tokyo.ac.jp

Abstract: A newly designed Gemini-shaped hexabenzocoronene amphiphile (**1**), carrying an isothiouronium ion-appended side chain, self-assembles in CH_2Cl_2 to form a nanotubular object, whose graphitic wall is densely covered by a positively charged molecular layer of isothiouronium ion pendants. The graphitic nanotube can be dispersed uniformly in aqueous media owing to effective hydration as well as electrostatic repulsion. Post-supramolecular functionalization of the nanotube surface is possible, without disruption of the tubular morphology, by taking advantage of a specific interaction of the isothiouronium ion pendants with oxoanion guests. Mixing with sodium poly(4-styrenesulfonate) results in wrapping of the nanotube, while complexation with an electron-accepting oxoanion such as anthraquinone carboxylate allows photoinduced electron transfer from the graphitic wall to the bound guest molecules.

Introduction

Self-assembled π-electronic nano-objects[1] with post-functionalizable surface groups via noncovalent interactions are expected to serve as potential scaffolds for the ultimate molecular design of finely integrated electronic and optoelectronic materials.[2] To achieve this goal, the nano-objects must be sufficiently robust to allow the accommodation of a guest without structural disruption. Furthermore, proper choice of surface groups that enable selective noncovalent interactions is essential. However, such π-electronic molecular assemblies that fulfill the above requisites are very rare.[3] Here, we report successful formation of a hexa-*peri*-hexabenzocoronene (HBC) graphitic nanotube[4] with isothiouronium ion surface pendants (Figure 1) that can be functionalized without disruption by oxoanion guests via a specific hydrogen-bonding interaction.[5,6] HBC[7] is one of the representatives of polycyclic aromatic hydrocarbons that attracts considerable attention, since they tend to form columnar assemblies important for electronic and optoelectronic applications.[8] Müllen and co-workers are

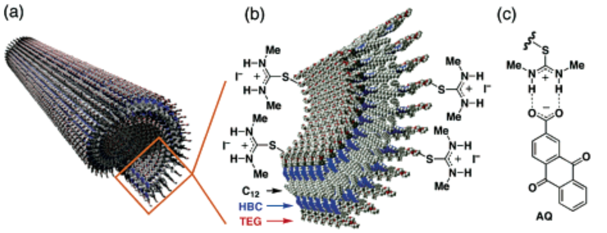


Figure 1. Schematic illustrations of (a) the graphitic nanotube from HBC **1** and (b) its bilayer wall (C_{12}; dodecyl chain), and (c) a possible binding mechanism for the complexation with AQ.

---

† JST.
‡ The University of Tokyo.
§ AIST.

(1) For recent reviews, see: (a) Simpson, C. D.; Wu, J.; Watson, M. D.; Müllen, K. *J. Mater. Chem.* **2004**, *14*, 494−504. (b) Würthner, F. *Chem. Commun.* **2004**, 1564−1579. (c) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491−1546. (d) Elemans, J. A. A. W.; van Hameren, R.; Nolte, R. J. M.; Rowan, A. E. *Adv. Mater.* **2006**, *18*, 1251−1266.

(2) For recent reviews, see: (a) Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378−4400. (b) Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2005**, 3245−3258.

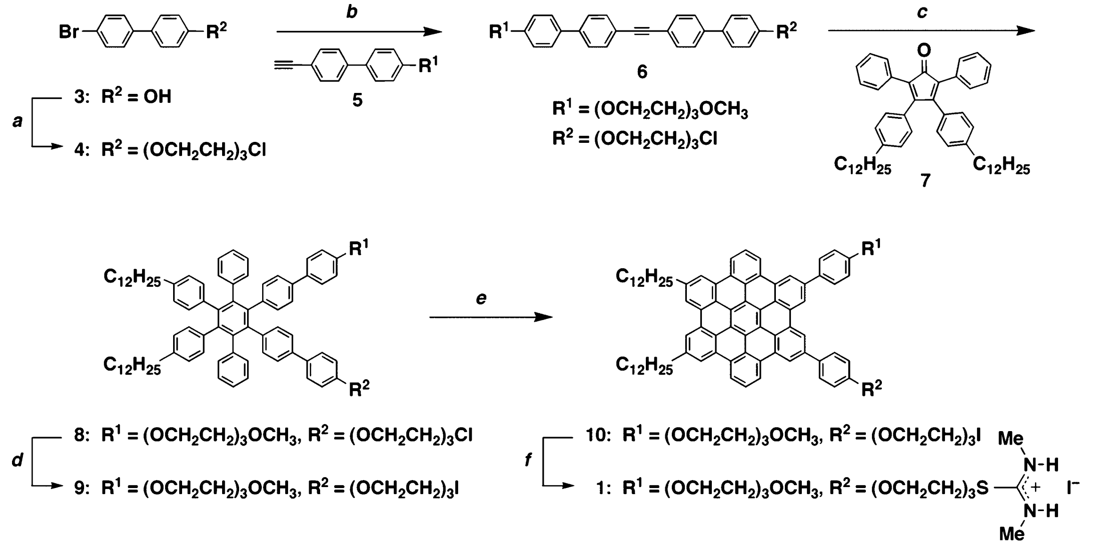
(3) Praveen, V. K.; George, S. J.; Varghese, R.; Vijayakumar, C.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2006**, *128*, 7542−7550.

(4) (a) Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. *Science* **2004**, *304*, 1481−1483. (b) Jin, W.; Fukushima, T.; Niki, M.; Kosaka, A.; Ishii, N.; Aida, T. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10801−10806. (c) Jin, W.; Fukushima, T.; Kosaka, A.; Niki, M.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 8284−8285. (d) Motoyanagi, J.; Fukushima, T.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 4220−4221. (e) Motoyanagi, J.; Fukushima, T.; Kosaka, A.; Ishii, N.; Aida, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5120−5127. (f) Yamamoto, T.; Fukushima, T.; Yamamoto, Y.; Kosaka, A.; Jin, W.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 14337−14340. (g) Yamamoto, Y.; Fukushima, T.; Jin, W.; Kosaka, A.; Hara, T.; Nakamura, T.; Saeki, A.; Seki, S.; Tagawa, S.; Aida, T. *Adv. Mater.* **2006**, *18*, 1297−1300.

(5) For recent reviews, see: (a) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*; The Royal Society of Chemistry: Cambridge, 2006. (b) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419−4476. (c) Best, M. D.; Tobey, S. L.; Anslyn, E. V. *Coord. Chem. Rev.* **2003**, *240*, 3−15.

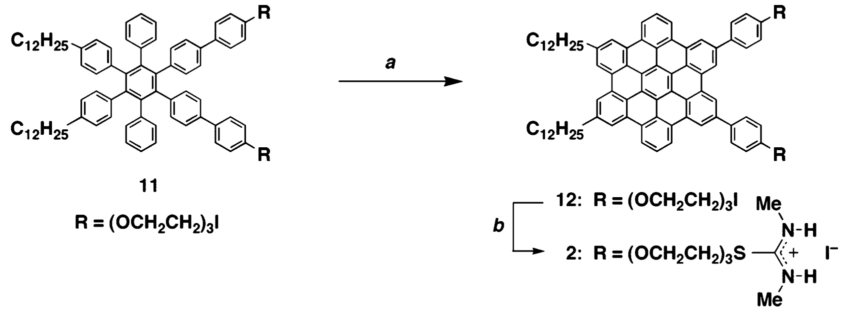
10.1021/ja0671518 CCC: $37.00

Scheme 1. Synthesis of Isothiouronium Ion-Appended HBC **1**[a]



[a] (a) 2-[2-(2-Chloroethoxy)ethoxy]ethyl *p*-toluenesulfonate, K_2CO_3, 18-crown-6, DMF, 60 °C, 90%; (b) $PdCl_2(PPh_3)_2$, CuI, DBU, benzene, 60 °C, 42%; (c) Ph_2O, reflux, 22%; (d) NaI, acetone, reflux, 86%; (e) $FeCl_3$, $MeNO_2$, CH_2Cl_2, 25 °C, 46%; (f) 1,3-dimethylthiourea, THF, reflux, 77%.

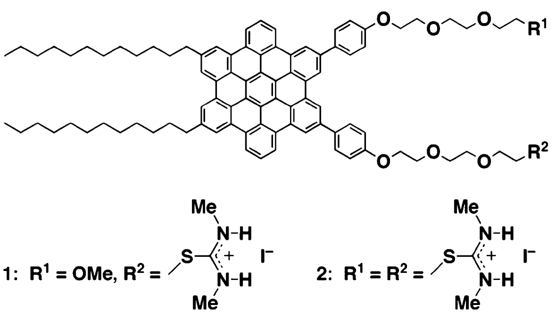
Scheme 2. Synthesis of Isothiouronium Ion-Appended HBC **2**[a]



[a] (a) $FeCl_3$, $MeNO_2$, CH_2Cl_2, 25 °C, 61%; (b) 1,3-dimethylthiourea, THF, reflux, 52%.

pioneers in columnar assemblies of HBC derivatives with paraffinic side chains[9] that display anisotropic carrier transport properties.

Recently, we have reported the formation of graphitic nanotubes by controlled self-assembly of HBC-based nonionic amphiphiles, where a graphitic bilayer wall consisting of π-stacked HBC is covered by densely packed triethylene glycol (TEG) chains.[4] On the basis of this approach, surface-modified graphitic nanotubes are available by self-assembly of HBC amphiphiles carrying end-functionalized TEG chains.[4c−f] However, such a covalent molecular design strategy always requires time-consuming optimization of self-assembling conditions to ensure the formation of nanotubular structures. In this sense, noncovalent, post-functionalization of preformed nanotubes is considered to be more advantageous for diversifying



the range of available functional groups. In the present work, we designed isothiouronium ion-appended HBC amphiphiles **1** and **2**, since the guanidinium ion family are known to bind a variety of oxoanions.[5,6] Fortunately, compound **1** formed

---

(6) (a) Yeo, W.-S.; Hong, J.-I. *Tetrahedron Lett.* **1998**, *39*, 3769−3772. (b) Kubo, Y.; Tsukahara, M.; Ishihara, S.; Tokita, S. *Chem. Commun.* **2000**, 653−654. (c) Kubo, Y.; Ishihara, S.; Tsukahara, M.; Tokita, S. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1455−1460. (d) Nishizawa, S.; Cui, Y.-Y.; Minagawa, M.; Morita, K.; Kato, Y.; Taniguchi, S.; Kato, R.; Teramae, N. *J. Chem. Soc., Perkin Trans. 2* **2002**, 866−870. (e) Kato, Y.; Nishizawa, S.; Teramae, N. *Org. Lett.* **2002**, *4*, 4407−4410. (f) Kato, R.; Cui, Y.-Y.; Nishizawa, S.; Yokobori, T.; Teramae, N. *Tetrahedron Lett.* **2004**, *45*, 4273−4276.

(7) Clar, E.; Ironside, C. T.; Zander, M. *J. Chem. Soc.* **1959**, 142−147.

(8) (a) Boden, N.; Bushby, R. J.; Clements, J.; Movaghar, B.; Donovan, K. J.; Kreouzis, T. *Phys. Rev. B* **1995**, *52*, 13274−13280. (b) van de Craats, A. M.; Warman, J. M.; Fechtenkötter, A.; Brand, J. D.; Harbison, M. A.; Müllen, K. *Adv. Mater.* **1999**, *11*, 1469−1472. (c) Kreouzis, T.; Donovan, K. J.; Boden, N.; Bushby, R. J.; Lozman, O. R.; Liu, Q. *J. Chem. Phys.* **2001**, *114*, 1797−1802. (d) van de Craats, A. M.; Stutzmann, N.; Bunk, O.; Nielsen, M. M.; Watson, M.; Müllen, K.; Chanzy, H. D.; Sirringhaus, H.; Friend, R. H. *Adv. Mater.* **2003**, *15*, 495−499. (e) O'Neill, M.; Kelly, S. M. *Adv. Mater.* **2003**, *15*, 1135−1146.

(9) (a) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1785. (b) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267−1300. (c) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119−1122. (d) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592−5629.

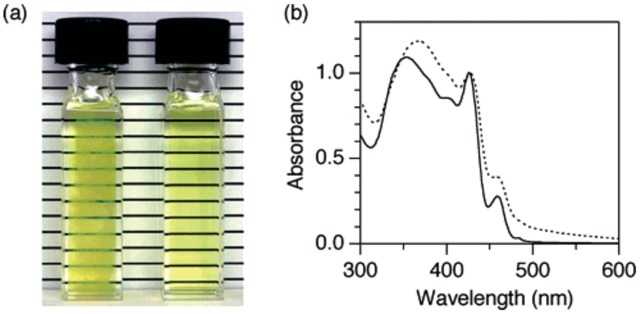


Figure 2. (a) Photograph of a CH_2Cl_2 suspension (left) and a water dispersion (right) of tubularly assembled **1**. (b) Electronic absorption spectra at 25 °C of an air-dried CH_2Cl_2 suspension (broken curve) and a water dispersion (2.5×10^{-5} M; solid curve) of tubularly assembled **1**. The spectra were normalized at 427 nm.

nanotubes that were highly dispersible in water, necessary for the uniform surface functionalization.

Results and Discussion

Isothiouronium ion-appended HBC amphiphile **1** was synthesized over six steps according to Scheme 1.[10] 2-[2-(2-Chloroethoxy)ethoxy]ethyl *p*-toluenesulfonate was allowed to react with **3** in DMF in the presence of K_2CO_3/18-crown-6-ether, yielding **4** in 90%. Sonogashira coupling reaction of **4** with biphenylacetylene **5** using $PdCl_2(PPh_3)_2$/CuI/DBU afforded **6** in 42% yield. The resultant unsymmetrical alkyne was subjected to Diels−Alder reaction with cyclopentadienone derivative **7**,[4b] giving hexaphenylbenzene **8** in 22% yield. Compound **8** was converted by the reaction with NaI into the corresponding iodide **9** in 86% yield. Oxidative cyclization of **9** by $FeCl_3$/$MeNO_2$ in CH_2Cl_2 resulted in the formation of HBC derivative **10** in 46% yield. This substance was allowed to react with 1,3-dimethylthiourea in THF, affording target compound **1** in 77% yield. Likewise, HBC amphiphile **2** was prepared over two steps from hexaphenylbenzene derivative **11**[4e] (Scheme 2).[10]

Compound **1**, a new class of ionically charged amphiphilic HBC, showed a much different solubility from previously reported nonionic versions. After many trials, we succeeded in obtaining a nanotubular object from **1** in CH_2Cl_2, which is a good solvent for other amphiphilic HBCs.[4] Thus, a CH_2Cl_2 suspension of **1** (1 mg/mL) was once heated to reflux, and the resulting hot solution was allowed to cool to 25 °C, whereupon a yellow suspension resulted (Figure 2a). Electronic absorption spectroscopy of an air-dried suspension showed a main absorption band at 366 nm with red-shifted absorption bands at 427 and 459 nm (Figure 2b), characteristic of tubularly assembled HBCs.[4] SEM and TEM micrographs revealed the formation of a nanotubular assembly with a uniform diameter of 18 nm and a wall thickness of 3 nm (Figure 3a,b). The observed dimensions of the nanotube are quite similar to those of previously reported nanotubular objects from nonionic HBC amphiphiles.[4] Infrared spectroscopy of a cast film of the nanotubes displayed CH_2 stretching vibration bands at 2917 (υ_{anti}) and 2848 cm^{-1} (υ_{sym}),[10] indicating that the dodecyl chains of **1** are stretched to form a crystalline domain by interdigitation. Moreover, a solid sample of tubularly assembled **1** exhibited an X-ray diffraction peak at $2\theta = 25.8°$,[10] assignable to a regularly stacked HBC with a *d* spacing of 3.45 Å.

In contrast with **1**, HBC amphiphile **2** possessing two isothiouronium groups has an extremely low solubility. It was hardly soluble in CH_2Cl_2 even upon heating. Exceptionally, a hot water/THF mixture (1:1 v/v) was able to solubilize **2**. However, cooling of this hot solution resulted in the formation of nontubular, ill-defined fibrous aggregates (Figure 3c,d).

Of interest, tubularly assembled **1** was finely dispersed in water at 25 °C, where component **1**, in contrast, was insoluble even under reflux. Thus, a CH_2Cl_2 suspension of the nanotubes (1 mg/mL, 1 mL) was centrifuged at 25 °C, and the resulting solid substance was subjected to immersion in MeCN (2 mL) followed by centrifugation. After the repetition of this solvent-

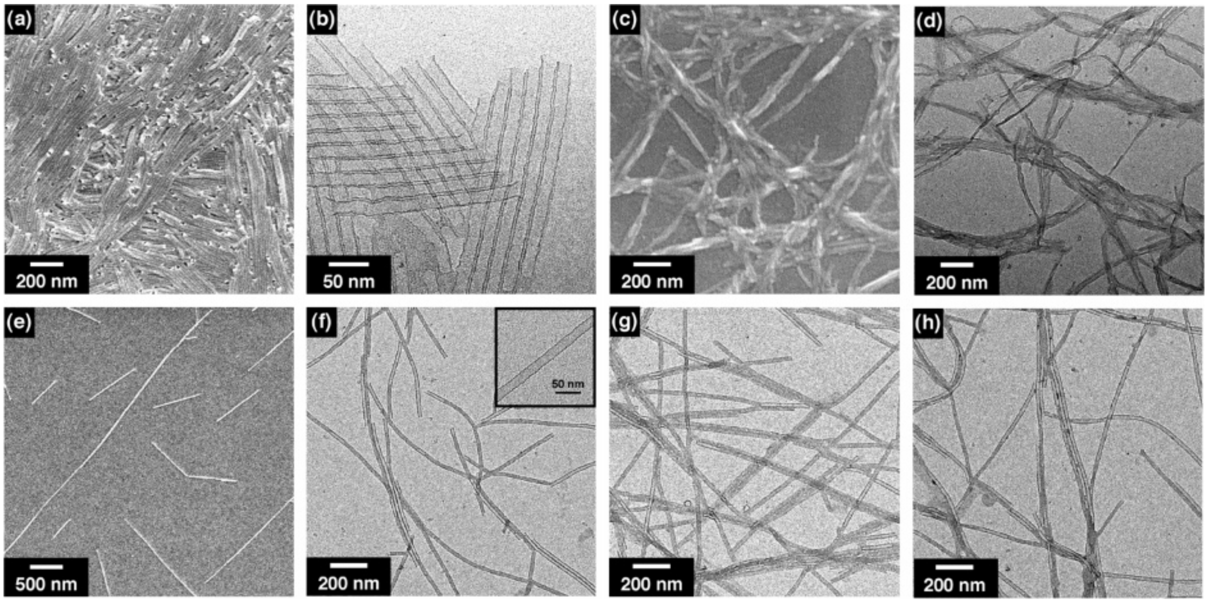


Figure 3. (a) SEM and (b) TEM micrographs of an air-dried CH_2Cl_2 suspension of tubularly assembled **1**. (c) SEM and (d) TEM micrographs of an air-dried suspension, formed upon cooling a hot water/THF (1:1 v/v) solution of **2** from 60 to 25 °C. (e) SEM and (f) TEM micrographs of an air-dried water dispersion of tubularly assembled **1** obtained by solvent exchange of CH_2Cl_2 with water. (g) TEM micrograph of an air-dried suspension, formed by mixing tubularly assembled **1** and PSS at a ratio [**1**]/[SO_3^-] of 1:2 in water. (h) TEM micrograph of an air-dried sample of a water/MeCN (1:1 v/v) dispersion of tubularly assembled **1** containing AQ at a ratio [**1**]/[AQ] of 1:6.

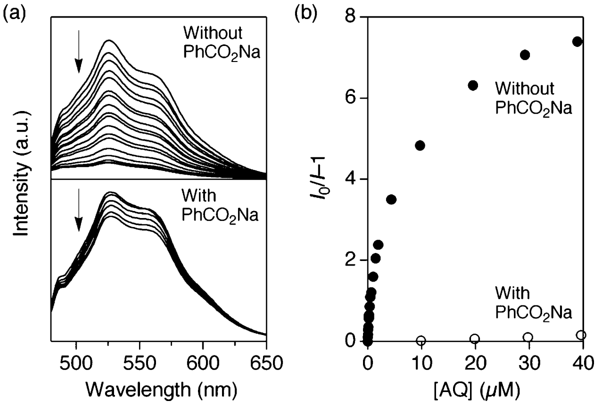


Figure 4. Fluorescence quenching of tubularly assembled **1** (11 μM) upon titration with AQ in water/MeCN (1:1 v/v) at 25 °C. (a) Fluorescence spectral changes and (b) their Stern−Volmer plots upon excitation at 427 nm in the absence ([AQ] = 0, 0.02, 0.03, 0.07, 0.10, 0.17, 0.21, 0.35, 0.49, 0.63, 0.97, 1.5, 1.9, 4.4, 9.7, 19, 29, 39 μM) and presence ([AQ] = 0, 10, 20, 30, 40, 50 μM) of sodium benzoate (220 μM).

exchange treatment, deionized water (2 mL) was added to the residue, whereupon a yellow-colored, transparent solution resulted (Figure 2a). Electronic absorption spectroscopy of this solution showed red-shifted absorption bands due to π-stacked HBCs (Figure 2b), whose maxima are the same as those observed for the nanotube formed in CH_2Cl_2. By means of TEM microscopy (Figure 3f), we found that the dimensions of the nanotube in water are nearly identical to those in CH_2Cl_2. SEM microscopy of an air-dried water dispersion clearly displayed that the individual nanotubes are well separated from one another (Figure 3e). Considering the fact that all the precedent nanotubes from nonionic HBC amphiphiles tend to form thick bundles,[4] this observation is remarkable and indicates that effective hydration of the positively charged surface pendants as well as their electrostatic repulsion should play an essential role in the dispersion of the nanotubes in water.

By taking advantage of a specific interaction of the isothiouronium ion pendants with oxoanions,[5,6] post surface functionalization of the uniformly dispersed nanotubes is possible. For example, by using a polymer having multiple oxoanion groups such as sodium poly(4-styrenesulfonate) (PSS), we demonstrated noncovalent surface stitching[4c−f] of tubularly assembled **1**. Thus, an aqueous dispersion of the nanotube (2.5×10^{-5} M, 80 mL) was mixed with an aqueous solution of PSS (5.4×10^{-3} M, 0.74 mL), whereupon a yellow precipitate formed. TEM microscopy of an air-dried suspension revealed that the included nanotubes preserve their morphology without disruption (Figure 3g). Even though the precipitate, collected by filtration, was washed thoroughly with water, a good solvent for PSS, the resulting solid still contained PSS. Infrared spectroscopy[10] showed vibration bands characteristic of phenyl sulfonate at 1038 and 1008 cm^{-1},[11] along with those due to tubularly assembled **1**. The PSS/nanotube composite, thus formed, was no longer soluble in common organic solvents including $CHCl_3$ and THF, where unstitched nanotubes are readily disrupted by dissociation. The successful noncovalent stitching is due to a multivalent interaction of the isothiouronium ion-appended nanotube with PSS.

Not only such a polymeric compound with multiple oxoanion groups but also guest molecules with a single oxoanion functionality such as sodium anthraquinone-2-carboxylate (AQ; Figure 1c) are able to bind to the nanotube surface. As observed by TEM microscopy (Figure 3h), the nanotubular morphology remained unchanged upon complexation with AQ. Excitation of the nanotubes (1.1×10^{-5} M) in water/MeCN (1:1 v/v)[12] at 427 nm resulted in a fluorescence emission at 526 nm with a shoulder at 562 nm. On the other hand, upon titration with AQ, the fluorescence intensity of the nanotubes decreased monotonically at the initial stage and leveled off later (Figure 4a). This observation indicates the occurrence of a static quenching as the consequence of a long-range photoinduced electron transfer from the HBC units in the graphitic tubular wall to surface-bound AQ molecules. The Stern−Volmer constant (K_{SV}), as determined from the initial fluorescence intensity change at 526 nm, was 3.3×10^6 M^{-1} (Figure 4b). As expected, the fluorescence quenching by AQ was significantly less explicit ($K_{SV} = 3.7 \times 10^3$ M^{-1}) in the presence of a large excess of sodium benzoate (20 equiv) as a competitive oxoanion without electron-accepting capability (Figure 4). While the guanidinium ion family in aqueous media hardly forms stable 1:1 complexes with oxoanions, those aligned on vesicular surfaces or liquid−liquid interfaces have been reported to capture oxoanions strongly.[13] Thus, the notably large K_{SV} value in the absence of sodium benzoate justifies our expectation that AQ molecules can be tightly trapped on the nanotube surface by the densely aligned isothiouronium ion groups.

Conclusions

In conclusion, incorporation of an isothiouronium ion end group into one of the TEG chains of the amphiphilic HBC did not hamper its nanotubular self-assembly. The resultant nanotube was highly dispersible in water and displayed a sufficient structural robustness despite possible electrostatic repulsions among the surface pendants. Therefore, this new graphitic nanotube may serve as a promising electroactive nanoscaffold via post-functionalization with a wide variety of oxoanion guests.

Supporting Information Available: Details of synthesis and characterization of **1** and **2**, infrared spectra, and X-ray diffraction pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0671518

---

(10) See Supporting Information.

(11) Weiss, R. A.; Sen, A.; Willis, C. L.; Pottick, L. A. *Polymer* **1991**, *32*, 1867−1874.

(12) To avoid solubility problems of AQ and the resulting composite, water/MeCN (1:1 v/v) was employed in place of water.

(13) (a) Ariga, K.; Kunitake, T. *Acc. Chem. Res.* **1998**, *31*, 371−378. (b) Sakai, N.; Matile, S. *J. Am. Chem. Soc.* **2003**, *125*, 14348−14356.