Bull. Chem. Soc. Jpn. Vol. 81, No. 6, 754–756 (2008)

Study on Facile Synthesis, Crystal Structure, and Solid-State Fluorescence of Dicyclohexane-Annelated Anthracene

Chitoshi Kitamura,*[1] **Chika Matsumoto,**[1]
Nobuhiro Kawatsuki,[1] **Akio Yoneda,**[1]
Kohei Asada,[2] **Takashi Kobayashi,**[2]
and Hiroyoshi Naito[2]

[1]Department of Materials Science and Chemistry,
Graduate School of Engineering, University of Hyogo,
2167 Shosha, Himeji 671-2280

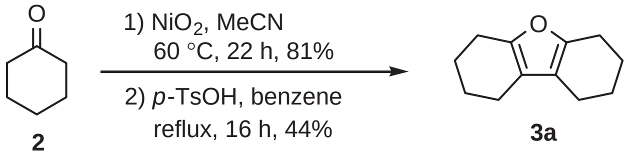
[2]Department of Physics and Electronics,
Graduate School of Engineering,
Osaka Prefecture University,
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531

Received October 23, 2007; E-mail: kitamura@eng.u-hyogo.ac.jp

Dicyclohexane-annelated anthracene was synthesized by a new efficient method, which employed the Diels–Alder reaction between in situ-generated 2,3-dehydronaphthalene and dicyclohexane-fused furan. The molecule adopted anti-parallel face-to-face slipped π-stacking in its crystal structure, which induced an excimer-like emission in the solid state.

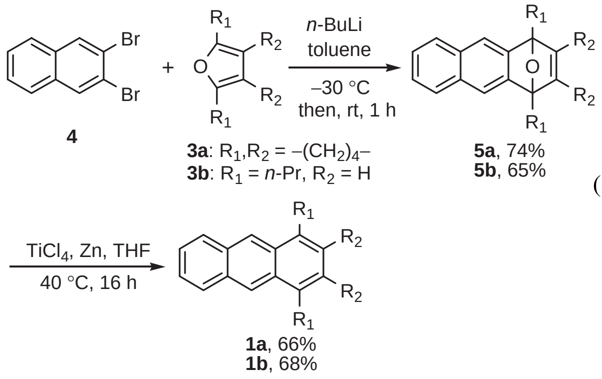
The design and synthesis of organic materials that can fluoresce in the solid state received considerable attention because of their promising applications, such as light-emitting diodes and solar cells.[1] Solid-state packing effects are now being recognized as critical factors for understanding fluorescence properties such as spectral shape and quantum efficiency.[2–6] However, molecular design for controlling solid-state fluorescence is not completely understood;[5] therefore, this topic will be discussed in the following sections. Anthracene is a representative member of fluorophores. For example, solid-state fluorescence studies concerning chain-bridged anthracene derivatives,[7] organic salts of anthracene-2,6-disulfonic acid with amines,[4] and supramolecular complexes of anthracene–resorcinol hosts with guest molecules[8] have been reported. Recently, we prepared a high-symmetry structure of 1,4,5,8-tetraalkylanthracenes,[9] where alkyl substituents varied from methyl to hexyl. In addition, we elucidated the relationship between the fluorescence properties in the solid state and the corresponding packing patterns. Then, we demonstrated that the alkyl chains can act as spacers and modulate the intermolecular distance and position between anthracene cores. To further investigate the substituent effect on the solid-state fluorescence, we studied the low-symmetry structure of anthracenes. We planned to synthesize some 1,4-disubstituted anthracene derivatives. 1,2,3,4,5,6,7,8-Octahydrodibenz[*a*,*c*]anthracene (**1a**) as well as 1,4-dialkylanthracene were selected as target molecules. The former can be ascribed to an extended 1,4-dialkylanthracene, which has two cyclohexane rings annelated to anthracene. Anthracene **1a** was first prepared by Lawrence et al. in 1935 by a classical anthracene synthesis method in five steps that involves a Friedel–Crafts reaction between phthalic anhydride and octahydrophenanthrene.[10] However, detailed description of the experimental procedure was not provided. In addition, although octahydrophenanthrene is commercially available, it is expensive, which reflects the difficulty in its preparation. To prepare the tetraalkylanthracenes mentioned above, we developed a new, efficient, and easily achievable synthetic approach, which involved the Diels–Alder reaction of dibenzyne and 2,5-disubstituted furans, and subsequent deoxygenation. The success led to the preparation of **1a** using the Diels–Alder reaction of a type of aryne, namely 2,3-dehydronaphthalene, with dicyclohexane-annelated furan **3a**. In this paper, we report on the facile synthesis, crystal structure, and solid-state fluorescence of **1a**. In addition, for comparison, the results of 1,4-dipropylanthracene (**1b**) are also presented.

The cyclohexane-fused furan **3a**[11] was obtained as shown in eq 1.



(1)

Thus, the homocoupling of cyclohexanone **2** with NiO_2, followed by Paal–Knorr furan synthesis using *p*-toluenesulfonic acid, resulted in a moderate yield of **3a**. Next, anthracene **1a** was synthesized as shown in eq 2.



(2)

Treatment of 2,3-dibromonaphthalene (**4**)[12] with excess *n*-BuLi and **3a** at −30 °C in toluene, where 2,3-dehydronaphthalene was generated in situ and then trapped with **3a**, resulted in a 74% yield of adduct **5a**. For the transformation into **1a**, the widely used two-step sequence of hydrogenation and acid treatment could not be applied because hydrogenation of **5a** was not possible. Instead, one-step deoxygenation with low-valent titanium[12] was employed for the synthesis of **1a**, which was obtained in 66% yield. The yields of the Diels–Alder reaction and the deoxygenation employed for the preparation of **1b** were 65 and 68%, respectively. This two-step anthracene

Published on the web June 11, 2008; doi:10.1246/bcsj.81.754

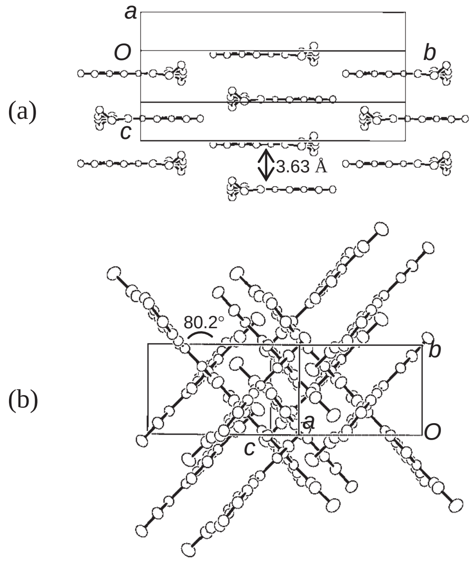


Figure 1. Crystal structures of (a) **1a** and (b) **1b**.

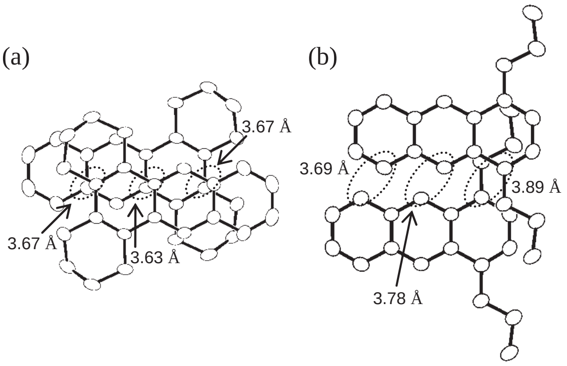


Figure 2. Stacking patterns of two vicinal molecules of (a) **1a** and (b) **1b**.

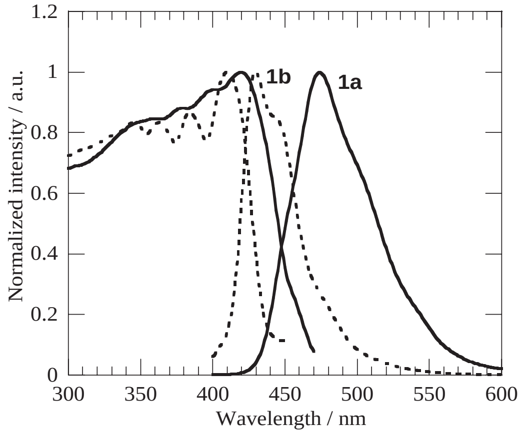


Figure 3. Excitation and fluorescence spectra of **1a** (solid line) and **1b** (dotted line) in the solid state.

Table 1. Spectroscopic Data of **1a** and **1b** in the Solid State

	λ_{ex} /nm	λ_{em}[a)] /nm	Φ[b)]	Lifetime /ns	Radiative lifetime/ns
1a	419	474	0.92	27	29
1b	410	429	0.88	4.4	5.0

a) Excitation at 325 nm. b) Absolute quantum yield.

synthesis is very simple, and would be a versatile tool for obtaining alkyl-substituted anthracenes.

X-ray analysis of **1a** and **1b** revealed that a large difference in packing patterns of molecules exists, as shown in Figures 1 and 2. Thus, **1a** showed face-to-face slipped π-stacking (Figures 1a and 2a); however, **1b** had a herringbone structure in which the interplanar tilt angle between anthracene rings in two adjacent columns was 80.2° (Figure 1b). The anthracene rings of **1b** in one column slipped relative to each other along the long molecular axis by 1.12 Å and along the short molecular axis by 3.89 Å. On the other hand, **1a** had an antiparallel arrangement in the stacked column direction, and the intermolecular distance between the adjacent anthracene planes was 3.63 Å (Figure 1a). The antiparallel molecular π-overlap has been recently reported in the intramolecular donor–acceptor system of tetracenes.[13] In the case of **1b**, neither a π-overlap nor an antiparallel arrangement was observed (Figure 2b). Even in the case of 1,4,5,8-tetraalkylanthracenes, the π-overlap was not observed.[9] The shortest distance for overlapping non-bonded atoms in anthracene for **1a** was 3.63–3.67 Å, which is shorter than that for **1b** (3.69–3.89 Å). The formation of the antiparallel arrangement for **1a** could be mainly ascribed to weak dipole–dipole interactions between neighboring molecules because **1a** has a dipole along the long molecular axis due to the presence of weak electron-donating alkyl groups. From B3LYP/6-31G* calculations, the dipole moment of **1a** was calculated to be 1.1 debye. In contrast, the dipole moment of **1b** was 0.1 debye, which indicated that the dipole was almost nonexistent. The calculation results confirmed that the alkyl substituents at the 2,3-positions in anthracene and not those at the 1,4-positions were responsible for the dipole moment.

The excitation and fluorescence spectra of **1a** and **1b** in the solid state are shown in Figure 3. **1a** illustrates a non-structured emission band at 474 nm. On the other hand, **1b** exhibits structured emission bands at 429, 445 (sh), and 474 (sh) nm, indicating the similarity to the fluorescence spectra of 1,4,5,8-tetraalkylanthracenes.[9] Both fluorescence spectra are red-shifted with respect to those in dilute solutions, although the shift of **1a** is much larger than that of **1b**. A comparison between the fluorescence and the corresponding excitation spectra in the solid state reveals that the larger red-shift of **1a** mainly results from its larger Stokes shift. In fact, the Stokes shifts of **1a** and **1b** are estimated to be 2769 and 1080 cm^{-1}, respectively. Broad spectral shape and large Stokes shift are characteristic features of excimer emission due to the face-to-face slipped π-stacking, which was studied in great detail in the case of pyrene crystals.[14] Thus, the fluorescence of **1a** can be classified as an excimer-like emission, whereas the fluorescence of **1b** is an exciton-like (or monomer-like) emission. This assignment is also supported by fluorescence quantum yield and lifetime measurements, which indicated that the radiative lifetime of **1b** is 6 times greater than that of **1a**, as shown in Table 1. In the face-to-face slipped π-stacking of **1a**, molecules can form an excimer although the distance between the molecules is slightly greater than the distance of 3.56 Å in pyrene crystals. However, the formation of an excimer is energetically not possible because the herringbone structure of **1b** does not contain a pair of molecules that lie exactly face-to-face. Our results suggest that the shape effect of the side chains on the anthracene backbone tuned not only the molecular arrangement in the crystal but also the solid-state fluorescence. The design of the molecule possessing a dipole along the long molecular axis is important for achieving an antiparallel π-stacked structure.

Experimental

Preparation of Dicyclohexane-Annelated Furan 3a. **3a** was prepared by a slightly modified procedure of Hawkins and Large.[11] A mixture of cyclohexanone (8.5 mL, 82.0 mmol) and freshly prepared NiO_2 (35.9 g, 396 mmol) in acetonitrile (60 mL) was stirred at 60 °C for 22 h. Then, $CHCl_3$ was added, and the mixture was filtered, washed with brine, and dried over Na_2SO_4. After evaporation, the residue was heated at 70 °C under vacuum to obtain bicyclohexanone (6.46 g, 81%) as a crude yellow oil. The oil was dissolved in benzene (70 mL), and p-TsOH•H_2O (189 mg, 1.0 mmol) was added to the solution. The mixture was refluxed for 16 h with a Dean–Stark trap. The reaction mixture was washed with brine and dried over Na_2SO_4. After evaporation, column chromatography (SiO_2, 1:1 (v/v) $CHCl_3$/hexane) afforded **3a** (2.59 g, 44%) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.69–1.73 (m, 4H), 1.79–1.83 (m, 4H), 2.30–2.32 (m, 4H), 2.54–2.57 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 20.60, 23.01, 23.14, 23.20, 116.74, 148.13.

Preparation of Dicyclohexane-Annelated Anthracene 1a. A 1.64 M solution of n-BuLi in hexane was added dropwise (2.6 mL, 4.11 mmol) to a suspension of **4** (614 mg, 2.15 mmol) and **3a** (557 mg, 3.16 mmol) in toluene (20 mL) at −30 °C. After 1 h, the mixture gradually warmed up to room temperature, and was stirred for one more hour. MeOH (5 mL) was added, and the mixture was washed with brine and dried over Na_2SO_4. After evaporation, column chromatography (SiO_2, 1:1 (v/v) $CHCl_3$/hexane) afforded **5a** (478 g, 74%) as a yellow solid; mp 75–76 °C. $TiCl_4$ (0.4 mL, 3.65 mmol) was added to a suspension of zinc dust (410 mg, 6.27 mmol) in THF (10 mL) at 0 °C, and the mixture was refluxed for 10 min. After cooling to 0 °C, a solution of **5a** (205 mg, 0.68 mmol) in THF (10 mL) was added gradually. The mixture was stirred at 40 °C for 16 h, and then cooled to 0 °C. Conc. HCl (25 mL) was added carefully, and the organic product was extracted with $CHCl_3$. The combined organic layers were washed with aqueous K_2CO_3 and brine, and dried over Na_2SO_4. After evaporation, column chromatography (SiO_2, 1:1 (v/v) $CHCl_3$/hexane) yielded **1a** (132 mg, 68%) as a yellow solid; mp 131–132 °C (lit.[10] 129 °C). ^{1}H NMR ($CDCl_3$) δ 1.97–2.04 (m, 8H), 2.81 (t, $J = 5.9$ Hz, 4H), 3.32 (t, $J = 5.9$ Hz, 4H), 7.48 (dd, $J = 3.2$, 6.4 Hz, 2H), 8.05 (dd, $J = 3.2$, 6.4 Hz, 2H), 8.56 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 22.84, 23.23, 26.50, 27.26, 121.38, 124.80, 128.23, 128.89, 130.17, 130.85, 133.65. Anal. Found: C, 91.99; H, 7.81%. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74%.

Preparation of 1,4-Dipropylanthracene (1b). Using a procedure similar to that for **1a**, **1b** was prepared as a yellow solid; mp 77–78 °C. ^{1}H NMR ($CDCl_3$) δ 1.09 (t, $J = 7.3$ Hz, 6H), 1.84–1.92 (m, 4H), 3.16 (t, $J = 7.7$ Hz, 4H), 7.23 (s, 2H), 7.47 (dd, $J = 3.2$, 6.4 Hz, 2H), 8.03 (dd, $J = 3.2$, 6.4 Hz, 2H), 8.61 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 14.41, 23.54, 35.42, 123.10, 124.61, 125.22, 128.28, 130.94, 131.01, 136.66. Anal. Found: C, 91.69; H, 8.77%. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45%.

X-ray Crystallography. Crystallographic data have been deposited at Cambridge Crystallographic Data Centre: the deposition numbers are CCDC-662236 (**1a**) and 662235 (**1b**). Copies of this information can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; FAX: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

This work was partly supported by a Grant-in-Aid (No. 18750123) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank the Instrument Center, the Institute for Molecular Science, for assistance in obtaining X-ray data. We also thank Dr. Yoshiaki Matsuo, University of Hyogo, for the measurement of diffuse reflectance spectra.

Supporting Information

Materials, fluorescence measurements in the solid state, crystallographic data of **1a** and **1b**, and UV–vis absorption and fluorescence spectra in hexane. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

References

1 a) C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913. b) C. W. Tang, S. A. VanSlyke, C. H. Chen, *J. Appl. Phys.* **1989**, *65*, 3610. c) J. Shi, C. W. Tang, *Appl. Phys. Lett.* **1997**, *70*, 1665.

2 H. Langhals, T. Potrawa, H. Nöth, G. Linti, *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 478.

3 a) Y. Ooyama, T. Nakamura, K. Yoshida, *New J. Chem.* **2005**, *29*, 447. b) Y. Ooyama, K. Yoshida, *New J. Chem.* **2005**, *29*, 1204. c) Y. Ooyama, T. Okamoto, T. Yamaguchi, T. Suzuki, A. Hayashi, K. Yoshida, *Chem.—Eur. J.* **2006**, *12*, 7827.

4 a) Y. Mizobe, N. Tohnai, M. Miyata, Y. Hasegawa, *Chem. Commun.* **2005**, 1839. b) Y. Mizobe, H. Ito, I. Hisaki, M. Miyata, Y. Hasegawa, N. Tohnai, *Chem. Commun.* **2006**, 2126. c) Y. Mizobe, M. Miyata, I. Hisaki, Y. Hasegawa, N. Tohnai, *Org. Lett.* **2006**, *8*, 4295.

5 a) E. Horiguchi, S. Matsumoto, K. Funabiki, M. Matsui, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1167. b) S. Matsumoto, Y. Uchida, M. Yanagita, *Chem. Lett.* **2006**, *35*, 654. c) E. Horiguchi, S. Matsumoto, K. Funabiki, M. Matsui, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 799.

6 A. Dreuw, J. Plötner, L. Lorenz, J. Wachtveitl, J. E. Djanhan, J. Brüning, T. Metz, M. Bolte, M. U. Schmidt, *Angew. Chem., Int. Ed.* **2005**, *44*, 7783.

7 M. Cotrait, P. Marsau, L. Kessab, S. Grelier, A. Nourmanode, A. Castellan, *Aust. J. Chem.* **1994**, *47*, 423.

8 K. Endo, T. Ezuhara, M. Koyanagi, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1997**, *119*, 499.

9 C. Kitamura, Y. Abe, N. Kawatsuki, A. Yoneda, K. Asada, T. Kobayashi, H. Naito, *Mol. Cryst. Liq. Cryst.* **2007**, *474*, 119.

10 E. de Barry Barnett, N. F. Goodway, C. A. Lawrence, *J. Chem. Soc.* **1935**, 1684.

11 E. G. E. Hawkins, R. Large, *J. Chem. Soc., Perkin Trans. 1* **1974**, 280.

12 H. Hart, A. Bashir-Hashemi, J. Luo, M. A. Meador, *Tetrahedron* **1986**, *42*, 1641.

13 Z. Chen, P. Müller, T. M. Swager, *Org. Lett.* **2006**, *8*, 273.

14 For example: J. B. Birks, A. A. Kazzaz, *Proc. R. Soc. London, Ser. A* **1968**, *304*, 291.