Molecular folding screen: folding and unfolding of 1,8-anthrylene–ethynylene oligomers by photochemical cycloaddition and thermal cycloreversion[1]†

Shinji Toyota,* Makoto Kuga, Akiko Takatsu, Michio Goichi and Tetsuo Iwanaga

Received (in Cambridge, UK) 12th November 2007, Accepted 12th December 2007
First published as an Advance Article on the web 15th January 2008
DOI: 10.1039/b717496a

Molecular folding screens consisting of anthracene plates and acetylene linkers stereoselectively fold into a zigzag form by [4 + 4]-photocycloaddition, and unfold by thermal cycloreversion.

The construction of novel molecular devices and machines to realize specific functions or motions at the molecular level is one of the challenges in molecular science.[2,3] Folding and unfolding triggered by external energy are fundamental molecular functions that not only change the molecular shape or volume but also influence properties related to reactivity and dynamics for a wide range of artificial and biological molecules.[4–9] In many cases, these functions occasionally arise from conformational changes, where the folded structures are stabilized by attractive interactions such as hydrogen bonds and coordination bond interactions.

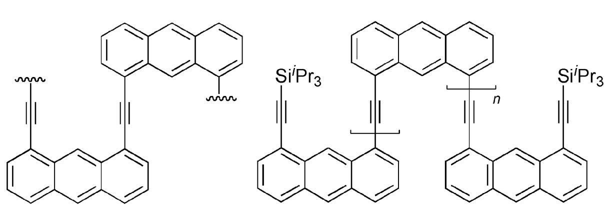
We tried to realize such functions through the [4 + 4]photodimerization of anthracene moieties[10,11] in the 1,8-anthrylene–ethynylene oligomeric system **1**, which we have used for the molecular design of novel π-conjugated compounds (Chart 1).[12] However, we failed to obtain significant photoproducts of the cyclic oligomers due to structural restrictions. This drawback prompted us to use acyclic oligomers because of the increased mobility of anthracene moieties. In fact, trimer **2** and tetramer **3** underwent intramolecular cycloaddition in good yields, and the products reverted to the original compounds upon heating. These processes, accompanied by the formation and cleavage of C–C covalent bonds, mimic the folding and unfolding of a folding screen (a *byobu* in Japanese). We herein report the mechanical like motion of 1,8-anthrylene–ethynylene acyclic oligomers and the structural determination of the photoproducts.

We used acyclic oligomers consisting of three or four anthracene panels with TIPS-ethynyl groups (TIPS = triisopropylsilyl) at both ends, which reasonably improved solubility. Trimer **2**, a known compound, was converted into the tetrameric monoiodide with a known procedure.[12] The Sonogashira coupling of this iodide with TIPS-acetylene gave tetramer **3** in 61% yield. Compound **3** was obtained as a yellow solid showing fluorescence in solution, and was reasonably characterized by NMR and mass spectroscopy (see ESI†).

A degassed solution of **2** in benzene was irradiated with a high-pressure Hg lamp through an L42 filter at room temperature for 8 h to give a photoproduct in 90% yield (Scheme 1).‡ Its NMR spectra showed one set of anthracene signals in the aromatic region and two signals in the aliphatic region (δ 4.59, 6.77 ppm), indicating a [4 + 4]cycloaddition between the terminal anthracene moieties. The structure of this product was determined by X-ray analysis (Fig. 1).§ An ORTEP drawing shows chiral structure **4a** cyclized in the *anti* mode rather than achiral **4b** in the *syn* mode. The both sides of the central anthracene ring are blocked by two TIPS groups to prevent further reactions. This chiral structure is also supported the nonequivalent proton signals due to the two methyl groups in each isopropyl group as well as the resolution of its enantiomers by chiral HPLC.[13]

The photoreaction was similarly carried out with tetramer **3**. The irradiation initially formed a singly cyclized product that was converted into another product after 21 h in 73% isolated yield. Although we could not isolate the intermediate product from the reaction mixture, this compound was identical with that converted from **4a** by monodesilylation and Sonogashira coupling with 1-iodo-8-(TIPS-ethynyl)anthracene to establish the structure of **6**. The photoreaction of the independently prepared **6** gave the same compound as the final product from **3**. Its NMR spectra suggested that that two pairs of anthracene moieties cyclized in a symmetric way. Therefore, the final product is unambiguously assigned to doubly cyclized form **5** in the *anti–anti* mode.[14]

The photochemical cycloaddition of **2** and **3** takes place diastereoselectively so that two reacting anthracene rings approach in the *anti* conformation relative to the central anthracene, creating a zigzag folded structure. Using a molecular model, we found that the bond-forming carbon atoms in the terminal anthracene panels can come within the distance required for photodimerization[15] only for the *anti* conformation *via* a large folding, and the approach was less easy for the



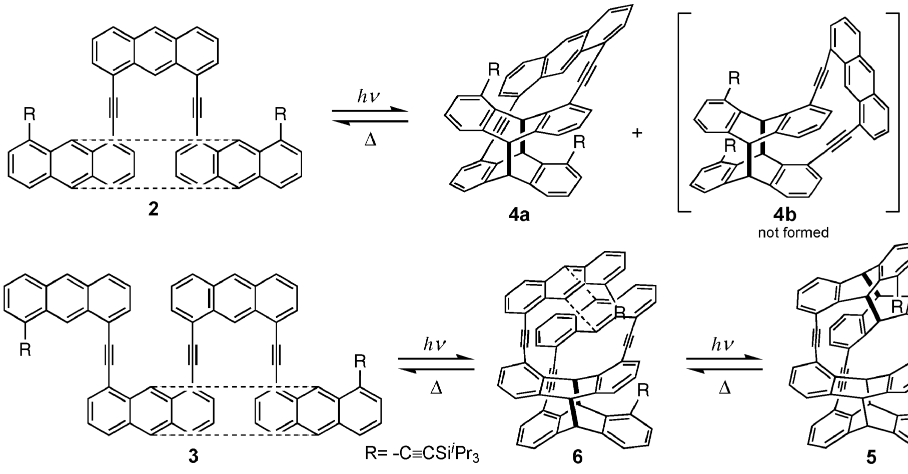
1

2(*n*=1) **3**(*n*=2)

Chart 1

Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Okayama 700-0005, Japan. E-mail: stoyo@chem.ous.ac.jp; Fax: +81 86-256-9457

† Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data. See DOI: 10.1039/b717496a



Scheme 1 Photocycloaddition of acyclic oligomers **2** and **3** and thermal cycloreversion of photoproducts **4** and **5**. Newly formed bonds by photoreactions are indicated by bold lines.

syn conformation irrespective of the folding angle (Fig. 2). Furthermore, the steric hindrance between the terminal silyl groups makes the cycloaddition difficult in the *syn* form; namely, the diastereoselective cyclization in the zigzag mode is attributed to the geometrical constraint inherent in the oligomeric chain. A similar structural situation is found for the two pairs of anthracene rings in tetramer **3** to give only one stereoisomeric photoproduct **5**.

A solid sample of photoproduct **4a** was heated at 180 °C for 30 min to afford the original acyclic trimer **2** in almost quantitative yield. This process was monitored by differential scanning calorimetry (DSC) measurements: an exothermic band due to cycloreversion was observed at 157 °C[16] and an endothermic band due to melting at 281 °C. The solid state was preserved even after the thermal reaction until the temperature reached the melting point. Fluorescence spectra measured in the solid state (Fig. 3) revealed that the thermally reverted sample of **2** (**2X**) was different from a solid sample of **2** obtained by crystallization from chloroform solution (**2Y**). The emission band of **2X** is red-shifted, broad, and long-lived (τ_F 2.2, 15.7 ns) compared with that of **2Y** (τ_F 0.6, 3.2 ns).[17] It is likely that molecules of **4a** undergo cycloreversion with small changes in molecular conformation and arrangement to preserve the zigzag form in the packing (Scheme 2). These spectral features of **2X** are attributable to strong interactions between anthracene groups, leading to the increased contribution of an excimer-type emission.[18] In contrast, the molecule adopted an approximately L-shape conformation in the crystal of **2Y**.[19] The NMR spectra of **2X** and **2Y** in solutions were identical because of the facile conformational interconversion by rotation about acetylenic axes. Hence, the thermal reaction in the solid state just unlocked the folded structure, which then unfolded upon dissolution. The thermal cycloreversion of **4a** also took place in 1,2-dichlorobenzene at 180 °C within 30 min, where the molecules unfolded immediately after the unlocking. Compound **5** similarly afforded **3** in good yield upon heating in the solid state. Although the DSC measurement of **5** gave very broad exothermic peaks above 160 °C, we obtained no clear evidence of structural changes and stepwise ring opening.

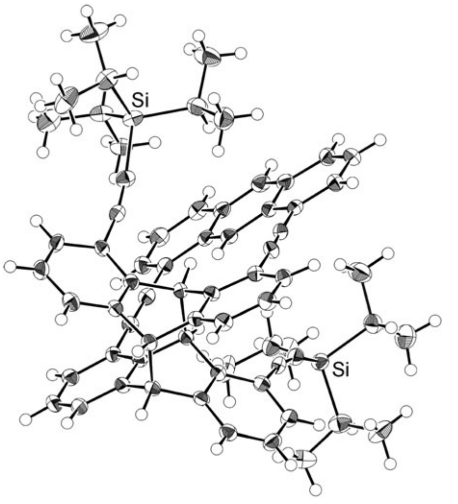


Fig. 1 X-Ray structure of photoproduct **4a** with thermal ellipsoids at 50% probabilities. One of the two molecules in an asymmetric unit is shown here, because their structures are almost the same except the absolute stereochemistry.

In summary, acyclic anthrylene–ethynylene trimer **2** and tetramer **3** were converted into the corresponding folded forms upon irradiation, which unfolded back to the open forms upon heating followed by dissolution in a manner similar to three- and four-panel folding screens, respectively. These processes

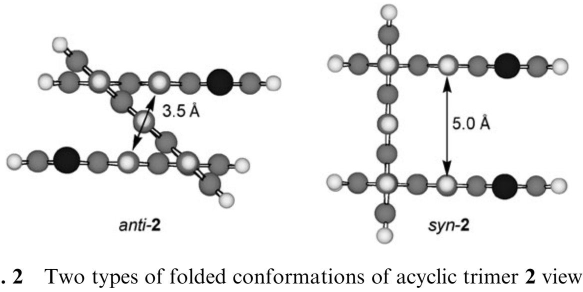


Fig. 2 Two types of folded conformations of acyclic trimer **2** viewed along the acetylenic axes. (Rigid models generated by Chem3D. Dihedral angles between anthracene groups are −42°/−42° and −90°/+90° for *anti*-**2** and *syn*-**2**, respectively. The TIPS group is indicated by a single black ball for clarity).

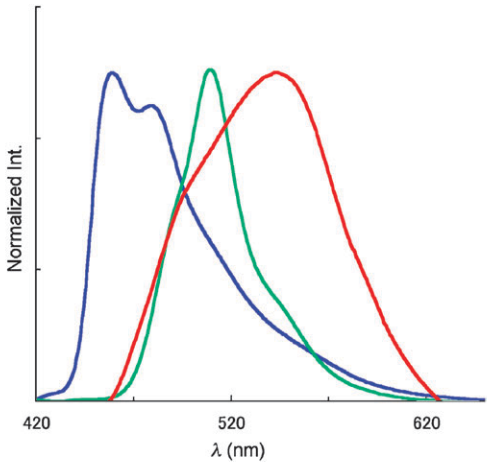
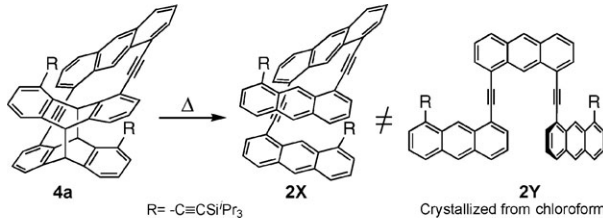


Fig. 3 Fluorescence spectra of **2** (λ_{ex} 393 nm). Red (**2X**): solid sample obtained by thermal cycloreversion of **4a**. Green (**2Y**): solid sample obtained by crystallization from chloroform solution of **2**. Blue: chloroform solution.



Scheme 2 Thermal cycloreversion of **4a** in the solid state.

provide a fundamental design of structural switch caused by external energies. Further studies of the improvement of function to realize rapid response and the photoreaction in the solid state are in progress.

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformations of Carbon Resources" (No. 19020069) from MEXT (the Ministry of Education, Culture, Sports, Science and Technology, Japan) and by "High-Tech Research Center" Project for Private Universities: matching fund subsidy from MEXT. The authors thank Prof. T. Shinmyozu of Kyushu University for use of the X-ray diffractomer, and Prof. T. Ohtani of Okayama University of Science for use of the DSC apparatus.

Notes and references

‡ Selected data of the photoproducts. **4a**: yield 90%; mp 280–282 °C; ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = -0.41$ (septet, 6H, J = 7.3 Hz), 0.44 (d, 18H, J = 7.3 Hz), 0.49 (d, 18H, J = 7.3 Hz), 4.59 (s, 2H), 6.77 (s, 2H), 6.80–6.94 (m, 8H), 7.07 (d, 2H, J = 7.3 Hz), 7.21 (d, 2H, J = 7.3 Hz), 7.46 (dd, 2H, J = 7.3, 8.3 Hz), 7.86 (d, 2H, J = 6.8 Hz), 8.03 (d, 2H, J = 8.8 Hz), 8.51 (s, 1H), 10.09 ppm (s, 1H); UV-vis (CHCl$_3$): λ_{max} (ε) = 271 (90 500), 296 (17 400), 367 (2400), 386 (9100), 408 (20 500), 432 (23 200) nm; HR FAB MS: m/z 938.4704 [M$^+$]; calcd for $C_{68}H_{66}Si_2$; m/z 938.4703 [M$^+$]. **5**: yield 73%; mp 285–288 °C (dec); ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = -0.01$ (septet, 6H, J = 7.8 Hz), 0.51 (d, 18H, J = 7.3 Hz), 0.57 (d, 18H, J = 7.3 Hz), 4.42 (d, 2H, J = 10.7 Hz), 4.57 (d, 2H, J = 10.7 Hz), 6.47 (d, 2H, J = 10.7 Hz), 6.63 (d, 2H, J = 10.7 Hz), 6.72 (d, 2H, J = 6.8 Hz), 6.76–6.96 (m, 14H), 7.04 (m, 2H), 7.15–7.19 ppm (m, 6H); UV-vis (CHCl$_3$): λ_{max} (ε) = 294 (35 000), 331 (9400), 391 (930), 411 (1070), 434 (750); HR FAB MS: m/z 1138.5294 [M$^+$]; calcd for $C_{84}H_{74}Si_2$; m/z 1138.5329 [M$^+$].

§ Crystal data for **4a**: $C_{68}H_{66}Si_2$, M = 939.39, monoclinic, $P2_1$, a = 22.625(3), b = 9.6582(11), c = 24.852(4) Å, β = 99.565(6)°, U = 5355.2(12) Å, T = 123 K, Z = 4, ρ = 1.165 g cm^{-3}, μ(Mo Kα) = 0.108 mm^{-1}, λ = 0.71073 Å. 88 674 reflections measured, 23 529 unique reflections [R_{int} = 0.0732]. Refinement on F^2, R_1 = 0.0618, wR_2 = 0.1612 for [$I > 2\sigma(I)$]. CCDC 667544. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717496a

1 Part 8 of "Chemistry of Anthracene–Acetylene Oligomers." For Part 7, see: S. Toyota, M. Kurokawa, M. Araki, K. Nakamura and T. Iwanaga, *Org. Lett.*, 2007, **9**, 3655.
2 V. Balzani, M. Venturi and A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003.
3 *Top. Curr. Chem.*, 2005, **262**.
4 K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377.
5 (*a*) Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, Y.-H. Chiu, L. B. Alemany, T. Sasaki, J.-F. Morin, J. M. Guerrero, K. F. Kelly and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 484; (*b*) J.-F. Morin, Y. Shirai and J. M. Tour, *Org. Lett.*, 2006, **8**, 1713; (*c*) C. Joachim, H. Tang, F. Moresco, G. Rapenne and G. Meyer, *Nanotechnology*, 2002, **13**, 330.
6 (*a*) R. A. van Delden, M. K. J. ter Wiel, H. de Jong, A. Meetsma and B. L. Feringa, *Org. Biomol. Chem.*, 2004, **2**, 1531; (*b*) J. Vicario, M. Walko, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2006, **128**, 5127; (*c*) R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer and B. L. Feringa, *Nature*, 2006, **440**, 163.
7 (*a*) B. X. Colasson, C. Dietrich-Buchecker, M. C. Jimenez-Molero and J.-P. Sauvage, *J. Phys. Org. Chem.*, 2002, **15**, 476; (*b*) J.-P. Collin, V. Heitz and J.-P. Sauvage, ref. 2, pp. 29.
8 (*a*) S. Witt and W. Baumeister, *Biopolymers*, 2003, **7**, 439; (*b*) V. Balzani, M. Venturi and A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003, ch. 12.5.
9 F. Ciardelli and O. Pieroni, in *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001.
10 (*a*) W. Horspool and D. Armesto, *Organic Photochemistry*, Ellis Horwood Limited, Chichester, 1992, pp. 88; (*b*) L. Burnelle, J. Lahiri and R. Detrano, *Tetrahedron*, 1968, **24**, 3517; (*c*) H.-D. Becker, *Chem. Rev.*, 1993, **93**, 145, and references therein.
11 Recent examples of photodimerization of anthracenes (*a*) A. Nakamura and Y. Inoue, *J. Am. Chem. Soc.*, 2003, **125**, 699; (*b*) C. Yang, A. Nakamura, G. Fukuhara, Y. Origane, T. Mori, T. Wada and Y. Inoue, *J. Org. Chem.*, 2006, **71**, 3126; (*c*) Y. Takaguchi, T. Tajima, Y. Yanagimoto, S. Tsuboi, K. Ohta, J. Motoyoshiya and H. Aoyama, *Org. Lett.*, 2003, **5**, 1677.
12 (*a*) S. Toyota, M. Goichi and M. Kotani, *Angew. Chem., Int. Ed.*, 2004, **43**, 2248; (*b*) S. Toyota, M. Goichi, M. Kotani and M. Takezaki, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 2214.
13 Conditions for chiral HPLC: Daicel Chiralcel OD column (10 mm ϕ × 250 mm), eluent: hexane–2-propanol (100 : 1), flow rate: 1.0 mL min^{-1}, injected sample: 0.25 mg in 0.5 mL, retention time: 22.5, 24.1 min. The specific rotations of the easily and less easily eluted enantiomers were $[\alpha]_D^{25}$ −232 and + 222, respectively. Their CD spectra are shown in ESI†.
14 We failed to resolve the enantiomers of tetrameric photoproduct **5** by chiral HPLC even though we used three types of columns under various conditions.
15 As Schmidt claimed, face-to-face oriented π systems within 4.2 Å can undergo photodimerization: G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.
16 This temperature is higher than those observed for the photodimers of various 9-alkylanthracenes: S. Grimme, S. D. Peyerimhoff, H. Bouas-Laurent, J.-P. Desvergne, H.-D. Becker, S. M. Sarge and H. Dreeskamp, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2457.
17 The difference in emission bands of the two types of solid sample was insignificant for the tetrameric system.
18 Fluorescence properties are sensitively influenced by the orientation of anthracene chromophores as revealed by studies on anthracenophanes (*a*) T. Hayashi, M. Mataga, Y. Sakata, S. Misumi, M. Morita and J. Tanaka, *J. Am. Chem. Soc.*, 1976, **98**, 5910; (*b*) B. F. Anderson, J. Ferguson, M. Morita and G. B. Robertson, *J. Am. Chem. Soc.*, 1979, **101**, 1832.
19 In the X-ray structure of **2**, dihedral angles between the anthracene groups are +73° and −162°. See ref. 12b.