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Multibridged Chiral Naphthalene Oligomers with Continuous Extreme-Cisoid Conformation

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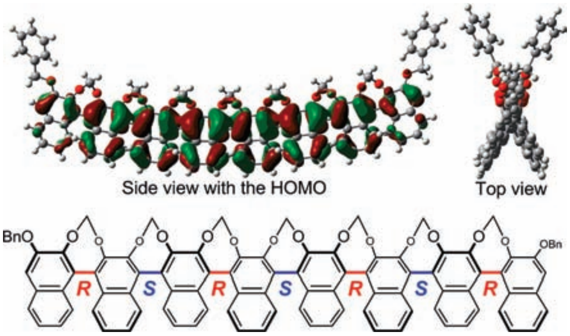
ABSTRACT



Axially chiral 2,2′-methylenedioxy-bridged-1,1′-binaphthyls, quaternaphthalenes, and octinaphthalenes were synthesized and their optical properties researched. 2,2′-Methylenedioxy bridges led to a continuous extremely cisoid conformation and subsequent extensive conjugation in the rod direction. Therefore, the absorption and fluorescence regions were red-shifted as the number of naphthalene rings increased. These oligonaphthalenes fluoresced in both solution and the solid state. Furthermore, DFT calculations showed that the LUMO and HOMO of these bridged oligonaphthalenes were spread over a wide range.

π-Conjugated linear oligomers such as oligothiophenes, oligophenylenes, and oligofluorenes are typically synthesized and designed as wire-type functional materials.[1] Previously, we have synthesized optically active 1,1′-oligonaphthalenes **1** (4mers to 32mers) as representative axially chiral oligomers by the bottom-up method, which maintains asymmetry and precisely constructs oligomers without a molecular weight distribution, to elucidate the asymmetric and optical properties.[2] Although energy transfer via the axes was detected, **1** did not realize extensive conjugation because the dihedral angles of adjacent naphthalene units were nearly 90°.[2c,g]

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Therefore, the potential of these orthogonal type oligomers has yet to be fully exploited. Thus, we speculated that oligonaphthalenes consisting of nearly planar, tiered naphthalene rings will behave as oligomers by a strong interaction between adjacent naphthalene rings and will show unique properties.

The dihedral angles for adjacent naphthalene rings in the optimized structure of (*R*,*S*,*R*)-**2** are 74.5° (C(1)−C(2)−C(3)−C(4)), 97.2° (C(5)−C(6)−C(7)−C(8)), and 89.6° (C(9)−C(10)−C(11)−C(12)) (Figure 1). In contrast, each 1,1′-axial rotation of oligonaphthalene **3** is limited, and these naphthalene rings form an extreme-cisoid conformation by the 2,2′-methylenedioxy bridges[3,4] and *peri*-hydrogens. For the simplest tetramer, (*R*,*S*,*R*)-**4**, which is the bridged form of (*R*,*S*,*R*)-**2**, the dihedral angles are 48.9° (C(1′)−C(2′)−C(3′)−C(4′)), 48.6° (C(5′)−C(6′)−C(7′)−C(8′)), and 49.0° (C(9′)−C(10′)−C(11′)−C(12′)),[5] suggesting the possibility of the extended conjugation of **4** or higher order bridged oligonaphthalene **3**. Based on the calculation results, we synthesized 2,2′-bridged-1,1′-oligonaphthalenes and analyzed their optical behaviors. These 1,1′-oligonaphthalenes have continuous axial chiralities. The oxy-functional groups of the alternating-chiral (*R*,*S*,*R*,*S*,*R*,*S*,...) form are arranged linearly, whereas those of the homochiral (*R*,*R*,*R*,*R*,*R*,... or *S*,*S*,*S*,*S*,*S*,...) form are arranged helically. Although examining the homochiral form would be structurally interesting, herein we selected the alternating-chiral form because it has the potential to form β-barrel structures[6] in the future (this point is not discussed in this paper).

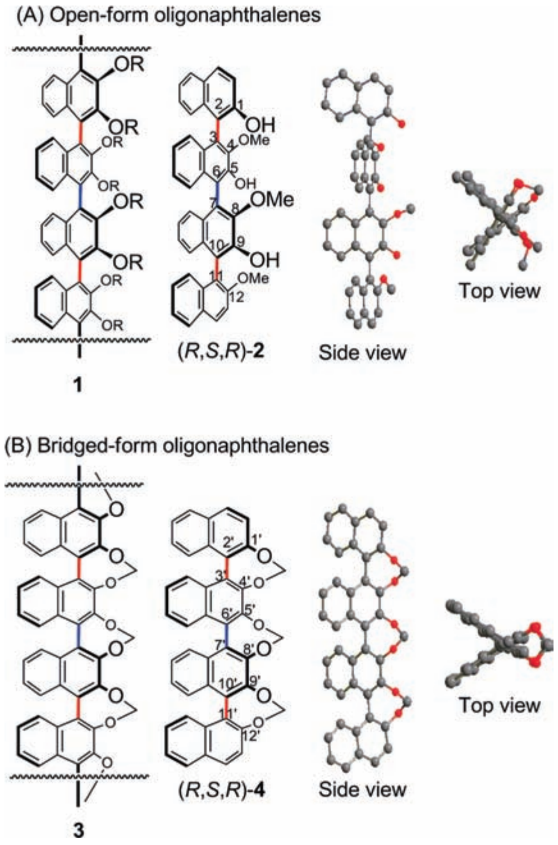
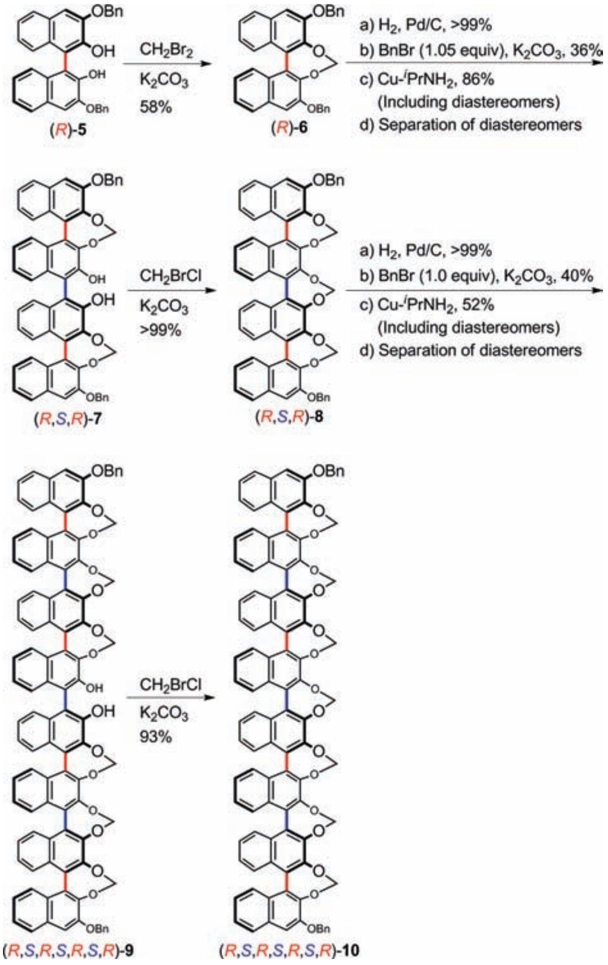


Figure 1. Optimized geometries obtained by DFT calculations at the B3LYP/6-31G(d) level for the (A) open- and (B) bridged-form oligonaphthalenes; Red axes denote *R* configuration and blue axes denote *S* configuration.

2,2′-Bridged naphthalene oligomers **6**, **8**, and **10** were synthesized by the double Williamson ether synthesis using dibromomethane or bromochloromethane and diols **5**, **7**, and **9**, respectively (Scheme 1). These diols were prepared via repeated oxidative homodimerization reactions with a Cu^{II}−amine complex and subsequent optical resolutions, and their absolute configurations were determined by the exciton chi-

Scheme 1. Synthesis of Bridged Oligonaphthalenes



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(3) For examples of 2,2′-bridged-1,1′-binaphthyls, see: (a) Ernesstimpson, J. E.; Daub, G.; Hayes, F. N. *J. Org. Chem.* **1973**, *38*, 1771. (b) Zhang, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 4852. (c) Deussen, H.-J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841. (d) Schafer, L. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 2683. (e) Minatti, A.; Dötz, K. H. *Tetrahedron: Asymmetry* **2005**, *16*, 3256. (f) Tu, T.; Maris, T.; Wuest, J. D. *J. Org. Chem.* **2008**, *73*, 5255.

(4) For examples of Geländer-type molecules, see: (a) Kiupel, B.; Niederalt, C.; Nieger, M.; Grimme, S.; Vögtle, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3031. (b) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893. (c) Hu, Z.-Q.; Chen, C.-F. *Tetrahedron* **2006**, *62*, 3446. (d) Modjewski, M.; Lindeman, S. V.; Rathore, R. *Org. Lett.* **2009**, *11*, 4656.

rality method[2c,h,7] with respect to the two TPP(Zn) (tetraphenylporphyrin zinc complex) adducts (see the Supporting Information). As the number of naphthalene units increased, the solubility decreased. Among the diastereomers, alternating-chiral naphthalenes with the oxy-functional groups concentrated on one side were less soluble because the dipole moment of the entire molecule is larger than that of the other diastereomers. Octamer **10** was the upper limit without solubilizing substituted groups. These methylenedioxy bridges were stable under heat, at least up to 80 °C, as well as under moderate acidic or basic conditions. Moreover, epimerization did not occur under these conditions.[8]

Figure 2 depicts the optical properties. Figure 2A shows the absorption spectra; as the number of naphthalene rings increased, the longer wavelength absorption region (320−400 nm) became broader and the spectra was red-shifted, while the change in the maximum absorption wavelength of the short wavelength side (220−240 nm) was insignificant. These results indicate that ^1L_a (transition moment of the short axes of the naphthalene rings) rather than ^1B_b (transition moment of the long axes of the naphthalene rings) is affected,[9] and adjacent naphthalene rings interact strongly in the rod direction. Each diastereomer displayed similar characteristics, but the spectral shape varied slightly (Figure S2, Supporting Information). Open-form compounds **1**, which are even higher order oligonaphthalenes, did not exhibit a red-shift.[2a,g] In Figure 2B, the CD intensity of (*R*)-**6** was much higher than that of (*R*)-**5**, although both had identical Cotton effect patterns. Moreover, debenzylated analogues of (*R*)-**6** showed similar spectra (Figure S4, Supporting Information). Therefore, the optical properties directly reflect differences in the torsion angle of the naphthalene rings. Higher order (*R*,*S*,*R*)-**8** and (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**10** had CD intensities almost identical to that of (*R*)-**6**. Because each naphthalene ring of **8** and **10** interacted with distant naphthalene rings, the CDs of *S* and *R* binaphthalene units canceled each other on a whole. Figure 2C shows the emission spectra in solution. Along with the absorption, the emission shifted bathochromically with the number of naphthalene rings. Each compound showed relatively high FL quantum yields in solution; ϕ_{310} of (*R*)-**6** was 0.44, ϕ_{330} of (*R*,*S*,*R*)-**8** was 0.79, and ϕ_{330} of (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**10** was 0.64. In contrast, ϕ_{fl} of the open-form dimers was relatively low; ϕ_{310} of (*R*)-**5** was 0.045,[10] and ϕ_{310} for compounds with methoxy groups instead of hydroxy groups of (*R*)-**5** was 0.16. The reason that bridged oligonaphthalenes exhibited a high fluorescence is unknown. However, plausible explanations include that the bridges provide the entire molecule with rigidity, especially the constraint axial rotation, or as suggested by the relatively small Stokes shifts (for example, the Stokes shift of (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**10** is 36 nm), the dihedral angles of the naphthalene rings of the S_0 state are inherently similar to that of the S_1 state,[11] tand hus, the excitation energy is more likely to be converted into fluorescence than axial vibration. Moreover, the bridged oligonaphthalenes strongly fluoresced in the solid state under UV light (Figure 2D, $\phi = 0.08-0.21$); (*R*)-**6** was pale blue

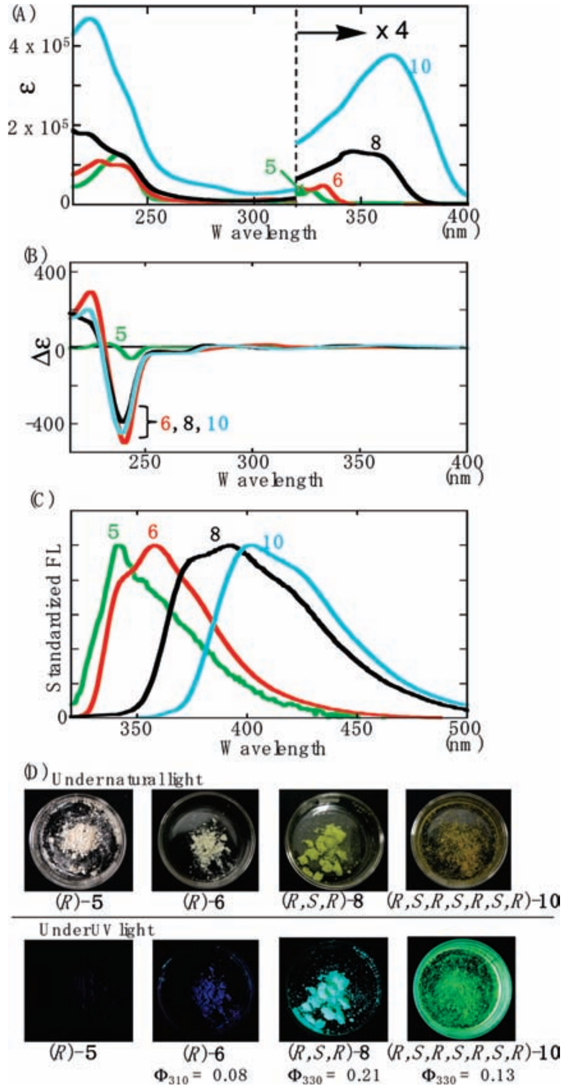

Figure 2. Optical properties of bridged oligonaphthalene (*R*)-**6** (red line), (*R*,*S*,*R*)-**8** (black line), (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**10** (aqua line), and nonbridged (*R*)-**5** (green line): (A) absorption spectra in 1,4-dioxane; (B) CD spectra in 1,4-dioxane; (C) fluorescence spectra in 1,4-dioxane (excitation wavelengths are 310 nm for **5** and **6** and 330 nm for **8** and **10**); (D) pictures of solid-state fluorescence under UV light (254 nm).

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(9) Rosini, C.; Superchi, S.; Peerlings, H. W. I.; Meijer, E. W. *Eur. J. Org. Chem.* **2000**, 61.

(10) Hydroxy groups of BINOL are involved in its fluorescence quenching, see: Wang, Q.; Chen, X.; Tao, L.; Wang, L.; Xiao, D.; Yu, X.-Q.; Pu, L. *J. Org. Chem.* **2007**, *72*, 97.

(11) Dihedral angles of the S_0 and S_1 state have been studied; see: Fujiyoshi, S.; Takeuchi, S.; Tahara, T. *J. Phys. Chem. A* **2004**, *108*, 5938.

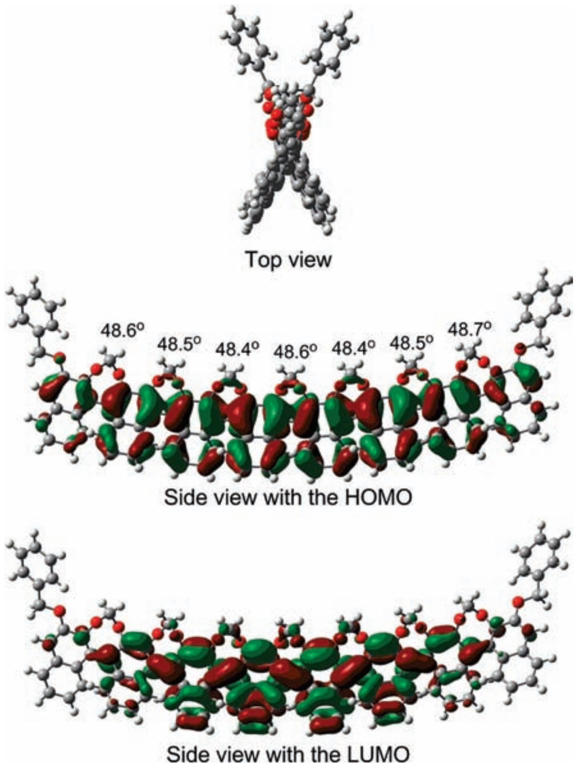

Figure 3. Optimized structure with the HOMO, LUMO, and consistent dihedral angles of adjacent naphthalene rings of (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**10** obtained by DFT calculations at the B3LYP/6-31G(d) level.

($\lambda_{\text{max,emm}}$ = 370 nm), (*R*,*S*,*R*)-**8** was light blue ($\lambda_{\text{max,emm}}$ = 416 nm), and (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**10** was yellow-green ($\lambda_{\text{max,emm}}$ = 443 nm). Figure S5 (, Supporting Information) shows the solid-state fluorescence spectra.

Figure 3 shows the calculated HOMO, LUMO, and dihedral angles of (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**10**. The dihedral angles held steady at 48−49°, which is between planar and orthogonal, but the oligonaphthalene skeleton had minor deviations toward the 2,2′-bridges. Except for the bridges and terminal benzyloxy groups, both the HOMO and LUMO are spread throughout the molecule[12] but gravitate somewhat toward the central naphthalene rings. These bridged oligonaphthalenes show a peculiar conjugation, that is, molecular-wide graduated-twisted π-conjugation.

In conclusion, we developed multibridged, chiral oligonaphthalenes. The 2,2′-methylenedioxy bridges gave them a continuous extremely cisoid conformation and, consequently, a notably extensive conjugation in the rod direction and high fluorescence. Although a lengthy process is currently required to synthesize these types of oligonaphthalenes with a specified number of naphthalene units and axial chirality, these compounds and their analogues may contribute to the development of photo- and electrochemistry with asymmetric properties.

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Supporting Information Available: Synthetic details, determination of the absolute configuration, and structural and optical characterization of various compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Both the HOMO and LUMO of an open form octinaphthalene are localized on about three naphthalene rings (Figure S6, Supporting Information).