Synthesis and Properties of Bay-Functionalized 9,9'-Bifluorenylidene Derivatives

Junichiro Hirano,1 Hiroshi Shinokubo,1 and Norihiro Fukui*1,2

1 Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, and Integrated Research Consortium on Chemical Science (IRCCS), Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan
2 PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012

E-mail: fukui@chembio.nagoya-u.ac.jp

Here, we disclose the substitution effect at the bay-region of 9,9'-bifluorenylidene on its optical and electrochemical properties. Bay-brominated 9,9'-bifluorenylidene was synthesized by the reductive dimerization of 4,5-dibromofluorenone with triethyl phosphite. The subsequent Suzuki–Miyaura cross-coupling afforded arylated derivatives. X-ray diffraction analysis revealed that the bulky bay-substituents twist the overall structure through the relay of the steric repulsion from the bay-region to the iodide-region. The π-extension at the bay-region with tolyl and 4-dimethylaminophenyl groups increases the electron-donating ability, while the introduction of bromo groups enhances the electron-accepting ability.

Keywords: 9,9'-Bifluorenylidene, Overcrowded alkene, Twisted structure

9,9'-Bifluorenylidene (1) represents an overcrowded alkene consisting of two fused five-membered rings (Figure 1).1,2 Owing to the steric repulsion between two fluorenylidene units, 9,9'-bifluorenylidene adopts a twisted conformation.3,4 The incorporation of fused five-membered rings decreases the LUMO level, enhancing electron-accepting character and light-harvesting ability in the visible region. Consequently, 9,9'-bifluorenylidene and its derivatives have offered diverse applications including conjugated polymers,5,6 covalent organic frameworks (COFs),7 hole-transporting materials for perovskite solar cells,8 and organic photovoltaics.9–18 To date, various functionalized 9,9'-bifluorenylidenes with various substituents or fused rings at their 1,2,3,6,7,8-positions have been reported.5–28 However, the substituent effect at the 4,5-positions (bay-region) has been underexplored, especially limited to benzo-fused derivatives.29,30 This situation is due to the lack of an appropriate precursor for derivatization at the bay-region.

Figure 1. 9,9'-Bifluorenylidene (1) and its crystal structure.

The current study started with our unexpected finding during the synthesis of 1,8,9,16-tetraphenyldimethylamino[9H-fluorene-9,9'(10'H)-phenanthren]-10'-on 3 as an intermediate.31 According to the reported procedure, we treated 4,5-dibromofluorenone 4 with triethyl phosphite at 175 °C to afford 4,5,4',5'-tetrabromo-9,9'-bifluorenylidene (6) in 24% yield along with the desired product 5 in 34% yield (Scheme 1). Contrastingly, the reaction of non-substituted fluorenone with P(OEt)3 under the same conditions provided spiro[9H-fluorene-9,9'(10'H)-phenanthren]-10'-on 3 in 65% yield with a trace amount of 9,9'-bifluorenylidene (1). It is worth noting that the attempted McMurry coupling of 4 did not afford 6 as shown Scheme S1, although the same transformation of fluorenone 2 furnished 1 in 60% yield.33 These results highlight the usefulness of the present procedure for the preparation of 6.

Scheme 1. Treatment of fluorenone 2 and 4,5-dibromofluorenone 4 with P(OEt)3 at 175 °C.

We examined the Suzuki–Miyaura cross-coupling reactions of bay-brominated 9,9'-bifluorenylidene 6 (Scheme 2). Treatment of 6 with p-tolylboronic acid in the presence of Pd(dba)3•CHCl3 and SPhos afforded 4,5,4',5'-tetra(p-toly)-9,9'-bifluorenylidene 7 in 55% yield. Electron-rich 4-dimethylaminophenyl and bulky 3,5-di-tert-butylphenyl groups were also introduced under the same conditions, furnishing 8 and 9 in 18% and 51% yields, respectively. However, the reactions with electron-deficient boronic acids, i.e., 4-nitrophenylboronic acid and 4-trifluoromethylphenylboronic acid, and bulkier mesitylboronic acid did not afford the corresponding arylated products.
The structures of 6, 7, and 8 were unambiguously determined by X-ray diffraction analysis (Figure 2). In all the cases, the crystal packing consists of a pair of enantiomers. For bromo derivative 6, one of two crystallographically inequivalent molecules is shown in Figure 2a. Compounds 6, 7, and 8 have helical chirality due to the steric repulsion at the bay- and fjord-regions. In the cases of bromo derivative 6 and p-tolyl derivative 7, the sense of the helicity at the bay-regions is opposite to that at the fjord-regions, leading to the twisting along the longitudinal molecular axis. Dimethylaminophenyl derivative 8 adopts a low-symmetric structure, in which the helicities at the two bay-regions are opposite. The density functional theory (DFT) calculations at the B3LYP/6-31G(d) level suggest that a stereoisomer with (P,M,M,M) configuration is energetically unfavorable by 1.2 kcal mol
-1 than that with (P,M,P,M) configuration.

We further investigated the detailed structural features of 1, 6, 7, and 8 by analyzing their X-ray crystal structures and optimized structures given by DFT calculations. The C(9)–C(9') bond lengths (d), dihedral angles at the fjord-regions (\(\phi\), and mean plane deviations (MPDs) of fluorenylidene segments are listed in Table 1. The experimental C(9)–C(9') bond lengths of 6, 7, and 8 are 1.378(8)/1.343(9), 1.370(4), and 1.379(2) Å, respectively, which are comparable to that of 9,9'-bifluorenylidene 1 (1.367(5) Å).The DFT calculations also support the negligible effect of bay-substituents on the C(9)–C(9') bond lengths. Contrastingly, the experimental torsion angles \(\phi\) of 6 (39°), 7 (31–40°), and 8 (36–37°) are larger than that of 1 (32–34°) (Figure S19). The DFT calculations reproduced the change of the torsion angles, suggesting that the structural change by the crystal packing force is negligible. The MPDs of 6 (0.13–0.16 Å), 7 (0.10–0.14 Å), 8 (0.11–0.14 Å) are larger than that of 1 (0.05 Å). These results indicate that the steric repulsion at the bay-regions enhances the twisting of the overall structure due to the relay of the steric repulsion: (1) the bulky bay-substituents twist the inherently planar fluorenylidene segment and (2) the resulting twist increases the steric repulsion at the fjord-regions.

The UV/vis absorption spectra of 1, 6, 7, 8, and 9 in CHCl
3 are shown in Figure 3. Non-substituted 9,9'-bifluorenylidene 1, bromo-derivative 6, tolyl-derivative 7, and 3,5-di-tert-butylphenyl derivative 9 exhibit characteristic absorption bands in the range of 350–600 nm. The peak tops of 6 (502 nm), 7 (496 nm), and 9 (491 nm) are more red-shifted than that of 1 (457 nm). The broad absorption of 4-dimethylaminophenyl-derivative 8 tails to approximately 660 nm, covering the entire visible region. These results demonstrate that the functionalization of 9,9'-bifluorenylidene at the bay-regions is effective to modulate the electronic properties.
their optical HOMO–LUMO gaps. The electrochemical HOMO–LUMO gaps
(eV) > 0.33 (0.23) implies the occurrence of dynamic structural
displacement between the oxidation and reduction peaks
around 0.44 V, while the following back-sweeping gave a re-
sweeping in the positive direction afforded an oxidation peak
donating ability due to the 4-dimethylaminophenyl groups.
derivatives 8 and 9 display significant differences in their first oxidation potentials (0.10 V) . The opposite trend has been observed for tolyl-
derivative 6 (–0.153 V). 4-Dimethylaminophenyl derivative
exhibits substantial orbital distribution at the bay-region, while the 6 reduction potential is negatively shifted compared to other
derivatives 6, 7, and 9, indicating the enhanced electron-
donating ability due to the 4-dimethylaminophenyl groups.
Sweeping in the positive direction afforded an oxidation peak
around 0.44 V, while the following back-sweeping gave a re-
duction peak around 0.05 V (Figure S21). The large
displacement between the oxidation and reduction peaks
(0.39 V) implies the occurrence of dynamic structural changes. The electrochemical HOMO–LUMO gaps
decrease in the order of 1 (2.45 eV) > 9 (2.41 eV) > 7 (2.30
eV) > 6 (2.26 eV) > 8 (1.90 eV). This trend is in line with
their optical HOMO–LUMO gaps.

Table 1. Redox potentials of 1, 6, 7, 8, and 9

<table>
<thead>
<tr>
<th>Oxidation [V]</th>
<th>Reduction [V]</th>
<th>$\Delta E^{[b]}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ox1}$</td>
<td>$E_{red}$</td>
<td>$E_{red}$</td>
</tr>
<tr>
<td>1 0.92</td>
<td>— —</td>
<td>1.53</td>
</tr>
<tr>
<td>6 1.02</td>
<td>— —</td>
<td>1.24</td>
</tr>
<tr>
<td>7 0.70</td>
<td>— —</td>
<td>1.60</td>
</tr>
</tbody>
</table>

[a] Redox potentials were measured by cyclic voltammetry in anhydrous
CH$_2$Cl$_2$ using 0.1 M [Bu$_4$N][PF$_6$] as the supporting electrolyte and
Ag/AgNO$_3$ as the reference electrode. The ferrocene/ferrocenium ion
couple was used as an external reference. [b] Electrochemical HOMO–
LUMO gap ($\Delta E = E_{ox1} - E_{red}$) determined by DPV.

To get more insight into the substitution effect at the
bay-region of 9,9'-bifluorenylidene, we conducted DFT
calculations for 1, 6, and 7 at the B3LYP/6-31G(d) level
(Figures S22–S25). The HOMO of 9,9'-bifluorenylidene 1
exhibits substantial orbital distribution at the bay-region,
which is a nodal position in its LUMO. Consequently, the
introduction of tolyl groups at the bay-region raises the
HOMO level of 7 by 0.3 eV, which nicely accords with the
observed redox behavior of 7. The LUMO level of bromo-
substituted derivative 6 is stabilized by 0.6 eV than that of 1.
Considering that the LUMO of 6 has no orbital distribution
at the bay-region, the stabilization of LUMO is attributed to
the inductive effect of bromo groups. The HOMO of 6 has
contributed to the antibonding interaction of the C–Br bonds.
The destabilization of the orbital energy by mesomeric effect
offsets the stabilization by inductive effect, leading to the
moderately stabilized HOMO level compared to non-
substituted 9,9'-bifluorenylidene 1. Pu and co-workers have
reported that the increase of a dihedral angle $\phi$ between two
fluorenylidene segments by 19° from the optimized structure
($\phi = 31°$) results in a small decrease of $S_\text{HOMO}$–LUMO gap
(approximately 0.3 eV).11 Our calculations also suggest the
subtle effect of torsion angle on the HOMO–LUMO gap
($\Delta E_{\text{HOMO–LUMO}} = 2.842 \text{ eV for } \phi = 34°$; $\Delta E_{\text{HOMO–LUMO}} = 2.798 \text{ eV for } \phi = 40°$;
$\Delta E_{\text{HOMO–LUMO}} = 2.719 \text{ eV for } \phi = 50°$). These results suggest that
the electronic modulation by bay-functionalized 9,9'-
bifluorenylidene originates from the mesomeric and/or
inductive effects of the substituents rather than the structural
changes.

Figure 3. UV/vis absorption spectra of 1 (black), 6 (green), 7 (red), 8
(blue), and 9 (pink) in CH$_2$Cl$_2$; $\lambda$ = wavelength; $\epsilon$ = extinction coefficient.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation [V]</th>
<th>Reduction [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0.92</td>
<td>— —</td>
<td>1.53</td>
</tr>
<tr>
<td>6 1.02</td>
<td>— —</td>
<td>1.24</td>
</tr>
<tr>
<td>7 0.70</td>
<td>— —</td>
<td>1.60</td>
</tr>
</tbody>
</table>

(a) 1

HOMO (–5.34 eV)  LUMO (–2.50 eV)

(b) 6

HOMO (–5.78 eV)  LUMO (–3.16 eV)

(c) 7

HOMO (–5.06 eV)  LUMO (–2.40 eV)
Figure 4. Frontier orbitals of (a) 1, (b) 6, and (c) 7. DFT calculations were conducted at the B3LYP/6-31G(d) level.

We have also conducted time-dependent DFT (TD-DFT) calculations for 1, 6, 7, and 8 at the B3LYP/6-31G(d) level, evaluating the substituent effect on the absorption spectra. These calculations assign their longest-wavelength absorption to the HOMO–LUMO transition. The simulated absorption spectra undergo red-shift in the order of 1 (463 nm) < 6 (508 nm) < 5 (511 nm) < 8 (595 nm), which nicely accords with the observed trend. The HOMO of 8 is delocalized on not only the fluorenylidene segment, but also the peripheral 4-dimethylaminophenyl groups (Figure S25), suggesting the contribution of charge-transfer character on the HOMO–LUMO transition of 8.

In summary, we synthesized bay-brominated 9,9'-bifluorenylidene derivative 6 by the reductive dimerization of 4,5-dibromofluorenone 4 with (P(OEt)). The Suzuki–Miyaura cross-coupling of 6 afforded three arylated derivatives 7, 8, and 9. The X-ray diffraction analysis revealed that bay-brominated derivative 6 exhibits a larger dihedral angle between the fluorenylidene segments due to the relay of the steric repulsion from the bay-region to the fjord-region. The electronic effect by bay-substituents was examined by UV/vis absorption spectroscopy, cyclic voltammetry, and DFT calculations, revealing that (1) bromo-substituents stabilize the LUMO level mainly due to the inductive effect and (2) aryl-substituents raises the HOMO. The current work should be helpful in designing advanced functional materials consisting of 9,9'-bifluorenylidene.

This work was supported by JSPS KAKENHI grants JP20H05863, JP20H05867, JP22K14663, and JP23H03947 as well as JST, PRESTO grant JPMJP21Q7 (Japan).

Supporting Information is available online as well as JST, PRESTO grant JPMJPR21Q7 (Japan).

References and Notes

26. D. Schollmeyer, H. Deter, IUCrData 2022, x220169.
**Graphical Abstract**

**Textual Information**

We disclose the substitution effect at the bay-region of 9,9'-bifluorenylidene on its optical and electrochemical properties. X-ray diffraction analysis revealed that the bulky bay-substituents twist the overall structure through the relay of the steric repulsion from the bay-region to the fjord-region. The π-extension at the bay-region with toyl and 4-dimethylaminophenyl groups increases the electron-donating ability, while the introduction of bromo groups enhances the electron-accepting ability.

**Title (required)**

Synthesis and Properties of Bay-Functionalized 9,9'-Bifluorenylidene Derivatives

**Authors’ Names (required)**

Junichiro Hirano, Hiroshi Shinokubo, Norihito Fukui

---

**Graphical Information**

![Bay-functionalization diagram](https://example.com/bay-functionalization-diagram)
Figure 1. 9,9'-Bifluorenylidene (1) and its crystal structure.

93x38mm (250 x 250 DPI)
Figure 2. X-ray crystal structures of (a) 6, (b) 7, and (c) 8. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are omitted for clarity.

207x137mm (250 x 250 DPI)
Figure 3. UV/vis absorption spectra of 1 (black), 6 (green), 7 (red), 8 (blue), and 9 (pink) in CH2Cl2; λ = wavelength; ε = extinction coefficient.
Figure 4. Frontier orbitals of (a) 1, (b) 6, and (c) 7. DFT calculations were conducted at the B3LYP/6-31G(d) level.
Scheme 1. Treatment of fluorenone 2 and 4,5-dibromofluorenone 4 with P(OEt)₃ at 175 °C.

112x69mm (600 x 600 DPI)
Table 1. Structural parameters of 1, 6, 7, and 8.a

41x26mm (600 x 600 DPI)