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One-Step Synthesis of a 2,2′-Directly-Linked Perylene Dimer from a 2,5,8,11-Tetraborylated Perylene

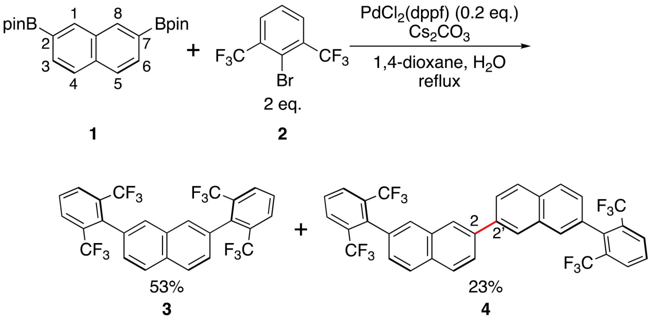
Ryuichi Fujita,[a] Miho Hirakawa,[a] Ryoko Oyama,[a] Kyohei Matsuo,[b] Hironobu Hayashi,[c] Mitsuaki Yamauchi,[b] Hiroko Yamada,*[b] and Naoki Aratani*[a]

One-step Suzuki-Miyaura cross-coupling reaction of 2,5,8,11-tetra-borylated perylene with 2,6-bis(trifluoromethyl)bromobenzene gave 2,2′-linked perylene dimer for the first time in 7.3 % yield under the standard conditions. The single-crystal X-ray structure exhibits three independent dimers in the unit cell, reflecting the low rotational energy around 2,2′-linkage. Excited state properties of 2,2′-dimer were compared with the corresponding 3,3′-linked congener. The facile synthetic method developed in this study could be a general route to access polycyclic aromatic hydrocarbon oligomers linked at less reactive positions.

Introduction

π-Conjugation of polycyclic aromatic hydrocarbons (PAHs) can be expanded by ring-fusion or oligomerization, resulting in a significant effect on photophysical properties such as a long-wavelength shift in the absorption spectrum.[1] In general, when PAHs are oligomerized at the position having the highest reactivity, the reaction pathway is simple and rapid.[2] For example, facile coupling methods based on oxidation reactions have been developed for the homogeneous oligomerization of pyrene[3] and porphyrin.[4] On the other hand, to synthesize PAH oligomers linked at positions with low reactivity, it is often necessary to take a multi-step route.[5] This is why there are no practical reports on 2,2′-linked perylene dimers despite their symmetric structure.[6]

When two 2,6-bis(trifluoromethyl)phenyl groups **2** were introduced into bis-borylated naphthalene **1**[7] at the 2,7-positions, 2,2′-linked dimer **4** was formed under standard Suzuki-Miyaura cross-coupling conditions in 23 % yield, along with the corresponding monomer **3** in 53 % yield (Scheme 1).[8] We therefore applied this side reaction to synthesize a 2,2′-linked perylene dimer. Consequently, the 2,2′-directly linked hexaaryl-substituted perylene dimer was obtained from pristine perylene in only two steps. Due to the small coefficients of the frontier orbitals at the 2,5,8,11-positions of perylene, the electronic communication between perylenes are expected to be limited even though the 2,2′-dimer takes co-planar (*vide infra*). A 3,3′-linked perylene dimer[9] possessing the same substituents was also synthesized, and the differences in optical properties depending on the bonding positions were compared.



Scheme 1. Synthesis of 2,7-di-substituted naphthalene **3** and 7,7′-di-substituted-2,2′-binaphthyl **4** from 2,7-diboryl naphthalene **1**.

Results and Discussion

Synthesis

2,5,8,11-Tetra-borylated perylene **5** was prepared by the iridium-catalyzed direct borylation of perylene.[10] The Suzuki-Miyaura cross-coupling reaction of **5** with 2,6-bis(trifluoromethyl)bromobenzene **2** not only afforded tetraaryl-substituted perylene monomer **6**[8] in 16 % but also simultaneously led to the formation of hexaaryl-substituted perylene dimer **7** in 7.3 % yield (Scheme 2). In this reaction, we used $PdCl_2$(dppf) (20 mol %) and 6 equivalents of **2** in a mixed solvent

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[a] R. Fujita, M. Hirakawa, Dr. R. Oyama, Prof. Dr. N. Aratani
Division of Materials Science, Nara Institute of Science and Technology (NAIST), 8916–5 Takayama-cho, Ikoma, Nara 630–0192, Japan
E-mail: aratani@ms.naist.jp

[b] Dr. K. Matsuo, Dr. M. Yamauchi, Prof. Dr. H. Yamada
Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611–0011, Japan
E-mail: hyamada@scl.kyoto-u.ac.jp

[c] Dr. H. Hayashi
Center for Basic Research on Materials, National Institute for Materials Science (NIMS), 1–2–1 Sengen, Tsukuba, Ibaraki 305–0047, Japan

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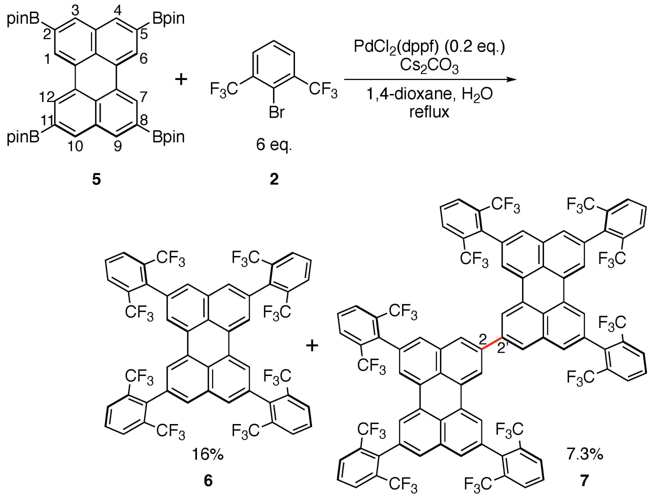
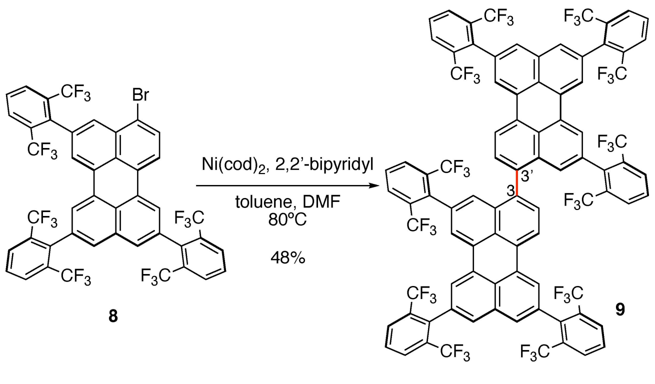


Scheme 2. One step synthesis of 5,5′,8,8′,11,11′-hexaaryl-2,2′-bisperylene **7** from tetraborylperylene **5**.

of 1,4-dioxane and water. The structure of **7** was confirmed by mass spectrometry and ^{1}H- and ^{19}F-NMR spectroscopy (Supporting Information: SI). High-resolution matrix-assisted laser-desorption/ionization time-of-flight (HR-MALDI-TOF) mass spectrometry detected the parent ion peak at $m/z = 1774.2083$ (calcd for $C_{88}H_{34}F_{36} = 1774.2080$ $[M]^+$). Notably, the ^{19}F-NMR spectrum of **7** shows three singlet peaks at room temperature, suggesting that **7** is fully co-planar or free-rotating around the 2,2′-linkage in solution (Figure S4).

It is well known that the homo-coupling reaction in the Suzuki-Miyaura couplings such as polymer synthesis occurs in a certain percentage.[11] A plausible mechanism to form the direct linkage between 2-positions is a concomitant side reaction of palladium-catalyzed cross-coupling reaction; the boronic acids (esters) are used as sacrificial nucleophiles, and transmetalation of 2 equivalents of **5** onto Pd(II) followed by reductive elimination generates Pd(0) species accompanying formation of a C–C homo-coupling product.[12]

For comparison, 3,3′-perylene dimer was prepared from 2,5,8-triarylperylene as shown in Scheme 3.[9] Ni(0)-mediated homo-coupling reaction of bromoperylene **8**[8] afforded 3,3′-perylene dimer **9** in 48% yield. The structure of **9** was also characterized by HR-MALDI-TOF mass spectrometry and ^{1}H- and ^{19}F-NMR spectroscopy.



Scheme 3. Synthesis of 5,5′,8,8′,11,11′-hexaaryl-3,3′-bisperylene **9** from triarylbromoperylene **8**.

Noteworthy here again is the ^{19}F-NMR spectrum. Six singlet peaks are observed at room temperature, indicating that the rotation at the 3,3′ linkage is inhibited in solution (Figure S6).

Single-Crystal X-Ray Analysis

The single-crystals suitable for X-ray diffraction were obtained by vapor diffusion of methanol into a solution of **7** in CH_2Cl_2 (Figure 1).[13] In the crystal, three independent 2,2′-dimers exist in the unit cell ($Z = 12$), one of which takes co-planar configuration, and the others are perpendicular. The dihedral angles between perylene cores are 3°, 81°, and 87°, respectively. The fact that the dimers have various dihedral angles in the crystal suggests that the rotational energy of the 2,2′-linkage is considerably small.

The single-crystals suitable for X-ray diffraction were also obtained by vapor diffusion of methanol into a solution of **9** in CH_2Cl_2 (Figure 2).[13] In case of 3,3′-dimer, only one kind of an independent molecule was analyzed in the unit cell and the dihedral angle between perylene cores is 86° since the hydrogen atoms at the peri-positions restrict the rotation of the two perylenes compared to the 2,2′-perylene dimer. This result is consistent with the ^{19}F-NMR spectrum in solution (Figure S6).

Photophysical Properties

To gain insight into the electronic communications between perylenes, UV-vis absorption spectra of **6**, **7**, and **9** in CH_2Cl_2 were measured (Figure 3a). The absorption spectrum of **7** showed only a small red-shift relative to that of monomer **6**, even though the co-planar configuration of **7**, due to the small coefficients of the frontier orbitals at the 2-position of perylene. On the other hand, the shape of the red-shifted UV-vis absorption spectrum of **9** was clearly different from those of **6** and **7**, presumably due to the strong electron correlation via the 3-position.

Photo-excited charge transfer due to "symmetry breaking" between the identical dyes has been studied in detail for directly-linked PAH dimers,[9,14] as in the case of 9,9′-anthryl.[15] To evaluate the interaction at the excited states in different bonding positions, photophysical properties of **7** and **9** were measures in cyclohexane, toluene, THF, $CHCl_3$, and CH_2Cl_2 (Figures 3b and c). For the 2,2′-dimer, no significant changes were observed in either the absorption and fluorescence spectra (Figure 3b). This indicates that the effect of solvent polarity on both the ground and excited states of the molecule is negligible.

UV-vis absorption spectra of **9** are also nearly invariant across solvents like that of **7** (Figure 3c). Fluorescence spectra, on the other hand, are affected by solvent. A progressive red-shift in the emission wavelength is observed with increasing solvent polarity, accompanied by a concomitant broadening

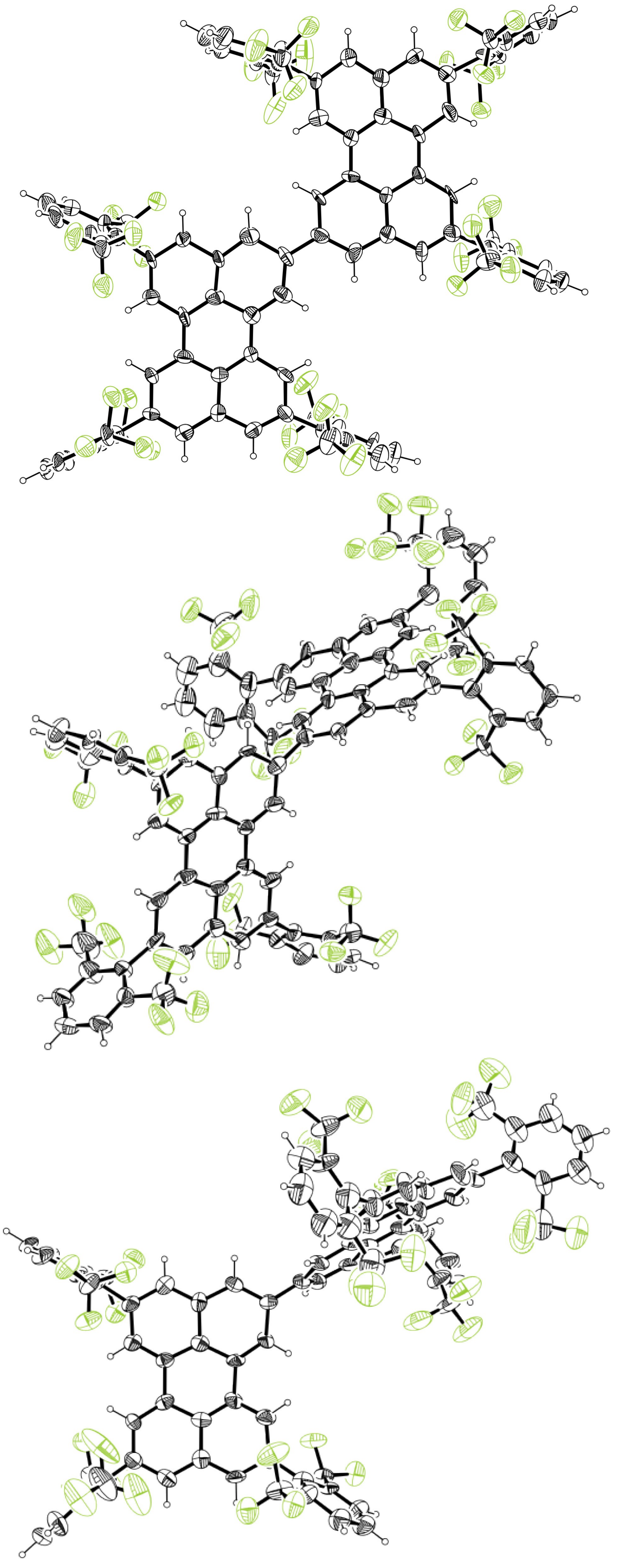


Figure 1. Single-crystal X-ray structures of three independent 2,2′-perylene dimers **7** in the unit cell. Fluorine atoms are represented by yellow-green color. Thermal ellipsoids are scaled at 25 % probability.

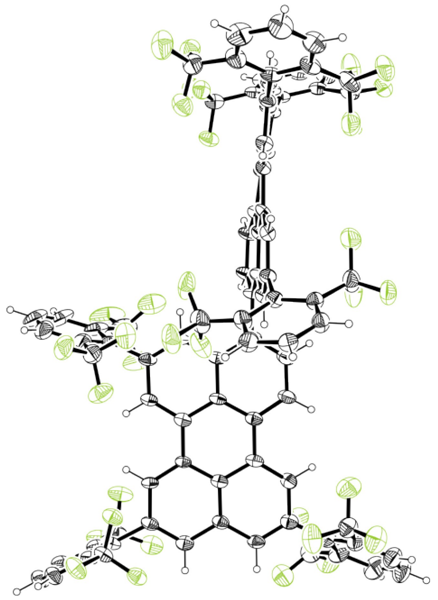


Figure 2. Single-crystal X-ray structure of **9**. Fluorine atoms are represented by yellow-green color. Thermal ellipsoids are scaled at 30 % probability.

(Figure 3c). The spectra indicate that **9** has a nonpolar ground state and a higher dipole moment in the excited state, even though the two constituent chromophores are identical. Similar behavior is observed for the 9,9′-bianthryl.[15] In fact, these Stokes shifts of the 3,3′-perylene dimer were analyzed using Mataga-Lippert plots with a straight line having a positive slope due to the effect of solvent relaxation, i.e., charge transfer after photo-excitation (Figure S10).

We also measured the fluorescence lifetimes of **6**, **7**, and **9** in cyclohexane, toluene, CH_2Cl_2, $CHCl_3$ and THF, with the results summarized in Figures S11–S13 and Table S1. In the case of monomer **6**, the fluorescence lifetimes were almost constant regardless of the solvents, but in the cases of compounds **7** and **9**, the fluorescence lifetimes tended to increase as the polarity of the solvent increased. Moreover, the effect was more pronounced for the 3,3′-dimer than for the 2,2′-dimer.

The photochemical measurements for 3,3′-dimer with *tert*-Bu substituents at 8 and 11 positions[9] showed almost the same fluorescence lifetimes. Therefore, the effect of CF_3 substituents on CT could be small.

In addition, the stability of the perylene dimers in CH_2Cl_2 solution was evaluated by monitoring changes their UV-vis absorption spectra The solutions of **7** and **9** were exposed to LED room light (400 to 700 nm) under air, showing practically no degradation after 24 h.

Electrochemical Measurements

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements in CH_2Cl_2 were performed to investigate the redox properties of the series of perylene derivatives (Figure 4). The working, counter, and reference electrodes are glassy carbon, Pt wire, and $Ag/AgNO_3$, respectively. With 0.1 M $n\mathrm{Bu_4NPF_6}$ as the electrolyte, the potentials were determined based on the ferrocene/ferrocenium (Fc/Fc^+) couple. The results

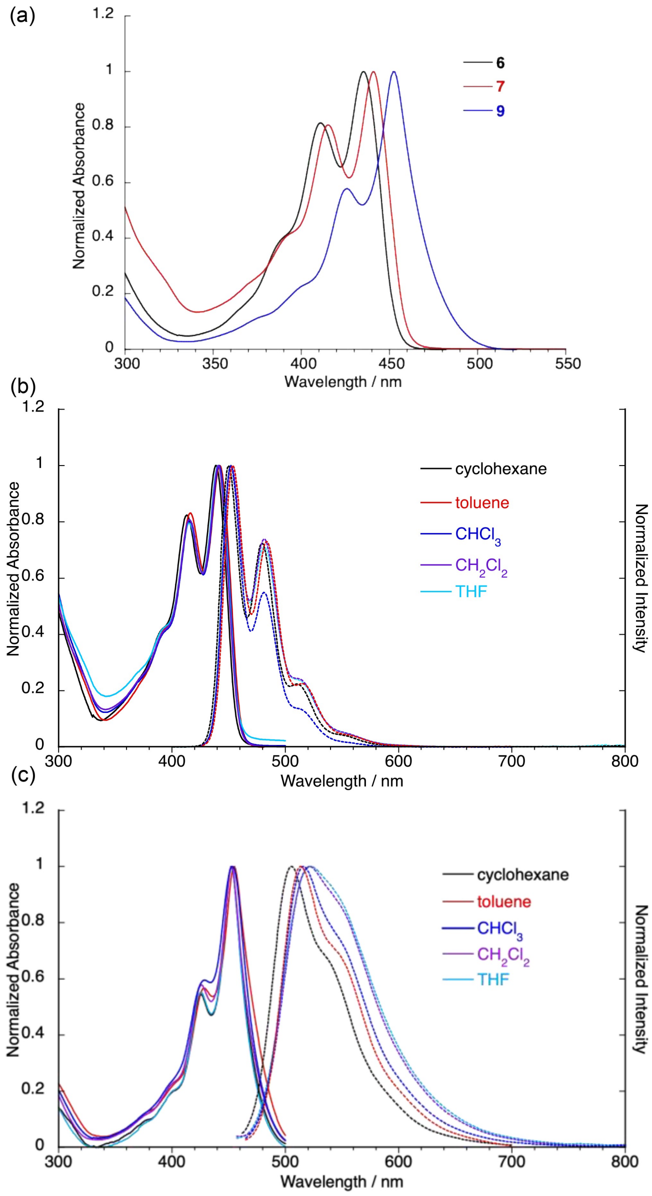


Figure 3. (a) UV-vis absorption spectra of **6**, **7**, and **9** in CH_2Cl_2. UV-vis absorption (solid line) and fluorescence (broken line) spectra of (b) **7** and (c) **9** in various solvents.

are summarized in Figure 4. Reversible oxidation and reduction waves were observed at 0.84 and −2.10 V for the monomer **6**. The CV of **7** and **9** exhibited two separated reversible oxidation and two reversible reduction waves, at 0.91, 0.78, −1.98 and −2.10 V for the dimer **7**, and at 0.95, 0.68,−2.05 and −2.11 V for the dimer **9**, respectively. The difference between the first (E_{ox1}) and second (E_{ox2}) oxidation potentials of **9** (0.27 V) is much larger than that of **7** (0.13 V). On the reduction side, two separated waves were also observed, but the difference is not as great as on the oxidation side. Thus, it is again confirmed that the electronic communication between perylene units in the 3,3′-dimer is larger than that of the 2,2′-dimer. This also evident in the lowering of the first oxidation potential (0.78 V to 0.68 V).

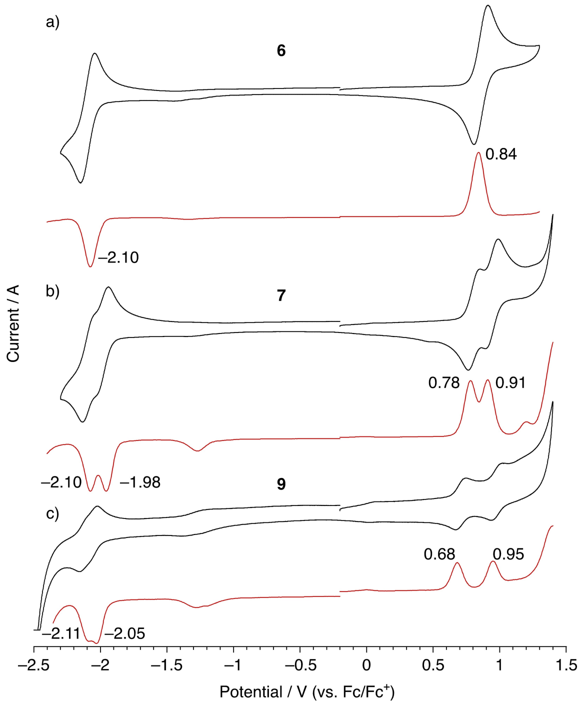


Figure 4. Cyclic (black line) and differential pulse (red line) voltammograms of a) **6**, b) **7**, and c) **9** at a scan rate of 0.1 V/s in CH_2Cl_2 (0.1 M nBu$_4$NPF$_6$).

Conclusions

In summary, we have succeeded in synthesizing the hexaaryl-substituted 2,2′-perylene dimer **7** in two steps from perylene even the coupling was achieved at the less reactive 2-positions. To the best our knowledge, this is the first practical report of 2,2′-perylene dimer. The photophysical properties of the 2,2′-perylene dimer were experimentally investigated and compared with those of the 3,3′-directly linked perylene dimer. Although no significant changes in absorption and fluorescence spectra were observed in the 2,2′-dimer due to the decoupled electronic communication, the fluorescence spectra of the 3,3′-dimer showed certain change depending on solvent polarity, indicating intramolecular charge transfer of **9** in the excited state.

The facile synthetic method developed in this study could be a general route to access PAH oligomers linked at less reactive positions.

Supporting Information Summary

Full details of synthesis, additional spectra, details of data collections are available in the Supporting Information.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Cross coupling · Oligomer · One step synthesis · Symmetry breaking · π-Conjugation

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