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Synthesis and Properties of BF_2 Complexes to Dihydroxydiones of Tetracene and Perylene: Novel Electron Acceptors Showing n-Type Semiconducting Behavior

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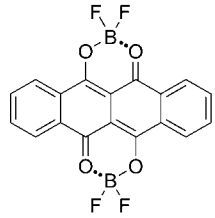
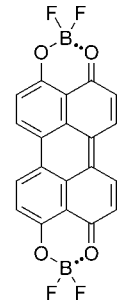
ABSTRACT





BF_2 complexes containing tetracene and perylene moieties were synthesized as new types of electron-deficient arene compounds. These compounds exhibit long wavelength absorption and high electron affinities, as revealed through spectral and electrochemical studies, due to their quadrupolar structures represented by resonance contributors. The BF_2 complex containing tetracene exhibits an n-type semiconducting behavior. These compounds are new types of electron acceptors functionalized by BF_2 chelation.

Currently, research on organic field-effect transistors (OFETs)[1] based on π-extended aromatic compounds is being actively pursued because of their potential applications in organoelectronic devices such as flexible displays, low-cost memories, and photovoltaic cells. A synthetic study of n-type semiconductors is crucial for the development of p-n junctions because the number of electron-transporting materials is still limited compared to that of p-type semiconductors.[2] Among these semiconductors, polycyclic aromatic compounds have been extensively studied. These compounds have extended π-conjugation and rigid planarity, thereby resulting in suitable intermolecular $\pi-\pi$ overlap and face-to-edge interactions in the solid state.[3] For the synthesis of n-type semiconductors with high electron affinities, introduction of fluorine and trifluoromethyl groups into arene moieties

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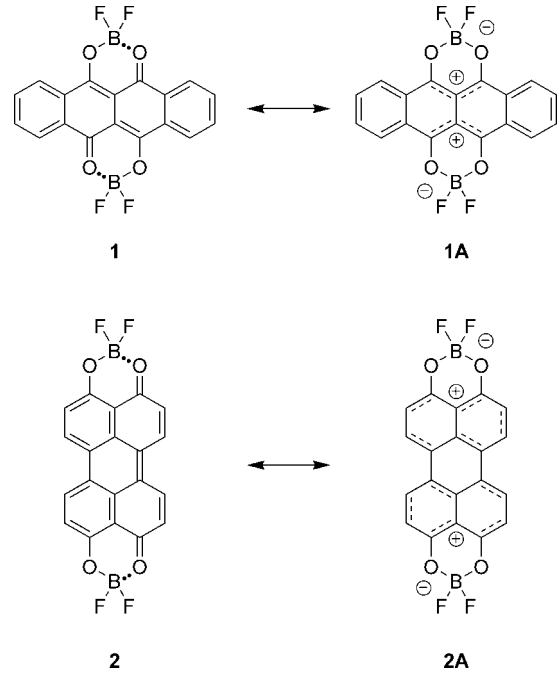
is effective, for example, perfluoropentacene,[2c] hexafluorohexa-*peri*-hexabenzocoronene,[4] and 2,6-bis(4-trifluoromethylphenyl)anthracene.[5] Furthermore, electron-withdrawing imide substituents yield naphthalene-, anthracene-, and perylene-based materials.[6] Electron-deficient heterocyclic compounds such as pyrazinoquinoxaline[7] and anthrazoline[8] are investigated as building blocks for electron-transporting materials. On the other hand, BF_2 complexes have been studied as potential electron-transporting materials.[9] In these compounds, the BF_2-chelating moieties behave as electron-accepting units.[9c] An OFET device that uses a BF_2 complex with 1,6-diphenyl-1,3,4,6-hexanetetrone exhibits an n-type semiconducting behavior.[9a] We synthesize BF_2 complexes containing tetracene (**1**) and perylene (**2**) as new types of electron-deficient arene compounds (Scheme 1). The BF_2 chelation contributes toward electron withdrawal and π-electron delocalization of the tetracene and perylene moieties, as represented by the resonance contributors **1A** and **2A**.[10] The quadrupolar structures yield small HOMO−LUMO energy gaps.[11] These molecules have rigid, planar structures leading to effective intermolecular $\pi-\pi$ overlap in the solid state. In this paper, we report the synthesis and properties of BF_2 complexes **1** and **2** and the application of **1** to OFET devices.

Scheme 1. Structures of BF_2 Complexes **1** and **2**



The synthesis of BF_2 complexes **1** and **2** was performed by chelation of 6,11-dihydroxy-5,12-naphthacenedione (DHND)[12] and 4,9-dihydroxy-3,10-perylenedione (DHPD)[13] with boron trifluoride−diethyl etherate (BF_3•OEt_2). Compound **1** was obtained in the form of red crystals with a yield of 61% after sublimation at 400 °C under 10^{-3} Torr. Compound **2** was prepared as a dark red solid with a crude yield of 88%, but it could not be sublimed. Compound **1** was slightly soluble in common organic solvents such as chloroform, dichloromethane, DMF, toluene, and acetonitrile, whereas compound **2** was insoluble in common solvents and very slightly soluble in DMF and acetonitrile. The structure of **1** was determined by ^{1}H NMR, IR, and EI mass spectrometry and elemental analysis. The structure of **2** was determined by IR and MALDI-TOF mass spectrometry. The molecular ion peak of **2** was observed by using the negative mode (see Supporting Information) instead of the positive mode. This suggests that compound **2** had high electron affinity. Both compounds were stable in air in the solid state. The stability of **1** to moisture considerably increased as compared to that of the BF_2 complex of 1,4-dihydroxyanthraquinone (quinizarin), which decomposed in air in the solid state within 5 h. The BF_2-chelating moieties of **1** and **2** were thermally stable in the solid state under nitrogen. The differential scanning calorimetry (DSC) of **1** revealed a melting point of 368.6 °C. The thermogravimetric analysis (TGA) of **2** exhibited the decomposition of a BF_2 moiety between 350 and 450 °C. The melting point of **1** was comparable to those of DHND (mp 351 °C) and tetracene (mp 357 °C), suggesting the strong intermolecular $\pi-\pi$ interactions.

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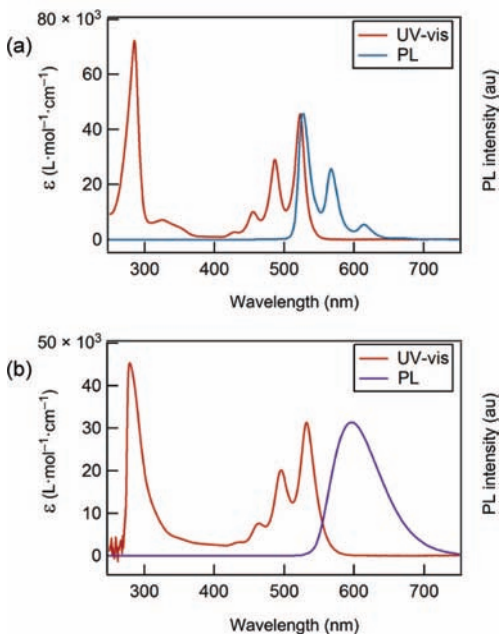

Figure 1. Absorption and PL spectra of **1** in (a) CH_2Cl_2 and (b) toluene.

The absorption and photoluminescence (PL) spectra of compound **1** in dichloromethane are shown in Figure 1a, and the optical properties of the compounds are listed in Table 1. The absorption bands between 420−550 nm and the PL bands between 500−650 nm are attributed to the tetracene moiety. These maxima are similar to those of DHND and are red-shifted relative to those of tetracene. The absorption and PL spectra of compound **2** in 1,1,2,2-tetrachloroethane are analogous to those of **1** in dichloromethane, and the maxima of **2** are red-shifted as compared to those of **1** (Table 1). According to the absorption edges, the energy gaps between the HOMO and LUMO levels for compounds **1** and **2** are found to be 2.15 and 2.04 eV, respectively. These values are smaller than that of tetracene and larger than that of perfluoropentacene (1.95 eV).[2c] The Stokes shifts are found to be 6 and 3 nm for compounds **1** and **2**, respectively. These results confirm that the BF_2-chelated complexes **1** and **2** have a rigid geometry such as those of tetracene (4 nm) and DHND (10 nm). Figure 1b shows the absorption and PL spectra of compound **1** in toluene. The absorption bands are slightly red-shifted as compared to those measured in dichloromethane (Table 1). Furthermore, the broadening of the PL bands is observed, and the PL maximum is red-shifted by 66 nm as compared to that of the shortest wavelength emission in dichloromethane. This phenomenon can be rationalized on the basis of an exciplex formation between compound **1** and electron-donating toluene. DHND exhibits a similar behavior in toluene, whereas tetracene does not show such a red-shift and broadening of PL bands.

Table 1. Optical Properties of **1** and **2**

compound	λ_{abs} (nm)	λ_{PL} (nm)	λ_{edge} (eV)
1[a]	523, 487, 455	529, 567, 615	2.15
1[b]	532, 495, 464	595	
2[c]	575, 533, 468, 440	578, 624	2.04
DHND[a]	518, 484, 457	528, 566, 604 sh	2.16
tetracene[a]	473, 444, 418, 395	477, 511, 549	2.45

[a] In CH_2Cl_2. [b] In toluene. [c] In $CHCl_2CHCl_2$.

Table 2. CV Data for **1** and **2**[a]

compound	E^{red1} (V)	E^{red2} (V)	E_p^{ox} (V)
1	−0.36	−0.90	
2	−0.18	−0.50	
DHND	−1.20	−1.77	
tetracene	−2.06		+0.52

[a] 0.1 M *n*-Bu_4NClO_4 in DMF, Pt electrode, scanning rate 100 mV s^{-1}, V versus Fc/Fc^+.

To investigate the electron affinity of compounds **1** and **2**, cyclic voltammetry (CV) is performed. The voltammograms of the compounds display two reversible reduction waves; the half-wave potentials are listed in Table 2. The reduction potentials of **1** and **2** are more positive than those of DHND and tetracene, indicating that compounds **1** and **2** have higher electron affinities. The electron-accepting ability of **2** is larger than that of **1**. These electron affinities are attributed to contribution by quadrupolar structures based on **1A** and **2A** (Scheme 1). The difference between the first and second reduction potentials for **1** (0.54 V) is similar to that for DHND (0.57 V), indicating that the on-site Coulomb repulsion is not affected by BF_2 chelation. The on-site Coulomb repulsion in compound **2** (0.32 V) is smaller than that observed in compound **1** owing to expansion of the arene skeleton. The reduction potentials of **1** and **2** are more positive than that of perfluoropentacene (−1.13 V versus Fc/Fc^+).[2c] Compounds **1** and **2** do not exhibit oxidation waves, whereas the oxidation potential of perfluoropentacene is reported to be +0.79 V. This indicates that both the HOMO and LUMO energies of **1** and **2** are lower than those of perfluoropentacene.

Table 3. B3LYP/6-31G(d) Calculations for **1** and **2**

compound	HOMO (eV)	LUMO (eV)	energy gap (eV)
1	−6.59	−3.86	2.73
2	−6.88	−4.35	2.53
DHND	−5.61	−2.88	2.73
tetracene	−4.84	−2.07	2.77

The molecular orbital (MO) calculations[14] of compounds **1** and **2** were performed using B3LYP/6-31G(d) in order to estimate the π-electronic states, which are summarized in Table 3. The HOMO and LUMO energies of **1** are lower

(14) See Supporting Information for the MO calculations.

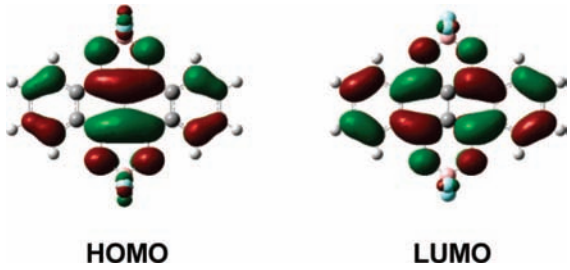

Figure 2. HOMO and LUMO of **1**.

than those of DHND and tetracene. This result demonstrates that the BF_2 chelation decreases the HOMO and LUMO energies of the arene π-electron systems. Furthermore, the HOMO and LUMO energies of **1** and **2** are lower than those of perfluoropentacene (HOMO, −5.39 eV; LUMO, −3.35 eV). The HOMO−LUMO energy gap of **2** is smaller than those of **1** and DHND (Table 3), although the energy gaps of **1** and **2** are larger than that of perfluoropentacene (2.04 eV).[15] These calculations support the high electron affinities and long wavelength absorption of **1** and **2**. The HOMO and LUMO energies of **1** are delocalized on the entire moiety of tetracene, as shown in Figure 2. The delocalization of molecular orbitals on the tetracene skeleton is favorable for the intermolecular $\pi-\pi$ overlap, which provides effective carrier transport.

The OFET device developed using compound **1** was fabricated on an SiO_2/Si substrate by a high-vacuum (ca. 10^{-6} Pa) evaporation method with bottom contact geometry at room temperature. Gold electrodes were prepared with L/W of 5 μm/38 mm. The OFET measurement was carried out under vacuum conditions. Figure 3 shows the output characteristics for the OFET device. The drain current increases as the gate voltage (V_g) becomes more positive; this means that the film of compound **1** exhibits n-type semiconducting behavior. The electron mobility and on/off ratio are calculated to be 1.5×10^{-5} cm^2 V^{-1} s^{-1} and 4000, respectively. This result is the first example of BF_2-chelated polycyclic aromatic compounds showing n-type semiconducting behavior.

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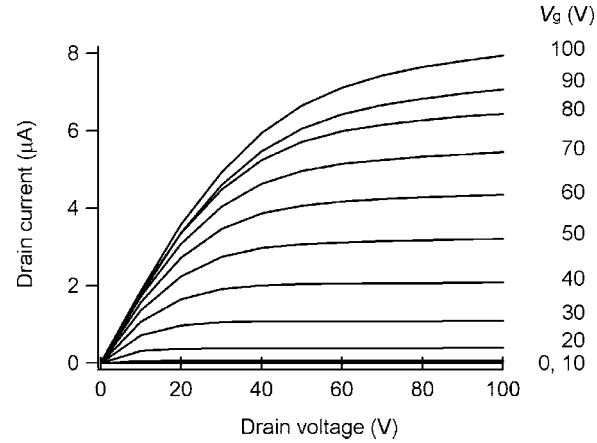

Figure 3. OFET characteristics for the film of **1** deposited at room temperature. Gate voltage (V_g) was applied in the range between 0 and 100 V.

In conclusion, we synthesized BF_2 complexes containing tetracene and perylene moieties as new types of electron-accepting compounds. These compounds exhibited small HOMO−LUMO gaps and high electron affinities, as observed from spectral and electrochemical studies. The properties of these compounds were attributed to the quadrupolar structures represented by resonance contributors. The BF_2 complex containing tetracene showed an n-type semiconducting behavior. This indicates that BF_2 chelation to arene moieties is a useful method for developing n-type semiconductors. Further investigation on the OFET applications of the BF_2 complexes is in progress.

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Supporting Information Available: Synthetic procedures and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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