Synthesis and luminescent properties of pyrenylvinylene-substituted tripylborane

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ARTICLE INFO

ABSTRACT

A novel luminescent compound, bis((E)-2-pyren-1-yl-vinyl)-2,4,6-triisopropylphenylborane (**3**) was synthesized by hydroboration reaction and was fully characterized. The obtained compound was further investigated by single-crystal X-ray diffraction analysis and DFT calculations. The extended structure tells us their herringbone structures with closely faced pairs of the molecules. Comparing the photoluminescent spectra between solution-state and solid state, the spectrum of the solid state of the compound **3** exhibited dramatically red-shifted fluorescent emission. This change also supports the efficient π-stacking behavior of the compound **3**.

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1. Introduction

Organic field-effect transistors (OFETs) have attracted a considerable interest for electronic applications, and even light-emitting OFETs have recently been developed. Air-stable n-type organic semiconducting materials are quite important for the p–n junction diodes. Fluorinated fused aromatics [1], heterocyclics [2–5] and diimide derivatives [6–9] are promising n-type materials. The design strategy of these n-type semiconductive materials has been based on the modification of the π-extended p-type semiconductive materials by electron-withdrawing groups. There have been some attempts to incorporate pyrene into conjugated oligomers for the generation of semiconducting layers in OFETs [10,11]. Furthermore, pyrene derivatives are chemically and photochemically stable comparing with linear polyacenes such as anthracene, tetracene and pentacene.

On the other hand, we have synthesized a wide variety of organoboron polymers including boron atoms in the polymer backbone by means of hydroboration polymerization [12–14]. These polymers exhibited strong fluorescence emission and n-type electronic conductivity [15,16] due to the high electron affinity of boron atoms. Especially, the extension of π-conjugation by hydroboration reaction has some inherit advantages. For example, this method does not require any transition metal catalyst which is usually used to prepare π-extended molecules. Therefore, metal catalysts that sometimes cause adverse affect for electronic properties cannot be in the obtained products in principle. We report here on the synthesis and the properties of the first example of 2-pyren-1-ylethenyl-substituted trivalent organoborane. The crystal structure and the packing diagrams were determined by single-crystal X-ray diffraction analysis.

2. Results and discussion

2.1. Synthesis

First, the reaction between 1-ethynylpyrene **2** and 2,4,6-triisopropylphenylborane (tripylborane, **1**) [tripyl = 2,4,6-triisopropylphenyl] was carried out as shown in Scheme 1. To a dehydrated and degassed THF solution of **2** was added a half equivalent of **1** in THF dropwise at room temperature in dry argon atmosphere. After 24 h of stirring, the solvent THF was removed under vacuum. The orange residue was purified by recrystallization from hot hexane to give orange crystals in 25% isolated yield. The structure of the compound **3** was confirmed by ^{1}H, ^{11}B and ^{13}C NMR, elemental analysis and single-crystal X-ray diffraction analysis. The ^{1}H NMR spectrum of the compound **3** showed the peaks assignable to the protons of two pyrenyl groups, a tripyl group and vinyl groups. The high value of the coupling constant (J = 17.54 Hz) shows that the vinyl protons are in the trans configuration. The integral ratios of the peaks for the compound **3** were in good agreement with the theoretical values. In the ^{11}B NMR spectrum, a peak around 63 ppm corresponding to the typical three-coordinated boron atom was observed.

2.2. Crystal structure

The crystal structure of the compound **3** was determined by single-crystal X-ray diffraction analysis. The boron center displays

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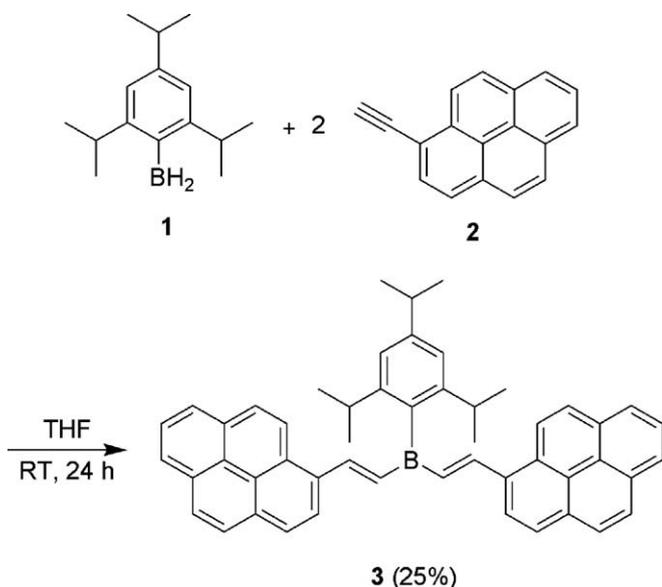
Scheme 1. Synthesis of compound **3**.

Table 1
Selected bond lengths (Å) and angles (°) for **3**.

3 (X-ray)			
B(1)–C(1)	1.531(4)	C(1)–B(1)–C(19)	115.6(2)
B(1)–C(19)	1.549(3)	C(1)–B(1)–C(37)	124.2(2)
B(1)–C(37)	1.579(4)	C(19)–B(1)–C(37)	120.1(2)
3 (DFT)			
B(1)–C(1)	1.5511	C(1)–B(1)–C(19)	118.3
B(1)–C(19)	1.5512	C(1)–B(1)–C(37)	120.9
B(1)–C(37)	1.5905	C(19)–B(1)–C(37)	120.9

Fig. 2. Plot illustrating the extended structure of compound **3**. All hydrogen atoms and tripyl groups were omitted for clarity.

a plane geometry, as shown in Fig. 1 and Table 1. Two pyrenyl groups were found to be in the same plane and the tripyl group was perpendicular to the pyrenyl groups. The extended structure illustrates herringbone structures with closely faced pairs of the molecules as shown in Fig. 2. The π-stacking distance is a critical parameter for efficient charge hopping in the solid state material. The distance between a pair of the pyrenyl groups was approximately 2.8 Å. According to the previous study [17], the crystal packing of the non-substituted pyrene was similar to that of the

compound **3** and the distance between a pair of pyrene molecules was about 3.5 Å. Therefore, the compound **3** seems to be promising as an organic electronic material.

2.3. DFT calculation

DFT calculation was carried out using GAUSSIAN 03 suit of program [18] for further understanding of the behavior of the luminescence. The structure of the compound **3** was optimized using the B3LYP/6-31(d) method. The orbital diagrams were generated by using the GAUSSVIEW program [19] as shown in Fig. 3. There was a good agreement between the geometry of the compound **3** optimized by DFT method and the structure determined by single-crystal X-ray diffraction as shown in Table 1. The lowest unoccupied molecular orbital (LUMO) is located on boron atom and the extension of the π-conjugation length via the boron atom was observed as pointed

Fig. 1. Structure of compound **3** with thermal ellipsoids drawn to the 50% probability level.

HOMO (-5.17 eV)   LUMO (-2.37 eV)

Fig. 3. HOMO and LUMO diagrams of compound **3**. Scaling radius is 75% and molecular orbital surface isovalue is 0.02.

before. We carried out TD–DFT calculations to obtain further insight into the origin of the electronic transitions for the compound **3**. The calculation reveals that the lowest energy transition of the compound **3** corresponds to promotion of electrons from the HOMO to the LUMO levels. The calculated excitation wavelength of the compound **3** was 492 nm with 1.4642 of the oscillator strength *f*. This wavelength was in approximately consistent with the result of UV–Vis absorption spectroscopy.

2.4. Optical properties

The optical properties of the compound **3** were investigated by UV–Vis absorption and fluorescence emission spectroscopy. The absorption of the compound **3** is shown in Fig. 4. The compound **3** showed the strong absorption peak at 437 nm (ε = 49 800). This absorption peak should be caused by the HOMO–LUMO transition on the plate of the pyrenylvinylene–borane–pyrenylvinylene from the DFT calculation. Fig. 5 shows the fluorescence spectra of the compound **3** in dichloromethane and in the solid state. The sample of the solid state of the compound **3** was prepared by using chloroform as a solvent (10 mg ml^{-1}) and by spinning the solution onto quartz substrates at 2000 rpm for 30 s. The excitation wavelength of 437 nm was set to the absorption maximum from the UV–Vis
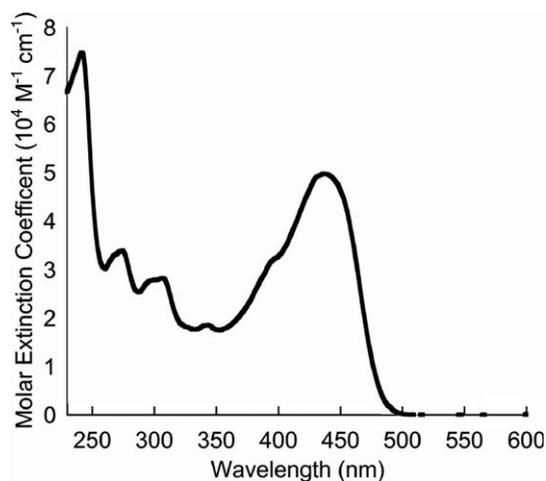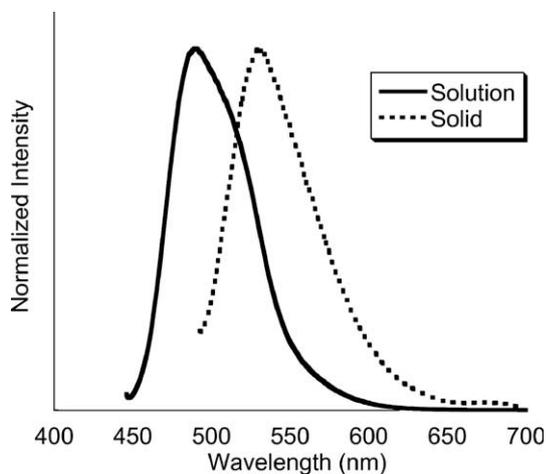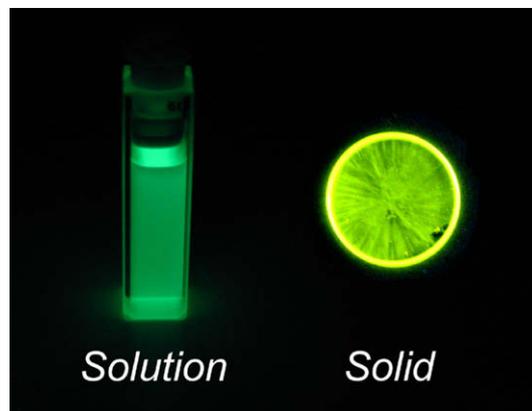
Fig. 6. Photographs of fluorescence of the compound **3** under UV light at 365 nm. Left: dichloromethane solution. Right: solid state.

absorption spectrum. The fluorescence emission peak from the dichloromethane solution was 490 nm. On the other hand, the solid state of the compound **3** showed dramatically red-shifted emission peak at 530 nm. This large red-shift should be due to an efficient π-stacking of the plane molecules of the compound **3**. Photographs of photoluminescence of the solution and the solid state are shown in Fig. 6. The dichloromethane solution exhibited a green emission and the spin-coated solid exhibited a yellow-green emission.

2.5. Conclusion

In conclusion, a pyrenylvinylene-substituted tripylborane was successfully prepared by hydroboration of ethynylpyrene with tripylborane. The crystal structure was revealed by single-crystal X-ray diffraction analysis. The packing diagram displayed herringbone structures with closely faced pairs of the molecules. DFT calculation and UV–Vis absorption spectroscopy indicated the delocalization of π-electron via the boron center. The fluorescence emission spectra reflected the strong π-stacking of the compound **3**. Efforts are underway to fabricate and evaluate OFETs utilizing the compound **3**.

3. Experimental

3.1. General

^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a JEOL JNM-EX400 instrument. The chemical shift values were expressed relative to Me$_4$Si (^{1}H and ^{13}C NMR) as an internal standard and BF$_3 \cdot$ OEt$_2$ (^{11}B NMR) as an external standard. UV–Vis spectra were obtained on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in CH$_2$Cl$_2$ at room temperature. Fluorescence spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer, and samples were analyzed in CH$_2$Cl$_2$ at room temperature. The melting point (m.p.) of the compound **3** was measured with a Yanaco Micro Melting Point apparatus (Model MP-S3). Elemental analysis was performed at the Microanalytical Center of Kyoto University. All procedures were performed under argon atmosphere. X-ray diffractions were collected on a Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation diffractometer with an imaging plate. A symmetry related absorption correction was carried out by using the program **abscor** [20]. The analysis was carried out with direct methods (SHELX-97 [21] or SIR92 [22]) using YADOKARI-XG [23]. The program ORTEP3 [24] was used to generate the X-ray structural diagrams.

Fig. 4. UV–Vis spectra of compound **3** in CH$_2$Cl$_2$ (5.0 × 10^{-5} M).

Fig. 5. Fluorescence spectra of compound **3** in CH$_2$Cl$_2$ (1.0 × 10^{-7} M) and in the solid state excited at 437 nm.

3.2. Materials

Tetrahydrofuran (THF) was purified using a two-column solid state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). Tripylborane **1** was prepared according to the literature [25]. 1-Ethynylpyrene was commercially available from Aldrich and purified by SiO$_2$ column chromatography. All other reagents were commercially available and used as received.

3.2.1. Bis((E)-2-pyren-1-yl-vinyl)-2,4,6-triisopropylphenylborane (**3**)

Tripylborane **1** (108 mg, 0.50 mmol) in THF (1 ml) was slowly added to 1-ethynylpyrene (226 mg, 1.00 mmol) in THF (4 ml). After stirring the mixture for 24 h at room temperature, the solvent was evaporated and the crude product was purified by recrystallization from hexane. After the emerged crystals were dried under reduced pressure, the model compound **4** (83 mg, yield 25%) was obtained as an orange solid. m.p. 245 °C. ^{1}H NMR (CDCl$_3$, δ, ppm): 8.61 (2H, d, J = 17.54 Hz, –CH=CH–B–), 8.55 (2H, d, J = 8.04 Hz), 8.36 (2H, d, J = 9.50 Hz), 8.22–8.16 (6H, m), 8.12–8.04 (6H, m), 8.00 (2H, t, J = 7.55 Hz, pyrene-7H), 7.80 (2H, d, J = 17.54 Hz, –CH=CH–B–), 7.17 (2H, s, tripyl-H), 3.12–3.01 (1H, m, –CH–(CH$_3$)$_2$ on 4-position of tripyl), 2.87–2.77 (2H, m, –CH–(CH$_3$)$_2$ on 2 and 6-position of tripyl), 1.43 (6H, d, J = 7.07 Hz, –CH–(CH$_3$)$_2$ on 4-position of tripyl), 1.28 (12H, d, J = 6.58 Hz, –CH–(CH$_3$)$_2$ on 2 and 6-position of tripyl). ^{13}C NMR (CDCl$_3$, δ ppm): 150.73, 149.75, 148.18, 139.90, 138.07, 132.21, 132.07, 131.40, 130.77, 129.41, 128.14, 127.45, 126.09, 125.70, 125.46, 125.11, 124.98, 124.82, 124.54, 122.69, 120.05, 35.31, 34.40, 24.60, 24.28. ^{11}B NMR (CDCl$_3$, δ, ppm): 63.67. Anal. Calc. for C$_{51}$H$_{45}$B: C, 91.60; H, 6.78; B, 1.62. Found: C, 91.35; H, 6.88%.

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