

Synthesis of π -Conjugated Dendrimers
Based on Azaborines

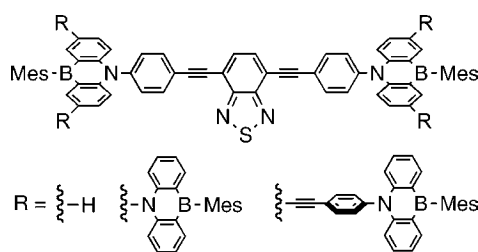
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ABSTRACT



π -Conjugated dendrons and dendrimers based on dibenzoazaborine were synthesized. The azaborine dendrons exhibited strong light absorption and photoluminescence, reflecting the optical properties of the azaborine. The fluorescence from the azaborine dendrimers bearing a benzothiadiazole core was strongly red-shifted or quenched, indicating photoinduced electron transfer from the azaborine dendrons to the core unit.

The spherical shape of dendrimers, as well as the core-branch-shell-type hierarchical structures, often provides useful features that are not accessible by ordinary small molecules or macromolecules (dendritic effects).¹ Therefore, the construction of new dendrimers featuring unique structures is an attractive strategy for the development of novel functions, such as self-assembly,² catalyst,³ drug-delivery,⁴ electrooptical devices,⁵ and so on.

π -Conjugated dendrimers have several advantages compared with a flexible one: (1) because of their rigidity, internal molecular motions are suppressed, and the spatial arrangement of the functional units in the dendritic structure can be precisely controlled, which is important for the design of the electronic interaction between the units. (2) The solubility

and amorphousness can be improved by their rigid and bulky three-dimensional structure. (3) Because of the dense packing of conjugated units, such dendrimers are expected to show efficient intramolecular energy or charge transfer ability. These potentials of the π -conjugated dendrimers are highly prized from the viewpoint of organic electrooptical materials, and thus π -conjugated dendrimers bearing various π -systems have been synthesized recently. For example, π -conjugated dendrimers based on electron-donating units, such as thiophene,⁶ carbazole,⁷ and phenothiazine,⁸ exhibited interesting optical and electronic properties. In contrast, electron-accepting units have not been widely utilized as a component unit of π -conjugated dendrimers,^{9,10} and π -conjugated dendrimers bearing both electron donors and acceptors are still

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unknown. Such dendrimers are expected to show n-type or ambipolar charge transfer ability, both of which have recently become important in the field of highly functionalized organic field effect transistors.¹¹

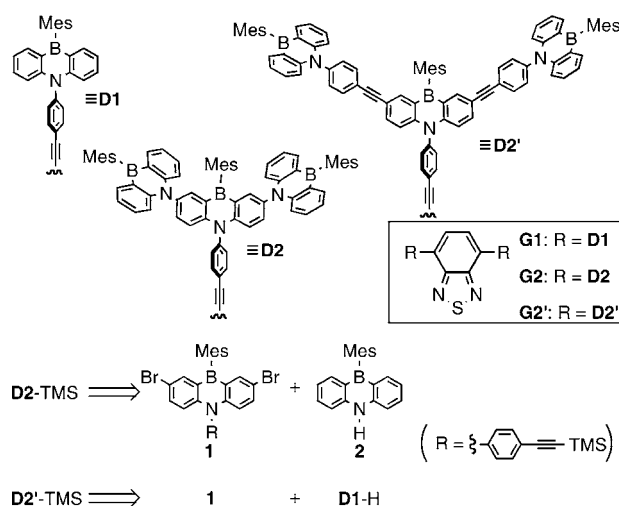


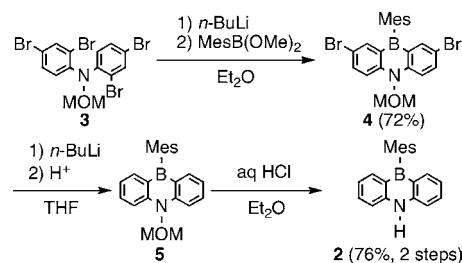
Figure 1. Azaborine-based dendrons **D1**, **D2**, and **D2'** and dendrimers **G1**, **G2**, and **G2'**. Synthetic strategy of the dendrons is also shown.

Recently, we have been investigating the properties of dibenzoheteraborines and their π -extended derivatives.^{12,13} In particular, dibenzoazaborines and their π -extended derivatives exhibited strong light absorption and emission because of the intramolecular charge-transfer interaction between electron-donating nitrogen atoms and electron-withdrawing boron atoms in the acene-like rigid structures. These results implied to us that an accumulation of dibenzoazaborine units in the dendritic architecture would provide dendrimers with beneficial characteristics, including light-harvesting antenna, ambipolar charge transfer, and charge separation upon photoexcitation of the dibenzoazaborine units.¹⁴ Here, we report the syntheses and optical properties of azaborine-based conjugated dendrons and their dendrimers bearing a strongly

electron-accepting benzothiadiazole unit as the core.¹⁵ The structures of azaborine dendrons and dendrimers are shown in Figure 1. These dendrons could be synthesized by palladium-catalyzed coupling reactions between branching unit **1** and terminal unit **2** or **D1-H**.

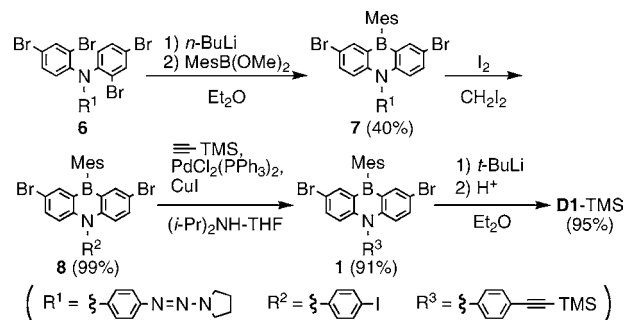
The synthesis of terminal unit **2** is shown in Scheme 1. *Ortho*-selective bromine–lithium exchange of MOM-protected diarylamine **3** followed by the reaction with MesB(OMe)₂ gave azaborine **4** in good yield.^{12c} The bromine atoms of **4** were removed, and deprotection of the MOM group of **5** under acidic conditions produced terminal unit **2**.

Scheme 1. Synthesis of Terminal Unit **2**



Branching unit **1** and first-generation dendron **D1-TMS** were synthesized from triarylamine **6** (Scheme 2). Triaz-enylphenyl azaborine **7** was synthesized from **6**, and the triaz-enyl group was quantitatively substituted with an iodine atom by treatment with I₂ in CH₂Cl₂.¹⁶ Sonogashira coupling of **8** with TMS-CCH gave **1** in good yield, and the bromo substituents of **1** were removed to give **D1-TMS**.

Scheme 2. Syntheses of Branching Unit **1** and Dendron **D1-TMS**



Second-generation dendrons **D2-TMS** and **D2'-TMS** were obtained by Buchwald–Hartwig coupling and Sonogashira coupling of **1** and the corresponding terminal unit, respec-

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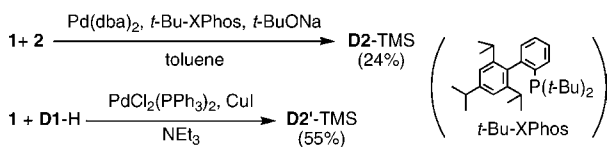
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tively (Scheme 3).¹⁷ The use of *t*-Bu-XPhos is critical to facilitate the coupling between **1** and **2**.

Scheme 3. Synthesis of Dendrons **D2-TMS** and **D2'-TMS**



The longest absorption maximum of **D2-TMS** hardly changed from that of **D1-TMS**, and the absorption coefficient of **D2-TMS** was almost three times as great as that of **D1-TMS** (Figure 2, Table 1). These results indicate that the three

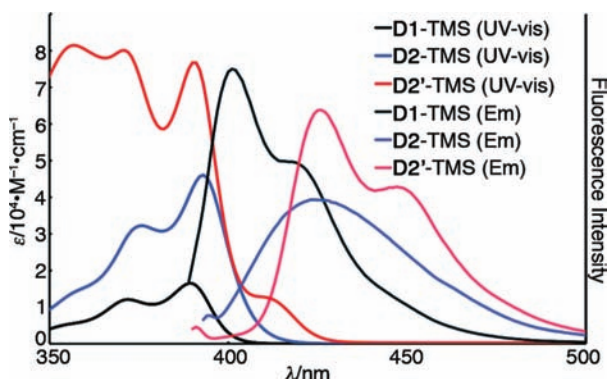
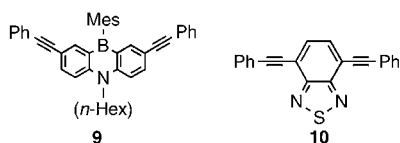


Figure 2. Optical spectra of the dendrons in CH_2Cl_2 .

Table 1. Optical Data of the Dendrons and Dendrimers in CH_2Cl_2

	$\lambda_{\text{max}}/\text{nm}$ (log ϵ)	$\lambda_{\text{em}}/\text{nm}$ (Φ)
D1-TMS	391 (4.2)	401 (0.80)
D2-TMS	393 (4.7)	423 (0.56)
D2'-TMS	391 (4.9), 415 (4.0)	426 (0.48)
G1	392 (4.6)	620 (0.19)
G2	393 (5.0)	429 (0.01)
G2'	391 (5.1), 414 (4.5)	450, 635 (0.08)
9	417 (3.9)	433 (0.33)
10	412 (4.4)	505 (0.87)



azaborine units in **D2-TMS** are electronically independent and behave as isolated chromophores.⁷ **D2'-TMS** showed a more intense light-absorption band for the azaborine units

at 391 nm and a new band at 415 nm. The new absorption band is assigned to the localized excitation on the branching unit by comparison with the optical data of **9** (λ_{max} 417 nm). The second longest maximum is due to the absorption of the terminal units, but the absorption coefficient increased substantially compared with that of **D2-TMS**. Such a strong light-absorbing property is useful for various applications, such as light-harvesting antennas.¹⁸

D1-TMS exhibited strong fluorescence with a small Stokes shift. The photoluminescence of **D2-TMS** was somewhat red-shifted and broadened, and the fluorescence quantum yield decreased, probably because of a deactivation process such as internal rotations. **D2'-TMS** also showed red-shifted emission at 426 nm, which is assigned to fluorescence from the branching unit, because **9** exhibits strong fluorescence at nearly the same wavelength. In addition, excitation of the terminal units also gave the same emission, indicating an efficient energy transfer from the terminal units to the branching unit.¹⁹

The TMS group of azaborine-based dendrons **D1-TMS**, **D2-TMS**, and **D2'-TMS** was removed by basic alcoholysis. The resulting terminal acetylene was coupled with 4,7-dibromobenzo[*c*][1,2,5]thiadiazole to give dendrimers **G1**, **G2**, and **G2'**, respectively (Table 2).

Table 2. Synthesis of the Azaborine-Based Dendrimers

TMS-protected dendron	dendrimer	yield (%)
D1-TMS	G1	52
D2-TMS	G2	62
D2'-TMS	G2'	13

The absorption profiles of **G1**, **G2**, and **G2'** are the superposition of those of the core unit and the corresponding dendrons (Figure 3, Table 1). This means that the dendrons and the core do not interact with each other in their ground states.

Irradiation of **G1** resulted in a broad and red-shifted emission, and the fluorescence from the dendrons was completely quenched. An excitation spectrum of **G1** revealed that the excitation of the dendrons contributes to the emission.¹⁹ The large bathochromic shift of the emission maximum from that of **10** indicates that the emissive state is not a local excited state of the core but an intramolecular charge-transfer (ICT) state formed between the core and the dendrons.²⁰

Density functional theory (DFT) calculations on **G1** show that its LUMO is a π^* orbital of the core unit, and its

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(19) See the Supporting Information for detail.

(20) In benzonitrile, the emission maximum of **G1** was shifted to 660 nm, suggesting the highly polar nature of the emissive state.

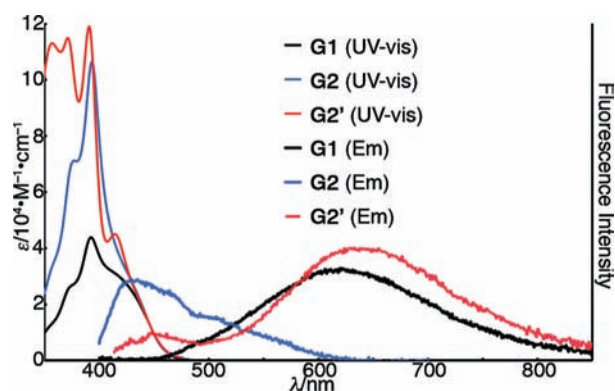


Figure 3. Optical spectra of the dendrimers in CH_2Cl_2 .

degenerate HOMO and HOMO-1 are π orbitals of the two dendrons, suggesting that electron transfer (ET) from the dendrons to the core unit to give the ICT state is a favorable process. TD-DFT calculations also revealed that the lowest excited state of **G1** is an ICT state between the dendrons and the core, and local excited states of the dendrons or the core are located at higher energy levels. Therefore, a Franck–Condon state of **G1** can be transformed to the ICT state, which may give the observed fluorescence emission.²¹

G2 did not exhibit a long-wavelength emission similar to that of **G1**. Instead, it showed a very weak and broad photoluminescence band that is ascribed to the emission from the dendrons (λ_{em} 429 nm) and the core (around 500 nm). The depression in its fluorescence intensity may be due to the fluorescence quenching by the ET from the dendrons to the core. On the other hand, the fluorescence of **G2'** contained not only a short-wavelength emission (λ_{em} 450 nm) but also a long-wavelength one (λ_{em} 635 nm), and the fluorescence quantum yield was moderate. The short-wavelength emission is ascribed to the dendron- and core-based fluorescence, and the long-wavelength one may be from the ICT state of **G2'**. Therefore, the fluorescence property of **G2'** can be described as a mixture of those of **G1** and **G2**.

The feasibility of such ET processes was analyzed on the basis of the Rehm–Weller equations (Table 3).^{22,23} In all

(21) In CH_2Cl_2 , pulsed laser irradiation (355 nm) of **G1** gave a development of transient absorption maxima at 473, 525, and 560 nm, and their lifetime was ca. 27 μs . Almost the same transient absorption profiles were observed in benzonitrile, indicating little solvent effect on the excited states. In addition, an air-saturated CH_2Cl_2 or benzonitrile solution of **G1** did not exhibit clear transient absorptions. These results suggest that the intermediate observed in these measurements is not an ICT state but a triplet state. A pathway from the Franck–Condon state of **G1** to the triplet state is not elucidated yet, but the ICT state is assumed to be formed as a primary intermediate that gives the fluorescence and is transformed into the triplet state to some extent.

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(23) The Coulomb interaction term ($Ze_0^2/\epsilon\alpha$) was neglected here because both the electron donor and acceptor are neutral molecules, and hence, the Coulomb interaction between them should be quite small.

Table 3. Parameters of Rehm–Weller Equation and the Estimated Free Energy Change on the Electron Transfer (ΔG_{ET})^a

	E_{ox}^b/V	$E_{\text{red}}^b/\text{V}$	E_{00}^c/eV	$\Delta G_{\text{ET}}^d/\text{eV}$
D1-TMS	1.0 ^e		3.4	
D2-TMS	1.0 ^e		3.3	
D2'-TMS	1.1 ^e		3.2	
10		−1.7 ^f		
G1				−0.7
G2				−0.6
G2'				−0.4

^a In CH_2Cl_2 . ^b The redox potentials (vs Fc/Fc^+) were measured by cyclic voltammetry in CH_2Cl_2 containing 0.1 M TBAP with a scan rate of 0.1 $\text{V}\cdot\text{s}^{-1}$. ^c E_{00} was estimated by the absorption edge of the UV–vis spectrum. ^d $\Delta G_{\text{ET}} = E_{\text{ox}} - E_{\text{red}} - E_{00} - Ze_0^2/\epsilon\alpha$. ^e Irreversible, peak potential. ^f Reversible, peak potential.

cases, ΔG_{ET} values are negative, and thus, the ET from the dendrons to the core is a thermodynamically favorable process, indicating the fast formation of the ICT states soon after the photoexcitation.

The difference in the fate of the ICT states between these dendrimers is quite intriguing. While the ICT state of **G1** and **G2'** resulted in a long-wavelength emission, **G2** exhibited only weak dendron- and core-based fluorescence, indicating that its ICT state is not emissive and participates in the fluorescence quenching, unlike **G1** and **G2'**. Further investigation to clarify the origin of such a difference is now underway in our laboratory.

In summary, the first donor–acceptor-type π -conjugated dendrons and dendrimers based on dibenzoazaborines have been synthesized. The optical properties of the dendrons are similar to those of the parent azaborines, indicating that the azaborine units are aligned perpendicularly to each other. Dendrimers containing the azaborine dendrons and the benzothiadiazole core form ICT excited states, but the fate of these excited states strongly depends on the generation of the dendrons.

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Supporting Information Available: Experimental and spectral data for all compounds and a description of theoretical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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