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Zwitterionic Ladder Bis(arylethenyl)benzenes with Large Two-Photon Absorption Cross Sections

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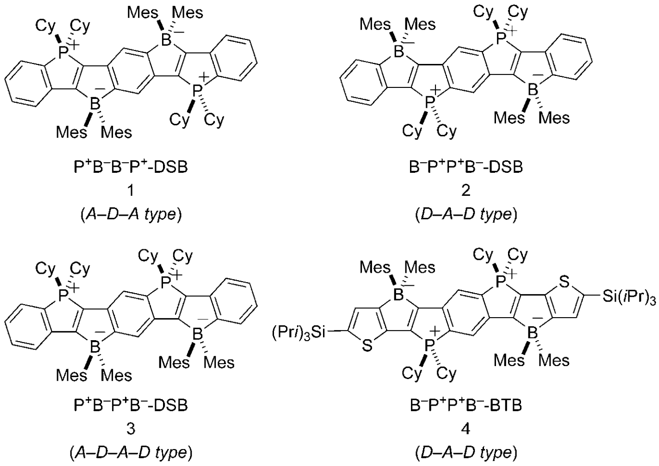
Dedicated to the 150th anniversary of Japan–UK diplomatic relations

The two-photon absorption (TPA) properties of organic chromophores have recently attracted much attention owing to a variety of potential applications, such as 3D microfabrication, ultra-high-density optical data storage, optical-limiting devices, up-converted lasing, and photodynamic therapy.[1] Considerable effort has been devoted to developing an excellent organic TPA material with a large TPA cross section (δ). Several TPA materials with δ values of several hundreds to thousands GM (1 GM $= 10^{-50}$ cm^4 s photon^{-1}) have already been reported, including dipolar[2] or quadrupolar[2a,3] π-conjugated chromophores, oligomeric porphyrin derivatives,[4,5] and giant macrocycles.[6] These studies have provided important guidelines for the molecular design of excellent TPA materials. Namely, 1) a sufficiently long π-conjugation length, 2) introduction of strong donor and acceptor moieties into a π-conjugated skeleton, and 3) a planar and rigid molecular structure are important structural requirements for large δ values. Regarding these guidelines, one promising class of TPA materials may be the ladder-type π-conjugated compounds with polar electronic structures. We have recently succeeded in synthesizing such compounds categorized into this class, i.e., phosphonium- and borate-bridged distyrylbenzenes (DSBs) **1** and **2** (Figure 1).[7] In these compounds, the zwitterionic bridges not only fix the DSB framework in a rigid and coplanar fashion, but also provide a highly polar electronic structure. The phosphonium and borate functionalities serve as strong electron-accepting and -donating moieties, respectively. All these features seem to well satisfy the foregoing requirements for excellent TPA properties. Whereas it has already been reported that several π-electron systems with zwitterionic groups have excellent nonlinear optical properties,[8–13] our current interest lies in the effects of the zwitterionic bridges in the completely planar π skeleton. We now report the TPA characteristics of a series of phosphonium- and borate-bridged ladder π-electron systems. In particular, we newly synthesized dipolar $P^+B^-P^+B^-$-DSB **3** (A-D-A-D type, Figure 1) and compared its photophysical properties with those of the quadrupolar $P^+B^-B^-P^+$-DSB **1** (A-D-A type) and $B^-P^+P^+B^-$-DSB **2** (D-A-D type) to address the effect of the bridging patterns (D and A denote the donor and acceptor, respectively). Furthermore, we designed and synthesized a thiophene-terminated analogue, the $B^-P^+P^+$



$P^+B^-B^-P^+$-DSB
1
(*A–D–A type*)

$B^-P^+P^+B^-$-DSB
2
(*D–A–D type*)

$P^+B^-P^+B^-$-DSB
3
(*A–D–A–D type*)

$B^-P^+P^+B^-$-BTB
4
(*D–A–D type*)

Figure 1. Zwitterion-bridged ladder π-conjugated compounds.

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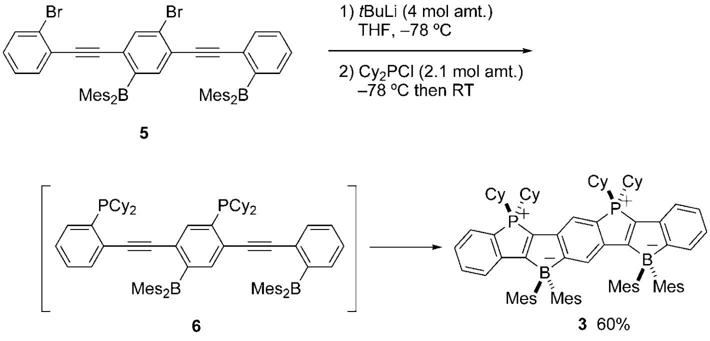
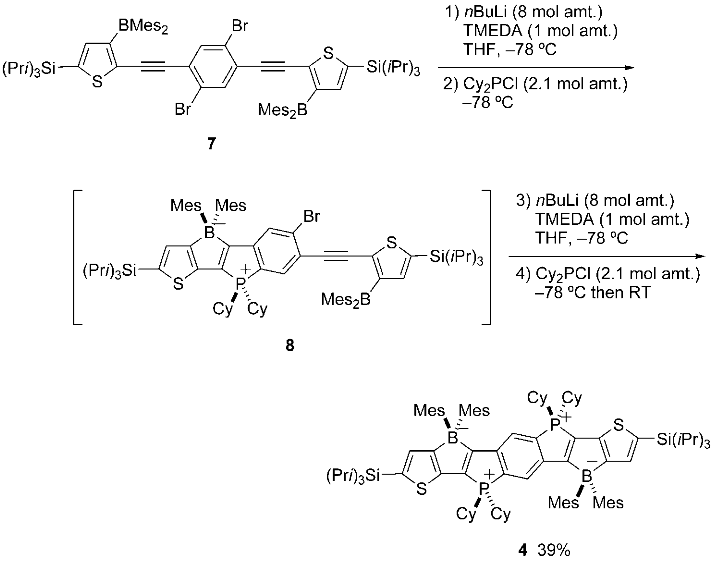
$\mathrm{B^-}$-bridged bis(thienylethenyl)benzene (BTB) **4**, as a potential TPA material in the near-infrared (NIR) region.

The syntheses of $\mathrm{P^+B^-P^+B^-}$-DSB **3** and $\mathrm{B^-P^+P^+B^-}$-BTB **4** were accomplished by intramolecular cyclization protocols, as shown in Scheme 1 and 2. For the synthesis of **3**, an unsymmetrically diborylated bis(phenylethynyl)benzene **5** was employed as a starting material. This compound was obtained from 1,4-dibromo-2,5-bis(trimethylsilylethynyl)benzene in seven steps with a total yield of 17% (see the Supporting Information). The dilithiation of **5** with *t*BuLi in THF followed by treatment with $\mathrm{Cy_2PCl}$ produced a bis(boryl)bis(phosphanyl) intermediate **6**, which spontaneously underwent nucleophilic double cyclization to give $\mathrm{P^+B^-P^+B^-}$-DSB **3** as bright orange solids in 60% yield. On the other hand, for the synthesis of **4**, we employed borylthienyl-terminated diethynylbenzene **7** as a starting material and first tried the dilithiation using various bases. However, all attempts were unsuccessful, presumably owing to the instability of the resulting dilithiated species. Therefore, we conducted the intramolecular cyclization in a stepwise manner. Thus, the monolithiation of **7** with excess *n*BuLi in the presence of TMEDA, followed by trapping with $\mathrm{Cy_2PCl}$, produced a mono-phosphanyl intermediate, which smoothly underwent the cyclization to give the partially cyclized product **8**. The mixture was again subsequently treated with an excess amount of *n*BuLi and then with $\mathrm{Cy_2PCl}$. This one-pot protocol successfully produced the fully fused compound **4** in 39% yield as deep blue solids. Notably, both compounds **3** and **4** were sufficiently stable in the air and moisture.



Scheme 1. Synthesis of compound **3** (Cy = cyclohexyl, Mes = mesityl).



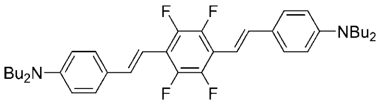
Scheme 2. Synthesis of compound **4**.

As summarized in Table 1, the photophysical properties of the phosphonium- and borate-bridged DSBs significantly depend on their bridging patterns. In the absorption spectra, among the three positional isomers **1**–**3**, the dipolar $\mathrm{P^+B^-P^+B^-}$-DSB **3** has the shortest absorption maximum (λ_{abs} = 480 nm in benzene), which is 40–50 nm shorter than those of quadrupolar **1** and **2**. In the fluorescence spectra, all the DSB derivatives showed intense emissions with quantum yields of 0.3–0.5 in benzene. The D-A-D type $\mathrm{B^-P^+P^+B^-}$-DSB **2** has the longest emission maximum wavelength (λ_{em}), while those of **1** and **3** are comparable to each other. In terms of the Stokes shift, the dipolar A-D-A-D type **3** has the largest value of 4200 $\mathrm{cm^{-1}}$, while those of the quadrupolar **1** and **2** are 2500 and 3100 $\mathrm{cm^{-1}}$, respectively. These results indicate that the dipolar compound **3** has a significant intramolecular charge-transfer (CT) character in the lowest-energy transition.

Table 1. Photophysical data for a series of bis(arylethenyl)benzenes **1**–**5** and **9**.[a]

	Absorption		Fluorescence		TPA
Cmpd	λ_{abs} [nm][b]	log ε	λ_{em} [nm][c]	Φ_{F}	δ [GM][d]
1	522	4.30	599	0.52[e]	349[i]
2	531	4.06	636	0.47[e]	469[i]
3	480	4.06	601	0.35[e]	476[i]
4	620	4.24	734	0.021[f]	784[j]
9[g]	439[h]	4.63[h]	528[h]	0.31[h]	216[i]

[a] In benzene unless stated otherwise. [b] Only longest absorption maxima are shown. [c] Emission maxima upon excitation at the absorption maximum wavelengths. [d] Two-photon absorption cross sections; 1 GM = 10^{-50} $\mathrm{cm^4\,s\,photon^{-1}}$. [e] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error. [f] Relative fluorescence quantum yields determined with cresyl violet perchlorate[14] as a standard. [g] Reference [17]. [h] In toluene. [i] Excited at 900 nm. [j] Excited at 1200 nm.



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To elucidate the effect of the bridging patterns on the electronic structures, we conducted DFT calculations on the model compounds **1′**–**3′** at the B3LYP/6-31G(d) level of theory, in which the cyclohexyl and mesityl groups in **1**–**3** are replaced with methyl and phenyl groups, respectively.[15] Dipolar **3′** has its HOMO and LUMO energy levels in the middle of those of quadrupolar **1′** and **2′**, as shown in Figure 2. This suggests that, in the A-D-A-D system, the electronic effects of the electron-donating borate and elec-

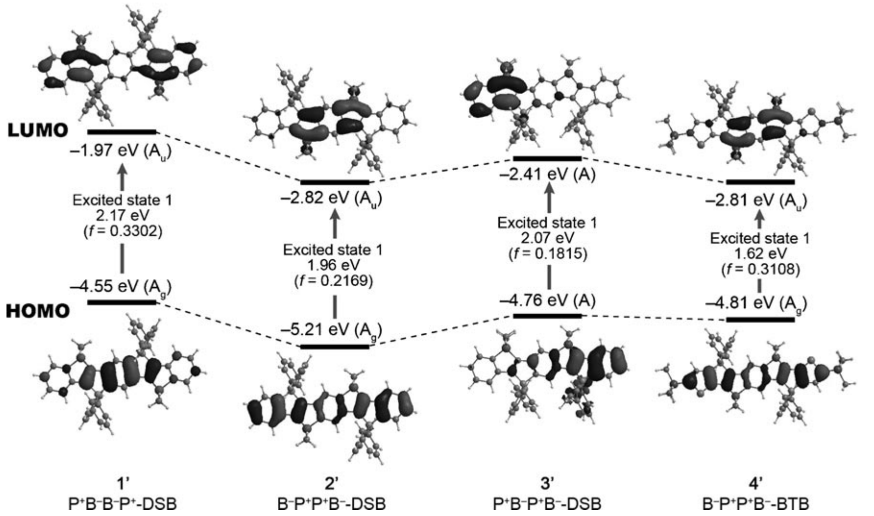

Figure 2. Energy diagrams and pictorial representations of the frontier MOs for the phosphonium- and borate-bridged DSBs **1′**–**3′** and BTB **4′** calculated at the B3LYP/6-31G(d) level, and their lowest-energy transitions estimated by TD-DFT calculations at the B3PW91/6-31+G(d)//B3LYP/6-31G(d) level. Methyl and phenyl groups were used instead of the cyclohexyl and mesityl groups in the corresponding compounds **1**–**4**, respectively. The trimethylsilyl groups were used instead of the triisopropylsilyl groups in **4**.

tron-accepting phosphonium located at the inner positions cancel the electronic effects of each other. Indeed, the HOMO and LUMO of **3′** are mostly localized on the terminal benzoborole and the terminal benzophosphole moieties, respectively. These rather localized frontier MOs may enhance the intramolecular CT character and thus result in the large Stokes shift.

The replacement of the terminal benzene rings in the B$^-$P$^+$P$^+$B$^-$-DSB **2** with thiophene rings significantly affects the linear absorption and fluorescence properties. The B$^-$P$^+$P$^+$B$^-$-BTB **4** has an absorption maximum at 620 nm in benzene, which is nearly 90 nm longer than that of the DSB analogue **2**. Moreover, **4** exhibits an emission in the red to NIR region with a λ_{em} value of 734 nm, although the fluorescence quantum yield is low ($\Phi_F = 0.021$). As shown in Figure 2, the DFT calculations of their model compounds **2′** and **4′** at the B3LYP/6-31G(d) level revealed that the HOMO level of **4′** (−4.81 eV) is higher than that of **2′** (−5.21 eV), while their LUMO levels are comparable to each other (−2.82 eV for **2′**, and −2.81 eV for **4′**). This fact clearly demonstrates that the enhancement of the electron-donating character of the terminal borate moieties by replacing the benzene rings with thiophene rings is responsible for the significantly red-shifted absorption and fluorescence bands.

Two-photon absorption properties for a series of zwitterionic ladder bis(arylethenyl)benzenes **1**–**4** were evaluated by the Z-scan method using a femtosecond optical parametric amplifier.[16] The TPA cross sections δ are also collected in Table 1, together with the data of a representative quadrupolar distyrylbenzene derivative **9**[17] for comparison.[18] The obtained δ values of quadrupolar P$^+$B$^-$B$^-$P$^+$-DSB **1** and B$^-$P$^+$P$^+$B$^-$-DSB **2**, and dipolar P$^+$B$^-$P$^+$B$^-$-DSB **3** in benzene, were 349, 469, and 476 GM, respectively, upon excitation at 900 nm.[19] These δ values are approximately twice as high as that of the reference compound **9** ($\delta = 216$ GM at 900 nm). These results demonstrate that the zwitterionic modulation of the distyrylbenzene chromophore is useful for the design of high-performance TPA materials, while the bridging pattern does not significantly affect the TPA properties, and dipolar **3** shows a slightly larger δ value among the three DSB derivatives. Besides, we found that the increment of the electron-donating ability of the terminal borate moieties in the B$^-$P$^+$P$^+$B$^-$-DSB **2** by replacing the benzene rings with thiophene rings resulted in a much larger TPA cross section. The δ value of the B$^-$P$^+$P$^+$B$^-$-BTB **4** was 784 GM even upon excitation at 1200 nm. It is worth noting that there are only a few examples of excellent TPA materials that can be excited with a NIR light, such as the highly polarized D-π-A type π-conjugated compounds[2b] and the oligomeric porphyrin derivatives with inherently long-wavelength absorption bands.[4] These facts clearly demonstrate that the present zwitterionic modulation is also useful for attaining a large δ value in the NIR region.

In summary, we investigated the linear absorption, fluorescence, and two-photon absorption properties of a series of phosphonium- and borate-bridged distyrylbenzenes **1**–**3**. All these compounds showed larger δ values compared to the previously known TPA-active distyrylbenzene derivative, regardless of the bridging patterns. Moreover, a large TPA cross section, even upon excitation at 1200 nm, was also attained in the thienyl-terminated derivative **4**. These results clearly demonstrate that the introduction of zwitterionic bridges into the ladder π-conjugated framework is a powerful strategy for the molecular design of excellent TPA materials.

Acknowledgements

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Keywords: boron · phosphorus · pi interactions · two-photon absorption · zwitterions

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[18] Since the values of TPA cross section δ are highly sensitive to the experimental conditions, it is not meaningful to simply compare the δ values reported by different research groups. Therefore, the hitherto known compounds were measured as a reference compound under the same conditions as those for our compounds. See reference [1] for details.

[19] These δ values do not necessarily represent maximum values, since the TPA measurements were conducted at a single wavelength.

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