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# Triaryl Boron-Based A-$\pi$-A vs Triaryl Nitrogen-Based D-$\pi$-D Quadrupolar Compounds for Single- and Two-Photon Excited Fluorescence

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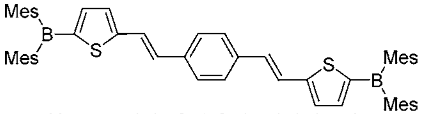
## ABSTRACT



Mes = mesityl = 2, 4, 6-trimethyl-phenyl
$\sigma$ = 1340 GM at 775 nm (fs pulse)
$\Phi$ = 0.61

**Three new A-$\pi$-A-type compounds with trivalent boron, protected by two mesityl groups, as electron acceptor have been synthesized and investigated together with their two diphenylamino-ended D-$\pi$-D analogues. These boranes exhibit large two-photon absorption cross sections and high fluorescence quantum yields.**

In recent years, two-photon excited fluorescence (TPEF), which is based on molecular two-photon absorption (TPA), has received increasing attention for its various applications such as multiphoton fluorescence imaging and microscopy.[1,2] Meantime, various organic TPEF compounds with high quantum yields, large TPA cross sections $\sigma$, and good stability have been designed and synthesized. These compounds can be typically classified as D-$\pi$-A dipoles,[3] D-$\pi$-D or A-$\pi$-A quadrupoles (D, electron donor; A, electron acceptor),[4−6] and multibranched octupoles or dendrimers.[7−12]

It has been recognized that the symmetrical quadrupolar charge transfer, from the terminal donors to the middle of a D-$\pi$-D molecule or conversely from the middle to the acceptor ends of a A-$\pi$-A molecule, is the most important structural factor for having strong TPA.[4] Conceptually, both D-$\pi$-D and A-$\pi$-A types of molecules are equally available for having large $\sigma$ values. In practice, however, the reports about the D-$\pi$-D type of TPEF emitters are more abundant in comparison with that of A-$\pi$-A type, and there is a

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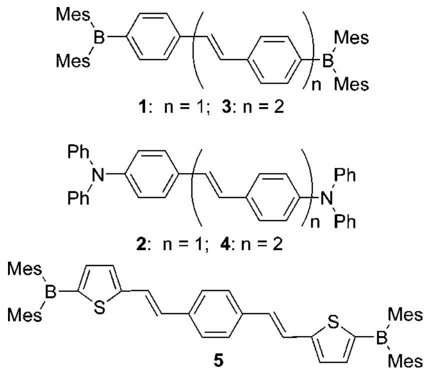


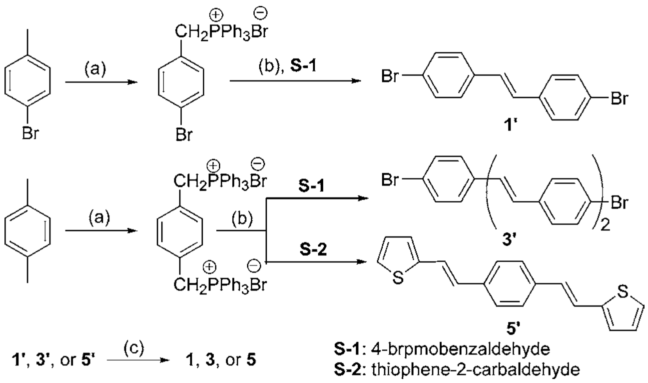
**Figure 1.** Molecular structure of compounds **1**−**5**; Mes = 2,4,6-trimethyl-phenyl.

tendency that the $\sigma$ values of A-$\pi$-A molecules are smaller than those of their D-$\pi$-D analogues with identical $\pi$-bridges.[5a]

To systematically explore the TPA and TPEF potentials of A-$\pi$-A-type quadrupoles, three new A-$\pi$-A-type compounds with dimesitylboryl as acceptors, together with other two related D-$\pi$-D-type compounds, have been synthesized and investigated in this letter. Noticing that a trivalent nitrogen atom, with a lone pair of electrons in its p-orbital, has been widely adopted as the donor center,[3−12] we chose the three-coordinate boron atom, which has an empty p-orbital, as the acceptor center. Indeed, trivalent boranes have found application as optoelectronic materials in recent years.[13] However, the reports concerning the role of boron in TPA materials are very few.[14]

Compounds **1** and **3** differ from **2** and **4** mainly in the terminal electron-donating/-accepting groups. The difference between compound **5** and **3** is at the $\pi$-bridge, in which two phenyls in **3** are replaced by two thienyls in **5**. Compounds **2** and **4**, which have been reported by others,[15,16] were synthesized by a $TiCl_4$/Zn-induced reductive coupling and standard Wittig reaction, respectively. The synthesis of boron-containing compounds **1**, **3**, and **5** are shown in Scheme 1. The Wittig reactions were used to prepare the precursors **1′**, **3′**, and **5′**. Substituting the Br atoms of **1′** and **3′** or the α-H of the thienyls of **5′** with a dimesitylboryl group by means of the lithium derivative at low temperature affords object compounds **1**, **3**, and **5** in good yield. All of these compounds are stable in air and in common solvents. The detailed characterization data can be found in Supporting Information.

**Scheme 1**[a]



[a] Reagents and condition: (a) (i) NBS/BPO/$CCl_4$/reflux/3 h, (ii) $PPh_3$/toluene/reflux/3 h; (b) *t*-KOBu/THF/0 °C to rt/24 h; (c) *n*-LiBu/FB$(Mes)_2$/THF/−78 °C to rt/24 h.

As summarized in Table 1, the spectra (both absorption and emission) positions of the A-$\pi$-A type compounds are considerably blue-shifted relative to those of their D-$\pi$-D analogues. The quantum yields $\Phi$ of **1** and **3** are also slightly higher than that of **2** and **4**, respectively. Due to the electron-rich nature of thienyl and its low stabilization energy relative to benzene,[17] both the absorption and emission spectra of **5** are greatly red-shifted compared with those of **3** (see Table 1 and Figure 2). On the other hand, the quantum yield of **5** is slightly smaller than that of others. Despite this, compound **5** is still the strongest emitter among **1**−**5** because of its largest absorbance and higher product of $\epsilon \cdot \Phi$.

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**Table 1.** Photophysical Properties of Compounds **1**−**5** in THF

| | UV−vis linear absorption[a,d] | | single-photon excited fluorescence (SPEF) | | | two-photon excited fluorescence (TPEF)[e] | | |
|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ (nm) | $\epsilon$ ($10^4$) | $\lambda_{max}{}^b$ (nm) | $\Phi^c$ | $\tau$ (ns) | $\lambda_{max}$ (nm) | $\sigma'$ (GM) | $\sigma^f$ (GM) |
| 1 | 372 | 3.99 | 407, 429 | 0.83 | 0.9 | 431 | 34 | 41 (720 nm) |
| 2 | 389 | 4.80 | 431, 453 | 0.78 | 1.2 | 436, 455 | 58 | 75 (720 nm) |
| 3 | 397 | 8.20 | 441, 467 | 0.71 | 1.0 | 445, 468 | 593 | 835 (730 nm) |
| 4 | 412 | 8.27 | 459, 489 | 0.68 | 1.2 | 466, 488 | 626 | 920 (745 nm) |
| 5 | 435 | 9.32 | 482, 515 | 0.61 | 1.2 | 491, 514 | 817 | 1340 (775 nm) |

[a] Only the longest absorption maxima are shown. [b] Emission maximum wavelength excited at the absorption maximum. [c] Determined using fluorescein as the standard. [d] All single-photon properties were measured at $5.0 \times 10^{-6}$ mol/L. [e] TPA properties were measured at $5.0 \times 10^{-4}$ mol/L. [f] TPA cross section determined using fluorescein as the standard; the data in parentheses are the excitation wavelengths of the laser.

The pulse width and repetition rate of the laser are 200 fs and 76 MHz, respectively. As shown in Figure 3, the output intensity of frequency up-converted fluorescence of **5** has a square dependence on the input laser intensity, i.e., the experimental $I_{out} - I_{in}$ data can fit in well with the quadratic parabolas. This gives direct experimental evidence of a two-photon excitation mechanism.

As shown in Figure 4, the peak position ($\lambda_{max}$) of the single-photon excitation (SPE) spectrum of compound **5** is at 435 nm, with that of the two-photon excitation (TPE) spectrum at 775 nm. If the absorption quantum is scaled by two-photon, the resonance absorption position will be at 387.5 nm. This indicates that the energy level of TPE state is about 0.35 eV higher than that of the SPE state and means that TPE-allowed $A_g$ state is above the SPE-allowed $B_u$ state for this kind of centro-symmetric quadrupoles. This electronic structure ($A_g$ above $B_u$) also applies to compounds **2** and **4**. As reported by Rumi et al.,[4b] the TPE peak positions of **2** and a very similar analogue of **4** are located at 690 and 745 nm, respectively. Their two-photon vertical transitions will be then at 345 and 372.5 nm, which are greatly blue-shifted relative to the corresponding linear absorption positions (389 and 412 nm, respectively, in Table 1).

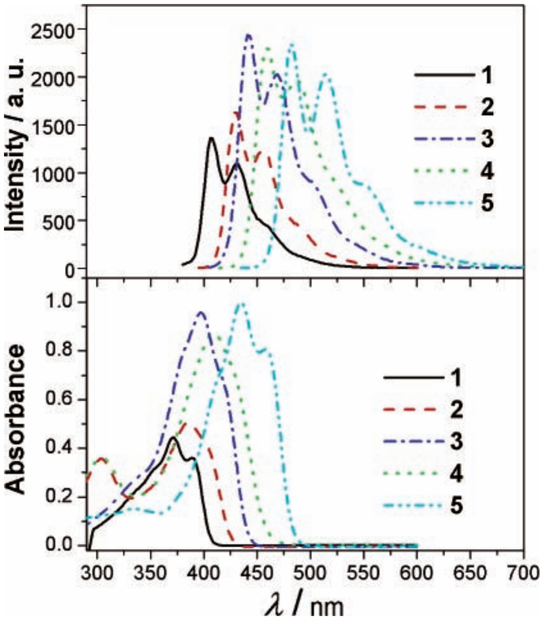

**Figure 2.** Linear absorption and SPEF spectra of **1**−**5** in toluene ($C = 5.0 \times 10^{-6}$ mol/L).

For a certain compound, the spectral profiles and peak positions of SPEF and TPEF are basically the same. As an example, Figure 4 shows the similar vibronic structures in the SPEF and TPEF spectra of compound **5**. This implies that SPEF and TPEF come from the same fluorescent excited state. Although the spectral selection rule of TPA (g → g) is different from that of single-photon absorption (g → u) for the centrosymmetric structures, both SPEF and TPEF emission processes, with only one photon involved, should abide by the same rule (u → g).

TPEF spectrum of compound **5** in Figure 4 shows a small red shift relative to the SPEF spectrum. In detail, the left part of the double peak is weaker in comparison with the profile of the SPEF spectrum. This is due to the reabsorption effect, considering the partial overlap of the SPE and SPEF spectra and the quite high concentration of the samples.

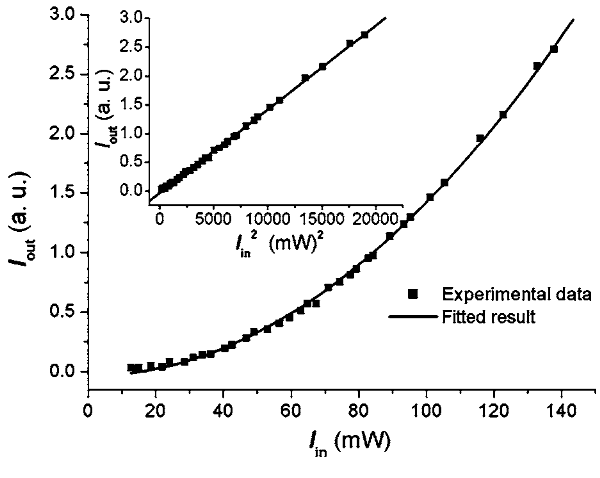

**Figure 3.** Dependence of the output fluorescence intensity ($I_{out}$) of compound **5** in THF on the input laser power ($I_{in}$). The insert shows the linear dependence of $I_{out}$ on $I_{in}{}^2$.

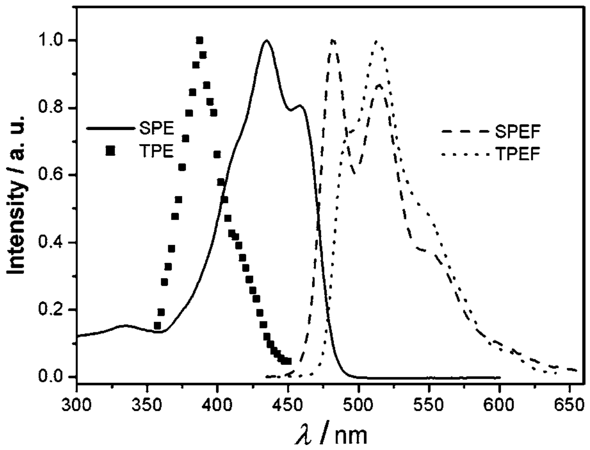

**Figure 4.** Normalized single-photon excitation (SPE) and two-photon excitation (TPE) spectra (left) and SPEF and TPEF spectra (right) of **5** in THF. In the TPE spectrum, the wavelengths data are divided by 2, considering the TPA characteristic.

The TPEF emission cross section $\sigma'$ and TPA cross section $\sigma$ were measured on the basis of the following expressions[18]

$$\sigma' = \sigma'_{\mathrm{ref}} \frac{C_{\mathrm{ref}}}{C} \frac{n_{\mathrm{ref}}}{n} \frac{F}{F_{\mathrm{ref}}}$$

$$\sigma = \sigma'/\Phi$$

where $C$ and $n$ are the concentration and refractive index of the sample solution, respectively, $F$ is the TPEF integral intensity and $\Phi$ is the quantum yield; the subscript ref means the reference. The $\sigma'_{\mathrm{ref}}$ value of the fluorescein reference was taken from the literature.[19]

As shown in Table 1, D-$\pi$-D-type compounds possess $\sigma$ values larger than that of their A-$\pi$-A analogues. The $\sigma$ value of **2** is nearly double that of **1**, whereas the $\sigma$ difference between **4** and **3** is slight. With increasing length of the $\pi$-bridge, the $\sigma$ difference between D-$\pi$-D and A-$\pi$-A types seems to become vanishing. This may be interpreted in terms of quadrupolar charge transfer. Some pioneer reports have concluded that the extent of the symmetrical charge transfer and the length of the $\pi$-bridge greatly influence TPA intensity.[4] In comparison with the electron-excessive D-$\pi$-D systems, A-$\pi$-A molecules are relatively electron-deficient systems. For compounds with shorter $\pi$-bridges, there is a distinct difference in charge density and charge transfer between D-$\pi$-D and A-$\pi$-A types. When the $\pi$-conjugation and quadrupolar charge transfer are greatly enhanced, the relative difference between D-$\pi$-D and A-$\pi$-A types becomes insignificant.

The tradeoff between nonlinear efficiency and transparency in second-order nonlinear optics seems to work here. All spectral positions ($\lambda_{\max}$) of SPEF and TPEF of A-$\pi$-A compounds are blue-shifted about 20 nm relative to those of their D-$\pi$-D analogues. A careful check on the photophysical data in Table 1 seems to mean that the $\sigma$ difference between compound **1** and **2** should not be so large. Because the absorption of A-$\pi$-A compound **1** is at a more blue region and the TPE-allowed $A_g$ state must be above the SPE-allowed $B_u$ state, the optimal TPE wavelength for **1** must be shorter than 720 nm and farther away from 720 nm in comparison with that of **2**. Unfortunately, our Ti:sapphire laser failed to be tuned to a shorter wavelength.

In regard to our special acceptor of dimesitylboryl and typical donor of diphenylamino, A-$\pi$-A-type quadrupoles are not essentially inferior to their D-$\pi$-D analogues. Significantly, from **3** to **5**, when two phenyls of **3** are replaced by two thienyls, which has been described as a good electronic transmitter,[17] we get a A-$\pi$-A-type TPEF emitter (compound **5**) with a $\sigma$ value as large as 1340 GM.

In conclusion, three new A-$\pi$-A-type compounds with dimesityl-protected trivalent boron as electron acceptor were synthesized. All of these triaryl boron-based A-$\pi$-A compounds show strong TPEF and large TPA cross sections that are comparable to other reported triaryl nitrogen-based D-$\pi$-D analogues. The appropriately tuned $\pi$-bridge will greatly improve the TPA and TPEF properties.

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**Supporting Information Available:** Synthesis and characterization of **1**, **3**, and **5**, and the single- and two-photon related optical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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