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Fluorene as the π–spacer for new two-photon absorption chromophores

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ABSTRACT

We report herein the design and synthesis of two new quadrupolar D–π–A–π–D chromophores containing diphenyl amine and dicyanobenzene or 2,1,3-benzothiadiazole as electron donor (D) and acceptor (A), respectively, which are bridged by fluorene linkage (π). The introduction of coplanar fluorenes is highly beneficial for the enhancement of two-photon absorption (TPA), where **1b** displays a TPA cross section (σ_2) of up to 1975±207 GM.

1. Introduction

The two-photon absorption (TPA) process, predicted theoretically in 1931[1] and observed experimentally in 1960s,[2] is a nonlinear absorption process invoking the simultaneous absorption of two photons, either degenerate or nondegenerate. Ever since, it has been receiving considerable attention due to its wide practical applications, such as three-dimensional optical data storage and microfabrication,[1–5] two-photon fluorescence microscopy,[6–8] optical limiting,[9] and photodynamic therapy.[10,11] Chromophores with high capability of two-photon absorption are desired for all these applications, because a greater degree of excitation can be achieved while lower laser intensity is sufficient for pumping. Thus, in order to shed light onto the design of molecules for increasing the two-photon absorption cross section (σ_2) and for tuning the position of the two-photon absorption peak wavelength, there is an urgent need to unveil the structure–property relationship for two-photon absorbing molecules. In theory, TPA cross sections of chromophores are governed by several factors, such as the properties of the π-conjugated segment, the strength of the donor and/or acceptor substituents, molecular symmetry, and the molecular dimensionality. So far, a variety of elegant molecular structures have been designed to improve the TPA cross section, including dipolar,[12,13] quadrupolar,[14–17] octupolar, and multipolar molecules.[18–21]

Among these molecules, the quadrupolar D–π–A–π–D structure, where D is an electron-donating group, A an electron-accepting group, and π a conjugating moiety, is highlighted by its excellent TPA property.[22] In this type of system, a large σ_2 value has been achieved by charge transfer from the periphery donors to the central acceptor (A) through various conjugated linkages upon optical excitation. In an aim to enhance the TPA cross section, one promising strategy is to maintain the coplanar conformation, which will increase the dimension of π electron delocalization. Adopting the most successful molecular design strategy for highly efficient TPA chromophores, we have strategically designed and synthesized two new quadrupolar chromophores **1a** and **1b** (Scheme 1) with high TPA cross sections.

In these new chromophores, we selected diphenyl amine as the donor (D) and dicyanobenzene or quinonoid 2,1,3-benzothiadiazole (BTD) as the acceptor (A), which are then bridged by fluorene linkages (π). In particular, we incorporated the coplanar fluorene linker in replacement for bridging units, such as the styryl group in model compound **2**[23] and biphenylene in molecule **3**,[24] since the coplanar fluorenes are beneficial for facilitating D–A electronic coupling and coplanar fluorene derivatives usually exhibit excellent TPA properties.[12,25–27] In addition, the 9-position of fluorene was alkylated to enhance the solubility and to enable future functionalization for latent applications.

2. Results and discussions

2.1. Molecular structures and synthesis

The synthetic routes of the two new TPA chromophores are depicted in Scheme 2.

In the presence of electron rich bis(diphenyl-phosphino)ferrocene (dppf) ligand, and a catalytic amount of Pd(dba)$_2$ catalyst, selective C–N bond formation of 9,9-dioctyl-2,7-dibromofluorene

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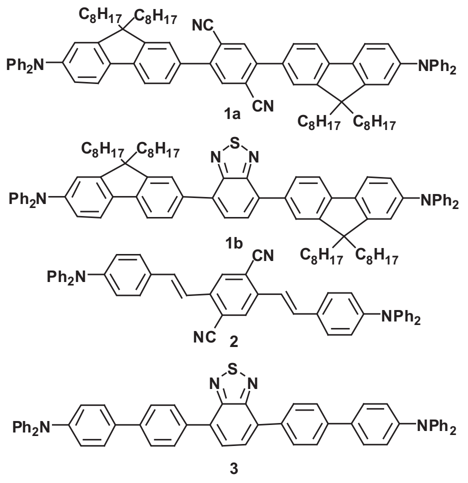
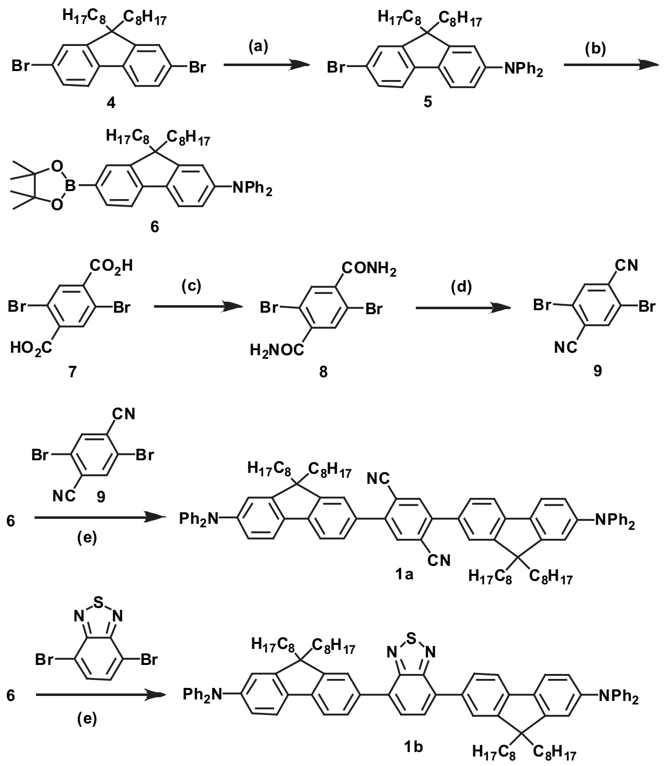


Scheme 1. Structures of **1a**, **1b**, **2**, and **3**.



Scheme 2. Synthesis of TPA chromophores of **1a** and **1b**. (a) **4** (1 equiv), diphenyl amine (0.5 equiv), Pd(dba)$_2$ (0.01 equiv), dppf (0.012 equiv), NaO^{t}Bu (1 equiv) in toluene, 100 °C, 5 h (70%); (b) **5** (1 equiv), *n*-BuLi (1.5 equiv), bis(pinacolato)diboron (1.5 equiv) in THF (99%); (c) **7** in SOCl$_2$, reflux, 3 h, and then remove SOCl$_2$, added NH$_4$OH concd in dioxane (76%); (d) **8** in POCl$_3$, 135 °C, 12 h (99%); (e) **6** (2 equiv), **9** or 4,7-dibromothiadiazode (1 equiv), Pd(PPh$_3$)$_4$ (0.05 equiv), K$_2$CO$_3$ (2 M) in toluene, 85 °C, 3 day (43% for **1a**, 13% for **1b**).

(**4**) with diphenyl amine was achieved to furnish compound **5** with an isolated yield of 70%. The bromo group of compound **5** was then converted to boronic ester by treating it with *n*-BuLi at −78 °C followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to produce the intermediate **6** in 99% yield. The synthesis of acceptor **9** began with the oxidation of 1,4-dibromo-2,5-dimethylbenzene to afford diacid **7** in 84% yield. The acid groups of compound **7** were subsequently transformed into amides by reacting with SOCl$_2$, followed by the treatment of concentrated NH$_4$OH to afford diamide compound **8** in 76% yield. Finally, the dehydration of **8** with POCl$_3$ gave the acceptor core **9** with an isolated yield of 99%. The new TPA chromophores **1a** and **1b** were obtained by Suzuki coupling reaction of the intermediate **6** with acceptor **9** in 43% yield and 4,7-dibromobenzothiadiazole in 13% yield.

2.2. Optical properties characterization

Fig. 1 depicts the single-photon absorption and emission spectra of chromophores **1a** and **1b** in CH$_2$Cl$_2$. Pertinent photophysical data are summarized in Table 1. The higher energy absorbing bands (310–360 nm) for both **1a** and **1b** can be ascribed to the π–π* transitions of local chromophores, such as fluorene[28] and 2-aminofluorene.[29]

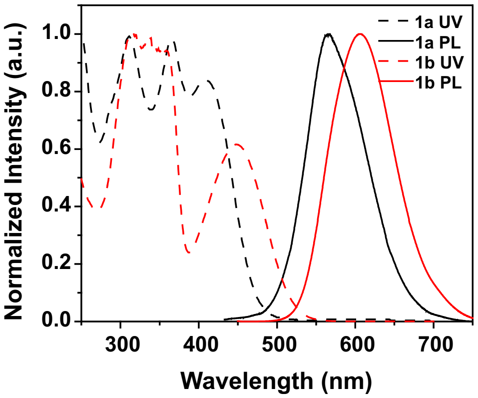


Fig. 1. Normalized UV–vis absorption (dashed lines) and photoluminescence (solid lines) spectra of chromophores **1a** (λ_{ex}=410 nm, black) and **1b** (λ_{ex}=449 nm, red) in CH$_2$Cl$_2$ at 298 K.

Table 1
Photophysical data for **1a**, **1b**, **2**, and **3**

Cmpd	λ_{abs}[a]	λ_{em}[b]	Φ_f	λ_{ex}[c]	Σ_2 (TPEF)	σ_2 (Z-scan)
1a	413	565	0.17	780	753±82	623±28[f]
1b	449	610	0.61	800	1975±207	1620±110[f]
2[d]	473	527	0.73	840	1370	—
3[e]	422	657	0.14	780	—	200

[a] λ_{abs}: one-photon absorption maximum.
[b] λ_{em}: emission maximum, excited at λ_{abs}.
[c] λ_{TPA}: maximum of TPA spectrum.
[d] Compound **2**: in accordance with Cho and co-workers report.[23]
[e] Compound **3**: in accordance with Mataka and co-workers report.[24]
[f] Measured at 800 nm.

Compound **1a** exhibits lowest-lying absorption maximum at 413 nm, whereas the absorption maximum of **1b** shifts to longer wavelength at 449 nm. Compared with a green emitting chromophore of 2,1,3-benzothiadiazole core end-capped with fluorenes, which displays an absorption maximum at 420 nm,[30] the absorption maximum of **1b** can be reasonably assigned to the electronic transition of the whole conjugated backbone including the diphenylamino terminus. It is noteworthy that chromophore **3**, with a similar structure to that of **1b**, shows a blue-shifted absorption maximum at 422 nm, indicating that the introduction of coplanar fluorene bridges leads to better molecular conjugation. Moreover, the red-shifted absorption maximum of **1b** relative to that of **1a** suggests that