Tetrahedron 67 (2011) 734–739

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

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

Jian-Zhang Cheng, Chao-Chen Lin, Pi-Tai Chou *, Atul Chaskar, Ken-Tsung Wong *

*Department of Chemistry, National Taiwan University, Taipei 106, Taiwan*

ARTICLE INFO

*Article history:*
Received 9 June 2010
Received in revised form 3 November 2010
Accepted 19 November 2010
Available online 27 November 2010

*Keywords:*
Two-photon absorption
Fluorene
Quadrupolar

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 ($\sigma_2$) 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 ($\sigma_2$) 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 $\sigma_2$ 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

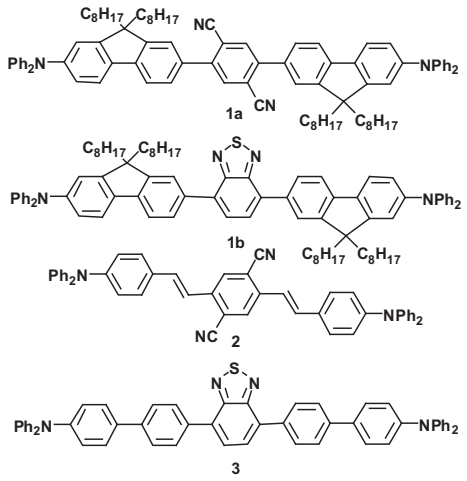
### 2.1. Molecular structures and synthesis

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

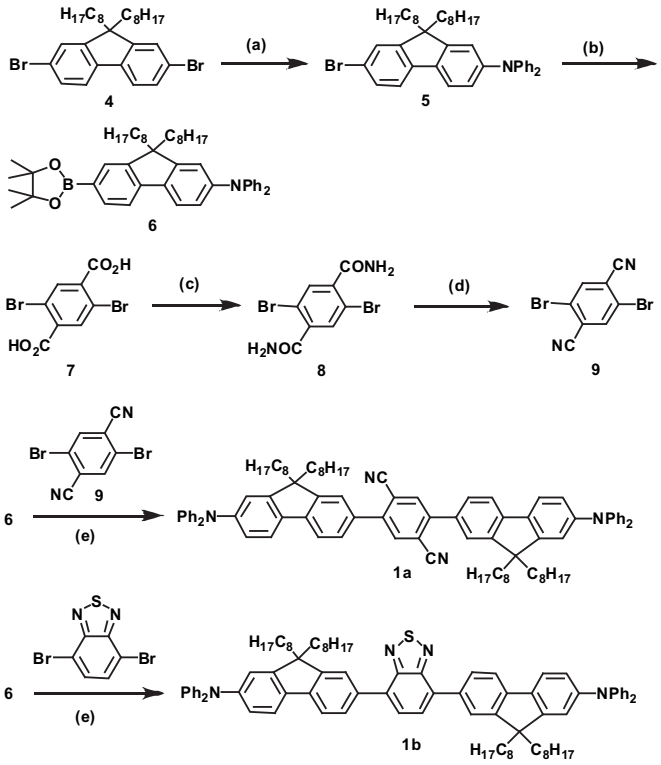
In the presence of electron rich bis(diphenyl-phosphino)ferrocene (dppf) ligand, and a catalytic amount of $Pd(dba)_2$ catalyst, selective C–N bond formation of 9,9-dioctyl-2,7-dibromofluorene

* Corresponding authors. Tel.: +886 2 33663894; fax: +886 2 23695208 (P.-T.C.); tel.: +886 2 33661665; fax: +886 2 33661667 (K.-T.W.); e-mail addresses: chop@ntu.edu.tw (P.-T. Chou), kenwong@ntu.edu.tw (K.-T. Wong).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.11.071




**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), $NaO^tBu$ (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 $NH_4OH$ 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), $K_2CO_3$ (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 $NH_4OH$ 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 $CH_2Cl_2$. 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]

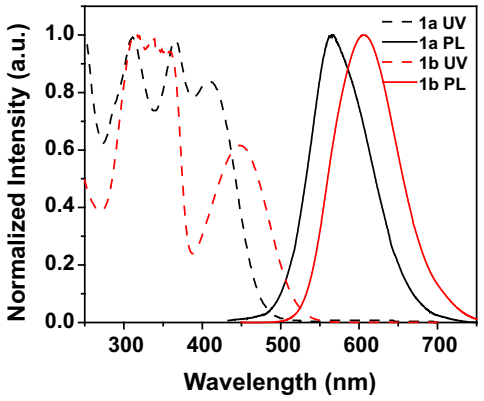



**Fig. 1.** Normalized UV–vis absorption (dashed lines) and photoluminescence (solid lines) spectra of chromophores **1a** ($\lambda_{ex}$=410 nm, black) and **1b** ($\lambda_{ex}$=449 nm, red) in $CH_2Cl_2$ at 298 K.

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

| Cmpd | $\lambda_{abs}$[a] | $\lambda_{em}$[b] | $\Phi_f$ | $\lambda_{ex}$[c] | $\Sigma_2$ (TPEF) | $\sigma_2$ (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] $\lambda_{abs}$: one-photon absorption maximum.
[b] $\lambda_{em}$: emission maximum, excited at $\lambda_{abs}$.
[c] $\lambda_{TPA}$: 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

the steric interactions between fluorene and dicyanobenzene in **1a** leads to a twisted conformation and thus poorer π-conjugation. A similar behavior was also observed in recently reported dipolar compounds containing an internal cyanovinyl unit.[31,32] In **2**, such interactions can be avoided when the cyano substituents and the vinyl groups are in the anti configuration so that planarity can be better maintained. On the other hand, quinoidal type chromophores[33,34] typically possess a more coplanar conformation. The coplanar structural feature also renders compound **1b** a red-shifted emission maximum (610 nm) in $CH_2Cl_2$ as compared to that of **1a** (565 nm) as well as in other solvents. Apparently, the more rigid and coplanar structure imposed by the quinoidal benzothiadiazole and fluorene moieties suppress the nonradiative decay pathways induced possibly by internal rotations. Likewise, the acceptor quinoidal benzothiadiazole in **1b** renders less steric effect relative to dicyanobenzene in **1a**. This may result in a more planar structure for **1b**. As a result, **1b** exhibits a high fluorescence quantum yield ($\Phi_f$=61%) as opposed to **1a** ($\Phi_f$=17%) and **3** ($\Phi_f$=14%).

Fig. 2 depicts the absorption and emission spectra of **1a** and **1b** in solvents with various polarity. The absorption spectra of both **1a** and **1b** show only limited solvent polarity dependence. In contrast, the emission peak wavelength red-shifts significantly as the solvent polarity increases, accompanied by gradual reduction in emission quantum yield. For example, the emission maxima of **1a** (474 nm) and **1b** (544 nm) in cyclohexane shift to 565 and 610 nm in $CH_2Cl_2$, respectively. The results are the manifestation of the charge transfer character of the corresponding electronic transition, in which a non-equilibrated excited state species is created upon Franck–Condon excitation, followed by solvent relaxation to the equilibrated emitting state. As a result, it is inferred that while the dipole moment is relatively small in the ground state, significant charge separation (with $D^{\delta+}$ and $A^{\delta-}$) is present in the excited state.

Herein, the TPA cross sections ($\sigma_2$) were measured by both the two-photon excited fluorescence (TPEF) and the Z-scan methods. The upper panel of Fig. 3 illustrates the two-photon excitation spectra of **1a** ($1.05\times10^{-5}$ M) and **1b** ($9.62\times10^{-6}$ M) from 720 to 900 nm in $CH_2Cl_2$, while the lower panel shows the Z-scan experimental data with the best-fitting curves for **1a** ($1.16\times10^{-3}$ M) and **1b** ($1.07\times10^{-3}$ M) in $CH_2Cl_2$ at 800 nm. The obtained $\sigma_2$ values are also summarized in Table 1, and the results of the two methods are mutually consistent. Chromophore **1a** exhibits maximum $\sigma_2$ of 753 GM at 780 nm, which is inferior to that of the model compound **2** ($\sigma_2$=1370 GM at 840 nm). The result can once again be attributed to the twisted structure between cyanobenzene and fluorene in the ground state. Remarkably, the effect of introducing coplanar fluorene linkages is clearly demonstrated with an eightfold increase in the TPA cross section of **1b** ($\sigma_2$=1975 GM at 800 nm) as compared to that of **3** ($\sigma_2$=200 GM at 780 nm). This suggests that the coplanarity of the π-conjugated spacers plays an important role in enhancing the TPA cross sections. Moreover, it is worthy to note that the TPA maxima shift to shorter wavelength compared to one-photon absorption, typical for centrosymmetric TPA chromophores in which the lowest excited states are one-photon allowed but two-photon forbidden.[35] For various practical applications, such as optical limiting, 3D microfabrication, strong TPEF agents in bioimaging, molecules with large TPA cross section per molecular weight ($\sigma_2$/MW) or large two-photon action cross section per molecular weight (e.g., $\Phi_f\sigma_2$/MW) are highly desired.[36] It has been established that TPA active chromophores with $\sigma_2$/MW>1.0 are useful for these applications.[4,37] Therefore, our new TPA chromophore **1b** ($\sigma_2$/MW=1.9 and $\Phi_f$=0.61), with appropriate functionalization on the pendant alkyl chains may present highly potential application in bioimaging.

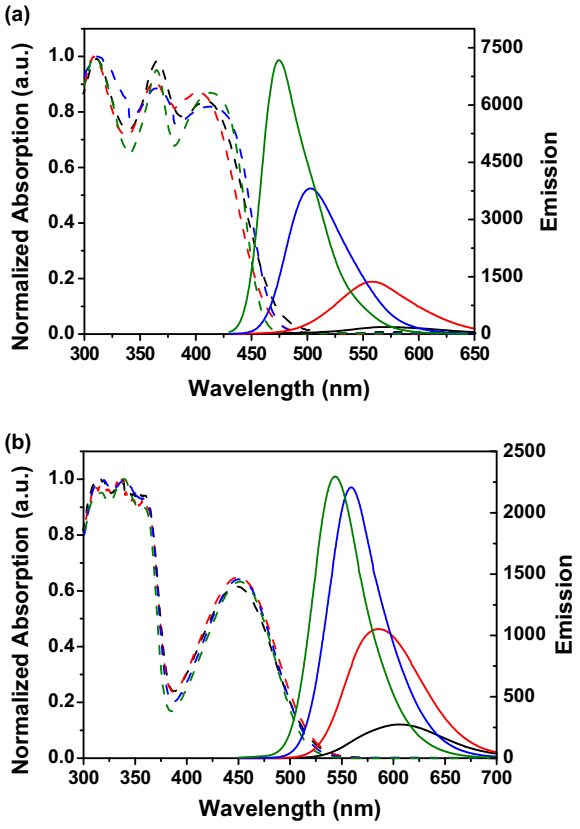



**Fig. 2.** UV–vis absorption (dashed lines) and photoluminescence (solid lines) spectra of chromophores **1a** and **1b** in cyclohexane (green), toluene (blue), THF (red), and $CH_2Cl_2$ (black).

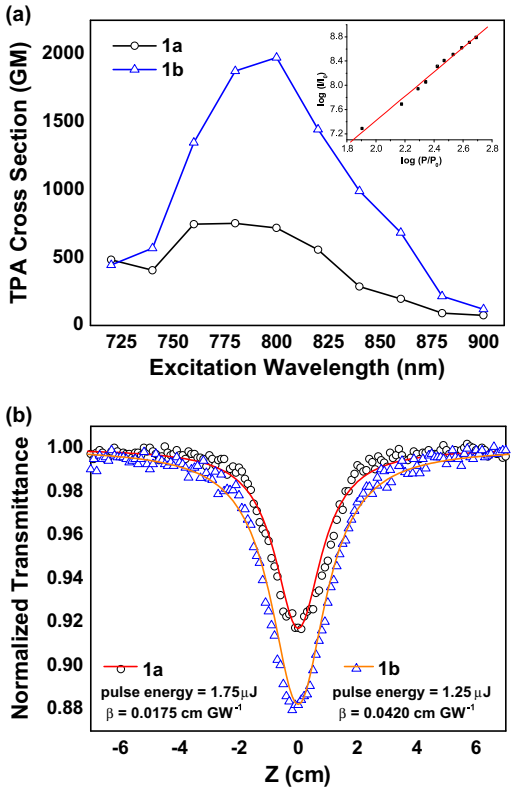



**Fig. 3.** Two-photon excitation spectra (upper) and Z-scan experimental data (lower) of **1a** and **1b** in $CH_2Cl_2$. Inset: the log–log plot of normalized two-photon emission intensity ($I/I_0$) versus normalized excitation power ($P/P_0$).

## 3. Conclusion

In summary, we have synthesized two new quadrupolar D–π–A–π–D chromophores by incorporating diphenylamino groups as the electron donor, dicyanobenzene (**1a**) or 2,1,3-benzothiadiazole (**1b**) as the electron acceptor, and fluorenes as the coplanar π-conjugation linkers. The significant solvent effect observed for **1a** and **1b** clearly indicates that charge separation in the excited state is efficient through the π linkers. The red-shifted absorption maximum and high fluorescence quantum yield of **1b** suggest better coplanarity and rigidity as compared to **1a**, which is also manifested in a remarkable enhancement of TPA cross section ($\sigma_2$=1975 GM) as compared to those of **1a** ($\sigma_2$=753 GM) and **3** ($\sigma_2$=200 GM). The successful increase in $\sigma_2$ values demonstrates the key of fluorene linkers in TPA chromophores to achieve a greater degree of excitation.

## 4. Experimental

### 4.1. General procedures

Unless otherwise noted, all reagents were used as received and without further purification. Tetrahydrofuran (THF) and toluene were distilled under $N_2$ from sodium/benzophenone immediately prior to use. Chromatography was carried out with Merck silica gel for flash columns, and preparative thin-layer chromatography (TLC) was conducted on 1000 μm Whatman plates. $^1$H and $^{13}$C NMR spectra were collected on a 400 MHz spectrometer at room temperature. High-resolution mass spectrometry (HRMS) was performed with Micromass ProSpec using fast atom bombardment (FAB).

### 4.2. Spectroscopic measurements

Photophysical properties were collected at room temperature with $5\times10^{-6}$ M $CH_2Cl_2$ solutions of **1a** and **1b**. The TPA cross section ($\sigma_2$) values were measured by both the TPEF and Z-scan method.

*4.2.1. The setup for TPEF measurements is similar to that used by Xu and co-workers[27b].* First, a femtosecond mode-locked Ti–sapphire laser (Spectra Physics) generates 120 fs pulses at 80 MHz repetition rate (700–1000 nm). The laser beam is focused on the sample cell (1 cm) by a lens with a focal length 15 cm. Two-photon induced fluorescence is then detected in the direction perpendicular to excitation. To minimize re-absorption, the excitation beam is focused as close as possible to the side of the quartz cell, which faces the entrance slit of the imaging spectrograph. The emission is focused by a lens with a focal length 8 cm into a monochromator (SP2300i, Acton Research Corporation) in conjunction with a CCD (PI-MAX camera, Princeton Instruments Inc.). TPEF spectra of Coumarin 480 ($1.02\times10^{-5}$ M in MeOH, $\sigma_2$=160 GM) were measured under the same experimental conditions as the reference.[38] TPA cross sections ($\sigma_2$) are evaluated with Eqs. 1 and 2:

$$\sigma_{\mathrm{TPE}} = \sigma_{\mathrm{TPE,r}}\frac{Fn_{\mathrm{r}}C_{\mathrm{r}}}{F_{\mathrm{r}}nC} \tag{1}$$

$$\sigma_2 \times \Phi_{\mathrm{f}} = \sigma_{\mathrm{TPE}} \tag{2}$$

where subscript r stands for the reference, $F$ represents the integrated emission intensity, $n$ denotes the refractive index of the solvent, and $C$ is the sample concentration. The spectra were recorded in a regime where the emission intensity is quadratically dependent on excitation power to ensure a pure TPA process.

*4.2.2. The open aperture Z-scan experiments were conducted with the experimental setup and procedure described in literature[39].* In this study, a mode-locked Ti–sapphire laser (Tsunami, Spectra Physics) produced a single Gaussian pulse, which was then coupled to a regenerative amplifier that generated a ~180 fs, 1 mJ pulse (800 nm, 1 kHz, Spitfire Pro, Spectra Physics). The pulse energy, after proper attenuation, was reduced to 1.00–2.00 μJ and the repetition rate was further reduced to 20 Hz. After passing through an $f$=30 cm lens, the laser beam was focused and passed through a 1.00 mm cell filled with the sample solution and the beam radius at the focal position was $5.09\times10^{-3}$ cm. When the sample cell was translated along the beam direction ($z$-axis), the transmitted laser intensity was detected by a photodiode (PD-10, Ophir). The TPA-induced decrease in transmittance, $T$(z), can be fitted with Eqs. 3 and 3, in which the TPA coefficient ($\beta$) is incorporated:

$$T(z) = \sum_{n=0}^{\infty}\frac{(-q)^n}{n+1^{3/2}} \tag{3}$$

$$q = \frac{\beta I_0 L}{1+\frac{z^2}{z_0^2}} \tag{4}$$

where $n$ is an integer number from 0 to ∞ and has been truncated at $n$=1000, $L$ is the sample length, $I_0$ is the input intensity, z represents the sample position with respect to the focal plane, and $z_0$ denotes the diffraction length of the incident beam (Rayleigh range). After obtaining the TPA coefficient ($\beta$), TPA cross section ($\sigma_2$) can be deduced with Eq. 5:

$$\beta = \frac{\sigma_2 N_{\mathrm{A}} d \times 10^{-3}}{h\upsilon} \tag{5}$$

where $N_{\mathrm{A}}$ is the Avogadro constant, $d$ is the sample concentration, and $h\upsilon$ is the incident photon energy.

### 4.3. Synthesis

*4.3.1. 7-Bromo-9,9-dioctyl-N,N-diphenyl-9H-fluoren-2-amine (**5**).* The mixture of 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (10.0 g, 15.4 mmol), diphenyl amine (1.3 g, 7.7 mmol), bis-(dibenzylideneacetone) palladium (88 mg, 0.153 mmol), bis(diphenylphosphine)ferrocene (102 mg, 0.184 mmol), sodium *tert*-butoxide (1.48 g, 15.4 mmol), and toluene (50 mL) was stirred under nitrogen at 100 °C for 5 h. The mixture was cooled and partitioned between toluene and brine. The organic layer was separated and dried over $MgSO_4$, concentrated under vacuum to give a brown liquid. The crude was purified by chromatography over silica gel (elution with hexane) to afford the pure product as a orange-red oil (3.88 g, 70%). IR (neat) $\nu$ 3064, 3034, 2924, 2892, 1592, 1491, 1456, 1432, 1340, 812, 752, 696 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.51 (d, $J$=8.4 Hz, 1H), 7.44–7.40 (m, 3H), 7.26–7.22 (m, 4H), 7.12–7.09 (m, 5H), 7.02–6.99 (m, 3H), 1.84 (t, $J$=5.6 Hz, 4H), 1.28–1.07 (m, 20H), 0.86 (t, $J$=7.2 Hz, 6H), 0.67–0.64 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 152.9, 151.8, 147.9, 147.6, 140.0, 135.1, 130.0, 129.3, 126.1, 124.0, 123.5, 122.7, 120.6, 120.5, 120.2, 119.2, 55.6, 40.4, 32.1, 30.2, 29.6, 29.5, 24.1, 23.0, 14.5; MS ($m/z$, FAB$^+$) 635 (18); HRMS ($m/z$, FAB$^+$) calcd for $C_{41}H_{50}BrN$ 635.3127, found 635.3127.

*4.3.2. 7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-octyl-N,N-diphenyl-9H-fluoren-2-amine (**6**).* To the solution of 7-bromo-9,9-dioctyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (0.8 g, 1.26 mmol) in THF (30 mL) was added *n*-butyl lithium (1.6 M solution in hexanes, 1.2 mL, 1.9 mmol) at −78 °C and stirred for 30 min, and then to the solution was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5 M solution in THF, 378 μL, 1.89 mmol), stirred for 1 h

after warming to room temperature. The mixture was quenched with brine, extracted into ether, dried over $MgSO_4$, concentrated under vacuum to give yellow oil. The crude was purified by chromatography over silica gel (elution with hexane/ethyl acetate=98/2) to afford the pure product as a yellow oil (0.86 g, 99%). IR (neat) $\nu$ 3061, 3035, 2955, 2926, 2854, 1595, 1492, 1467, 1415, 1354, 1275, 1144, 1113, 1081, 1029, 963, 821, 696, 622 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.78 (d, $J$=7.6 Hz, 1H), 7.70 (s, 1H), 7.62–7.57 (m, 2H), 7.26–7.22 (m, 4H), 7.13–7.11 (m, 5H), 7.03–6.99 (m, 3H), 1.93–1.85 (m, 4H), 1.40 (s, 12H), 1.28–1.05 (m, 20H), 0.85 (t, $J$=7.2 Hz, 6H), 0.66–0.64 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 152.8, 149.8, 148.0, 147.6, 144.0, 136.1, 133.9, 129.2, 128.7, 123.9, 123.5, 122.6, 120.9, 119.4, 118.5, 83.8, 55.3, 40.4, 32.1, 30.3, 29.6, 29.5, 25.3, 24.11, 23.0, 14.5; MS ($m/z$, $FAB^+$) 683 (5); HRMS ($m/z$, $FAB^+$) calcd for $C_{47}H_{62}BNO_2$ 683.4874, found 683.4879.

*4.3.3. 2,5-Dibromobenzene-1,4-diamide (**8**).* The mixture of 2,5-dibromotetrephthalic acid (1.5 g, 4.6 mmol), thionyl chloride (20 mL), a drop of DMF was refluxed for 3 h. Thionyl chloride was removed by co-evaporation with toluene (20 mL) with rotary evaporation. The concentrated crude product was dissolved in dioxane (20 mL). Ammonium hydroxide (20 mL, concd) was added dropwisely to the mixture and stirred overnight at room temperature. The precipitate was filtered and washed with dioxane to afford the pure product as a white solid (1.22 g, 76%). Mp=338–341 °C; IR (KBr) $\nu$ 3176, 1653, 1615, 1527, 1483, 1393, 1352, 1319, 1264, 1205, 1153, 1125, 1057, 887, 802, 735, 662, 609, 502 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.98 (s, 2H), 7.70 (s, 2H), 7.63 (s, 2H); $^{13}C$ NMR (DMSO-$d_6$, 100 MHz) $\delta$ 166.9, 140.6, 132.1, 117.5; MS ($m/z$, $FAB^+$) 321 (4); HRMS ($m/z$, $FAB^+$) calcd for $C_8H_6Br_2N_2O_2$ 320.8874, found 320.8875.

*4.3.4. 2,5-Dibromobenzene-1,4-dinitrile (**9**).* 2,5-Dibromobenzene-1,4-diamide (1.0 g, 3.2 mmol) in phosphorus oxychloride (40.0 mL) was heated at 135 °C for 12 h. The mixture was slowly poured into ice water, and stirred for 10 min. The precipitate was filtered and washed with water to afford the pure product as a white solid[40] (**9**) (0.90 g, 99%). Mp=260–262 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.96 (s, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 138.0, 124.3, 121.3, 114.7.

*4.3.5. 2,5-Bis(2-(diphenylamino)-9,9-dioctyl-9H-fluoren-7-yl) benzene-1,4-dinitrile (**1a**).* To the mixture of 2,5-dibromobenzene-1,4-dinitrile (33 mg, 0.12 mmol) and tetrakis(triphenylphosphine) palladium (7 mg, 0.006 mmol) was added the solution of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (167 mg, 0.244 mmol) in toluene (6 mL) and $K_2CO_3$ (2 M, 3 mL) under nitrogen, and then stirred for 3 days at 85 °C. The mixture was partitioned between toluene and brine, dried over $MgSO_4$, and concentrated under vacuum to get orange oil. The orange oil was purified by chromatography over silica gel (elution with hexane/toluene=5/2) to afford the pure product as a white solid (60 mg, 43%). Mp=198–200 °C; IR (KBr) $\nu$ 3062, 3035, 2954, 2924, 2852, 2229, 1594, 1492, 1462, 1341, 1275, 1076, 1028, 891, 821, 751, 696, 511 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.00 (s, 2H), 7.77 (d, $J$=7.6 Hz, 2H), 7.63 (d, $J$=8.0 Hz, 2H), 7.57–7.54 (m, 4H), 7.30–7.26 (m, 8H), 7.17–7.15 (m, 10H), 7.08–7.03 (m, 6H), 2.01–1.90 (m, 8H), 1.26–1.11 (m, 40H), 0.87 (t, $J$=6.8 Hz, 12H), 0.77–0.75 (m, 8H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 152.4, 151.3, 147.7, 147.5, 144.1, 142.3, 134.9, 134.6, 133.2, 129.0, 127.4, 124.0, 123.1, 122.9, 122.7, 120.8, 119.5, 118.8, 115.2, 55.8, 40.7, 32.4, 30.5, 30.3, 29.9, 29.8, 24.5, 23.3, 14.8; MS ($m/z$, $FAB^+$) 1240 (4); HRMS ($m/z$, $FAB^+$) calcd for $C_{90}H_{102}N_4$ 1239.8183, found 1239.8195.

*4.3.6. 4,7-Bis(2-(diphenylamino)-9,9-dioctyl-9H-fluoren-7-yl) benzo [1,2,5]thiadiazole (**1b**).* In the mixture of 4,7-dibromo[1,2,5]thiadiazole (23.5 mg, 0.08 mmol) and tetrakis(triphenyl phosphine) palladium (6 mg, 0.004 mmol) was added the solution of 7-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-9,9-dioctyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (117 mg, 0.171 mmol) in toluene (6 mL) and $K_2CO_3$ (2 M, 3 mL) under nitrogen, and then stirred for 3 days at 85 °C. The mixture was partitioned between ether and brine, dried over $MgSO_4$, and concentrated under vacuum to get brown oil. The brown oil was purified by chromatography over silica gel (elution with hexane/toluene=4/1) to afford the pure product as an orange solid (0.012 g, 13%). Mp=152–153 °C; IR (KBr) $\nu$ 3034, 2924, 2851, 1594, 1492, 1462, 1274, 1028, 893, 816, 752, 696, 511 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 8.03 (d, $J$=8.0 Hz, 2H), 7.94 (s, 2H), 7.89 (s, 2H), 7.79 (d, $J$=8.0 Hz, 2H), 7.64 (d, $J$=8.8 Hz, 2H), 7.30–7.16 (m, 18H), 7.08–7.02 (m, 6H), 2.04–1.90 (m, 8H), 1.29–1.14 (m, 40H), 0.92–0.84 (m, 20H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 154.0, 152.4, 150.7, 147.7, 147.0, 140.9, 135.6, 135.2, 133.3, 129.0, 128.0, 127.6, 123.8, 123.5, 123.3, 122.4, 120.5, 119.2, 119.0, 55.6, 40.7, 32.4, 30.6, 29.9, 29.8, 24.6, 23.3, 14.8; MS ($m/z$, $FAB^+$) 1247 (12); HRMS ($m/z$, $FAB^+$) calcd for $C_{88}H_{102}N_4S$ 1247.7903, found 1247.7892.

## Acknowledgements

This work was financially supported by the National Science Council of Taiwan.

## Supplementary data

$^1H$ and $^{13}C$ NMR spectra of new compounds. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.11.071.

## References and notes

1. Göppert-mayer, M. *Ann. Phys.* **1931**, *9*, 273–294.
2. Peticolas, W. L. *Annu. Rev. Phys. Chem.* **1967**, *18*, 233–260.
3. Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843–845.
4. Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X. L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51–54.
5. Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777–1788.
6. Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 83–85.
7. Köhler, R. H.; Cao, J.; Zipfel, W. R.; Webb, W. W.; Hansen, M. R. *Science* **1997**, *276*, 2039–2042.
8. Xu, C.; Zipfel, W. R.; Shear, J. B.; William, R. M.; Webb, W. W. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 10763–10768.
9. Spangler, C. W. *J. Mater. Chem.* **1999**, *9*, 2013–2020.
10. Pettit, D. L.; Wang, S. S. H.; Gee, K. R.; Augustine, G. *Neuron* **1997**, *19*, 465–733.
11. Fisher, W. G.; Partridge, W. P.; Dees, J. C.; Wachter, E. A. *Photochem. Photobiol.* **1997**, *66*, 141–155.
12. Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863–1874.
13. Adronov, A.; Fre'chet, J. M.; He, G. S.; Kim, K.-S.; Chung, S.-J.; Swiatkiewicz, J.; Prasad, P. N. *Chem. Mater.* **2000**, *12*, 2838–2841.
14. Albota, M.; Beljonne, D.; Bre'das, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, C.; Webb, W. W.; Wu, X. L.; Xu, C. *Science* **1998**, *281*, 1653–1656.
15. Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z.; McCord-Maughon, D.; Parker, T. C.; Röckel, H.; Thayumanavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J. L *J. Am. Chem. Soc.* **2000**, *122*, 9500–9510.
16. Ventelon, L.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. *Chem. Commun.* **1999**, *45*, 2055–2056.
17. Entwistle, C. D.; Collings, J. C.; Steffen, A.; Palsson, L.-O.; Beeby, A.; Albesa-Jove, D.; Burke, J. M.; Batsanov, A. S.; Howard, J. A. K.; Mosely, J. A.; Poon, S.-Y.; Wong, W.-Y.; Ibersiene, F.; Fathallah, S.; Boucekkine, A.; Halet, J.-F.; Marder, T. B. *J.Mater. Chem.* **2009**, *19*, 7532–7544.
18. Beljonne, D.; Wenseleers, W.; Zojer, E.; Shuai, Z.; Vogel, H.; Pond, S. J. K.; Perry, J. W.; Marder, S. R.; Brédas, J. L *Adv. Funct. Mater.* **2002**, *12*, 631–632.
19. Cho, B. R.; Son, K. H.; Lee, S. H.; Song, Y.-S.; Lee, Y.-K.; Jeon, S.-J.; Choi, J.-H.; Lee, H.; Cho, M. *J. Am. Chem. Soc.* **2001**, *123*, 10039–10045.
20. Cho, B. R.; Piao, M. J.; Son, K. H.; Lee, S. H.; Yoon, S.-J.; Jeon, S.-J.; Choi, J. H.; Lee, H.; Cho, M. *Chem.—Eur. J.* **2002**, *8*, 3907–3916.
21. Jiang, Y.; Wang, Y.; Hua, J.; Tang, J.; Li, B.; Qian, S.; Tian, H. *Chem. Commun.* **2010**, *46*, 4689–4691.
22. Das, S.; Nag, D.; Goswami, D.; Bharadwaj, P. K. *J. Am. Chem. Soc.* **2006**, *128*, 402–403.

23. Yoo, J.; Yang, S. K.; Jeong, M.-Y.; Ahn, H. C.; Jeon, S.-J.; Cho, B. R. *Org. Lett.* **2003**, *5*, 645–648.
24. Kato, S.-I.; Matsumoto, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Ishi- I. T.; Mataka, S. *Chem.—Eur. J.* **2006**, *12*, 2303–2317.
25. Kannan, R.; He, G. S.; Yuan, L.; Xu, F.; Prasad, P. N.; Dombroskie, A. G.; Reinhardt, B. A.; Baur, J. W.; Vaia, R. A.; Tan, L.-S. *Chem. Mater.* **2001**, *13*, 1896–1904.
26. Belfield, K. D.; Morales, A. R.; Kang, B.-S.; Hales, T. M.; Hagan, D. J.; VanStryland, E. W.; Chapela, V. M.; Percino, J. *Chem. Mater.* **2004**, *16*, 4634–4641.
27. (a) Albota, M. A.; Xu, C.; Webb, W. W. *Appl. Opt.* **1998**, *37*, 7352–7356; (b) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481–491.
28. Justin Thomas, K. R.; Velusamy, M.; Lin, J. T.; Chuen, C.-H.; Tao, Y.-T. *Chem. Mater.* **2005**, *17*, 1860–1866.
29. Liao, Y.-L.; Hung, W.-Y.; Hou, T.-H.; Lin, C.-Y.; Wong, K.-T. *Chem. Mater.* **2007**, *19*, 6350–6357.
30. Ku, S.-Y.; Chi, L.-C.; Hung, W.-Y.; Yang, S.-W.; Tsai, T.-C.; Wong, K.-T.; Chen, Y.-H.; Wu, C.-I. *J. Mater. Chem.* **2009**, *19*, 773–780.
31. Huang, S.-T.; Hsu, Y.-C.; Yen, Y.-S.; Chou, H. H.; Lin, J. T.; Chang, C.-W.; Hsu, C.-P.; Tsai, C.; Yin, D.-J. *J. Phys. Chem. C* **2008**, *112*, 19739–19747.
32. Pond, S. J. K.; Rumi, M.; Levin, M. D.; Parker, T. C.; Beljonne, D.; Day, M. W.; Bredas, J.-L.; Marder, S. R.; Perry, J. W. *J. Phys. Chem. A* **2002**, *106*, 11470–11480.
33. Yamashita, Y. *Chem. Lett.* **2009**, *38*, 870–878.
34. Suzuki, T.; Yamashita, Y.; Kabuto, C.; Miyashi, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1102–1103.
35. Katan, C.; Tretiak, S.; Werts, M. H. V.; Bain, A. J.; Marsh, R. J.; Leonczek, N.; Nicolaou, N.; Badaeva, E.; Mongin, O.; Blanchard-Desce, M. *J. Phys. Chem. B* **2007**, *111*, 9468–9483.
36. Kimw, H. M.; Cho, B. R. *Chem. Commun.* **2009**, *45*, 153–164.
37. Kim, H. M.; Fang, X. Z.; Yang, P. R.; Yi, J. S.; Ko, Y. G.; Piao, M. J.; Chung, Y. D.; Park, Y. W.; Jeon, S. J.; Cho, B. R. *Tetrahedron Lett.* **2007**, *48*, 2791–2795.
38. Fisher, W. G.; Wachter, E. A.; Lytle, F. E.; Armas, M.; Seaton, C. *Appl. Spectrosc.* **1998**, *52*, 536–545.
39. Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.
40. Bukeikhanov, N. R.; Kudinova, V. S.; Suvorov, B. V. *Dokl. Akad. Nauk SSSR* **1968**, *178*, 591–594.