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Synthesis and properties of new two-photon absorption chromophores containing 3,5-dicyano-2,4,6-tristyrylpyridine as the core

Hongli Wang,[a] Zhen Li,[a] Pin Shao,[a] Yanke Liang,[a] Hui Wang,[a] Jingui Qin*[a] and Qihuang Gong[b]

[a] *Department of Chemistry, Wuhan University, Wuhan, 430072, P. R. China. E-mail: jgqin@whu.edu.cn; Fax: +86-27-68756757; Tel: +86-27-68756757*
[b] *State Key Laboratory for Mesoscopic Physics, Department of Physics, Peking University, Beijing, 100871, P. R. China*

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This paper reports the synthesis of a series of donor-substituted 3,5-dicyano-2,4,6-tristyrylpyridine derivatives, having two-dimensional branched D-π-A structures, as new two-photon absorption (TPA) chromophores. These chromophores are stilbene-type chromophores containing the same acceptor group but end-capped with different aromatic groups as the donors. Measured as the two-photon-induced fluorescence in chloroform solvent, using a femtosecond multipass Ti : sapphire amplifier as the irradiation source, the TPA cross section values of some compounds are on the order of 10^{-48} cm^4 s $photon^{-1}$. These chromophores also have relatively high two-photon-excited fluorescence (TPEF) action cross sections. Pumped by the laser at 800 nm, these chromophores show efficient two-photon-induced orange-red fluorescence emission. The experimental results indicate that the different end-capped functional electronic donors and the number of branches of these chromophores affect their one-photon properties, two-photon up-conversion emission behavior and TPA cross section values. Especially, with increasing numbers of branches, λ_{max}^{abs} and λ_{max}^{spf} exhibit bathochromic shifts, while their two-photon absorption cross sections also increase. Compared with the two-branched chromophore **6**, the tribranched chromophore **4** shows a larger TPA cross section, and the cooperative enhancement of the TPA cross section from **6** to **4** is 1.2-fold at 800 nm.

Introduction

The two-photon absorption (TPA) properties of organic materials have attracted much attention in the last decade because of various potential applications in optical data storage,[1–4] fabrication of microstructures,[4–7] optical limiting,[8,9] and in other fields such as analytical chemistry, biology and medicine.[10,11] For these applications, it is important to prepare materials exhibiting large TPA cross sections (δ) at the wavelengths of available laser sources.[12,13] Marder *et al.* have demonstrated that symmetrical stilbenes containing bis-donor (D) or bis-acceptor (A) groups linked by a π-conjugated bridge (D-π-D or A-π-A) exhibit large δ with the π-conjugation length as well as the strength of D and A being important parameters.[14,15] On the other hand, Prasad *et al.* have pointed out that D-π-A type molecules, containing dithienothiophene or other aromatic rings as the rigid π-conjugated backbone, also have large TPA cross sections.[12,13,16] Many additional structural designs such as heterocyclic π-bridges have also been proposed by Abbotto *et al.*, and their TPA molecules exhibit high TPA cross section values.[17] Rebane *et al.* also have presented a series of porphyrin dimers that show extremely large TPA cross sections of up to 1×10^4 GM (GM = Göppert–Mayer = 10^{-50} cm^4 s $photon^{-1}$) in the near-IR.[18]

Recently, molecules with branched structures such as octupolar molecules [19–24] have attracted much research interest due to their potential utilization in TPA and two-photon-excited fluorescence (TPEF) microscopy. Differing from other dipolar molecules, these symmetrical octupolar compounds with a three-fold rotational symmetry axis can enhance the two-dimensional charge transfer between the core and the conjugated peripheral substituents to obtain high TPA cross section values.[24] However, the number of existing octupolar structural materials is still low. In particular, only some symmetrically octupolar compounds have been reported for TPA,[19,21,24] and until now, there are still few reports on nonsymmetrical octupolar materials. Similarly, the dependence of the TPA cross section values on the number of branches in the chromophores has only been rarely reported.[17,19]

Within this context, we herein describe the syntheses and the one- and two-photon photophysical properties of two new nonsymmetrical three-branched chromophores, **3** and **4**, having an $A(-\pi-D)_3$ structure, and three new two-branched chromophores, **5–7** with the $A(-\pi-D)_2$ structural design. These new compounds all contain the same 3,5-dicyano-2,4,6-tristyrylpyridine core but are end-capped with varied donor aromatic groups. The different terminal functions of the aromatic donor components of these chromophores result in their different single-photon and two-photon properties. Measured with a femtosecond laser at ~800 nm as the two-photon-induced fluorescence, these compounds showed relatively high TPA cross sections (δ); they also exhibited relatively high two-photon-excited fluorescence (TPEF) action cross sections. Comparing the TPA cross section value of tribranched chromophore **4** at 800 nm with that of the two-branched chromophore **6**, we find that the cooperative enhancement from **6** to **4** is 1.2-fold.

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Experimental

Chemicals and measurements

2,4,6-Trimethylpyridine (**1**; 98%), triphenylamine and *N*-ethylaniline were commercially available from Acros Organics. Bromine, piperidine, *n*-propyl alcohol were AR grade. The above chemicals were used without further purification. Phosphorus oxychloride ($POCl_3$) was distilled before use. *N*,*N*-Dimethylformamide (DMF) was dried and distilled under reduced pressure over calcium hydride (CaH_2) before use. 4-(*N*,*N*-Diphenylamino)benzaldehyde (**8**),[25] *N*-ethyl-*N*-cetylaminobenzaldehyde (**10**)[26] and 3,5-dicyano-2,4,6-trimethylpyridine (**2**)[27] were synthesized following the literature. Other chemicals were used as received without further purification.

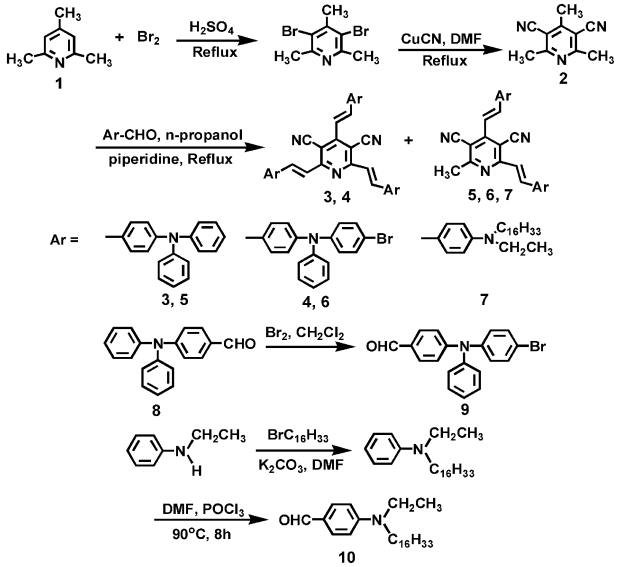
^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian-Mercury 300 spectrophotometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as a reference. IR spectra were obtained as KBr pellets on a Nicolet-170 SKFT-IR spectrometer. UV-Vis absorption spectra were measured on a Shimadzu-12106 recording spectrophotometer. The steady-state fluorescence spectrum measurements were performed using a Hitachi 5000 spectrofluorimeter. Elemental analysis was performed using a PE 2400 elemental analyzer. Mass spectra were recorded using a VJ-ZAB-3F mass spectrometer. The melting points and decomposition temperatures were measured on a Perkin Elmer DTA 1700 differential thermal analyzer and on a Shimadzu DT-40 thermal analyzer at a heating rate of 15 °C min^{-1} under nitrogen atmosphere, respectively. The two-photon-absorption fluorescence experiments were performed using a femtosecond multipass Ti : sapphire amplifier (Quantronix Odin, pulse width 130 fs, repetition frequency 1 KHz, at ~800 nm) as the irradiation source.

Single-photon UV-Vis absorption was conducted in chloroform at the concentration of 1×10^{-5} M, and their single-photon fluorescence was also measured in chloroform but at the concentration of 1×10^{-6} M. The chloroform was anhydrous grade after further purification. For the single-photon fluorescence measurements, the solutions were freshly prepared and kept in the dark before the measurements. The fluorescence quantum yield was determined using Rhodamine B as the reference by the literature method.[28] The two-photon absorption cross sections of all samples (1.0×10^{-4} M in chloroform) were measured at 800 nm using Rhodamine 6G (1.0×10^{-4} M in MeOH) as the reference. The intensity of the two-photon-induced fluorescence spectra of the reference and of the samples emitting at the same excitation wavelength were determined. Their TPA cross sections were calculated by using eqn. (1) and eqn. (2) below[14,21,29] (see the Results and discussion section).

Syntheses

The synthetic routes for compounds **9** and **3–7** are outlined in Scheme 1 and the details are given below.

4-*N*-(*p*-Bromophenyl)-*N*-phenylaminobenzaldehyde (9). 4-(*N*,*N*-Diphenylamino)benzaldehyde (**8**, 0.7 g, 2.56 mmol) was dissolved in 10 mL of methylene chloride; bromine (0.45 g, 2.82 mmol) dissolved in 40 ml of methylene chloride was added slowly with vigorous stirring at room temperature over 8 h. The mixture was stirred at room temperature overnight and poured into a large excess of 1 M sodium hydroxide solution. The methylene chloride layer was then separated. After methylene chloride was removed by distillation using a rotary evaporator, the residue was purified by column chromatography over a silica gel column using petroleum ether–ethyl acetate (v/v, 4 : 1) as the eluent to afford **9** as yellow solids. Yield: 94% (0.85 g). M.p. 151–153 °C. ^{1}H NMR ($CDCl_3$, δ): 9.81 (s, 1H, C*H*O), 7.66 (m, 2H, Ar–*H*), 7.44 (t, 2H, J = 8.0 Hz, Ar–*H*), 7.32 (m, 2H, Ar–*H*), 7.17 (m, 3H, J = 7.2 Hz, Ar–*H*), 7.01 (m, 4H, Ar–*H*). MS (*m*/*z*): 352.



Scheme 1 Synthetic routes to compounds **3–7**, **9** and **10**.

Preparation of compounds 3–7. The preparations were all very similar and the method described here for compounds **3–7** is typical. In a 100 mL round-bottomed flask equipped with a reflux condenser and nitrogen bubbler were placed 3,5-dicyano-2,4,6-trimethylpyridine (**2**, 0.1 g, 0.585 mmol) and 3.1 (2.1 for **7**) equiv. of the aromatic benzylaldehyde in 20 mL *n*-propyl alcohol; a catalytic amount piperidine (about 8 drops) was added to the mixture. The mixture was refluxed for 2 days. After cooling to room temperature, crude products were precipitated, which were isolated by suction filtration and air dried. Then they were dissolved in chloroform and chromatographed over a silica gel column using chloroform–petroleum ether (3 : 1 v/v) as the eluent to get the desired products; the first band collected was **3** or **4**, the second band collected was **5** or **6**. For the reaction of **2** with *N*-ethyl-*N*-cetylaminobenzaldehyde (**10**), the crude production could not be precipitated in *n*-propyl alcohol, so that after concentration of the reaction mixture to dryness *in vacuo*, the residue was chromatographed over silica using chloroform–petroleum ether (v/v) as the eluent to get the product, the first band collected was **7**.

3,5-Dicyano-2,4,6-tri(triphenylaminostyryl)pyridine (3) and 3,5-dicyano-2,4-di(triphenylaminostyryl)-6-methylpyridine (5). After **2** and 4-(*N*,*N*-diphenylamino)benzaldehyde (**8**) reacted completely, the crude product was chromatographed as described above. The first band was collected to give **3** as a red solid; 22% yield (0.12 g); m.p. 232–234 °C and T_d 250 °C. ^{1}H NMR ($CDCl_3$, δ) 8.15 (d, 2H, J = 14.5 Hz, *o*-Py–CH=C*H*–), 7.88 (d, 1H, J = 15.5 Hz, *p*-Py–CH=C*H*–), 7.55 (d, 2H, J = 14.5 Hz, *o*-Py–C*H*=CH–), 7.51 (m, 2H, J = 8 Hz, Ar), 7.47 (d, 2H, J = 6.5 Hz, Ar), 7.41 (d, 1H, J = 15.5 Hz, *p*-Py–C*H*=CH–), 7.30 (m, 18H, Ar), 7.10 (m, 20H, Ar). FTIR (cm^{-1}): 1623, 971 (CH=CH), 2214 (CN). Anal. calcd for $C_{67}H_{48}N_6$: C, 85.90; H, 5.13; N, 8.97. Found: 86.57; H, 5.23; N, 9.25%. The second band gave compound **5** as a red solid; 57% yield (0.23 g); m.p. 184–186 °C and T_d 232 °C. ^{1}H NMR ($CDCl_3$, δ) 8.07 (d, 1H, J = 15.0 Hz, *o*-Py–CH=C*H*–), 7.89 (d, 1H, J = 15.0 Hz, *p*-Py–CH=C*H*–), 7.50 (t, 3H, J = 15.0 Hz, *o*-Py–C*H*=CH– and Ar), 7.40 (d, 1H, J = 15.0 Hz, *p*-Py–C*H*=CH–), 7.29 (m, 10H, Ar), 7.14 (m, 10H, Ar), 7.04 (m, 6H, Ar), 2.84 (s, 3H, C*H*$_3$). Anal. calcd for $C_{48}H_{35}N_5$: C, 84.58; H, 5.14; N, 10.28. Found: 84.87; H, 5.43; N, 9.98%.

3,5-Dicyano-2,4,6-tri[*N*-(*p*-bromophenyl)-*N*,*N*-diphenylamino]styrylpyridine (4) and 3,5-dicyano-2,4-di[*N*-(*p*-bromophenyl)-*N*,*N*-diphenylamino]styryl-6-methylpyridine (6). After **2** and 4-*N*-(*p*-bromophenyl)-*N*-phenylaminobenzaldehyde (**9**) reacted completely, the crude product was chromatographed as described above. The first band was collected to give **4** as a red solid; 27% yield (0.19 g); m.p. 257–259 °C and T_d 359 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.12 (d, 2H, J = 14.5 Hz, *o*-Py–CH=C*H*), 7.85 (d, 1H, J = 15.5 Hz, *p*-Py–CH=C*H*), 7.54 (m, 4H, *o*-Py–C*H*=CH and Ar–*H*), 7.46 (m, 3H, *p*-Py–C*H*=CH and Ar–*H*), 7.36 (t, 4H, J = 7.5 Hz, Ar–*H*), 7.29 (t, 4H, J = 6.5 Hz, Ar–*H*), 7.10 (dd, 12H, J = 6.5 Hz, Ar–*H*), 7.01 (q, 15H, J = 8.0 Hz, Ar–*H*). ^{13}C NMR ($CDCl_3$, 300 MHz, δ): 104.47, 114.89, 114.97, 115.97, 116.73, 117.17, 118.12, 119.28, 122.71, 122.93, 124.01, 124.26, 124.48, 125.36, 125.73, 126.07, 126.41, 126.68, 129.09, 129.28, 129.53, 130.14, 132.54, 132.67, 132.81, 139.01, 141.91, 145.44, 145.63, 145.81, 146.20, 147.77, 149.21, 150.83, 154.41, 155.05, 164.44, 165.02, 165.27. FTIR (cm^{-1}):1622, 967 (CH=CH), 2214 (CN). Anal. calcd for $C_{67}H_{45}N_6Br_3$: C, 68.54; H, 3.84; N, 7.16. Found: 68.76; H, 4.02; N, 6.91. The second band gave compound **6** as a red solid; 66% yield (0.32 g); m.p. 196–198 °C and T_d 249 °C. ^{1}H NMR ($CDCl_3$, δ): 8.07 (d, 1H, J = 14.5 Hz, *o*-Py–C*H*=CH–), 7.86 (d, 1H, J = 15.5 Hz, *o*-Py–CH=C*H*–), 7.48 (m, 3H, *p*-Py–C*H*=CH and Ar–*H*–), 7.36 (m, 3H, *p*-Py–CH=C*H*– and Ar–*H*), 7.28 (m, 4H, J = 6.5 Hz, Ar–*H*), 7.12 (t, 8H, J = 8.1 Hz, Ar–*H*), 7.03 (t, 10H, J = 7.2 Hz, Ar–*H*), 2.83 (s, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 300 MHz, δ): 25.42, 102.24, 103.19, 116.67, 117.68, 118.16, 119.73, 120.18, 121.71, 121.89, 122.22, 122.40, 124.32, 124.68, 125.66, 126.67, 129.01, 129.45, 129.68, 129.84, 132.66, 132.84, 141.03, 141.68, 146.09, 146.52, 146.89, 149.43, 149.63, 149.99, 151.46, 159.81, 164.95. FTIR (cm^{-1}): 1630, 967 (CH=CH), 2217 (CN). Anal. calcd for $C_{48}H_{33}N_5Br_2$: C, 68.65; H, 3.93; N, 8.34. Found: 68.78; H, 4.16; N, 7.89.

3,5-Dicyano-2,4-di(*N*-ethyl-*N*-cetylaminobenzylstyryl)-6-methylpyridine (7). After **2** and *N*-ethyl-*N*-cetylaminobenzaldehyde (**10**) reacted completely, the crude product was chromatographed as described above to give compound **7** as a red solid; 36% yield (0.19 g); m.p. 123–125 °C and T_d 317 °C. ^{1}H NMR ($CDCl_3$, δ): 8.04 (d, 1H, J = 15.5 Hz, *o*-Py–CH=C*H*–), 7.94 (d, 1H, J = 15.5 Hz, *p*-Py–CH=C*H*–), 7.48 (t, 4H, J = 8.5 Hz, Ar), 7.25 (d, 1H, J = 15.5 Hz, *o*-Py–C*H*=CH–), 7.03 (d, 1H, J = 15.5 Hz, *p*-Py–C*H*=CH–), 6.60 (d, 4H, J = 8.5 Hz, Ar), 3.40 (d, 4H, J = 7.5 Hz, N–C*H*$_2$), 3.29 (t, 4H, J = 7.2 Hz, N–C*H*$_2$), 2.78 (s, 3H, C*H*$_3$–Py), 1.25 (m, 56H, C*H*$_2$), 0.88 (t, 12H, J = 6.6 Hz, C*H*$_3$). FTIR (cm^{-1}): 1598, 967 (CH=CH), 2216 (CN). Anal. calcd for $C_{60}H_{91}N_5$: C, 81.73; H, 10.33; N, 7.95. Found: 81.84; H, 10.52; N, 8.22. FAB-MS (m/z) 882 (M + 1).

Results and discussion

Syntheses and structural characterization

The synthetic routes to the aromatic aldehydes and compounds **3–10** are shown in Scheme 1. In the literature[20] 4-[*N*,*N*-di(4-bromophenyl)amino]benzaldehyde was synthesized in a yield of 63%. In the present work, 4-*N*-(*p*-bromophenyl)-*N*-phenylaminobenzaldehyde (**9**) was obtained by the bromination of 4-(*N*,*N*-diphenylamino)benzaldehyde (**8**) in a yield of 94%, which is higher than that reported in ref. 20. In our case, the dropping rate of bromine in diluted methylene chloride was very slow to prevent the formation of the 4-[*N*,*N*-di(4-bromophenyl)amino]benzaldehyde as the by-product. After the reaction was completed, the crude product was not washed with methanol, as was done in ref. 20, because we found that our crude product could slightly dissolve in methanol. So this may be the reason for the higher yield of compound **4** than that of 4-[*N*,*N*-di(4-bromophenyl)amino]benzaldehyde in ref. 20.

The five chromophores were synthesized by the Knoevenagel reaction between 3,5-dicyano-2,4,6-trimethylpyridine (**2**) and aromatic aldehydes with piperidine as a catalyst. Compounds **4** and **6** were prepared simultaneously in yields of 27% and 66%, respectively, with a molar ratio of reagents of 1 : 3.1 (Table 1). The structure of **6** was proved by its ^{1}H NMR spectrum with the chemical shift of the unsubstituted methyl group being around 2.83 ppm, and also by its ^{13}C NMR spectrum with the CN group of the compound **6** split into two peaks at 102.24 and 103.19 ppm, as theoretically the CN group of the 2,6-disubstituent could not be split in its ^{13}C NMR spectrum. Also, the CN group of tri-substituted **4** only had its chemical shift at 104.47 ppm. Compounds **3** and **5** were also prepared simultaneously in yields of 22% and 57%, respectively, with a molar ratio of the reagents of 1 : 3.1 also (Table 1). However, when a molar ratio for 3,5-dicyano-2,4,6-trimethylpyridine (**2**) and *N*-ethyl-*N*-cetylaminobenzaldehyde (**10**) of 1 : 3.1 was used, the main product was **7**; its 2,4,6-trisubstituted derivative cannot be obtained and some unreacted **10** was also recovered. The possible reason the trisubstituted derivative was not obtained might be related to its distorted structure due to its long alkyl group, which prevents the reaction from occurring. So, in this study, a molar ratio of 1 : 2.1 for compounds **2** and **10** was used (Table 1) to prepare **7**, whose structure was proved by its ^{1}H NMR spectrum with the chemical shift of the unsubstituted methyl group being around 2.78 ppm, and also proved by the peak at 882 (M + 1) in the mass spectrum; no higher mass peaks appear.

All of the above compounds are characterized by ^{1}H NMR, FTIR, UV-Vis and elemental analysis; some compounds have ^{13}C NMR analysis; these data are given above in the Experimental. Characteristic resonances of the vinylic protons of these compounds at 8.12–7.03 ppm with large trans coupling constants were evident in their ^{1}H NMR spectra; the shift of the unsubstituted methyl groups of these compounds were around 2.8 ppm. The absorptions around 2221 and 969 cm^{-1} in their FTIR spectra correspond to CN stretching and out-of-plane bending motions, respectively, of *trans*-vinylene. Thermogravimetric analyses of these compounds show they all have a relatively high thermal stability with a 5% weight loss at relatively high temperatures in argon. All of the compounds are soluble in common organic solvents such as toluene, chloroform, acetone, THF, DMF and DMSO.

Table 1 Syntheses and experimental photophysical properties of compounds **3–7** in chloroform solution

Molar ratio[a]	Product	λ_{max}^{abs} [b]	λ_{max}^{spf} [b]	λ_{max}^{tpf} [b]	Φ_f/%[c]	δ/GM (at 10^{-4} M)[d]	δ'/GM (at 10^{-4} M)[e]
1 : 3.1	**3**	480	586	592	54	187	101
	5	471	581	—[f]	50	—[f]	—[f]
1 : 3.1	**4**	476	575	587	51	204	110
	6	468	570	588	45	118	53
1 : 2.1	**7**	482	569	575	38	109	66

[a] When the molar ratio of the regents [3,5-dicyano-2,4,6-trimethylpyridine (**2**) and aromatic benzylaldehydes] was 1 : 3.1, the first product was **3** or **4**, and the second product was **5** or **6**; when the molar ratio of the regents was 1 : 2.1, the first product was **7**. [b] λ_{max}^{abs}, λ_{max}^{spf}, λ_{max}^{tpf}: peak wavelengths in the linear absorption, single photon fluorescence emission, two-photon absorption (at 800 nm) induced fluorescence emission. [c] Rhodamine B was used as in ref. 27. [d] TPA cross-section values are given in GM at 800 nm, measured at a concentration of 10^{-4} M, with Rhodamine 6G used as in ref. 1. GM (Göppert–Mayer) = 10^{-50} cm^4 s $photon^{-1}$. [e] Two-photon-excited fluorescence (TPEF) action cross section at a concentration of 10^{-4} M. [f] Not obtained.

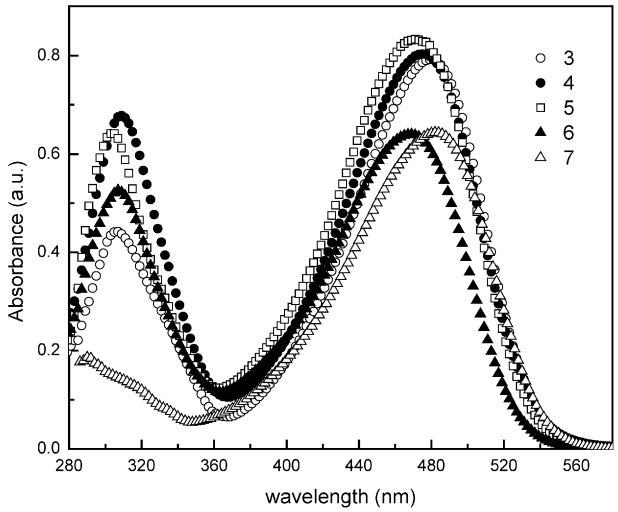


Fig. 1 Absorption spectra of compounds **3–7** in chloroform solution.

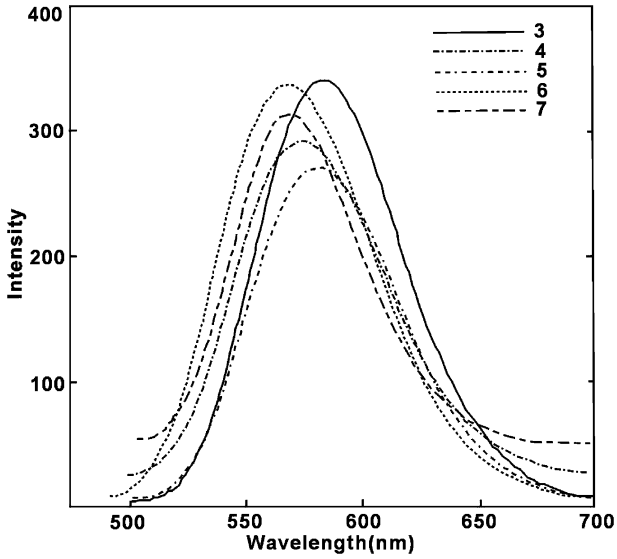


Fig. 2 Steady-state single-photon fluorescence spectra of compounds **3–7** in chloroform solution.

One-photon optical properties

Fig. 1 exhibits the one-photon absorption spectra of the five compounds at a concentration of 1×10^{-5} M in chloroform. There are two bands in their spectra, one near 300–310 nm and the other at around 468–482 nm. The former band can be assigned to a π–π* transition whereas the latter, lower energy and more intense band, is largely of intramolecular charge transfer character. This charge transfer occurs between 3,5-dicyanopyridine, a strong electron acceptor, and the other various aromatic groups. Table 1 summarizes single-photon absorption wavelengths (λ_{max}^{abs}). Their absorption maxima exhibit a blue shift in the order of $\lambda_3 > \lambda_4$ and $\lambda_7 > \lambda_5 > \lambda_6$, which would be related with the decrease in the electron-donating ability of the corresponding terminal amino group: *N*-ethyl-*N*-cetylamino > diphenylamino > *N*-(*p*-bromophenyl)-*N*-phenylamino. The diphenylamino group of **5** seems to be a weaker donor than the *N*-ethyl-*N*-cetylamino group of **7**, due to the delocalization of the lone pair electrons of the N atom onto the phenyl groups. The bromo group of **4**, as an electron-withdrawing functional group, can also result in the delocalization of lone pair electrons onto phenyl groups to a certain degree. Fig. 1 is also shows that the λ_{max}^{abs} of the tribranched chromophores is, in turn, higher than that of the two-branched chromophores, as $\lambda_3 > \lambda_5$, $\lambda_4 > \lambda_6$, which is associated with the much larger enhancements of electronic delocalization in octupolar molecules. Namely, their charge transfer and redistribution would occur between the ends and the core of the molecules along three axes, which leads to the extension of the conjugated systems.

The one-photon fluorescence spectra of these chromophores at a concentration of 1×10^{-6} M in chloroform are displayed in Fig. 2. Table 1 summarizes the single-photon fluorescence wavelengths (λ_{max}^{spf}). Their fluorescence spectra exhibit the same tendency as above, that is $\lambda_3 > \lambda_4$ and $\lambda_5 > \lambda_6$, except that $\lambda_7 < \lambda_5$. On the other hand, upon increasing the numbers of conjugated branches from two to three, the red shift from **5** to **3** of 5 nm and from **6** to **4** of 5 nm (Table 1) is obvious. Some compounds have high Φ_f values of over 50%. It is noted that only a few organic chromophores are reported to have red or orange luminescence, such as DCM {4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran} and its analogs.[30] In this context, these chromophores show orange-red fluorescence and have high Φ_f values in chloroform solution (using Rhodamine B as the standard chromophore); they might have potential use in organic light-emitting devices and the testing of their electroluminescence properties is now under way.

Two-photon absorption properties

Table 1 summarizes the wavelengths of the two-photon absorption (at 800 nm) induced up-converted fluorescence (λ_{max}^{tpf}) and the two-photon absorption cross sections (δ) of these compounds. Fig. 3 presents the two-photon-induced fluorescence emission spectra of compounds **3–7**. These chromophore solutions display manifest TPA-induced frequency up-converted fluorescence emission. All the sample solutions were prepared in the same manner at a concentration of 1.0×10^{-4} M in chloroform for this measurement. The excitation laser pulses were generated from the Ti : sapphire laser amplifier system. When a bromo group is attached to the triphenylamino, the position of two-photon absorption peak shifts to the blue, moving from 592 (**3**) to 587 (**4**) nm, which would be related with the donor strength the of end-capped aromatic moieties. It is interesting to note that the branch numbers do not affect the λ_{max}^{tpf} of these compounds, since **4** and **6** have the nearly same wavelengths. Compound **7** is an exception, with a strong donor, having the smallest value of λ_{max}^{tpf} at 575 nm.

The dependence of the two-photon absorption induced fluorescence intensity on the excitation intensity of these chromophore solutions was also examined. As an example, Fig. 4 shows the measured relative intensity of TPA-induced fluorescence as a function of the input pump intensity for

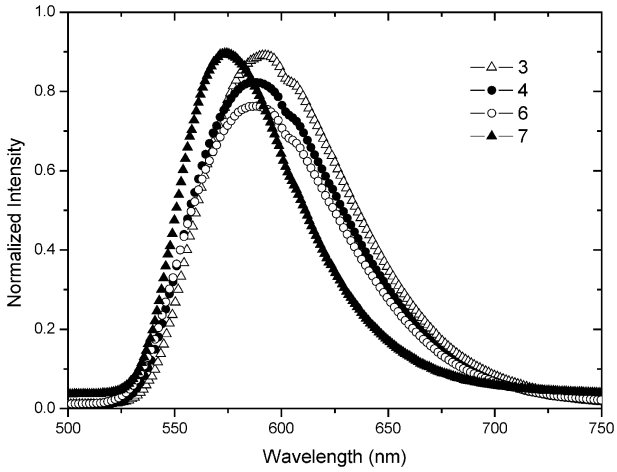


Fig. 3 Two-photon absorption (at 800 nm) induced fluorescence emission spectra of compounds **3**, **4**, **6** and **7**.

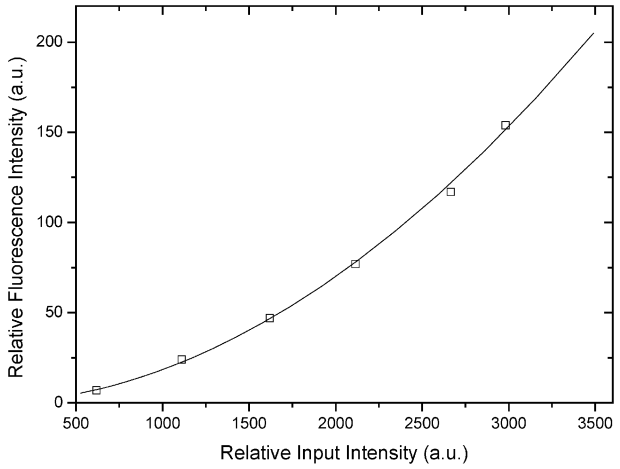


Fig. 4 Measured intensity dependence of the two-photon-induced fluorescence on the relative input intensity of the 800 nm laser pulses for compound **6** (1.0×10^{-4} M in chloroform).

chromophore **6** solution at a concentration of 1.0×10^{-4} M. The measured data (open squares) are in good agreement with the solid fitting curve following the square law, which confirms that the TPA process is responsible for the observed up-converted fluorescence emission.

The two-photon absorption cross section (δ) and two-photon excited fluorescence (TPEF) cross-section (δ') are fundamental parameters for TPA and/or TPEF materials. We adopted a TPEF-based method for the measurement of δ and δ'. Rhodamine 6G was selected as a reference in our experiment, as the δ values of Rhodamine 6G (δ_r) at different wavelengths have been carefully measured by Webb *et al.*[29] and it has been used as a reliable standard by other research groups.[14,21,24] In addition, the emission range of Rhodamine 6G is similar to that of our samples. The TPEF cross-section values of these samples (δ'_s) were measured by comparing their TPEF integral intensities S_s with that of Rhodamine 6G (S_r) under the same conditions, according to eqn. (1):[14,21,29]

$$\delta'_s = \delta_r S_s \Phi_r \phi_r c_r / S_r \phi_s c_s \quad (1)$$

$$\delta'_s = \delta_s \Phi_s \quad (2)$$

The subscripts r and s stand for the reference and sample, respectively; c is the number density of the molecules in solution, Φ is the fluorescence quantum yield and ϕ is the overall fluorescence collection efficiency of the experiment apparatus. Until now, we have not measured the two-photon absorption spectra of compounds **3–7** with an exciting laser wavelength ranging from 700–1000 nm, but have only obtained the TPA properties of compounds **3**, **4**, **6** and **7** at 800 nm. The TPA cross section values for the four compounds have been calculated and are listed in Table 1.

Comparing the TPA cross section value of the two-branched chromophore **6** with that of the tribranched chromophore **4**, the latter is higher than the former, which reveals the presence of a strong cooperative enhancement among the three branches of the octupolar molecule **4**. Significant cooperative enhancement was first reported by Prasad and coworkers for a tribranched chromophore compared with single-branched chromophores (6.8 : 1, corresponding to a 6.8 : 3 = 2.3-fold enhancement at 796 or 810 nm),[19] and later by Drobizhev *et al.* for a 29 repeat unit dendrimer compared with the unit (1.2-fold enhancement),[31] and Abbotto *et al.* for two heteroaromatic-based tribranched chromophores compared with its single-branched derivatives (7.5-fold, that is 22.6 : 3, and 4.5-fold, that is 13.4 : 3, enhancement, respectively, at 800 nm).[32] In our work, the TPA cross section value of **4** is 1.2-fold higher than that of **6** (that is 204/3 : 118/2 = 1.2 : 1) at 800 nm. Therefore, the increase of the TPA cross section value per branch is 1.2-fold in our study, which is different from the above references in which the number of branches increased by two or more. This result may be attributed to the electronic coupling[32] among the core and the three individual branches of the octupolar molecule **4**. The electronic coupling of **4** is quite strong, due to its intramolecular charge transfer and the fact that electronic redistribution can occur along its three branches from the core to the periphery (or *vice versa*), compared with that among the two branches and the core of compound **6**. However, the above TPA measurement was carried out only at the single wavelength of 800 nm, and the effect of the branches is strongly wavelength dependant. Therefore, the factor of 1.2 may be different at other wavelengths.

Among the four known TPA cross section values, the maximum value is shown by compound **4**, with a value of 204 GM. Without the δ value of **5**, we cannot compare the δ value of **5** with that of **3**. It is well-known that the TPA cross section values of compounds increase not only as the conjugation length increases, but also with the donor strength.[14,15,21] But the following two preliminary TPA results are not consistent with the ordering of donor strength. It is of interest to note that the TPA cross section values of **4** and **3** are close to each other. It is also noted that **7**, with the dialkylaminobenzyl group as its donor, and **6**, having the *N*-(*p*-bromophenyl)-*N*,*N*-diphenylamino group as its donor, have nearly equal TPA cross section values. **7** has the smallest TPA cross section value, which maybe related with its distorted structure coming from its long alkyl group, as did some 1,3,5-tricyano-2,4,6-tristyrylbenzene derivatives studied by Cho *et al.*[21] Theoretical calculations on the relationship between the donor and acceptor strengths and TPA cross section values of these chromophores are under way.

Furthermore, multiphoton microscopy is currently a blooming field, owing to the advantages that it provides for biological imaging. Besides the ongoing developments of optical systems, the design of novel fluorescence systems with optimized characteristics is of timely importance. In our work, these chromophores, with elongated conjugated systems, display relatively large δ values at 800 nm, which is in the visible red/NIR region (700–900 nm), a spectral window of particular interest for the imaging of biological tissues. These chromophores also have high fluorescence quantum yields; namely, they have relatively high TPEF action cross sections (δ') and, therefore, they have potential value in biological imaging applications..

Conclusions

In this paper, new stilbene-type branched derivatives with two-dimensional D-π-A structures have been synthesized. They are terminated with various electronic donors and the same 3,5-dicyanopyridine acceptor group. The synthesis is very convenient, the crude products are separated easily and the yields of some compounds are relatively high. Using a TPEF-based method, the TPA cross sections of some compounds are on the order around 10^{-48} cm^4 s photon^{-1}. The end-capped functional electronic donor strength affects their one-photon properties, two-photon up-conversion emission behavior and TPA cross sections. With increasing numbers of branches, the λ_{max}^{abs} and λ_{max}^{spf} wavelengths exhibit bathochromic shifts, while the TPA cross sections (δ) also become larger. Comparing the TPA cross section of the tribranched chromophore **4** at 800 nm with that of the two-branched chromophore **6**, we found that the cooperative enhancement is 1.2-fold per branch group. These chromophores also have relatively high two-photon excited fluorescence (TPEF) action cross sections, so they have potential use in biological imaging applications. Although a number of push-pull polyenes and linear quadrupolar molecules have been synthesized and extensively studied because of their large TPA cross sections, in this context, an additional

structural motif based on the 3,5-dicyano-2,4,6-tristyrylpyridine derivatives appears to be a promising direction for further development of novel TPA and TPEF chromophores.

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