

# Bis-1,4-(*p*-diarylaminostryl)-2,5-dicyanobenzene Derivatives with Large Two-Photon Absorption Cross-Sections

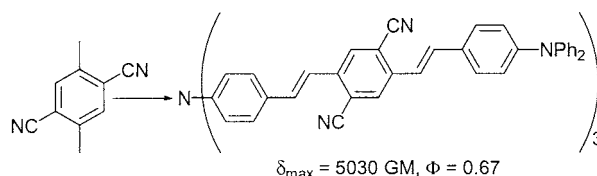
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## ABSTRACT



Synthesis and physical properties of novel multibranch two-photon materials are reported. The compound with three units of 4-(*p*-diphenylaminostryl)-2,5-dicyanostyryl moieties attached to the central triphenylamine core exhibits a very large two-photon absorption cross-section.

Extensive research is being conducted to develop organic materials with large two-photon absorption (TPA) cross-sections because of their potential applications in optical power limiting,<sup>1–3</sup> two-photon upconversion lasing,<sup>4,5</sup> two-photon fluorescence excitation microscopy,<sup>6–10</sup> three-dimensional optical data storage,<sup>11–13</sup> and photodynamic therapy.<sup>14</sup>

A variety of compounds including donor–bridge–acceptor (D– $\pi$ –A) dipoles,<sup>15</sup> donor–bridge–donor (D– $\pi$ –D) quadrupoles,<sup>16–18</sup> multibranch compounds,<sup>19</sup> dendrimers,<sup>20</sup> and octupoles<sup>21</sup> have been synthesized and their structure–property relationships established.<sup>15–22</sup> The results of these studies reveal that the TPA cross-section increases monotonically with the extent of charge transfer. Also, a significant increase in the TPA cross-section was noted in

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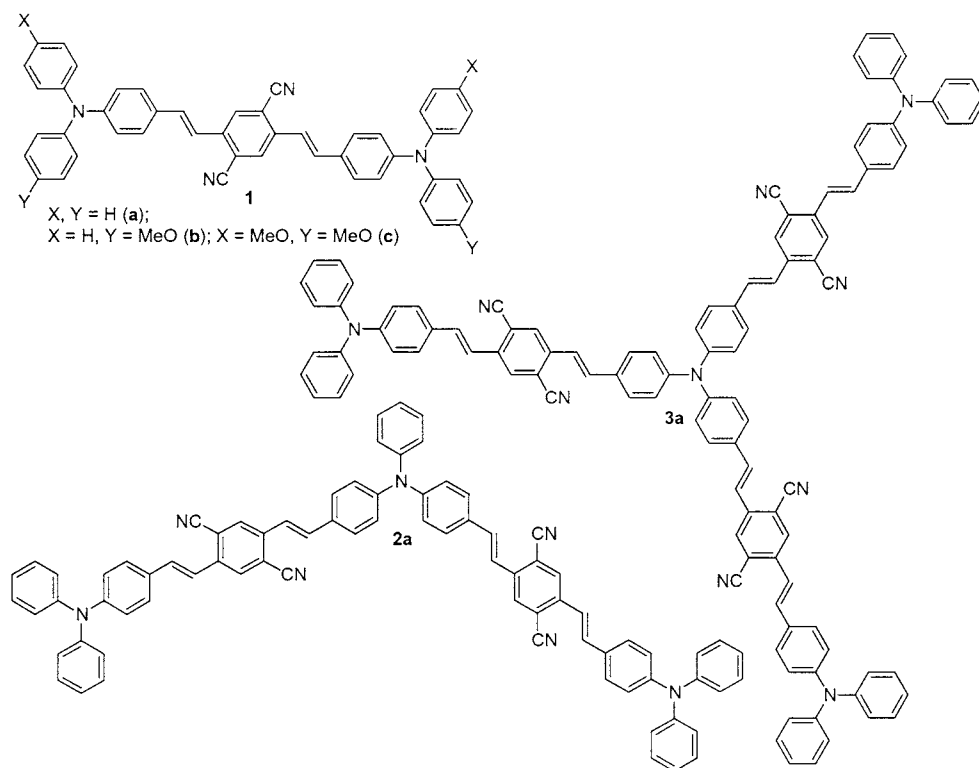
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**Figure 1.** Structures of **1–3**.

the multibranching structures indicating a cooperative enhancement.<sup>19</sup> Therefore, a useful design strategy for the synthesis of efficient TPA materials would be to incorporate D- $\pi$ -A- or D- $\pi$ -D-types of TPA dye into the multibranching structure. We have now synthesized a series of bis-1,4-(*p*-diphenylaminostryl)-2,5-dicyanobenzene derivatives with unprecedentedly large two-photon crosssections by using this design strategy (Figure 1).

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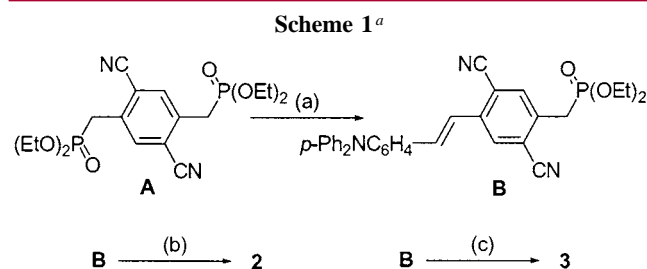
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All of the compounds were synthesized by the condensation between phosphonate ylids and benzaldehyde derivatives as shown in Scheme 1. Compounds **1a–c** were prepared by

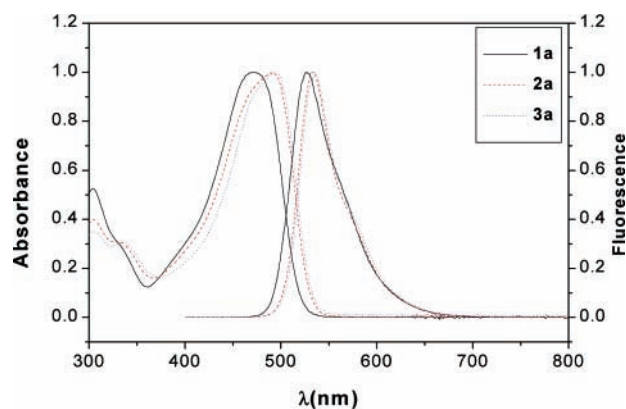


<sup>a</sup> Reagents and condition: (a) *p*-Ph<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO (1 equiv)/LDA/THF, 0 °C–rt, 40–43%. (b) PhN(C<sub>6</sub>H<sub>4</sub>CHO)<sub>2</sub> (0.5 equiv)/LDA/THF, 0 °C–rt, 56%. (c) N(Ph<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO)<sub>3</sub> (0.3 equiv)/LDA/THF, 0 °C–rt, 21–62%.

the condensation between **A** and the appropriate benzaldehyde as reported.<sup>17c,23</sup> To prepare **2** and **3**, intermediate **B** was prepared by the same procedure as described for **1** except that 1 equiv of benzaldehyde was used. Reactions of *N,N*-bis(4-formylphenyl)aniline and *N,N,N*-tris(4-formylphenyl)-

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**Figure 2.** Normalized one-photon absorption and emission spectra of **1a–3a** in toluene.

amine with **B** afforded **2** and **3**, respectively (Scheme 1). The experimental procedures for the synthesis of **2** and **3** are described in Supporting Information.

One-photon absorption and fluorescence spectra of **1a–3a** in toluene solution are depicted in Figure 2. The corresponding spectra for **1b,c** are shown in Figure S1 in Supporting Information. The results indicate that  $\lambda_{\max}^{(1)}$  of **1a–c** increases with a stronger donor (Table 1). It also

**Table 1.** One- and Two-Photon Properties of **1–3** in Toluene

compd	$\lambda_{\max}^{(1)a}$	$\lambda_{\max}^{(f)b}$	$\Delta\bar{\nu}^c$	$\Phi^d$	$\lambda_{\max}^{(2)e}$	$\delta_{\max}^{f,g}$
<b>1a</b>	473 (77.2)	527	2170	0.73	840	1370 (1.0)
<b>1b</b>	485 (66.2)	543	2200	0.62	880	1350
<b>1c</b>	488 (70.9)	560	2640	0.53	890	2250
<b>2a</b>	492 (125)	534	1600	0.69	840	3130 (1.4)
<b>3a</b>	495 (239)	536	1550	0.67	840	5030 (1.6)

<sup>a</sup>  $\lambda_{\max}^{(1)}$  of the one-photon absorption spectra in nm. The numbers in parentheses are the molar extinction coefficients ( $10^3\epsilon$ ). <sup>b</sup>  $\lambda_{\max}^{(f)}$  of the one-photon emission spectra in nm. <sup>c</sup> Stokes shift in  $\text{cm}^{-1}$ . <sup>d</sup> Fluorescence quantum yield. <sup>e</sup>  $\lambda_{\max}^{(2)}$  of the two-photon absorption spectra in nm. <sup>f</sup> Peak two-photon absorptivity in  $10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$  (GM). <sup>g</sup> Numbers in the parenthesis are relative  $\delta_{\max}/\text{MW}$ .

increases as the number of branching increases from **1a** to **2a**, indicating that the central triphenylamine moiety participates in the conjugation. However, a further increase in the branching to **3a** resulted in only a small increase in the  $\lambda_{\max}^{(1)}$  probably because the cross-conjugation effect is relatively unimportant.<sup>24</sup> It is interesting to note that the ratio between the molar absorptivity of **1a** and **3a** is close to 1:3, as expected if the three branches in **3a** are effectively separated and noninteracting.

A similar result was observed in the fluorescence spectra except that the substituent effect was larger. Compared with the absorption spectra, the  $\lambda_{\max}^{(f)}$  of **1c** shows a greater

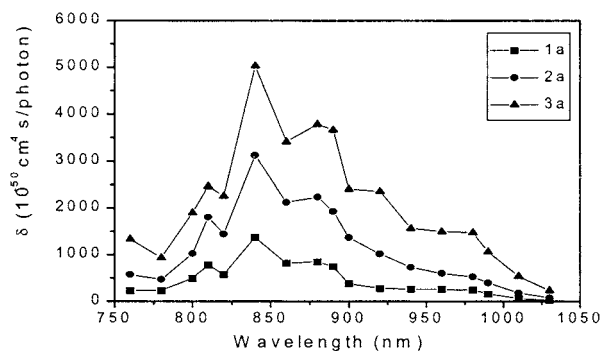
bathochromic shift and hence a larger Stokes shift in comparison to **1a,b**, indicating that the donor stabilizes the lowest excited state more than the ground state (Table 1). On the other hand, the Stokes shift decreased from **1a** to **2a**, probably because two dicyanophenyl groups in **2a** must share the central nitrogen donor to diminish the excited-state charge transfer. A further increase in the branching to **3a** had little influence on the Stokes shift, indicating that there is little difference in the excited-state charge transfer between **2a** and **3a**.

The slight decrease in the fluorescence quantum yields with a stronger donor could be due to the increased charge transfer. This would facilitate the solute–solvent interaction, by which the excited state could be rapidly quenched and decrease the quantum yield.<sup>25</sup> Note that compound **1c** with the largest Stokes shifts shows the smallest quantum yield. Also, the quantum yields of **2a** and **3a** are nearly the same probably because their Stokes shifts are very similar.

The two-photon cross-section  $\delta$  was measured by using the two-photon-induced fluorescence measurement technique with the following equation,

$$\delta = \frac{S_s \Phi_r \phi_r c_r}{S_r \Phi_s \phi_s c_s} \delta_r$$

where the subscripts s and r stand for the sample and reference molecules, respectively.<sup>17</sup> The intensity of the signal collected by a PMT detector was denoted as  $S$ .  $\Phi$  is the fluorescence quantum yield.  $\phi$  is the overall fluorescence collection efficiency of the experimental apparatus. The number density of the molecules in solution was denoted as  $c$ .  $\delta_r$  is the TPA cross-section of the reference molecule (see Supporting Information).



**Figure 3.** Two-photon excitation spectra of **1a–3a** in toluene.

Figure 3 shows the two-photon-induced fluorescence excitation spectra of **1a–3a**. The corresponding spectra for **1b,c** are shown in Figure S2 in Supporting Information. All of the compounds show two peaks at 840–890 nm, indicating the existence of the common two-photon allowed states.

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Table 1 summarizes the  $\lambda_{\max}$  of one-photon absorption and fluorescence spectra, wavelengths of the two-photon absorption maxima ( $\lambda_{\max}^{(2)}$ ), and the maximum values of the two-photon absorption cross-section ( $\delta_{\max}$ ). The value of  $\delta_{\max} = 1370$  GM for **1a** is somewhat smaller than the reported value by Marder's group.<sup>17</sup> The  $\lambda_{\max}^{(2)}$  values of **1a–c** increase as the electron-donating ability of the aryl substituent increases. This result indicates the interesting possibility that the wavelength of the maximum two-photon cross-section could be tuned by using an appropriate substituent. It is also shown that the  $\delta_{\max}$  values of **1a,b** are similar, but that of **1c** is much larger. Note that **1c** has a much larger  $\lambda_{\max}^{\{\text{fl}\}}$  than **1a,b** and, hence, a larger Stokes shift (Table 1). This could be explained if the two-photon allowed states are close to the lowest excited states. As discussed above, the donor stabilizes the latter more than the ground state to diminish the energy gap between the ground- and two-photon allowed states. This would predict a larger two-photon cross-section, because the smaller the energy gap is, the higher the probability of the excitation will be.

The most interesting result of the present study is that the value of  $\delta_{\max}/\text{MW}$  for **1a–3a** increases from 1.0 to 1.4 to 1.6 with increased branching, indicating significant enhancement in the multibranching structure. To our knowledge,  $\delta_{\max} = 5030$  GM determined for **3a** is the largest value reported in the literature.<sup>26</sup>

Chung et al. reported similar enhancement in the triphenylamine-based multibranching structure and attributed their result partly to the electronic coupling between the branches.<sup>19a</sup> However, a theoretical study revealed that such an enhance-

ment is mainly caused by the vibronic coupling.<sup>19b</sup> The electronic coupling is weak probably because the central amino group is used as the connecting unit, which breaks the conjugation of the whole network. On the other hand, increasing the size of the system will increase the density of state, providing more effective coupling channels, which would in turn increase the TPA cross-section.

A similar explanation could be applied to the present result. As stated above,  $\delta_{\max}/\text{MW}$  increases with the applied branching despite the smaller Stokes shift (Table 1). This is in contrast to the parallel increase of  $\delta_{\max}$  and Stokes shift for **1a–c**, where the electronic interactions are important (vide supra). Hence, the possibility of the electronic coupling being the cause of such an enhancement could be ruled out, and the vibronic coupling appears to be the favored alternative.

In conclusion, we have synthesized a series of efficient TPA molecules. The wavelength of the maximum TPA cross-section could be tuned by using a different substituent. The TPA cross-section increased with a stronger donor and with the number of branching to reach the maximum value of 5030 GM for **3a**. Noteworthy is the significant enhancement of the TPA cross-section in the multibranching structure. This result underlines the importance of incorporating the TPA chromophores in the multibranching structure to obtain a very large TPA cross-section.

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**Supporting Information Available:** Experimental procedures for the synthesis of compounds **2** and **3** and one-photon absorption and fluorescence, as well as two-photon excitation spectra of compounds **1b,c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(26) The most efficient two-photon chromophores and their two-photon cross-sections measured by the two-photon-induced fluorescence using the nanosecond pulses are 2,7-bis[[7-(*p*-dioctylaminostryl)-9,10-dihydrophenathren-2-yl]vinyl]-9,10-dihydrophenathrene ( $\lambda_{\max} = 422$  nm,  $\Phi = 0.66$ ,  $\delta_{\max} = 3760$  GM),<sup>18a</sup> 4,4'-bis[4-(*p*-dihexylaminophenylethynyl)styryl]-biphenyl ( $\lambda_{\max} = 400$  nm,  $\Phi = 0.80$ ,  $\delta_{\max} = 1050$  GM), and 1,3,5-tricyano-2,4,6-tris(*p*-diphenylaminostyryl)benzene ( $\lambda_{\max} = 488$  nm,  $\Phi = 0.25$ ,  $\delta_{\max} = 2480$  GM).<sup>21a</sup>