

Enhanced Two-photon Properties of Tri-branched Styryl Derivatives Based on 1,3,5-Triazine

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Novel styryl derivatives with triphenylamine as donor and 1,3,5-triazine as acceptor were synthesized and their one- and two-photon properties were investigated. These molecules show large two-photon absorption (TPA) cross sections and strong two-photon fluorescence. TPA cross section is as large as $1.64 \times 10^{-20} \text{ cm}^4/\text{GW}$ for the tri-branched molecule.

Organic materials that can simultaneously absorb two photons have attracted considerable attention due to their increasing applications in two-photon upconversion laser,¹ two-photon laser scanning fluorescence imaging,² 3D optical data storage,³ optical limiting,⁴ and photodynamic therapy.⁵ These applications request the materials with large two-photon absorption (TPA) cross sections (σ) and strong two-photon excited fluorescence. The connection of donor and acceptor by π -conjugated bridge to form D- π -D, A- π -A, or D- π -A structure is an effective way to improve TPA cross sections.⁶⁻¹¹ Recently, more research has focused on octupolar,¹² multi-branched,¹³⁻¹⁶ or dendrimeric¹⁷⁻¹⁹ molecules, whose TPA cross sections can be significantly improved by the increased chromophore density of the molecules and the cooperative enhancement effect among the chromophores.

In this letter, we describe the synthesis, one- and two-photon properties of novel styryl derivatives (Figure 1). In these compounds, triphenylamine serves as electron donor, 1,3,5-triazine as electron acceptor and styryl as chromophore. T01 and T02 form D- π -A and D- π -A- π -D linear structure, while T03 forms

octupolar tri-branched structure containing three D- π -A sub-units.

Equivalent 4-formyl-4'-methoxytriphenylamine and *o*-chloroaniline were refluxed in ethanol for 4 h to give 4-[[2-chlorophenyl]imino]methyl-*N*-(*p*-methoxyphenyl)-*N*-phenylbenzenamine (1). The crude product was dried under high vacuum and used directly without further purification. The reactions of 2,4,6-tris(*p*-methylphenyl)-1,3,5-triazine and 1 with the ratio of 1:1, 1:2, and 1:3 were performed in the presence of *t*-BuOK at 100 °C in DMF for 4 h to give styryl derivatives T01, T02, and T03 in 51–67% yield, respectively. The final products were purified with chromatography (silica gel) and characterized with ¹H NMR, ¹³C NMR and TOF-MS.²⁰

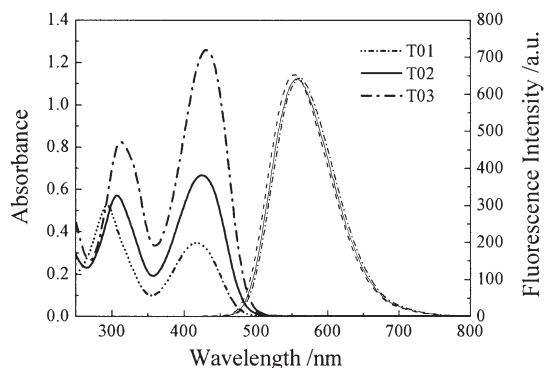


Figure 2. The absorption ($1 \times 10^{-5} \text{ M}$) and fluorescence (at the same absorbance) spectra of T01, T02, and T03 in chloroform.

Table 1. The optical properties of T01, T02, and T03 in chloroform

	$\lambda_{\text{max}}^{\text{ab}}$ (nm)	$\lambda_{\text{max}}^{\text{fl}}$ /nm	Φ^{a}	σ^{b} / $10^{-20} \text{ cm}^4/\text{GW}$	$\lambda_{\text{max}}^{\text{TPF}}$ /nm
T01	293, 418	552	0.49	0.31	578
T02	307, 425	554	0.47	0.365	577
T03	312, 430	555	0.47	1.64	576

^aFluorescence quantum yield determined using fluorescein in 0.1 N NaOH as the standard. ^bTPA cross sections measured at 800 nm (140 fs).

As shown in Figure 2 and Table 1, there are two strong absorption bands in the UV and visible regions. T01 shows the maximum absorption wavelength at 418 nm, while the maximum absorption peaks for T02 and T03 are red-shifted to 425 and 430 nm, respectively. The absorption peak at longer wavelength corresponds to π - π^* excitation of the whole molecules, whereas the shorter absorption peak attributes to localized excitation. Both the maximum absorption wavelengths and the molar extinction coefficients are increased with increasing chromophore intensity, which means that the electrons are delocalized over the whole molecules and interaction among the chromo-

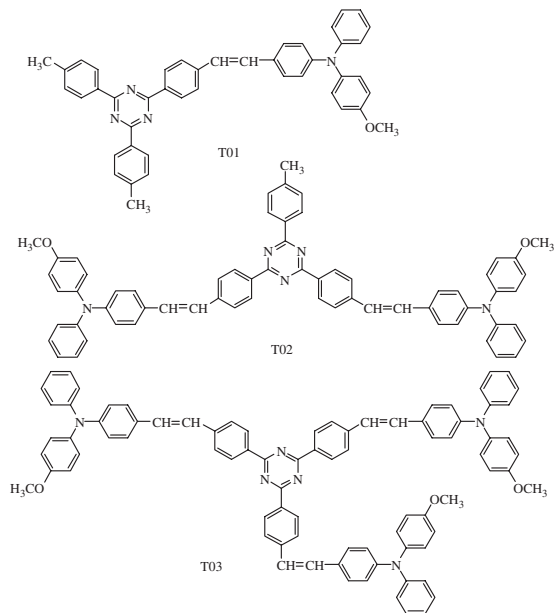


Figure 1. The chemical structures of T01, T02 and T03.

phores exist. Compounds T01, T02, and T03 emit strong fluorescence under the irradiation of light at the maximum absorption wavelengths. The fluorescence quantum yield was determined to be about 0.47 using fluorescein in 0.1 N NaOH as the standard. Although the absorption spectra are of great difference, these compounds show similar fluorescence spectra with the peaks located at about 554 nm. The Stokes' shifts for T01, T02, and T03 are 134, 129 and 125 nm, respectively.

TPA cross sections of these compounds were determined by femtosecond open aperture Z-scan technique according to previously described method.²¹ As shown in Table 1, the TPA cross sections for T01, T02, and T03 are $0.31 \times 10^{-20} \text{ cm}^4/\text{GW}$, $0.365 \times 10^{-20} \text{ cm}^4/\text{GW}$ and $1.64 \times 10^{-20} \text{ cm}^4/\text{GW}$, respectively. These values are comparable to those of the most representative materials reported in the literatures measured with similar molecular weight.^{9,11,13} The TPA cross section of T02 is only slightly higher than that of T01 although its chromophore density is much larger. But, the TPA cross section of T03 is nearly 5 times higher than those of T01 and T02. In compound T03, 1,3,5-triazine is connected with three styryl units and forms tri-branched octupolar structure. The increased chromophore density, delocalization interaction and the octupolar structure are responsible for its much larger TPA cross sections than the other two molecules.

Under the excitation of 800 nm laser pulse (140 fs), compounds T01, T02, and T03 emit strong frequency upconverted fluorescence with the peaks located at 578, 577, and 576 nm, respectively. The maximum wavelengths of two-photon fluorescence are red-shifted about 21 to 26 nm compared with those of linear fluorescence emission. Since there is no absorption at wavelength longer than 550 nm, the upconverted fluorescence comes from two-photon process. As an example, the two-photon fluorescence spectra of T03 under different laser intensity are shown in Figure 3. The linear dependence of fluorescence intensity on the square of the excitation intensity as shown in the inset confirms that TPA is the main excitation mechanism of two-photon fluorescence.

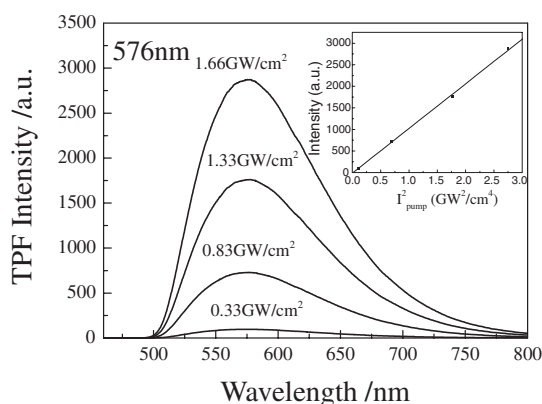


Figure 3. The two-photon excited fluorescence spectra of T03 in chloroform.

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- 20 **T01**: mp 174–176 °C. ¹H NMR (CDCl₃, 500 MHz): δ 2.48 (s, 6H), 3.82 (s, 3H), 6.87 (d, 2H, *J* = 8.72 Hz), 7.02 (m, 3H), 7.10 (m, 4H), 7.26 (m, 4H), 7.37 (d, 4H, *J* = 7.90 Hz), 7.41 (d, 2H, *J* = 8.36 Hz), 7.66 (d, 2H, *J* = 8.07 Hz), 8.66 (d, 4H, *J* = 7.87 Hz), 8.73 (d, 2H, *J* = 8.02 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 22.39, 56.14, 115.51, 122.63, 123.21, 124.31, 126.53, 126.97, 128.19, 128.26, 129.59, 129.87, 129.95, 129.99, 130.80, 130.85, 134.41, 135.68, 140.98, 142.37, 143.52, 148.33, 148.79, 157.11, 171.66, 172.02. TOF-MS (ES⁺): 636.3 (M, 8%), 637.4 (M + 1, 100%), 638.3 (M + 2, 30%). **T02**: mp 106–108 °C. ¹H NMR (CDCl₃, 500 MHz): δ 2.48 (s, 3H), 3.82 (s, 6H), 6.87 (m, 4H), 7.02 (m, 7H), 7.10 (m, 9H), 7.25 (m, 6H), 7.37 (d, 2H, *J* = 8.10 Hz), 7.41 (d, 4H, *J* = 8.64 Hz), 7.66 (d, 4H, *J* = 8.41 Hz), 8.66 (d, 2H, *J* = 7.15 Hz), 8.73 (d, 4H, *J* = 8.33 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 21.745, 55.45, 114.79, 121.90, 122.50, 123.60, 125.80, 126.26, 127.50, 127.57, 128.89, 129.18, 129.25, 129.30, 130.06, 130.11, 133.64, 134.90, 140.25, 141.64, 142.84, 147.60, 148.05, 156.38, 170.87, 171.23. TOF-MS (ES⁺): 921.5 (M, 37%), 922.5 (M + 1, 100%), 923.5 (M + 2, 30%). **T03**: mp 256–258 °C. ¹H NMR (CDCl₃, 500 MHz): δ 3.81 (s, 9H), 6.87 (d, 6H, *J* = 8.81 Hz), 7.02 (m, 12H), 7.09 (m, 12H), 7.18 (d, 3H, *J* = 16.23 Hz), 7.24 (t, 6H), 7.39 (d, 6H, *J* = 8.55 Hz), 7.62 (d, 6H, *J* = 8.30 Hz), 8.68 (d, 6H, *J* = 8.32 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 56.16, 115.49, 122.60, 123.20, 124.31, 126.51, 126.98, 128.21, 128.28, 129.88, 129.96, 130.80, 135.58, 140.95, 142.37, 148.29, 148.75, 157.06, 171.57. TOF-MS (ES⁺): 1206.6 (M, 43%), 1207.6 (M + 1, 100%), 1208.7 (M + 2, 60%), 1209.7 (M + 3, 20%).
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