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Triphenylamine Derivatives with Large Two-Photon Cross-Sections

Wen Jun Yang, Dae Young Kim, Chang Ho Kim, Mi-Yun Jeong, Seung Kyu Lee, Seung-Joon Jeon,* and Bong Rae Cho*

Molecular Opto-Electronics Laboratory, Department of Chemistry and
Center for Electro- and Photo-Responsive Molecules, Korea University,
1-Anamdong, Seoul 136-701, Korea

chobr@korea.ac.kr

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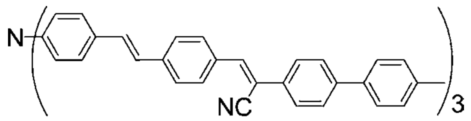
ABSTRACT



δ_{ns} = 1360 GM (800 nm), ϕ = 0.69
δ_{fs} = 790 GM (800 nm)

Triphenylamine derivatives have been synthesized and shown to exhibit large two-photon cross-sections at a wide range of wavelengths and the largest value measured by fs Z-scan experiment. Moreover, a linear relationship is noted between the two-photon cross-sections measured by ns fluorescence and fs Z-scan methods.

Synthesis of nonlinear optical materials exhibiting large two-photon (TPA) cross-sections (δ_{TPA}) is of current research interest due to their potential applications in a number of new areas, including three-dimensional fluorescence imaging, optical limiting, photodynamic therapy, and three-dimensional optical data storage and microfabrication.[1−14] Various derivatives of donor−bridge−acceptor (D−π−A) dipoles, donor−bridge−donor (D−π−D) quadrupoles, multibranched compounds, dendrimers, and octupoles have been synthesized and their δ_{TPA} reported.[15−19] Recently, we and others have reported that triphenylamine derivatives show appreciable enhancement in the δ_{TPA} compared with their monobranched analogue.[17a,18c−f,19a] However, these studies employed a

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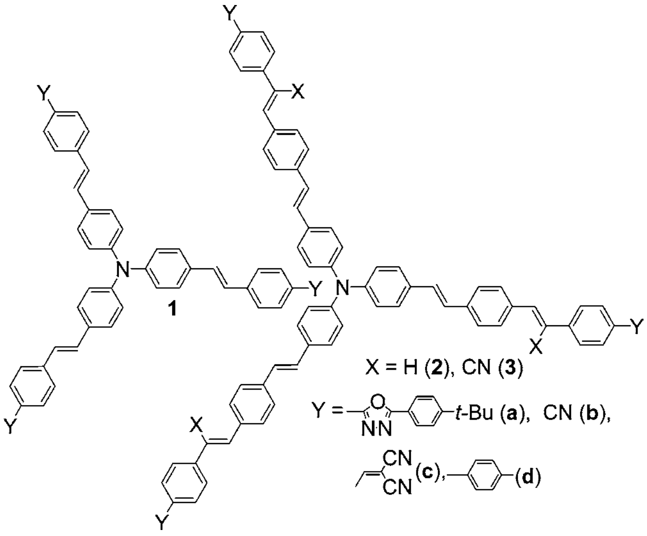
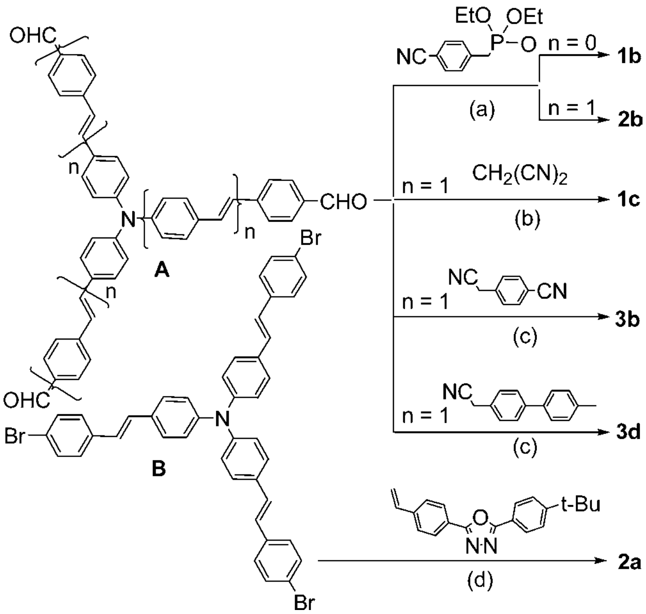


Figure 1.

limited number of acceptors. Moreover, although most of the results are based on either fluorescence measurement or Z-scan experiments, it has not been possible to make a direct comparison between them due to the lack of data on δ_{TPA} measured by both methods for the same series of compounds.

In this work, we have synthesized a series of triphenylamine derivatives **1**−**3** with a variety of acceptors (Figure 1) and measured their δ_{TPA} by nanosecond (ns) fluorescence measurement and femtosecond (fs) Z-scan experiments. We now report that **3d** having a cyano group at the vinylene double bond and a biphenyl group at the periphery not only shows large δ_{TPA} at a wide range of wavelengths but also exhibits the largest value measured by the fs Z-scan experiment. Moreover, a linear relationship is noted between the δ_{TPA}values measured by ns fluorescence and fs Z-scan methods.

Scheme 1[a]



[a] Reagents and conditions: (a) LDA/THF, 0 °C rt; (b) pyridine/molecular sieves/NH_4OAc/AcOH, rt; (c) *t*-BuOK/EtOH/benzene, reflux; (d) $Pd(OAc)_2$/$P(o\text{-tolyl})_3$/NEt_3/MeCN, reflux.

Synthesis of **1**−**3** is shown in Scheme 1. Condensation of **A** with (*p*-cyanophenyl)methylphosphonate, malononitrile, (*p*-cyanophenyl) acetonitriles, and (4-methylbiphenyl) acetonitriles afforded **1b**, **2b**, **1c**, **3b**, and **3d**, respectively. Compound **2a** was prepared by the Heck coupling between **B** and 4-[5-(4′-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]styrene. The structures of **1**−**3** were unambiguously confirmed by IR, ^{1}H and ^{13}C NMR, and elemental analysis.

Figure 2 shows the absorption spectra for **1**−**3** in toluene. The one-photon absorption maximum ($\lambda^{(1)}_{\max}$) is shifted to a longer wavelength with the conjugation length, i.e., **1a** < **2a**, **1b** < **2b**, and as the acceptor is changed to a stronger

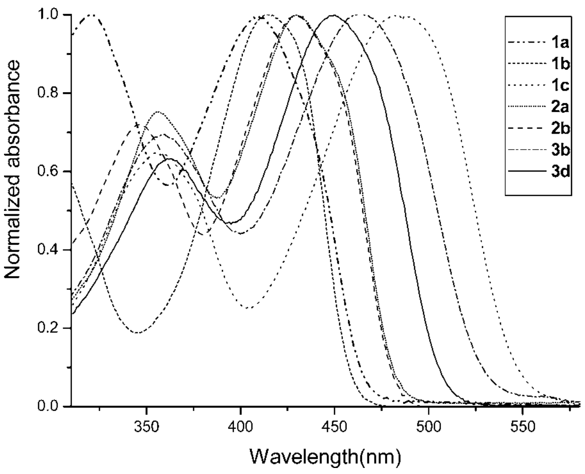


Figure 2. Normalized absorption spectra of **1**−**3** in toluene.

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

cmpd	$\lambda_{max}^{(1)}$ [a]	λ_{max}^{fl} [b]	$\Delta\tilde{\nu}$ [c]	Φ [d]	$\lambda_{max}^{(2)}$ [e]	δ_{max}^{ns} [f]
1a	410 (8.91)	471	3160	0.98	760	430
1b	415 (6.21)	467	2680	0.95	760	220
1c	487 (9.42)	570	2990	0.41	890	1200
2a	429 (12.4)	487	2780	1.0	780	950
2b	429 (11.4)	488	2820	0.97	780	870
3b	464 (9.11)	550	3420	0.33	890	740
3d	450 (13.4)	519	2960	0.69	800	1360

[a] λ_{max} of the one-photon absorption spectra in nm. The numbers in the parentheses are the molar extinction coefficients ($\times 10^4\epsilon$). [b] λ_{max} of the one-photon fluorescence spectra in nm. [c] Stokes shift in cm^{-1}. [d] Fluorescence quantum yield. [e] λ_{max} of the two-photon excitation spectra in nm. [f] Peak two-photon absorptivity in 10^{-50} cm^4 s $photon^{-1}$ (GM).

one, i.e., **1a** < **1b** < **1c** (Table 1). This indicates a gradual decrease in the HOMO−LUMO energy gap in the same order. Moreover, the cyano group bound to the π-backbone double bond induces a significant bathochromic shift, i.e., **2b** < **3b**, as expected for substitution with an electron-accepting group. A similar result is observed in the fluorescence spectra, i.e., (i) both emission maxima (λ_{max}^{fl}) and Stokes shift increase with the conjugation length, and (ii) except for **1a**, λ_{max}^{fl} for **1**−**3** show a parallel increase with $\lambda_{max}^{(1)}$ (Figure S1). Interestingly, the Stokes shift increases in the order **1b** < **1c** < **1a**, indicating that the acceptors with extended conjugation and/or stronger electron-withdrawing ability stabilize the emitting states more than the Franck−Condon singlet states (Table 1). However, the very similar Stokes shifts for **2a** and **2b** reveal that this effect becomes less important as the conjugation length increases. Most of the compounds are strongly fluorescent with large fluorescence quantum yields ranging from 0.3 to 1.0. Note that the larger the λ_{max}^{fl}, the smaller the quantum yields. This may be due to the lower energy of the emitting states, which may in turn facilitate the nonradiative pathways.

The two-photon cross section δ_{TPA} was measured by the two-photon-induced fluorescence measurement technique using nanosecond (ns) laser pulses.[16b,19c] Figure 3 shows the two-photon excitation spectra for **1**−**3**. The results are summarized in Table 1.

Table 1 shows that $\lambda_{max}^{(2)}$ of **1**−**3** are in the range of 760−890 nm. Moreover, δ_{max}^{ns} for **1** and **2** increases monotonically with the conjugation length, i.e., **1a** < **2a**, **1b** < **2b**, and as the acceptor is changed in the order **1b** < **1a** < **1c**, reaching the maximum at a value of 1200 GM for **1c**. It is well established that the two-photon cross-section of octupolar molecules increases with the extent of charge transfer.[19] The gradual increase in both $\lambda_{max}^{(1)}$ and λ_{max}^{fl} in the same order provides additional support for this conclusion.

It is interesting to compare the relative efficiency of the oxadiazol and cyano groups as the acceptor. As stated above, δ_{max}^{ns} of **1a** is larger than that of **1b**. Also, δ_{max}^{ns} of **2a** is larger than that of **2b**, despite that $\lambda_{max}^{(1)}$ and λ_{max}^{fl} are nearly the same. This indicates that the former is a more efficient acceptor than the latter as long as δ_{max}^{ns} is considered. Because of the extended π-conjugation, the former may have a larger number of density of states, providing more effective coupling channels between the ground and two-photon allowed states, which would in turn increase the TPA cross-section.

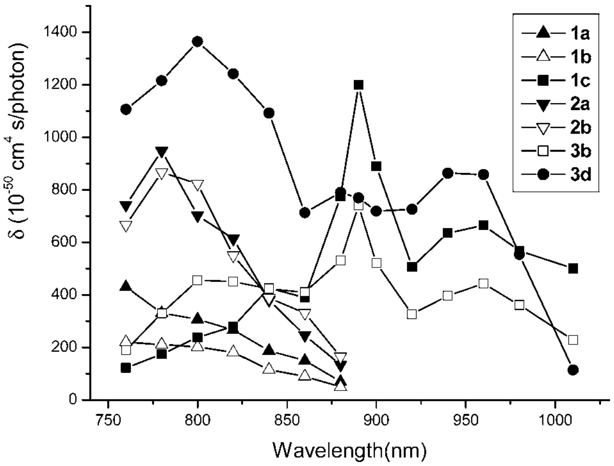

Figure 3. Two-photon excitation spectra of **1**−**3** in toluene.

The cyano group at the vinylene double bond has different effects depending on the conjugation length. The value of δ_{max}^{ns} for **3b** is smaller than **2b**, probably because of the distorted structure.[16c] However, **3d**, having the biphenyl group at the periphery, shows the largest δ_{max}^{ns} in this series of compounds. Here again, the increased number of density of states provided by the biphenyl fluorophore seems to play an important role. Moreover, it exhibits a large two-photon cross-section over a wide range of wavelengths. This may be due to the fact that **3d** consists of two components, **1c** with one less CN and **2d**, both of which may have two-photon allowed states at different wavelength ranges. A similar result is observed for **3b**, although δ_{TPA} is smaller. This result suggests the interesting possibility that one can design an efficient two-photon chromophore with large two-photon cross-section over a wide range of wavelengths by introducing an acceptor at the vinylene double bond and an additional fluorophore at the periphery. Although the origin of this interesting property is not clear, such molecules will be useful for a variety of applications, including optical limiting.

The fs Z-scan experiment has been conducted as reported.[5,20] Figure 4 shows the Z-scan data for **3d** measured at 800 nm by changing the input intensity (I_o). The corresponding data for other compounds and for **1**−**3** obtained by varying the dye concentration (d_o) are shown in Figures S2 and S3, respectively, in the Supporting Information.

Table 2 summarizes the fs Z-scan results for **1**−**3**, measured at 800 nm by changing the input intensity (I_o) and by varying the dye concentration (d_o).[5,20] The TPA cross-sections (δ_{fs}) determined by both methods are very similar, indicating the reliability of the measurements. In all cases, the values of δ_{fs} are always smaller than δ_{ns}, indicating a

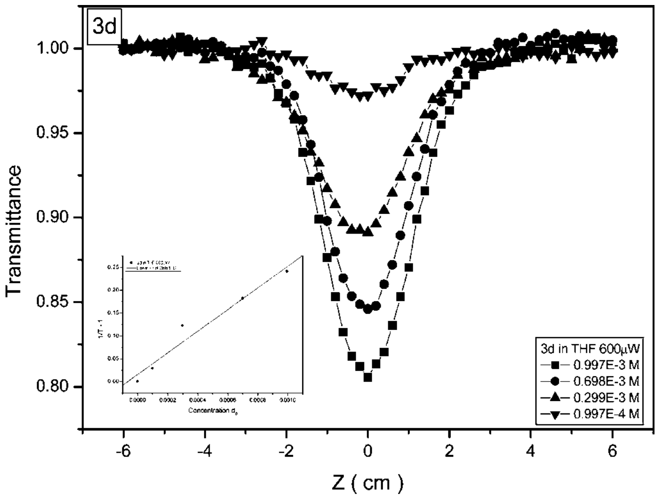

Figure 4. Z-Scan experimental data for **3d** measured at 800 nm by changing the input intensity of laser beam. Inset: the plot of ($1/T(L) - 1$) vs I_o (GW/cm^2) (see Supporting Information for details).

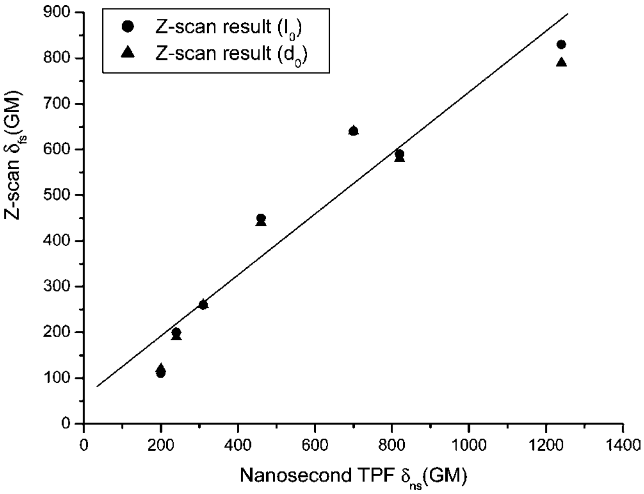

Figure 5. Plot of δ_{fs} vs δ_{ns}.

significant contribution by the excited-state absorption in the latter. Moreover, the results of the structure−TPA property relationship studies from both experiments are qualitatively the same, i.e., (i) TPA cross-section (δ_{fs}) increases with the conjugation length and with a stronger acceptor, (ii) compounds with an oxadiazole group show larger δ_{fs} than the cyano derivatives, and (iii) **3d** shows the largest δ_{fs} in this series of compounds. Furthermore, there is qualitatively a linear relationship between δ_{fs} vs δ_{ns}(Figure 5). Although most of the structure−TPA property relationship studies have been based on either ns fluorescence measurement or fs Z-scan experiments, it has not been possible to make a comparison between them. Hence, this result may provide a useful guideline for making such comparisons. Finally, $\delta_{\mathrm{fs}} = 790{-}830$ GM determined for **3d** is among the largest values determined by the Z-scan method.[22]

Table 2. Comparison of the Two-Photon Cross-Sections Measured by Femtosecond Z-Scan and Nanosecond Fluorescence Measurement Methods at 800 nm

cmpd	δ_{fs} (I_o)[a−c]	δ_{fs}(d_o)[b−d]	δ_{ns} [b,c,e]
1a	260 (10.4)[f]	260 (10.3)	310
1b	110 (4.45)	120 (0.95)	200
1c	200 (8.30)	190 (7.76)	240
2a	640 (25.8)	640 (25.9)	700
2b	590 (23.6)	580 (23.4)	820
3b	450 (18.3)	440 (17.7)	460
3d	830 (33.4)	790 (32.0)	1360

[a] Measured by fs Z-scan method by varying the input intensity (I_o). The chromophore concentration was 1.0×10^{-3} M in THF. [b] Unit is GM, where 1 GM (Goppert−Mayer) $= 1 \times 10^{-50}$ cm^4 s photon^{-1} molecule^{-1}. [c] Estimated uncertainty, ±15%. [d] Measured by fs Z-scan method by varying the dye concentration (d_o) in the range of $(0.10{-}1.0) \times 10^{-3}$ M in THF. [e] Determined by the two-photon-induced fluorescence measurement technique using the nanosecond (ns) laser pulses in toluene. [f] Numbers in the parenthesis are the two-photon cross-section in 10^{-21} cm^4/GW.

In conclusion, we have synthesized a series of triphenylamine derivatives with large two-photon cross-sections. Compound **3d** having the cyano group at the vinylene double bond and biphenyl group at the periphery not only shows large δ_{TPA} at a wide range of wavelengths but also exhibits the largest value measured by the Z-scan method. Noteworthy is the linear relationship between the δ_{TPA} values measured by ns fluorescence and fs Z-scan methods.

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Supporting Information Available: Synthesis of **1**−**3**, fluorescence spectra of **1**−**3**, and the measurements of two-photon cross-section by ns fluorescence measurement and fs Z-scan methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) The most efficient TPA chromophores showing the largest TPA cross-sections measured by fs Z-scan experiments are TP-DTT-TP (270 GM)[17c] and PRL-701 (587 GM).[17a]