Communication

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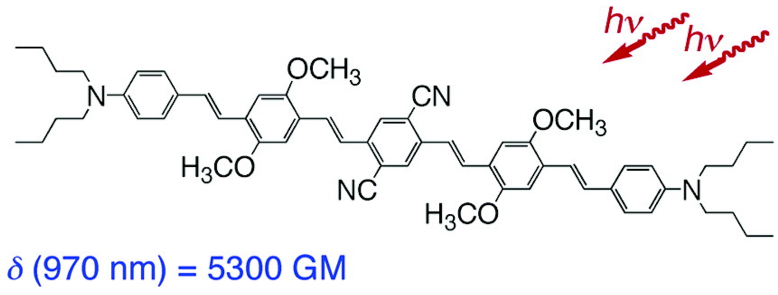

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Strong, Low-Energy Two-Photon Absorption in Extended Amine-Terminated Cyano-Substituted Phenylenevinylene Oligomers

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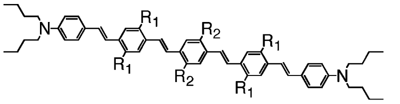
Interest in two-photon absorption (TPA) and its applications, including three-dimensional (3D) fluorescence imaging,[1,2] photodynamic therapy,[3] nonlinear optical transmission,[4] and 3D microfabrication,[5−7] has been growing significantly in recent years. To realize the full potential of these applications, it is necessary to identify chromophores with large TPA cross-sections, δ. Molecular systems investigated experimentally or theoretically, to date, include: donor−bridge−acceptor (D−π−A) dipolar molecules,[8,9] donor−bridge−donor (D−π−D) or donor−acceptor−donor quadrupolar molecules,[10,11] multibranched compounds,[12] octupolar molecules,[13,14] and porphyrins.[15]

We have shown that quasi-linear quadrupolar D−π−D molecules exhibit peak δ values at least an order of magnitude larger than the corresponding unsubstituted counterparts and that the additional presence of acceptors on the π-bridge (D−A−D) can augment the cross section further, as these substitutions can enhance the degree of intramolecular charge transfer upon excitation.[10,16,17] It was also shown that the magnitude of δ increases and the position of the two-photon band can be red-shifted when the conjugated bridge is elongated.[13,16] Here we report on a series of symmetrically substituted phenylenevinylene chromophores with long conjugation length and a D−A−D motif, to investigate whether δ can be increased further and the position of the two-photon maximum red-shifted with respect to the shorter analogues. The three molecules examined are shown in Figure 1 (the substitution patterns can be described as: D−A−π−A−D, D−A−D−A−D, and D−D−A−D−D, respectively, where the letters represent the type of substituent on each phenylene and π indicates that the ring is unsubstituted). Compounds **A**−**C** were synthesized using successive Horner-Emmons reactions (see Supporting Information).

The one-photon absorption (OPA) and fluorescence spectroscopic parameters of compounds **A**−**C** in toluene are summarized in Table 1 (spectra are in the Supporting Information). The absorption bands peak between 499 and 509 nm and are relatively broad and unstructured for all compounds. The absorption maximum ($\lambda^{(1)}_{max}$) is observed at slightly longer wavelength for **B** and **C** than for **A**, presumably due to the destabilization of the HOMO (highest occupied molecular orbital) by the presence of the additional alkoxy donors in **B** and **C**. The extinction coefficients are consistent with the values reported for other molecules with similar conjugation length ($\epsilon_{max} \approx 1 \times 10^5$ M^{-1} cm^{-1}).[16,18] The absorption band of **C** is broader than for the other two chromophores; this is probably responsible for the slightly smaller ϵ_{max} of **C**. The molecules are highly fluorescent in toluene, and all the fluorescence bands are 0−0 peaked, with a 1−0 vibronic shoulder.



A: R_1 = CN, R_2 = H
B: R_1 = CN, R_2 = $OC_{12}H_{25}$
C: R_1 = OCH_3, R_2 = CN

Figure 1. Molecular structure of compounds **A**−**C**.

Table 1. Linear Absorption and Fluorescence Parameters for Compounds **A**−**C** in Toluene

	$\lambda^{(1)}_{max}$ (nm)[a]	$E^{(1)}$ (eV)[b]	ϵ_{max} (M^{-1}cm^{-1})[a]	λ^{em}_{max} (nm)[c]	η[d]
A	499	2.48	1.00×10^5	564	0.73
B	507	2.45	1.21×10^5	570	0.79
C	509	2.44	9.19×10^4	599	0.71

[a] Peak of the OPA band ($\lambda^{(1)}_{max}$) and maximum molar extinction coefficient (ϵ_{max}). [b] Energy of the peak in the absorption band. [c] Peak of the fluorescence band. [d] Fluorescence quantum yield.

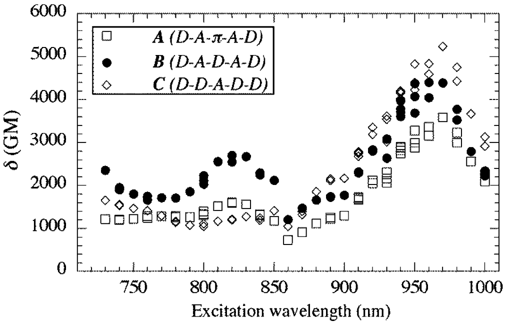


Figure 2. Two-photon-induced fluorescence excitation spectra of **A**−**C** in toluene (using fs pulses and fluorescein as reference compound).

Table 2. Two-Photon Absorption Parameters for **A**−**C** in Toluene

	low-energy peak			high-energy peak		
	$\lambda^{(2)}_{max}$[a]	$E^{(2)}$ [b]	δ_{max}[a]	$\lambda^{(2)}_{max}$[a]	$E^{(2)}$ [b]	δ_{max}[a]
A	970	2.56	3.6×10^3	820	3.02	1.6×10^3
B	960	2.58	4.4×10^3	820	3.02	2.7×10^3
C	970	2.56	5.3×10^3	830	2.99	1.3×10^3

[a] $\lambda^{(2)}_{max}$ and δ_{max} are the TPA peak (in nm) and cross section (in GM; 1 GM $\equiv 1 \times 10^{-50}$ cm^4 s/photon-molecule). [b] $E^{(2)}$ (in eV) is the total two-photon excitation energy.

The TPA cross sections were determined by the two-photon-induced fluorescence method (see Supporting Information). The most notable characteristic of the two-photon spectra of **A**−**C** in toluene (Figure 2 and Table 2) is the presence of two distinct bands: one at 960−970 nm ("low-energy peak") and the other at 820−830 nm ("high-energy peak"). The low-energy peak is stronger than the high-energy one and is largest for **B** and **C**, compounds that have substituents on all the phenylene rings. The number of acceptors seems to influence δ_{max} for the high-energy peak to some extent, as δ for **A** and **B** is larger than for **C**. It is observed that

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only for compound **B** is the value of δ for the high-energy peak significantly larger than for the corresponding cyano-substituted distyrylbenzene (1700 GM for compound **1** in ref 17) and for a 5-ring compound with $R_1 = OCH_3$ and $R_2 = OC_{12}H_{25}$ (1420 GM for compound **12** in ref 16). Overall, because of the large peak cross sections and the presence of two TPA bands, these chromophores exhibit δ values above 1000 GM in a range at least 250 nm wide. These chromophores could be promising candidates for broad-band nonlinear transmission based on two-photon-induced excited-state absorption. Large δ values at 980 nm ($\delta = 3600-5500$ GM) have also been reported for two compounds similar to **C**, but in which the central phenylene is replaced by anthracene.[19] However, for the anthracene derivatives the quantum yield was relatively low and the lowest two-photon state was at significantly higher energy than the one-photon state, in contrast to the present case (see below).

It is interesting to note that in **C**, which possesses the largest low-energy band δ, strong charge transfer can occur over the longest distance from the dialkylamino donors to the cyano acceptors. In **A** and **B**, instead, there can be strong charge transfer over a shorter distance or weak charge transfer from the dialkylamino donors to the central phenylene, and the low-energy band δ's are smaller for these compounds. Some insight into the behavior of the new chromophores can be gleaned by using the simplified few-level model described by eqs 6−7 of ref 16. On the basis of the two-photon properties obtained for distyrylbenzene D−A−D molecules,[10,16,17] one would expect smaller δ's for the 5-ring molecules than those observed experimentally for the low-energy peak, because of the increase in the energy detuning term, which overrides the increase in the M_{ge} transition moment. This suggests that there is a sizable increase in the excited-state transition moment, $M_{ee'}$, that leads to large δ in the extended systems. On the other hand, the δ's for the high-energy band should be larger than those observed due to an increase in M_{ge} and a decrease in detuning energy. These observations are consistent with the effects of electron correlation and intramolecular charge transfer in the extended molecules, which lead to both an energy stabilization of the lowest two-photon state and to a redistribution of oscillator strength from higher-lying excited states toward the lowest two-photon state.[20]

An unusual characteristic of these compounds is the small (<0.15 eV) separation in energy between the peak of the OPA maximum ($E^{(1)}$) and the low-energy TPA band ($E^{(2)}$). The difference $E^{(2)} - E^{(1)}$ was found to be larger (0.3−0.5 eV) in the quadrupolar distyrylbenzenes we studied previously.[16] While this TPA band appears to be due to a strongly allowed low-lying two-photon state, it is also possible that symmetry-lowering distortions of the molecules or vibronic coupling, whose effect on TPA intensities has already been recognized for other molecular systems,[15,21,22] could explain the observed band. However, preliminary investigations on molecules **A**−**C** indicate that the spacing between the peak of the two-photon band and the 0−0 component of the one-photon band is about 2000 cm^{-1}, larger than expected for vibronic coupling (1200−1500 cm^{-1}). It should also be noted that for some phenylenevinylene derivatives (e. g., compounds **11** and **12** of ref 16) measurable TPA activity, but not a separate low-energy peak, was observed in the energy range around $E^{(1)}$. Additional experimental and theoretical work is underway to understand the nature of the electronic states of these and related chromophores.

In summary, we have shown that extended D−A−D oligophenylenevinylenes show large TPA cross sections (over 1000 GM) in a wide wavelength range and peak cross sections up to 5300 GM at almost twice the wavelength of the one-photon peak. These findings, which differ from those of similar molecules previously studied, indicate that relatively small changes in molecular structure can lead to large effects on the optical properties in this class of materials.

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Supporting Information Available: Synthetic procedures, characterization, spectroscopic information, and complete list of authors for refs 7, 10, and 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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