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Enhanced Two-Photon Absorption with Novel Octupolar Propeller-Shaped Fluorophores Derived from Triphenylamine

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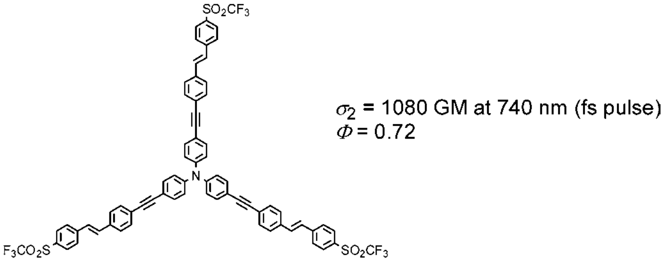
ABSTRACT



σ_2 = 1080 GM at 740 nm (fs pulse)
Φ = 0.72

Novel octupolar fluorophores derived from the symmetrical functionalization of a triphenylamine core with strong acceptor peripheral groups via phenylene-ethynylene linkers have been synthesized and shown to exhibit high fluorescence quantum yields, very large TPA cross-sections in the red–NIR region, and suitable photostability.

Molecular two-photon absorption (TPA) has attracted growing interest over recent years due to the many applications it offers both in material science and in biological imaging. These include microfabrication,[1] three-dimensional optical data storage,[2] optical power limitation,[3] localized photodynamic therapy,[4] and two-photon laser scanning fluorescence imaging.[5] These applications call for the design of specifically engineered compounds displaying enhanced TPA cross-sections. In the case of two-photon excited fluorescence

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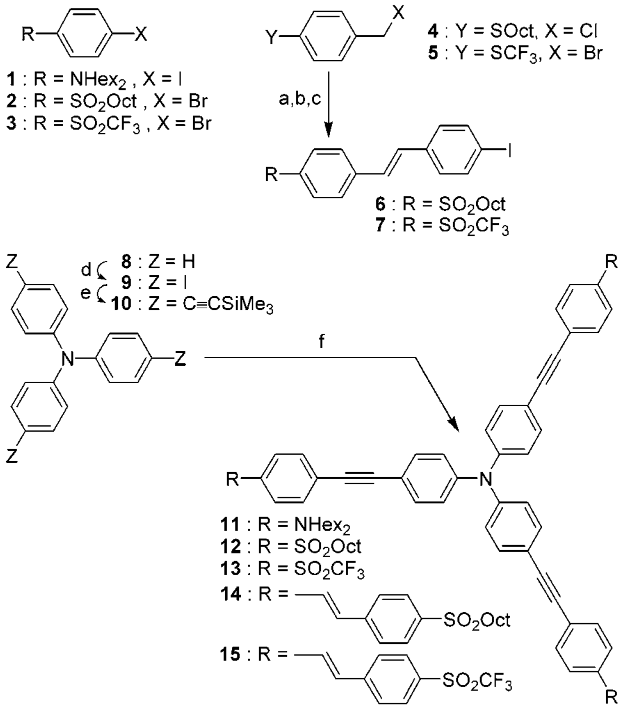
(TPEF) microscopy, high-performance fluorophores must exhibit both high fluorescence quantum yields (ϕ) and large TPA cross-sections (σ_2) in the red−NIR range (700−1200 nm), corresponding to the biological optimal window for reduced photodamage.[5] Photostability is also an important feature to consider for TPEF-based applications.

The optimization of molecular TPA has largely focused on one-dimensional dipolar[6,7] or quadrupolar[3,7,8] structures, and so far little attention has been devoted to the design of optimized octupolar structures,[9] although it has been realized that increased dimensionality and branched structures[10,11] could lead to highly effective multiphoton absorption. In this perspective, we have investigated a series of novel three-branched octupolar fluorophores with the aim of optimizing their TPEF cross-section ($\sigma_2\phi$) in the NIR region, as well as ensuring suitable photostability.

Our trigonal derivatives are derived from the symmetrical functionalization of an electron-donating triphenylamine core with three conjugated branches (Scheme 1) bearing electron-withdrawing (A) end-groups (**12**−**15**). Although octupolar derivatives based on triphenylamine cores have been shown to lead to high quadratic polarizabilities,[12] only a few examples of such derivatives have been shown to display large TPA cross-sections,[9a−c] calling for further engineering of the basic structures.

Scheme 1[a]



[a] Reagents and conditions: (a) $P(OEt)_3$, reflux, 10 h (80−84%); (b) H_2O_2, AcOH, reflux, 4 h (77−82%); (c) 4-iodobenzaldehyde, NaH, THF, rt, 15 h (51−61%); (d) KI (2 equiv), KIO_3 (1 equiv), AcOH, 85 °C, 5 h (88%); (e) $HC{\equiv}CSiMe_3$, $Pd(PPh_3)_2Cl_2$, CuI, toluene/Et_3N, 40 °C, 2.5 h (96%); (f) TBAF, R-π-X (**1**−**3**, **6**, or **7**, 3.5 equiv), Pd_2dba_3, PPh_3, CuI, toluene/Et_3N, 35 °C (72−89%).

To examine the role of octupolar symmetry, we also have investigated a structurally related analogue bearing only electron-releasing D peripheral groups (**11**). Following the same line of reasoning, we have selected strong acceptor peripheral groups using, in particular, the triflyl moiety (compounds **13**, **15**), a powerful acceptor,[13] which has not been considered yet in molecular engineering of TPA. Rigid

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Table 1. Photophysical and Two-Photon Absorption Characteristics of Fluorophores **11**−**15**

	λ_{abs}^{OPA} (nm)^a			λ_{em}^{OPA} (nm)^c					σ_2(GM)^{b,g}	
compd	toluene	$CHCl_3$	log ϵ^b	toluene	$CHCl_3$	Stokes shift (cm^{-1})^{b,d}	$\phi^{b,e}$	τ (ns)^{b,f}	at 2 λ_{abs}^{OPA}	at 740 nm
11	385	384	5.06	411	450	1600	0.77	0.88	15	30
12	388	392	4.91	424	449	2200	0.77	1.27	150	160
13	405	409	4.78	450	502	2500	0.78	1.49	420	495
14	397	399	5.13	446	500	2800	0.79	1.07	660	1065
15	408	409	4.97	473	542	3400	0.72	1.29	740	1080

[a] One-photon absorption maximum. [b] In toluene. [c] One-photon emission maximum. [d] Stokes shift = $(1/\lambda_{abs} - 1/\lambda_{em})$. [e] Fluorescence quantum yield relative to fluorescein in 0.1 N NaOH as a standard (λ_{ex} = 470 nm). [f] Experimental fluorescence lifetime. [g] TPA cross-sections; 1 GM = 10^{-50} cm^4 s photon^{-1}; TPEF measurements were performed using a mode-locked Ti:sapphire laser delivering 80 fs pulses at 80 MHz, calibrating with fluorescein.

(**11**−**13**) or semirigid (**14**, **15**) conjugated rods built from phenylene-ethynylene and phenylene-vinylene units were used to allow Intramolecular Charge Transfer (ICT) to take place between the core and the peripheral groups while maintaining fluorescence. To enhance the TPA cross-section, we have investigated molecules of increasing size from 2.9 to 4.3 nm in diameter. B3LYP ab initio calculations indicate that the molecules adopt a propeller-shaped structure (Figure 1), the core nitrogen being trigonal and the conjugated branches twisted by about 40°.

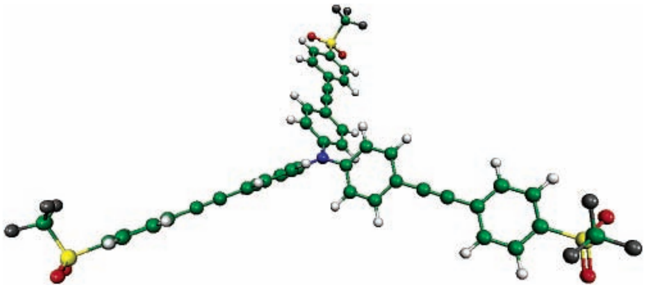

Figure 1. B3LYP-optimized geometry of fluorophore **13**.

The synthesis of these fluorophores is based on the threefold Pd(0)-catalyzed cross-coupling reaction of the nitrogen-cored building block **10** (Scheme 1) with aromatic iodide (**1**,[14] **6**, **7**) or bromide (**2**[15], **3**[16]) derivatives. The synthesis of the triphenylamine reagent **10** was achieved by triiodination[17] of triphenylamine, followed by a triple Sonogashira coupling with ethynyltrimethylsilane. The extended building blocks **6** and **7** were obtained from the halo derivatives **4** and **5**, respectively, in a three-step sequence (Michaelis−Arbuzov reaction, oxidation, and Horner−Wadsworth−Emmons condensation with 4-iodobenzaldehyde). All new fluorophores have been fully characterized by NMR, HRMS, and elemental analysis data.

The photophysical properties of the new series of trigonal fluorophores are shown in Table 1 and Figure 2.

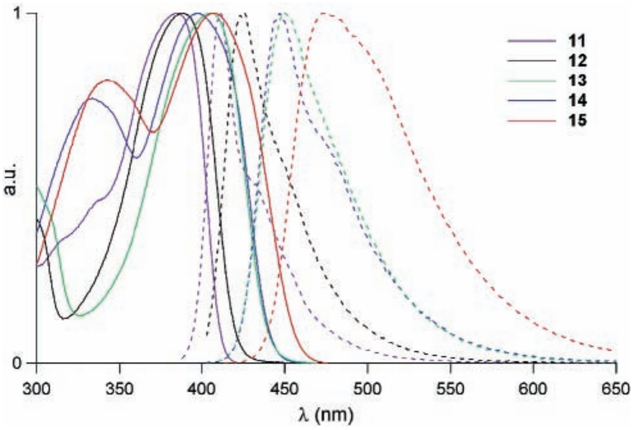

Figure 2. Normalized absorption and emission spectra of fluorophores **11**−**15** in toluene.

We observe that all fluorophores display a broad absorption in the near UV−visible violet region and exhibit high fluorescence quantum yield (about 0.8) independently of their end-groups (D or A) or conjugated branch nature. In contrast, their fluorescence lifetimes are significantly affected by the nature of the peripheral groups. We observe that the octupolar derivatives (**12**−**15**) display longer fluorescence lifetimes than the analogue bearing only donor peripheral groups (**11**). Interestingly, the powerful triflyl acceptor leads to a noticeable increase of the fluorescence lifetime, while an increase in the length of the branches by the addition of a phenylene-vinylene unit results in a decrease of the fluorescence lifetime.

Increasing the polarity of the solvent leads to a slight bathochromic shift of the absorption band of octupolar fluorophores (**12**−**15**) and to a more pronounced red shift in their emission band (Table 1). Such positive solvatochromic behavior can be related to an ICT phenomenon taking place between the fluorophore center and periphery.[18,19]

The TPA spectra of fluorophores **11**−**15** in the 740−950 nm range were determined by investigating their TPEF in

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solution according to the protocol described by Webb and co-workers[20] in the femtosecond regime. We note that the TPA spectra of the octupolar fluorophores **12**−**15** (Figure 3) exhibit a relative maximum close to $2\lambda_{abs}^{OPA}$, indicating that the lowest energy excited-state is both one-photon and two-photon allowed.[21]

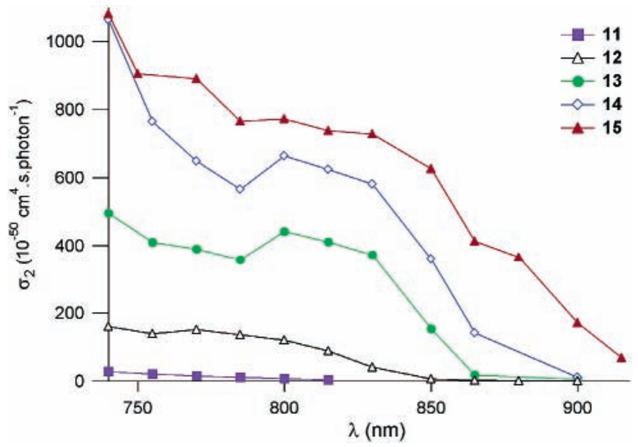

Figure 3. TPA spectra of fluorophores **11**−**15** in toluene.

We note that the character of the end-groups significantly affects the TPA response. The tris-acceptor octupolar fluorophores display much larger TPA cross-sections than their tris-donor counterpart (**11**). For instance, molecule **13** shows a TPA cross-section more than one-order of magnitude larger than molecule **11** of similar size. Moreover, we observe from the comparison of fluorophores **12** and **13** that increasing the acceptor character of the end-group does lead to an important increase in the TPA cross-section (Figure 3), in correlation with a concomitant increase in the Stokes shift (Table 1) and a red shift of both the absorption and emission spectra (Figure 2).

By increasing the distance between the core and peripheral electroactive groups, we aimed at extending the multidimensional charge-transfer phenomenon and increasing the nonlinear response.[23] This strategy turned out to be effective, as observed from the comparison of fluorophores **12** and **14**, which bear similar acceptor end-groups: increasing the molecular weight of the molecule by 30% (and increasing the size by about 50%) leads to a 4-fold (and 6-fold, respectively) enhancement in the TPA cross-section at $2\lambda_{abs}^{OPA}$ (respectively 740 nm). This also leads to a red-shift and broadening of both absorption and emission bands (Figure 2), as well as to an increase in the Stokes shifts, consistent with an increase of the core-to-periphery ICT. A similar trend is noted when comparing fluorophores **13** and **15** (Table 1) (but to a lesser extent), while the main effect lies in the major broadening of the TPA spectrum toward the NIR region. As a result, the elongated octupolar fluorophore **15** bearing strong acceptor peripheral groups maintains a sizable TPA cross-section at 900 nm (Figure 3). Finally, we stress that the use of phenylene-ethynylene linkers in the conjugated branches (in place of the more classical phenylene-vinylene linkers) leads to improved photostability, as indicated by the absence of photodegradation either upon pulsed-laser or prolonged lamp irradiation for derivatives **12** and **13**.

In summary, we have designed and investigated novel multipolar fluorophores derived from a triphenylamine core. By enhancing the multidimensional ICT between the core and the peripheral groups, we produced fluorophores that combine very large TPA cross-sections in the red−NIR region, high fluorescence quantum yields, and suitable photostability. This strategy led to octupolar fluorophores that exhibit some of the highest TPA cross-sections measured to date in the NIR region and in the femtosecond regime.[24]

Furthermore, our study provides evidence that the TPA cross-sections of such derivatives can be significantly enhanced in the NIR region with elongated derivatives bearing strong electron-withdrawing peripheral groups, leading to new directions for further engineering of their TPA properties. In particular by modifying and lengthening the conjugated branches, even larger TPA cross-sections should be attainable.[25]

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Supporting Information Available: Computational details, photophysical methods (absorption, fluorescence, and TPEF), and descriptions of all new fluorophores. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] This is corroborated by HOMO−LUMO calculations, which indicate that a significant electronic redistribution takes place from the core to the branches upon excitation.

[19] On the basis of the low sensitivity of the one-photon absorption spectra to solvent polarity, we expect the TPA spectra in the NIR region to depend only weakly on solvent polarity, except for possible spectral broadening due to inhomogeneous broadening.

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[21] This excited state is doubly degenerated, and our experimental results are in agreement with models presented in the literature for trigonal octupolar molecules.[9e,22]

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[23] Such a strategy has proven to be valid in the case of nanoscale octupoles derived from triphenylbenzene leading to enhanced first-order hyperpolarizability: Brunel, J.; Mongin, O.; Jutand, A.; Ledoux, I.; Zyss, J.; Blanchard-Desce, M. *Chem. Mater.* **2003**, *15*, 4139−4148.

[24] PRL-701: $\sigma_2 = 600$ GM at 796 nm (Z-scan).[9b] Crystal violet: $\sigma_2 = 1980$ GM at 752 nm, (TPEF, $\phi = 0.015$).[9e] Compound **9** from ref 10f: $\sigma_2 = 1265$ GM at 770 nm, (TPEF, $\phi = 0.80$).

[25] In particular by replacing the phenyl moieties with a fluorene unit[10f] and/or triple bonds with double bonds (but at the expense of reduced photostability).