New chromophores from click chemistry for two-photon absorption and tuneable photoluminescence

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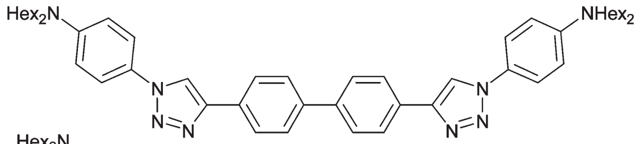
New multipolar derivatives built from triazole moieties that combine full transparency and strong TPA in the visible region as well as fully tuneable fluorescence have been designed; such chromophores open a new route for optical limiting.

For more than a decade, two-photon absorption (TPA) has attracted increasing attention in relation to various applications such as optical data storage, high-resolution 3-dimensional imaging of biological systems, laser up-conversion, photodynamic therapy, 3D microfabrication, and optical power limiting.[1] Depending on the desired application, different features are required in addition to strong TPA. In the case of optical limiting based on multiphoton absorption, chromophores combining high solubility, high linear transparency and strong nonlinear absorptivities in the visible region are required. In addition intense excited-state absorption and long excited-state lifetimes are looked for to favour a two-photon induced excited-state absorption phenomenon (*i.e.* sequential three-photon absorption) leading to the synergic effects of TPA and excited-state absorption.[2]



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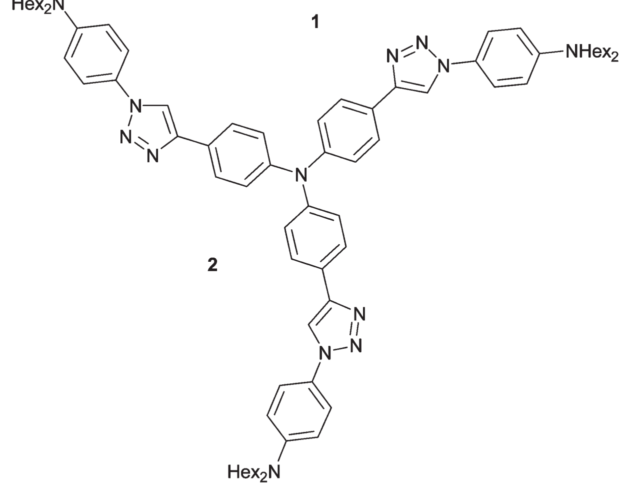

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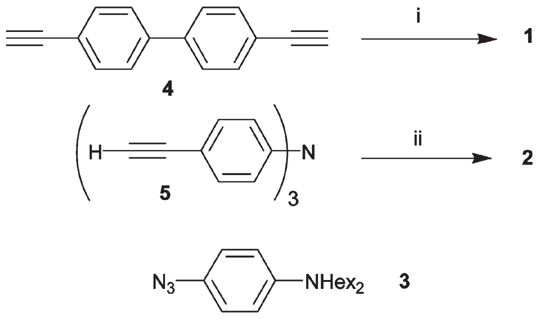
Molecular engineering directed towards TPA optimisation has become very active lately leading to a range of molecules of various symmetries including dipoles,[3] quadrupoles,[4] octupoles[5] and branched structures.[6] In particular several quadrupolar derivatives and dendrimers have been shown to lead to giant TPA cross-sections in the NIR region but at the expense of reduced transparency in the visible region. Here we present a new approach based on derivatives built from triazole moieties that combine full transparency and strong TPA in the visible region. Indeed heterocyclic moieties which are either electron-donating such as pyrrole[4f,6f] or electron-withdrawing such as pyridine,[3] benzothiazole,[1f] oxadiazoles[6a,b] or benzothiadiazole[7] have been used in the design of TPA active compounds. However the triazole unit has remained ignored although this electron-poor heterocycle can be readily synthesised in an efficient way using click chemistry.[8] Following this line, we designed and compared quadrupolar (**1**) and branched (**2**) systems where 1,2,3-triazole moieties are combined with electron-donating peripheral groups. The molecules could be obtained in good yields and with excellent regioselectivity using a two-fold or three-fold Huisgen 1,3-dipolar cycloaddition[8b] of azide **3** with bis-alkyne **4** or tris-alkyne **5**[5c] (Scheme 1).

The two chromophores show an intense absorption band in the near UV region but maintain full transparency in the visible region (Table 1). Both compounds exhibit large Stokes shifts, indicating that significant nuclear reorganisation takes place after excitation prior to emission.

In addition both compounds show strongly solvent dependent photoluminescence (PL) characteristics. The PL of molecule **1** can be tuned *in the whole visible range* by changing the solvent: a major red shift of the emission band is observed with increasing solvent polarity whereas the absorption is not affected (Fig. 1). This solvatochromic behaviour reveals a strongly polar emissive excited-state.

Interestingly, the excited-state lifetime can be markedly lengthened by increasing the solvent polarity (τ_1 = 2.23 ns in



Scheme 1 *Reagents and conditions*: i, **3** (2.7 equiv.), CuI (0.1 equiv.), DIPEA, THF, 35 °C, 15 h (86%); ii, **3** (3.1 equiv.), CuI (0.2 equiv.), DIPEA, THF, 35 °C, 15 h (68%).

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Table 1 Photophysical characteristics of fluorophores **1** and **2** in toluene

	λ_{max}(abs)/nm	log ε	λ_{max}(em)/nm	Φ_F	Stokes shift/cm^{-1}	τ^a/ns	$\sigma_2^{max b}$/GM	N_e^c	(σ_2/N_e)/GM
1	325	4.84	391	0.23	5100	0.39	99	36	2.75
2	347	4.92	387	0.49	3000	1.20	>240	31.2	>7.70

[a] Experimental fluorescence lifetime measured by TCSPC. [b] Two-photon absorption cross-section measured at 577 nm by Z-scan in 3–11 mM solutions; 1 GM = 10^{-50} cm^4 s photon^{-1}. [c] Effective number of π-electrons in the conjugated system.[13]

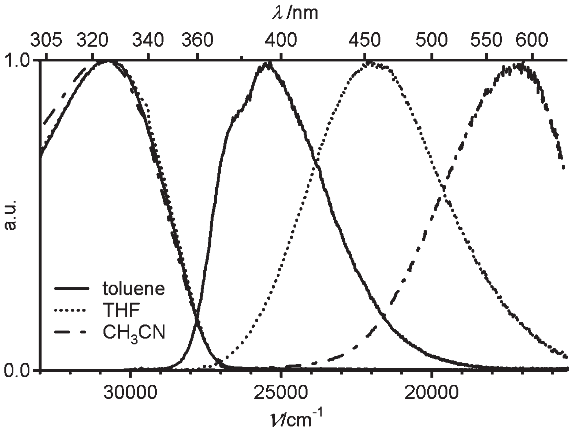

Fig. 1 Normalised absorption and fluorescence spectra of chromophore **1** in various solvents.

THF and 4.93 ns in CH_3CN). Indeed, it increases by more than *one order of magnitude* on changing from an apolar solvent like toluene to a polar solvent like acetonitrile. Such an effect is particularly important with regards to optical power limiting applications in the nanosecond regime based on two-photon induced excited state absorption[9] since the effective three-photon absorption coefficient increases significantly with the excited-state lifetime.[10]

The two-photon absorption characteristics of chromophores **1–2** were evaluated by performing Z-scan experiments in the 570–730 nm spectral range using femtosecond pulses.[11] This protocol allows prevention of any contribution from excited-state absorption which can lead to artificially enhanced effective TPA cross-section values when nanosecond pulses are used. As observed from Table 1, the two chromophores show strong TPA in the visible region. Interestingly the peak TPA cross-section of chromophore **1** is more than twice as large as that of AF-50,[12] a dipolar TPA benchmark. Comparison with recently reported quadrupolar D–π–A–π–D derivatives built from similar donating and π-linker units, but with benzothiadiazole heterocyclic acceptors indicates that quadrupole **1** exhibits comparable or stronger TPA while being more transparent. Hence the present study demonstrates that conjugated derivatives built from triazole moieties hold great promise for TPA-transparency optimisation. Furthermore, comparison of the TPA cross-sections normalised by the effective number of π-electrons in the conjugated system (N_e),[13] clearly indicates that 2D branched structures show superior TPA activity as compared to quasi-1D linear structures indicating a route for further improvement of TPA efficiency.

In conclusion by using an efficient click chemistry strategy, we have obtained quadrupolar and branched structures where electron-withdrawing triazole moieties combined with electron-donating peripheral groups create pronounced photo-induced intramolecular charge transfers resulting in both strong TPA and highly tuneable PL in the visible region. These chromophores combine excellent transparency, high solubility and excited-state lifetimes that can be markedly lengthened and thus hold great promise for optical limiting in the visible region.

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