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Novel heteroaromatic-based multi-branched dyes with enhanced two-photon absorption activity†

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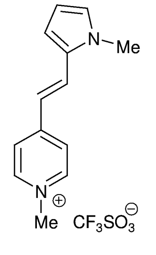
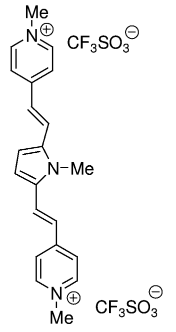
The first examples of heterocycle-based multi-branched dyes with efficient two-photon absorption (TPA) activity are reported; the novel chromophores exhibit large TPA cross sections (as high as 1600 × 10^{-50} cm^4 s photon^{-1} molecule^{-1}, measured with 150 fs laser pulses at 800 nm); a strong cooperative enhancement in the branched systems with respect to the one-dimensional sub-units is found.

The ability of an organic molecule to simultaneously absorb two or more photons[1] and be promoted to one of its excited states has recently attracted much interest due to its applicability in fields such as optical limiting,[2] upconverted lasing,[3] laser scanning fluorescence microscopy,[4] and microfabrication.[5] It is now known that an appropriate design of one-dimensional two-photon absorption (TPA) chromophores should rely either on a dipolar, such as A–π–D, or quadrupolar, such as A–π–D–π–A (D = donor, A = acceptor, π = conjugated spacer), general structure.[6] With few exceptions,[7] design has been so far vastly based on conventionally substituted benzenoid derivatives. We have recently shown the beneficial systematic use of heteroaromatic rings both as D and A components[8] of novel efficient dipolar[3] and quadrupolar[9] TPA dyes. In recent times some[10–14] reports have appeared on octupolar, branched, or dendrimeric structures for TPA activity, underlining the importance of cooperative effects in the TPA enhancement.[15] Once again, simple benzenoid derivatives and primary organic donor and acceptor functionalities have been commonly used.

We herein describe the first example of heterocycle-based multi-branched TPA dyes **1** and **2**, using π-deficient (pyridinium) and π-excessive (pyrrole) heteroaromatic rings as A and D units, respectively. Long alkyl chains were introduced on the pyridinium sites of **2** in order to increase solubility. We show that the new chromophores present a very large TPA cross-section σ in the femtoseconds (fs) regime. We also compare the TPA response of the branched systems with that of the corresponding dipolar **1-M**[8] and quadrupolar **2-M**[9] one-dimensional sub-units ("monomeric" units).



1-M

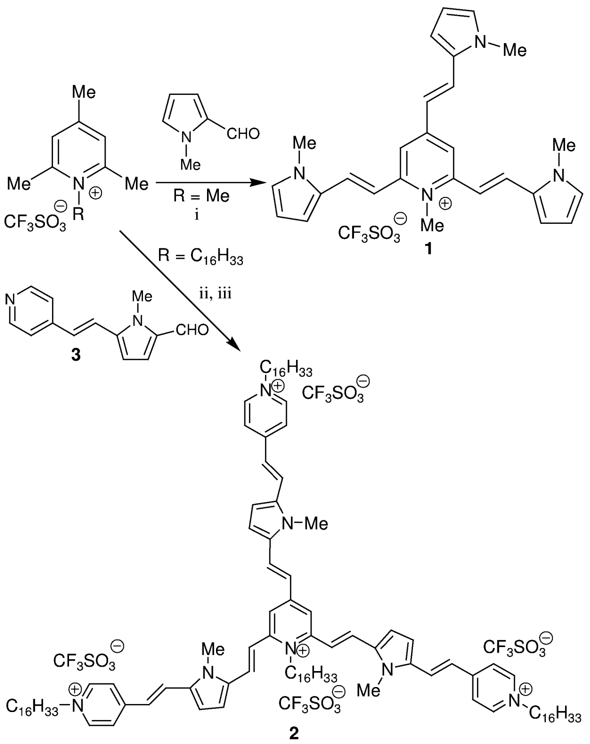


2-M

The new systems were prepared by triple Knoevenagel condensation of the quaternary salts of collidine with the appropriate aldehyde (Scheme 1). In the case of the synthesis of **2**, the reaction with **3**[16] becomes sluggish after the first two substitutions, even using a 100% excess of the aldehyde. We found that running the condensation in propylene glycol avoids the formation of a mixture of di- and tri-substituted compounds, difficult to separate because of their saline nature. The quaternarization of the peripheral pyridine moieties was accomplished in the last step in order to avoid retro-aldol cleavage during the Knoevenagel step and formation of undesired co-products.

Dyes **1** and **2** show a strong intramolecular charge transfer absorption band in the visible region and no NIR absorption. Despite their (multi)cationic nature, they present a fluorescence emission, although with moderate quantum yield. Table 1 lists the absorption and emission properties of **1** and **2**, compared to those of their counterparts **1-M** and **2-M**.

TPA cross sections were measured by open aperture Z-scan experiments with a fs-laser source. The fs-laser measurements provide a more accurate evaluation of the true TPA cross-sections with respect to nanosecond (ns) laser pulses.[17] In the latter, multiphoton sequential absorptions implying excited states populated by nonradiative processes become important. Table 2 collects σ values of molecules **1** and **2** together with



Scheme 1 *Reagents and conditions:* i, piperidine, *n*-BuOH, reflux, 6 h; ii, **3** (two fold excess), piperidine, propylene glycol, 130 °C, 6 h; iii, CF$_3$SO$_3$C$_{16}$H$_{33}$, anhyd. CH$_3$CN, overnight, rt.

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† Electronic supplementary information (ESI) available: Experimental section. See http://www.rsc.org/suppdata/cc/b3/b305995b/

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Table 1 Linear absorption and emission parameters of branched compounds **1** and **2** and monomers **1-M** and **2-M** in DMSO

Compd	λ_{max}(abs) /nm	ε /mol^{-1} l cm^{-1}	λ_{max}(em) /nm	Stokes shift^a /cm^{-1}	Φ_F^b
1	475	62 100	596	4270	0.11
1-M	437	29 800	523	3760	0.22
2	562	192 000	658	2600	0.0001
2-M	524	72 100	620	2960	0.14

[a] $1/\lambda$(abs) − $1/\lambda$(em). [b] Fluorescence quantum yield relative to 9,10-diphenylanthracene (Φ_F = 0.90 in cyclohexane).

those of monomers **1-M** and **2-M** and of the most representative one-dimensional and branched known examples of comparable molecular weight.

AF-50 has one of the largest σ values so far observed for a D–π–A structure and is usually referred as a TPA benchmark for 800 nm measurements. To our knowledge, the remaining literature examples are the most efficient branched TPA dyes in the fs regime known to date. Although we emphasize that valid comparisons are only possible when TPA peaks of different molecules are approximately at the same wavelength, systems **1** and **2** compare well with the best previously available data. It is commonly known[6] that the increase of the effective conjugation length (*i.e.*, number of π-electrons) should also lead to an increase of the TPA activity. Thus, it appears more appropriate to compare different systems by looking at their σ values normalized to the number of π electrons (σ/e_π). The normalized values of the new branched TPA dyes are either very similar or larger (almost four fold increase) than best literature values (Table 2).

Analysis of the σ data of the three-arm dyes **1** and **2** compared to those of the corresponding one-dimensional sub-units **1-M** and **2-M** reveals the presence of a strong cooperative enhancement. In fact, the found increase from the one- to the three-arm systems is 22.6 : 1 for **1** and 13.4 : 1 for **2**, that is much larger than those predicted simply on the basis of the chromophore number density increase (*i.e.*, 3 : 1). Significant cooperative enhancements were firstly reported by Prasad and coworkers[10] for a tri-branched chromophore (6.8 : 1, corresponding to a 6.8 : 3 = 2.3 fold enhancement) and later only by Drobizhev *et al.*[12] for a 29-repeat-unit dendrimer (1.2 fold enhancement) and Cho[14] for a triphenylamine tri-branched derivative (1.2 fold enhancement). We report here unprecedented large cooperative enhancements for **1** (7.5 fold enhancement, that is 22.6 : 3) and **2** (4.5 fold enhancement, that is 13.4 : 3).[18]

Table 2 TPA cross-section σ of branched compounds **1** and **2** and monomers **1-M** and **2-M** in DMSO, and comparison with literature data

	Pulse laser				
Compd.	λ/nm	fwhm/fs	e_π^a	σ /GM^c	$(\sigma/e_\pi)^b$ /GM^c
1	800	150	30	113	3.8
1-M	800	150	14	5	0.4
2	800	150	54	1600	29.6
2-M[9]	800	150	22	119	5.4
AF-50[17]	796	150	34	22	0.6
PRL-701[10]	796	173	80	600	7.5
ET-101[11]	790	131	138	380	2.7
Tri-branched[13]	755	80	162	798	4.9

[a] Number of π-electrons. [b] TPA cross-section normalized to the number of π electrons. [c] 1 GM (Göppert-Mayer) = 1 × 10^{-50} cm^4 s photon^{-1} molecule$^{-.1}$.

In conclusion, we have presented the first example of heteroaromatic-based multi-branched TPA dyes. These systems are highly ranked among the best dipolar, quadrupolar, and branched chromophores in the fs regime. The TPA response of **2** is more than 70 times that of benchmark AF-50. The strong cooperative enhancement observed in the branched architectures support the hypothesis that even larger values could originate by highly branched and dendrimeric systems based on heteroaromatic donor and acceptor components. Being the TPA response in the ns-regime orders of magnitude stronger than that measured with fs-laser pulses,[10,17] this family of chromophores could become very attractive for practical applications.

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18 TPA cross sections were all measured at a single wavelength. The integral value of the distribution of the TPA cross-section as a function of the excitation wavelength should provide a more accurate evaluation of the cooperative enhancement in the nonlinear optical response. We are currently pursuing these data by means of two-photon excited fluorescence measurements.