

Cooperative Enhancement of Two-photon Absorption of Multibranching Compounds with Vinylenes Attaching to the *s*-Triazine Core

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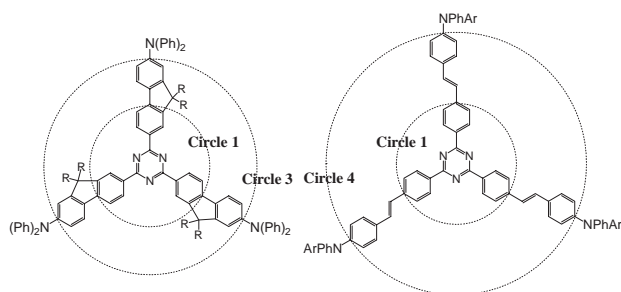
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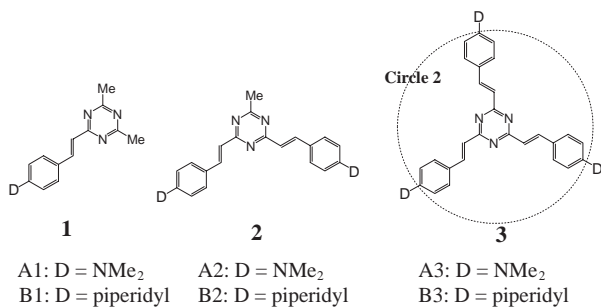
Two series of multibranching compounds with vinylenes attaching to the *s*-triazine core have been synthesized. The two-photon absorption cross section (σ) increases significantly as the branch number increases, with the ratios of σ between one-, two-, and three-branched compounds being 1.0:3.3:7.0 for series A and 1.0:3.7:7.0 for series B respectively, indicating remarkable cooperative enhancement.

Considerable effort has been placed in developing molecule-based materials with strong two-photon absorption (TPA) in recent years owing to their applications in many fields, such as in optical power limitation.¹ The molecular design for large TPA cross section (σ) has been mainly focusing on one-dimensional D- π -A type dipoles or D- π -D/A- π -A type quadrupoles.² Additionally, several two-dimensional π -systems of square porphyrin derivatives show strong TPA.³ Recently, some octupolar compounds, such as those based on N atom core⁴ and triazine core,⁵ have been reported to exhibit large TPA σ values or significant TPA enhancement.

Recently, Tan et al. reported some novel octupolar *s*-triazine derivatives with large σ values.^{5a} Tian et al. also reported several multibranching *s*-triazine derivatives with their σ values increas-



Scheme 1. The *s*-triazine derivatives in Refs. 5a (left) and 5b (right).



Scheme 2. The *s*-triazine derivatives in this work.

ing in a ratio of 1.0:1.2:5.3 when the branch number increases from 1 to 3.^{5b} As shown in Scheme 1, the compounds in Refs. 5a and 5b have the same local structure at the central hub (within the circle 1) which has been identified to be planar, whereas the planarity of whole molecules (in the region of circle 3 or circle 4) remains to be experimentally identified.

In this work, we connected vinylenes to *s*-triazine and synthesized two series of new *s*-triazine derivatives, named as A1–A3 and B1–B3 (shown in Scheme 2), by the Aldol condensation between 1,3,5-trimethyl-*s*-triazine and 4-*N,N*-dimethylamino-benzaldehyde or 4-*(N-piperidyl)*benzaldehyde. On the basis of our X-ray structural analysis earlier on the similar octupolar *s*-triazine derivatives,⁶ the A3 and B3 should take a planar C_{3h} conformation and can be distinguished from the reported compounds by the central local hub (within the circle 2) which has a planar structure and less steric hindrance.

The one-branched (A1 and B1) are typical D- π -A dipoles with a triazine acceptor and a dimethylamino/piperidyl donor, while the two-branched (A2 and B2) and the three-branched (A3 and B3) contain two and three this D- π -A unit, respectively. The X-ray structures of A1, A2, and B2 crystals have been determined by a Bruker P4 four-circle diffractometer.⁷ For any one of the structures, styryl moiety is conjugated with the *s*-triazine ring, forming a planar conformation. Molecule A1 is bar-shaped, while A2 and B2 are V-shaped. Most bond-lengths of these molecules are characterized by conjugacy. This bond character, combined with the molecular planarity, indicates quite good π -delocalization of the molecules.

For each series, the linear absorption spectra, the single-photon excited fluorescence (SPEF) spectra and the two-photon excited fluorescence (TPEF) spectra show red-shift as the branch

Table 1. The photophysical properties of *s*-triazine in THF

	i $\lambda^{a(1)}$	ii ϵ_{\max}	iii $\lambda^{e(1)}$	iv φ	v $\lambda^{e(2)}$	vi σ	vii σ/MW
A1	400	2.7	486	2.4	485	343	1.4
A2	416	6.6	514	4.5	516	1140	3.0
A3	418	10.0	516	3.3	520	2405	4.7
B1	391	2.1	488	4.4	488	363	1.2
B2	408	5.9	526	3.1	530	1345	2.9
B3	409	9.3	530	2.2	533	2523	4.0

ⁱAbsorption peak position in nm (1.0×10^{-5} mol L⁻¹).

ⁱⁱMaximum molar extinction coefficient in 10^4 mol⁻¹ L cm⁻¹.

ⁱⁱⁱSPEF peak position in nm (1.0×10^{-5} mol L⁻¹), measured at the exciting wavelength of 410 nm for all compounds.

^{iv}quantum yield in %.

^vTPEF peak position in nm (1.0×10^{-3} mol L⁻¹), measured at the exciting wavelength of 800 nm using a femtosecond Ti:sapphire laser as pump source.

^{vi}TPA cross section in GM (10^{-50} cm⁴s).

^{vii}Reduced TPA cross section, i.e., TPA cross section being divided by molecular weight.

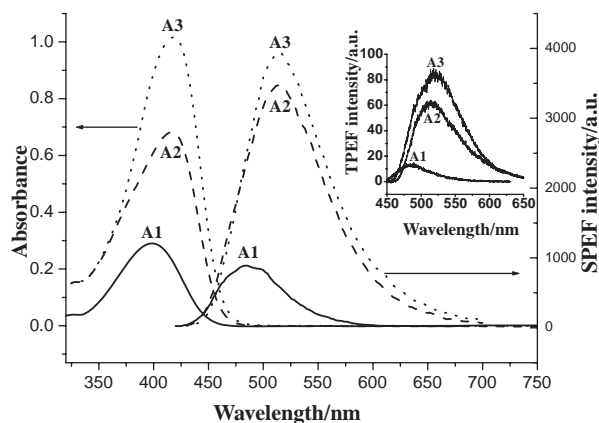


Figure 1. The absorption and emission (SPEF) spectra of A1, A2, and A3 in THF along with their TPEF spectra (inset) in THF.

number increases (Table 1 and Figure 1). This may be attributed to the extended π -conjugation of the multibranched molecules, and to the two-dimensional intramolecular charge-transfer characters along their individual branches. The spectral intensities, including the molar extinction coefficient (ϵ_{\max}), the SPEF intensity, and the TPEF intensity, also increase regularly as the branch number increases. The ratios of ϵ_{\max} between the one-, two-, and three-branched compounds are 1.0:2.4:3.7 (for series A) and 1.0:2.8:4.4 (for series B), both of which are larger than the ratio of branch numbers (1:2:3). As shown in Table 1, the TPEF peak position ($\lambda^{\text{e}(2)}$) of any of these compounds is very close to its SPEF peak position ($\lambda^{\text{e}(1)}$), indicating that both the emissions for a given compound are from the same excited state, though their initial Frank–Condon states may be different.

The TPA cross-section (σ) was obtained by comparing the TPEF intensity of the sample with that of coumarine 307 which serves as the reference compound.⁸ For each series, both σ and σ/MW (MW, the molecular weight) increase significantly as the branch number increases. The ratios of σ between one-, two-, and three-branched compounds are 1.0:3.3:7.0 for series A and 1.0:3.7:7.0 for series B, respectively. Both the ratios are much larger than the ratio of the branch numbers (1:2:3). The value of σ/MW , which measures the TPA efficiency of a compound, increases in a proportion of 1.0:2.2:3.5 for series A and 1.0:2.3:3.2 for series B, respectively. This kind of cooperative enhancement is much larger than that reported by Tian et al.^{5b} The enhanced σ and σ/MW by increasing branch number indicate that our structure motif of vinylenes attaching to the *s*-triazine core is in favor of interactions between the individual styryl branches.

All of our molecules are basically planar. Such π -conjugated structure must allow electronic coupling (π -conjugation) between the individual branches. The spectral red-shifts of linear absorption and the spectral enhancement of SPEF and TPEF with the increase of branch number are the clear evidences for the electronic coupling between branches. Such interaction between branches may play an important role in the remarkable cooperative enhancement of σ .

In conclusion, the multibranched *s*-triazine derivatives with vinylenes attaching to the core exhibit remarkable cooperative enhancement of TPA. This study reveals a new structural character which may be useful for designing new multibranched type of molecular materials.

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