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Synthesis and Two-photon Absorption Properties of s-Triazine Derivatives

Lei YIN[1], Yue Zhi CUI[2], Qi FANG[1,3]*, Gang XUE[1], Gui Bao XU[1], Wen Tao YU[1]

[1]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100
[2] Department of Chemical Engineering, Light Industry College of Shandong, Jinan 250100
[3] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093

Abstract: Two new s-triazine derivatives, which belong to linear dipolar type and triangle octupolar type respectively, have been synthesized. The structure of the dipolar compound has been determined by X-ray diffraction. The two-photon absorption cross-section σ, and the two-photon excited fluorescence (TPEF) intensities are increased significantly from dipolar compound to octupolar compound.

Keywords: s-Triazine, crystal structure, two-photon absorption, two-photon excited fluorescence.

Recently, organic molecules with large two-photon absorption (TPA) and intense two-photon excited fluorescence (TPEF) have attracted considerable attention due to their applications in various fields, such as optical limiting[1] and frequency up-converted fluorescence and lasing[2,3]. General structural motifs for TPA and TPEF are D- π -A dipoles, D- π -D or A- π -A quadrupoles, (D = donor, A = acceptor, π = conjugating linker), most of which are linear compounds with some exceptions of Λ-shaped compounds. In 1999, the first octupolar compound, which shows significantly enhanced TPA cross section [4], was reported. Since then, octupolar TPA compounds became one of the researching focuses in organic opto-electronic materials. In this work, we report two new s-triazine derivatives (see **Figure 1**) which belong to single-branched dipolar type and three-branched octupolar type respectively.

Experimental

As shown in **Figure 1**, compound I was synthesized by Aldol condensation. Heating 100 mL methanol solution of 2,4,6-trimethyl-s-triazine [5] (3.7 g, 0.03 mol) and potassium hydroxide (1.0 g) to reflux, then the solution of 4-N, N-dimethylaminobenzaldehyde (2.24 g, 0.015 mol) in 50 mL methanol was added dropwise in the period of 3 h. The reaction mixture was refluxed for further 24 h. The crude products were purified by column chromatography on silica gel using benzene/ethanol (10/1) as eluent. Compound **II** was synthesized by the same procedure as above except that the molar

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[*] E-mail: fangqi@icm.sdu.edu.cn

ratio of 4-N,N-dimethylaminobenzaldehyde and 2,4,6-trimethyl-s-triazine was changed to 6:1, and 1,3,5-trimethyl-s-triazine was added into 4-N,N-dimethylaminobenzaldehyde.

2,4-Dimethyl-6-[2-(4-N,N-dimethylamino)phenylethenyl]-1,3,5-s-triazine (compound **I**):

m.p. 147~149°C; H-NMR ($CDCl_3$, δppm): 8.14 (d, 1H, J = 16.09 Hz), 7.53 (d, 2H, J = 8.78 Hz), 6.82 (d, 1H, J = 16.09 Hz), 6.69 (d, 2H, J = 8.78 Hz), 3.03 (s, 6H), 2.60 (s, 6H). E.A.Calcd for $C_{15}H_{18}N_4$: C, 70.87; H,7.08; N, 22.05. Found: C, 70.95; H, 7.05; N, 21.88.

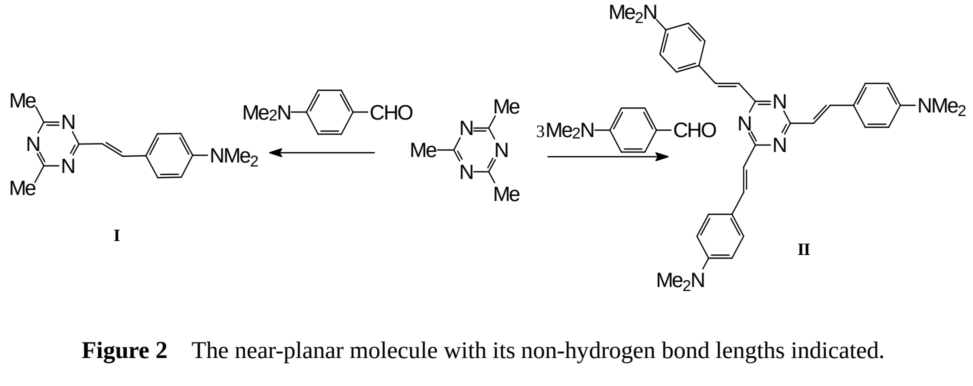
2,4,6-Tris[2-(4-N,N-dimethylamino)phenylethenyl]-1,3,5-s-triazine (compound **II**):

m.p. 276~278°C; ^{1}H-NMR ($CDCl_3$, δppm): 8.21(d, 3H, J=15.60 Hz), 7.59 (d, 6H, J = 8.77 Hz), 6.95 (d, 3H, J = 15.60 Hz), 6.71 (d, 6H, J = 8.78 Hz), 3.03 (s, 9H). MS (70eV) *m/z* (%): 516 (M^+,100), 517(37.39), 343 (46.82), 329 (18.60), 258 (14.88), 171 (59.61), 172 (40.82), 158 (16.45). E.A.Calcd for $C_{33}H_{36}N_6$: C, 76.74; H, 6.98; N, 16.28. Found: C, 76.57; H, 7.02; N, 15.88.

Crystallographic data and structural features

Compound **I** crystallized to triclicnic system, $P\bar{1}$ space group, a = 0.7834(5), b = 0.7852(5), c = 1.3105(5) nm, α = 88.966(5), β = 88.966(5), γ = 62.259(5)°, V = 0.7035(7) nm^3, Z = 2. R_1 = 0.0775, ωR_2 = 0.1951 for $I > 2\sigma(I)$.

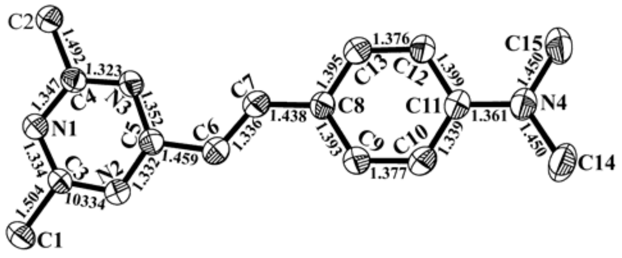
Figure 1 Synthesis route and structures of compounds I- II



I

II

Figure 2 The near-planar molecule with its non-hydrogen bond lengths indicated.



As shown in **Figure 2**, compound **I** has a linear polar structure. It is roughly planar with the dihedral angle between the triazine plane and the benzene plane, being only 6.8°, which indicates that the molecule is high conjugated. The conjugation character of compound **I** can also be presented by the bond length data. The NC_3 fragment in dimethylamino is co-planar, and the dihedral angles between NC_3 plane and its neighboring benzene plane is only 2.7°, which indicated the sp^2-hybrization of the nitrogen atom (N_4) in molecule **I**.

Linear Absorption and Emission Properties

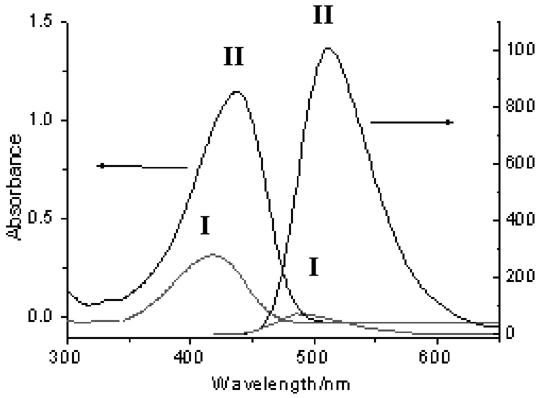
As shown in **Table 1** and **Figure 3**, both the absorption and the single-photon excited fluorescence (SPEF) spectra show regular red-shift from **I** to **II**, which can be attributed to the extended π-delocalization. It is interesting to note the spectral intensity of **II** was enhanced than that of **I**: At the peak positions, the ratio of ε between **II** and **I** is 3.4 : 1.0 and the ratio of Φ between **II** and **I** is also 3.4: 1.0, which are close to the ratio of the branch number of compound **II** and **I** (3: 1). Resultantly, the ratio of fluorescence intensity (defined here as the product of ε and Φ) between **II** and **I** is quadratically increased to 11.5:1.0, which closed to 3^2: 1.

Table 1 The linear and non-linear optical properties of I and II in chloroform

	$\lambda_{max}{}^a$	$\varepsilon_{max}{}^b$	$\lambda_{max}{}^c$	$\Delta\tilde{\nu}{}^d$	Φ^e	$I_{max}{}^f$	$\lambda_{max}{}^g$	σ^h
I	406	2.92×10^4	489	4180	1.98	578	491	220
II	426	10.02×10^4	511	3905	6.64	6653	515	534

[a] Absorption peak position in nm, c = 1.0×10^{-5} mol L^{-1}. [b] Maximum molar absorbance in mol^{-1} L cm^{-1}. [c] SPEF peak position in nm. [d] Stokes shift in cm^{-1}. [e] SPEF quantum yield in %. [f] Maximum SPEF intensities defined as the product of ε_{max} and the quantum yield Φ. [g] TPEF peak position in nm. [h] TPA cross section in GM (1GM = 10^{-50} cm^4s.$molecule^{-1}$.$photon^{-1}$), c = 5×10^{-3} mol L^{-1}.

Figure 3 The absorption and SPEF spectra of **I** and **II** in chloroform (c = 1.0×10^{-5} mol L^{-1})



The two-photon excited fluorescence properties

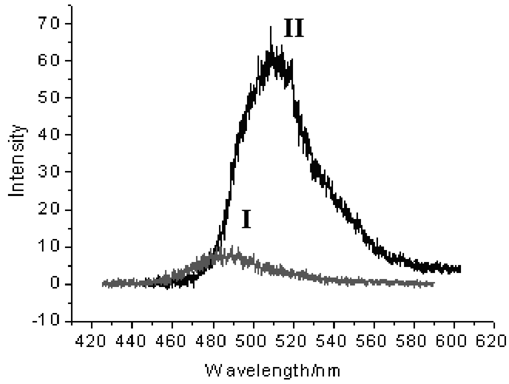
The TPA cross-section (σ) values were obtained by the following equation[6]:

$$\sigma = \sigma_{ref} \frac{\Phi_{ref}}{\Phi} \frac{c_{ref}}{c} \frac{n_{ref}}{n} \frac{F}{F_{ref}}$$

In the above equation, n is the refractive index, Φ is the TPEF quantum yield and can be supposed to be equal to the SPEF quantum yield [7], c is the concentration, F is the integral intensity of TPEF and the subscript *ref* refers to the reference sample. Coumarine 307 in MeOH was selected as the reference in this work[7].

As shown in **Table 1**, the value of σ increased significantly from **I** to **II**. Obviously, three-branched octupolar compound is a stronger TPEF emitter, compared with their dipolar counterpart (see **Figure 4**).

Figure 4 The two-photon fluorescence spectra of **I** and **II** in choloroform (c = 5 × 10^{-3} mol L^{-1}).



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