

Synthesis and Nonlinear Optical Properties of New Quadrupolar Chromophores

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Abstract: Two new symmetric chromophores: 2, 8-bis-[(2-4'-ethoxy phenyl-5-4'-styryl)-1, 3, 4-oxadiazole] didibenzothiophene (abbreviated as SO-G₁) and 2, 8-bis-[(2-4'-ethoxy phenyl-5-4'-styryl)-1, 3, 4-oxadiazole]-N-ethyl carbazole (abbreviated as NO-G₁) have been synthesized and characterized. Both chromophores exhibit strong two-photon absorption (TPA) with the cross-sections of 2.99×10^{-48} and 3.48×10^{-48} cm⁴·s·photon⁻¹ in THF and large up-conversion emission, when pumped by Ti:sapphire femto-second laser at 720 nm.

Keywords: 2, 8-Bis-[(2-4'-ethoxy phenyl-5-4'-styryl)-1, 3, 4-oxadiazole] didibenzothiophene, 2, 8-Bis-[(2-4'-ethoxy phenyl-5-4'-styryl)-1, 3, 4-oxadiazole]-N-ethyl carbazole, two-photon excited fluorescence, two-photon absorption .

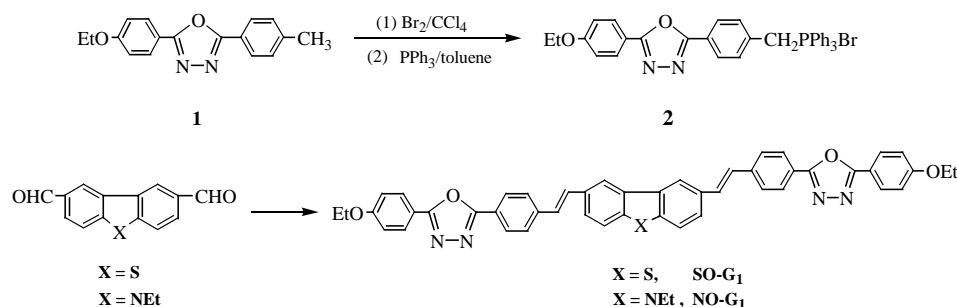
Two-photon absorption (TPA) has recently received considerable attention because they offer opportunities for both fundamental research and technological applications. The potential applications, including optical data storage, two-photon photodynamic therapy and optical limiting mainly depend on the materials with large two-photon cross section (δ_{TPA})¹. Here, we reported two novel chromophores based on symmetric structure of "D-A-Core-A-D", where D and A stand for electron-donor and electron-acceptor groups, respectively. The fused aromatic heterocyclic ring of dibenzothiophene or carbazole group is designed for rigid conjugated central core to improve π -electron delocalization resulting in better TPA property. Using 4-hydroxyl-benzoic acid as the starting material, the synthesis of chromophores SO-G₁ and NO-G₁ was shown in **Scheme 1**.

Experimental

Nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR), mass spectra, absorption spectra and one-photon excited (OPE) fluorescence spectra have been measured by the same apparatus previously². Two-photon excited (TPE) fluorescence spectra, pumped by Ti:sapphire femto-second laser tuned in the range of 700 nm-800 nm, were recorded

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Scheme 1



on a C5680-01 streak camera with a 2 ps resolution. TPA cross-section (δ_{TPA}) for SO-G₁ and NO-G₁ are calculated by assuming the value of δ_{TPA} to be 30 GM for fluoresce in reference³.

2-(4-Methylphenyl)-5-(4-ethoxyphenyl)-1, 3, 4-oxadiazole (1): This compound was synthesized according to the similar method reported⁴.

2-(4-Bromomethyl) phenyl-5-(4-ethoxyphenyl)-1, 3, 4-oxadiazole phosphonium bromide (2). A 250 mL, three-necked round-bottom flask was equipped with a reflux condenser, an argon inlet tube and a magnetic stirrer bar. The flask was charged 8.6 g (30.7 mmol) of **1**, then 5.6 g (31.5 mmol) of N-bromosuccinimide and 1.6 g (6.6 mmol) of benzoyl peroxide dissolved in the fresh distilled carbon tetrachloride as a catalyst were added dropwise. The mixture was refluxed for 5 h under an argon atmosphere, then cooled to room temperature and filtered. The solvent was removed by evaporation under reduced pressure. The light orange solid was washed with *n*-hexane three times. 2-(4-bromomethyl) phenyl-5-(4-ethoxyphenyl)-1, 3, 4-oxadiazole was obtained as pale orange solid. Yield 8.8 g (80.0%), mp 104~108°C. To 4.4 g of above obtained solid, 3.3 g of triphenylphosphine dissolved in fresh distilled toluene were added. The reaction solution was refluxed for 4 h, cooled to room temperature and filtered. 7.2 g white crystal of **2** was obtained after recrystallized from ethanol, yield 94 %, mp > 300°C. ¹H NMR (CDCl₃, δ ppm) 1.450-1.482 (t, 3H, *J*=6.4 Hz, CH₃), 4.081-4.131 (q, 2H, *J*=6.7 Hz, CH₂), 7.949-6.957 (m, 25H, Ar-H).

2, 8-Bis-[(2-4'-ethoxyphenyl-5-4'-styryl)-1, 3, 4-oxadiazole]dibenzothiophene (SO-G₁). Under anhydrous and oxygen-free conditions, a solution of 0.33 g (13.8 mmol) of sodium hydrid in 1,4-dioxane was added to a flask in the presence of 0.33 g (1.38 mmol) 2, 8-benzothiophene dialdehyde⁵ and 1.72 g (2.8 mmol) of **2**. After finishing the addition, the mixture was refluxed for 3 days while the color of mixture changed from pale yellow to deep orange. After removal of the half of the solvent, the mixture was poured into warm water. The precipitate was filtered and washed with ethyl alcohol and 3.1 g yellow powders (SO-G₁) were obtained after recrystallized from chloroform, yield 44 %. Mass spectrum: *m/z* 765.2 (+H⁺), 787.1 (+Na⁺). ¹H NMR (CDCl₃, δ ppm) 1.462-1.497 (t, 6H, *J*=7.0 Hz, 2CH₃), 4.083-4.139 (q, 4H, *J*=7.5 Hz, 2CH₂), 7.048, 7.254 (d, 4H, *J*=8.4 Hz, Ar-H), 7.325, 7.346 (d, 2H, *J*=8.4 Hz, Ar-H), 7.411 (d, 2H, *J*=8.0 Hz, Ar-H), 7.452, 7.473 (d, 2H, *J*=8.0 Hz, Ar-H), 7.736-7.635 (m, 6H, heterocyclic), 7.883,

7.863 (d, 2H, $J=8.0$ Hz, Ar-H), 8.025, 8.007 (d, 2H, $J=8.4$ Hz, Ar-H), 8.057, 8.078 (d, 4H, $J=8.4$ Hz, Ar-H), 8.143, 8.161 (d, 2H, $J=8.4$ Hz, Ar-H). ^{13}C NMR (CDCl_3 , δ ppm) 164.72, 164.45, 162.08, 140.58, 139.92, 132.57, 132.47, 130.15, 129.03, 127.39, 127.17, 125.61, 123.35, 120.30, 116.43, 115.29, 64.15, 15.14.

2, 8-Bis-[(2-4'-ethoxyphenyl-5-4'-styryl)-1, 3, 4-oxadiazole]-N-ethylcarbazole (NO-G₁). This chromophore was synthesized and purified according to the similar method mentioned of SO-G₁. Mass spectrum: m/z 775.3 (M^+), 789.3 (+Na⁺). ^1H NMR (CDCl_3 , δ ppm) 1.462-1.497 (t, 6H, $J=7.0$ Hz, 2CH₃), 4.083-4.139 (q, 4H, $J=7.5$ Hz, 2CH₂), 7.048, 7.254 (d, 4H, $J=8.4$ Hz, Ar-H), 7.325, 7.346 (d, 2H, $J=8.4$ Hz, Ar-H), 7.411 (d, 2H, $J=8.0$ Hz, Ar-H), 7.452, 7.473 (d, 2H, $J=8.0$ Hz, Ar-H), 7.736-7.635 (m, 6H, heterocyclic), 7.883, 7.863 (d, 2H, $J=8.0$ Hz, Ar-H), 8.025, 8.007 (d, 2H, $J=8.4$ Hz, Ar-H), 8.057, 8.078 (d, 4H, $J=8.4$ Hz, Ar-H), 8.143, 8.161 (d, 2H, $J=8.4$ Hz, Ar-H). ^{13}C NMR (CDCl_3 , δ ppm): 164.76, 164.49, 162.11, 140.80, 133.36, 132.59, 132.49, 130.17, 129.05, 128.93, 127.51, 126.99, 125.13, 123.73, 122.43, 119.63, 116.63, 115.30, 64.17, 15.17.

One-photon and two-photon properties

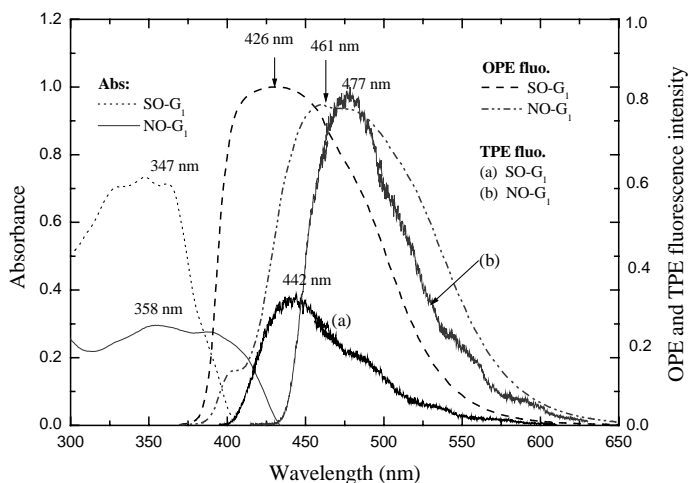
Table 1 and **Figure 1** show that the linear absorption peaks ($\lambda_{\text{max}}^{\text{OPA}}$) of both chromophores locate at 347 and 358 nm. The maximum peaks of one-photon ($\lambda_{\text{max}}^{\text{OPF}}$) and two-photon fluorescence ($\lambda_{\text{max}}^{\text{TPF}}$) are at 426 nm and 442 nm for SO-G₁ and at 461 nm and 477 nm for NO-G₁ under the excitation by a Xe lamp at 366 nm and by the Ti:sapphire femto-second laser irradiation at 720 nm, respectively, that is, the central wavelengths for OPE and TPE fluorescence are almost the same although they are obtained by different excitation mode. It is interesting to find that both chromophores possess large TPA cross-section value (δ_{TPA}) of 299 GM for SO-G₁ and 348 GM for NO-G₁ by assigning the δ_{TPA} of fluorescein to be 30 GM³. Concomitant with high fluorescence quantum yield (Φ_f) of 0.89, NO-G₁ exhibits relatively larger two-photon emission cross-section (δ_{TPF}) of 17.2 by assigning the δ_{TPF} of fluorescein to be 1. These show that NO-G₁ and SO-G₁ that have large TPA cross section and strong TPF emission accompanying with highly transparent across almost the whole visible spectrum can be the better candidates for potential applications in optical power limiting and two-photon fluorescence imaging.

Table 1 Summary of one-photon and two-photon parameters in THF

Compd.	Solvent	one-photo properties			two-photo properties		
		λ^{OPA} (nm)	λ^{OPF} (nm)	Φ_f	λ^{TPF} (nm)	δ_{TPA} (GM)	δ_{TPF}
SO-G ₁	THF	347	432	0.39	444	299	6.5
NO-G ₁	THF	358	458	0.89	477	348	17.2

$$1\text{GM} = 1 \times 10^{-50} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$$

Figure 1 One-photon (1×10^{-5} mol/L) and two-photon (1×10^{-3} mol/L) optical properties of SO-G₁ and NO-G₁ in THF



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