

Two-photon Absorption Properties of Novel Conjugated Dyes Containing a Benzophenone Unit

Jian Liu, Fang Gao,* Long Yang, Chunfeng Wang, Hongru Li,* and Shengtao Zhang
 College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, P. R. China

(Received December 24, 2009; CL-091140; E-mail: hrli@cqu.edu.cn)

A variety of new conjugated dyes bearing a benzophenone unit were synthesized, and the linear absorption and emission were determined. Two-photon absorption properties of the derivatives have been measured by a Ti:sapphire femtosecond laser tuning from 720 to 880 nm at intervals of 20 nm. One- and two-photon optical properties of the derivatives were found to be significantly dependent on their chemical structures.

In recent decades, two-photon absorption (TPA) has been a subject which attracts intensive attention in chemistry.¹ One of the central themes in organic and material chemistry is to develop highly fluorescent and remarkable two-photon absorption dyes since they can be applied widely in optical and biomedical fields, such as two-photon fluorescence sensors,² two-photon fluorescence excitation microscopy,³ three-dimensional optical data storage and microfabrication,⁴ optical limiting materials,⁵ and two-photon photodynamic therapy.⁶ Thus, many efforts have been devoted to develop new TPA dyes and survey the relationship between molecular structure and optical properties.⁷ Benzophenone is a well-known photoactive compound and is used extensively in material and biomedical fields.⁸ We can imagine that if a two-photon chromophore is linked with benzophenone via conjugated bond, the new dyes have great application potentials in various fields. Furthermore, the introduction of benzophenone branch could enhance two-photon absorption due to the donor–acceptor moiety. Novel conjugated derivatives with benzophenone unit, namely, 4-(*p*-benzoylstyryl)-4'-styryltriphenylamine (**C1**), 4-(*p*-benzoylstyryl)-4'-(3,4,5-trimethoxystyryl)triphenylamine (**C2**), and 4-(*p*-benzoylstyryl)-4'-(*p*-nitrostyryl)triphenylamine (**C3**) (Figure 1) were developed in this letter. As shown in Figure 1, the substituent group is in one branch, and benzophenone locates at the other branch. Each branch forms a π -conjugated structure and the overall conjugation of the derivatives are efficiently extended.

The derivatives were synthesized by different synthetic strategy to construct conjugated double bonds.⁹ The branch without benzophenone was first introduced to triphenylamine-core. For **C1**, this branch was constructed by Wittig reaction. For

C2, this branch was synthesized by Wittig–Horner reaction. While for **C3**, this branch was built by thermal condensation. Then, benzophenone was coupled as the other branch of the derivatives by Wittig–Horner reaction. The final products were purified by chromatography (silica gel) in the yield of approximate 60%, and the structures were characterized by ¹H, ¹³C NMR, IR, and elemental analysis.⁹

The linear optical properties of the derivatives **C1**, **C2**, and **C3** were investigated in benzene and ethyl acetate (EtOAc), and the data are listed in Table 1. As shown in Figure 2, the derivatives exhibit double absorption peaks in 275–500 nm. The first absorption band is similar to the absorption of triphenylamine, indicating that it may arise from the localized electronic transition of triphenylamine core. The second absorption band around 400 nm (for **C1** and **C2**) and 430 nm (for **C3**) could be assigned to π – π^* electron transition with large molar extinction coefficients in the order of $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. As compared with those of **C1** and **C2**, the absorption maxima of **C3** are red-shifted, indicating that **C3** has a larger internal charge transfer.

The derivatives **C1** and **C2** exhibit remarkably strong fluorescence emission in benzene with the quantum yields as high as 0.97 and 0.93, respectively. This is presumably due to the increased structural stiffness by benzophenone unit. Although one-photon emission of **C1** and **C2** is somewhat reduced in EtOAc, they still exhibit remarkable emission with the quantum yields as large as 0.52 and 0.29, respectively. The reduction could be mainly ascribed to increases in the molecular geometry twist and the extent of the internal charge transfer in EtOAc, and thus nonradiative deactivation of the excited state is increased.⁹ As compared with the emission maxima of the derivatives in benzene, they shift more to longer wavelength in EtOAc. The emission displays more remarkable solvent effect than the absorption, which could be due to the enhancement of internal charge-transfer of (π , π^*) transition of the derivatives by benzophenone unit, and the linear emission thus is more pronouncedly sensitive solvent polarity in the excited state. While, one-photon fluorescence intensity of **C3** is lower than that of **C1** and **C2**, especially much lower in EtOAc. This could be ascribed to larger internal conversion in the excited state of **C3** due to the nitro group and the fluorescence emission is thus prohibited.¹⁰

TPA emission and TPA cross sections of these derivatives were determined with a Ti:sapphire femtosecond laser. TPA cross sections were estimated by fluorescence based technique.⁹ The maximal TPA emission wavelength and TPA cross sections (measured by 800 nm laser) of these derivatives are shown in Table 1. It is interesting to observe that the maximal TPA emission is almost identical to one-photon emission wavelength. As compared with **C1** and **C2**, **C3** has not only red-shifted TPA emission but a larger cross section (1443 GM in benzene, 1687 GM in EtOAc, $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$). We notice that two-photon cross section of **C3** is much larger than that of (*p*-nitrostyryl)triphenylamine,¹¹ indicating that benzophenone

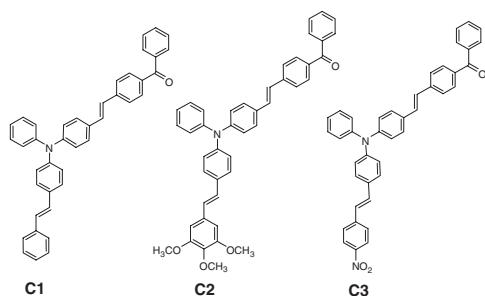
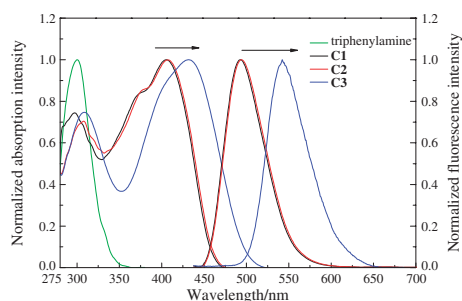


Figure 1. Chemical structures of **C1**, **C2**, and **C3**.

Table 1. Optical properties of **C1**, **C2**, and **C3**⁹

Compounds	$\lambda_{\text{abs}}^{\text{OPA}}/\text{nm}$		$\varepsilon/10^5$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$		$\lambda_{\text{em}}^{\text{OPF}}/\text{nm}$		Φ		$\lambda^{\text{TPA}}/\text{nm}$	$\sigma^{\text{TPA}}/\text{GM}$	
	Benzene	EtOAc	Benzene	EtOAc	Benzene	EtOAc	Benzene	EtOAc		Benzene	EtOAc
C1	406	407	0.40	0.46	493	527	0.97	0.52	495	181	147
C2	406	407	0.44	0.51	494	529	0.93	0.29	497	241	142
C3	432	431	0.42	0.50	542	590	0.44	0.0025	548	1443	1687

**Figure 2.** Normalized absorption and fluorescence spectra of triphenylamine, **C1**, **C2**, and **C3** in benzene.

unit makes a contribution to TPA of the derivatives. It plays the role of donor–acceptor due to the electron-withdrawing effect of carbonyl. **C3** was used as an example to check the relationship between TPA intensity and the pumped powers, which follows well the square law in the excitation laser frequency 800 nm. The slope of 2.03 demonstrates that the derivative has excellent two-photon absorption nature.⁹

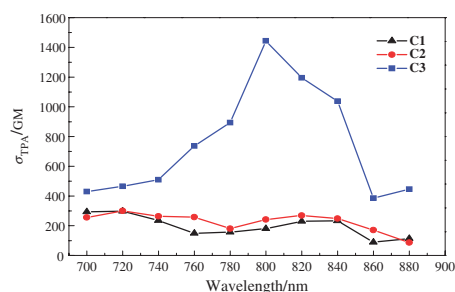
We further determined TPA cross sections of the derivatives by tuning laser frequency from 720 to 880 nm at intervals of 20 nm. TPA cross sections of **C3** are larger than those of **C1** and **C2** in benzene at various laser frequencies (Figure 3). The high TPA properties of **C3** could be attributed to the larger changes in the dipole moment between the excited state and the ground state. It could be understood as **C3** has a stronger electron-withdrawing group than **C1** and **C2**. As a matter of fact, **C3** has a higher dipole moment change between the excited state and the ground state (**C1**, 1.63 D; **C2**, 1.43 D; **C3**, 2.33 D, $1 \text{ D} = 6.695 \times 10^{-30} \text{ C m}$, calculated with Gaussian 03⁹). As a consequence, the linear absorption, emission and TPA emission of **C3** is red-shifted and TPA cross section is enhanced. The data also interpret why the derivatives **C1** and **C2** have similar linear and two-photon optical properties.

To summarize, new conjugated dyes carrying benzophenone were synthesized, and the linear absorption, emission, and two-photon properties were investigated. The optical properties have been shown to have a strong relationship with their molecular structures. The results presented in this letter would be of great interest in the development of new organic dyes carrying benzophenone moiety with ideal optical characteristics.

The authors appreciate NSFC (Nos. 20776165, 20702065, and 20872184) and (CSTC 2009BB4216 and CSTC 2008BA4020).

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**Figure 3.** TPA cross sections (σ^{TPA}) of **C1**, **C2**, and **C3** in benzene in laser frequency from 720 to 880 nm ($c = 5 \times 10^{-4} \text{ mol L}^{-1}$).

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