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Coumarin derivatives with enhanced two-photon absorption cross-sections

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Abstract

A series of ketocoumarin derivatives were synthesized using Aldol condensation and Wittig reactions and their one- and two-photon photophysical properties were investigated. Two-photon absorption cross-sections (δ) of the derivatives revealed that most of the new compounds possessed δ values that were some one to two orders of magnitudes larger than those of commercial coumarin dyes. The largest δ value within measured range was obtained as 1570 GM, which is comparable to that of reported strong two-photon absorption compounds. These novel derivatives containing the functional ketocoumarin group should open new opportunities for two-photon polymerization.

Keywords: Coumarin derivatives; Two-photon absorption; Charge transfer; TPEF

1. Introduction

In 1931, Göeppert-Mayer predicted that an atom or a molecule could absorb two photons simultaneously in the same quantum event [1]; 30 years later, this prediction was confirmed by Kaiser and Garrett [2]. As the transition probability of two-photon absorption depends quadratically on the excitation intensity, any initiated photochemical or photophysical processes will only happen in the focus point with a tightly focused excitation beam, which provides high penetration depth and high resolution of the excitation volume. Based on these characteristics, studies of two-photon absorbing materials have attracted increasing attention in terms of their potential application in two-photon-excited fluorescence microscopy [3], high-density optical data storage [4], three-dimensional microfabrication [5], two-photon up-converted lasing [6], and photodynamic therapy [7].

Coumarin derivatives have been extensively investigated for electronic and photonic applications [8–11], such as fluorescence probe, charge-transfer agents, solar energy collectors, and nonlinear optical properties due to their inherent photochemical characteristics, reasonable stability, good solubility and their relative ease of synthesis. However, as with other commercial dyes, their two-photon absorption cross-sections (δ) are too small to find usage in practical application. Thus, there is a need to improve the δ of commercial coumarins to promote their application in two-photon technology. It is well known that ketocoumarins are highly efficient photosensitizers and photoinitiators in UV–vis curable systems [12]. Given their improved δ, they are liable to be highly efficient photosensitizers or photoinitiators in the NIR region. This paper concerns a series of styrene-modified ketocoumarin derivatives **C2–C11** (Scheme 1) with a variety of terminated substituents and the study of their one- and two-photon photophysical properties using UV–vis spectra, steady-state fluorescence spectra, and

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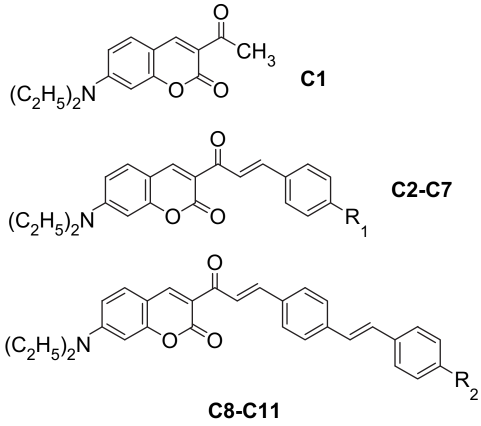


R_1 = -CHO (**C2**); -CN (**C3**); -Cl (**C4**);-OCH_3(**C5**);
-$N(CH_3)_2$ (**C6**); -$N(C_2H_5)_2$ (**C7**)
R_2 = -CH_3 (**C8**); -OCH_3(**C9**); -$N(CH_3)_2$ (**C10**); -$N(C_2H_5)_2$ (**C11**)

Scheme 1. The structures of compounds **C1**–**C11**.

two-photon-excited fluorescence (TPEF) technique with femtosecond laser pulses.

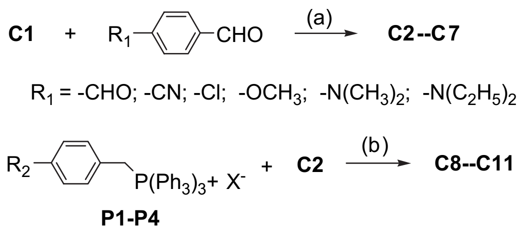
2. Experimental

2.1. Synthesis

α-Bromo-*p*-xylene, 4-methoxybenzylchloride and 4-cyanobenzaldehyde were purchased from Arcos Organics and were used as received. 4-(*N*,*N*-diethylamino)salicyaldehyde was obtained from Tianjin De'ai Co. Ltd. All other reagents (A.R.) were all from Beijing Beihua Co. Ltd. and were employed after purification using common methods.

3-Acetyl-7-diethylaminocoumarin (**C1**) was synthesized according to Ref. [12]. [4-Methylbenzyl]triphenylphosphonium bromide (**P1**) and [4-methoxylbenzyl]triphenylphosphonium chloride (**P2**) were synthesized according to literature [13]. [4-(*N*,*N*-dimethylamino)benzyl]triphenylphosphonium iodide (**P3**) and [4-(*N*,*N*-diethylamino)benzyl]triphenylphosphonium iodide (**P4**) were synthesized according to Ref. [14].

The synthetic routes to the target compounds **C2**–**C11** are shown in Scheme 2.



P1: R_2= -CH_3, X = Br; **P2**: R_2= -OCH_3, X = Cl;
P3: R_2= -$N(CH_3)_2$, X = I; **P4**: R_2= -$N(C_2H_5)_2$, X = I

Scheme 2. Reagents and conditions: (a) piperidine/ethanol:acetonitrile (v:v = 1:1) refluxed 20 h; (b) NaOH (aqueous 2 M)/CH_2Cl_2, 40 °C, then I_2, heated.

The general process for the synthesis of compounds **C2**–**C7** was as follows. In a reaction flask, 1 mmol of 3-acetyl-7-diethylaminocoumarin (**C1**) and 1 mmol appropriate benzoaldehyde derivatives were dissolved in 8 ml of ethanol/acetonitrile (v:v = 1:1) mixed solvents, three drops of piperidine were added as catalyst. The mixture was heated to reflux for about 20 h, and then cooled down to room temperature. The precipitate was collected by filtration and recrystallized twice in ethanol/acetonitrile. The pure products were characterized by ^1H NMR and elemental analysis.

C2: yield 56%; ^1H NMR (300 MHz, $CDCl_3$) δ10.042 (s, 1H), 8.612 (s, 1H), 8.254 (d, $J = 15.75$ Hz, 1H), 7.923 (d, $J = 8.21$ Hz, 2H), 7.856 (d, $J = 15.45$ Hz, 1H), 7.834 (d, $J = 8.31$ Hz, 2H), 7.520 (d, $J = 8.79$ Hz, 1H), 6.8413 (d, $J = 8.73$ Hz, 1H), 6.664 (s, 1H), 3.505 (q, 4H), 1.277 (t, 6H); Anal. Calcd (%) for $C_{23}H_{21}NO_4$: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.27; H, 5.71; N, 3.55.

C3: yield 61%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.586 (s, 1H), 8.249 (d, $J = 15.87$ Hz, 1H), 7.765 (d, $J = 8.31$ Hz, 2H), 7.722 (d, $J = 15.66$ Hz, 1H), 7.689 (d, $J = 8.14$ Hz, 2H), 7.469 (d, $J = 8.81$ Hz, 1H), 6.702 (d, $J = 8.70$ Hz, 1H), 6.552 (s, 1H), 3.493 (q, 4H), 1.272 (t, 6H); Anal. Calcd (%) for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52. Found: C, 74.09; H, 5.44; N, 7.45.

C4: yield 60%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.577 (s, 1H), 8.144 (d, $J = 15.60$ Hz, 1H), 7.778 (d, $J = 15.82$ Hz, 1H), 7.621 (d, $J = 6.03$ Hz, 2H), 7.462 (d, $J = 8.1$ Hz, 1H), 7.374 (d, $J = 5.92$ Hz, 2H), 6.686 (d, $J = 8.02$ Hz, 1H), 3.484 (q, 4H), 1.270 (t, 6H); Anal. Calcd (%) for $C_{22}H_{20}ClNO_3$: C, 69.20; H, 5.28; Cl, 9.28; N, 3.67. Found: C, 69.30; H, 5.29; Cl, 9.31; N, 3.64.

C5: yield 65%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.564 (s, 1H), 8.053 (d, $J = 15.66$ Hz, 1H), 7.826 (d, $J = 15.72$ Hz, 1H), 7.656 (d, $J = 8.28$ Hz, 2H), 7.441 (d, $J = 8.79$ Hz, 1H), 6.925 (d, $J = 8.25$ Hz, 2H), 6.651 (d, $J = 8.64$ Hz, 1H), 6.517 (s, 1H), 3.858 (s, 3H), 3.474 (q, 4H), 1.257 (t, 6H); Anal. Calcd (%) for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.12; H, 6.22; N, 3.79.

C6: yield 50%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.560 (s, 1H), 7.988 (d, $J = 15.60$ Hz, 1H), 7.846 (d, $J = 15.60$ Hz, 1H), 7.616 (d, $J = 8.46$ Hz, 2H), 7.429 (d, $J = 8.79$ Hz, 1H), 6.732 (d, $J = 8.31$ Hz, 2H), 6.629 (d, $J = 8.84$ Hz, 1H), 6.504 (s, 1H), 3.468 (q, $J = 13.97$ Hz, 4H), 3.052 (s, 6H), 1.254 (t, 6H); Anal. Calcd (%) for $C_{24}H_{26}N_2O_3$: C, 73.82; H, 6.71; N, 7.17. Found: C, 73.72; H, 6.78; N, 7.09.

C7: Yield 46%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.554 (s, 1H), 7.954 (d, $J = 15.45$ Hz, 1H), 7.839 (d, $J = 15.51$ Hz, 1H), 7.582 (d, $J = 8.52$ Hz, 2H), 7.422 (d, $J = 8.78$ Hz, 1H), 6.647 (d, $J = 8.34$ Hz, 2H), 6.608 (d, $J = 8.72$ Hz, 1H), 6.497 (s, 1H), 3.438 (m, 8H), 1.225 (m, 12H); Anal. Calcd (%) for $C_{26}H_{30}N_2O_3$: C, 74.61; H, 7.22; N, 6.69. Found: C, 74.65; H, 7.22; N, 6.73.

The general process for the synthesis of compounds **C8**–**C11** was as follows. A mixed solution of 1 mmol of **C2** in 20 ml of methylene chloride and 40 ml of 2 M NaOH (aqueous) was stirred at room temperature, then a corresponding triphenylphosphonate (1 mmol) in 20 ml of methylene chloride was added dropwise. The mixture was heated to reflux for 2 h. After cooling, the organic phase was separated off and the aqueous phase was extracted with chloroform twice. The combined organic phases were washed with water. After drying with sodium sulfate, the solvent was rotary evaporated. The crude oily product was purified by chromatography on silica gel (eluent: chloroform/ethyl acetate). After treatment with a catalytic amount of iodine by heating in chloroform, pure *trans*-products were obtained. The pure products were characterized by ^{1}H NMR, MS and elemental analysis.

C8: yield: 57.2%; mp: 238–239 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ1.26 (t, $J = 6.99$ Hz, 6H), 2.37 (s, 3H), 3.46 (q, $J = 7.14$ Hz, 4H), 6.54 (d, $J = 1.8$ Hz, 1H), 6.69 (d, $J = 8.85$ Hz, 1H), 7.14 (m, 4H), 7.42 (m, 3H), 7.54 (d, $J = 8.07$ Hz, 2H), 7.66 (d, $J = 8.19$ Hz 2H), 7.86 (d, $J = 15.66$ Hz, 1H), 8.14 (d, $J = 15.69$ Hz, 1H), 8.57 (s, 1H); MS (*m*/*z*): 463.3; Anal. Calcd (%) for $C_{31}H_{29}NO_3$: C, 80.32; H, 6.31; N, 3.02. Found: C, 79.97; H, 6.52; N, 2.88.

C9: yield: 39.2%; mp: 223–225 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ1.26 (t, $J = 7.08$ Hz, 6H), 3.46 (q, $J = 7.08$ Hz, 4H), 3.84 (s, 3H), 6.51 (s, $J = 8.52$ Hz, 1H), 6.27 (d, $J = 8.85$ Hz, 1H), 6.90 (d, $J = 8.52$ Hz, 2H), 7.01 (d, $J = 16.47$ Hz, 1H), 7.12 (d, = 16.41 Hz, 1H), 7.47 (m, 5H), 7.66 (d, $J = 8.04$ Hz, 2H), 7.86 (d, $J = 15.63$ Hz, 1H), 8.14 (d, $J = 15.60$ Hz, 1H), 8.57 (s, 1H); MS (*m*/*z*): 479.5; Anal. Calcd (%) for $C_{31}H_{29}NO_4$: C, 77.64; H, 6.10; N, 2.92. Found: C, 77.84; H, 6.37; N, 2.67.

C10: yield: 53.4%; mp: 242–244 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ1.26 (t, $J = 7.14$ Hz, 6H), 3.02 (s, 6H), 3.46 (q, $J = 7.08$ Hz, 4H), 6.50 (d, $J = 2.22$ Hz, 1H), 6.65 (m, 3H), 6.97 (d, $J = 16.20$ Hz, 1H), 7.11 (d, $J = 16.20$ Hz, 1H), 7.45 (m, 5H), 7.65 (d, $J = 8.25$ Hz, 2H), 7.86 (d, $J = 15.72$ Hz, 1H), 8.13 (d, $J = 15.66$ Hz, 1H), 8.57 (s, 1H); MS (*m*/*z*): 492.4; Anal. Calcd (%) for $C_{32}H_{32}N_2O_3$: C, 78.02; H, 6.55; N, 5.69. Found: C, 77.85; H, 6.62; N, 5.53.

C11: yield: 48.6%; mp: 227–228 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, $J = 7.14$ Hz, 6H), 1.23 (t, $J = 6.99$ Hz, 6H), 3.38 (q, $J = 7.14$ Hz, 4H), 3.46 (q, $J = 7.14$ Hz, 4H), 6.50 (d, $J = 2.13$ Hz, 1H), 6.62 (m, 3H), 6.91 (d, $J = 16.20$ Hz, 1H), 7.09 (d, $J = 16.20$ Hz, 1H), 7.45 (m, 5H), 7.64 (d, $J = 8.16$ Hz, 2H), 7.86 (d, $J = 15.66$ Hz, 1H), 8.12 (d, $J = 15.66$ Hz, 1H), 8.56 (1H, s); MS (*m*/*z*): 520.3; Anal. Calcd (%) for $C_{34}H_{36}N_2O_3$: C, 78.43; H, 6.97; N, 5.38. Found: C, 78.19; H, 6.83; N, 5.41.

2.2. *Photophysical methods*

UV–vis spectra were recorded on a Jasco V-530 spectrophotometer. Steady-state fluorescence measurements were performed at room temperature using a Hitachi F-4500 spectrophotometer. Fluorescence quantum yields were measured in diluted solutions (10^{-6} M) using fluorescein in 0.1 N NaOH as standard ($\Phi = 0.90$); refractive index correction was performed [15]. Two-photon absorption cross-sections of all compounds in chloroform solution (10^{-4}–10^{-3} M) were determined using a two-photon-excited fluorescence technique with femtosecond laser pulses (from a Tsunami mode-locked Ti: sapphire, 695–880 nm, 80 MHz, <130 fs) following the experimental protocol described in detail by Xu and Webb [16]. Fluorescein in 0.1 N NaOH (10^{-4} M) and Rhodamine B in methanol solution (10^{-4} M) were used as references to calibrate our measurement. The experimental uncertainty amounts to ±15%.

3. Results and discussions

The UV–vis absorption spectra and steady-state fluorescence spectra of all compounds in chloroform are shown in Figs. 1 and 2, respectively. Their photophysical characteristics are listed in Table 1. The linear absorption peak of **C1** exists at 435 nm; other compounds present an intense red-shift absorption peak at 456–489 nm due to their elongated conjugations. The fluorescence spectra of these compounds also exhibit systematic red shifts with increase in the electron-donating ability of terminated substituents or elongation of conjugation moieties. Compounds **C10** and **C11** display very large Stokes shifts of 5781 and 6305 cm^{-1}, respectively, which suggests that their lowest excited state are more likely to be a charge-transfer state and the difference of charge distribution between their

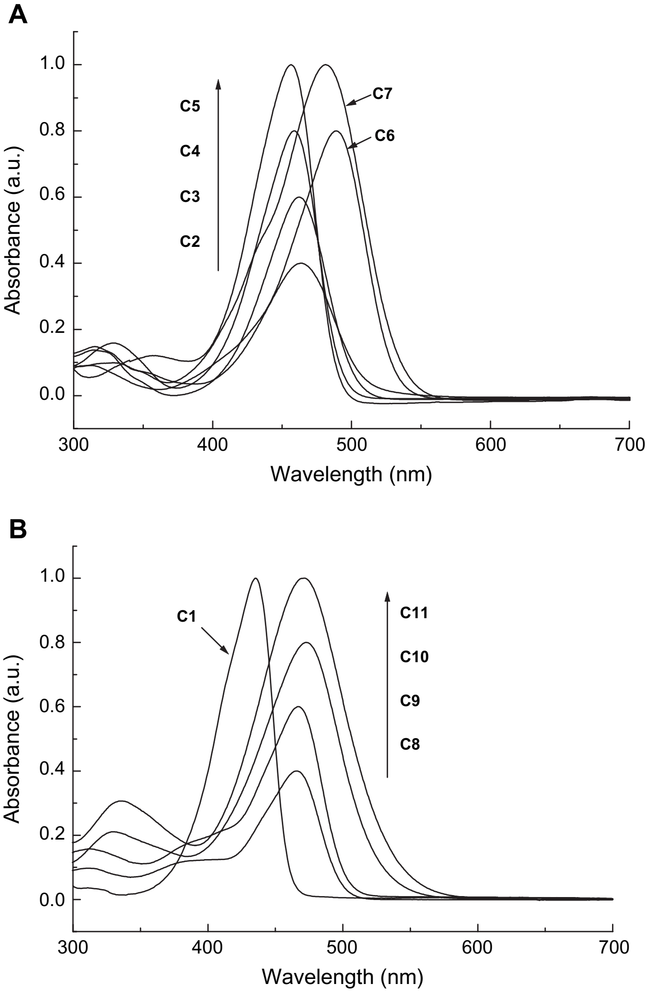


Fig. 1. UV–vis absorption spectra of compounds **C1**–**C11** in chloroform.

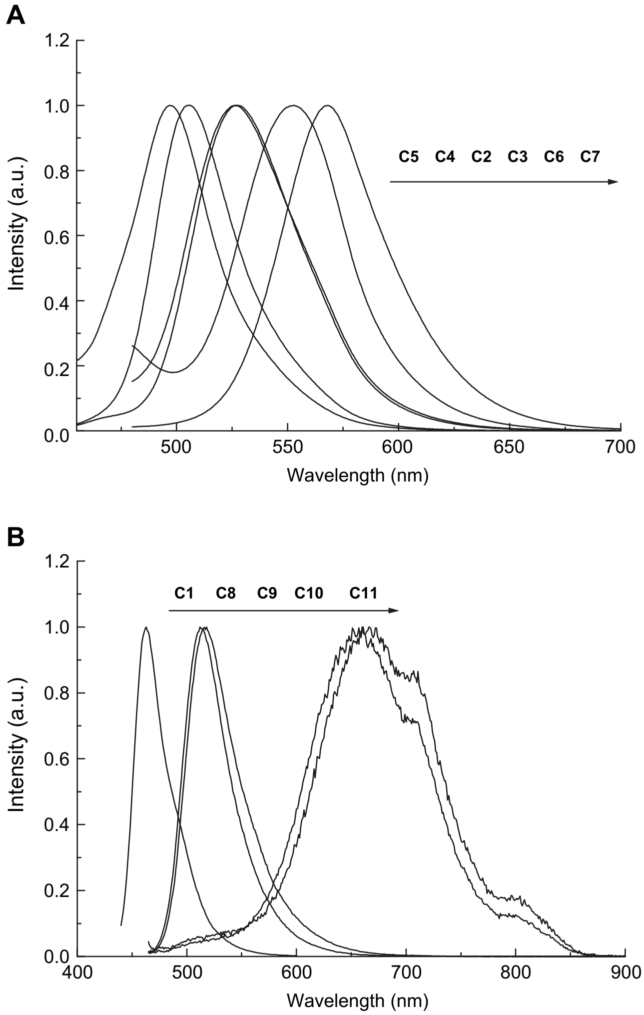


Fig. 2. Normalized fluorescence spectra of compounds **C1–C11** in chloroform at room temperature, performed at the λmax of each sample.

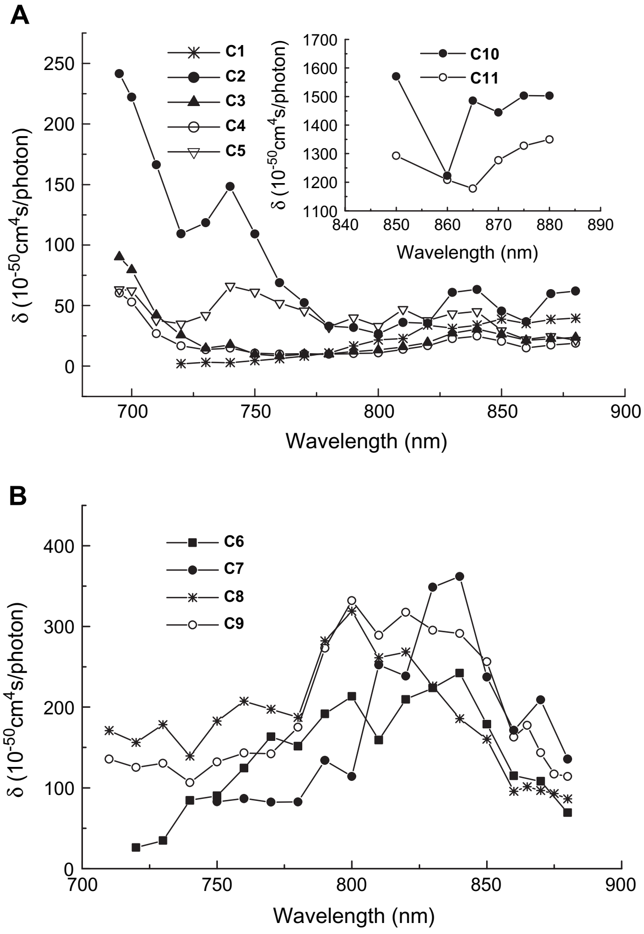


Fig. 3. Two-photon excitation spectra of compounds **C1–C11** in chloroform.

molecular ground state and excited state is more significant than those of other compounds. The low fluorescence quantum yields (Φ) of compounds **C10** and **C11** also indicated their increased excited state charge transfer [17]; dissipation processes other than fluorescence emission may occur due to the lower energy of their emitting states.

The two-photon-excited spectra of all compounds are shown in Fig. 3. As the TPEF spectra of **C10** and **C11** overlapped the residual excitation light when the excited wavelength was shorter than 850 nm, only their two-photon-excited spectra between 850 and 880 nm were determined. For compound **C1**, a δ of 39 GM was obtained at 850 nm. Compounds **C2–C11** showed enhanced δ values, especially compounds **C10** and **C11** with δ_{max} of 1570 and 1349 GM, respectively, within the measured wavelength range (Table 2). The δ values of compounds **C10** and **C11** are comparable with the data of other strong two-photon absorption compounds measured by the same method [18,19]. Considering the large Stokes shifts of compounds **C10** and **C11**, the reason for their significant enhancement of δ can be ascribed to the large change of dipole moment between their ground state and excited state according to the reported structure–property relationships [18]. Obviously, through relatively easy synthesis

Table 1
Linear photophysical characteristics of compounds **C1–C11**

Compounds	$\lambda_{max}^{(1)}$ (nm)	log ε_{max}	$\lambda_{max}^{(fl)}$ (nm)	$\Delta\nu$ (cm^{-1})	Φ
C1	435	4.75	463	1390	0.95
C2	463	4.82	526	2587	0.18
C3	462	4.77	527	2670	0.24
C4	459	4.76	505	1985	0.41
C5	456	4.75	497	1809	0.50
C6	489	4.84	552	2334	0.32
C7	481	4.91	568	3184	0.29
C8	466	4.90	512	1928	0.31
C9	467	4.98	516	2033	0.40
C10	473	4.93	651	5781	0.023
C11	472	4.89	672	6305	0.015

Table 2
The maximum TPA cross-sections of compounds **C1–C11** within measured region

Compounds	$\lambda_{max}^{(2)}$ (nm)	δ_{max} (GM)	Compounds	$\lambda_{max}^{(2)}$ (nm)	δ_{max} (GM)
C1	850	39	**C7**	840	362
C2	695	241	**C8**	800	318
C3	695	90	**C9**	800	332
C4	695	60	**C10**	850	1570
C5	740	66	**C11**	880	1349
C6	840	242			

to obtain significant increase of δ is an attractive way for exploring compounds with large δ values.

In addition, the terminated substituents (R_1 or R_2) had distinct effects on the two-photon absorption properties of these compounds. With the same conjugated moiety, compounds containing stronger electron-donor exhibited much larger δ values than compounds containing weaker electron-donor. The $\delta_{\max}$ of **C6** and **C7** were nearly four to six times larger than those of **C4** and **C5**. Similarly, **C10** and **C11** show the same extent enhancement compared to **C8** and **C9**.

Theoretically, the two-photon-excited fluorescence should quadratically depend on excitation intensities. We tried to ensure that this relationship was obtained for each compound insofar as the concentrations of the solutions were 10^{-4} M for **C1–C9** and 10^{-3} M for **C10** and **C11**, with the result that a near quadratic dependence of the fluorescence intensity on excitation intensity was obtained. This indicates that, apart from two-photon absorption, other photophysical processes such as reabsorption, excited-state absorption, stimulated emission, and excited-state saturation may be involved. It is more likely to be an "effective" two-photon absorption cross-section, which means the overall cross-sections besides a true two-photon absorption, consisting of other photophysical processes [20]. Nonetheless, the values of δ determined in this work are also useful to elucidate the two-photon absorption response of the samples [21].

4. Conclusions

A series of ketocoumarin derivatives were synthesized, for which it was shown that, by appropriately modifying terminated substituents and/or elongating conjugations, the two-photon absorption cross-sections of common coumarin dyes are significantly enhanced by one to two orders of magnitudes. The maximum δ is obtained as 1570 GM, which is comparable to the values of other reported compounds with strong two-photon absorption properties. These novel derivatives containing the functional group ketocoumarin are promising candidates for two-photon polymerization.

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