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Dyes and Pigments 75 (2007) 104–110

DYES and PIGMENTS

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The synthesis of novel coumarin dyes and the study of their photoreaction properties

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Received 28 April 2005; received in revised form 11 July 2005; accepted 24 April 2006
Available online 11 July 2006

Abstract

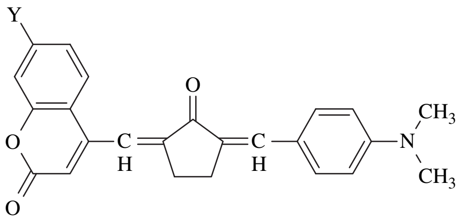
A series of novel coumarin derivatives linked with an *N*,*N*-dimethylaniline group via cyclopentanonediene on position 4 of the coumarin ring were synthesized and their two-photon absorbing (TPA) properties were investigated by femtosecond laser pulses. Compared to commercial coumarin dyes, novel compounds presented greatly enhanced TPA cross-sections around 100–400 GM. The photoreaction kinetic study showed that these dyes had fast electron transfer with commercial coinitiators, such as hexaarylbisimidazoles or iodonium salt. The dye/coinitiator combination can be used as highly efficient photoinitiating component in photopolymerization materials. In addition, a self-accelerating phenomenon was observed in the photoreaction process of the dye/iodonium salt.

Keywords: Coumarin derivatives; Two-photon absorption; Photoinitiator; Photobleaching; Photopolymerization

1. Introduction

In recent years, two-photon polymerization (TPP) technique has been paid much attention for its potential applications on high-density optical storage [1,2] and three-dimensional microfabrication [3,4]. Compounds with large two-photon absorbing (TPA) cross-section and high photoinitiating efficiency are required as the key issue for exploring TPP materials. Triplet coumarin dyes are well-known high efficient photosensitizers in UV–vis curable systems. When excited by light, they can transfer electrons with high efficiencies to coinitiators, such as iodonium salts or hexaarylbisimidazoles [5–9]. In addition, they can initiate the polymerization of crylic acid monomers directly as initiators [10]. However, the TPA cross-sections of commercial coumarin dyes are only around 1–50 GM [11], which limits their applications on two-photon polymerization. In our previous work, it was proved that *N*,*N*-dimethylaminobenzylidene cycloalkanones had strong TPA properties, and could be used as photoinitiators in two-photon curable materials [12]. For exploring novel TPP photonsensitizers with large TPA cross-section and high initiating efficiency, it is considered a valuable strategy to design and synthesize compounds containing both coumarin and cycloalkanones structures.

In this paper, we designed a series of novel coumarin/cyclopentanone derivatives with a donor–π-acceptor–π-donor structural motif (shown in Scheme 1), studied their structure/



Y : -CH_3 **1**, -OCH_3 **2**, -OC_2H_5 **3**, -OC_4H_9 **4**

Scheme 1. Structural formulas of compounds **1–4**.

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doi:10.1016/j.dyepig.2006.04.019

TPA property relationship, and investigated their photoreaction kinetics and photopolymerization initiating efficiency.

2. Results and discussions

2.1. The absorption and fluorescence spectra of compounds

The linear absorption spectra and fluorescence spectra of compounds are depicted in Fig. 1. All linear optical data are listed in Table 1. It was shown that the effect of the different electron-donating groups in four compounds on the positions of their absorption or emission peaks was very weak. The λ^{a}_{max} and the λ^{f}_{max} of four compounds only have 2 nm and 4 nm shifts, respectively.

2.2. The TPA cross-section of compounds

The results of four compounds' TPA cross-section at 730–840 nm are shown in Fig. 2. Their TPA cross-section have an order as **1** > **2**> **3**> **4** (see Table 2). It is considered that when the electron-donating ability of Y is increased, the electron transfer and the charge separation within coumarin groups will be enhanced, which could decrease the electron-donating ability on the position 4 of coumarin ring and induce decrease of the TPA cross-section of compounds **1–4**. Compared to commercial coumarin dyes (1–50 GM), these novel dyes presented large two-photon absorbing properties. The maximum TPA cross-section was obtained as 406 GM for compound **1**.

Table 1
Linear optical data of compounds **1–4** in chloroform

Compound	Y	ε_{max} (10^4 l/mol cm)	λ^{a}_{max} (nm)	λ^{f}_{max} (nm)	τ (ns)
1	$-CH_3$	3.7	480	635	0.67
2	$-OCH_3$	3.04	480	633	0.66
3	$-OC_2H_5$	3.26	479	632	0.51
4	$-OC_4H_9$	3.06	478	631	0.63

λ^{a}_{max}– Absorption peak, λ^{f}_{max} – emission peak, ε_{max} – molar extinction coefficients at λ^{a}_{max}, and τ – fluorescence lifetime.

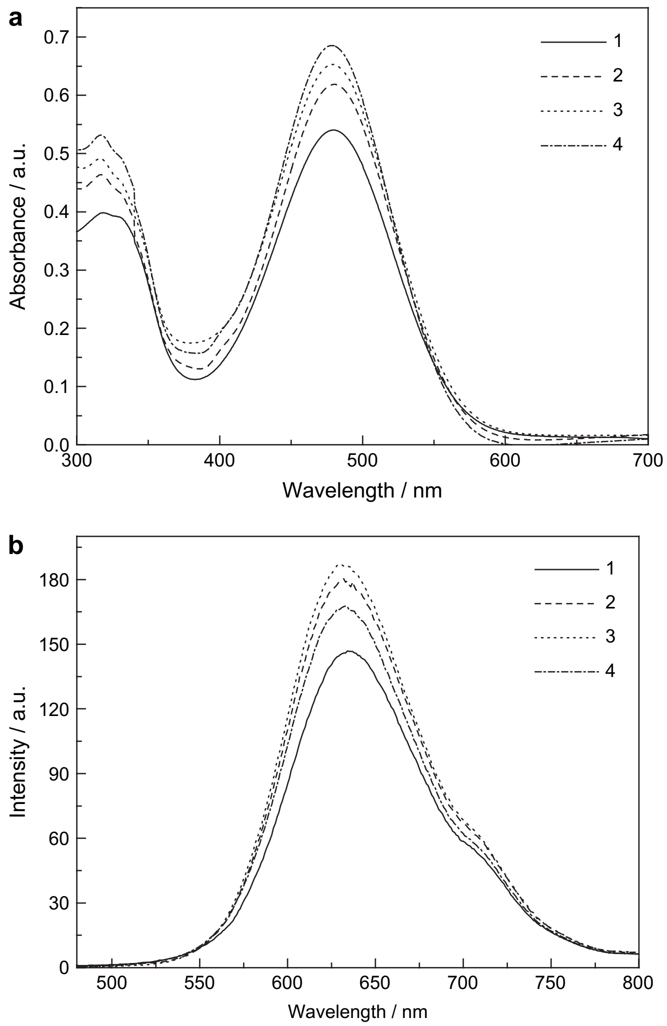


Fig. 1. The linear absorption spectra (a) and the fluorescence emission spectra (b) of compounds in chloroform.

2.3. The photoinitiating efficiency of compounds

2.3.1. The photoreaction kinetics of compounds *1–4*/HABI

The photoreaction kinetics study was carried out by monitoring the relative changes in the optical density of dye's absorption maximum with irradiation time. In Fig. 3, the photobleaching of dyes **1–4**/HABI was carried out under the same experimental condition. It is shown that compound **1** has the fastest photoreaction speed with HABI. Fig. 4 shows that the effect of oxygen on the photoreaction is very clear. In addition, HABI has almost no effect on the fluorescence intensity of four compounds, indicating that all these compounds are triplet photosensitizers.

2.3.2. The photopolymerization initiating efficiency of dye/HABI combination

The study of photopolymerization initiating efficiency was carried out by monitoring the change of the absorption peak at

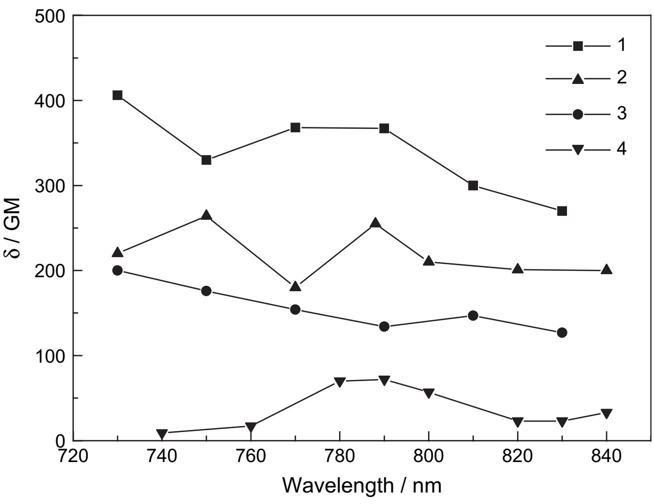


Fig. 2. Two-photon excitation spectra of compounds **1–4** in chloroform.

Table 2
The TPA cross-section of compounds **1**–**4**

Compound	R	δ_{max}(GM)
1	$-CH_3$	406
2	$-OCH_3$	264
3	$-OC_2H_5$	200
4	$-OC_4H_9$	92

810 cm^{-1}, the typical absorption band of double bonds, of the photocurable resin film with irradiation time. For comparison, the well-known high efficient triplet photosensitizer, 3,3′-bis(7-diethylamino)-ketocoumarin (R), was used as reference. In Fig. 5, it is shown that **1**/HABI and **3**/HABI presented an equivalent or even high photopolymerization initiating efficiency compared to R/HABI as bis-component initiating systems in UV curable resin films.

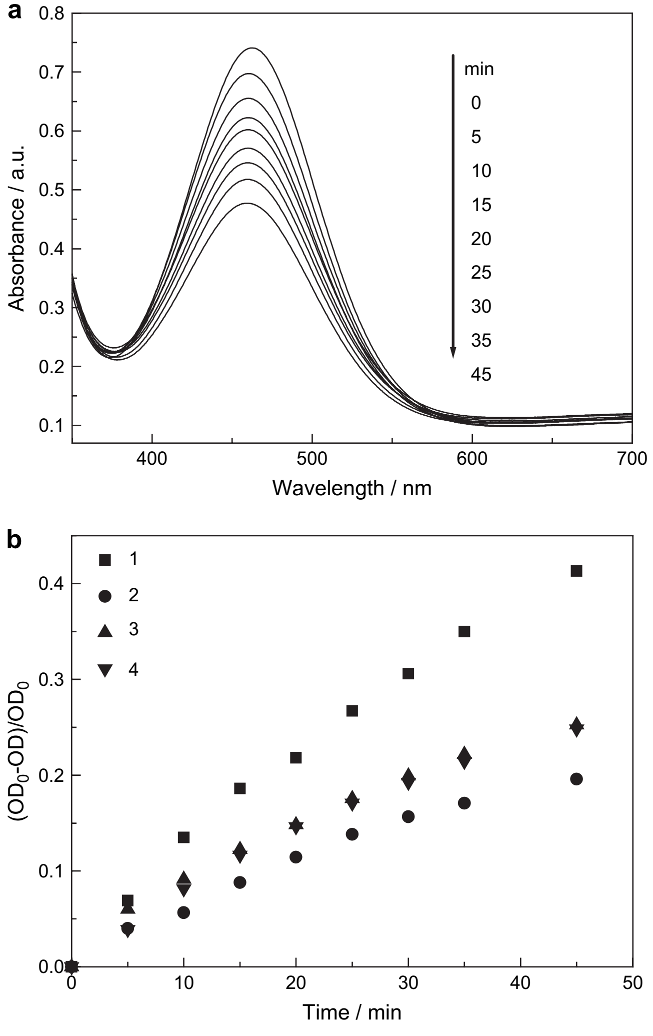


Fig. 3. (a) Change of the absorption spectra of **1**/HABI with irradiation time; (b) photobleaching of different dyes with HABI, [dye] = 2 × 10^{-5} mol/l, [HABI] = 8 × 10^{-5} mol/l, in acetonitrile, N$_2$.

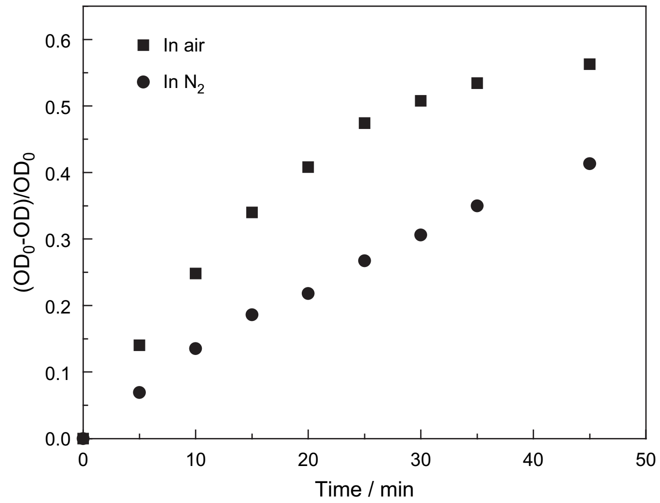


Fig. 4. Influences of oxygen on the photobleaching of dye **1**/HABI.

2.3.3. The photoreaction kinetics of compounds **1–4**/iodonium salt

In Fig. 6, it is shown that compound **1** also has the fastest photoreaction speed with iodonium salt. The quenching effect of oxygen on the photoreaction is very clear (shown in Fig. 7), in addition, iodonium salt has almost no effect on the fluorescence intensity of four compounds, indicating that these compounds transfer their electron to iodonium salt through their triplet excited states.

It is interesting to note that the photobleaching process of all dyes present a self-accelerating phenomenon. During photobleaching, a novel four-finger peak appeared with irradiation time at long wavelength region. When a small amount of hydroxyl sodium or trichloroethyl amine was added into the solution, these peaks disappeared and the absorption at 454 nm increased a little again, which indicated that a new acid material was generated in the photoreaction process. We consider

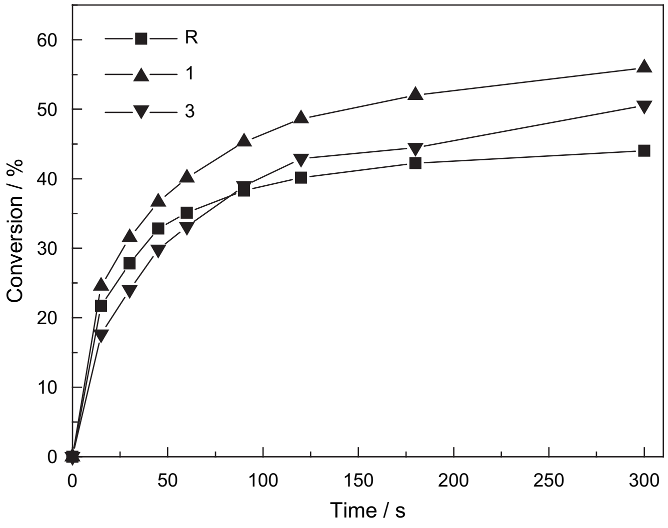


Fig. 5. The conversion rate of double bond in photocurable resin containing dye/HABI with irradiation time, [dye] = 5 × 10^{-3} mol/kg, and [HABI] = 2 × 10^{-2} mol/kg.

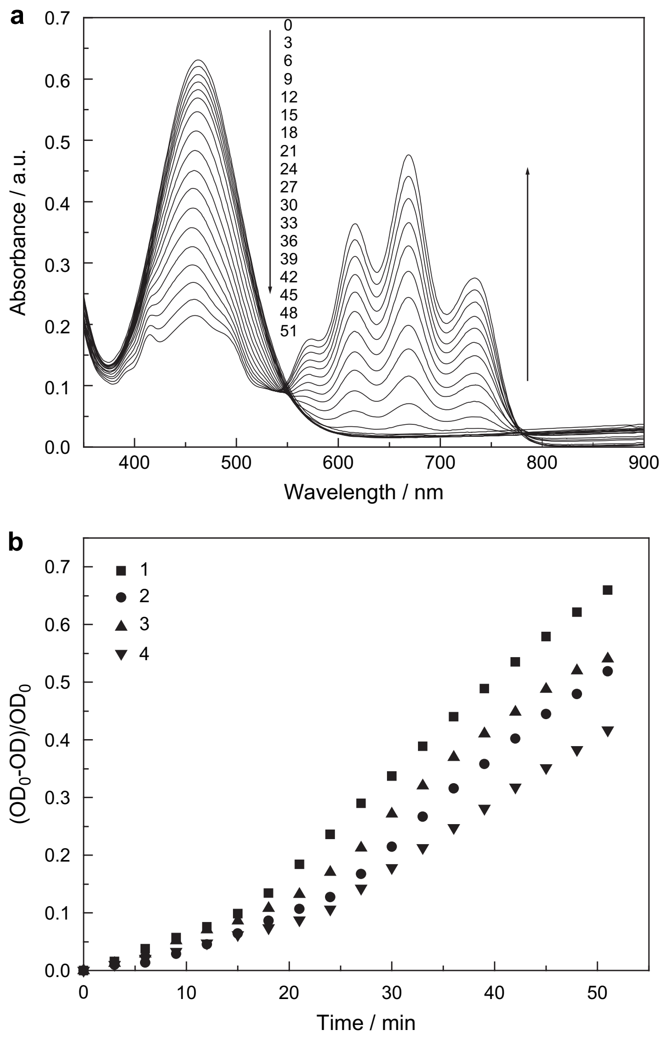


Fig. 6. (a) Change of the absorption spectra of **1**/iodonium salt with irradiation time; (b) photobleaching of different dyes with iodonium salt (IS), [dye] $= 2 \times 10^{-5}$ mol/l, [IS] $= 8 \times 10^{-5}$ mol/l, in acetonitrile, N_2.

the self-accelerating phenomenon of the photoreaction may be due to this new material's effect. However, it needs further studies to explore the basic reason.

2.3.4. The photopolymerization initiating efficiency of dye *1*/iodonium salt

Fig. 8 shows that **1**/iodonium salt also presents higher photopolymerization initiating efficiency than that of R/iodonium salt as bis-component initiating systems. In addition, the self-accelerating phenomenon also appeared during the photopolymerization process.

3. Experimental

3.1. Instruments

The infrared spectra were measured with a Bio-Rad FTS165 system, the absorption spectra were recorded with a Jasco V530 UV–vis spectrometer, the mass spectra were obtained with an MSGC-MC E1 system, the fluorescence emission spectra were determined using Rhodamine B as the reference on an F-4500 fluorescence spectrometer, ^1H NMR spectra were taken on a Varian Gemini 300 system, and a mode-locked Tsunami laser system (Ti:sapphire, 720–980 nm, 80 MHz, <130 fs) was used for measurement of two-photon absorbing properties of compounds.

3.2. Synthesis

The synthesis route of our target compounds is presented in Scheme 2.

3.2.1. 4,7-Dimethylcoumarin

3-Methylphenol (10.8 g, 0.1 mol) was dissolved in 15 ml of 75% concentrated H_2SO_4, then the solution was heated to 75 °C and 13 g (0.1 mol) acetylacetic ether was added dropwise. After 40 min, the reaction solution was poured into 100 g ice. The precipitate was collected, washed with water and recrystallized with ethanol. White crystal product (7.5 g) was obtained. Yield 43%, mp 128–130 °C [13].

3.2.2. 4-Formyl-7-methylcoumarin

4,7-Dimethylcoumarin (1.74 g, 0.01 mol) was dissolved in 50 ml dimethylbenzene during heating. Following this, seleninic acid (2.0 g) was added. The reaction solution was refluxed for 14 h, then filtered during heating to recycle selenium. After the filtrate was cooled, 1.65 g yellow crystal product was separated out, yield 88%. ^1H NMR ($CDCl_3$): 300 MHz, $\delta = 10.120$ (s, 1H), 8.459 (d, 1H, $J = 7.98$ Hz), 7.202 (s, 1H), 7.172 (d, 1H, $J = 8.01$ Hz), 6.829 (s, 1H), 2.480 (s, 3H).

3.2.3. Compound *1*

2-(4-Dimethylamino-benzylidene)-cyclopentanone (0.21 g, 1 mmol) and 0.19 g (1 mmol) of 4-formyl-7-methylcoumarin were dissolved in 15 ml ethanol during heating. After 0.03 g NaOH was added, the reaction solution became red colour

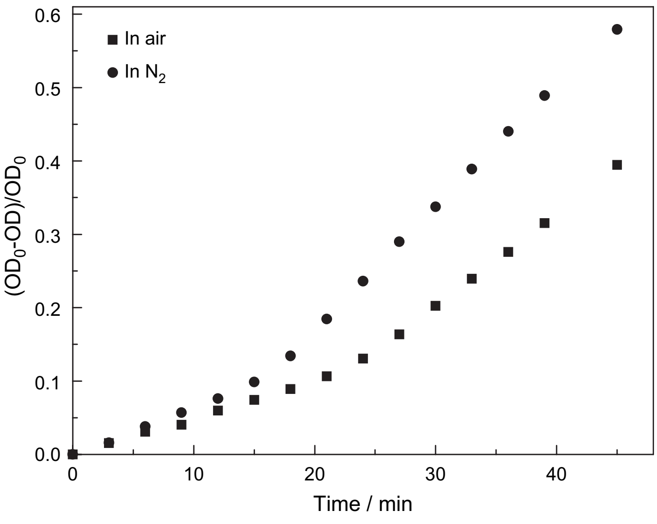


Fig. 7. Influences of oxygen on the photobleaching of dye **1**/iodonium salt.

immediately and some precipitate was produced. The mixture was refluxed for 1 h, then cooled to room temperature. The red precipitate was collected and recrystallized with dimethylbenzene. Pure product (0.15 g) was obtained, yield 40%. ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 7.669$ (d, 1H, $J = 8.22$ Hz), 7.662 (s, 2H), 7.558 (d, 2H, $J = 8.25$ Hz), 7.188 (s, 1H), 7.138 (d, 1H, $J = 8.22$ Hz), 6.759 (d, 2H, $J = 8.46$ Hz), 6.469 (s, 1H), 3.079 (s, 6H), 3.051 (s, 4H), 2.470 (s, 3H).

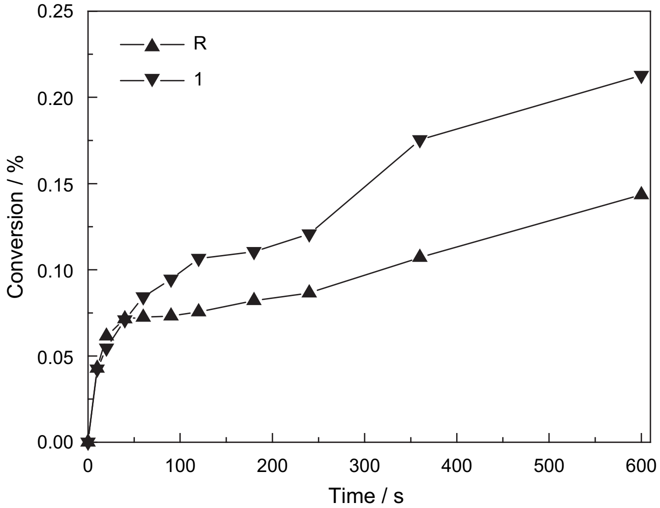


Fig. 8. The conversion rate of double bond in photocurable resin containing dye/iodonium salt with irradiation time, [dye] = 5×10^{-3} mol/kg, and [IS] = 0.13 mol/kg.

3.2.4. *4-Methyl-7-hydroxylcoumarin*

3-Hydroxylphenol (11 g) was dissolved in 20 ml 1,4-dioxane followed by the addition of 2 ml concentrated H_2SO_4. Then 13 g (0.1 mol) acetylacetic ether was added dropwise at room temperature. The reaction solution was heated to 60 °C for 6 h. After cooling, white precipitate was separated out. The precipitate was collected, washed with water/ethanol and pure water for several times, then dissolved in 60 ml of 10% NaOH solution. H_2SO_4 solution (5%) was used to neutralize the solution till pH = 4. White product was precipitated and collected as 14 g, yield 75%.

3.2.5. *4-Methyl-7-methoxylcoumarin*

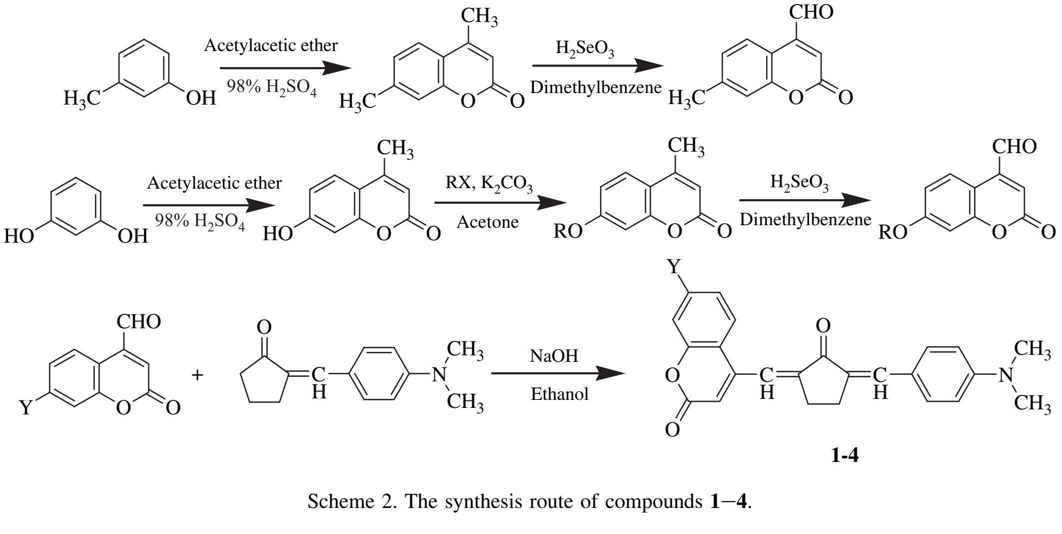
4-Methyl-7-hyroxylcoumarin (3.52 g, 0.02 mol) was dissolved in 50 ml acetone. To it, anhydrous K_2CO_3 (5.5 g, 0.04 mol) was added. The reaction solution was refluxed for 10 min, then 2.9 g (0.02 mol) methyl iodide added, and continuously refluxed for 6 h. The reaction mixture was filtered during heating. White product (3.45 g) was obtained by evaporating off the solvent from the filtrate, yield 90%. ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 7.489$ (d, 1H, $J = 8.79$ Hz), 6.856 (d, 1H, $J = 8.61$ Hz), 6.807 (s, 1H), 6.132 (s, 1H), 3.899 (s, 3H), 2.365 (s, 3H).

3.2.6. *4-Methyl-7-ethoxylcoumarin*

4-Methyl-7-hyroxylcoumarin (3.52 g, 0.02 mol) was dissolved in 50 ml acetone. To it, anhydrous K_2CO_3 (5.5 g, 0.04 mol) was added. The reaction solution was refluxed for 10 min, followed by the addition of 3.1 g (0.02 mol) ethyl iodide, and continuously refluxed for 6 h. The reaction mixture was filtered during heating. White product (3.51 g) was obtained by evaporating off the solvent from the filtrate, yield 86%. ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 7.487$ (d, 1H, $J = 8.81$ Hz), 6.854 (d, 1H, $J = 8.71$ Hz), 6.802 (s, 1H), 6.132 (s, 1H), 4.114 (q, 2H, $J = 7.01$ Hz), 2.334 (s, 3H), 1.458 (t, 3H, $J = 6.98$ Hz).

3.2.7. *4-Methyl-7-butanoxycoumarin*

4-Methyl-7-hydroxylcoumarin (3.52 g, 0.02 mol) was dissolved in 50 ml acetone. To it, anhydrous K_2CO_3 (5.5 g, 0.04 mol) was added. The reaction solution was refluxed for 10 min, followed by the addition of 2.7 g (0.02 mol) of bromobutane, and continuously refluxed for 6 h. The reaction mixture was filtered during heating. White product (4.1 g) was obtained by evaporating off the solvent from the filtrate, yield 89%. ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 7.487$ (d, 1H, $J = 8.81$ Hz), 6.856 (d, 1H, $J = 8.79$ Hz), 6.808 (s, 1H), 6.133 (s, 1H), 4.022 (t, 2H, $J = 6.33$ Hz), 2.401 (s, 3H), 1.806 (m, 2H, $J = 6.84$ Hz), 1.526 (m, 2H, $J = 7.14$ Hz), 0.992 (t, 3H, $J = 7.28$ Hz).



1-4

Scheme 2. The synthesis route of compounds **1–4**.

3.2.8. 4-Formyl-7-methoxylcoumarin

4-Methyl-7-methoxylcoumarin (3.8 g, 0.02 mol) was dissolved in 50 ml dimethylbenzene during heating. To it, seleninic acid (3.8 g, 0.027 mol) was added. The reaction solution was refluxed for 20 h, and then filtered during heating to recycle Selenium. After the filtrate was cooled, 3.7 g of yellow crystal product was separated out, yield 90%. ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 10.080$ (s, 1H), 8.502 (d, 1H, $J = 9$ Hz), 6.944 (d, 1H, $J = 9.06$ Hz), 6.878 (s, 1H), 6.723 (s, 1H), 3.905 (s, 3H).

4-Formyl-7-ethoxylcoumarin and 4-formyl-7-butanoxylcoumarin could be prepared according to the same method.

3.2.9. Compounds **2–4**

2-(4-Dimethylamino-benzylidene)-cyclopentanone (0.21 g, 1 mmol) and 0.19 g (1 mmol) 4-formyl-7-methoxylcoumain were dissolved in 10 ml ethanol and 3 ml dimethylbenzene during heating. After 0.03 g NaOH was added, the reaction solution became red colour immediately and some precipitate was produced. The mixture was refluxed for 1 h, and then cooled to room temperature. The red precipitate was collected and recrystallized with dimethylbenzene. Pure product (2 g) was obtained, yield 38%. ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 7.704$ (d, 1H), 7.668 (s, 1H), 7.630 (s, 1H), 7.562 (d, 2H, $J = 8.67$ Hz), 6.904 (d, 1H), 6.870 (s, 1H), 6.789 (d, 2H, $J = 8.37$ Hz), 6.373 (s, 1H), 3.896 (s, 3H), 3.083 (s, 6H), 3.052 (s, 4H).

Compounds **3** (yield 35%) and **4** (yield 38%) were prepared according to the same method. Compound **3**, ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 7.697$ (d, 1H), 7.668 (s, 1H), 7.632 (s, 1H), 7.563 (d, 2H, $J = 8.79$ Hz), 6.884 (d, 1H), 6.853 (s, 1H), 6.792 (d, 2H, $J = 8.46$ Hz), 6.367 (s, 1H), 4.114 (q, 2H, $J = 7.08$ Hz), 3.084 (s, 6H), 3.053 (s, 4H), 1.469 (t, 3H, $J = 6.9$ Hz). Compound **4**, ^{1}H NMR ($CDCl_3$): 300 MHz, $\delta = 7.696$ (d, 1H), 7.665 (s, 1H), 7.630 (s, 1H), 7.562 (d, 2H, $J = 8.81$ Hz), 6.883 (d, 1H), 6.852 (s, 1H), 6.791 (d, 2H, $J = 8.52$ Hz), 6.366 (s, 1H), 4.044 (t, 2H), 3.082 (s, 6H), 3.051 (s, 4H), 1.816 (m, 2H), 1.532 (m, 2H), 1.001 (t, 3H).

3.3. Measurement of the TPA cross-section of compounds

The TPA cross-section of compounds was measured by nonlinear absorption method [14] with femtosecond laser pulses. Samples were dissolved in chloroform at concentrations of 1×10^{-2} mol/l. The incident intensity (I_0) and the transmitted intensity (I) were recorded and their relationship could be expressed as the following function:

$$I(L) = [\ln(1 + I_0 L\beta)]/L\beta \qquad (1)$$

where, L is the thickness of the solution and β is the TPA coefficient of the solution.

TPA cross-section σ_2' (in units of cm^4/GW) or σ_2 (in units of cm^4 s/photon or GM, 1 GM $= 10^{-50}$ cm^4 s/photon) has relationship with β as follows:

$$\beta = \sigma_2' N_0 = \sigma_2' N_A C \times 10^{-3} \text{ and } \sigma_2 = h\nu\sigma_2' \qquad (2)$$

where, N_0 is the molecular density of TPA compound (in units of 1/cm^3), C is the concentration of the TPA compound in the solution (in units of mol/L), and hν is the energy of an incident photon.

3.4. The photoreaction kinetics of compounds

The light source for photobleaching was 400 W Xenon lamps, light below 300 nm was filtered off with Pyrex glass and the intensity of irradiation was 25 mW/cm^2. The dye/coinitiator (iodonium salts or *o*-Cl-hexaarylbisimidazoles (HABI)) solution was bubbled with high purity nitrogen for 20 min before exposing to light. The change of the absorption spectra of the solution with irradiation time was recorded on Jasco 50 UV–vis spectrometer.

3.5. The photopolymerization initiating efficiency of compounds

The photocurable resin films were prepared by coating the mixed resin solution containing cellulose acetate butyrate (CAB)/2-phenoxyethyl acrylate (POEA)/*N*-vinyl carbzole (NVC) as monomers, chloroform/methanol as solvents, compounds **1–4** as sensitizers and HABI or iodonium salts as coinitiator onto KBr substrates and dried in vacuum oven for 3 h to evaporate all solvents. The film thickness was controlled to be about 10 μm. The light source was the same as used for photobleaching. The change of the absorption peak at 810 cm^{-1} of the resin film following irradiation time was recorded on Bio-Rad FTS 165 spectrometer.

Acknowledgement

We acknowledge the financial support from the National Science Foundation of China (50173031 and 50403030).

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