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Study of the absorption and emission spectroscopy of "A–B" type photosensitive compounds including two-photon chromophore and benzophenone moiety

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Abstract

"A–B" type photosensitive compounds including two-photon chromophore and benzophenone moiety have been designed, synthesized and characterized. The UV–vis absorption and fluorescence emission of the compounds have been extensively studied in various solvents. The results show that the absorption of "A–B" type compounds displays obvious double absorption bands, one of which at short-wavelength is related to the benzophenone moiety, the other at long-wavelength is mainly contributed by chromophore. The emission of "A–B" type compounds at 500–700 nm shows an "unexpected" blue-shift comparing with that of the sole chromophore. The photosensitive compounds with amino group display strong emission in apolar solvents and have a low fluorescence quantum yields in polar solvents. In contrast, the compounds without amino group exhibit strong fluorescence emission in polar solvents, and low fluorescence quantum yields in apolar solvents. The fluorescence quantum yields of "A–B" type compounds are higher than those of the sole chromophore. The discoveries suggest that charge redistribution induced by the introduction of benzophenone moiety plays a key role on the absorption and emission spectroscopy. © 2007 Elsevier B.V. All rights reserved.

Keywords: Absorption; Emission; Chromophore; Photoinitiator; Fluorescence quantum yield

1. Introduction

Since the first time realization of two-photon fabrication [1], it has shown an important role in many fields, for instance data storage [1], micro-fabrication of medical device [2], microstructure of hydrogel [3], microstructure of protein [4], DNA loading [5]. As compared to one-photon polymerization, two-photon microfabrication offers many advantages, such as space resolution and deep fabrication [1]. However, the resolution of two-photon fabrication still needs to be further increased for the more extensive application, especially for nanoscale materials fabrication [6].

Till now, three approaches have been established to achieve two-photon polymerization: (1) Free radical for photopolymerization is produced from common UV-photoinitiators via two-photon dye-sensitization. This requires suitable dyes with

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1386-1425/\$ – see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2007.07.064 large two-photon absorption cross-section and high-efficient UV-photoinitiators. When the dyes are excited by two-photon, an intermolecular electron transfer occurs between dyes and photoinitiators, free radicals are then formed, and monomers are initiated. This pathway has been confirmed by several research groups [7-10]. It is convenient because numerous sensitizers and UV-photoinitiators can be chosen from compounds' library. On the other hand, because free radical is produced from two-photon intermolecular electron transfer, the possibility of one to two orders of magnitude improvement of photopolymerization efficiency decreases. (2) Monomer is initiated by two-photon absorption dyes. Marder and co-workers firstly utilized "D- π -A" molecules as two-photon initiators to obtain photopolymer [1], and a substantial number of other researchers have also explored such molecules as two-photon initiators [11–13], and the recent feather article of Marder is especially comprehensive review on the advance of this field [14]. While, the issue of this approach is that the mechanism of two-photon polymerization is not clear [11]. (3) Common UV photoinitiators are directly used as two-photon initiators. This method, of course, is easy to be used. However, two-photon absorption cross-section of UV photoinitiators generally is small and their absorption wavelength is short, consequently, their application future in two-photon polymerization becomes gloomy [15].

In a word, controlling the two-photon polymerization at the molecular level has not been realized. In 2002, Marder and co-workers have covalently attached sulfonium moieties to the two-photon dyes and achieved high-efficient significant twophoton polymerization [16]. It is well known that compounds with sulfonium moieties are typical cationic photoinitiator [17], therefore, the "Marder Molecule" has a "twin" nature, which has an absorption cross-section and is a typical cationic photoinitiator at the same time. The results indicate that it is feasible to increase two-photon polymerization efficiency and achieve the goal of the molecular-based controlling two-photon polymerization through the molecular design and construction. This paper is a part of our endeavour of realization the above target, of which particular interest concentrates on the design and synthesis of "A-B" type compounds including chromophore and common UV photoinitiator, and on the extensive study of their absorption and emission spectroscopy in various solvents. The two-photon chemistry and physics, and more "A-B", "A-2B" and "A-nB" type compounds will be reported soon.

2. Experimental

p-Nitro-phenylacetic acid was purchased from Jiangshu Jinguan Chemical Corp. and further purification by recrystallization from ethanol/methylene chloride before use. *N*-Methyl-*N*-hydroxyethylamino benzaldehyde was a gift from Zhejiang Le'an Chemical Corp. and further purification by recrystallization from benzene/hexane before use. *p*-Hydroxylbenzaldehyde was purchased from Chongqing Yiyao Corp. and used as received. NaH (60% dispersion in mineral oil) was purchased from Chongqing Yiyao Corp. 4-Methylbenzophenone (Scheme 1, compound 1) was a gift from Zhengjiang Zhengdan Chemical Corp. and recrystallization from benzene/cyclohexane before use. *N*-Bromosuccinimide (NBS) was obtained from Chongqing Yiyao Corp. and used as received. 18-Crown-6 was obtained from Zhejiang Xianju Chemical Corp. The organic solvents were purchased from Chongqing Oritental Chemical Corp. and dried using standard laboratory techniques according to methods published [18]. The compounds **2–6** (Scheme 1) were synthesized in our laboratory.

The UV–vis absorption spectra were recorded with a Cintra spectrophotometer. The emission spectra were checked with Shimadzu RF-531PC spectrofluorophotometer. Rodamin 6G in ethanol ($\phi = 0.94$, 1×10^{-5} mol/L [19]) was used as reference to determine the fluorescence quantum yields of the compounds herein. The melting point was determined on a Sichuan University 2X-1 melting point apparatus and was uncorrected. Nuclear magnetic resonance (NMR) was done with a Bruker 500 MHz apparatus with tetramethylsilane (TMS) as internal standard. Element analysis was detected by CE440 elemental analysis meter from Exeter Analytical Inc.

2.1. Synthesis

2.1.1. Compound 2: 4-bromomethyl benzophenone

The compound was synthesized according to a well-known method with modified procedure [20].

2.1.2. Compound 3: p-hydroxyl-p'-nitro-stilbene

The compound was synthesized according to a similar method with modified procedure [21]. Two *p*-nitro-phenylacetic acid (11 mmol) and 1.0 g *p*-hydroxy-benzaldehyde (8 mmol) were mixed fully and 1.04 g (12 mmol) piperidine was added into the mixture. The resulting mixture was heated at 100 °C for 2 h, then at 120 °C for 1 h till a black solid was formed.



Scheme 1. The structure of compounds studied in this paper.

The product 1.5 g (yield: 76%) was obtained as a brown solid after twice recrystallization from ethanol. ¹H NMR: δ , 6.788–6.818 (d, 2H, **3**, **15**), 7.125–7.157 (d, 1H, **6**), 7.373–7.390 (d, 1H, **13**), 7.502–7.515 (d, 2H, **4**, **14**), 8.125–8.179 (d, 4H, **7**, **8**, **10**, **11**), 9.236 (s, 1H, **1**), melting point (196.5–200.5 °C).



(number 1-15 refers to the carbon or oxygen position)

2.1.3. Compound 4:

(p-nitro-stilbene)-(methylenebenzophenone) ether

The compound was synthesized according to Scheme 2. Compounds 2 (1.37 g, 5 mmol) and 3 (1 g, 4 mmol) were dissolved in 0.05 g 18-C-6/1.45 g $K_2CO_3/50$ ml dry acetone solution, the mixture was stirred at room temperature under argon for 24 h. The solid was got rid of solution by filtration and acetone was removed fully by evaporation. The resultant mixture was dissolved in CHCl₃ and washed by water for 3 times. The organic layer was dried with anhydrous sodium sulfate and then concentrated. The product was purified by column chromatography. Further purification was done by twice recrystallization from benzene to yield bright yellow 0.6 g (1.4 mmol, 30% yield) compound **4**. ¹H NMR: δ, 5.122 (s, 1H, **8**), 6.934–6.966 (t, 2H, 6, 22), 6.966-7.139 (q, 2H, 3, 24), 7.405-7.448 (m, 2H, 10, 21), 7.482-7.544 (m, 3H, 16, 17, 18), 7.729-7.782 (m, 6H, **5**, **11**, **15**, **19**, **20**, **23**), 8.125–8.143 (d, 4H, **1**, **2**, **26**, **27**); ¹³C NMR, δ, 70.172, 115.981, 124.863, 127.254, 127.668, 129.043, 129.194, 129.928, 130.233, 130.780, 131.217, 138.006, 138.234, 142.028, 144.855, 147.196, 159.763, 197.267. Melt-



Scheme 2. The synthesis route of compound 4.

ing point (136–137 °C), Anal. Calcd for $C_{28}H_{21}NO_4$: C, 77.23; H, 4.86; N, 3.22; O, 14.70. Found: C, 77.13; H, 4.86; N, 3.23.



(number 1-28 refers to the carbon position)

2.1.4. Compound 5:

p-(N-methyl-N-hydroxyethyl)-p'-nitro-stilbene

2.68 g (14.8 mmol) *p*-nitro-phenylacetic acid and 2.0 g (11.8 mmol) *p*-(*N*-methyl-*N*-hydroxyethyl)-*p*'-nitrobenzaldehyde were mixed fully and 1.5 g piperdine (17.6 mmol) was added into the mixture. The resultant mixture was heated at 100 °C for 2 h, then at 120 °C for 1 h till a black solid was formed. 2.5 g (yield: 71.4%) compound **5** was obtained as a brown solid after twice crystallization from ethanol. ¹H NMR: δ , 2.098 (s, 1H, **7**), 3.049 (s, 1H, **6**), 3.520–3.570 (m, 1H, **8**), 3.803–3.823 (t, 1H, **9**), 6.935–6.968 (d, 2H, **5**, **10**), 7.066–7.172 (q, 2H, **3**, **12**), 7.563–7.581 (d, 2H, **4**, **11**), 8.094–8.165 (d, 4H, **1**, **2**, **13**, **d14**). Melting point (143–146 °C).



(number 1-14 refers to the carbon or oxygen position)

2.1.5. Compound 6: [p-(N-methyl-N-hydroxyethyl)-p'nitro-stilbene]-(methylenebezophone) ether

The compound was synthesized according to Scheme 3. 0.24 g (60%, 10 mmol) NaH was washed by dry cyclohexane twice to remove mineral oil. 2.77 g (10 mmol) compounds 2 and 5 (1.5 g, 5 mmol) were dissolved in NaH/50 ml dry THF, the mixture was stirred at room temperature under argon for 24 h. The solid was got rid of solution by filtration and THF was removed fully by evaporation. The resulting mixture was dissolved in CHCl₃ and washed by water for 3 times. The organic layer was dried with anhydrous sodium sulfate and then concentrated. The product was purified by column chromatography. Further purification was carried out with twice recrystallization from benzene to yield 0.8 g (1.6 mmol) deep red solid of compound **6** (yield 32.3%). ¹H NMR: δ , (3.030, s, 1H, **10**), 3.579–3.602 (t, 1H, **25**), 3.369-3.700 (t, 1H, 26), 4.521 (s, 1H, 11), 6.861-6.893 (d, 2H, 8, 27), 7.107–7.210 (q, 2H, 5, 29), 7.287–7.316 (t, 2H, 12, 23), 7.376-7.410 (m, 3H, 18, 19, 20), 7.480-7.517 (m, 4H, 13, 17, 21, 22), 7.694-7.711 (t, 2H, 7, 28), 8.098-8.116 (d, 2, 3, 30, 31), 13 C NMR: δ , (18.442, 58.472, 68.582, 72.738, 124.160, 126.142, 126.978, 128.293, 128.515, 130.013, 130.272, 132.436, 136.877, 137.606, 196.377). Melting point



Scheme 3. The synthesis route of compound 6.

(110–110.5 °C), Anal. Calcd for $C_{31}H_{28}N_2O_4$: C, 75.59; H, 5.73; N, 5.69; O, 12.29. Found: C, 75.58; H, 5.83; N, 5.65.



(number1-31 refers to the carbon or oxygen position)

3. Results and discussion

3.1. Construction of the compounds 4 and 6

It was demonstrated that p-nitro-stilbene has significant nonlinear optical (NLO) nature [22] and benzophenone is a free radical type photoinitiator [23–26], they were chosen as chromophore and photoinitiator moieties to build the compounds for two-photon polymerization in this paper.

Compound 2, which play a role of the introduction of benzophenone moiety to the chromophore backbone, was obtained from bromide reaction of compound 1 and NBS. Reference compounds 3 and 5 were obtained by condensation reaction of *p*-nitro-phenylacetic acid and benzaldehyde in the presence of piperidine as catalyst at high temperature. Compounds 4 and 6 have been constructed by compound 2 and compounds 3, 5, respectively. The preparation of compound 4 was achieved by Williason reaction of compound 2 and compound 3 in the presence of weak base K_2CO_3 as catalyst, and 18-C-6 as phase transfer reagent. Compound 6 was prepared from compound 2 and compound 5 in the presence of strong base NaH.



Fig. 1. A typical absorption of compounds 1,~5 and 6 in $CH_3CN~(1\times 10^{-5}~mol/L).$

3.2. The UV-vis absorption spectroscopy

As shown in Fig. 1, compound 4 or 6 shows obvious double absorption bands, one of which locates around 225-300 nm, the other is at long-wavelength (350-550 nm). Benzophenone moiety makes major contribution to the short-wavelength absorption band, and the long-wavelength absorption band is related to the absorption of chromophore. The absorption of compound 4 or 6 shows an overlap effect of that of compound 1 and compound 3 or 5, respectively. While, the molar extinction coefficient of compound 6 or 4 at long-wavelength generally is less than that of the sole chromophore, which indicates that the introduction

of benzophenone to the chromophore has an influence on charge distribution of compound **4** or **6**, and the electron transmission process thus is affected.

As compared to compound 3 or 4, the absorption of compound 5 or 6 at long-wavelength shows a red-shift (Fig. 2), which suggests that the long-wavelength absorption is induced by



Fig. 2. A typical absorption of compounds 4 and 6 in CH_2Cl_2 (1 × 10⁻⁵ mol/L).

intramolecular charge transfer (ICT). With a stronger electrondonor group, compound **5** or **6** shows obvious absorption in visible light region till 550 nm. Moreover, compared to apolar solvents, for instance CCl₄ and benzene, the absorption of the four compounds at long-wavelength show obvious red-shift in polar solvent, for example CH₂Cl₂ and CH₃CN. It is further evident that the absorption at long-wavelength is induced from intramolecular charge transfer (ICT).

3.3. The fluorescence spectroscopy

It is interesting to observe that compounds **3** and **4** display obvious emission in polar solvents, for example in CH_2Cl_2 and CH_3CN , while very weak or none emission in apolar solvents, such as in CCl_4 and benzene, at 500–700 nm while excited at 350 nm. In contrast, compounds **5** and **6** display a strong emission in apolar solvents, for example in CCl_4 and benzene, while very weak or none emission in polar solvents, such as in CH_2Cl_2 and CH_3CN , at 500–700 nm when excited at 350 nm as well. A typical example was shown in Fig. 3. The results suggest that stronger intramolecular charge transfer causes the fluorescence quenching of compounds **5** and **6** at 500–700 nm in polar solvents.

A fluorescence quenched and red-shift phenomenon at 500-700 nm was observed with the increasing of CH₂Cl₂ ratio in benzene/CH2Cl2 mixed solvents when compound 6 was excited at 350 nm. In contrast, with the increasing of benzene ratio in benzene/CH2Cl2 mixed solvents, the fluorescence of compound 4 at 500–700 nm was quenched continuously and a blue-shift phenomenon took place when it was excited at 350 nm. On the other hand, no change of the emission band at 360–440 nm was observed with the change of CH₂Cl₂ or benzene ratio in benzene/CH2Cl2 mixed solvents. A typical example was shown in Fig. 4. This suggests that: (1) The emission of compounds 4 and 6 at 500-700 nm is related to the intramolecular charge transfer. As compared to compound 4, compound 6 has a stronger intramolecular charge transfer nature, therefore, only in apolar solvents it can have a high fluorescence yield at 500–700 nm. (2) The emission band at 360-440 nm is produced from a similar excited state of compounds 4 and 6, respectively.

As shown in Fig. 5, the emission of compounds 5 and 6 display remarkable red-shift (approximately 100 nm) comparing



Fig. 3. The typical fluorescence spectra of compound **4** in benzene and acetonitrile (Ex: 350 nm, silt width—Ex: 5 nm, Em: 5 nm, $C = 1 \times 10^{-5}$ mol/L).



Fig. 4. The fluorescence quenching of compound **6** with the increasing CH₂Cl₂ ratio to CH₂Cl₂/benzene mixed solvents (Ex: 350 nm, slit width—Ex: 5 nm, Em: 5 nm, $C = 1 \times 10^{-5}$ mol/L).

with those of compounds **3** and **4** in modest polar solvents, such as in tetrahydrofuran or ethyl acetate, when excited at 350 nm. This gives further solid evidence that compounds **5** and **6** have a nature of a stronger intramolecular charge transfer because of the better electron-donor group. As compared to compounds **3** and **5**, an "unexpected" blue-shift of emission at 500–700 nm of compounds **4** and **6** is observed. A charge redistribution induced by the introduction of benzophenone moiety to chromophore causes "the abnormal" emission behavior [27].

3.4. The fluorescence quantum yields

In order to further assess the effect of benzophenone moiety on the emission of compounds 4 and 6, the fluorescence quantum yields of compounds 4, 6 and reference compounds 3, 5 have been studied. As shown in Table 1, compounds 3, 4 have low fluorescence quantum yields in apolar solvents and high fluorescence quantum yields in polar solvents. On the contrary, compounds 5 and 6 display strong fluorescence emission in apolar solvents, and low fluorescence quantum yields in polar solvents. As discussed above, "the contrary" is related to the intramolecular charge transfer.

For compounds **3** and **4**, the emission at 360-500 nm makes a major contribution to the fluorescence quantum yields in apolar solvents when they are excited at 350 nm. And for compounds **5** and **6**, the major contribution to the fluorescence quantum yield



Fig. 5. The fluorescence spectra of compounds **3–6** in tetrahydrofuran (Ex: 350 nm, for convenient observation, the slit width of excitation and emission was not the same, $C = 1 \times 10^{-5}$ mol/L).

Table 1	
The fluorescence quantum	yields of the compounds $3-6$

Solvents	Compound 3	Compound 4	Compound 5	Compound 6
Carbon tetrachloride	6.86×10^{-4}	2.96×10^{-3}	0.15	0.12
Benzene	3.86×10^{-3}	6.82×10^{-3}	0.18	0.36
Ethyl acetate	0.091	0.023	0.032	0.054
Tetrahydrofuran	0.17	0.034	0.017	0.056
Methylene chloride	0.12	0.20	0.013	0.019
Acetonitrile	0.03	0.03	$6.4 imes 10^{-4}$	$2.6 imes 10^{-4}$

also comes from the emission at 360-440 nm in polar solvents when they are excited at 350 nm. The emission at 500-700 nm makes a very minor contribution to the fluorescence quantum yields of these compounds at the above situation. It is interesting to observe that the emission at 360-440 nm of these compounds always can be detected in solvents, despite sometimes it is very small comparing with the emission at 360-440 nm. This further demonstrates that the emission band at 360-440 nm is produced from the similar excited state of all compounds. Seen from the chemical structures, this may be related to the *p*-nitro-benzene moiety.

Moreover, the fluorescence yields of compounds 4 and 6 (compound 4: $\phi = 0.20$ in CH₂Cl₂, compound 6: $\phi = 0.36$ in benzene) are higher than those of compounds 3 and 5 (compound 3: $\phi = 0.17$ in THF, compound 5: $\phi = 0.18$ in benzene). It is well known that benzophenone is a typical triplet molecule with an intersystem crossing (ISC) efficiency of 100% [23], and displays typical spectroscopy of ketone [28]. While, as compared to compounds 3 and 5, an occurring of charge redistribution of compounds 4 and 6 induced by the introduction of benzophenone moiety causes the reduction of the molar extinction coefficients, an "unexpected" blue-shift of fluorescence emission, and an "abnormal" increasing of fluorescence quantum yields.

4. Conclusions

In conclusions, we present the design, synthesis and characterization of some "A–B" type photosensitive compounds. The absorption and emission spectroscopy has been studied in various solvents. The discoveries demonstrate that the intramolecular charge transfer has not only an effect on the maximum absorption and emission wavelength, but on the fluorescence quantum yields. The results confirm that the charge redistribution induced by the introduction of benzophenone moiety has a close internal relationship with the absorption and emission spectroscopy of "A–B" type photosensitive compounds.

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