

Synthesis, Crystal, Absorption and Fluorescence Spectroscopy of Nitro-Stilbene Derivatives with Benzophenones

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Abstract In this paper, we have presented a range of new nitro-stilbene derivatives with benzophenones via ether or ester bridged bond. These nitro-stilbene derivatives with benzophenones have been conveniently obtained by condensation reaction. The linked benzophenones were efficiently introduced to nitro-stilbene dyes. The structures of these compounds have been characterized with NMR and element analysis. The single crystals of two target compounds (**11** and **12**) have been obtained, and their X-ray crystallographic data have been determined and discussed. Remarkably different absorption and fluorescence spectroscopy was observed for nitro-stilbene derivatives with benzophenones via different linked bonds. The results show that electron-donating or electron withdrawing bridged bonds have significant influence on the absorption and fluorescence spectroscopy, which makes it possible for the development of ideal nitro-stilbene dyes with benzophenones through chemical strategy.

Keywords Synthesis · Single crystal · Nitro-stilbene · Benzophenone · Absorption spectroscopy · Fluorescence spectroscopy

Introduction

In recent years, development of novel organic dyes with different luminescent characteristics has attracted considerable attention, since these compounds can be applied

widely in many fields such as material science and biomedical fields [1–6]. As a result, the study of influence of chemical structures on the absorption and emission spectroscopy characteristics of organic dyes has become a research subject intensively studied in photochemistry and photophysics [7–10]. The chemical structures have been shown to have a strong interrelationship with the absorption and fluorescence spectroscopy of dyes. For instance, intersystem crossing from excited singlet state to triplet state of dyes can be increased by heavy atoms [11, 12], and this has been employed to produce singlet oxygen by one or two-photon dye-sensitization [13–15]. Marder and coworkers have reported that bis(styryl)benzene derivatives with donor- π -donor donor-acceptor-donor, and acceptor-donor-acceptor structural motifs exhibit exceptionally large multi-photon effects [16, 17]. It was demonstrated that photoinduced intramolecular electron transfer is a useful approach on the quenching fluorescence of cyanine dye [18–21]. The formation of intramolecular nonfluorescent ground-state complexes causes the quenching of fluorescence of dyes [22, 23]. Geddes and coauthor have proposed and demonstrated metal-assisted approach on the enhancement of fluorescence quantum yields of dyes [24, 25].

It is well-known that benzophenone is widely used in biomedical and material fields [26–31], and nitro-stilbene dyes have non-linear optical characteristics [32, 33]. Recently, we are interesting in developing new nitro-stilbene dyes with benzophenones which have great potential as multi-photon materials, laser dyes and biomedical reagents. Of its particular interest is if we can control their luminescent characteristics of nitro-stilbene dyes with benzophenones through chemical strategy. Very few comparable investigations on the synthesis and spectroscopy properties of nitro-stilbene dye-linked benzophenone compounds with different linked bonds have been performed.

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Furthermore, to our best knowledge, there is no report on the single crystals of nitro-stilbene dye-linked benzophenone compounds. In this paper, we described the design and synthesis of a series of nitro-stilbene dyes with benzophenones. Two single crystals of nitro-stilbene dyes with benzophenones were prepared and their X-ray crystallography was analyzed and discussed. In order to investigate the effects of bridged bonds on the photo-physical properties of nitro-stilbene derivatives with benzophenone, the absorption and fluorescence spectroscopy of the model and target compounds was investigated in various solvents.

Experimental

Reagents

p-Nitro-phenylacetic acid was purchased from Jiangsu Jinguang Chemical Corp. and further purification by recrystallization from ethanol/methylene chloride before use. 2-Benzoylbenzoic acid was a present from Zhejiang Shengxiao Corp. The organic solvents were purchased from Chongqing Oriental Chemical Corp. and dried using standard laboratory techniques according to published methods [34]. Other reagents were purchased from Chongqing Yiyao Corp. and used without further purification. The compounds **2**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11** and **12** (Fig. 1) were synthesized in our laboratory.

Instruments

The UV/visible absorption spectra were recorded with a Cintra spectrophotometer. The emission spectra were checked with uncorrected for detector response by Shimadzu RF-531PC spectrofluorophotonmeter. Rodamin 6G in ethanol ($\Phi=0.94$, 1×10^{-5} mol/l [35]) was used as reference to determine the fluorescence quantum yields of the compounds. The melting point was determined using an uncorrected Sichuan University 2X-1 melting point apparatus. Nuclear magnetic resonance (NMR) was done at room temperature with a Bruker 500 MHz apparatus with tetramethylsilane (TMS) as internal standard and CDCl_3 as solvent. Element analysis was determined with CE440 elemental analysis meter of Exeter Analytical Inc.

The fluorescence quantum yields of the compounds in solvents with different polarities are measured based on the following equation [36, 37]:

$$\Phi_f = \Phi_f^0 \frac{n_0^2 A^0 \int I_f(\lambda_f) d\lambda_f}{n^2 A \int I_f^0(\lambda_f) d\lambda_f}$$

where n_0 and n are the refractive indices of the solvents, A^0 and A are the absorption at excited wavelength, Φ_f and Φ_f^0

are the quantum yields, and the integrals denote the area of the fluorescence bands for the reference and sample, respectively.

Synthesis

Cautious: thionyl chloride and pyridine must be redistilled before the reaction Unless otherwise noted, all operations were carried out under a dry, oxygen-free argon atmosphere.

In this paper, target compounds **8** and **9** were prepared according to the strategy listed as Fig. 2a and b respectively. Compounds **10** and **11** were synthesized Fig. 2c and d respectively.

1. Compound **2**: 4-bromomethyl benzophenone

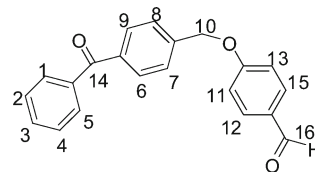
The compound was synthesized according to a well-known method with modified procedure [38].

2. Compound **4**, 2-benzoylbenzoic acetic chloride

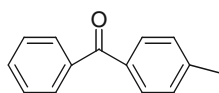
Redistilled thionyl chloride (11 ml; 0.15 mol) was dissolved in dry benzene, and the mixture was dropped gradually into 2.0 g 2-benzoylbenzoic acid (9 mmol) in an ice bath. The reactant mixture was kept stirring at refluxing for about 6 h. The excessive thionyl chloride and solvent were removed by vacuum distillation. The final product 2.08 g (yield: 95%) was used in next step without further purification.

3. Compound **5**: (4-benzophenemethoxyl)-benzaldehyde

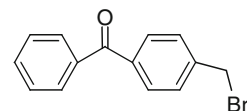
4-Hydroxy-benzaldehyde (1.22 g, 10 mmol) and compound **2** (3.3 g, 12.5 mmol) were dissolved in 0.03 g 18-C-6/ K_2CO_3 (1.72 g, 12.5 mmol)/50 ml dry acetone solution. The mixture was stirred at room temperature under argon for 24 h. The solid was removed by filtration, and the solvent as removed fully by evaporation. The resultant mixture was dissolved in CHCl_3 and washed by water for three times. The organic layer was collected and dried with anhydrous sodium sulfate and then concentrated. The compound **5** was purified by column chromatography. The light yellow solid product 1.64 g (yield: 51.8%) was obtained.



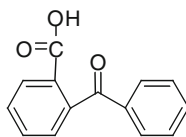
$^1\text{H-NMR}$: δ , 5.168 (d, 2H, 10), 6.572–6.598 (d, 2H, 11,13), 7.443–7.456 (d, 2H, 7, 8), 7.475–7.492 (d, 2H, 2,

Fig. 1 The chemical structures of the compounds in this paper

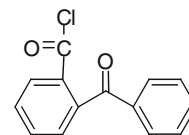
compound 1



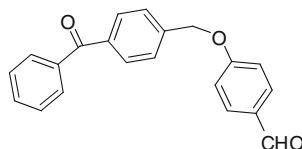
compound 2



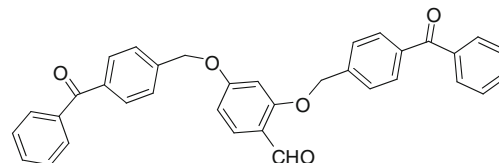
compound 3



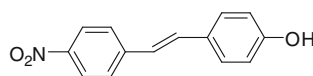
compound 4



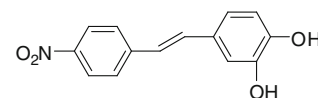
compound 5



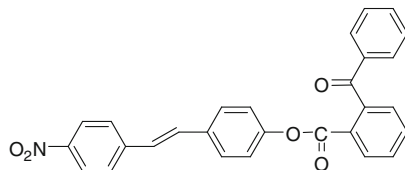
compound 6



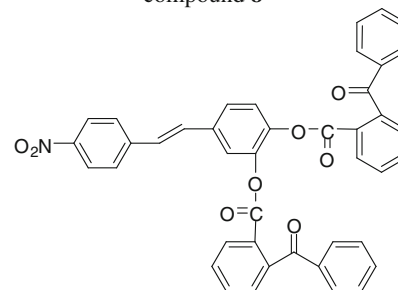
compound 7



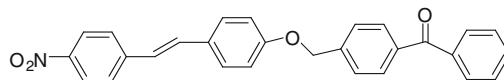
compound 8



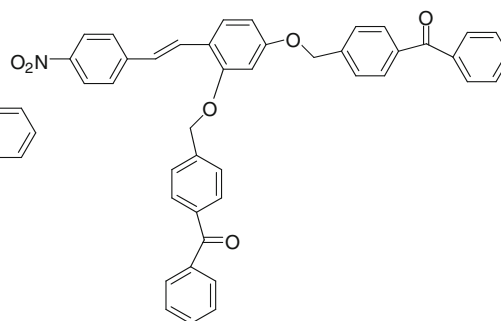
compound 9



compound 10



compound 11



compound 12

4), 7.521–7.529 (t, 1H, 3), 7.560–7.579 (d, 2H, 12, 15), 7.751–7.760 (d, 2H, 6, 9), 7.793–7.828 (d, 2H, 1, 5), 10.341 (s, 1H, 16). Anal. calcd for $C_{12}H_{21}O_3$, C, 79.73, H, 5.10, O, 15.17, found: C, 78.62, H, 4.93.

4. Compound 6: 2, 4-dibenzophenonemethoxyl-benzaldehyde

2,4-Hydroxy-benzaldehyde (1 g, 7.2 mmol) and compound 2 (7.9 g, 29.6 mmol) were dissolved in 0.05 g 18-C-

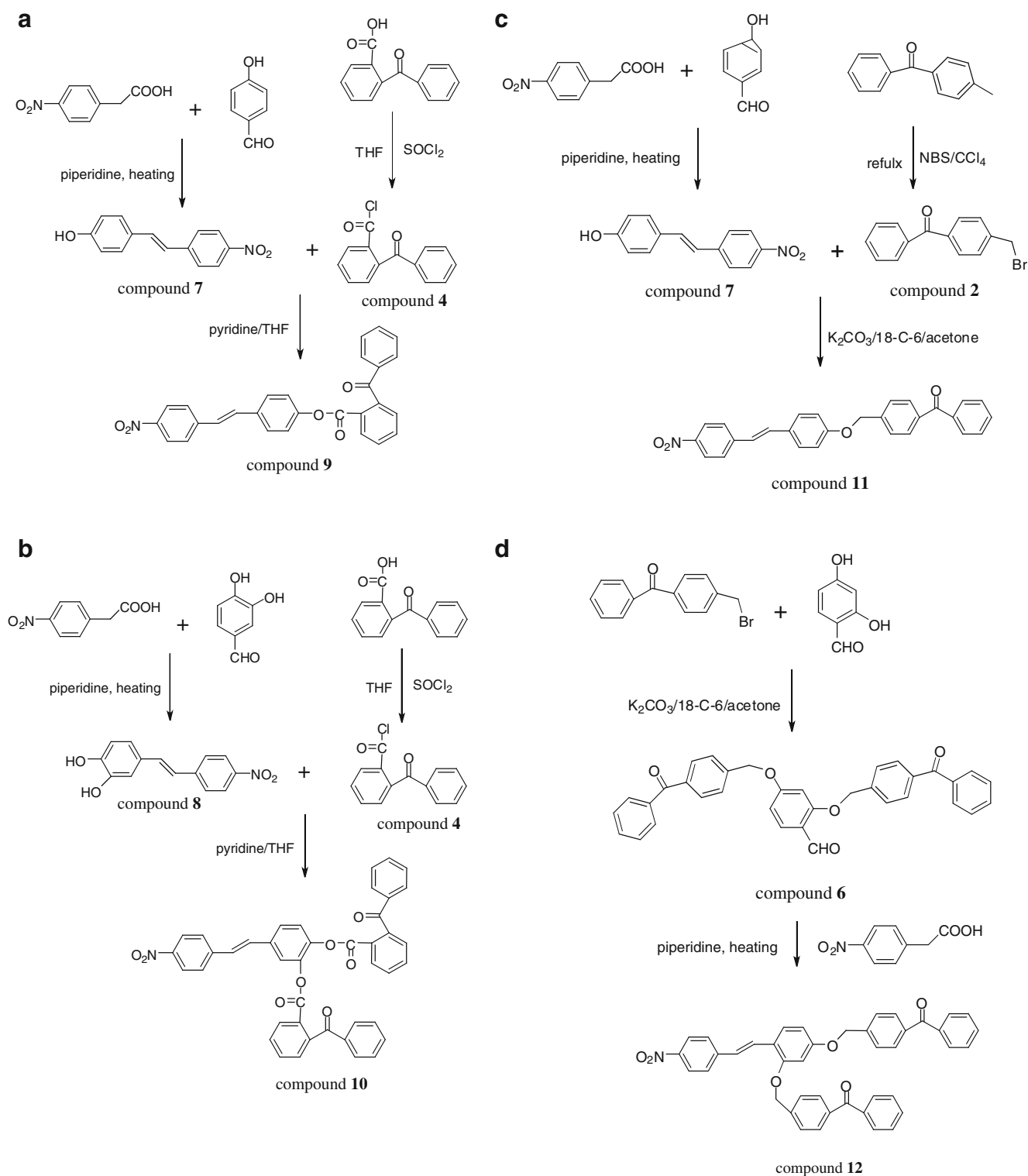
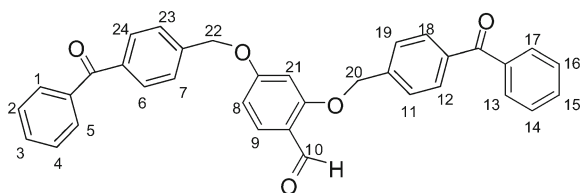


Fig. 2 **a** Synthesis route of compound 9. **b** Synthesis route of compound 10. **c** Synthesis route of compound 11. **d** Synthesis route of compound 12

6/ K_2CO_3 (4.08 g, 29.6 mmol)/50 ml dry acetone solution, the mixture was stirred at room temperature under argon for 24 h. The solid was removed by filtration, and the solvent was removed fully by evaporation. The resultant

mixture was dissolved in $CHCl_3$ and washed by water for three times. The organic layer was collected and dried with anhydrous sodium sulfate and then concentrated. The compound 4 was purified by column chromatogra-

phy. The yellow solid product 1.25 g (yield: 33%) was obtained.



(number 1–24 denotes the carbon position)

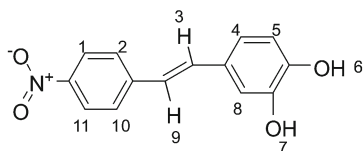
$^1\text{H-NMR}$: δ , 5.166 (d, 4H, 20, 22), 6.576–6.592 (d, 2H, 8, 21), 7.442–7.458 (d, 4H, 7, 11, 19, 23), 7.480–7.496 (d, 4H, 2, 4, 14, 16), 7.511–7.525 (t, 2H, 3, 15), 7.565–7.578 (d, 1H, 9), 7.753–7.763 (d, 4H, 6, 12, 18, 24), 7.791–7.826 (d, 1, 5, 13, 17), 10.340 (s, 1H, 10). Anal. calcd for $\text{C}_{35}\text{H}_{26}\text{O}_5$, C, 79.83, H, 4.98, O, 15.19 found: C, 79.51, H, 4.96.

5. Compound 7, 4'-hydroxyl-4-nitro-stilbene

The compound was prepared according to a published method [39].

6. Compound 8, 3', 4'-dihydroxyl-4-nitro-stilbene

The compound was synthesized according to a similar approach for the synthesis of compound 7. A 1.6-g (8.6 mmol) *p*-nitro-phenylacetic acid and 1.0 g (7.2 mmol) 3,4-hydroxy-benzaldehyde were mixed fully, and 0.7 g (8.6 mmol) piperidine was then 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. The product 1.4 g (yield: 76%) was obtained as a brown solid after twice recrystallization from ethanol.



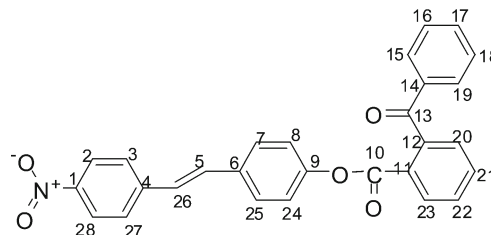
(number 1–11 denotes the carbon position)

$^1\text{H-NMR}$: δ , 6.954–7.309 (d, 1H, 5), 7.059–7.104 (d, 1H, 9), 7.158–7.245 (d, 1H, 3), 7.316–7.325 (d, 1H, 4), 7.315 (s, 1H, 8), 8.173–8.191 (m, 4H, 1, 11, 2, 10), 9.455 (s, 2H, 6, 7), anal. calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_4$, C, 65.37, H, 4.31, N, 5.44, O, 24.88 found: C, 64.82, H, 4.28, N, 5.51. Melting point, (184–187°C).

7. Compound 9, (2-benzoylbenzoic acetic)-(4'-nitro-stilbene)-ester

Compounds 4 (2.08 g, 8.5 mmol) and 7 (1.0 g, 4.15 mmol) were dissolved in dry THF, 1.0 g (12.6 mmol)

dry pyridine was dropped gradually. The reactant mixture was kept stirring at refluxing for about 5 h. The solvent was removed by vacuum distillation. The products were dissolved in methylene chloride and washed with water for three times. The bright yellow final product 0.79 g (1.76 mmol, yield: 42.5%) was obtained by flash chromatography.

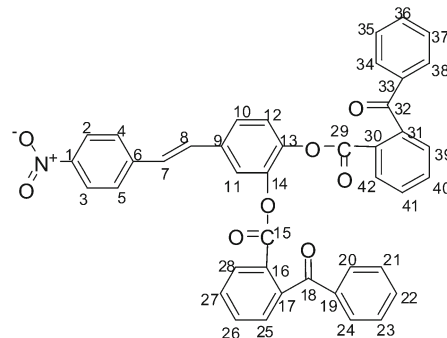


(number 1–28 denotes the carbon position)

$^1\text{H-NMR}$, δ , 6.860–6.877 (d, 1H, 26), 6.933–6.951 (d, 1H, 5), 7.011–7.083 (d, 2H, 8, 24), 7.130–7.224 (t, 2H, 16, 18), 7.324–7.360 (t, 1H, 17), 7.357–7.460 (m, 3H, 15, 19, 22), 7.523–7.539 (d, 2H, 7, 25), 7.546–7.563 (d, 1H, 20), 8.001–8.088 (d, 2H, 3, 27), 8.103–8.175 (d, 2H, 2, 28), 8.191–8.207 (m, 2H, 21, 23). $^{13}\text{C-NMR}$, δ , 122.632, 124.791, 126.561, 127.380, 128.440, 129.014, 129.611, 130.286, 131.598, 132.740, 133.015, 133.888, 134.545, 137.604, 144.512, 147.115, 149.231, 170.679, 197.903. Melt point: 189–189.5°C. Anal. calcd for $\text{C}_{28}\text{H}_{21}\text{NO}_4$, C, 74.82, H, 4.26, N, 3.12, O, 17.80. Found: C, 73.96, H, 4.32, N, 3.14

8. Compound 10, [3',4'-bis (2-benzoylbenzoic acetic)]-(4-nitro-stilbene)-ester

Compounds 4 (4.15 g, 17 mmol) and 8 (1.06 g, 4.15 mmol) were dissolved in THF, 2.0 g (25.2 mmol) dry pyridine was dropped gradually. The reactant mixture was kept stirring at refluxing for about 5 h. The solvent was removed by vacuum distillation. The products were dissolved in methylene chloride and washed with water for three times. The yellow final product 1.45 g (2.2 mmol, yield: 52%) was obtained by flash chromatography.



(number 1–42 denotes the carbon position)

$^1\text{H-NMR}$, δ , 6.929–6.963 (d, 1H, 7), 7.062–7.093 (d, 1H, 8), 7.368–7.384 (m, 2H, 11, 12), 7.399–7.414 (t, 4H, 21, 23,

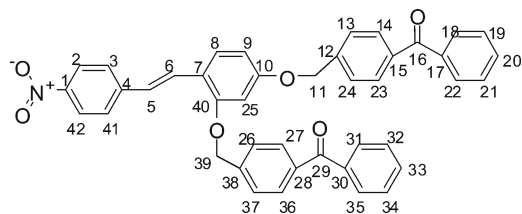
35,37), 7.439–7.451 (t, 2H, 22, 36), 7.538–7.548 (m, 6H, 20, 24, 27, 34, 38, 41), 7.565–7.582 (d, 1H, 10), 7.698–7.710 (d, 2H, 25, 39), 8.093–8.125 (m, 4H, 2, 3, 4, 5), 8.201–8.218 (m, 4H, 26, 28, 40, 42) $^{13}\text{C-NMR}$, δ , 121.789, 124.099, 124.838, 127.515, 127.657, 128.139, 128.399, 128.431, 128.691, 129.206, 130.208, 130.470, 131.508, 131.971, 133.837, 133.921, 135.903, 137.548, 142.849, 143.245, 143.948, 147.640, 164.034, 197.136. Melt point: 135.5–136°C. Anal. calcd for $\text{C}_{42}\text{H}_{27}\text{NO}_8$, C, 74.88, H, 4.04, N, 2.08, O, 19.00. Found: C, 75.16, H, 4.25, N, 1.97

9. Compound **11**: (4*ϕ*-benzopheonemethoxy)-(4-nitro-stilbene)

The compound was prepared according to the method developed in our laboratory [40].

10. Compound **12**: [2',4*ϕ*-bis(benzopheonemethoxy)-(4-nitro-stilbene)

A 0.5-g *p*-nitro-phenylacetic acid (2.76 mmol) and 0.526 g (1 mmol) compound **6** were mixed fully, and 0.24 g (2.76 mmol) piperidine was then 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. The product 0.48 g (yield: 74.8%) was obtained as a yellow solid was obtained as a yellow solid after purification with flash chromatography.



$^1\text{H-NMR}$: δ , 5.249 (d, 4H, 11, 39), 6.636–6.662 (t, 2H, 9, 25), 7.101–7.135 (d, 1H, 5), 7.480–7.495 (d, 4H, 13, 24, 26, 37), 7.510–7.542 (d, 1H, 6), 7.558–7.585 (d, 4H, 19, 21, 32, 34), 7.606–7.628 (d, 2H, 20, 33), 7.807–7.821 (d, 2H, 14, 23, 27, 36), 7.839–7.875 (d, 2H, 19, 22, 31, 35), 8.182–8.199 (m, 5H, 2, 3, 8, 41, 42). $^{13}\text{C-NMR}$, δ , 70.330, 70.691, 101.650, 107.474, 107.863, 124.843, 125.887, 127.226, 127.567, 127.724, 129.035, 129.058, 130.727, 131.178, 133.249, 133.299, 138.055, 141.807, 145.444, 158.127, 160.891, 196.926. Anal. calcd for $\text{C}_{42}\text{H}_{31}\text{NO}_6$, C, 78.12, H, 4.84, N, 2.17, O, 14.87, found: C, 78.83, H, 4.62, N, 2.20. Melting point (128–130°C).

Preparation of single crystals

Growing of single crystals of compounds **11** and **12** is done with slow volatilization of the solvent of their benzene solution at 25°C ($C = 1 \times 10^{-3}$ mol/l).

X-ray crystallography

The crystal structures of the title compounds were determined by X-ray single crystal diffraction. XRD data were collected on a Bruker-AXS CCD area detector equipped with diffractometer with $\text{Mo } K_{\alpha}$ ($\lambda = 0.71073 \text{ \AA}$) at 298 K. A single crystal suitable for determination was mounted inside a glass fiber capillary. The structures of the compounds were solved by direct methods and refined by full-matrix least squares on F^2 . All the hydrogen atoms were added in their calculated positions and all the non-hydrogen atoms were refined with anisotropic temperature factors. SHELXS97 were used to solve the structure and SHELTL were used to refine the structure [41, 42].

Results and discussion

Synthesis

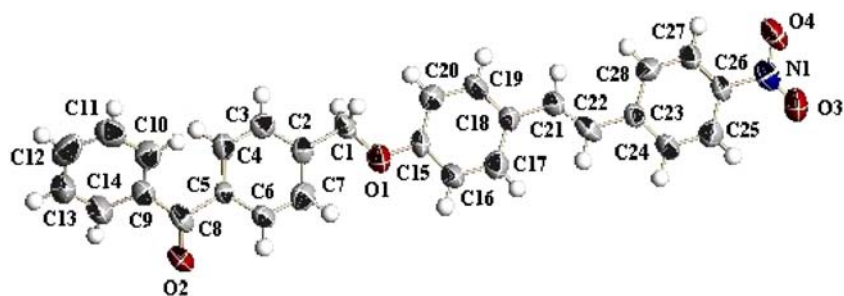
Target compounds **9** to **12** were prepared via condensation reaction, which used a weak base as catalyst. Compounds **9** and **10** were easily synthesized by a similar condensation reaction of acetyl chloride and phenol in dry THF. Compound **12** was obtained from a different synthesis route from compound **11**. We found that normally the product is a coumarin dye, not compound **12** if we follow same strategy. All target compounds with benzophenones were conveniently synthesized in three steps with satisfied yields. Growing of single crystals of compounds **10** and **11** must be kept at a slow rate at room temperature. Otherwise, fine powder or multi crystals are generally formed instead of single crystal.

X-ray crystallography

Compound **11** consists of four benzene rings. As shown in Figs. 3 and 4, the crystal data (see “Supplementary information available”) shows that rings 1–4 are composed of C atoms from C23 to C28, C15 to C20, C2 to C7, C9 to C14, respectively. Rings 1 and 2 are almost coplanar. The dihedral angle between planes 1 and 2 is 4.7°. The ring 3 is slightly deviated from plane 1 (dihedral angle: 18.0°), whereas ring 4 is obviously deviated from ring 1 (dihedral angle: 33.9°). Ring 5 is composed of C atoms from C15A to C20A (atom with additional label A refers to the symmetry operation: $-x, 1-y, -z$). A strong offset face-to-face π – π stacking interaction exists between planes 1 and 5 (perpendicular distance: 3.5 Å, centroid–centroid distance: 3.751 Å; Fig. 4).

In contrast, compound **12** crystallizes in the triclinic system, *P*-1 space group. The crystal data (see “Supplementary information available”) show that the benzene

Fig. 3 ORTEP drawing of the title compound with thermal ellipsoids at 50% probability



rings C9–C14 and C1–C6 are not coplanar (dihedral angle: 15.2°) though the two planes are connected by C=C double bond (Fig. 5). The rings C30–C35 and C37–C42 are deviated from plane C1–C6, and the deviated angles are 44.6° and 29.8° , respectively. The dihedral angles between planes C30–C35 and C37–C42 is 50.5° (Fig. 5). Similarly, the rings C16–C21 and C23–C28 are deviated from plane C1–C6, and the deviated angles are 28.2° and 46.2° , respectively. The dihedral angles between planes C16–C21 and C23–C28 is 56.5° (Fig. 5).

The UV-visible absorption spectroscopy

Typical UV/visible absorption spectroscopy of compounds **8**, **10** and **12** in CH_2Cl_2 was shown as Fig. 6. It clearly shows that compounds **10** and **12** exhibit obvious dual UV/visible absorption bands. On the other hand, we observed that compounds **5** and **6** only show absorption spectral characteristics of benzophenone part. Therefore, it is confirmed that the short wavelength absorption band around 250 nm of compounds **9** to **12** should mainly arise from benzophenone part, and the long-wavelength absorption is from nitro-stilbene part. As compared with compound **8**, the maximal absorption wavelength of compound **10** display obvious hypsochromic shift. While, compound **12** shows some hypsochromic shift.

Some spectral data of compounds **7**, **8**, **9**, **10**, **12** in different polar solvents were presented in Table 1. As shown in Table 1, the maximal wavelength of compounds **9**, **10** and **12** shows much difference in various solvents. This suggests that the bridged bond has an influence on the absorption spectroscopy of nitro-stilbene derivatives. Ester bridged bond leads to a hypsochromic shift of the long-wavelength absorption of nitro-stilbene derivatives. Fur-

thermore, two linked ester bonds induce a more hypsochromic shift. In contrast, two bridged ether bonds lead to a bathochromic shift of the long-wavelength absorption of nitro-stilbene derivatives. For instance, comparing with the maximal absorption wavelength of compounds **8** in CH_2Cl_2 , compound **9** exhibits approximate 30 nm hypsochromic shift, and compound **10** shows 44 nm hypsochromic shift, and compound **12** displays 8 nm bathochromic shift. The results suggest that the maximal absorption wavelength of nitro-stilbene derivatives with benzophenone can be medicated by linked bonds.

When nitro-stilbene is connected with benzophenones through ester bridged bond, intramolecular charge transfer is diminished due to electron deficiency of the electron-withdrawing effect of benzoyl ester groups. In comparison, owing to the electron-donating of the phenyl methoxyl group, intramolecular charge transfer is enhanced while nitro-stilbene is connected with benzophenones through ether linkage bond. As a consequence, this arrangement shows dramatic different effects on the absorption spectroscopy of nitro-stilbene with benzophenones. The maximal absorption wavelength of compounds **9** and **10** does not display obvious shift in different polar solvents due to their weak intramolecular charge transfer. In contrast, the maximal absorption wavelength of compounds **12** exhibits bathochromic shift with the increasing of polarity of solvents. The molar extinction coefficients of long-wavelength absorption of compounds **9** to **12** are smaller than those of compounds **7** and **8** in various solvents. The results indicate that the electron transmission process of nitro-stilbene is affected by the substituents groups.

The fluorescence spectroscopy and the fluorescence quantum yields

Generally, compounds **7** to **12** exhibits dual fluorescence emission bands as excited at 350 nm. The fluorescence band at 370–450 nm is found for compounds **7** to **12** in various solvents, but it is extremely weak. The other fluorescence band at 500–700 nm is observed for compounds **7** to **12** in some conditions. A typical change of fluorescence emission of compound **9** in a binary solvents

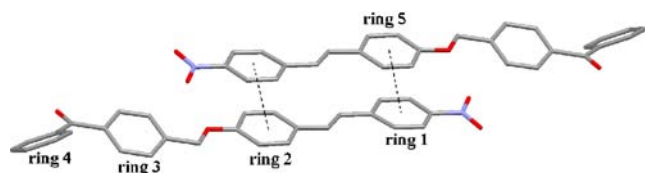
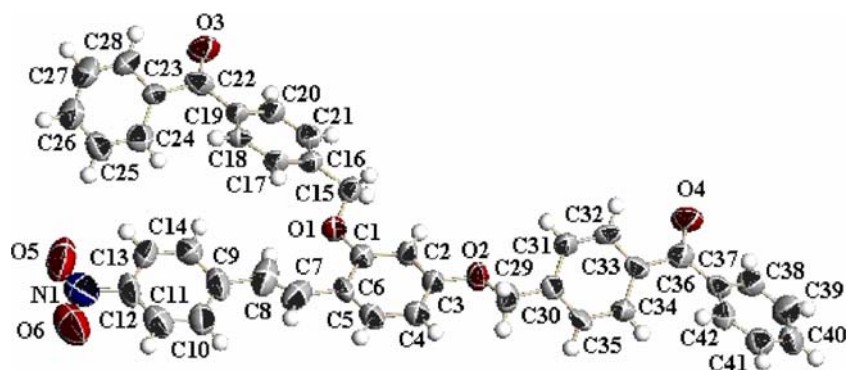


Fig. 4 The π - π stacking interactions in the title compound (H atoms omitted for clarity)

Fig. 5 ORTEP drawing of compound **6** with thermal ellipsoids at 50% probability



is shown in Fig. 7. It shows that small fluorescence band from 370–450 nm does not display remarkable change, but in contrast, the intensity and maximal emission wavelength at 500–700 nm exhibits changes gradually with the increasing of benzene. Similar phenomena were observed for compounds **7** to **12** in some binary solvents. This shows that maximal fluorescence wavelength (500–700) has a large dependence on the polarity of solvents, suggesting that the fluorescence is caused by intramolecular charge transfer.

(In order to conveniently observe the fluorescence spectroscopy shape and maximal emission wavelength, the slit widths for the survey of fluorescence spectroscopy were not kept same. For compound **10** in CH_2Cl_2 and CH_3CN , slit width: Ex: 10 nm, Em: 10 nm; for compounds **9** and **12** in CH_2Cl_2 , slit width: Ex: 5 nm, Em: 3 nm; for compounds **9** and **12** in CH_3CN , slit width: Ex: 5 nm, Em: 5 nm)

The bridged bond shows significant influence on the fluorescence emission spectroscopy of nitro-stilbene derivatives as well. Typical fluorescence spectroscopy of compounds **9**, **10** and **12** in CH_2Cl_2 and CH_3CN as excited at 350 nm was shown in Fig. 8. We found that only in strong

polar solvent CH_3CN , compound **10** displays weak fluorescence emission at long-wavelength region (500–700 nm), and its maximal emission wavelength show remarkable blue-shift to that of compound **9** in CH_3CN . Compound **9** shows fluorescence emission at long-wavelength region (500–700 nm) in CH_2Cl_2 and CH_3CN , and its maximal emission wavelength in CH_3CN does not display obvious red shift to that in CH_2Cl_2 , though their polarity is different. In contrast, compound **12** displays strong fluorescence emission at long-wavelength region (500–700 nm) in CH_2Cl_2 and CH_3CN , and its maximal emission wavelength in CH_3CN display obvious red shift to that in CH_2Cl_2 . Furthermore, the maximal fluorescence wavelength of compound **12** at long-wavelength region (500–700 nm) shows remarkable red-shift to that of compound **10** in CH_3CN . In modest solvents such as in THF, compounds **9** and **10** display very weak fluorescence emission at 370–450 nm as excited at 350 nm. While, compounds **11** and **12** show strong fluorescence emission at 500–700 nm as excited at 350 nm in various modest and strong polar solvents, and their maximal emission wavelength displays remarkable red-shift with the increasing of polarity. A typical comparisons of fluorescence spectroscopy

Fig. 6 Typical absorption spectroscopy of compounds **1**, **8**, **10** and **12** in CH_2Cl_2

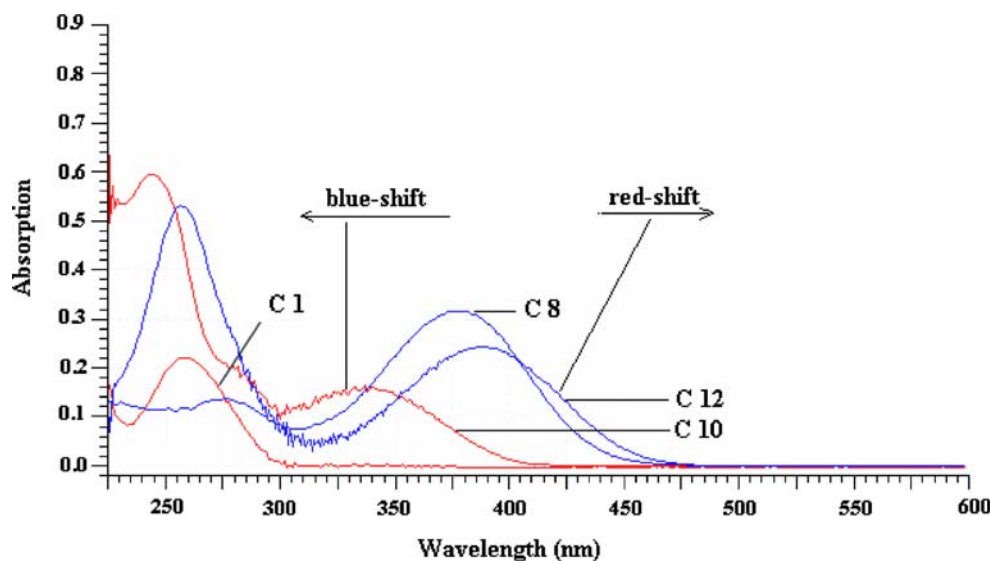


Table 1 Some spectral data of compounds **7**, **8**, **9**, **10**, **12** in different polar solvents

Compounds	Benzene		CH ₂ Cl ₂		CH ₃ CN	
	λ_{\max}	ϵ	λ_{\max}	ϵ	λ_{\max}	ϵ
7	359	0.183	372	0.331	375	0.319
8	371	0.220	377	0.318	378	0.334
9	345	0.111	347	0.162	349	0.171
10	332	0.120	333	0.160	333	0.163
12	372	0.119	385	0.244	386	0.242

$\epsilon \times 10^5$ l/mol cm, λ_{\max} nm

py of compound **10** and compound **12** in THF was shown in Fig. 9. However, compounds **5** and **6** do not show any fluorescence emission as excited at 350 nm in various solvents. The results suggest: (1) the long-wavelength fluorescence emission of nitro-stilbene derivatives is produced by intramolecular charge transfer, (2) intramolecular charge transfer of nitro-stilbene derivatives with electron-donating group (phenyl methoxyl group) is much stronger than that of the derivatives with electron-withdrawing group (benzoyl ester group).

Electron-donating group or electron-withdrawing group of nitro-stilbene derivatives has effects not only on the fluorescence emission wavelength (fluorescence spectroscopy shape), but on the intensity of the fluorescence emission. Table 2 listed some fluorescence quantum yields of nitro-stilbene derivatives in various solvents. Nitro-stilbene derivatives with electron-withdrawing benzoyl ester group have quite small fluorescence quantum yields. The fluorescence quantum yields of compounds **9** and **10** in CH₂Cl₂ and CH₃CN are higher than those in modest and

low polar solvents, which is due to more emission induced by intramolecular charge transfer. In contrast, nitro-stilbene derivatives with electron-donating phenyl methoxyl group have very high fluorescence quantum yields in various solvents. Compound **12** has a higher fluorescence quantum yield in modest polar such as solvent THF than in CH₂Cl₂ and CH₃CN. This is most probably due to non-luminescence TICT (twisted intramolecular charge transfer) state of such a “D-A” compound caused by strong intramolecular charge transfer in CH₂Cl₂ and CH₃CN [44]. In fact, similar observation was found for compounds **7** and **8** (typical “D- π -A” compounds). Seen from Table 2, the fluorescence quantum yields of compounds **9** and **10** are smaller than those of compound **8**, and much smaller than those of compound **12**. The data indicate that: (1) D- π -A structures exist in compounds **7** and **8** with electron-withdraw group (NO₂) and electron-donating group (OH). When compounds **7** and **8** are connected with benzophenones through benzoyl ester bridged bond, the D- π -A structures change to A- π -A structures due to strong electron-withdraw effect of ester group, resulting in much diminution of the extent of intramolecular charge transfer. This causes not only the blue-shift of long-wavelength absorption and fluorescence emission of compounds **9** and **10**, but remarkable small fluorescence quantum yields in various solvents. In comparison, when compounds **7** and **8** are connected with benzophenones through phenyl methoxyl linked bond, the weak D- π -A structures (relative weak electron-donating OH group) change to strong D- π -A structures due to strong electron-donating effect of phenyl methoxyl group. This leads to not only red-shift of long-wavelength absorption and fluorescence emission of compounds **11** and **12**, but dramatically increasing the fluorescence quantum yields in

Fig. 7 The changes of fluorescence of compound **9** with the increasing benzene ratio to CH₂Cl₂/benzene binary solvents. (Ex: 350 nm, slit width: Ex: 5 nm, Em: 5 nm, C=1 \times 10⁻⁵ mol/l)

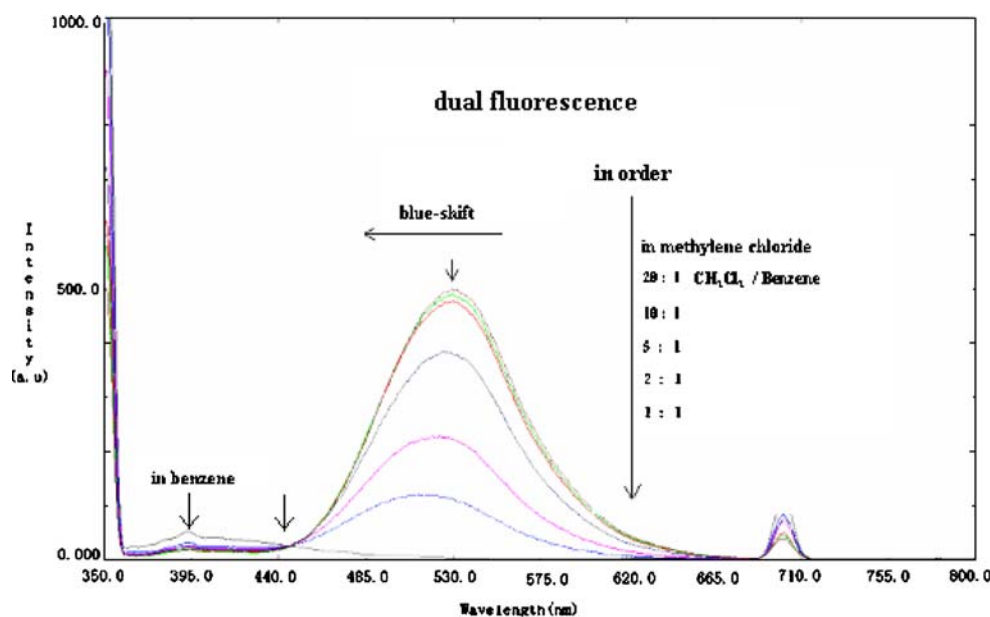
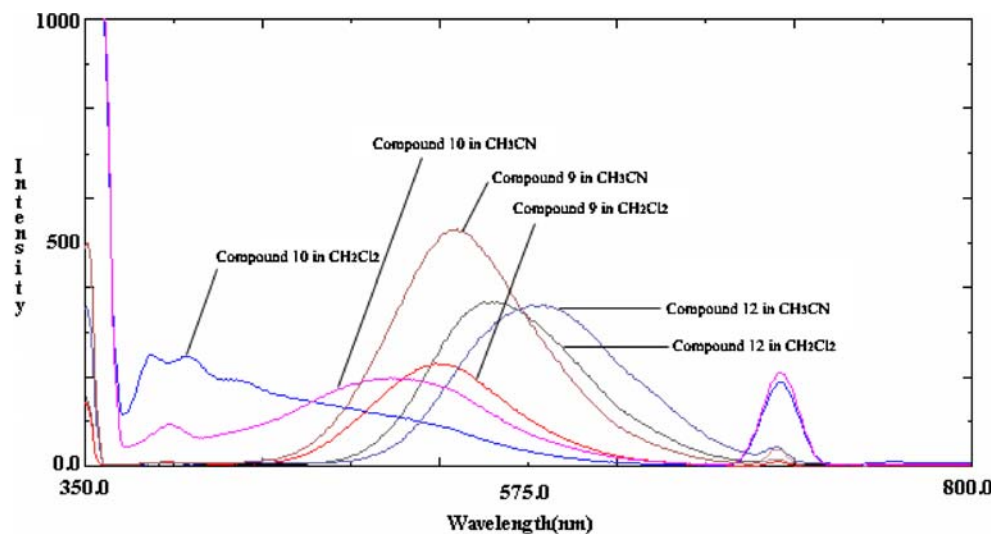


Fig. 8 Typical fluorescence spectroscopy of compounds **9**, **10** and **12** in CH_2Cl_2 and CH_3CN as excited at 350 nm. (In order to conveniently observe the fluorescence spectroscopy shape and maximal emission wavelength, the slit widths for the survey of fluorescence spectroscopy were not kept same. For compound **10** in CH_2Cl_2 and CH_3CN , slit width: Ex: 10 nm, Em: 10 nm; for compounds **9** and **12** in CH_2Cl_2 , slit width: Ex: 5 nm, Em: 3 nm; for compounds **9** and **12** in CH_3CN , slit width: Ex: 5 nm, Em: 5 nm)



various solvents. A simple sketch on the change of intramolecular charge transfer of nitro-stilbene derivatives with benzophenones (compounds **10** and **12**) caused by different bridged bond was shown in Fig. 10. (2) the luminescence properties of nitro-stilbene with benzophenones could be optimized or controlled by varying electron-donating or electron withdrawing bridged bonds.

Conclusions

In summary, we have developed a series of nitro-stilbene derivatives with benzophenones via different linked bonds. Single crystal X-ray crystallographic data show that the coplanar extent of two phenyl rings of nitro-stilbene derivatives is affected by substituents. It is evident that the intramolecular charge transfer of nitro-stilbene with benzophenones is largely affected by bridged bonds. The extent of intramolecular charge transfer is increased by

ether linking bond, however, it is diminished by ester linking bond. This thus in turn has significant influence on the absorption and fluorescence spectroscopy of nitro-stilbene derivatives with benzophenones. The results presented in this paper would be great interest in the development of ideal luminescent nitro-stilbene dyes with benzophenones by varying electron-donating or electron withdrawing bridged bonds.

Supplementary information available

CCDC 672472 and 658028 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or (from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033).

Fig. 9 Typical fluorescence spectroscopy of compounds **10** and **12** in THF as excited at 350 nm. slit width: Ex: 5 nm, Em: 3 nm

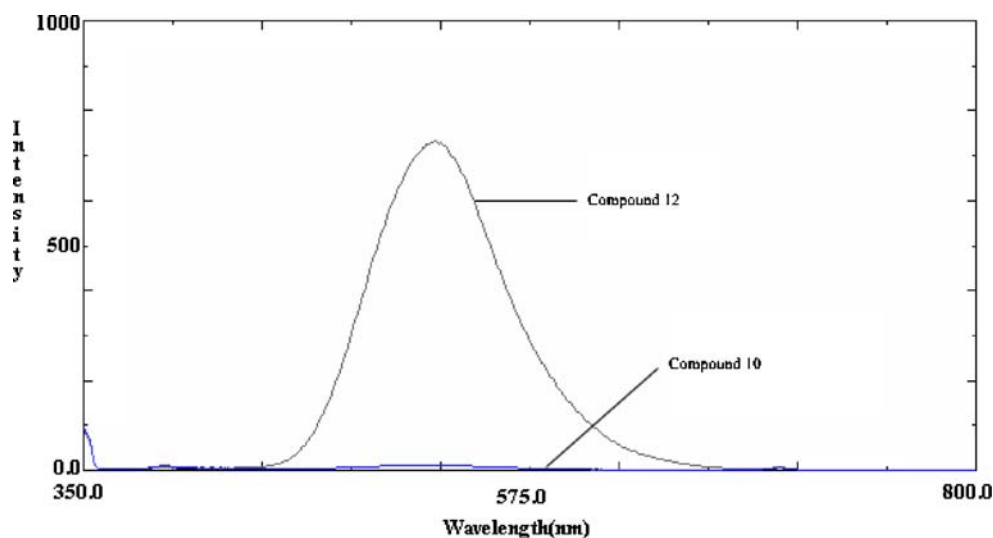


Fig. 10 a and b The sketch of change of intramolecular charge transfer of nitro-stilbene derivatives with benzophenones caused by bridged bonds

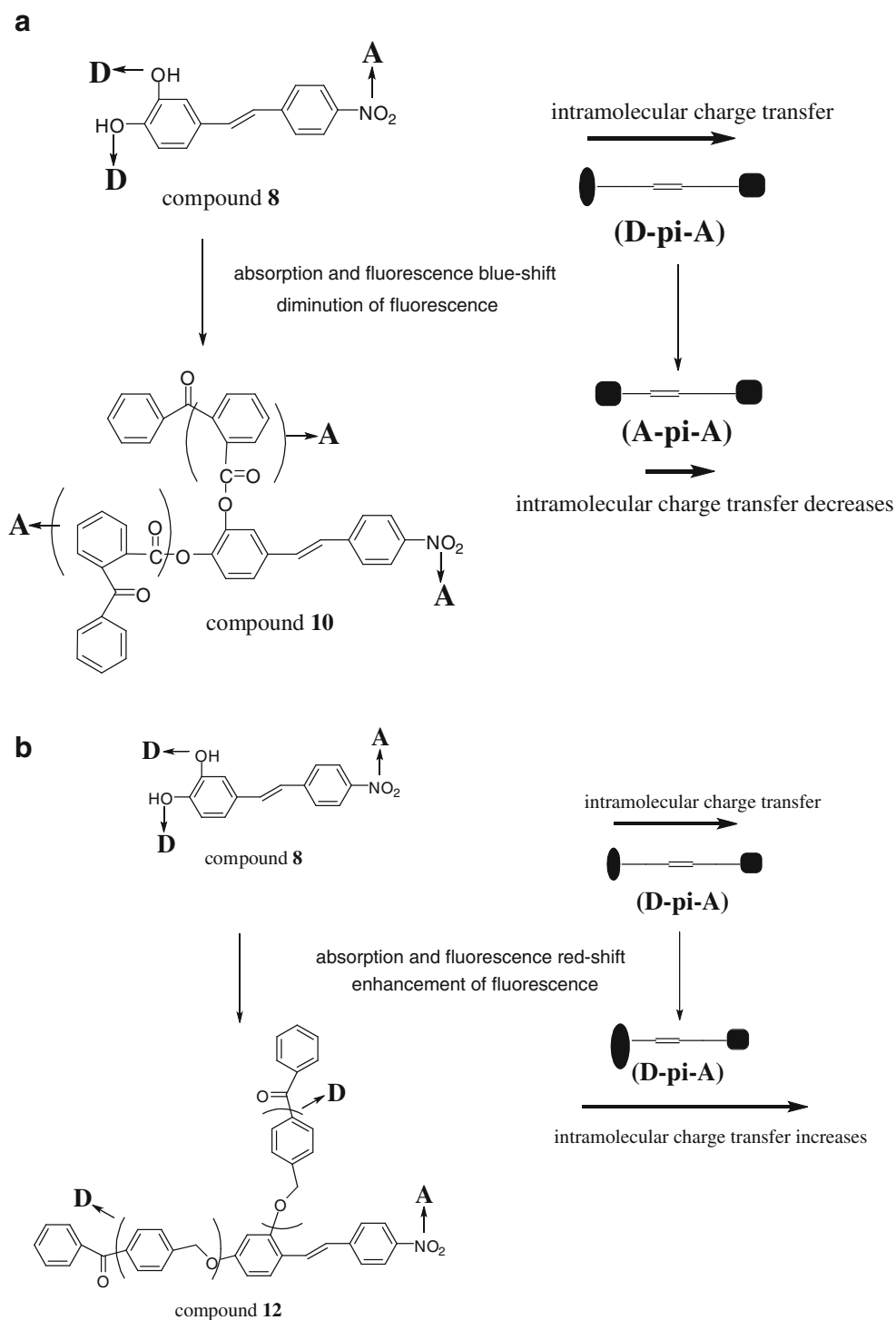


Table 2 The fluorescence quantum yields of compounds 8, 9, 10 and 12

Solvents	C 8	C 9	C 10	C 12
Benzene	0.018	0.0025	0.0021	0.035
Ethyl Acetate	0.10	0.0017	0.0012	0.27
Tetrahydrofuran	0.21	0.0017	0.0016	0.37
CH ₂ Cl ₂	0.13	0.046	0.004	0.19
Acetonitrile	0.031	0.043	0.0006	0.045

The fluorescence quantum yields of compounds 7 and 11 can be found elsewhere [40].

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