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A study on the synthesis and photophysical performances of some pyrazole and triazole fluorescent brightening agents

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Abstract

A series of fluorescent brightening agents containing pyrazolyl or triazolyl groups were synthesized in this work and their structures were confirmed by IR, ^{1}H NMR and ^{13}C NMR determination. UV absorption spectrometry was employed to investigate the process of photoisomerizations of some stilbene-derived fluorescent brightening agents. Their fluorescence spectra were also studied and discussed.

Keywords: Triazole; Pyrazole; Stilbene; Photoisomerization; Fluorescence spectra

1. Introduction

Triazolyl or pyrazolyl substituted stilbene derivatives are fluorescent brightening agents (FBAs) which show excellent fastness to chlorine and light, thereby they have found ubiquitous applications in detergents, papers, textiles, coatings and other industries [1]. Only recently they have been used as ultraviolet light absorbent. Because of their excellent properties, some other new applications are sure to be found in the future.

Although the literature on the manufacturing techniques of these FBAs is plentiful [2–6], published researches on their spectrometries are relatively fewer. UV and fluorescence spectra are two important ones among them. The UV absorption properties of these kinds of brightening agents were only investigated as a method to determine the proportion of *cis*/*trans* isomer in the reaction [7]. In this paper, we attempted to investigate the fluorescence spectra and the process of photoisomerization of some stilbene derivated fluorescent brightening agents. The chemical structures of investigated compounds are shown in Fig. 1.

2. Results and discussions

2.1. UV–visible absorption spectra

The UV–visible spectra of FWA1–FWA5 and DHS are given in Fig. 2, the solutions were water and methanol, respectively. The absorption data are summarized in Table 1. These compounds exhibited similar absorption curves as DHS, which indicated that these compounds had the same chromic structure, that is, stilbenedisulfonic acid sodium salt, as DHS. The absorption at about 206 nm is the E_2 band of benzene in stilbene backbone. The maximum absorption was also due to this stilbene backbone. Besides, FWA1 and FWA2 had an exceptional absorption at about 240 nm. It was attributed to the B bands of phenyl in 4 position of 2H-1,2,3-triazolyl group.

Moreover, the introduction of different modifying moieties into the stilbene backbone significantly

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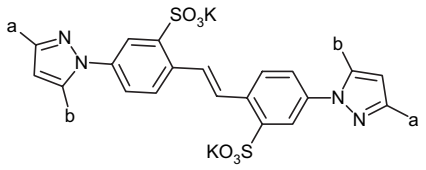
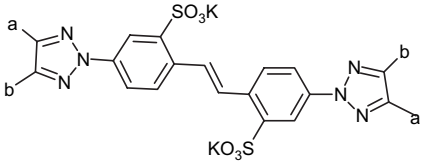
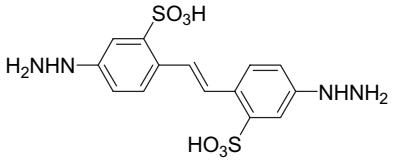


FWA2: a=b=methyl ; FWA3: a=methyl, b=carboxide



FWA1: a=hydrogen, b=phenyl; FWA4: a=b=methyl; FWA5: a=hydrogen, b=4-chlorophenyl



DHS: 4,4'-(hydrazine)-2,2-stibenesulfonic sodium

Fig. 1. Structures of FWA1–FWA5 and DHS.

influenced the maximum absorption wavelength λ_{max}. When 4-aryl substituted-2H-1,2,3-triazolyl group was introduced, the maximum absorption red shifted from 340 nm to more than 350 nm. However, the introduction of substituted pyrazolyl group resulted in blue shift while pyrazolonyl moiety caused a little change of the maximum absorption peak.

2.2. Fluorescence spectra

Fig. 3 shows the fluorescence spectra of FWA1–FWA4 excited at the maximum absorption wavelength of each compound, respectively. Obviously all the curves are very similar. Compared with their respective UV spectra, it was found that their fluorescence spectra were in symmetry with their UV spectra, respectively. Therefore, their Stokes shift could be evaluated. For example, the Stokes shifts of FWA1 and FWA2 were calculated at 220 nm and 131 nm, respectively. However, it is very strange that the spectrum of FWA3 is rather unorderly. It seems that there are two peaks in the range of 400–500 nm. In fact, the fluorescence of FWA-3 is very weak. It was found that the existence of carbonyl group may effect the electron excitation of the molecule. Thus the lowest singlet excitation state S_1 may be the n, π_1 type, or n, π_1 transition, which is an electron spin-forbidden transition with small molar absorbent coefficient and weak fluorescence.

From Fig. 3, we could see that introduction of oxygen group, such as carbonyl, made fluorescence highly quenched. And the larger conjugated groups introduced such as phenyl would decrease the fluorescence intensity. The reason may be that the introduction of a larger group broke the coplanarity of triazole and phenyl.

2.3. Photoisomerization

Photoisomerization is a common phenomenon for stilbene type compounds, and closely influences the light stability or light fastness of the FBAs. Here UV–visible absorption spectra at different irradiation time were employed to monitor the process of photoisomerization of different stilbene type fluorescent brightening agents containing triazolyl or pyrazolyl moieties. The spectra were recorded in pre-determined intervals after compounds had been irradiated (Fig. 4). Fig. 4 clearly showed that the maximum absorption peak decreased significantly at the initial irradiation time, with the lengthening of irradiating time the maximum absorption peak continued to decrease, while a new absorption peak occurred at about 300 nm. After a certain time of irradiation, the spectra changed very little, which indicated that the irradiated compounds' solutions had come to their respective photostationary state, that is, an equilibrium had been reached between *cis* and *trans* isomers.

The above changes of absorption curves can be easily understood, in *trans* isomer, two large groups lie at the

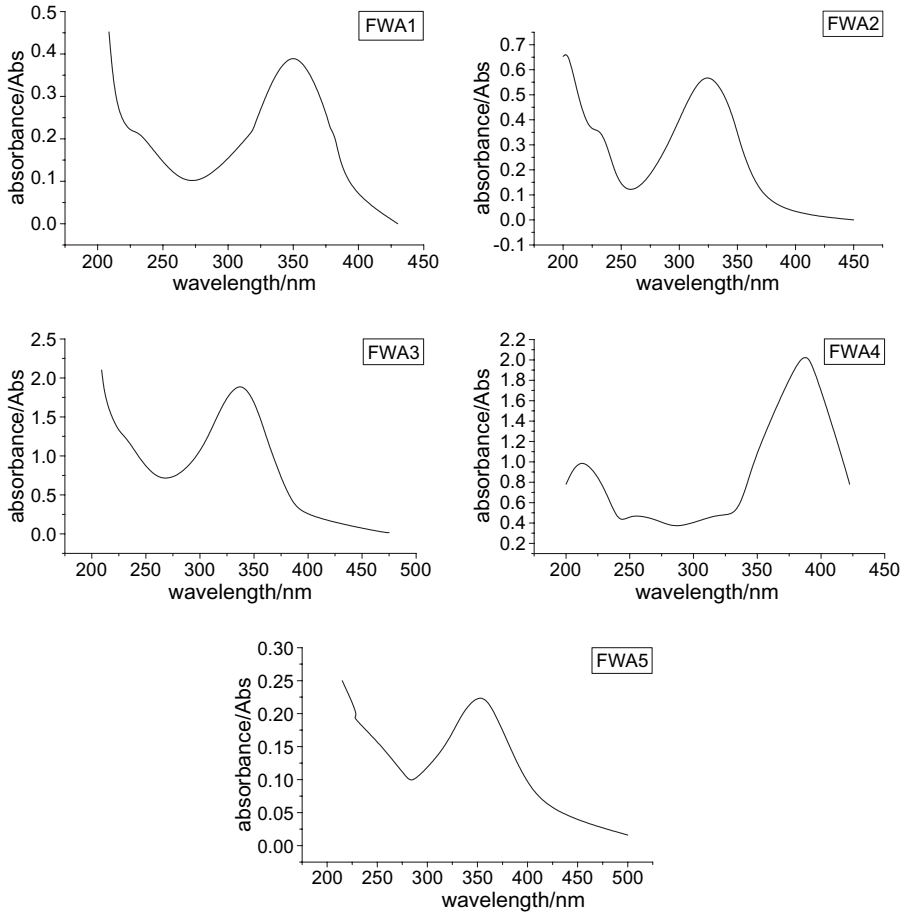


Fig. 2. The UV–visible spectra of FWA1–FWA5.

different side of the ethylene double bond which only produces small steric effect and has a better coplanarity. Therefore, *trans* isomers can form pretty good rigid structures and long π–π conjugative systems, which then help to result in bathochromic shifts in UV spectra and emit strong fluorescence.

But in *cis* isomer, in order to reduce the crowdness in the molecules caused by the strong steric effects, two aromatic rings were forced to rotate along C–C σ bonds. So the possible stable conformations should be oar-shaped, which have exterior rigidness and coplanarity and resulting in blue shifts in UV spectra and weak or no fluorescence was emitted.

From Fig. 4, it could be found that photoisomerization of compound FWA3 and FWA4, especially FWA4 was not obvious, for FWA1, FWA2, FWA5, the initial rate of isomerization was very quick; after they had been irradiated for 5 min, the velocity decreased sharply. The reason is that after the larger group was introduced, the heterocycle would rotate along C–C σ bonds to lower the influence of sterical hinderance. Here the coplanarity was broken harder between the heterocycle and the phenyl.

3. Conclusion

1. The introduction of substituted pyrazolyl group resulted in blue shift and pyrazolonyl moiety only caused a little shift, and that the introduction of substituted triazolyl resulted in red shift, benefited the creation of fluorescence.
2. Introduction of oxygen containing group and larger groups, especially oxygen containing group can lower the fluorescence intensity sharply.
3. All of these five compounds exhibit photoisomerization phenomenon, but introduction of large groups such as FWA1, FWA2 and FWA5, would influence photoisomerization, resulting in lowered fluorescence intensity.

Table 1
The absorption data of FWA1–FWA5 extracted from Fig. 2

	Wave crest (nm)	Peak value
FWA1	350	0.452
FWA2	324	0.611
FWA3	337	1.988
FWA4	387	2.001
FWA5	354	0.235

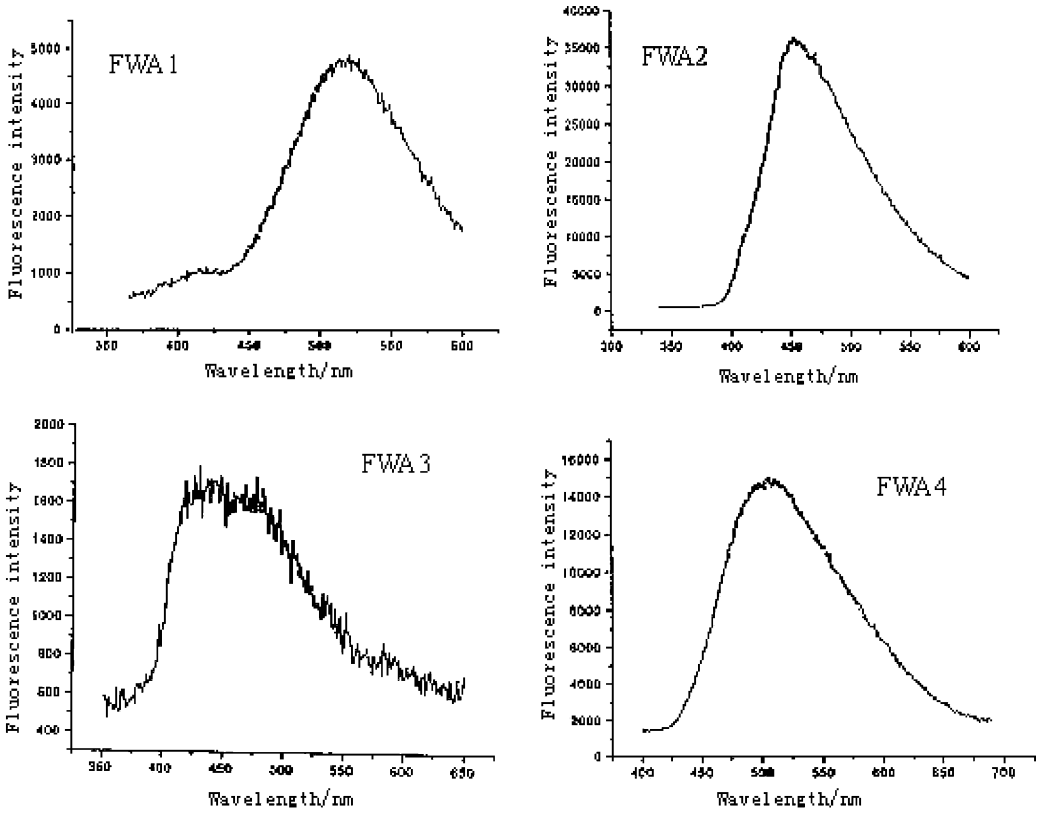


Fig. 3. The emitting fluorescence spectra of FWA1–FWA4.

4. Experimental

All chemical agents used are in chemical grade. The synthetic methods of compounds FWA1–FWA5 refer to respective literature [8–11]. UV–visible spectra were recorded on UV-1100 Spectrophotometer (Rayley Analytical Corp., Beijing). Fluorescence spectra were determined on SPEX-212 Spectrometer. ^{13}C NMR and ^{1}H NMR were determined by, respectively, Varian Unity-plus 400 and BRUKER AC-P 200.

4.1. FWA1 4,4′-bis(4-phenyl-2H-1,2,3-triazol-2-yl)-2,2′-disulfonic acid, dipotassium salt

A 100 mL four-necked flask equipped with a condenser and a stir was charged with 2.0 g of 4,4′-dihydrazinostilbene-2,2′-disulfonic acid, 5.0 g of urea, and 20 mL of methanol. The pH value of the mixture was regulated to 4.7–5.0 by addition of 2.0 g anhydrous CH_3COOK. Then 1.6 g of isonitrosoacetophenone was added when the mixture was heated to 50 °C, the reaction was proceeded at 50 °C for 2 h.

After the mixture was cooled to 30 °C, the pH value was regulated to 7.6–8.0 with 50% potassium hydroxide aqueous solution. Then 1.2 g of acetic anhydride was added with stirring. After the mixture was stirred for 15 min, 15 mL water was introduced and the pH value was regulated to 7.5 with potassium hydroxide aqueous solution.

The mixture was heated slowly to 90–98 °C to evaporate methanol and part of water and ammonia, the mixture was cooled to 80–85 °C. The precipitate was separated by filtration, washed with 15 mL of 3% potassium chloride aqueous solution and dried to yield 2.4 g yellowish product. Yield: 76.9%.

^{1}H NMR (200 MHz, DMSO-d_6): δ/ppm 2.49093, 3.33504 (d, solvent), 7.44800–7.54031 (q, 10H, H–C-1–C-3), 7.83749–7.88047 (d, 2H, $J = 8.596$, H–C-13), 7.99716–8.08123 (q, 2H, H–C-11, H–C-12), 8.24671 (s, 2H, H–C-12), 8.56351 (s, 2H, H–C-8), 8.65241 (s, 2H, H–C-6).

^{13}C NMR (400 MHz, DMSO-d_6): δ/ppm 117.259 (C-13), 118.559 (C-11), 126.000 (C-2), 126.925 (C-1), 127.521 (C-10), 129.028 (C-12), 129.074 (C-3), 129.326 (C-8), 133.784 (C-7), 134.121 (C-4), 137.149 (C-9), 147.045 (C-6), 148.589 (C-5).

4.2. FWA2 4,4′-bis (3,5-dimethylpyrazolyl)-2,2′-disulfonic acid, disodium salt

In a 250 mL four-necked flask was added 65 mL of anhydrous ethanol and 2.0 g of DHS. Then the mixture was heated to 45 °C in waterbath, 1.5 g of anhydrous CH_3CO_2Na and acetoacetone were added. The solution

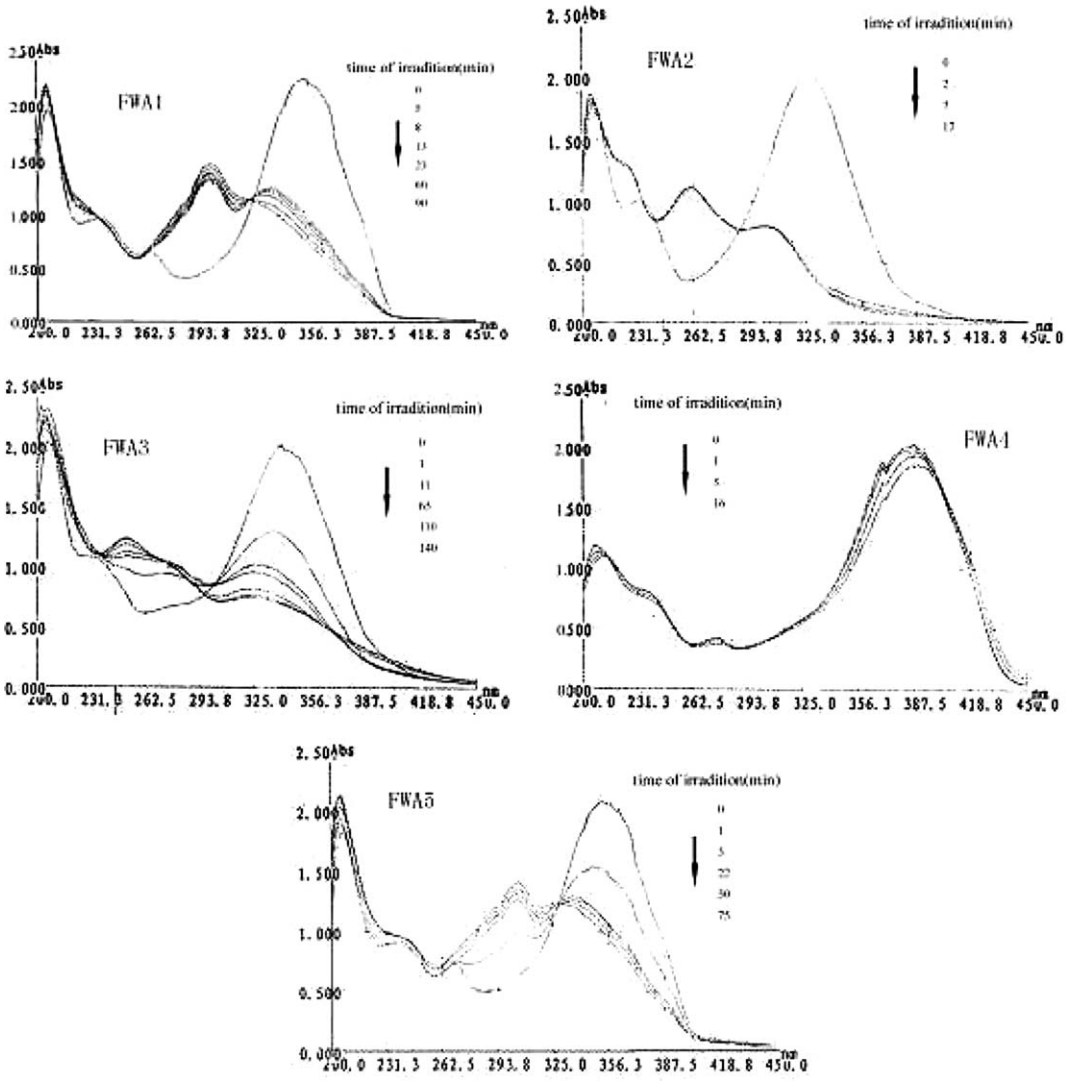


Fig. 4. The UV–visible spectra at different moments of FWA1–FWA5.

was then heated to 80 °C and refluxed for 3 h. After it cooled to room temperature, 1.5 g yellow precipitate was separated as the product. Yield: 69.9%.

^{1}H NMR (400 MHz, DMSO-d_6): δ/ppm 2.265 (s, 3H, H–C-5), 2.343 (s, 3H, H–C-1), 3.310, 4.873 (solvent), 6.103 (s, 2H, H–C-3), 7.555–7.581 (q, 2H, J = 8.4), 8.136–8.157 (d, 2H, H–C-11), 8.288 (s, 2H, H–C-7), 8.053–8.059 (d, 2H, H–C-10).

^{13}C NMR (400 MHz, DMSO-d_6): δ/ppm 12.428 (C-5), 13.308 (C-1), 108.385 (C-3), 125.071 (C-7), 127.717 (C-11), 129.277 (C-12), 129.728 (C-10), 136.481 (C-9), 139.456 (C-4), 142.094 (C-6), 145.069 (C-8), 150.873 (C-2).

4.3. FWA3 4,4′-bis(3-methyl-5-pyrazolonyl)-2,2′-disulfonic acid, disodium salt

In a 250 mL four-necked flask was added 50 mL of anhydrous methanol, 2.0 g of DHS, 2.0 g of anhydrous CH_3CO_2Na, and 2.6 mL of ethyl acetoacetate. Then the mixture was stirred and heated to reflux for 2 h. After cooling down to the room temperature, 3.3 g yellow powder was obtained as the product. Yield: 57.5%.

4.4. FWA4 4,4′-bis(3,5-dimethyl -2H-1,2,3-triazol-2-yl)-2,2′-disulfonic acid, dipotassium salt

The same procedure as that of FWA5 was used except that isonitrosoacetophenone was replaced by diacetyldioxime.

4.5. FWA5 4,4′-bis(4-chlorophenyl-2H-1,2,3-triazol-2-yl)-2,2′-disulfonic acid, dipotassium salt

The same procedure as that of FWA1 was used, except that isonitrosoacetophenone was replaced by 1.9 g of *p*-chloro-isonitrosoacetophenone. And the product was orange yellowish powder. Yield: 81.2%.

^{1}H NMR (200 MHz, DMSO-d_6): δ/ppm 7.57466–7.61632 (d, 4H, H–C-3), 7.66480 (d, 2H, H–C-13), 8.01794–8.06115 (d, 4H, H–C-2), 8.22792 (s, 2H, H–C-8), 8.54971 (s, 2H, H–C-12), 8.68544 (s, 2H, H–C-6).

^{13}C NMR (400 MHz, DMSO-d_6): δ/ppm 147.527 (C-5), 147.184 (C-6), 137.044 (C-11), 134.243 (C-4), 133.935 (C-7), 133.558 (C-1), 129.156 (C-3), 128.282 (C-10), 127.777 (C-2), 127.511 (C-12), 126.886 (C-9), 118.561 (C-8), 117.311 (C-13).

4.6. The general procedure for the preparation of corresponding solutions

Compounds FWA1–FWA5 were dissolved in deionized water and methanol, respectively, to give corresponding diluted solutions (concentration in the range of 10^{-5}–10^{-4} g/mL).

cis–trans isomerization of corresponding compounds was carried out in the solutions under UV monochromatographic light of 365 nm.

4.7. cis–trans photoisomerization

The solutions to be tested were prepared as above (2×10^{-5}–6×10^{-5} g/mL) and then irradiated under the light of a 10 W $\times$ 365 nm fluorescence tube. Samples were picked up and examined on UV-1100 Spectrophotometer in pre-determined interval time. After the sample solutions were irradiated for 24 h, the isomerized product mixture was separated on Shimadzu LC-4A.

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