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Synthesis and properties of new anionic fluorescent brighteners

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Abstract. Three new fluorescent brighteners (FBs) were synthesized and compared with traditional FBs. Their UV/visible absorption and fluorescence emission characteristics were studied. Compared with traditional products, the new fluorescent brighteners had better optical performance, high solution and low pollution.

Introduction

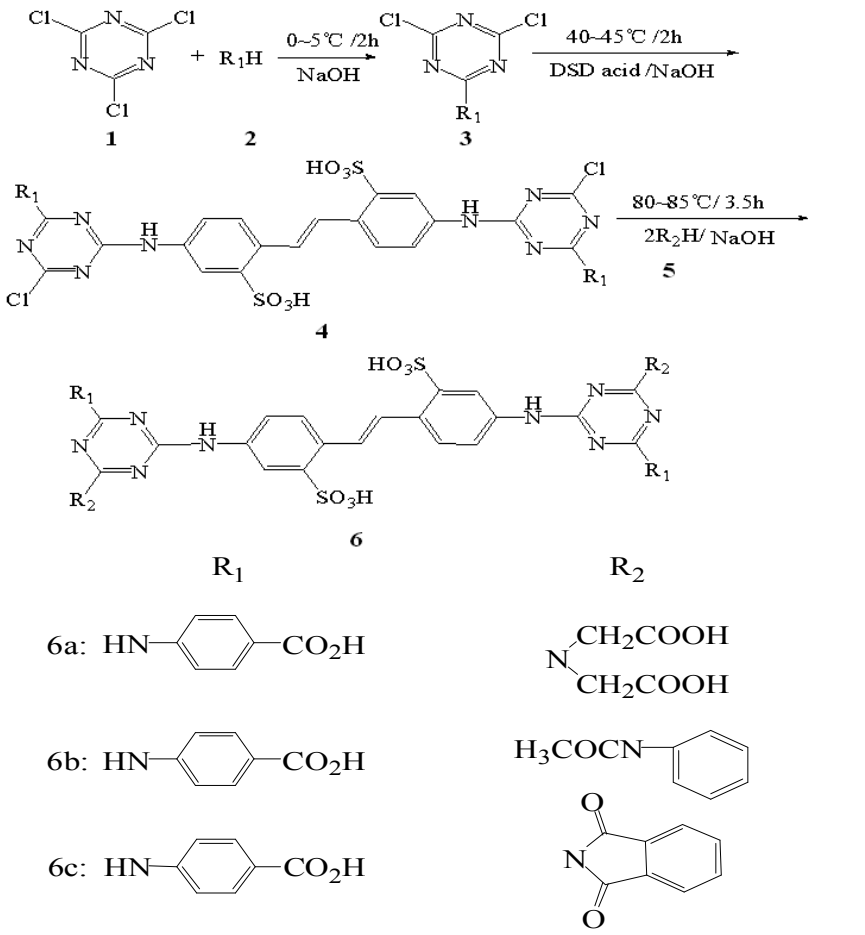
As an important class of optical brighteners, triazine-stilbene fluorescent brighteners（FBs） which include different substitutes in the triazine rings, were widely used for whitening textile, paper and so on [1-3]. They are especial fluorescent dyes. Materials treated with FBs obtain a high degree of whiteness based on photophysical and photochemical principle. They absorb light in the near ultraviolet region of the spectrum (340-380 nm) and reemit the light of violet-blue fluorescence in the visible region (400-450 nm) [4].

At present, it has been reported that there are about 15 types of fluorescent whitening agents. Among them, the two-amino-stilbene triazine fluorescent brighteners have the maximum demand, but some toxic raw materials which are used are in preparation, limiting its industrialization. Therefore, the application of non-toxic or low toxic synthetic materials, obtaining fluorescent whitening agents with specific functions, is still one of the focuses of current research.

In this paper, we have the conscious choice of three low or non-toxic raw materials and have synthesized three novel compounds with 85-90% yield. Three compounds were characterized by UV-visible absorption spectra and fluorescence emission spectra. The physical properties were performed by dying rate and dye concentration on the impact of whiteness. The result shows that the new synthesized compounds (6a~6c) had better optical performance, high solution and low pollution.

Experimental

2,4,6-Trichloro-1,3,5-triazine (1) (1 mol, 184 g) and 4-amino-benzoic acid (2) (1 mol, 137 g) in water (300 mL) were added to the flask , while maintaining pH at 2~3 with NaOH (30%), the reaction mixture was stirred at 0~5˚C for 3 h. The temperature was then increased to 45˚C and 4,4'-diaminostilbene-2,2'-disulfonic acid (DSD) (0.5 mol, 370 g) was added and stirred for 3.5 h at pH 4~4.5. At last different amino compound (5) (1 mol) was added to the reaction flask and adjusted to pH 8 with NaOH (30%). The reaction mixture was heated to 80 ˚C and stirred for 2~3 h. Then the mixture was cooled to room temperature and acidified to pH 3 with 4 N HCl, The precipitate was filtered and dried to obtain compound (6a-6c). The synthetic course is shown in Scheme 1.



Scheme 1. Synthesis of 6a-6c

UV/visible absorption measurement

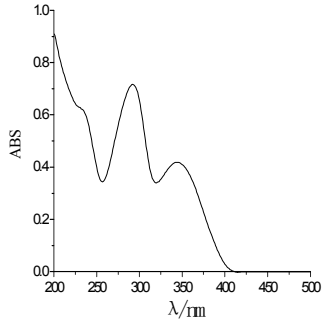


Fig.1. UV/visible absorption measurement of compound 6a

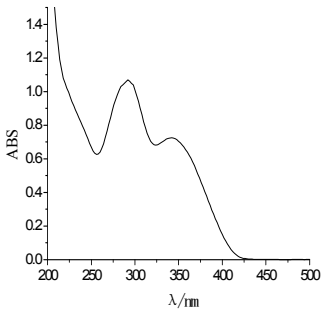


Fig.2. UV/visible absorption measurement of compound 6b

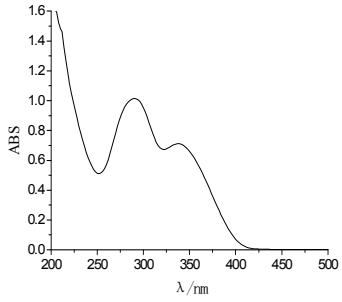


Fig.3. UV/visible absorption measurement of compound 6c

From the Fig.1~Fig.3, we can know that there are two isomers in the ultraviolet region, each has its maximum absorption. The FWA in aqueous solution, trans-isomer maximum absorption wavelength at 338~346 nm, Cis-isomer in the 290~292 nm region.

Fluorescence emission measurement

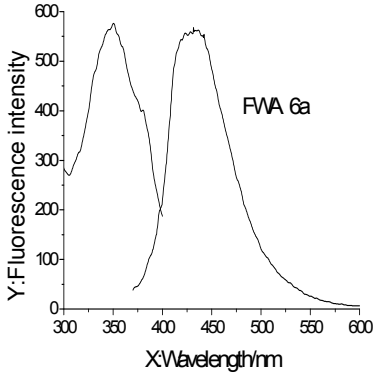


Fig.4. Fluorescence emission measurement of compound 6a

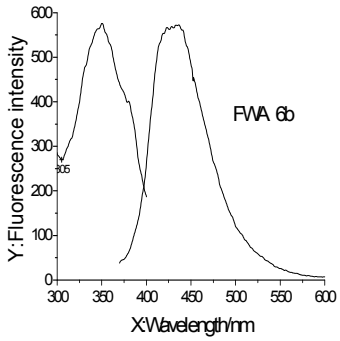


Fig.5. Fluorescence emission measurement of compound 6b

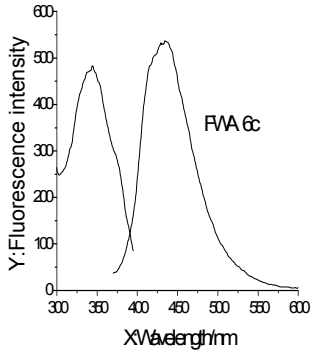


Fig.6. Fluorescence emission measurement of compound 6c

From the Fig.4~Fig.6, FWA1~3 emit fluorescence in the 370 ~ 540 nm, the most intense between the 425~465nm. Because of the common structure, the products have the similar shape of fluorescence excitation and emission spectra curve.

Dying rate and dye concentration on the impact of whiteness

A_0 is the absorbance of the FWA solution before staining and A_1 is the absorbance of the FWA solution after staining . the formula of the dye uptake as follows:

$$\text{Dye uptake} = \frac{m_0 \cdot A_0 - m_1 \cdot A_1}{m_0 \cdot A_0} \times 100\%$$

FWA concentration (o.w.f) on the impact of dyeing rate of dye, results are shown in Table1, Table 2.

Table 1. The relation between dyeing rate of dye and concentration about compounds (6a~6c)

FWA	o.w.f	6a	6b	6c
Dye uptake (U)	0.05%	48.0	38.3	50.2
	0.10%	35.2	25.2	28.6
	0.20%	35.9	17.1	17.4
	0.40%	31.1	12.2	11.0
	0.80%	28.5	11.8	10.2
	1.20%	24.3	9.8	8.8

Table 2. The relation between whiteness and concentrate on about compounds (6a~6c)

FWA	o.w.f	6a	6b	6c
whiteness	0.05%	86.9	88.2	87.6
	0.10%	88.2	90.0	89.5
	0.20%	89.6	91.6	90.9
	0.40%	91.2	92.3	92.1
	0.80%	92.5	92.8	92.9
	1.20%	93.1	93.3	93.4

From the table 1, FWA6a, 6b, 6c the dye uptake decreased with increase in concentration. From the table 2, whiteness has the following characteristic: As the dye concentration increases, the brightness value is also a corresponding increase. At a lower level, large increase in the value of whiteness, but at higher concentrations, whiteness of increase becomes smaller. The relationship between dye concentration and whiteness is shown in Fig.7.

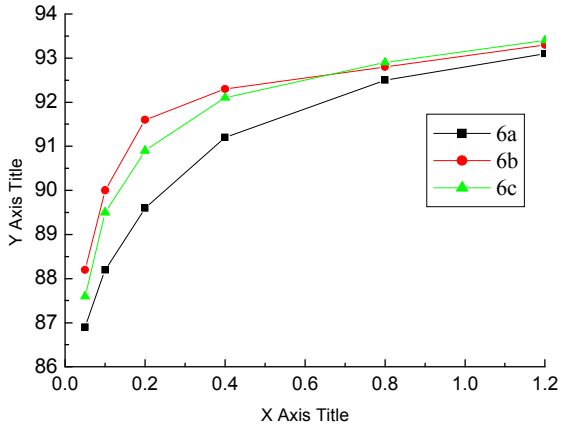


Fig.7. The relationship between dye concentration and whiteness

Conclusions

Through the use of low toxicity, high water-soluble aminobenzoic acid replace the toxicity of aniline which used for the production of VBL, we obtained three new anionic fluorescent brighteners with high yields. The obtained compounds were characterized by UV-visible absorption spectra, fluorescence emission spectra and different concentrations of dye rate and whiteness were investigated. The result showed that compounds (6a~6c) had better optical performance, high solution and low pollution during the synthetic experiment.

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