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Intramolecular energy and charge transfer in 5-(9-anthryl)-3-(4-nitrophenyl)-1-phenyl-2-pyrazoline

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Abstract

The absorption and photoluminescence of the newly synthesized 5-(9-anthryl)-3-(4-nitrophenyl)-1-phenyl-2-pyrazoline (ANPP) were investigated. The absorption is the absorption of anthryl moiety at about 325–400 nm, superimposed on the broader absorption of 3-(4-nitrophenyl)-1-phenyl-2-pyrazoline moiety peaked at 420 nm. On excitation at 420 nm, the fluorescence spectrum has only one emission band from the pyrazoline moiety. This emission band exhibits a larger red shift with an increase in the polarity of solvents. But on excitation at 365 nm, the fluorescence spectrum has two emission bands coming from the anthryl and pyrazoline moieties, respectively. The intensity ratio of the two bands is different in solvents of different polarity. It is concluded that photo-induced intramolecular energy transfer from the anthryl to pyrazoline moiety exists simultaneously with the charge transfer from N (1) to C (3) in the pyrazoline moiety in the excited state and both compete with each other. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pyrazoline; Photoluminescence; Energy transfer; Charge transfer

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1. Introduction

1,3,5-Triaryl-2-pyrazolines are fluorescent compounds, which are widely used for the whitening of textile fiber, plastics and paper [1,2]. More recently, these compounds have also been reported as hole transporting or emitting materials in organic EL devices [3,4]. In the past decades, attempts were made to elucidate the mechanism of fluorescence in these compounds by studying the effect of substituents on the absorption and fluorescence properties of this class of compounds [5–8]. It was reported that [5] an intramolecular conjugated charge transfer process exists in pyrazoline moiety in the excited state and evidence was presented that the aryl group at position 5 is also responsible for spiroconjugated charge transfer quenching of pyrazoline fluorescence. In this report, a new derivative of triaryl-2-pyrazoline, 5-(9-anthryl)-3-(4-nitrophenyl)-1-phenyl-2-pyrazoline (ANPP), was synthesized. For a thorough understanding of its properties, its absorption and photoluminescence behaviors were studied. It was

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found that intramolecular energy transfer also exists between the 5-arthyl and pyrazoline moiety in the photo-physical process in addition to the two charge-transfer processes mentioned above and has a great influence on the fluorescence of pyrazoline compounds.

2. Experimental

2.1. Materials

The procedure for the synthesis of ANPP is as follows: 1.65 g (10 mmol) 4-nitro-acetophenone and 2.06 g (10 mmol) 9-anthrylaldehyde in 20 ml ethanol were mixed with a solution of 0.72 g (12.8 mmol) potassium hydroxide in 6 ml water. The reaction mixture was stirred for 24 h at room temperature. The precipitate was filtered, washed with ethanol and recrystallized from ethanol to give 2.0 g 3-(9-anthryl)-1-phenylprop-2-en-1-one (ANPP precursor). 1.0 g (3 mmol) ANPP precursor and 0.7 g (6.5 mmol) of phenylhydrazine in 10 ml ethanol were refluxed for 8 h. The product was filtered and washed with ethanol to give a red solid product. It was then purified by silica gel chromatography (eluent chloroform) and recrystallized from ethanol to give 0.8 g red ANPP crystals. mp: 180–182°C. ^{1}HNMR($CDCl_3$): 3.56–3.59 (1 H), 4.02–4.08 (1 H), 6.71–6.74 (1 H), 6.77–8.58 (18 H); MS: M+, 443; Anal., calc. (found) for $C_{29}H_{21}N_3O_2$: C 78.54 (78.32), H 4.77 (4.81), N 9.47 (9.35).

Another derivative of pyrazoline, 1,5-diphenyl-3-(4-nitrophenyl)-2-pyrazoline (DNP) was synthesized in the same method for comparison. Anthracene was purchased from Aldrich. All solvents were purified by the usual methods before use. The synthetic route of ANPP and the structure of DNP are shown in Fig. 1.

2.2. Instrumentation

The absorption spectra were measured on a Shimadzu UV-2102 spectrophotometer. The fluorescence spectra were recorded using a Shimadzu RF-5000 spectrofluorophotometer. Fluorescence quantum yields of pyrazoline compounds in various solvents were obtained by comparison of the integrated areas under their corrected emission spectra with that of a 0.1 N sulfuric acid solution of quinine sulfate.

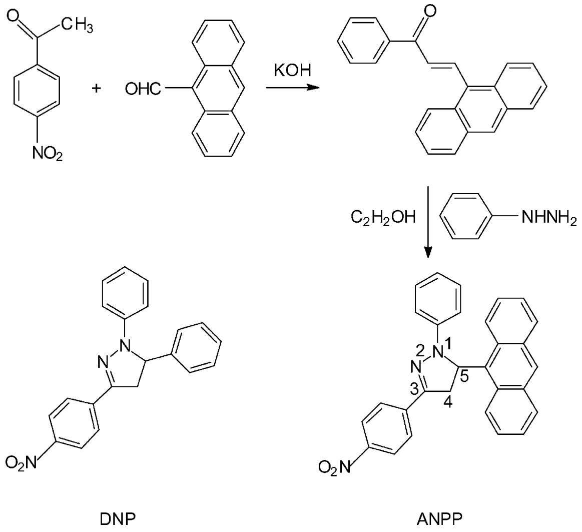

Fig. 1. Synthetic route of ANPP and molecular structure of DNP.

3. Results and discussion

3.1. Absorption spectra

Fig. 2 compares UV-vis spectra of ANPP, DNP and anthracene in cyclohexane. DNP exhibits a broad absorption peaking at 420 nm arising from the π–π* transition of 3-(4-nitrophenyl)-1-phenyl-2-pyrazoline moiety. It is because, when an electron-withdrawing group is located on the *p*-position of phenyl ring at position 3, the absorption peak is at a longer wavelength than other pyrazoline compounds in which the electron-withdrawing group is not present [5]. Anthracene exhibits several maximum peaks near 365 nm due to the different electronic excitations. The absorption of ANPP is a result of the combination of two chromophores (the anthryl and pyrazoline moieties). It exhibits four strong absorptions at about 325–400 nm superimposed on the absorption of pyrazoline moiety. The four absorptions (λ_{max} at 330, 350, 370, and 383 nm) in the shorter

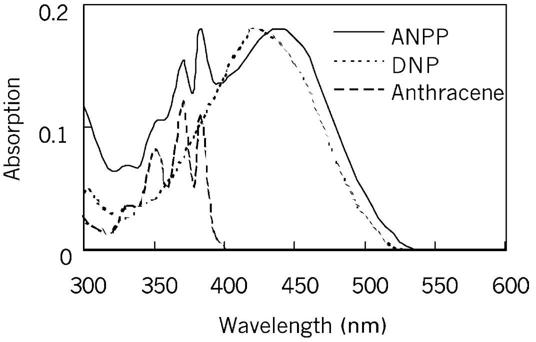

Fig. 2. Absorption of ANPP (1×10^{-5} M), anthracene (1×10^{-5} M) and DNP (1×10^{-5} M) in cyclohexane.

wavelength region originate from the anthryl group.

3.2. Fluorescence

Fig. 3 presents the fluorescence of ANPP and DNP (excitation at 420 nm) in solvents of different polarities. It can be found that both ANPP and DNP show two fluorescence maxima in cyclohexane but only one maximum in THF or methanol solution. Both exhibit a larger red shift with an increase in the polarity of solvents. When the solvent is changed from cyclohexane to methanol, this emission band has red shifted about 100 nm. These characters have been observed by Yan Zhenglin [5] and Strahle [9] in the fluorescence spectra of derivatives of 1,3-diphenyl-2-pyrazolines and 1,3,5-triphenyl-2-pyrazolines containing an electron-drawing substituent located in the *p*-position of the 1-phenyl or 3-phenyl. So this emission band in ANPP can be attributed to the fluorescence of 3-(4-nitrophenyl)-1-phenyl-2-pyrazoline moiety. All these results can be explained by the intramolecular charge transfer from N (1) to C (3) in the excited state of these compounds [5]. It is evident that the introduction of a *p*-nitrophenyl group at position 3 has a very strong effect on the molecular polarization in the excited state.

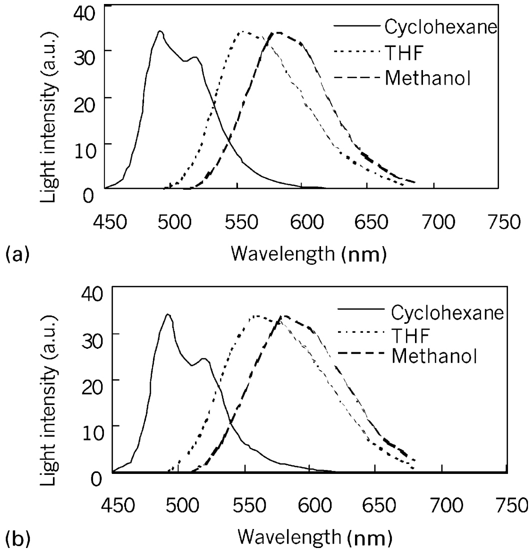

Fig. 3. Fluorescence spectra of ANPP (1×10^{-5} M) and DNP (1×10^{-5} M) in different solvents excited at 420 nm: (a) ANPP; (b) DNP.

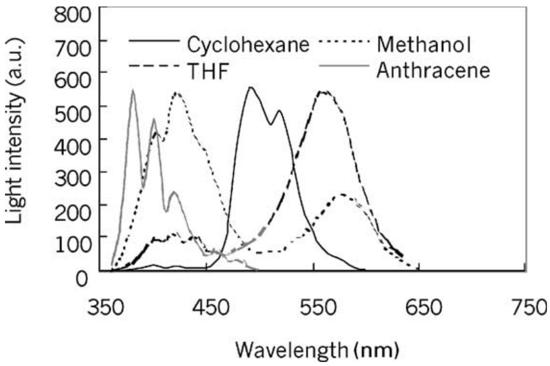

Fig. 4. Fluorescence spectra of ANPP (1×10^{-5} M) and anthracene (1×10^{-5} M) in different solvents excited at 365 nm.

However, on excitation at 365 nm (Fig. 4), which is the absorption of anthryl group, ANPP exhibits two emission bands. Except for the pyrazoline moiety emission band observed on excitation at 420 nm, a new emission band at shorter wavelength can be observed. This short-wavelength emission band near 440 nm which shows no obvious change in different solvents can be attributed to the fluorescence of anthryl group by comparing it with that of anthracene.

Since there is considerable overlap around 420 nm between the fluorescence spectrum of anthracene and the ground absorption of DNP, intramolecular energy transfer from anthryl to pyrazoline moiety should exist in ANPP. It can be found that (Fig. 4) the ratio of anthryl fluorescence to pyrazoline fluorescence is different in solvents of different polarity. This implies that the efficiency of intramolecular energy transfer changes with solvents. In cyclohexane, the fluorescence of anthryl group nearly disappears completely when excited at 365 nm where only the absorption of anthryl group can be found. It demonstrates that energy transfer from anthryl to pyrazoline moiety is very efficient in cyclohexane. But in methanol or THF, the fluorescence of anthryl group can be observed and the ratio of anthryl fluorescence to pyrazoline fluorescence is higher in methanol than in THF. This implies that the energy transfer in methanol is not as efficient as in THF and energy transfer in THF is not as efficient as in cyclohexane. The reabsorption is trivial even if it exists because it is a radiative energy transfer and the fluorescence of energy acceptor (pyrazoline group) has no influence on the fluorescence of energy donor (anthryl group) for this mechanism. However, Foerster-type overlap is of crucial importance. It was reported that spiroconjugation exists between aryl group in position 5 and pyrazoline moiety in 5-aryl-1,-3-diaryl-2-pyrazoline compounds because of the orbital overlap between the two moieties [10]. Foerster-type overlap is influenced by the solvent and it is smaller in methanol than in THF; thus the energy transfer is faster in the latter case.

This difference can also be found by comparing the corrected fluorescence excitation spectra of ANPP in different solvents with its absorption spectra in Fig. 5. On monitoring the pyrazoline emission at 518 nm and scanning through 350–550 nm, it can be found that the excitation spectrum agrees well with the absorption spectrum after normalization at 430 nm in cyclohexane indicating that energy transfer is very efficient. However, there is a discrepancy between the excitation spectrum in methanol and the absorption spectrum in the 325–400 nm region where anthryl absorbs. It indicates that nearly no photons absorbed by anthryl are transferred to the pyrazoline moiety in methanol. The large difference between the excitation in cyclohexane and methanol means also that the Foerster-type overlap is larger in cyclohexane than in methanol.

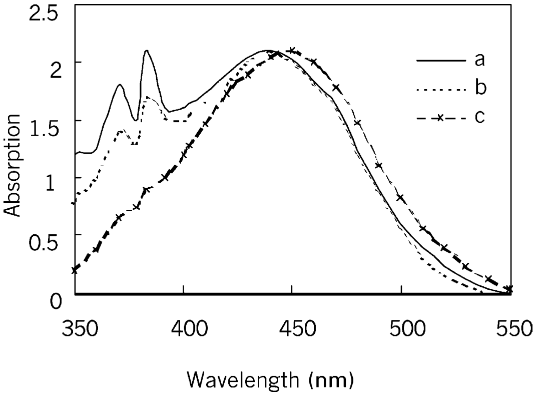

Fig. 5. Comparison of the excitation ($\lambda_{em} = 518$ nm) and absorption spectra of ANPP: (a) absorption spectrum in cyclohexane, 1×10^{-5} M; (b) excitation spectrum in cyclohexane, 1×10^{-5} M; (c) excitation spectrum in methanol, 1×10^{-5} M.

The fluorescence quantum yields of DNP and ANPP in different solvents are also investigated. For DNP, the fluorescence quantum yield is 0.43 in cyclohexane and 0.08 in methanol. For ANPP, the fluorescence quantum yield is 0.71 in cyclohexane and 0.12 in methanol. It is obvious that the decreased fluorescence quantum yield in methanol is caused by conjugated charge transfer from N (1) to C (3) in the excited state of DNP [5]. However, for ANPP several possible factors related to the interaction between the anthryl and pyrazoline moiety may complicate the interpretation of the reduced fluorescence quantum yield. For example, conjugated charge transfer from N (1) to C (3) and intramolecular energy transfer from anthryl to pyrazoline moiety exist simultaneously in the excited state. Moreover, spiroconjugation also exists between the two moieties. It means that charge transfer between the two moieties cannot be excluded from consideration although it may be trivial.

It is suggested that these two charge transfer processes compete with the energy transfer process in the excited state of ANPP. The energy transfer process is the main process in cyclohexane, but the charge transfer process becomes the main process because of a relatively greater polarity effect with an increase of the solvent polarity. The anthryl fluorescence is quenched mainly by energy transfer between the two chromophores and the pyrazoline fluorescence is mainly quenched by the conjugated charge transfer from N (1) to C (3).

4. Conclusion

A new pyrazoline derivative molecule is synthesized. Its absorption and photoluminescence in solution are studied. The absorption spectrum is the strong absorption of anthryl group at about 325–400 nm superimposed on the broader absorption of 3-(4-nitrophenyl)-1-phenyl-2-pyrazoline group peaked at 420 nm. The photoluminescence includes the contribution of both anthryl and the pyrazoline moieties. Intramolecular energy transfer and charge transfer exist simultaneously in the excited state. The anthryl fluorescence is quenched mainly by energy transfer from anthryl to pyrazoline moiety. The pyrazoline fluorescence is quenched mainly by conjugated charge transfer from N (1) to C (3). Spiroconjugated charge transfer between the two moieties may also exist at the same time. The energy transfer is the main process in cyclohexane and charge transfer becomes the main process in solvents with higher polarity.

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