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Synthesis and spectrum characteristic of four new organic fluorescent dyes of pyrazoline compounds

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Abstract

Four novel fluorescence dyes of the pyrazoline were synthesized, which were 1,3-diphenyl-5-(4-chlorophenyl)-2-pyrazoline (DCP), 1,5-diphenyl-3-biphenyl-2-pyrazoline (DBP), 1,5-diphenyl-3-(*N*-ethylcarbazole-3-yl)-2-pyrazole (DEP), and 1-phenyl-3-(*N*-ethylcarbazole-3-vinyl)-5-(*N*-ethylcarbazole-6-yl)-2-pyrazole (PEEP). The characteristic of the synthesis methods used is that the carbazole radical is linked with pyrazoline molecule. The products were characterized by IR spectra, ^{1}H NMR, elemental analysis and fluorescence spectra. The fluorescence emission spectra of the compounds were red-shifted evidently from DEP to PEEP in $CHCl_3$. The solvent effect on the fluorescence characteristics of the four compounds indicates that the emission wavelength was red-shifted with the increase of solvent polarity. The concentration effect on fluorescence intensities of the four compounds showed that the fluorescence intensities increased initially and then decreased with the concentration increasing. The fluorescence quantum yields of the four compounds were obtained and the fluorescence quantum yield of PEEP was the largest.

Keywords: Pyrazoline; Fluorescence dye; Carbazole; Synthesis

1. Introduction

Pyrazoline derivatives are formed by benzeno-hydrazone cyclization. These compounds show stronger fluorescence because of the double bond hindering which occurred due to cyclization. The pyrazoline has N atom which attains conjugation by donating electron, and it has higher hole-transport efficiency and some photoelectron characteristics [1]. Pyrazoline derivatives have not only excellent hole-transfer performance but also excellent emitting blueness property [2–4]. Therefore, it has widely been used as hole-transport materials in the electrophotography and electroluminescence fields [5–9]. Carbazole derivatives are also excellent hole-transfer compounds. For example, polyvinyl carbazole (PVCz) is an excellent electrophotoconductor, which has widely been used in electrophotography and laser printing and solar energy cells [10,11]. Carbazole derivatives can also emit blue fluorescence [12]. So if carbazole radical is linked to pyrazoline molecule, it would bring an excelsior efficiency.

Based on this target, carbazole radical was linked to pyrazoline molecule, and four pyrazoline compounds were synthesized (Scheme 1). Their structures were determined by IR, ^{1}H NMR, elemental analysis and fluorescence spectra. The fluorescence emission spectra were red-shifted evidently in $CHCl_3$ from DBP to PEEP. The solvent effects on the fluorescence characteristics of the four compounds were studied, which indicate that the emission wavelength of the compounds was red-shifted with the increase of solvent polarity. The concentration effects on fluorescence intensities of the four compounds were studied. It indicates that the fluorescence

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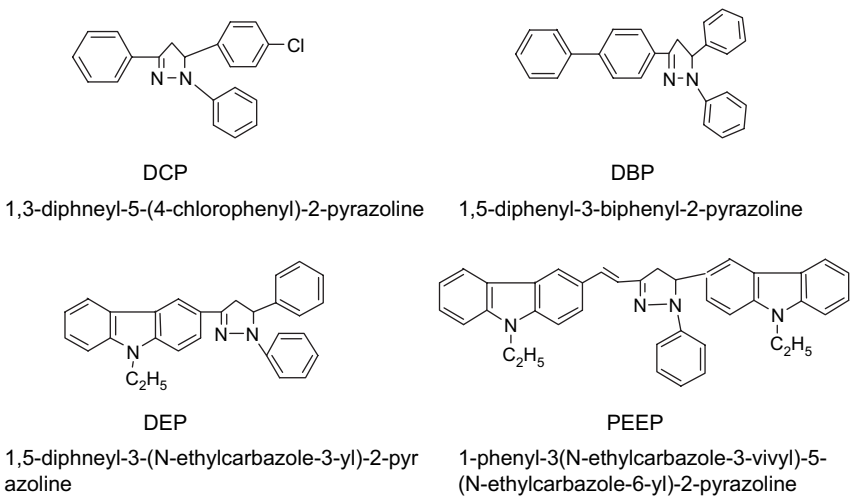
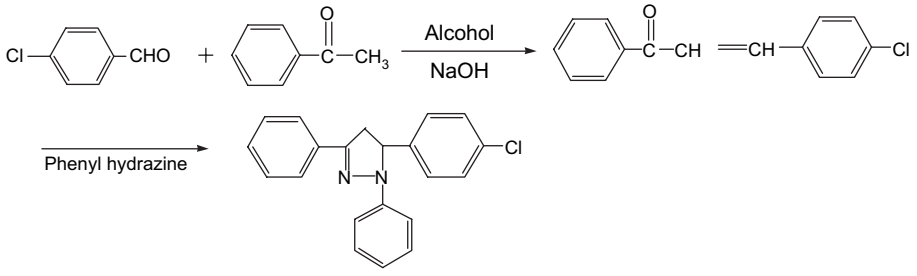
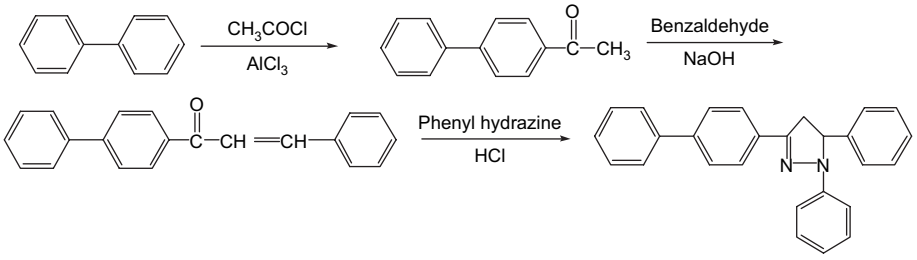


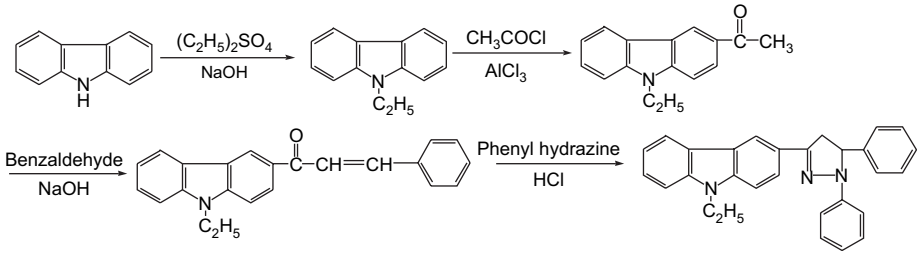
Scheme 1. The structure of four pyrazoline compounds.



Scheme 2. Synthesis of 1,3-diphenyl-5-(4-chloro)phenyl-2-pyrazoline (DCP).



Scheme 3. Synthesis of 1,5-diphenyl-3-biphenyl-2-pyrazoline (DBP).

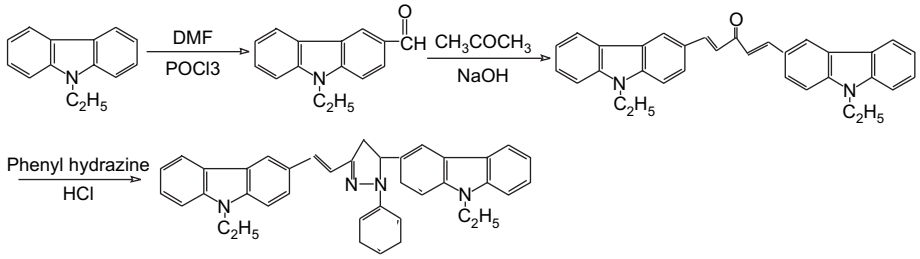


Scheme 4. Synthesis of 1,5-diphenyl-3-(*N*-ethylcarbazole-3-yl)-2-pyrazoline (DEP).

intensities increased initially and then decreased with the concentration increasing. The fluorescence quantum yields of the four compounds were obtained and the fluorescence quantum yield of PEEP was the largest.

2. Experimental

Melting points were determined on x-5 melting point detector. IR spectra were recorded with an FTIR 1730. ^{1}H NMR



Scheme 5. Synthesis of 1-phenyl-3-(*N*-ethylcarbazole-3-vinyl)-5-(*N*-ethylcarbazole-6-yl)-2-pyrazole (PEEP).

spectra were obtained on a Bruker 300 MHz instrument. Fluorescence spectra were obtained on F-4500 spectrofluorometer (Hitachi).

All the reagents were purchased from Beijing Chemical Plant without further purification prior to use.

2.1. Synthesis of DCP

The synthesis route of compound DCP is given in Scheme 2.

2.1.1. Synthesis of phenyl-p-chlorophenyl ketene

According to the method from Ref. [13a], *p*-chlorobenzaldehyde (2.3 g) was dissolved in 50 ml of absolute alcohol. Two millilitres of 15% NaOH aqueous solution was added dropwise in ice bath. Acetophenone (3 ml) was added and it was stirred for 3 h at ambient temperature. The reaction product was filtrated, dried and recrystallized from ethanol. Yellow needle crystalloid (3 g) was obtained. Yield: 70%. M.p. 111–112 °C.

2.1.2. Synthesis of DCP [13b]

Benzol-chlorophenyl-acetone (1 g) was dissolved in 20 ml of glycol monoethyl ether with a little hydrochloric acid being added dropwise. Phenyl hydrazine (1 g) was added and it was stirred at ambient temperature for 3 h. Some water was added to the reaction liquid. The yellow precipitate appeared at once. Recrystallized from ethanol, 1.1 g of light yellow crystalloid was obtained. Yield: 80%. M.p. 152–153 °C. ^{1}H NMR ($CDCl_3$) δ: 3.85 (2H, $-CH_2-$), 3.2 (1H, $-CH=$), 6.8–7.8 (14H, Ar). For $C_{21}H_{17}N_2Cl$ Calcd. (%): C, 75.70; H, 5.11; N, 8.42. Found (%): C, 75.30; H, 5.14; N, 8.34.

2.2. Synthesis of DBP

The synthesis route of compound DBP is described in Scheme 3.

Table 1
The maximum emission spectra of four compounds (1.0×10^{-3} mol/l) in $CHCl_3$

DBP (nm)	DCP (nm)	DEP (nm)	PEEP (nm)
471	463	421	601

2.2.1. Synthesis of p-phenylacetophenone

According to the method from reference, biphenyl (6 g), 28 ml of nitrobenzene, and 5 g of $AlCl_3$ were added into a 3-necked flask and stirred with 2.8 ml of acyl chloride being dropped at ambient temperature. The reaction lasted for 4 h. Nitrobenzene was removed by steam distillation. The residue was recrystallized from ethanol, 4 g of yellow crystals was obtained. Yield: 52%. M.p. 120–121 °C. ^{1}H NMR ($CDCl_3$) δ: 2.66 (3H, $-CH_3$), 7.27–8.1 (9H, diphenyl).

2.2.2. Synthesis of benzal-biphenylacetophenone

p-Phenylacetophenone (30 g) was dissolved in absolute ethanol with stirring. Benzaldehyde (1.2 ml) and 0.5 ml of a 15% KOH aqueous solution were added at ambient temperature. The reaction was kept for 1 h. A yellow powder was obtained. Yield: 69%. M.p. 153–154 °C. ^{1}H NMR ($CDCl_3$) δ: 7.28 (1H, $-COCH=$), 7.91 (1H, $=CH-Ph$), 7.45–8.2 (14H, Ph + diphenyl).

2.2.3. Synthesis of DBP

To a 3-necked flask equipped with a stirrer were added 15 g of benzal-biphenylacetophenone, 300 ml of glycol monoethyl ether, a little hydrochloric acid, and 9 ml of phenyl hydrazine.

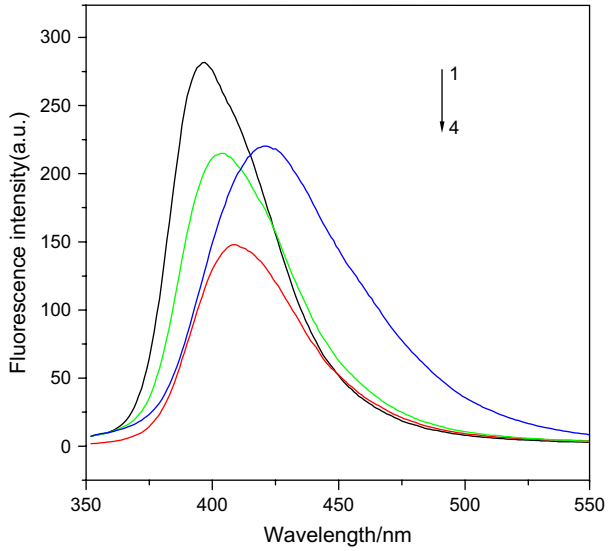


Fig. 1. Fluorescence emission spectra of DEP in different solvents. Solvents: (1) C_6H_6, (2) CH_3CN, (3) THF, and (4) $CHCl_3$.

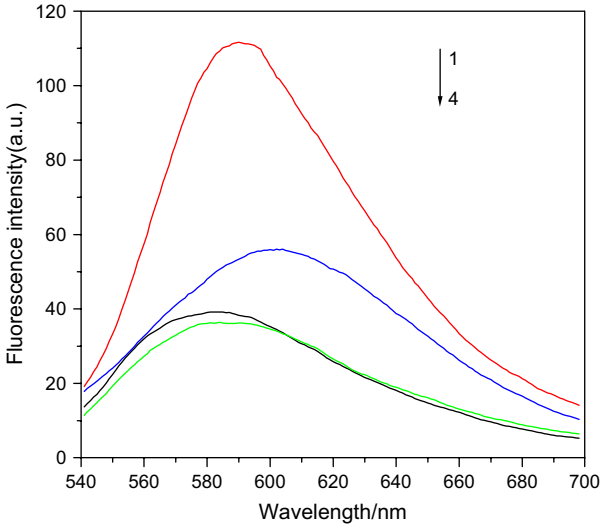


Fig. 2. Fluorescence emission spectra of PEEP in different solvents. Solvents: (1) $CHCl_3$, (2) CH_3CN, (3) C_6H_6, and (4) THF.

The mixture was stirred for 2 h at ambient temperature. A yellow needle crystal was obtained. Yield: 62%. M.p. 196–198 °C. ^{1}H NMR ($CDCl_3$) δ: 3.22 (2H, $-CH_2-$), 3.85 (1H, $-CH=$, pyrazoline), 6.8–7.83 (19H, Ph + diphenyl). For $C_{27}H_{22}N_2$ Calcd. (%): C, 87.33; H, 5.93; N, 7.55. Found: C, 87.23; H, 6.00; N, 7.21.

2.3. Synthesis of DEP

The synthesis route of compound DEP is described in Scheme 4.

2.3.1. Synthesis of N-ethylcarbazole

Carbazole (5 g) , 9.3 g of diethyl sulfate, 5.6 ml of acetone, 4.5 g of NaOH and 3 ml of water were added into a 3-necked flask with stirrer and fastly stirred for 15 min. The reaction mixture was poured into 700 ml of water, white precipitate appears at once. The product was filtrated and recrystallized from ethanol, 4.3 g of white needle crystal was obtained. Yield: 75%. M.p. 72–74 °C. ^{1}H NMR ($CDCl_3$) δ: 1.4 (3H, $-CH_3$), 4.4 (2H, $-CH_2-$), 7.2–8.2 (8H, carbazole).

2.3.2. Synthesis of N-ethyl-3-acetyl-carbazole

N-ethylcarbazole (5 g) was dissolved in 20 ml of benzene, and added 3.4 g of $AlCl_3$, and 2 ml of acetyl chloride was dropped into the mixture, at ambient temperature with stirring for 5 h. The precipitate was recrystallized from ethanol. Yellow-green crystal of 4.6 g was obtained. Yield: 75%. M.p. 116–118 °C. ^{1}H NMR ($CDCl_3$) δ: 1.4 (3H, $-CH_3$), 2.8 (3H, $-COCH_3$), 4.4 (2H, $-CH_2-$), 7.3–8.2 (7H, carbozole). IR (KBr) cm^{-1}: 1660 ($-COCH_3$).

Table 2
The maximum fluorescence emission wavelengths of DEP and PEEP in different solvents

Solvents	DEP (λ_{em}) (nm)	PEEP (λ_{em}) (nm)
Benzene	396	580
Tetrahydrofuran	401	583
Trichloromethane	408	589
Acrylonitrile	421	600

2.3.3. Synthesis of N-ethyl carbazole-3-yl-phenyl ketene

N-ethyl-3-acetylcarbazole (1 g) was dissolved in 20 ml of ethanol and added 1 ml of 10% NaOH aqueous solution, 0.5 ml of benzaldehyde was dropped into this mixture. The reaction solution was stirred for 24 h at ambient temperature. A yellow powder product was obtained after being filtrated and recrystallized from ethanol. Yield: 39%. M.p. 130–132 °C. ^{1}H NMR ($CDCl_3$) δ: 1.4 (3H, $-CH_3$), 4.4 (2H, $-CH_2-$), 7.15–8.18 (12H, Ph + carbozole), 7.3 (1H, $-COH=$), 7.7 (1H, $=CH-Ph$). IR (KBr) cm^{-1}: 1647 ($-CO-$).

2.3.4. Synthesis of DEP

N-ethylcarbazole-3-yl-phenyl ketene (0.4 g) was dissolved in 5 ml of ethyleneglycol monoethyl ether, and a little hydrochloric acid and phenyl hydrazine were added. The mixture was stirred for 8 h at 78 °C. A brown powder product was obtained. Yield: 40%. M.p. 108 °C. ^{1}H NMR ($CDCl_3$) δ: 1.4 (3H, $-CH_3$), 4.4 (2H, $-CH_2-$), 3.5 (2H, $-CH2$, pyrazole), 3.7 (1H, $-CH=$, pyrazole), 7.2–8.2 (17H, Ph + pyrazole). IR (KBr) cm^{-1}: 1540 (C=N).

2.4. Synthesis of PEED

The synthesis route of compound PEED is described in Scheme 5.

2.4.1. Synthesis of N-ethyl-3-formyl carbazole

N-ethylcarbazole (10 g), 100 ml of chlorobenzene, and 5 ml of DMF were added into a 4-necked flask equipped with a stirrer, after dropping 10 ml of $POCl_3$ was reacted at 65–70 °C for 5 h. Appropriate amount of water was added into the reaction mixture, and yellow solid was obtained. A yellow powder product was obtained after recrystallization from ethanol. Yield: 72%. M.p. 86–88 °C. ^{1}H NMR ($CDCl_3$) δ: 1.5 (3H, $-CH_3$), 4.4 (2H, $-CH_2-$), 10.1 (1H, $-CHO$), 7.3–8.7 (7H, carbazole). IR (KBr) cm^{-1}: 1682 ($-CHO$).

2.4.2. Synthesis of bi-(N-ethylcarbazole-3-yl) pentadienone

To a circular flask were added 5 g of *N*-ethyl-3-formyl carbazole, 300 ml of ethanol, and 0.65 ml of acetone. Then by dropping 15 ml of 10% NaOH aqueous solution, at ambient temperature and reacting for 24 h, 2.1 g of the yellow powder was obtained, and separated by the chromatography of silica gel (trichloromethane:ethyl acetate = 3:1). Yield: 30%. M.p. 254 °C. ^{1}H NMR ($CDCl_3$) δ: 1.45 (3H, $-CH_3$), 4.4 (2H, $-CH_2-$), 6.8–7.2 (1H, $-COCH-$), 7.9 (1H, =CH-Carbo). 7.3–8.6 (14H, carbazole). IR (KBr) cm^{-1}: 1610 ($-CO-$).

Table 3
The maximum fluorescence emission wavelength of the four compounds in $CHCl_3$ of different concentrations

DEP		PEEP		DBP		DCP	
C (mol/l)	λ_{em} (nm)	C (mol/l)	λ_{em} (nm)	C (mol/l)	λ_{em} (nm)	C (mol/l)	λ_{em} (nm)
1.0×10^{-3}	421	1.0×10^{-3}	601	1.2×10^{-2}	475	1.0×10^{-3}	463
1.0×10^{-4}	410	1.0×10^{-4}	593	1.0×10^{-3}	471	1.0×10^{-4}	455
1.0×10^{-5}	408	1.0×10^{-5}	588	3.6×10^{-5}	469	1.0×10^{-5}	450
1.0×10^{-6}	414	1.0×10^{-6}	580	8.0×10^{-6}	466	1.0×10^{-6}	446
1.0×10^{-7}	418	1.0×10^{-7}	578	8.0×10^{-7}	461		

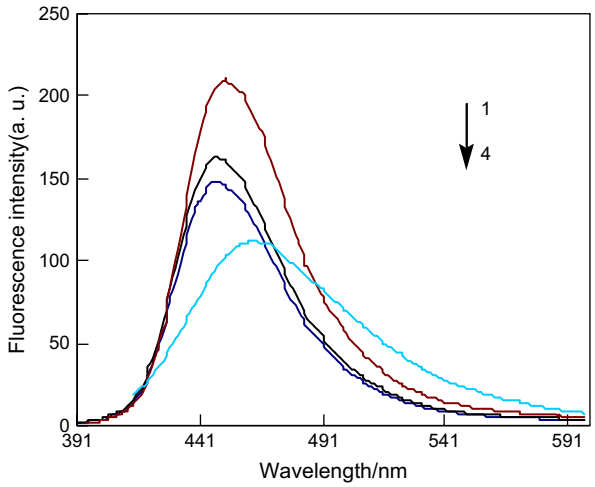


Fig. 3. The fluorescence emission spectra of DCP in $CHCl_3$ of different concentrations (mol/l). (1) 1.0×10^{-4}, (2) 1.0×10^{-5}, (3) 1.0×10^{-6}, and (4) 1.0×10^{-3}.

2.4.3. Synthesis of PEEP

Bi-(*N*-ethylcarbazole-3-yl) pentadienone (1.6 g) was dissolved in 200 ml of ethyleneglycol monoethyl ether, then added were a little hydrochloric acid and 0.4 ml of phenyl hydrazine. The mixture was stirred for 24 h at 110 °C. The reaction liquid was poured into water, which resulted in a brown precipitate at once, filtrated, and dried, then 0.8 g of brown powder was obtained. Yield: 42%. M.p. 110 °C. ^{1}H NMR ($CDCl_3$) δ: 1.5 (3H, $-CH_3$); 2.4 (2H, $-CH_2-$, pyrazoline), 3.6 (1H, $-CH=$, pyrazoline), 4.3 (2H, $-CH=CH-$), 7.2–8.8 (19H, Ph + carbazole). IR (KBr) cm^{-1}: 1566 (C=N).

3. Results and discussions

3.1. The maximum emission spectra of four compounds in $CHCl_3$

The maximum emission spectra of four compounds in $CHCl_3$ are shown in Table 1. It can be observed from Table 1 that a strong donating-electron radical on C-5 position of pyrazoline made the emission wavelength of PEEP red shifted after pyrazoline. The fluorescence emission spectra were red-shifted evidently from DEP (421 nm) to PEEP (λ_{em} = 601 nm). PEEP emits yellow fluorescence. It indicates that the pyrazoline derivatives emitting different colour fluorescence can be obtained by changing substitute radical of C-3 and C-5 positions of pyrazoline.

3.2. The solvent effect on fluorescence emission [14]

The solvent effects on the fluorescence characteristics of the four compounds were studied, which indicate that the

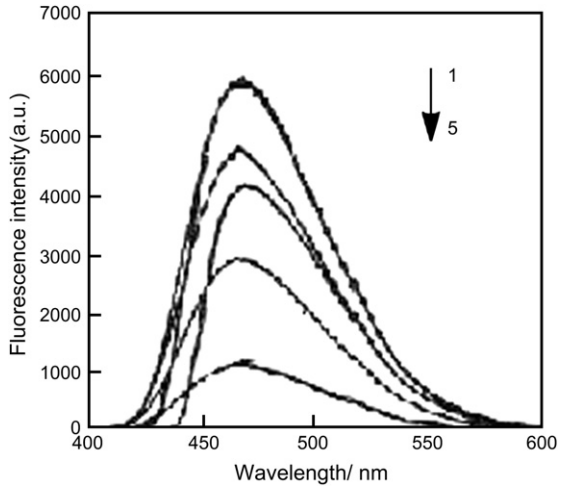


Fig. 4. The fluorescence emission spectra of DBP in $CHCl_3$ of different concentrations (mol/l). (1) 1.0×10^{-3}, (2) 3.6×10^{-5}, (3) 1.2×10^{-2}, (4) 8×10^{-6}, and (5) 8.0×10^{-7}.

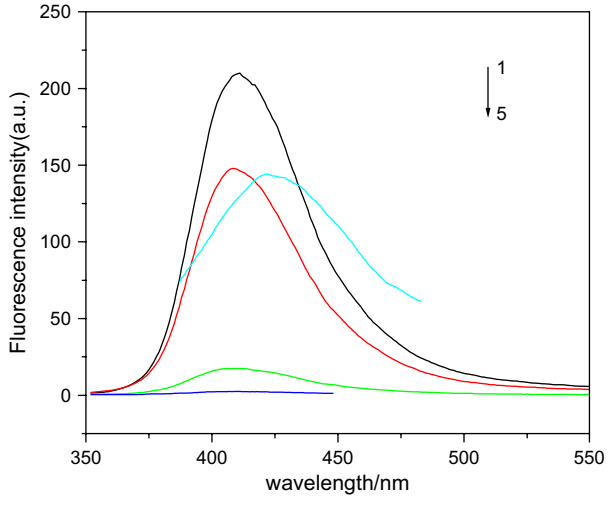


Fig. 5. The fluorescence emission spectra of DEP in $CHCl_3$ of different concentrations (mol/l). (1) 1.0×10^{-4}, (2) 1.0×10^{-5}, (3) 1.0×10^{-3}, (4) 1×10^{-6}, and (5) 1.0×10^{-7}.

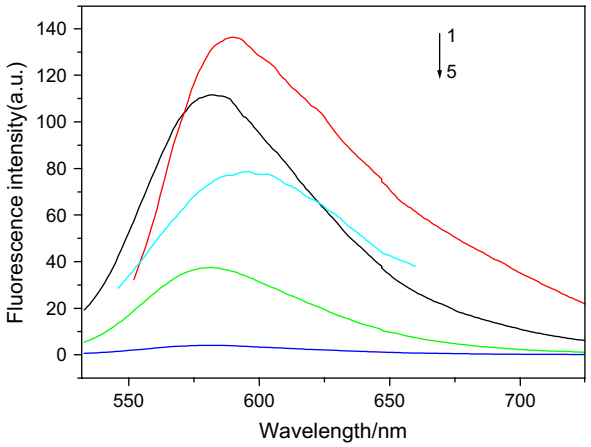


Fig. 6. The fluorescence emission spectra of PEEP in $CHCl_3$ of different concentrations (mol/l). (1) 1.0×10^{-4}, (2) 1.0×10^{-5}, (3) 1.0×10^{-3}, (4) 1×10^{-6}, and (5) 1.0×10^{-7}.

emission wavelength of the compounds was red-shifted with the increase of solvent polarity (Figs. 1–2 and Table 2).

3.3. The concentration effect of fluorescence emission

The concentration effects on fluorescence intensities of the four compounds were studied. The maximum fluorescence emission wavelengths of the four compounds in $CHCl_3$ in different concentrations were listed in Table 3 and their fluorescence spectra were shown in Figs. 3–6. It indicates that the fluorescence intensities increased initially and then decreased with the concentration increasing. The fluorescence was quenched because fluorescent dye molecules happened to collide with each other.

Maximum emission spectra of the compounds shifted to red, which are attributed to the di-aggregates, tri-aggregates or poly-aggregates which formed with concentration increasing and the conjugate system of the compounds are strengthened.

3.4. The photo-physical behavior [15,16]

The charge transfer mechanism of pyrazoline is the competition between N1 → N2 → C3 conjugate charge transfer and N1 → C5 non-conjugate charge transfer. The substituent in the 5-position of pyrazoline is donating-electron radical, which enhances donating-electron ability of the 1-position of it. When the compounds are in the excited state, the electron transfer occurs and the molecule is polarized, which is contributed due to the fact that intramolecular conjugated charge transfer is predominant and strong fluorescence occurs.

Table 4
The fluorescence quantum yields of four compounds

DBP	DCP	DEP	PEEP
0.56	0.58	0.576	0.68

3.5. The fluorescence quantum yields of four compounds

The fluorescence quantum yields of four compounds were listed in Table 4. It was observed that the fluorescence quantum yield of PEEP was the largest. Substitute radical in 3-position of PEEP has larger conjugation than DBP, DCP and DEP, and its 5-position also has a strong donating-electron radical. So in the excited state, the strong charge transfer of intramolecule occurred.

Acknowledgements

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