

Derivatives of 4-dihydroquinolinone and their fluorescent property

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Abstract: A series of donor- π -acceptor (D- π -A) compounds involving varied donors and acceptors as well as a dihydroquinolinone moiety were synthesized. Tuned fluorescent colors from blue to orange were successfully realized in them. Spectroscopic analysis exhibits that the increased conjugated system, enhanced electron-donating ability of acceptor, and electron-withdrawing ability of donor result in red shift in both absorption and fluorescence for these compounds. Both the absorption and fluorescence show strong bathochromic shift effect with the increase in the polarity of solvents. It indicates that they are intramolecular charge transfer (ICT) fluorescent compounds and may have potential application as novel electroluminescent material.

Key words: dihydroquinolinone; donor- π -acceptor (D- π -A); red shift; intramolecular charge transfer

Quinacridones (QAs)^[1] are widely used organic pigments for the applications of high-sensitivity photo-sensors or photoreceptors required for electro-photography^[2], solar cells^[3], and optical probes^[4], etc. QA was often used as a fluorescent guest in organic lighting emitting diodes (OLED) for their strong emissions in the solid film^[5-7]. However, the quinacridone derivatives can easily form an excimer or exciplex by hydrogen bond and the planar structure which may result in quenching or a non-radiative pathway. Multi-substitution of QA at N atom and benzene ring with long alkyl or alkyloxy was conducted to improve their properties^[8]. Here we synthesize a series of dihydroquinolinone derivatives with the skeleton of QA but much fewer conjugated rings than QA, which are unfavorable to form excimer or exciplex. These derivatives belong to the structural modes of D- π -A, where D is an electron-donating group, A is an electron-acceptor group, and π is a conjugating linker. Different fluorescent colors were obtained by modifying D, A, and their arrangement mode. These compounds with tuned fluorescent colors may meet some requirements in electroluminescence.

1 Experimental

¹HNMR spectroscopy was obtained from a Bruker DRX (300 MHz and 500 MHz, relative to TMS). IR spectroscopy was determined by Nicolet-170. The UV-vis absorption spectra were measured on a Shimadzu

UV-2201 spectrophotometer and the fluorescence spectra were recorded using a Hitachi-850 spectrofluorophotometer.

1) 2, 3-Dihydroquinolin-4(1H)-one (DHQ)

As shown in Fig. 1, the starting compound, N-tosyl- β -anilinopropionic acid, was prepared according to literature procedure^[9]. In a three neck 100-mL round bottom flask equipped with a condenser and thermometer, above acid (5 g, 15.7 mmol) was mixed with polyphosphoric acid (PPA) (45 g, 133 mmol), then it was kept at 110 °C for 0.5 h under stirring, and the orange melt was slowly decomposed with water, basified with sodium hydroxide and extracted with ether. The ethereal extract was washed with 5% NaOH aqueous solution and saturated brine, and dried with anhydrous magnesium sulfate. The ether was removed under reduced pressure to afford DHQ as a yellow solid (2.0 g, 85%). IR (KBr): $\nu = 3\ 311\ \text{cm}^{-1}$ (N—H), $\nu = 1\ 650\ \text{cm}^{-1}$ (C=O). ¹HNMR (300 MHz, CDCl₃, δ): 2.64 to 2.73 (m, 2H, $J = 7.8\ \text{Hz}$), 3.52 to 3.60 (m, 2H, $J = 6.9\ \text{Hz}$), 4.65 (s, 1H), 6.65 to 6.76 (m, 2H, $J = 4.5\ \text{Hz}$), 7.27 to 7.33 (m, 1H, $J = 3.0\ \text{Hz}$), 7.81 to 7.86 (m, 1H, $J = 6.6\ \text{Hz}$, 1.2 Hz); mp: 42 to 43 °C.

2) 1-Hexyl-2, 3-dihydroquinolin-4-one (HDHQ)

In a four neck 100-mL round bottom flask

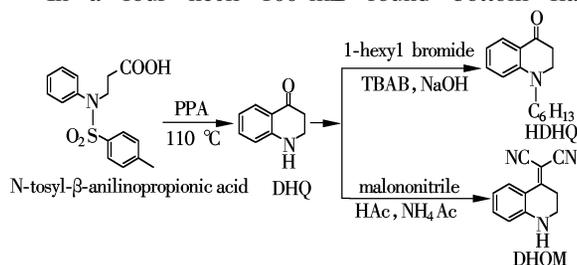


Fig. 1 Synthesis outline of DHQ, HDHQ and DHQM

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equipped with a condenser and thermometer, DHQ (1.47 g, 10 mmol), 1-hexyl bromide (2.1 g, 12.7 mmol), tetrabutylammonium bromide (TBAB) (0.5 g, 3.2 mmol) and 10 mL 50% NaOH aqueous solution in 25 mL 2-butanone were vigorously stirred and heated to reflux for 2.5 h. Then the reaction mixture was poured into water, extracted with cyclohexane, concentrated and purified by chromatography (silica gel, chloroform) to afford HDHQ as liquid (0.46 g, 20%). ¹HNMR (500 MHz, CDCl₃, δ): 0.90 to 0.92 (t, 3H, *J* = 5.65 Hz), 1.34 to 1.41 (m, 6H, *J* = 13 Hz), 1.59 to 1.65 (m, 2H, *J* = 7.5 Hz), 2.67 to 2.70 (t, 2H, *J* = 7.0 Hz), 3.33 to 3.36 (t, 2H, *J* = 7.0 Hz), 3.50 to 3.52 (t, 2H, *J* = 7.0 Hz), 6.66 to 6.71 (q, 2H, *J* = 10.5 Hz, 7.0 Hz), 7.34 to 7.37 (q, 1H, *J* = 7.0 Hz), 7.88 to 7.90 (d, 1H, *J* = 8.0 Hz).

3) 2-(2, 3-Dihydroquinolin-4(1H)-ylidene) malonitrile (DHQM)

In a 100-mL round bottom flask equipped with a water distributor, DHQ (4.4 g, 30 mmol), malonitrile (2.2 g, 34.4 mmol), NH₄Ac (0.3 g, 4mmol) and 1.3 mL HAc in 25 mL benzene were refluxed until no more water was separated. Then most solvent was removed under reduced pressure. The precipitated red solid was recrystallized in ethanol to afford DHQM (3.83 g, 65%). IR (KBr): $\nu = 3370 \text{ cm}^{-1}$ (N—H), $\nu = 2218 \text{ cm}^{-1}$ (C≡N). ¹HNMR (500 MHz, CDCl₃, δ): 3.07 to 3.10 (t, 2H, *J* = 6.65 Hz), 3.53 to 3.55 (t, 2H, *J* = 6.5 Hz), 4.66 (s, 1H), 6.61 to 6.63 (d, 1H, *J* = 8.25 Hz), 6.73 to 6.76 (t, 1H, *J* = 7.7 Hz), 7.30 to 7.33 (t, 1H, *J* = 7.75 Hz), 8.23 to 8.25 (d, 1H, *J* = 8.3 Hz); mp: 159 to 161 °C.

4) 1,6-Diketojulolidine (DKJD)

DKJD was synthesized according to Ref. [10] (see Fig. 2). IR (KBr): $\nu = 1676 \text{ cm}^{-1}$ (C=O). ¹HNMR (500 MHz, CDCl₃, δ): 2.83 to 2.86 (t, 4H, *J* = 7.0 Hz), 3.49 to 3.52 (t, 4H, *J* = 7.0 Hz), 6.86 to 6.89 (t, 1H, *J* = 7.5 Hz), 8.11 to 8.12 (d, 2H, *J* = 8.0 Hz); mp: 142 to 143 °C.

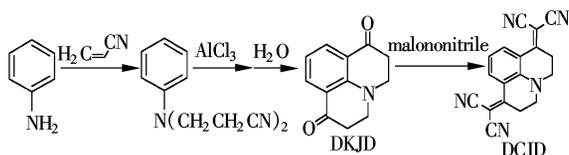


Fig. 2 Synthesis outline of DKJD and DCJD

5) 1,6-Bisdicyanomethylene julolidine (DCJD)

In a 100-mL round bottom flask equipped with a water distributor, DKJD (0.45 g, 2.2 mmol), malonitrile (0.53 g, 8 mmol), NH₄Ac (0.2 g, 2.6 mmol) and 0.7 mL HAc in 10 mL benzene were mixed and refluxed for 2 h. Then about two-thirds of solvent was

removed and the mixture was placed overnight, the precipitated deep red solid was recrystallized in HAc to afford a purple solid DCJD (0.46 g, 69%). IR (KBr): $\nu = 2219 \text{ cm}^{-1}$ (C≡N). ¹HNMR (500 MHz, CDCl₃, δ) 2.84 to 2.87 (t, 4H, *J* = 7.0 Hz), 3.50 to 3.52 (t, 4H, *J* = 7.0 Hz), 6.87 to 6.90 (t, 1H, *J* = 7.5 Hz), 8.12 to 8.14 (d, 2H, *J* = 8.0 Hz); mp: 204 to 206 °C.

2 Results and Discussion

2.1 Absorption

UV-vis spectra of HDHQ (0.1 mmol/L) in different solvents are investigated (see Fig. 3). The absorption consists of three bands in the 200 to 450 nm region. Moreover, the long-wavelength absorption band of HDHQ in different solvents shifts to a longer wavelength region with the increasing polarity of solvents. When the solvent is changed from cyclohexane to methanol, its maximal wavelength has red shift as much as 20 nm. Detailed peak wavelengths of the long-wavelength absorption band for DHQ, HDHQ, HDQM, DKJD and DCJD in different solvents are shown in Tab. 1. Obviously, they all show large red shift when solvent is changed from cyclohexane to ethanol. It means that there may exist dipole moments or charge transfer upon the excited state of the dye molecules in polar solvent^[11].

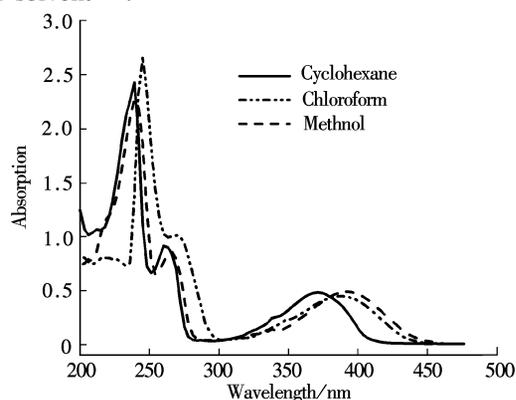


Fig. 3 Absorption of HDHQ (0.1 mmol/L) in different solvents

Tab. 1 Maximal wavelength of the long-wavelength absorption band for derivatives in different solvents

Solvent	λ_{max} of long-wavelength absorption/nm				
	DHQ	HDHQ	HDQM	DKJD	DCJD
Cyclohexane	360	371	430	392	490
Ethanol	381	390	464	406	507

Fig. 4 shows the UV-vis spectra of DHQ, HDHQ and DHQM (0.1 mmol/L) in chloroform. The shapes of the absorption spectra of compounds DHQ, HDHQ and DHQM are mainly similar to long characteristic absorption above 300 nm. The long-wavelength absorption peak of DHQ, HDHQ and DHQM can be

recognized at 365, 388 and 440 nm, respectively. It is observed that the maximum of a longer wavelength absorption band shows red shift from DHQ to HDHQ and DHQM. This can be ascribed to the enhanced electron-donating ability after N-alkylation in HDHQ and the electron-withdrawing ability of $C=C(CN)_2$ group after replacement of $C=O$ group in DHQM, respectively^[12]. As shown in Tab. 1, the same result is found for DKJD and DCJD. When the $C=O$ group in DKJD is replaced by the $C=C(CN)_2$ group, large red shift occurs both in non-polar solvent (cyclohexane) and polar solvent (ethanol).

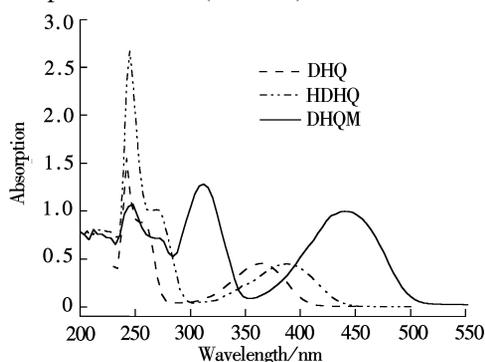


Fig. 4 Absorption of DHQ, HDHQ and DHQM (0.1 mmol/L) in chloroform

2.2 Fluorescence and intramolecular charge transfer (ICT)

Fluorescences of DHQ, HDHQ and DHQM in chloroform are shown in Fig. 5. Combining with Fig. 4, the Stoke's shifts of DHQ, HDHQ and DHQM in chloroform can be recognized for 77, 80 and 90 nm, respectively. The large Stoke's shifts can be attributed to D- π -A structure of these compounds^[13-14]. It is noted that the fluorescence shows red shift from DHQ to HDHQ and DHQM. This also can be explained by the intense electron-donating ability of N atom after N-alkylation in HDHQ, and the strong electron-withdrawing ability of $C=C(CN)_2$ moiety as well as long conjugated length in DHQM as discussed above.

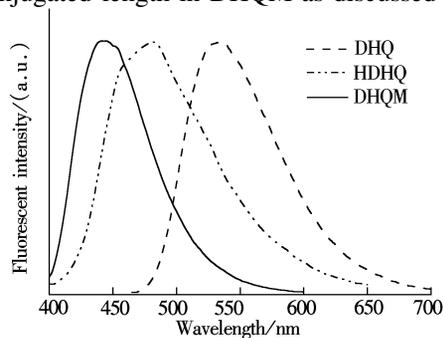


Fig. 5 Fluorescences of DHQ, HDHQ and DHQM in chloroform

The fluorescent peaks of DHQ, HDHQ, DHQM, DKJD and DCJD in different solvents are listed in Tab. 2. It is shown that the maximum of fluorescence shows red shift (30 nm) from DHQ to DKJD in cyclohexane. The reason may be that the excited conjugation system in DKJD is larger than that of DHQ. DCJD emits the longest wavelength of fluorescence in cyclohexane among the above compounds. It can be attributed to the strong electron-withdrawing ability of $C=C(CN)_2$ group and the largest excited conjugation system in DCJD. Furthermore, the emissions of these compounds range from blue to orange-red. This reveals that emitting materials with different colors, especially the red color, can be obtained by modifying the structure of 4-dihydroquinolinone.

Tab. 2 Maximal wavelength of fluorescence of derivatives in different solvents

Solvent	λ_{max} of emission/nm				
	DHQ	HDHQ	DHQM	DKJD	DCJD
Cyclohexane	412	430	502	442	538
Ether	421	455	532		
Dichloromethane				468	565
THF	430			468	591
DMF	442	464	540		
Ethanol				499	598
Methanol	503	491	593		
H ₂ O				521	

Variation in the fluorescence spectrum of DHQ in solvents is shown in Fig. 6. It is found that the fluorescent peaks of all compounds show large bathochromic shifts with the increase in the polarity of solvents. This means that dipole moments of these compounds increase upon excitation. It can be attributed to the intramolecular charge transfer (ICT) formed upon the excited state for these D- π -A structure compounds (see Fig. 7). The same conclusion was previously obtained from the results of PPP and CNDO/S quantum-chemical calculations for dihydroquinolinones by Bakalova^[15]. Other compounds involving HDHQ, DHQM DKJD, and DCJD have a similar D- π -A

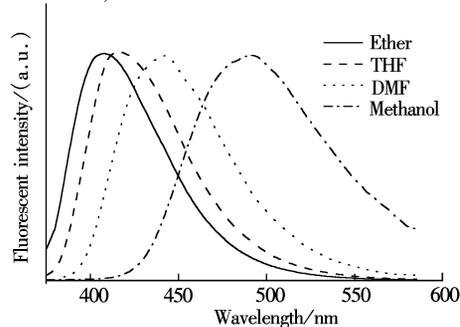


Fig. 6 Fluorescence of DHQ excited at 365 nm in different solvents

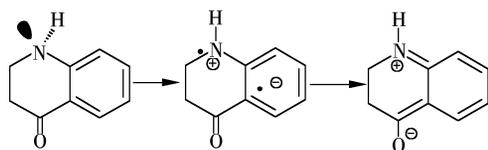


Fig. 7 Assumed ICT model in DHQ upon excited state

structure with DHQ, which results in ICT upon excited state and the large bathochromic shifts with the increase in the solvent polarity (see Tab. 2).

3 Conclusion

We synthesize a series of 4-dihydroquinolinone derivatives with D- π -A structure. The effects of structure and solvent on their absorption and fluorescence were investigated. The result indicates that a large conjugated system and groups with strong electron-withdrawing or electron-donating ability can result in large red shifts in both absorption and fluorescence. Both the absorption and photoluminescence show strong bathochromic shift effects with the increase in the polarity of solvents. It indicates that there exists ICT upon excited state. These derivatives may have potential application in electroluminescence as a novel organic dye.

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4-二氢喹啉酮衍生物及其荧光性质

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摘要: 在喹啉酮结构的基础上, 设计合成了一系列具有推拉电子结构且含二氢喹啉酮结构的化合物, 并研究了结构改变和不同溶剂对吸收光谱和荧光光谱的影响. 研究发现化合物中增大的共轭体系和增强的推拉电子基团会导致吸收峰和荧光峰产生大的红移; 随着结构的改变, 这些化合物的荧光从蓝色变成橙红色. 这些化合物随着溶剂极性的增加, 吸收峰和荧光峰都表现出强烈的红移. 并进一步研究了这类荧光化合物的分子内电荷转移现象. 它们作为一类新的荧光化合物在电致发光领域有潜在的应用价值.

关键词: 二氢喹啉酮; 推拉电子结构; 红移; 分子内电荷转移

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