Synthesis and luminescence properties of N-carbazole acetyl hydrazones Schiff-bases

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Three new N-carbazole acetyl hydrazones Schiff-bases were synthesized by the condensation reaction between N-carbazolyl acetyl hydrazine and the substituted benzaldehydes in anhydrous ethanol, and characterized by elemental analysis, Fourier transform-infrared (FT-IR), ^{1}H-NMR and mass spectral analysis. The relationships between the substituent type and the UV, fluorescence spectral properties as well as the fluorescence quantum yields of the title Schiff-bases were also investigated. The results indicate that the fluorescence quantum yields of the title Schiff-bases with accepting electron groups are decreased, while that of the title Schiff-bases with donating electron group are increased. The fluorescence quantum yield of the 2-(9H-carbazol-9-yl)-N'-(2-hydroxybenzylidene) acetohydrazide is up to 0.631.

1. Introduction

Schiff-base, which is a special type of compound containing C=N bond, possesses various coordination forms, strong coordination ability, peculiar pharmacological activities and nonlinear optical properties [1-4], and widely applied in such fields as biological activity, drug design, fluorescence assay reagent and catalysis [5-9]. The Schiff bases containing carbazolyl group possess the stronger conjugated system and the higher intramolecular electron transfer efficiency than the general Schiff bases, so they are expected to extend the potential applications in fluorescent material fields.

In this paper, three new carbazolyl acylhydrazones Schiff-bases were synthesized by the condensation reactions between the N-carbazole acetyl hydrazines and the substituted benzaldehydes. In order to fully discuss the effects of the different substituents on the UV and fluorescence spectral properties, other six carbazolyl acylhydrazones Schiff-bases were also synthesized. The synthesis route is shown in **Scheme 1**. All the as-synthesized title compounds as well as their intermediates have been characterized by Nuclear Magnetic Resonance Spectroscopy (NMR), Mass Spectroscopy (MS), Infrared Spectroscopy (IR) and elemental analysis. The effects of the different substituents on the fluorescence quantum yields of the title compounds have been investigated in detail.
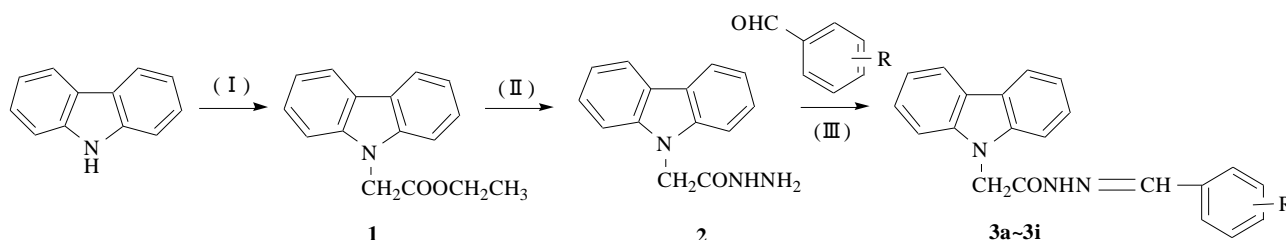
3a, R=4-CHO; **3b**, R=3-NO$_2$; **3c**, R=4-NO$_2$; **3d**, R=4-Cl ; **3e**, R=H; **3f**, R= 4-OH; **3g**, R=4-OCH$_3$; **3h**, R=4-CH$_3$; **3i**, R=2-OH

(I) BrCH$_2$COOC$_2$H$_5$, KOH, (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$NBr, (CH$_3$)$_2$CO; (II) NH$_2$NH$_2$H$_2$O, C$_2$H$_5$OH; (III) C$_2$H$_5$OH, CH$_3$COOH.

Scheme 1

2. Experimental

Materials

Carbazole, substituted benzaldehydes and ethyl bromoacetate were of AR grade and came from Sinopharm Chemical Reagent Co.,Ltd. Other reagents and solvents were also of AR grade and were obtained commercially.

Melting points are uncorrected. ^{1}H NMR spectra were recorded on Varian-400 spectrometers. Chemical shifts are reported as δ values in units of ppm relative to the Me$_4$Si as an internal standard (dimethysulfoxide (DMSO)-d$_6$ or CDCl$_3$ as solvent). Mass spectra were recorded on an Agilent 1100 and a VG Auto Spec-300 mass spectrometer. A Vario ELⅢ elemental analyser was used to collect microanalytical data (C, H, N). IR spectra were determined as KBr pallets, using a PerkinElmer Spectrum One Spectrophotometer. Fluorescence spectra were obtained on a Hiachi F-4500 Spectrophotometer.

Synthesis of *N*-carbazolyl ethyl acetate (1)

Carbazole (0.84 g, 5 mmol), potassium hydroxide (1.00 g, 17.8 mmol) and tetrabutyl ammonium bromide (0.05 g, 0.155 mmol) were dissolved in acetone (40 mL) in a 100 mL single aperture flask, and stirred for 20 min. Ethyl bromoacetate (1.67 g, 10 mmol) was then added to it, and the mixture was heated to reflux for another 5 hours. The acetone was evaporated under vacuum, the residual product was dissolved in dichloromethane (50 mL). The organic layer was washed with water, then evaporated to obtain a light yellow solid coarse product. This coarse product was purified over a silica gel column with the eluent of dichloromethane/benzin (1:1, v/v). The second band was collected, then evaporated and dried under vacuum. The product was a white solid, yield 85%. MS (EI) m/z (%): 253 (M, 21), 180 (100), 152 (21), 90 (12), 76(10).

Synthesis of *N*-carbazolyl acetyl hydrazine (2)

N-carbazolyl ethyl acetate (0.25 g, 1 mmol) were dissolved with anhydrous ethanol (25 ml) in a 100 mL single aperture flask. The 85% hydrazine hydrate (1.12 g, 20 mmol) was then added to it. The mixture was heated to reflux for 15 hours, and cooled down, then a large white precipitate was formed when diluted with 100 mL cold water. The product was washed with water, and then evaporated and dried under a vacuum, forming a white solid, yield 91%. ^{1}H NMR (400 MHz, CDCl$_3$) δ/ppm: 2.17 (d, 2H), 5.57 (s, 2H), 7.20(d, 2H, *J*=8.0 Hz), 7.27 (q, 4H, *J*=4.4 Hz), 7.33 (d, 2H, *J*=8.0 Hz), 7.44 (t, 2H, *J*=8.4 Hz), 7.69 (s, 1H), 8.14(d, 2H, *J*=7.6 Hz).

The general procedure for the synthesis of Schiff-bases (3a~3i)

The synthesis procedure of the as-synthesized nine acylhydrazone Schiff-bases is similar, so it is only illustated how to synthesize the *N'*-benzylidene-2-(9H-carbazol-9-yl)acetohydrazide (**3e**).

N-carbazolyl acetyl hydrazine (**2**) (0.239 g, 1 mmol)

and benzaldehyde (0.212 g, 2 mmol) were dissolved with anhydrous ethanol (10 mL) in the 100 mL three-necked flask, glacial acetic acid (0.5 mL) was then added to it. The mixture solution was heated to reflux for 1 hour at 80~85℃, then cooled to room temperature to form precipitates. The coarse product was filtered, and recrystallized, then dried to get the objective compound, yield 90%, m. p. 281~283℃. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ/ppm: 5.61 (s, 2H, N-CH$_2$) , 7.21 (m, 2H, *J*=8.0 Hz), 7.42 (m, 5H, aromatic protons), 7.54 (d, 2H, *J*=8.0 Hz, aromatic protons), 7.78 (s, 2H), 8.10 (s, 1H, N=CH), 8.15 (d, 2H, *J*=7.6 Hz), 11.74 (s, 1H, NH-N); IR (KBr), *v*/cm^{-1}: 3437, 3188, 3084, 2966, 1682, 1615, 1598, 1486, 1461, 1422, 1279, 1129, 881, 745, 721, 692. MS (EI) m/z (%): 327 (M, 25), 180 (100), 152 (23). Anal.calcd for C$_{21}$H$_{17}$N$_3$O: C 77.04, H 5.23, N 12.84; found C 77.10, H 5.26, N 12.67.

2-(9H-carbazol-9-yl)-*N'*-(4-formylbenzylidene)acetohydrazide (3a)

The product being a white solid, yield 80%, m. p. 264~266℃. ^{1}H NMR (400MHz, DMSO-d$_6$) δ/ppm: 5.62 (s, 2H), 7.20 (q, 2H, *J*=8.0 Hz), 7.36 (m, 2H), 7.55~7.65 (m, 4H), 7.84 (d, 2H, *J*=8.4 Hz), 8.06 (s, 1H), 8.17 (d, 2H, *J*=8.0 Hz), 9.98 (s, 1H), 11.90 (s, 1H); IR (KBr), *v*/cm^{-1}: 3436, 3090, 2928, 1649, 1599, 1485, 1460, 1545, 1278, 1207, 1132, 745, 721. MS (API) m/z (%):357 (M+2, 35), 356 (M＋1, 100). Anal.calcd for C$_{22}$H$_{17}$N$_3$O$_2$: C 74.35, H 4.82, N 11.82; found C 74.30, H 4.76, N 11.79.

2-(9H-carbazol-9-yl)-*N'*-(3-nitrobenzylidene)acetohydrazide (3b)

The product being a yellow solid, yield 76%, m. p. 234~235℃. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ/ppm: 5.77 (s, 2H), 7.18~7.25 (m, 2H), 7.40~7.47 (m, 2H), 7.53~7.59 (m, 2H), 7.74~7.78 (t, 1H, *J*=8.0 Hz), 8.13~8.18 (m, 2H), 8.25~8.29 (m, 2H), 8.40 (s, 1H), 8.63 (s, 1H), 12.00 (s, 1H); IR (KBr), *v*/cm^{-1}: 3435, 3307, 3084, 2926, 1681, 1659, 1610, 1503, 1485, 1460, 1345, 1271, 1269, 1154, 744, 722. MS (EI) m/z (%): 372 (M, 5), 180 (100), 152 (35), 77 (10), 63 (8). Anal.calcd for C$_{21}$H$_{16}$N$_4$O$_3$: C 67.73, H 4.33, N 15.05; found C 67.86, H 4.23, N 15.12.

2-(9H-carbazol-9-yl)-*N'*-(4-nitrobenzaldehyde)acetohydrazide (3c)

The product being a yellow solid, yield 81%, m. p. 278~282℃. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ/ppm: 5.75 (s, 2H), 7.21 (s, 2H), 7.42 (s, 2H) ,7.55 (d, 2H, *J*=8.4 Hz), 7.90(s, 2H) , 8.07 (d, 2H, *J*=8.4 Hz), 8.15 (t, 2H, *J*=8.0 Hz), 8.31 (d, 2H, *J*=8.4 Hz), 12.07 (s, 1H); IR (KBr), *v*/cm^{-1}: 3436, 3189, 3112, 2966, 2924, 2849, 1681, 1598, 1587, 1521, 1460, 1341, 1275, 1136, 1108, 880, 850, 748, 722, 690. MS (EI) m/z (%): 372 (M, 5), 180 (100), 152 (25), 76 (10). Anal.calcd for C$_{21}$H$_{16}$N$_4$O$_3$: C 67.73, H 4.33, N 15.05; found C 67.69, H 4.37, N 15.12.

2-(9H-carbazol-9-yl)-*N'*-(4-chlorobenzaldehyde)acetohydrazide (3d)

The product being a white solid, yield 80%, m. p.

265~267℃. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ/ppm: 5.65 (s, 2H), 7.23 (q, 2H, J=8.0 Hz), 7.42 (m, 2H), 7.53 (m, 4H), 7.82 (d, 2H, J=8.4 Hz), 8.07 (s, 1H), 8.15 (d, 2H, J=8.0 Hz), 11.79 (s, 1H); IR (KBr), ν/cm^{-1}: 3436, 3186, 3027, 2964, 2925, 1682, 1616, 1598, 1540, 1486, 1460, 1421, 1288, 1208, 1091, 881, 828, 743, 721. MS (EI) m/z (%): 362 (M+1, 100), 180 (60), 160 (20), 152 (23), 77 (10). Anal.calcd for C$_{21}$H$_{16}$ClN$_3$O: C 69.71, H 4.46, N 11.61; found C 69.60, H 4.37, N 11.56.

2-(9H-carbazol-9-yl)-N'-(4-hydroxybenzylidene)acetohydrazide (3f)

The product being a white solid, yield 89%, m. p. >300℃. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ/ppm: 5.60 (s, 2H), 6.82 (t, 2H, J=4.0 Hz), 7.19 (dd, 2H, J=4.0 Hz), 7.39~7.44 (m, 2H), 7.51~7.55 (m, 3H), 7.56~7.62 (m, 2H), 8.15 (d, 2H, J=8.0 Hz), 9.93 (s, 1H), 11.54 (s, 1H); IR (KBr), ν/cm^{-1}: 3248, 3069, 2927, 1665, 1648, 1621, 1515, 1454, 1277, 1244, 1155, 751, 722; MS (EI) m/z (%): 420 (M+1, 5), 419 (M, 20), 300 (30), 166 (60). Anal.calcd for C$_{22}$H$_{17}$N$_3$O$_2$: C 73.45, H 4.99, N 12.24; found C 73.36, H 4.89, N 12.31.

2-(9H-carbazol-9-yl)-N'-(4-methoxybenzaldehyde)acetohydrazide (3g)

The product being a white solid, yield 91%, m. p. 210~213℃. ^{1}H NMR (400MHz，DMSO-d$_6$) δ/ppm: 3.79 (s, 3H), 5.62 (s, 2H), 7.01 (t, 2H, J=8.4 Hz), 7.22 (q, 2H, J=8.0 Hz), 7.45 (q, 2H, J=8.4 Hz), 7.55 (q, 2H, J=8.4 Hz), 7.71 (d, 2H, J=8.8 Hz), 8.03 (s, 1H), 8.17 (d, 2H, J=8.0 Hz), 11.60 (s, 1H); IR (KBr), ν/cm^{-1}: 3436, 3187, 3047, 2964, 2836, 1678, 1602, 1518, 1485, 1461, 1282, 1168, 1034, 831, 744, 721. MS (EI) m/z (%): 358 (M+1, 3), 357 (M, 12), 152 (23), 136 (10), 77 (10). Anal.calcd for C$_{22}$H$_{19}$N$_3$O$_2$: C 73.93, H 5.36, N 11.76; found C 73.67, H 5.35, N 11.80.

2-(9H-carbazol-9-yl)-N'-(4-methylbenzaldehyde)acetohydrazide (3h)

The product being a white solid, yield 86%, m. p. >300℃. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ/ppm: 2.58 (s, 3H), 5.63(s, 2H), 7.24(dd, 2H, J=8.0 Hz), 7.32 (d, 2H, J=8.0 Hz), 7.39~7.45 (m, 3H), 7.53 (d, 2H, J=4.0 Hz), 7.68 (d, 2H, J=4.0 Hz), 8.17 (d, 2H, J=8 Hz), 11.67 (s, 1H); IR (KBr), ν/cm^{-1}: 3436, 3189, 3048, 2966, 1678, 1615, 1599, 1485, 1461, 1421, 1280, 1154, 880, 742, 721. MS (EI) m/z (%): 342 (M+1, 5), 341 (M, 25), 180 (100), 152 (23), 77 (10). Anal.calcd for C$_{22}$H$_{19}$N$_3$O: C 77.40, H 5.61, N 12.31; found C 77.33, H 5.69, N 12.28.

2-(9H-carbazol-9-yl)-N'-(2-hydroxybenzylidene)acetohydrazide (3i)

The product being a white solid, yield 90%, m. p. 234~235℃. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ/ppm: 5.77 (s, 2H), 7.18~7.25 (m, 2H), 7.40~7.47 (m, 2H), 7.53~7.59 (m, 2H), 7.74~7.78 (t, 1H, J=8.0 Hz), 8.13~8.18 (m, 2H), 8.25~8.29 (m, 2H), 8.40 (s, 1H), 8.63 (s, 1H), 12.00 (s, 1H); IR (KBr), ν/cm^{-1}: 3435, 3307, 3084, 2926, 1681, 1659, 1610, 1503, 1485, 1460, 1345, 1271, 1269, 1154, 744, 722. MS (EI) m/z (%): 372 (M, 5), 180 (100), 152 (35), 77 (10), 63 (8).Anal.calcd for C$_{21}$H$_{16}$N$_4$O$_3$: C 67.73, H 4.33, N 15.05; found C 67.86, H 4.23, N 15.12.

3. Results and discussion

The UV data, fluorescence data and the fluorescence quantum yields of the title Schiff bases are listed in Table 1. The fluorescence quantum yields are calculated by the following formula[10, 11]:

$$\Phi_X = \frac{n_X^2}{n_{std}^2} \cdot \frac{F_x}{F_{std}} \cdot \frac{A_{std}}{A_X} \cdot \Phi_{std}$$

where, n- index of refraction, F -the relative fluorescence determined by integrating the area beneath the corrected fluorescence spectrum, A-the absorbance. (X is referred to the unknown variable, std is the standard contrast, using quinine bisulphate as a reference $n_{std} = 1.3370$ and Φ_{std}=0.55).

Table 1. UV data, fluorescence data and the fluorescence quantum yields of the title Schiff bases.

Schiff base	R	$\lambda^{①}_a$/nm	$\lambda^{②}_e$/nm	Φ_x	I/a.u.
3a	4-CHO	296	430	0.153	230.8
3b	3-NO$_2$	294	430	0.170	280.5
3c	4-NO$_2$	295	431	0.204	322.6
3d	4-Cl	295	425	0.217	338.4
3e	H	294	409	0.302	420.9
3f	4-OH	317	431	0.386	444.35
3g	4-OCH$_3$	299	427	0.508	705.1
3h	4-CH$_3$	302	451	0.514	707.3
3i	2-OH	312	440	0.631	934.60

① the maximum UV characteristic absorption wavelength

② the maximum characteristic fluorescence emission wavelength

4. Effect of substituents on the UV spectral properties of the title Schiff bases

The UV characteristic absorption peaks generally appear red shift with the introduction of donating electron and almost without red shift with the introduction of accepting electron group. The UV spectra of the title Schiff bases are shown in Fig. 1 and Fig. 2.
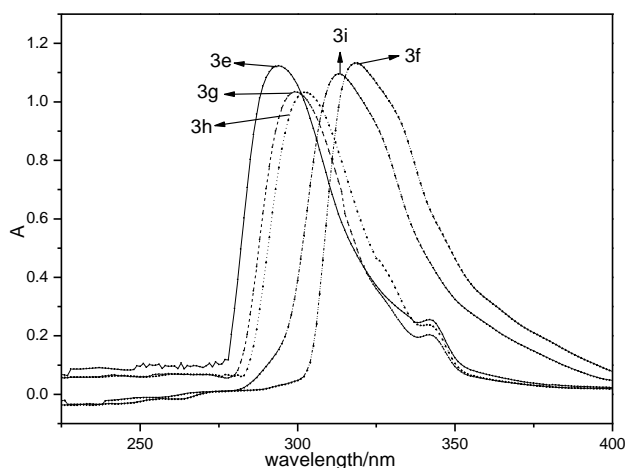

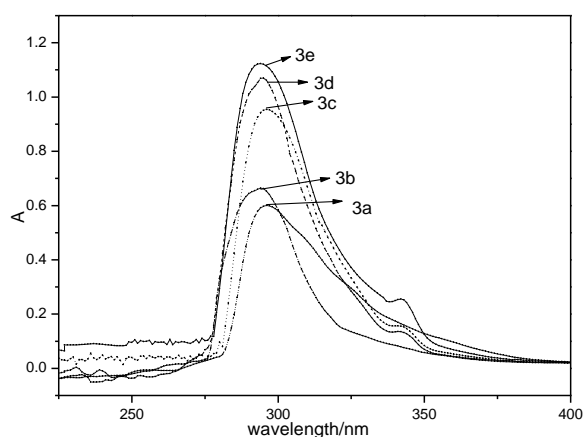*Fig. 1. The UV spectra of the Schiff base with the donating electron groups.*

Fig. 2. The UV spectra of the Schiff base with the accepting electron groups.

The introduction of the donating electron groups (4-CH$_3$, 4-OCH$_3$, 2-OH and 4-OH) causes the UV characteristic absorption peak of the title Schiff bases to occur various grade red shift (Fig. 1). As shown in Table 1, compared to that of the compound 3e, the absorption peaks of the hydroxy-substituted Schiff base and methoxy-substituted Schiff base appeared obvious red shift (23 nm for compound 3f, 5 nm for compound 3g, 18 nm for compound 3i). The reason producing the above phenomena is that the p→π conjugation effect between the

lone pair electrons of O atom and π electrons of phenyl ring decrease the required energy of π→π* transition, and cause the π→π* absorption band red shift. The peak position of the methyl-substituted Schiff base 3h appeared 8 nm red shift compared with that of compound 3e. The reason is that the hyperconjugation effects between the σ-electron of methylic C-H bond and π-electron of phenyl ring can increase electron density of phenyl ring and lead the increment of UV absorption peak wavelength of compound 3h. As shown in Fig. 2, the introduction of the accepting electron groups have rarely caused the change of the UV characteristic absorption peaks of the title Schiff bases.

5. Effect of substituents on the fluorescence spectral properties and the fluorescence quantum yields of the title Schiff bases

The fluorescence emission peaks of the title Schiff-bases apparently present red-shift with the introduction of the accepting and donating electron groups. Their fluorescence emission spectra of the title Schiff-bases are shown in Fig. 3. and Fig. 4.
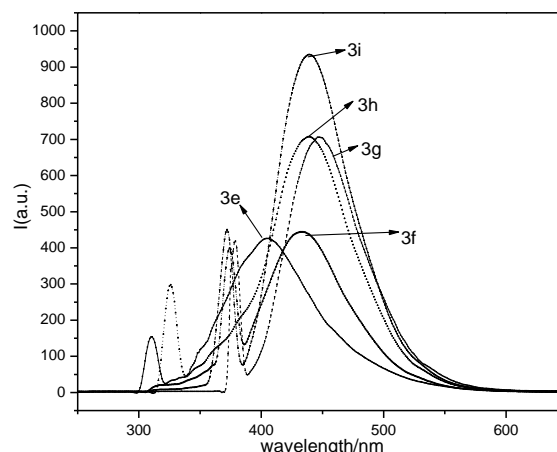

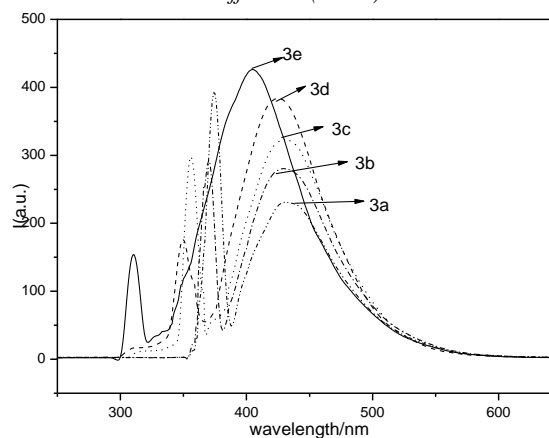*Fig. 3. The fluorescence emission spectra of the Schiff-bases (3e~3i).*

Fig. 4. The fluorescence emission spectra of the Schiff-bases (3a~3e).

As shown in Table 1, Fig. 3. and Fig. 4. the introduction of both the donating and accepting electron groups causes the red-shift of the fluorescence characteristic emission peaks of the title Schiff-bases in the range of 16 nm to 42 nm. The fluorescence quantum yield of the title Schiff-base with methyl substituent, compared to that (0.302) of the compound 3e, rises up to 0.514. The reason is that the electron density of the phenyl ring is increased with $\sigma \to \pi$ hyperconjugation effect. The title Schiff-base with methoxy substituent possesses the $p \to \pi$ conjugation structure that can increase its fluorescence emission intensity, so its fluorescence quantum yield is up to 0.508. The fluorescence quantum yield (0.631) of the o-hydroxyl-substituted Schiff-base 3i is quite different from that (0.386) of p-hydroxyl-substituent Schiff-base 3f, compared to that of the compound 3e. This is because the molecular structure of the Schiff-base 3i possesses good conjugated system and rigid plane. According to the intramolecular charge-transfer theory [12], the introduction of p-hydroxyl-substituent can prohibit the intramolecular charge-transfer, and result in the increase of molecular flexibility, and then decrease the fluorescence quantum yield of p-hydroxyl-substituted Schiff-base 3f.

The fluorescence intensity and quantum yields of the title Schiff-bases with accepting electron substituents have been reduced. The possible reasons are that the $n \to \pi^*$ transition of the accepting electron substituent belongs to the forbidden transition, the excited state molecules are obtained seldom, and the $S_1 \to T_1$ intersystem crossing occupy the dominant position. Furthermore, the introduction of the accepting electron groups easily causes the fluorescence quenching to reduce the fluorescence quantum yields of the title Schiff-bases.

6. Conclusions

Three new carbazolyl acylhydrazones Schiff-bases (3a, 3f, 3h) have been designed and synthesized. The introduction of the accepting and donating electron groups causes various grade red-shifts of the fluorescence characteristic emission peaks of the title Schiff-bases. The results indicate that the fluorescence quantum yields of the title Schiff-bases with accepting electron groups reduced, while that of the title Schiff-bases with donating electron groups increased. The fluorescence quantum yield of the o-hydroxyl-substituted Schiff-base is up to 0.631, and expected to be used as the hole transport optical material.

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