Journal of Photochemistry and Photobiology A: Chemistry 222 (2011) 241–248

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Studies of energy/electron transfer in the photoluminescence process of bipolar Al-complex containing phenothiazine group

Jianxin Luo[a,b,c], Chaolong Yang[a,c], Bihai Tong[d], Jie Zheng[a,c], Jianying Ma[a,c], Liyan Liang[a], Mangeng Lu[a,*]

[a] Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China
[b] Department of Materials and Chemical Engineering, Hunan Institute of Technology, Hengyang, Hunan 421002, PR China
[c] Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China
[d] Institute of Molecular Engineering & Applied Chemistry, Anhui University of Technology, Maanshan 243002, PR China

ARTICLE INFO

Article history:
Received 16 December 2010
Received in revised form 11 April 2011
Accepted 23 May 2011
Available online 13 June 2011

Keywords:
Phenothiazine
Tris-(8-hydoxyquinoline)aluminum (Alq_3)
Luminescence
Bipolar complex
Energy transfer
Electron transfer

ABSTRACT

The photophysical properties of three bipolar complexes, $Al(PHQ)_3$ (1), $AlQ(PHQ)_2$ (2), and $AlQ_2(PHQ)$ (3) (Q = 8-hydroxyquinoline, PHQ = 5-[(phenothiazine-9′-yl)methyl]-8-hydroxyquinoline) were studied by UV–vis absorption and fluorescent spectra. The results showed that both energy transfer and electron transfer from phenothiazine (Ptz) group to Alq_3-center had taken place in the photoluminescence (PL) process of the bipolar Al-complex. Förster non-radiative energy transfer theory together with fluorescent spectra were applied to investigate the energy transfer process of these bipolar Al-complexes. Additionally, thermodynamic analysis validated the possibility of the photo-induce electron transfer (PET) process. To further confirm the PET process, Cu^{2+} ion was used to oxidize aromatic amine of phenothiazine group to observe the variation of both the absorption and emission spectra of $Al(PHQ)_3$. Moreover, dynamics of the PET process were also studied by dynamic fluorescence, and some dynamic constants were obtained.

1. Introduction

More recently, tris-(8-hydoxyquinoline)aluminum (Alq_3) has been widely used as the emissive and electron-transporting material in organic light-emitting devices (OLEDs) [1–5] due to its high thermal stability, excellent electron-transporting properties and unique luminescent properties [6,7]. In order to improve the solubility and luminescent properties, many derivatives of 8-hydroxyquinoline were designed and the corresponding metal-complexes were obtained. 2, 5, and 7 positions of quinoline ring can easily be replaced by electron-donating and electron-withdrawing groups, such as halogen [8], alkoxy and alkylamine groups [9], fluorene [10], carbazole [11–14] and 1,3,4-oxadiazole derivatives [15]. Generally, these substituted groups were attached to quinoline ring through alkyl, alkoxy or alkylamine groups. Due to the introduction of these substituted groups, solubility, carrier-transporting and luminescent properties of the metalloquinolate have been improved. However, the effect of the conjugation or hyperconjugation of the substituted groups on the luminescence of metalloquinolate has not been reported systematically so far.

In the work, phenothiazine (Ptz) was attached to 8-hydroxyquinoline and a series of bipolar Al-complexes were obtained. The structures of the complexes are shown in Fig. 1, which consist of an Alq_3-center and different number of phenothiazine groups. Phenothiazine is a rich-electron group, which has been acted as good electron donor in long-distance hole/charge transfer materials [16–19]. The intermolecular and intramolecular electron transfer interaction between phenothiazine and the acceptor have been investigated extensively [20–24]. Therefore, these bipolar Al-complexes containing phenothiazine group were selected as research objective to study energy transfer and electron transfer from the attached phenothiazine group to Alq_3-center in the PL process.

2. Experimental

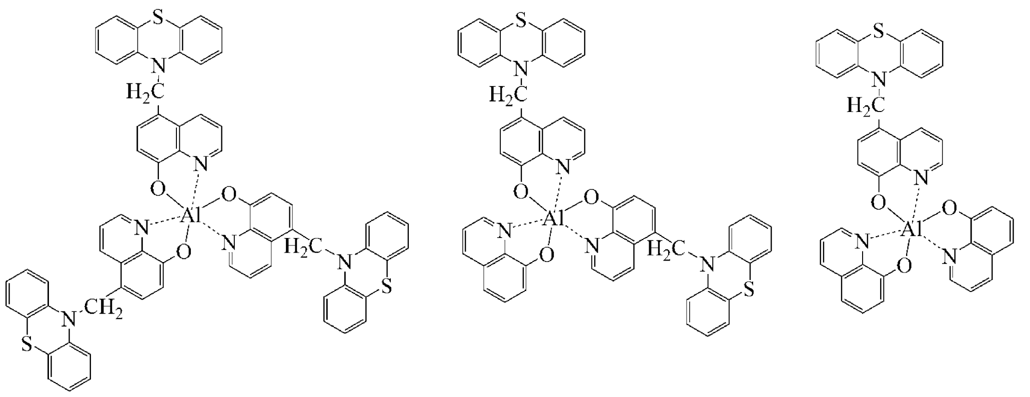
2.1. Materials

Solvents and chemicals were obtained commercially. Some of them were used as received, such as triethylaluminum ($AlEt_3$) of hexane solution and petroleum ether. Tetrahydrofuran (THF), acetonitrile (ACN), and chloroform were dried and treated according to standard methods before use. Perchlorate copper ($Cu(ClO_4)_2$) was prepared by standard method. $Al(HEMA\text{-}CH_2\text{-}Q)_3$ [1] and

---

* Corresponding author. Tel.: +86 020 85232978; fax: +86 020 85231119.
E-mail address: mglu@gic.ac.cn (M. Lu).

1010-6030/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2011.05.025



Al(PHQ)$_3$ (Complex **1**) AlQ(PHQ)$_2$ (Complex **2**) AlQ$_2$(PHQ) (Complex **3**)

Fig. 1. Structures of the bipolar Al-complexes (AlQ$_x$(PHQ)$_y$).

5-[(phenothiazine-9′-yl)methyl]-8-hydroxyquinoline (PHQ) [25] were prepared as described.

2.2. Characterization

The melting point of the sample was observed by SGW X-4 micro-melting point apparatus (Shanghai PSE Co. Ltd.). ^{1}H NMR spectra were recorded on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer. FT-IR spectra were carried out using a RFX-65A (Analects) Fourier Transform Infrared Spectrometer. Elemental analysis data were obtained from Vario EL elemental analyzer. UV–vis absorption spectrum was determined on a Shimadz spectrophotometer. The PL measurements were conducted in a Hitachi F-4600 florescence spectrophotometer. Fluorescence quantum yield of the complexes was calculated using quinine sulfate in 0.5 M H_2SO_4 solution ($\varphi_f = 0.55$) as a standard [26]. Fluorescence lifetimes were measured by time-correlated single photo counting method (PLSP20 steady state spectrophotometer) with excitation at 405 nm and the emission was monitored at 530 nm.

2.3. Synthesis of the bipolar Al-complexes

Al(PHQ)$_3$ (**Complex 1**). PHQ (1.068 g, 0.003 mol) was added into a 150 mL three-necked flask equipped with a nitrogen inlet and a magnetic stirrer and dissolved with 30 mL anhydrous THF. Triethylaluminum of hexane solution (1.0 mL, 0.001 mol), diluted with 10 mL dry THF, was added dropwise and the reaction mixture was stirred at room temperature for 1 day. After filtering through a G4 funnel to remove precipitate, a yellow solution was obtained and precipitated by addition of petroleum ether (200 mL). The precipitate was purified by several solution–precipitation cycles using minimum amount of THF to dissolve and plenty of petroleum ether to precipitate. Yield: 76%; mp > 300 °C. ^{1}H NMR ($CDCl_3$, δ): 8.87–8.48 (6H, m, aromatic-H), 7.41–6.70 (33H, m, aromatic-H), 5.28 (6H, s, $-CH_2-$). FT-IR (KBr, cm^{-1}): 3424 (–OH), 3058 ($-CH_2$), 1625, 1603 (pyridine ring), 1574, 1505, 1456 (aromatic), 1367, 1325 (C–N), 1090 (C–O), 746, 560 (Al–O). Element Anal. Calcd. for Al(PHQ)$_3$·5H$_2$O ($C_{66}H_{55}N_6S_3O_8Al$): C, 67.01; H, 4.65; N, 7.11. Found: C, 67.43; H, 4.41; N, 7.04.

AlQ(PHQ)$_2$ (**Complex 2**). To a 150 mL three-necked flask equipped with a nitrogen inlet and a magnetic stirrer, triethylaluminum of hexane solution (1.0 mL, 0.001 mol) was added via syringe, and then 8-hydroxyquinoline (0.145 g, 0.001 mol) in anhydrous THF was added dropwise into the solution. After stirring at room temperature for 1 day, PHQ (0.712 g, 0.002 mol) of THF solutions was added and stirred for another 1 day. The mixture was filtered through a G4 funnel to remove precipitate. The filtrate was added to petroleum ether (200 mL) and the precipitate was filtered off and washed by petroleum ether three times, and then dried at 50 °C in vacuum. Yield: 69%. mp > 300 °C. ^{1}H NMR ($CDCl_3$, δ): 8.87–8.18 (6H, m, aromatic-H), 7.47–6.70 (26H, m, aromatic-H), 5.28 (4H, s, $-CH_2-$). FT-IR (KBr, cm^{-1}): 3423 (–OH), 3058 ($-CH_2$), 1600 (pyridine ring), 1504, 1465 (aromatic), 1382, 1326 (C–N), 1101 (C–O), 748, 648, 546 (Al–O). Element Anal. Calcd. for AlQ(PHQ)$_2$·5H$_2$O ($C_{53}H_{46}N_5S_2O_8Al$): C, 65.50; H, 4.74; N, 7.21. Found: C, 65.24; H, 4.91; N, 7.32.

AlQ$_2$(PHQ) (**Complex 3**). The procedure followed was same as that of AlQ(PHQ)$_2$. Triethylaluminum of hexane solution (1.0 mL, 0.001 mol), 8-hydroxyquinoline (0.29 g, 0.002 mol) and PHQ (0.356 g, 0.001 mol) were used. Yield: 71%. mp > 300 °C. ^{1}H NMR ($CDCl_3$, δ): 8.84–8.18 (6H, m, aromatic-H), 7.49–6.73 (19H, m, aromatic-H), 5.29 (2H, s, $-CH_2-$). FT-IR (KBr, cm^{-1}): 3413 (–OH), 3056 ($-CH_2$), 1602 (pyridine ring), 1502, 1467 (aromatic), 1384, 1326 (C–N), 1112 (C–O), 750, 648, 546 (Al–O). Element Anal. Calcd. for AlQ$_2$(PHQ)·6H$_2$O ($C_{40}H_{39}N_4SO_9Al$): C, 61.70; H, 5.01; N, 7.20. Found: C, 61.50; H, 5.12; N, 7.13.

3. Results and discussion

3.1. Photophysical properties

UV–vis absorption spectra of PHQ and the bipolar Al-complexes are shown in Fig. 2. The characteristic absorption band of phenothiazine group located around 315 nm (from 290 to 380 nm),

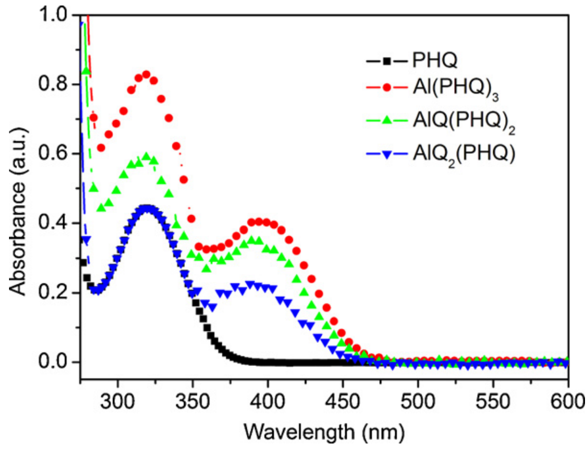


Fig. 2. UV–vis absorption spectra of the bipolar Al-complexes (AlQ$_x$(PHQ)$_y$) in chloroform (concentration: 2.5 × 10^{-5} M).

Table 1
UV–vis absorption and emission data of these complexes in chloroform.

Complexes	$\lambda_{abs}/\varepsilon^{a}$ (nm/×10^4 M^{-1} cm^{-1})	λ_{em}/I^{b} (nm/a.u.)	φ_f ^{c} (%)	τ_1/α_1 (ns/%)	τ_2/α_2 (ns/%)	$\langle\tau\rangle^{d}$ (ns)	k_{et}^{e} (×10^8 s^{-1})	φ_{et}^{f}
Al(PHQ)$_3$	398/1.64	532/12.06	5.90	1.96 (88%)	3.88 (12%)	2.37	3.66	0.98
AlQ(PHQ)$_2$	390/1.42	526/20.26	7.01	2.55 (91%)	6.92 (9%)	3.48	2.32	0.97
AlQ$_2$(PHQ)	386/0.92	523/43.86	7.24	2.83 (81%)	10.60 (19%)	6.46	0.99	0.94

[a] Absorption maxima and the corresponding extinction coefficients of the complexes in chloroform solution (concentration: 2.5×10^{-5} mol/L).
[b] Emission maxima of the complexes in chloroform solution (concentration: 1×10^{-4} mol/L, excitation wavelength λ_{ex} = 375 nm).
[c] Fluorescence quantum yields determined by relative method [26].
[d] Average lifetime calculated by Eq. (7).
[e] Average rate constant of electron transfer calculated by Eq. (8).
[f] Quantum efficiency of electron transfer calculated by Eq. (9).

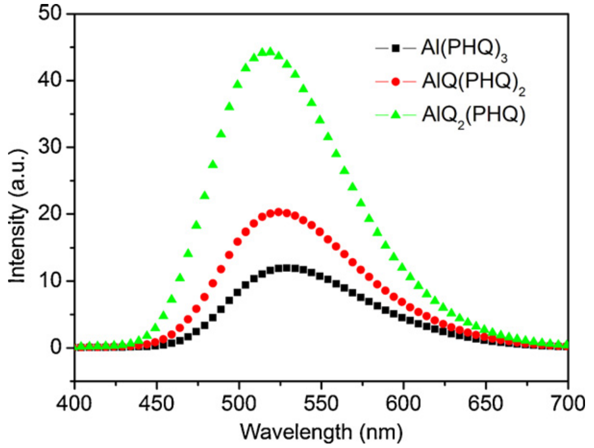


Fig. 3. PL emission spectra of the bipolar Al-complexes (AlQ$_x$(PHQ)$_y$) in chloroform (concentration: 10^{-4} M).

and the absorption of quinoline at 325 nm was covered. Compared with the absorption of PHQ, Alq$_3$'s characteristic absorption peak was observed around 390 nm in the absorption spectra of the Al-complexes. Depending on the number of phenothiazine moieties, the characteristic peak showed slight red shift. Upon going from AlQ$_2$(PHQ) to Al(PHQ)$_3$ the characteristic absorption peak of Alq$_3$ shifted from 386 to 398 nm with an increase in the extinction coefficient. Absorption maxima and extinction coefficients together with emission data are listed in Table 1.

As well known, the optical transition responsible for photoluminescence in Alq$_3$ is centered on the organic ligand, which is due to π–π* charge transfer from the electron rich phenoxide ring to the electron deficient pyridyl ring [27]. Moreover, in metalloquinolate system, the highest density HOMOs locates on phenoxide ring, particularly on C5-position [28]. In the bipolar Al-complex, the electron-donating group (phenothiazine) was attached at C5-position of quinoline, which affects its electronic structure to some extent due to hyperconjugation. Thus, the absorption and emission maxima of these Al-complexes showed some change, red-shifting with increasing of the number of phenothiazine groups, as shown in Fig. 2 and Fig. 3 respectively. All complexes exhibited the characteristic emission of Alq$_3$-center around 530 nm, and the emission band of phenothiazine group from 400 nm to 450 nm was not observed. In addition, the emission intensity of Al(PHQ)$_3$ exhibited considerable quenching compared with that of AlQ$_2$(PHQ). Therefore, fluorescence quantum yields of the complexes measured using the relative method [26] decreased while increasing the number of phenothiazine groups as shown in Table 1. Based on previous literature reports [21,22], we attribute the PL emission quenching to electron transfer from phenothiazine group to Alq$_3$-center.

PL emission spectra of Al(PHQ)$_3$ under different conditions are shown in Fig. 4. Excitated with different wavelength (300–390 nm) of UV light (Fig. 4(a)), which include the absorption band of both phenothiazine group (300–380 nm) and Alq$_3$-center (300–450 nm), the emission from phenothiazine (400-450 nm) was suppressed completely and only one broad band centered at 530 nm attributed to the emission of Alq$_3$-center was observed in chloroform solution (concentration: 10^{-4} M), indicating that there existed effective singlet energy transfer between phenothiazine group and Alq$_3$-center [12]. The concentration dependence of the PL emission spectra of Al(PHQ)$_3$ is displayed in Fig. 4(b). As the concentration increased, the PL emission of Alq$_3$-center intensified in the beginning. Thereafter, the emission intensity of Alq$_3$-center decreased steadily due to concentration quenching. However, the emission of phenothiazine group decreased with increasing in concentration all the time and disappeared completely in high concentration solution (concentration > 10^{-4} M), which is also the result of energy transfer. The similarity in the emission spectra of Alq$_3$ and the bipolar Al-complex indicated that introducing phenothiazine into Alq$_3$ does not substantially affect the metal-quinoline chromophoric core. However, the phenothiazine group acts as electron/energy donor has great effect on the photoluminescence of the Alq$_3$-center as

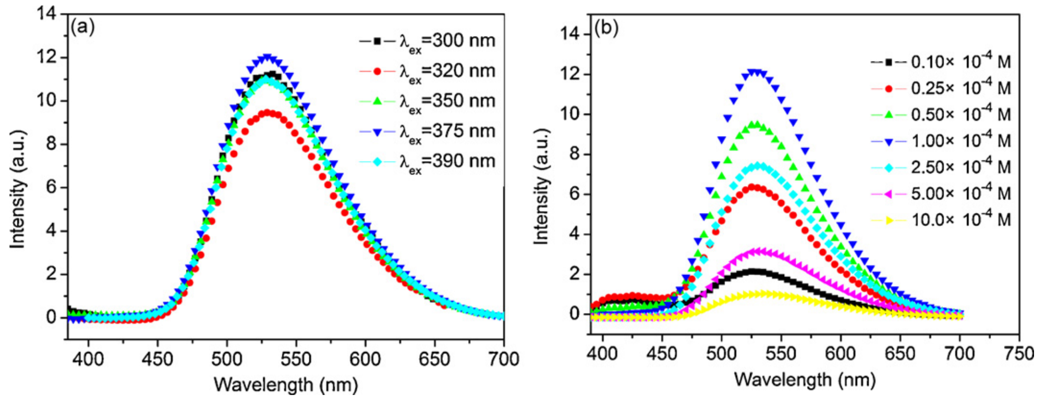


Fig. 4. (a) PL emission spectra of Al(PHQ)$_3$ excited with different excitation wavelength (solvent: chloroform, concentration: 10^{-4} M); (b) PL emission spectra of Al(PHQ)$_3$ in chloroform solution with different concentration (λ_{ex} = 375 nm).

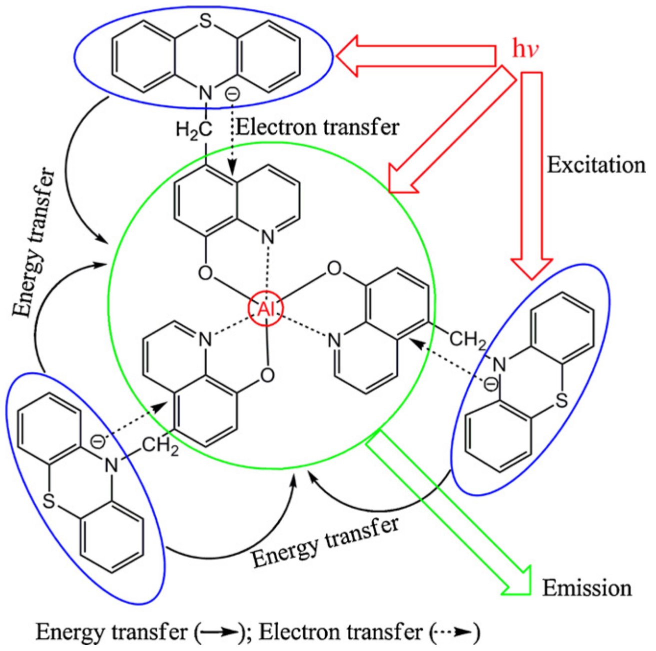


Fig. 5. Energy transfer and electron transfer in photoluminescence of Al(PHQ)$_3$.

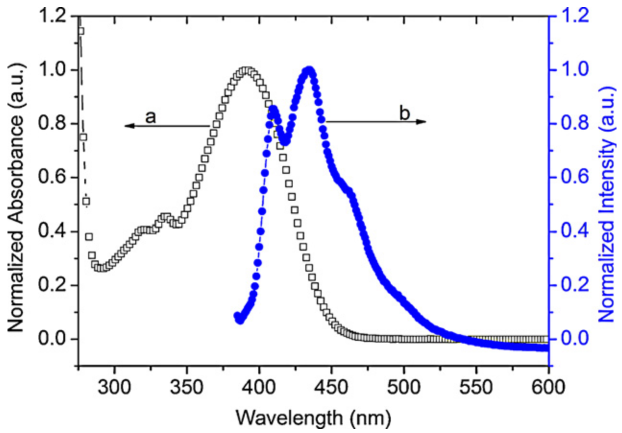


Fig. 6. Overlap of the UV–vis absorption spectrum of Alq$_3$ (model complex) (a) with the emission spectrum of phenothiazine (b) in chloroform (λ_{ex} = 375 nm). [Alq$_3$] = [phenothiazine] = 10^{-5} M.

demonstrated in Fig. 5. Both energy transfer and electron transfer can take place simultaneously in the photoluminescence process of the bipolar Al-complex. Thereinafter, luminescent measurements together with the theoretic assumption will be adopted to evaluate and quantitate these photophysical processes.

3.2. Energy transfer

As shown in Fig. 6, there was an appropriate overlap between the emission of phenothiazine (λ_{ex} = 375 nm) and the absorption of the Alq$_3$ (Model complex Al(HEMA-CH$_2$-Q)$_3$ was adopted to instead of Alq$_3$), so singlet-singlet energy transfer from the excited state of phenothiazine group to Alq$_3$-center would be favorable [12,29].

Based on the theory of Förster energy transfer [30–33], the efficiency of energy transfer (E) between a donor and acceptor is related to the average distance of separation (r_a) and the critical distance (R_0) for 50% energy transfer by Eq. (1). R_0 is defined by Eq. (2), where κ^2 is the spatial orientation factor related to the geometry of the donor-accepter of dipole; n is the average refracted index of the medium in the wavelength range where spectral overlap is significant; φ_D is the fluorescence quantum yield of the donor; and J is the spectral overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor. The value of J can be calculated by equation (3), where $F(\lambda)$ is the corrected emission intensity of the donor in the wavelength range from ν to $\nu + d\nu$; $\varepsilon(\nu)$ is the molar absorption coefficient in units of M^{-1} cm^{-1}, and ν is the frequency in cm^{-1}.

$$E = \frac{R_0^6}{R_0^6 + r_a^6} \tag{1}$$

$$R_0^6 = 8.78 \times 10^{-25} \kappa^2 \varphi_D n^{-4} J \tag{2}$$

$$J = \frac{\int F(\nu)\varepsilon(\nu)\nu^{-4}\, d\nu}{\int F(\nu) d\nu} \tag{3}$$

Based on the significant fluorescence quenching of the phenothiazine upon the attaching to Alq$_3$, the efficiency of energy transfer (E) is also given by Eq. (4), where F and F_0 are the emission intensity of phenothiazine in the presence and absence of acceptor Alq$_3$, respectively.

$$E = 1 - \frac{F}{F_0} \tag{4}$$

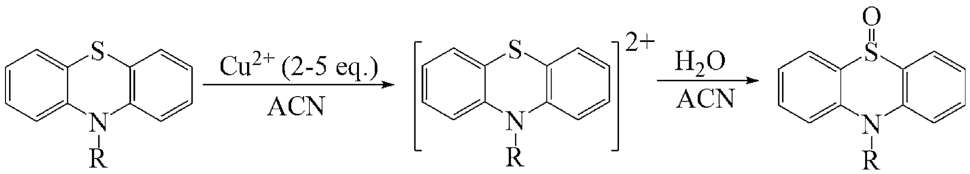
The value of J was calculated according to Eq. (3) by computer as 8.32×10^{-15} cm^3 L mol^{-1} [32]. The orientation factor, κ^2, was taken as 2/3 [30], and the refractive index, n, was the refractive index of the solvent. The quantum yield, φ_D, was determined by relative method as 0.02 [26]. With use of the values of J, κ^2, n and φ_D, R_0 value was calculated according to Eq. (2) as 1.68 nm. The efficiency of energy transfer (E) and the average distance (r_a) at different concentration were calculated according to the above equations and summarized in Table 2.

Generally, both intramolecular and intermolecular energy transfer can happen simultaneously in metal-complex [34,35]. In Al(PHQ)$_3$, three donors (phenothiazine) were attached to an Alq$_3$-center with methylene. The distance of intramolecular energy transfer (r_b), which approached to the distance between the center

Table 2
Energy transfer data of the bipolar complex (Al(PHQ)$_3$) at different concentration of chloroform solutions.

Concentration ($\times 10^{-4}$ M)	E[a] (%)	r_a[b] (nm)	r_b[c] (nm)	r_c[d] (nm)	%E_b[e] (%)	%E_c[e] (%)
0.10	77.7	1.36	0.473	54.9	100	0
0.25	89.9	1.17	0.473	40.5	100	0
0.50	92.2	1.11	0.473	32.1	100	0
1.00	99.3	0.74	0.473	25.5	100	0
2.50	100	–	–	–	–	–

[a] The efficiency of energy transfer calculated according to Eq. (4).
[b] The average distance of energy transfer calculated according to Eq. (1).
[c] The distance of intramolecular energy transfer calculated by Gauss soft [36,37].
[d] The distance of intermolecular energy transfer determined by concentration.
[e] The proportion of the two energy transfer routes calculated according to the equations $\%E_b = \frac{r_c^6}{r_b^6 + r_c^6}$ and $\%E_c = \frac{r_b^6}{r_b^6 + r_c^6}$.



Scheme 1. The oxidation of phenothiazine derivatives with $Cu(ClO_4)_2$ in acetonitrile.

of phenothiazine ring and the center of quinoline ring in the same molecule, was calculated as about 0.473 nm according to Gaussian soft [36,37]. The distance of intermolecular energy transfer (r_c) is approach to the distance of two neighboring molecules, which can be calculated by the concentration of the complex solution according to the formula:

$$r_c = \sqrt[3]{\frac{1}{N_A c}} \times 10^8\,\mathrm{nm}$$

(Supposed that every molecule occupy a cube). The value of r_b and r_c was used to evaluate the proportion of the two energy transfer routes, the results indicated that intramolecular energy transfer is dominant absolutely (nearly 100%). As shown in Table 2, the efficiency of energy transfer increased, as the solutions get thick, which is probably due to the fact that the average distance of energy transfer decreased slightly as the concentration increased.

3.3. Electron transfer

Phenothiazine bearing electron-rich sulfur and nitrogen atoms is a strong electron-donating group due to its low oxidation potentials [38]. Thus, phenothiazine as electron donor was used to construct donor (D)–acceptor (A) systems capable of undergoing photoinduced electron transfer (PET) reactions and generating long-lived charge separated (CS) states [20,21]. In these systems, electron transfer from the phenothiazine group to the excited metal-complexes to generate the charge separated state ML^+-$Ptz^{\bullet+}$. Similarly, the photo-induced electron transfer (PET) process can take place in $Al(PHQ)_3$, which has three donors (phenothiazine) and an acceptor (Alq_3-center). As discussed above, both energy transfer and electron transfer can take place simultaneously in the photoluminescence process of the bipolar Al-complex. Energy transfer from phenothiazine group to Alq_3-center is favorable for the photoluminescence of Alq_3-center. In contrast, photo-induced electron transfer restrains the photoluminescence of Alq_3-center. How and to what extent are the PL properties of the bipolar Al-complex affected by electron transfer from phenothiazine?

Similarly as $Ru(bpy)_3{}^{2+}$ complex [21], excitation of the Alq_3 chromophore leaded to formation of excited state, which was quenched by electron transfer from the phenothiazine group leading to the formation of Alq_3 anion (abbreviated as $Alq_3{}^-$) and phenothiazine radical cation (abbreviated as $Ptz^{\bullet+}$) as shown in Eq. (5).

$$\mathrm{A1q_3{-}Ptz}\quad (\mathrm{A1(PHQ)_3}) \xrightarrow{h\nu} {}^{*}(\mathrm{A1q_3}){-}\mathrm{Ptz} \xrightarrow{\mathrm{ET}} \mathrm{A1q_3}^{-}{-}\mathrm{Ptz}^{\bullet+} \tag{5}$$

As reported previously [22], in the presence of excess $Cu(ClO_4)_2$ (2–5 equiv.), phenothiazine derivatives were oxidized easily to dication compound, which further react with traces of water present in ACN to give the phenothiazine-5-oxide, as shown in Scheme 1. Based on this reaction, $Cu(ClO_4)_2$ was utilized for oxidation of phenothiazine group in $Al(PHQ)_3$. It was added stepwise into the solution of $Al(PHQ)_3$ (1×10^{-5} M) in ACN and the emission spectrum experienced dramatic variation as shown in Fig. 7. Initially, the emission intensity decreased with addition of Cu^{2+}. In this case, traces of Cu^{2+} only acted as fluorescence quencher. When the mole ratio of Cu^{2+} relative to the $Al(PHQ)_3$ approached to 1 (Fig. 7c), parts of phenothiazine group were oxidized and the peak located at 530 nm started to red-shift, the emission band turned to narrow and the intensity decreased gradually. As $[Cu^{2+}]/[Al(PHQ)_3] = 3.8$ equiv., the Alq_3's characteristic peak red-shifted to 546 nm and a new peak from the oxide ($Al(POHQ)_3$) appeared at about 482 nm. Further addition of Cu^{2+} caused the constantly enhancement of this emission intensity. UV–vis absorption spectra were also used to inspect the above process. As shown in Fig. 8, with addition of Cu^{2+}, all of absorption peaks red-shifted gradually and the intensity of Alq_3's characteristic absorption increased. Moreover, a new absorption due to $Ptz^{\bullet+}$ at about 520 nm appeared immediately after mixing and disappeared with time [20]. All of these phenomenons confirmed the occurrence of the oxidation reaction as shown in Scheme 2, which also revealed the difference of the effect of phenothiazine and its oxide (phenothiazine-5-oxide) on the photoluminescence of the Alq_3-center.

Both Alq_3 and phenothiazine's redox properties have been extensively studied. In order to further ascertain the PET between the photo-excited Alq_3-center and the attached phenothiazine or phenothiazine-5-oxide, redox potentials were used to calculate the free energy change (ΔG^0) for electron transfer using the Weller equation (6).

$$\Delta G^0 = E_{\mathrm{ox}} - E_{\mathrm{red}} - E_{0,0} - \frac{e^2}{\varepsilon_S d} \tag{6}$$

where E_{ox} is the oxidation potential of the donor and E_{red} is the reduction potential of the acceptor, $E_{0,0}$ is the energy of the excited state of the acceptor, ε_S is the dielectric constant of the solvent and d is the distance separating the donor and acceptor moieties. In solvents such as ACN, the fourth term in Eq. (6) is very small and hence neglected, $E_{0,0}$ for the system was calculated from the onset of the Alq_3 emission.

The oxidation potential of Alq_3 appeared at about 1.50 V (vs SCE) and the reduction potential occurred at around −1.60 V (vs SCE) [39], and while phenothiazine exhibited reduction peak at −2.20 V (vs SCE) and oxidation peak at 0.73 V (vs SCE) [20]. Phenothiazine is obviously easier to be oxidized than Alq_3 according to their redox potentials. PET from phenothiazine group to Alq_3 is thermodynamically favored, since its ΔG is a negative value obtained by:

$$\Delta G_{\mathrm{PET}} = E_{(\mathrm{PTZ/Ptz}^{\bullet+})} - E_{(\mathrm{Alq_3}^{\bullet-}/\mathrm{Alq_3})} - E_{0,0} = 0.73 - (-1.60) - 2.76 = -0.43\,\mathrm{eV}.$$

For emission quenching in $Al(POHQ)_3$, we have to consider both oxidative and reductive quenching mechanisms. For these calculations, redox potentials of phenothiazine-5-oxide (PO) moiety can be obtained in previous report [22]. For the oxidative quenching, E_{ox} of Alq_3 (=1.50 V vs SCE) and E_{red} of PO (=−1.27 V vs SCE) are relevant and we obtained ΔG^0 = +0.01 eV. For reductive quenching, E_{ox} of PO (=1.28 V vs SCE) and E_{red} of Alq_3 (=−1.60 V vs SCE) are relevant and we obtained ΔG^0 = +0.12 eV. ΔG^0 values are posi-

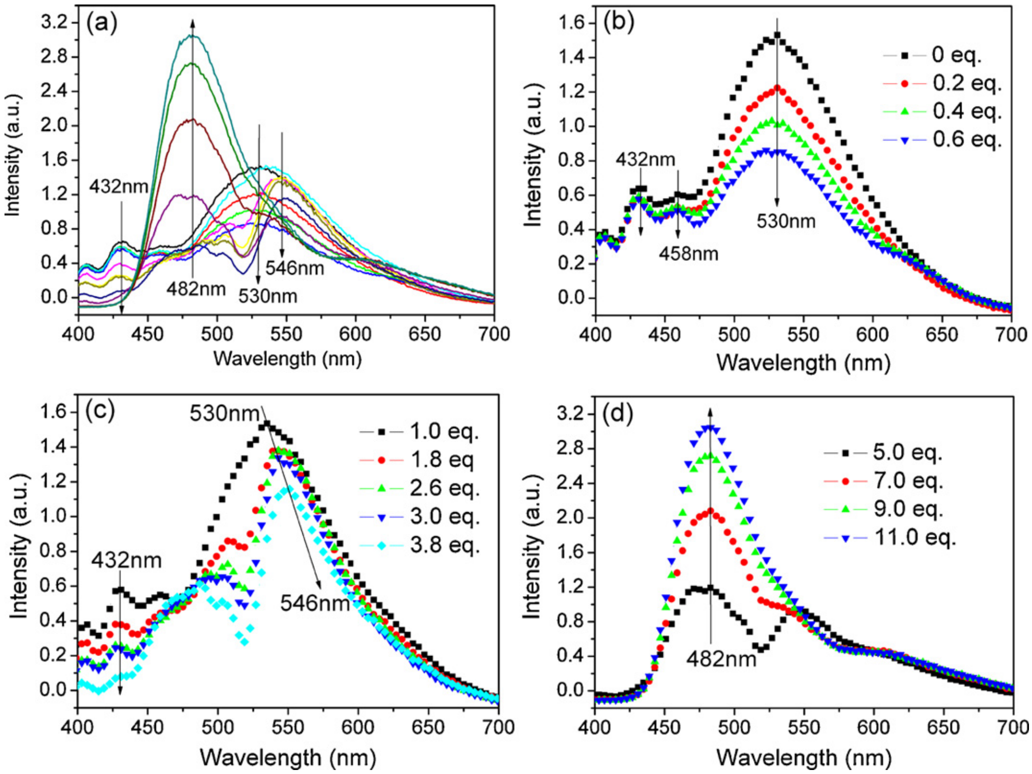


Fig. 7. The variation of emission spectra of Al(PHQ)$_3$ (concentration: 10^{-5} M) with addition of different equivalents (0–11.0 equiv.) of Cu(ClO$_4$)$_2$ in ACN. The arrows shown in the figure indicate the variation trend of all the emission peaks.

tive for both reactions and hence the emission of Alq$_3$ core will not be quenched by the attached phenothiazine-5-oxide (PO) moiety. Based on the redox properties of these groups, electron can easily transfer from phenothiazine group to Alq$_3$-center, but hardly transfer from phenothiazine-5-oxide to Alq$_3$-center, which lead to fluorescence quenching and enhancement, respectively. The electron transfer in the photoluminescence process of the complexes (Al(PHQ)$_3$ and Al(POHQ)$_3$) is shown in Fig. 9.

The fluorescence decays were monitored at 530 nm with excitation at 405 nm in chloroform. The emission of Alq$_3$ decays single exponential with lifetime of 18 ns in chloroform [40]. For all the bipolar Al-complexes the decays were bi-exponential, which may be due to different conformations of the phenothiazine group with respect to Alq$_3$-center or due to different electron transfer mechanism [21]. The lifetime values and their contributions are shown in Table 1. The contribution of the short lifetime (τ_1) was above 80%, and the value of τ_1 and τ_2 decreased with the number of phenothiazine groups. For all these complexes, average lifetimes $\langle\tau\rangle$ were calculated according to Eq. (7) [41], and these values are listed in Table 1.

$$\langle\tau\rangle = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \tag{7}$$

It can be seen that the $\langle\tau\rangle$ values were smaller than that of Alq$_3$ (18 ns), and also decreased while increasing in the number of phenothiazine groups. The reduction in the lifetime is attributed to electron transfer as shown in Eq. (5) and hence the average rate constant (k_{et}) for electron transfer can be calculated from the fluorescent lifetime using Eq. (8).

$$k_{et} = \frac{1}{\langle\tau\rangle} - \frac{1}{\langle\tau_0\rangle} \tag{8}$$

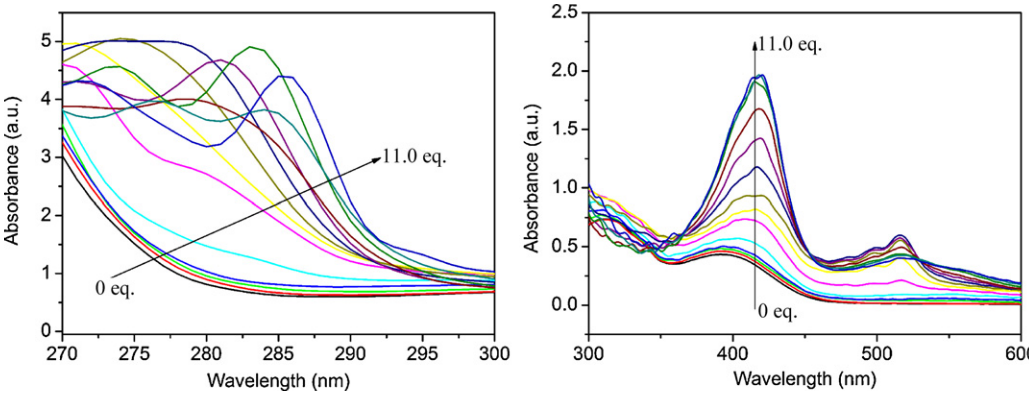
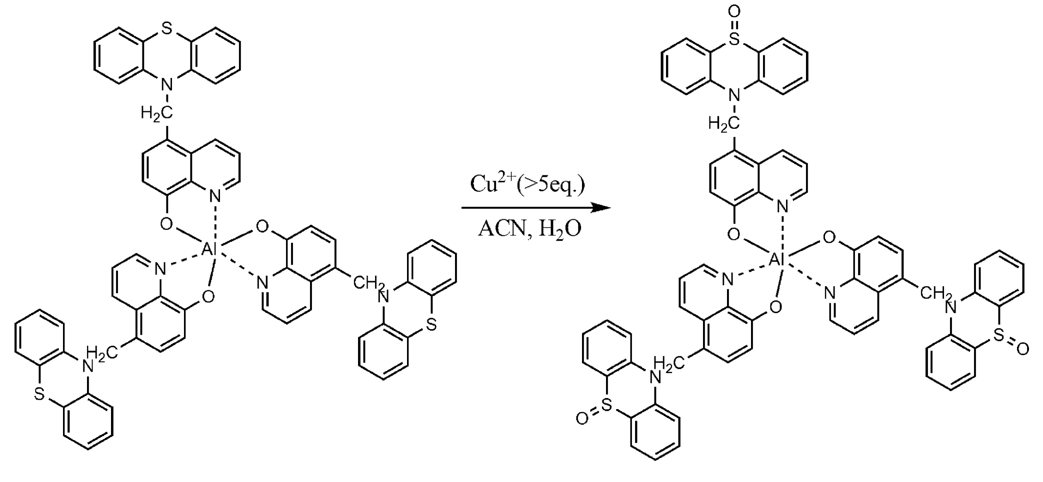


Fig. 8. The variation of UV–vis absorption spectra of Al(PHQ)$_3$ (concentration: 10^{-5} M) with addition of different equivalents (0–11.0 equiv.) of Cu(ClO$_4$)$_2$ in ACN. The arrows shown in the figure indicate the variation of the equivalent of Cu(ClO$_4$)$_2$.



$Al(PHQ)_3$ $Al(POHQ)_3$

Scheme 2. The oxidation of the bipolar complex ($Al(PHQ)_3$) with $Cu(ClO_4)_2$ in acetonitrile.

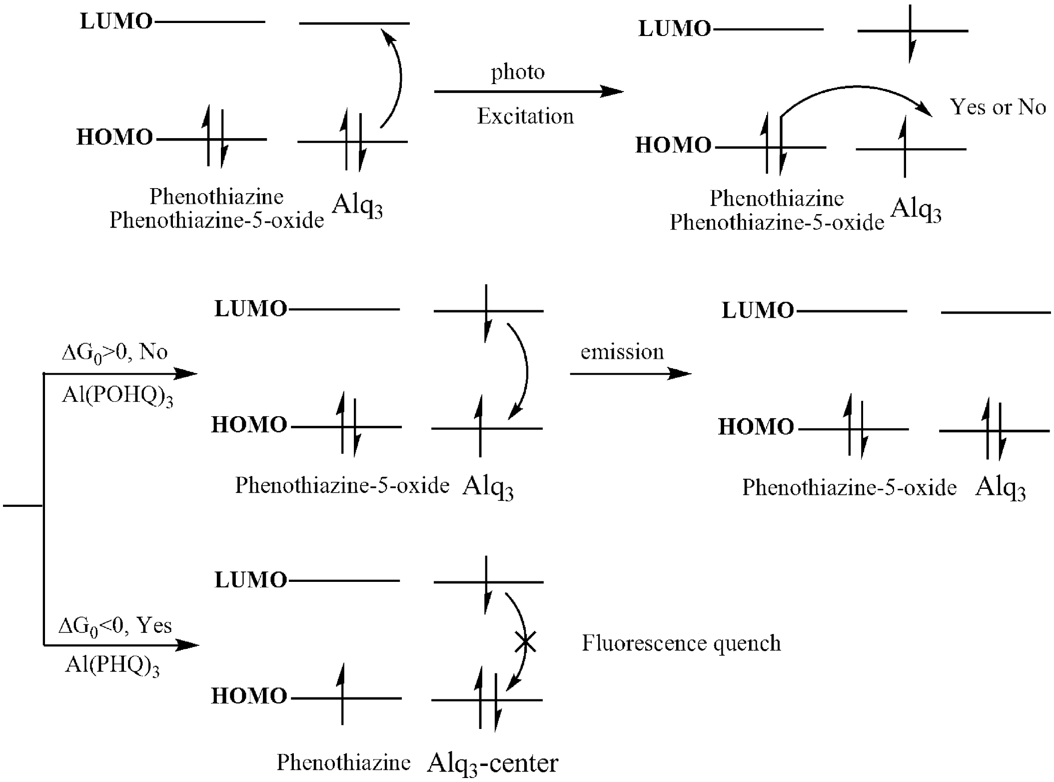


Fig. 9. Electron transfer in the PL process of the complexes ($Al(PHQ)_3$ and $Al(POHQ)_3$).

$$\varphi_{\mathrm{et}} = \frac{k_{\mathrm{et}}}{k_{\mathrm{et}} + 1/\tau_0} \tag{9}$$

The k_{et} values thus calculated are also shown in Table 1, and increased with number of phenothiazine groups. Using k_{et} values the quantum efficiency of electron transfer (φ_{et}) can be calculated according to Eq. (9). The values of φ_{et} are 0.98, 0.97 and 0.94 for $Al(PHQ)_3$, $AlQ(PHQ)_2$ and $AlQ_2(PHQ)$ respectively, which also increased with the number of phenothiazine groups (Table 1).

4. Conclusions

In this article, phenothiazine group was attached to Alq_3-center to obtain three bipolar Al-complexes. The attached phenothiazine group has great effects on the photoluminescence of the Alq_3-center due to energy and electron transfer from phenothiazine to Alq_3-center, which were studied through fluorescent spectra and corresponding theory. It is found that energy transfer is favorable for the photoluminescence of Alq_3-center and electron transfer is unfavorable for the photoluminescence of Alq_3-center. The paper provides an academic rule for designing perfect molecule to improve luminescent properties.

Acknowledgements

This project was supported by Guangdong-Hongkong Technology Cooperation Finding (Project No. 2009A091300012). We are grateful to Doctor Qunbo Mei from Jiangsu Key Lab of Organic Electronics & Information Displays, Nanjing University of Posts and Telecommunications (China) for help in Gaussian calculation. We are also grateful to Prof. Zhengzhi Zeng from College of Chemistry and Chemical Engineering and State Key Laboratory of Applied Organic Chemistry, Lanzhou University (China) for help in calculation of energy transfer.

References

[1] N.Y. Du, Q.B. Mei, M.G. Lu, Quinolinate aluminum and zinc complexes with multi-methyl methacrylate end groups: synthesis, photoluminescence, and electroluminescence characterization, Synth. Met. 149 (2005) 193–197.
[2] S.F. Hsu, C.C. Lee, S.W. Hwang, H.H. Chen, C.H. Chen, A.T. Hu, Color-saturated and highly efficient top-emitting organic light-emitting devices, Thin Solid Films 478 (2005) 271–274.
[3] N.Y. Du, R.Y. Tian, J.B. Peng, Q.B. Mei, M.G. Lu, Cross-linked Alq(3)-containing polymers with improved electroluminescence efficiency used for OLEDs, Macromol. Rapid Commun. 27 (2006) 412–417.
[4] M.A. Khan, W. Xu, F.X. Wei, Y. Bai, X.Y. Jiang, Z.L. Zhang, W.Q. Zhu, Highly efficient organic electroluminescent diodes realized by efficient charge balance with optimized electron and hole transport layers, Solid State Commun. 144 (2007) 343–346.
[5] S.K. Kim, B. Yang, Y.I. Park, Y.G. Ma, J.Y. Lee, H.J. Kim, J.W. Park, Synthesis and electroluminescent properties of highly efficient anthracene derivatives with bulky side groups, Org. Electron. 10 (2009) 822–833.
[6] G. Farruggia, S. Iotti, L. Prodi, M. Montalti, N. Zaccheroni, P.B. Savage, V. Trapani, P. Sale, F.I. Wolf, 8-Hydroxyquinoline derivatives as fluorescent sensors for magnesium in living cells, J. Am. Chem. Soc. 128 (2006) 344–350.
[7] M. Shirakawa, N. Fujita, T. Tani, K. Kaneko, S. Shinkai, Organogel of an 8-quinolinol platinum(II) chelate derivative and its efficient phosphorescence emission effected by inhibition of dioxygen quenching, Chem. Commun. (2005) 4149–4151.
[8] Y.W. Shi, M.M. Shi, J.C. Huang, H.Z. Chen, M. Wang, X.D. Liu, Y.G. Ma, H. Xu, B. Yang, Fluorinated Alq(3) derivatives with tunable optical properties, Chem. Commun. (2006) 1941–1943.
[9] A. Mishra, N. Periasamy, M.P. Patankar, K.L. Narasimhan, Synthesis and characterisation of soluble aluminium complex dyes based on 5-substituted-8-hydroxyquinoline derivatives for OLED applications, Dyes Pigments 66 (2005) 89–97.
[10] L.H. Feng, X.J. Wang, S.H. Zhao, Z.B. Chen, Synthesis and photophysics of novel 8-hydroxyquinoline aluminum metal complex with fluorene units, Spectrochim. Acta A 68 (2007) 646–650.
[11] L.H. Li, B. Xu, Synthesis and characterization of 5-substituted 8-hydroxyquinoline derivatives and their metal complexes, Tetrahedron 64 (2008) 10986–10995.
[12] J.T. Xie, Z.J. Ning, H. Tian, A soluble 5-carbazolium-8-hydroxyquinoline Al(III) complex as a dipolar luminescent material, Tetrahedron Lett. 46 (2005) 8559–8562.
[13] X.J. Wang, L.H. Feng, Z.B. Chen, Synthesis and photophysics of novel 8-hydroxyquinoline aluminum metal dye with hole transfer groups, Spectrochim. Acta A 71 (2008) 1433–1437.
[14] J.A. Cheng, C.H. Chen, H.P.D. Shieh, Organic light-emitting devices based on solution-processible quinolato-complex supramolecules, Mater. Chem. Phys. 113 (2009) 1003–1008.
[15] L.H. Feng, X.J. Wang, Z.B. Chen, Synthesis and photophysics of novel 8-hydroxyquinoline aluminum metal complex with 1,3,4-oxadiazole units, Spectrochim. Acta A 71 (2008) 312–316.
[16] T. Takada, K. Kawai, M. Fujitsuka, T. Majima, Rapid long-distance hole transfer through consecutive adenine sequence, J. Am. Chem. Soc. 128 (2006) 11012–11013.
[17] E.A. Weiss, M.J. Ahrens, L.E. Sinks, M.A. Ratner, M.R. Wasielewski, Solvent control of spin-dependent charge recombination mechanisms within donor-conjugated bridge-acceptor molecules, J. Am. Chem. Soc. 126 (2004) 9510–9511.
[18] W.J. Wu, J.B. Yang, J.L. Hua, J. Tang, L. Zhang, Y.T. Long, H. Tian, Efficient and stable dye-sensitized solar cells based on phenothiazine sensitizers with thiophene units, J. Mater. Chem. 20 (2010) 1772–1779.
[19] Y. Morishima, S. Nomura, M. Kamachi, Initiation of cationic polymerization of *n*-butyl vinyl ether by stable cation radicals of substituted phenothiazines, J. Polym. Sci. A: Polym. Chem. 32 (1994) 3141–3146.
[20] X.F. Zhang, H.W. Zheng, S.M. Jin, R.Y. Wang, Photoinduced electron transfer (PET) within D-4-A and D-A photosynthetic systems: enhanced intramolecular PET achieved by increasing the number of donors, Dyes Pigments 87 (2010) 139–143.
[21] G. Ajayakumar, K.R. Gopidas, Long-lived photoinduced charge separation in new $\text{Ru(bipyridine)}_3{}^{2+}$–phenothiazine dyads, Photochem. Photobiol. Sci. 7 (2008) 826–833.
[22] G. Ajayakumar, K. Sreenath, K.R. Gopidas, Phenothiazine attached $\text{Ru(bpy)}_3{}^{2+}$ derivative as highly selective "turn-ON" luminescence chemodosimeter for Cu^{2+}, Dalton Trans. (2009) 1180–1186.
[23] K. Meng, Y.L. Liu, W.K. Feng, Q. Zeng, X.J. Zhao, S.F. Wang, Q.H. Gong, Transient photophysics of phenothiazine-thiophene/furan copolymers in solvents, J. Photochem. Photobiol. A: Chem. 210 (2010) 44–47.
[24] J.E. McGarrah, J.T. Hupp, S.N. Smirnov, Electron transfer in platinum(II) diimine-centered triads: mechanistic insights from photoinduced transient displacement current measurements, J. Phys. Chem. A 113 (2009) 6430–6436.
[25] J.X. Luo, C.L. Yang, L.Y. Liang, M.G. Lu, Synthesis and characterization of a novel bipolar Alq_3-based copolymer containing carbazole and phenothiazine groups, J. Polym. Res., doi:10.1007/s10965-010-9523-0.
[26] G.A. Crosby, J.N. Demas, Measurement of photoluminescence quantum yields, J. Phys. Chem. 75 (1971) 991–1024.
[27] N. Li, X.T. Li, W. Wang, W.C. Geng, S.L. Qiu, Blue-shifting photoluminescence of Tris (8-hydroxyquinoline) aluminium encapsulated in the channel of functionalized mesoporous silica SBA-15, Mater. Chem. Phys. 100 (2006) 128–131.
[28] C.H. Chen, J.M. Shi, Metal chelates as emitting materials for organic electroluminescence, Coord. Chem. Rev. 171 (1998) 161–174.
[29] C.J. Liang, W.L. Li, J.Q. Yu, X.Y. Liu, D. Li, Y. Zhao, J.B. Peng, A new electroluminescent material $Eu(NO_3)_3$phen, Chin. J. Lumin. 17 (1996) 382–383.
[30] W.DeW. Horrocks Jr., W.E. Collier, Lanthanide ion luminescence probes. Measurement of distance between intrinsic protein fluorophores and bound metal ions: quantitation of energy transfer between tryptophan and terbium(III) or europium(III) in the calcium-binding protein parvalbumin, J. Am. Chem. Soc. 103 (1981) 2856–2862.
[31] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, second ed., Plenum Press, New York, 1999.
[32] X.H. Liu, P.X. Xi, F.J. Chen, Z.H. Xu, Z.Z. Zeng, Spectroscopic studies on binding of 1-phenyl-3-(coumarin-6-yl)sulfonylurea to bovine serum albumin, J. Photochem. Photobiol. B: Biol. 92 (2008) 98–102.
[33] X.J. Guo, L. Zhang, X.D. Sun, X.W. Han, C. Guo, P.L. Kang, Spectroscopic studies on the interaction between sodium ozagrel and bovine serum albumin, J. Mol. Struct. 928 (2009) 114–120.
[34] Z.G. Zhang, J.B. Yuan, H.J. Tang, H. Tang, L.N. Wang, K.L. Zhang, Nearly monochromatic red electroluminescence from a nonconjugated polymer containing carbazole segments and phenanthroline [Eu(beta-diketonate)(3)] moieties, J. Polym. Sci. A: Polym. Chem. 47 (2009) 210–221.
[35] Q.D. Ling, Q.J. Cai, E.T. Kang, K.G. Neoh, F.R. Zhu, W. Huang, Monochromatic light-emitting copolymers of *N*-vinylcarbazole and Eu-complexed 4-vinylbenzoate and their single layer high luminance PLEDs, J. Mater. Chem. 14 (2004) 2741–2748.
[36] S.H. Dong, W.L. Wang, S.W. Yin, C.Y. Li, J. Lu, Theoretical studies on charge transport character and optional properties of Alq_3 and its difluorinated derivatives, Synth. Met. 159 (2009) 385–390.
[37] M.J. Frisch, et al., Gaussian 03 Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
[38] Y.H. Gao, J.F. Chen, X.J. Zhuang, J.T. Wang, Y. Pan, L.M. Zhang, S.Q. Yu, Proton transfer in phenothiazine photochemical oxidation: laser flash photolysis and fluorescence studies, Chem. Phys. 334 (2007) 224–231.
[39] Y.C. Luo, H. Aziz, R. Klenkler, G. Xu, Z.D. Popovic, Temperature dependence of photoluminescence efficiency in doped and blended organic thin films, Chem. Phys. Lett. 458 (2008) 319–322.
[40] K.C. Tang, P.W. Cheng, V. Chien, C.P. Cheng, P.Y. Cheng, I.C. Chen, Fluorescence lifetime of tri-(8-hydroquinoline) aluminum thin film and solution, J. Chin. Chem. Soc. 47 (2000) 875–879.
[41] D.R. James, Y.S. Liu, P.De Mayo, W.R. Ware, Distributions of fluorescence lifetimes: consequences for the photophysics of molecules adsorbed on surfaces, Chem. Phys. Lett. 120 (1995) 460–465.