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Novel polymeric metal complexes based on bis-(8-hydroxylquinolinol)

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Abstract

Novel polymeric metal complexes based on bis(8-hydroxyquinolinol) were synthesized by a concise route. Substitution effects on their fluorescence spectra in the solution and in the solid state were tested and discussed preliminarily.

Keywords: Metal chelates; Synthesis; Fluorescence; bis(8-Hydroxyquinoline)

1. Introduction

Organic electroluminescent flat panel display is regarded as "technology of flat panel display of 21st century", and has been a hot research topic. Organometallic complexes such as Tris(8-hydroxyquinoline)-aluminum (Alq_3) seem to be the best materials for their excellent electroluminescent properties up to now [1]. A lot of research has been carried out in the field of organic electroluminescent devices (OELD) using organometallic complexes during the last decade [2].

Tang [1a] firstly reported the discovery of the double organic layer electroluminescent devices in 1987, which used Alq_3 as emitting and electron transporting layer and used the diamine as hole-transport layer. Subsequently other 8-hydroxyquinoline derivatives metal complexes were also used as both emitters and electron transport layers [3,4]. They are directly used as organic small molecules or adulterated with polymer. Comparing with small molecules which are hardly to form large scale uniform films and easily to be crystal in the process of operation so as to cut the lifetime of the devices, the polymers from 8-hydroxyquinolinol complexes might settle the questions, and the polymeric metal complex dyes containing hydroxyquinoline moiety were reported in recent years [5,6].

According to the relation between molecular structures and electroluminescent properties and the mechanism of electroluminescence, we report the new synthesis of polymeric metal complexes including bis(8-hydroxyquinoline) in this paper. And their fluorescence property was tested preliminarily.

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2. Results and discussion

2.1. Synthesis of the target compounds from 8-hydroxyquinoline

The synthetic routes and the target compounds were shown in Fig. 1. 8-Hydroxyquinoline was used as the starting material for the preparation of coordination of the polymeric metal complex dyes. 8-Hydroxyquinoline was reacted with formaldehyde in the environment of concentrated hydrochloric acid to give compound QQ **1**, and the compounds **2**, **3** and **4** were synthesized respectively from compound **1** and double molar

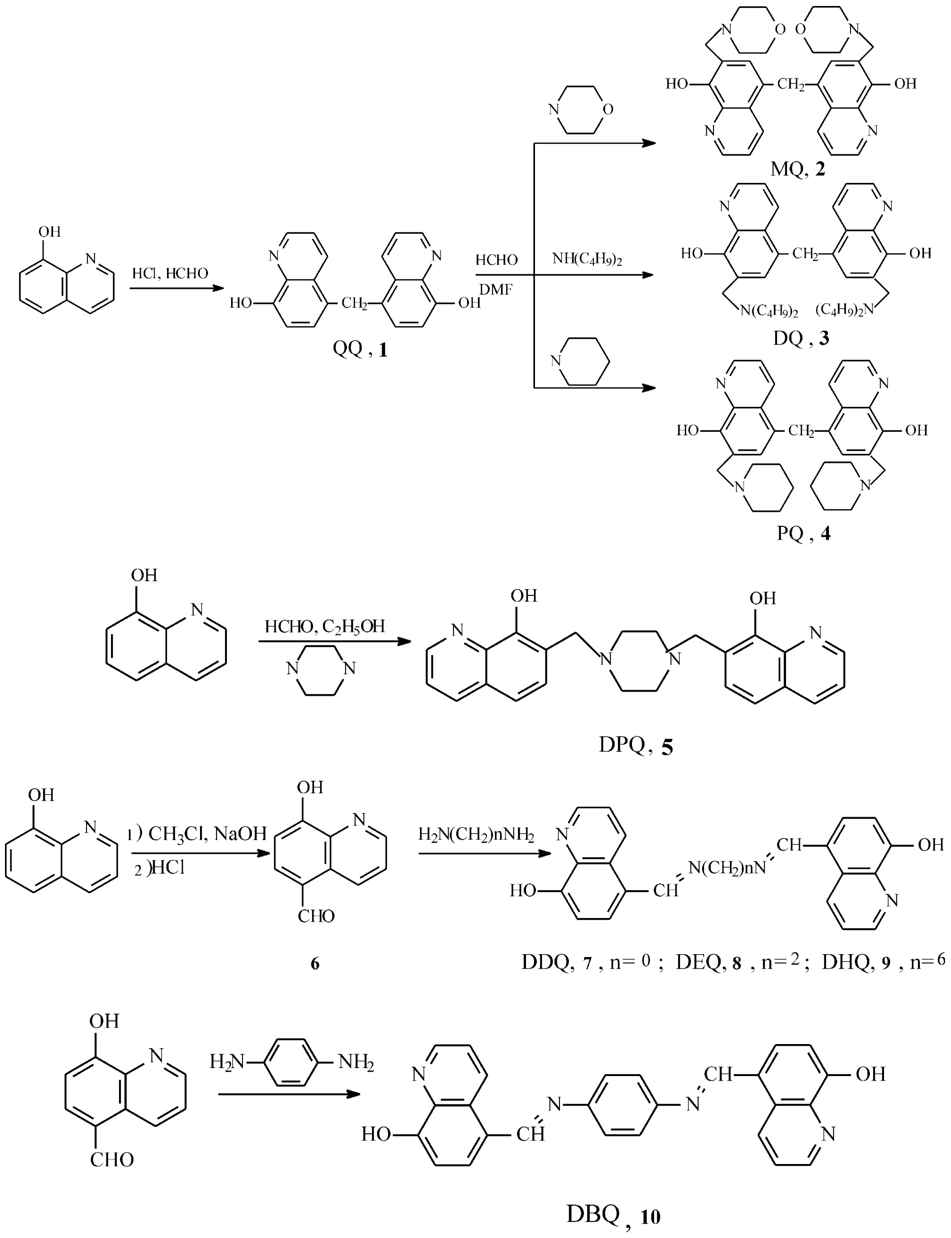

Fig. 1. Synthetic route of the compounds.

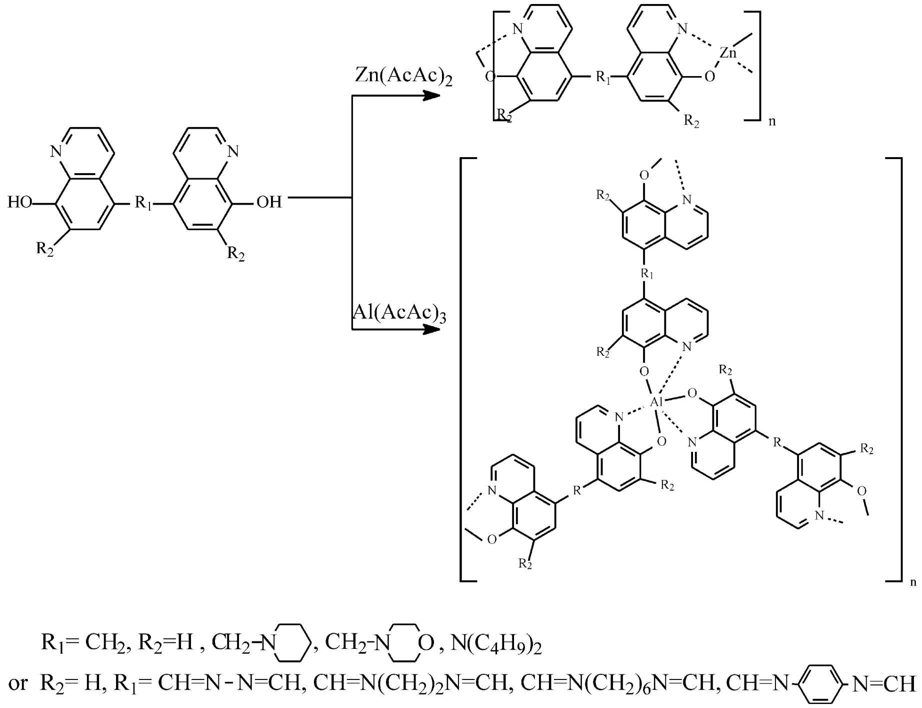

Fig. 1. (continued)

amount of morpholine, dibutylamine, piperidine through reaction. 8-Hydroxyquinoline was condensed with a half molar amount of piperazine hexahydrate and an equal molar amount of formaldehyde to give DPQ **5**. The coordination **7**, **8**, **9**, **10** were synthesized respectively from compound **6** and hydrazine monohydrate, ethylenediamine, 1, 6-hexanediamine, *p*-phenylendiamine. Every complex was prepared from a different coordination and metal ion. Among these compounds donating metal ion, aluminum acetylacetone and zinc acetylacetone were prepared by a different method. Acetylacetone was dropped into the solution of $Al(NO)_3{\cdot}9H_2O$ in hot water. The mixed solution was stirred for 1 h and ammonia was dropped into the solution of Al (III). After being stirred adequately and cooled, the aluminum acetylacetone obtained was filtered and dried. However, aqueous solution of $ZnAc_2{\cdot}2H_2O$ was dropped into the solution of acetylacetone, sodium hydroxide and water. The suspension was stirred for 30 min, and then filtered, washed with water, dried to give a white power (zinc acetylacetone).

According to the analysis, Alq_3 had a good characteristic property because it has an inner complex salts structure, which was the complex formed by the coordination including an acidic group and other coordination group and metallic ion. In the structure of Alq_3, 8-hydroxyquinoline has one acidic OH and the other N as coordination group, and then the inner complex salts was formed by 8-hydroxyquinoline and aluminum ion. In order to form the inner complex, the center ion should be chosen from the IIA, IIIA in the element period Table. For the trivalent metal, the coordination number of the metal selected is six; correspondingly the coordination number of the metal selected is four for the bivalent metal. The complex has an octahedral fabric when the ratio of the center metal and coordination is 1:3; similarly the complex has tetrahedral fabric when the ratio of the center metal and coordination is 1:2. The complexes have inner complex salts structure and high intensity fluorescence. Therefore, aluminum and zinc were selected as center metal to prepare metallic complexes.

The polymers samples were conformed by the IR spectra. For the Al(QQ) polymer, there is a sharp absorption hand at 1100 cm^{-1}, the Zn(QQ) polymer has a sharp absorption band at 1099 cm^{-1}, and so on. Charles et al. [7] suggested that the absorption band at about 1100 cm^{-1} should be associated with C–O vibrations at the C–O–M site. The new band at 1320 cm^{-1} in all spectra of the polymers was connected with the metal ions and monomers. All monomers also show strong bands around 1420 cm^{-1} due to OH deformation which appear as less intense bands in all polymers in the region 1400–1410 cm. The complexes of DDQ **7**, DEQ **8**, DHQ **9**, and DBQ **10** had the band of CH=N, which appeared at $\delta = 8.70$–9.25 in NMR spectra.

Compared the ^{1}H-NMR of Zn(MQ) with the ^{1}H-NMR of MQ, the δ of the hydrogen atom on the quinoline ring was moved forward low field and whose cracking was not obvious.

2.2. *Absorption and fluorescence properties*

The complex had an absorption peak at the band of 380–400 nm, which were the absorption peak of the 8-hydroxyquinoline metal complex and the peak was faintly influenced by the substituent. The fluorescence data show that the emissions of the polymer lie in the green region. The absorption and fluorescence data of complexes were shown in Table 1. The fluorescence data show that the fluorescence peak of the polymeric complexes had a blue shift than the fluorescence peak of the same metal complex of 8-hydroxyquinoline, which might be influenced by the 5-withdrawing group or the steric factor of the *p*-substitutes [8–10]. For example, Znq2 has a fluorescence peak at 560 nm in DMF, but the fluorescence of all zinc complexes is lower than 560 nm in DMF. The effect of blue shift of the fluorescence peak is unexpected.

Table 1
Absorption and fluorescence data of complexes: Al(MQ) and Zn(MQ) in methanol, others in DMF

Compound	λ_{max} (nm)	Log ϵ	PL (nm)
Al(MQ)	377	3.32	518
Zn(MQ)	388	3.87	546
Al(DEQ)	386	3.98	478
Zn(DEQ)	394	4.11	501
Al(DHQ)	390	4.02	483
Zn(DHQ)	400	4.09	502
Al(DBQ)	394	3.76	498
Zn(DBQ)	405	4.15	504

In order to show the influence that the concentration of metal ion affected the fluorescence of the complex, diverse ratio of the coordination MQ and metal ion was analysed. With the accretion of the concentration of the metal ion, the solubility of the complex was increased, and the fluorescence intensity was enhanced. It was conceivable that the complex formed by MQ and metal ion was not an ideal polymer but a small molar metallic complex with the accretion of the metal ion. Therefore, the theoretical ratio was adopted in order to perfect polymer of metal complex. Fig. 2 shows that

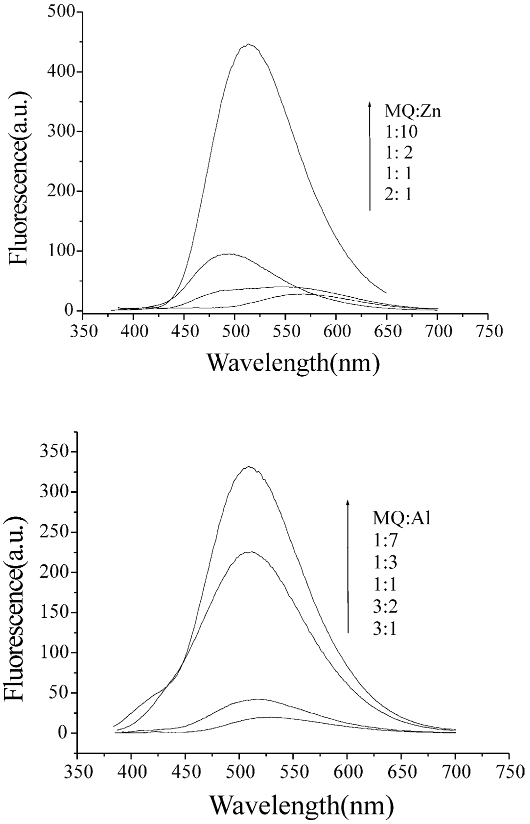

Fig. 2. Fluorescence spectra of complexes in DMF with various ratios of the metal: zinc complexes of MQ (top), aluminum complexes of MQ (bottom).

the difference of the fluorescence of the complex was produced by the diverse ratio of the coordination and metal ion.

Different Schiff-based substitute had the similar fluorescence peak in DMF, which shows that it is only the imine bond that influences the fluorescence peak. The existence of the electron-inductive imine bond results in the blue shift of fluorescence peak. Placing electron-withdrawing substituents in the 5-position of the quinoline ring is expected to increase the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Fig. 3 shows the fluorescence spectra of metal complexes containing hydroxyquinoline moiety with different Schiff based substituents. Table 2 shows fluorescence data of the complex in solid state. As shown in Fig. 3 and Table 2, these polymeric complexes have strong fluorescent emission in their solid state, which would be promising candidates with emitting metal complex for fabrication OLED by means of soluble casting technology. The preliminary studies of electroluminescent devices with the polymeric complexes in this work are being done in progress.

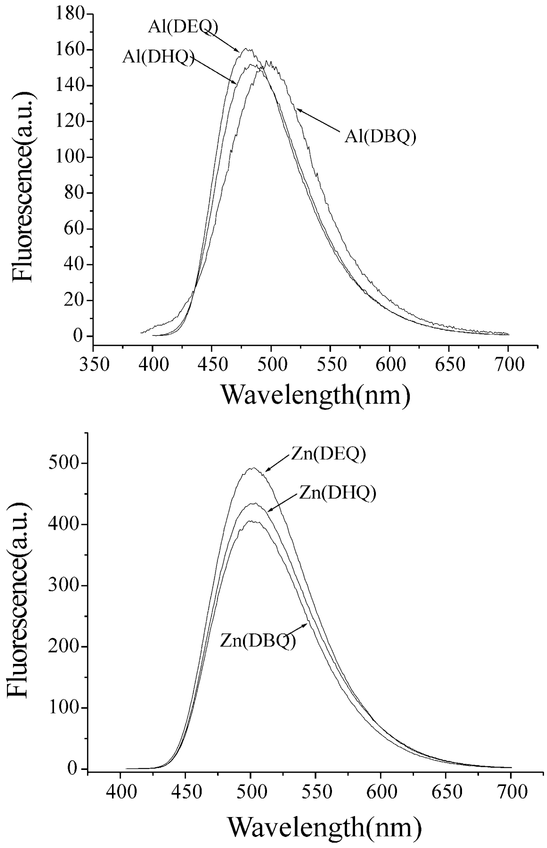

Fig. 3. Fluorescence spectra of metal complexes containing Schiff base: (top) aluminum complexes; (bottom) zinc complexes.

Table 2
Fluorescence data of the complexes in power

Compound	PL (nm)	Compound	PL (nm)
ZnQQ	540	AlQQ	522
Zn(DPQ)	514	Al(DPQ)	506
Zn(PQ)	542	Al(PQ)	528
Zn(MQ)	550	Al(MQ)	530
Zn(DQ)	560	Al(DQ)	533

In summary, the polymeric complexes consisting of 8-hydroxyquinoline moiety were prepared by a concise route. The compounds show good fluorescence property, in especially strong emission in solid state. According to the effect of placing electron-withdrawing substituents in the 5-position of the quinoline ring or the steric factors in the *p*-position, the fluorescence of the metal complexes containing hydroxyquinoline moiety is blue-shifted.

3. Experimental

^{1}H-NMR spectroscopy: Bruker 500 MHz (relative to TMS). Mass spectra were obtained with HP5989A, Mariner API time of flight (TOF, TIS ion source, PE Corp.) and API2000 (TIS, PE Corp.) spectrometers. Infrared spectra were measured on a Nicolet Magna IR550. UV–vis-NIR spectra were recorded on a Varian Cary500. Fluorescence spectroscopy was recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer.

Based on the synthetic methods in the references [11,12], 5, 5′-methylene-bis(8-hydroxyquinoline) (QQ, 1), 7, 7′-Di(*N*-piperidinomethyl)-5,5′-methylene-bis(8-hydroxyquinoline) (PQ, 4) and 5-Aldehydol-8-hydroxyquinoline (6) were synthesized.

*3.1. Synthesis of 7,7′-Di(*N*-morpholinomethyl)-5,5′-methylene-bis(8-hydroxy-quinoline) (MQ,* **2***)*

MQ was prepared from QQ and morpholine, formaldehyde in DMF. A mixture of QQ (0.579 g, 1.9 mmol), 37% aqueous formaldehyde (0.8 ml, 0.01 mol), morpholine (0.7 ml, 6 mmol), and DMF (30 ml) was stirred and heated at 100 °C for 4 h. After being cooled over night, the white crystal obtained was filtered, and then the filtrate was concentrated and cooled, the white power obtained was filtered. The whole white solid obtained was washed with acetone and dried. Yield 0.64 g, 66.5%. The sample obtained had a melting point of 195–197 °C.

^{1}H-NMR(CDCl$_3$): 2.56 (s, 8H, CH$_2$**C**H$_2$N), 3.73 (t, 8H, –CH$_2$O), 3.75 (s, 4H, –NCH$_2$Ar), 4.63 (s, 2H, ArCH$_2$Ar), 6.86 (s, 2H),7.39 (d×d, *J*=4.17 Hz, *J*=4.19 Hz, 2H), 8.23 (d×d, *J*=1.31 Hz, *J*=1.28 Hz, 2H), 8.90 (d×d, *J*=1.27 Hz, *J*=1.28 Hz, 2H).

*3.2. Synthesis of 7,7′-Di (*N*-dibutylaminomethyl)-5,5′-methylene-bis (8-hydroxy- quinoline) (DQ,* **3***)*

A mixture of QQ (0.725 g, 2.4 mmol), 37% aq formaldehyde (2.00 ml, 0.027 mol), dibutylamine (0.80 ml, 0.01 mol), and DMF (10 ml) was stirred and refluxed for 4 h. After cooled, the filtrate obtained was filtered and concentrated on vacuum. The solid obtained was filtered and added to benzene (20 ml). After refluxed for 30 min, the mixture was hot filtered. The solid obtained was filtered from the filtrate concentrated. Yield 0.56 g, 40.0%.

^{1}H-NMR(CDCl$_3$), 0.87 (t, 12H, –CH$_3$), 1.31 (m, 8H, –**C**H$_2$CH$_3$), 1.53 (m, 8H, R–CH$_2$–R), 2.52 (t, 8H, N–CH$_2$–R), 3.77 (s, 4H, N–CH$_2$–Ar), 4.60 (s, 2H, Ar–CH$_2$–Ar), 6.70 (s, 2H), 7.35 (d×d, *J*=4.09 Hz, *J*=4.09 Hz, 2H), 8.21 (d×d, *J*=1.27 Hz, *J*=1.28 Hz, 2H), 8.92 (d×d, *J*=1.32 Hz, *J*=1.60 Hz, 2H).

3.3. Synthesis of 2,2′-(1, 4-dimethylenepiperazino)-bis(8-hydroxyquinoline) (DPQ, **5***)*

A mixture of 8-hydroxyquinoline (2.9 g, 0.02 mol), paraformaldehyde (0.06 g, 0.02 mol), and piperazine hexahydrate (1.94 g, 0.01 mol) was mixed and melted on the steam bath without the use of solvent. After heating for 3 h, the reaction was allowed to stand several days. The solid contents of the flask was triturated with alcohol and then collected on a filter and dried. Yield 2.12 g, 56.4%. The white solid had a melting point of 160–161 °C.

^{1}H-NMR(CDCl$_3$): 2.25–3.0 (s, 8H, piperazine ring), 3.92 (s, 4H, N–CH$_2$–Ar), 7.26 (d×d, *J*=8.12 Hz, *J*=8.29 Hz, 4H), 7.39 (d×d, *J*=4.19 Hz, *J*=4.13 Hz, 2H), 8.09 (d×d, *J*=1.41 Hz, *J*=1.57 Hz, 2H), 8.87 (d×d, *J*=1.57 Hz, *J*=1.60 Hz, 2H).

*3.4. Synthesis of 5, 5′-(*N, N′*-dialdiminohydrazine)-bis(8-hydroxyquinoline) (DDQ,* **7***)*

A suspension of compound **6** (0.346 g, 2 mmol) in alcohol (50 ml) was stirred and heated until the suspended solid was dissolved completely, and then a solution of 80% hydrazine monohydrate (0.055 g, 1 mmol) in alcohol (10 ml) was added to the above solution. The mixed solution was heated to reflux and then a little of *p*-toluene sulfonic acid was added as catalyst. After being refluxed for 18 h, the yellow precipitate obtained was filtered off, washed completely with methanol and dried. Yield 0.29 g, 96.3%. Melting point is higher than 290 °C.

^{1}H-NMR(d_6-DMSO): 7.25 (d×d, *J*=8.30 Hz, *J*=8.06 Hz, 2H), 7.77 (d×d, *J*=4.07 Hz, *J*=4.08 Hz, 2H), 8.07 (d, *J*=8.13 Hz, 2H), 8.98 (d, *J*=3.92 Hz, 2H), 9.25 (s, 2H, –CH=N), 9.81 (d, *J*=8.60 Hz, 2H).

3.5. Synthesis of 5,5′-(N,N′-Dialdimino-1,2-ethyldiamine)bis(8-hydroxyquinoline) (DEQ, **8***)*

A suspension of compound **6** (0.346 g, 2 mmol) in alcohol (30 ml) was stirred and heated until the suspended solid was dissolved completely, and then a solution of 90% ethylenediamine (0.074 g, 1 mmol) in alcohol (10 ml) was added to the above solution. The mixed solution was heated to reflux and then a little of *p*-toluene sulfonic acid was added as catalyst. After refluxed for 16 h, the yellow precipitate obtained was filtered off, washed completely with methanol and dried. Yield 0.31 g, 83.8%. Melting point was 241–243°C.

^{1}H-NMR(d_6-DMSO): 4.0 (s, 4H, –CH_2CH_2–), 7.11 (d, $J = 8.00$ Hz, 2H), 7.53 (d×d, $J = 4.06$ Hz, $J = 4.09$ Hz, 2H), 7.78 (d, $J = 8.10$ Hz, 2H), 8.75 (s, 2H, –CH=N), 8.87 (d, $J = 2.78$ Hz, 2H), 9.70 (d×d, $J = 1.36$ Hz, $J = 1.08$ Hz, 2H).

3.6. Synthesis of 5,5′-(N,N′-dialdimino-1, 6-hexyldiamine)bis(8-hydroxyquinoline) (DHQ, 9)

A suspension of compound **6** (0.346 g, 2 mmol) in alcohol (35 ml) was stirred and heated until the suspended solid was dissolved completely, and then a solution of 1,6-hexanediamine (0.114 g, 1 mmol) in alcohol (5 ml) was added to the above solution. The mixed solution was heated to reflux and then a little of *p*-toluene sulfonic acid was added as catalyst. After refluxed for 46 h, the yellow precipitate obtained was filtered off, washed completely with methanol and dried. Yield 0.19 g, 44.6%. Melting point was 182–184 °C.

^{1}H-NMR(d_6-DMSO): 1.46 (m, 4H, –CH_2), 1.71 (m, 4H, –$\mathbf{CH_2}CH_2$–N), 3.62 (t, 4H, –CH_2N), 7.11 (d, $J = 8.03$ Hz, 2H), 7.65 (d×d, $J = 4.15$ Hz, $J = 4.09$ Hz, 2H), 7.81 (d, $J = 8.05$ Hz, 2H), 8.70 (s, 2H, –CH=N), 8.88 (d, $J = 2.9$ Hz, 2H), 10.40 (s, 2H, –OH).

3.7. Synthesis of 5,5′-(N,N′-dialdimino-1,4-benzyldiamine)bis(8-hydroxyquinoline) (DBQ, 10)

A mixture of compound **6** (0.173 g, 1 mmol), *p*-phenylendiamine (0.054 g, 0.5 mmol), and alcohol (30 ml) was stirred and heated to reflux. And then a little of *p*-toluene sulfonic acid was added as catalyst. After being refluxed for 20 h, the yellow precipitate obtained was filtered off, washed completely with methanol and dried. Yield 0.153 g, 73.2%. Melting point was higher than 290 °C.

^{1}H-NMR(d_6-DMSO): 7.25 (d, $J = 4.79$ Hz, 2H), 7.47 (s, 4H, ph-H), 7.76 (d×d, $J = 4.09$ Hz, $J = 4.11$ Hz, 2H), 8.13 (d, $J = 8.12$ Hz, 2H), 8.95 (d, $J = 2.82$, 2H), 9.08 (s, 2H, –CH=N), 9.90 (d, $J = 8.35$ Hz, 2H).

3.8. Preparation of aluminum complex of QQ 1: Al(MQ)

Under a dry argon atmosphere, in anhydrous DMF (20 ml) solution of QQ **1** (0.302 g, 1 mmol) and diethylamine (2.00 ml) as a proton scavenger, an anhydrous aluminum chloride (0.088 g, 0.67 mmol) was added. Then, the reaction mixture was refluxed for 5 h and filtered, washed with DMF and water. The yellow solid was dried under vacuum. Then the solid was washed by acetone over night and dried to give 0.2 g in yield 62.9%. Melting point was higher than 280 °C. The solid had a yellow-green fluorescence.

^{1}H-NMR(D_2SO_4): 9.10 (m, 3H), 8.87 (m, 1H), 8.19 (m, 1H), 7.97 (m, 1H), 7.25 (s, 1H), 4.89 (m, 2H).

3.9. Preparation of zinc complex of QQ 1: Zn(QQ)

With the similar synthetic method as Al(QQ), expect that anhydrous aluminum chloride was replaced by zinc chloride (0.135 g, 1 mmol), the solid had been prepared in yield 54.8%. The solid had a melting point higher than 280 °C and had yellow-green fluorescence.

3.10. Preparation of aluminum complex of MQ 2: Al(MQ)

An anhydrous methanol (20 ml) solution of anhydrous aluminum chloride (0.036 g, 0.27 mmol) was added drop-wise to a dichloromethane (20 ml) solution of MQ **2** (0.2 g, 0.4 mmol) over 3 h, under a dry argon atmosphere. The reaction solution was stirred for 72 h at room temperature. The yellow power was obtained until the solvent was removed at reduced pressure. The power was adequately washed with acetone. Melting point was higher than 280 °C.

3.11. Preparation of zinc complex of MQ 2: Zn(MQ)

An anhydrous methanol (10 ml) solution of anhydrous zinc chloride (0.095 g, 0.7 mmol) was added drop-wise to a dichloromethane (20 ml) solution of MQ **2** (0.35 g, 0.7 mmol) over 3 h, under a dry argon atmosphere. The reaction solution was stirred for 72 h at room temperature. The yellow precipitated solid was filtered and washed by dichloromethane, methanol and dried. The filtrate was removed at reduced pressure and dried.

Yield 0.3 g, 76.1%. Melting point was higher than 280 °C.

^{1}H-NMR(d_6-DMSO): 8.85 (s, 2H), 8.51 (s, 2H), 7.60 (s, 2H), 7.12 (s, 2H), 4.62 (s, 2H), 2.07 (s, 8H).

3.12. Preparation of aluminum complex of DQ 3: Al(DQ)

A mixture of DQ **3** (0.08 g, 0.14 mmmol) and alcohol (20 ml) was stirred until the DQ **3** was dissolved completely, and then a methanol (10 ml) solution of aluminum chloride (0.013 g, 0.1 mmol) was added drop-wise. The yellow-green precipitated solid was obtained instantly. The reaction was stirred for 3 h at room temperature under argon atmosphere. The yellow power was filtered and washed with alcohol adequately, and dried. Melting point was higher 280 °C.

3.13. Preparation of zinc complex of DQ 3: Zn(DQ)

With the similar synthetic method as Al(DQ), expect that anhydrous aluminum chloride was replaced by zinc chloride, the solid had a melting point higher than 280 °C and yellow-green fluorescence.

3.14. Preparation of aluminum complex of PQ 4: Al(PQ)

A mixture of PQ **4** (0.247 g, 0.5 mmol), anhydrous aluminum chloride (0.044 g, 0.3 mmol), toluene (20 ml), and a little of benzoic acid as catalyst was stirred and heated to reflux. After refluxed for 3 h under argon atmosphere, the precipitated solid was filtered and washed with acetone adequately and dried. Melting point was higher than 280 °C.

3.15. Preparation of zinc complex of PQ 4: Zn(PQ)

With the similar synthetic method as Al(PQ), expect that anhydrous aluminum chloride was replaced by zinc chloride, the solid had a melting point higher than 280 °C and yellow-green fluorescence.

3.16. Preparation of aluminum complex of DPQ 5: Al(DPQ)

An anhydrous methanol (20 ml) solution of anhydrous aluminum chloride (0.183 g, 1.4 mmol) was added drop-wise to a dichloromethane (15 ml) solution of DPQ **5** (0.83 g, 2.1 mmol) over 3 h, under a dry argon atmosphere. The reaction solution was stirred for 72 h at room temperature. The yellow power was obtained until the solvent was removed at reduced pressure. The power was adequately washed with acetone. Melting point was higher than 280 °C.

3.17. Preparation of zinc complex of DPQ 5: Zn(DPQ)

An anhydrous methanol (10 ml) solution of anhydrous zinc chloride (0.282 g, 2.1 mmol) was added drop-wise to a dichloromethane (20 ml) solution of DPQ **5** (0.83 g, 2.1 mmol) over 3 h, under a dry argon atmosphere. The reaction solution was stirred for 72 h at room temperature. The yellow precipitated solid was filtered and washed by dichloromethane, methanol and dried. Melting point was higher than 280 °C.

3.18. Preparation of aluminum complex of DDQ 7: Al(DDQ)

A mixture of DDQ **7** (0.103 g, 0.3 mmol) and DMF (30 ml) was stirred and heated until the DDQ **7** was dissolved completely. And then a methanol of aluminum chloride (4 ml, 0.2 mmol) was added to the solution of DDQ **7**. The precipitated solid was obtained instantly. The suspension had yellow-green fluorescence and was refluxed for 20 h. After cooled, the brown power was filtered, washed with water and dried. Yield 0.087 g, 82.9%. Melting point was higher than 280 °C.

3.19. Preparation of zinc complex of DDQ 7: Zn(DDQ)

A mixture of DDQ **7** (0.068 g, 0.2 mmol) and DMF (15 ml) was stirred and heated until the DDQ **7** was dissolved completely. And then a mixture of zinc acetate (0.044 g, 0.2 mmol) and DMF (5 ml) was added to the solution of DDQ **7**.

The precipitated solid was obtained instantly. The suspension had yellow-green fluorescence and was stirred for 20 h at 100 °C. After being cooled, the red-brown power was filtered, washed with water and dried. Yield 0.056 g, 70.0%. Melting point was higher than 280 °C.

*3.20. Preparation of aluminum complex of DEQ **8**: Al(DEQ)*

A mixture of DEQ **8** (0.111 g, 0.3 mmol) and DMF (30 ml) was stirred and heated until the DEQ **8** was dissolved completely. And then a mixture of aluminum acetylacetone (0.065 g, 0.2 mmol) and DMF (5 ml) was added to the solution of DEQ **8**. The mixed solution had yellow-green fluorescence. After stirred at about 100 °C for 10 h, the dark-red solution was cooled and removed at reduced pressure. The concentrated solution was poured into water (50 ml) and stirred adequately. The dark-brown power obtained was filtered and washed with water and acetone. Yield 0.097 g, 82.5%. Melting point was higher than 280 °C.

*3.21. Preparation of zinc complex of DEQ **8** : Zn(DEQ)*

A mixture of DEQ **8** (0.074 g, 0.2 mmol) and DMF (20 ml) was stirred and heated until the DEQ **8** was dissolved completely. And then a mixture of zinc acetylacetone (0.053 g, 0.2 mmol) and DMF (5 ml) was added to the solution of DEQ **8**. The precipitated solid was obtained instantly. The suspension had yellow-green fluorescence and was stirred at 100 °C. The precipitate disappeared slowly. After stirring for 10 h, the dark-red solution was cooled and removed at reduced pressure. The concentrated solution was poured into water (50 ml) and stirred adequately. The dark-brown power obtained was filtered and washed with water and acetone. Yield 0.083 g, 95.8%. Melting point was higher than 280 °C.

*3.22. Preparation of aluminum complex of DHQ **9** and DBQ **10**: Al(DHQ), Al(DBQ)*

With the similar synthetic method as Al(DEQ), expect that the compound DEQ **8** was replaced by DHQ **9** and DBQ **10**, the all dark-brown power obtained had melting point higher than 280 °C.

3.23. Preparation of zinc complex of DHQ and DBQ: Zn(DHQ), Zn(DBQ)

The complex of Zn(DHQ) was prepared with the similar synthetic method as Zn(DEQ), expect that DEQ **8** was replaced by DHQ. The preparation of Zn(DBQ) was similar with the synthetic method of Zn(DDQ), expect that DDQ **7** was replaced by DBQ **10**. All the complexes had melting point higher than 280 °C.

Acknowledgements

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