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Design and synthesis of 2-substituted-8-hydroxyquinline zinc complexes with hole-transporting ability for highly effective yellow-light emitters

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ABSTRACT

Four multifunctional 8-hydroxyquinoline derivatives were designed and synthesized, their structures were identified by FT-IR, ^{1}H NMR, MS and elemental analysis. Among them are (*E*)-2-(2-(9-(4-methoxyphenyl)-9H-carbazol-3-yl)vinyl) quinolato-zinc (**1**), (*E*)-2-(2-(9-p-tolyl-9H-carbazol-3-yl)vinyl)quinolato-zinc (**2**), (*E*)-2-(2-(9H-fluoren-2-yl)vinyl)quinolato-zinc (**3**), and (*E*)-2-(2-(phenanthren-9-yl)vinyl)quinolato-zinc (**4**). The electroluminescence (EL) and hole-transporting characteristics of these materials were investigated on four configurations: (A) ITO/2-TNATA/NPB/1, 2, 3 or 4/Alq_3/LiF/Al; (B) ITO/2-TNATA/NPB/1, 2, 3 or 4/LiF/Al; (C) ITO/2-TNATA/1, 2, 3 or 4/Alq_3/LiF/Al; and (D) ITO/2-TNATA/1 or 2/NPB/Alq_3/LiF/Al. The maximum luminescence and current efficiencies of are 3556 cd m^{-2} (at 13 V) and 2.17 cd A^{-1} (at 9 V) for compound **2**, 4624 cd m^{-2} (at 15 V) and 2.1 cd A^{-1} (at 7 V) for compound **3**, and 3164 cd m^{-2} (at 14 V) and 1.83 cd A^{-1} (at 13 V) for compound **4** in the configuration D, respectively, indicating that they are good multifunctional materials with strong hole-transporting abilities and luminescence properties.

1. Introduction

Organic photo- and electronic materials have commanded increasing attention since the discovery of organic conductors [1–3], which offer large-area, flexible, and lightweight devices through simple and low-cost processing. During the past twenty years, much effort has been paid to the development of highly efficient organic light-emitting diodes (OLEDs) [4–6], especially the white OLEDs [7–10]. To obtain white emission, various strategies have been developed. For small-molecule OLEDs, the general approach is to fabricate multiplayer devices by consecutive evaporation involving three primary colors (blue, green and red) or two special colors (blue and yellow). However, multiplayer construction of devices will increase of the cost of fabrication processes. In order to reduce the cost and obtain white OLEDs with minimal process of fabrication, it would be necessary to discover multifunction and highly efficient yellow-light emitting materials.

8-Hydroxyquinoline aluminum (Alq_3) has been identified as an excellent green-light emitting and electronic transporting material [11]. In order to retain the excellent photoelectron properties of 8-hydroxyquinoline itself and achieve yellow-light emission, a feasible approach is to extend the degree of π-conjugation in 8-hydroxyquinoline molecule, which will bring about a huge bathochromic effect. Meanwhile, some OLEDs with highly electroluminescent efficiencies can be also obtained by modifying the quinoline ring with differently functional groups. Active research in this area has been conducted over the past twenty years. For example, Mishra et al. [12] synthesized several 5-alkoxymethyl- and 5-aminomethy substituted 8-hydroxyquinoline alumina complexes, which were characteristic of strong green-light emissions with high quantum yields. Cui et al. [13] also reported 2-substitued-8-hydroxyquinoline molecules with large conjugated groups and tuned their luminescence to yellow-light ($\lambda_{ex} = 610$ nm). Likewise, Xie et al. [14] synthesized a new 5-substitued-8-hydroxyl quinoline exhibiting bi-functional and dipolar behavior. Their results showed that this molecule can be used as hole and electron transporter and emitter. Therefore, the incorporation of electron-donors (chemical structure suitable for capturing hole carriers) and electron-acceptors (chemical structure suitable for capturing electron carriers) into one molecule is highly desirable to enhance performance and improve fabrication technology.

In this paper, we report the synthesis, device fabrication and electroluminescence measurements of 2-substituted-8-hydroxyquinolato-Zn derivatives containing two different carbazole, fluorine and phenanthrene units owing to their abilities in luminescence and charge-transfer [15–18]. These four compounds

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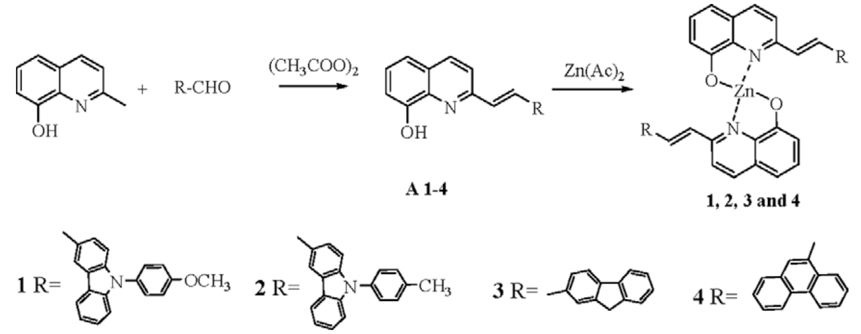

Scheme 1.

are: (E)-2-(2-(9-(4-methoxyphenyl)-9H-carbazol-3-yl)vinyl)quinolato-zinc (**1**), (E)-2-(2-(9-p-tolyl-9H-carbazol-3-yl)vinyl)quinolato-zinc (**2**), (E)-2-(2-(9H-fluoren-2-yl)vinyl)quinolato-zinc (**3**) and (E)-2-(2-(phenanthren-9-yl)vinyl)quinolato-zinc (**4**). The synthetic route of **1**, **2, 3** and **4** is shown in Scheme 1. In combination of 8-hydroxyquinoline with fluorene and carbazole, we anticipate the formation of new dipolar and multifunctional materials with excellent performance. Optical, thermal properties of these compounds were investigated, and electroluminescent devices using them as emission layers (EL), hole-transporting layers (HTL) or EL&HTL were fabricated and characterized.

2. Results and discussions

The thermal properties of the 8-hydroxyquinoline derivatives, investigated by differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA), are summarized in Table 1. The glass-transition temperatures (T_gs) of all four compounds are around 181–187 °C. **3** exhibits the highest T_g (187 °C), due to its rigid fluorene structure segment. Thermal decomposition temperatures (T_ds) of all compounds are around 360–480 °C. The results indicate that the incorporation of π-conjugated bridges into the 8-hydroxyquninoline system enhances the thermal properties significantly, especially with the fluorene derivative comparing with the publications about 2-methyl-8-hydroxylquinolato-zinc (T_g, 103 °C) [19].

The absorption data for the four compounds are also summarized in Table 1 and Fig. 1a. Among the four compounds, the maximal absorptive peaks of **1** and **2** are very similar and centered at about 380 nm, and the absorption spectra of **3** and **4** are also almost identical and at a maximum wavelength of ~350 nm, due to their similar π-conjugation structures and lengths. In the meanwhile, we also plotted the absorptive spectra of **A1**–**A4** in Fig. 1a, it can be seen the spectra appeared clear difference between the samples **A1**–**A4** and samples 1–4, which indicated there were interactions among them. The phenomena can be attributed to charge-transfer form metal-to-ligand transitions (MLCT) or ligand-to-metal transitions (LMCT). Photoluminescence (PL) data for these samples in solution and in solid state are recorded in Table 1 and Fig. 1b. The PL emissions of the four compounds appear around 567–585 nm in solution state and 591–628 nm in solid state. The spectra obtained for the solid state are red-shifted in relation to the solution measurements, as can be seen in Table 1, due to the molecular aggregation. Molecular aggregation leads to shifts of the state energies depending on the mutual orientation of the molecules forming a dimer, different transitions in the system can be forbidden or allowed. The optical properties associated with H-aggregates and J-aggregates [20]. It has been shown that H-type molecular aggregates result in the shift of the luminescence band. The insertion of π-conjugation bridging moieties also causes a significant red-shift in the spectra: **1**, **2**, **3** and **4** exhibit yellow to orange-red emission at peak wavelengths ($\lambda_{\max}^{PL}$) at 591, 593, 602 and 628 nm, respectively. Thus, the photophysical properties of these emitters are strongly affected by the π-conjugation lengths. Similar to the absorption spectra, the PL spectrum of **4** is red-shifted

Table 1
Summary of physical properties of compounds **1, 2, 3** and **4**.

	$\lambda_{\max}^{abs}$ (nm)	$\lambda_{\max}^{em}$ (nm) in DMF	$\lambda_{\max}^{em}$ (nm) in solid	Φ	T_g (°C)	T_d (°C)	τ (ns)
1	382	576	591	0.096	184	372	3.23
2	383	571	593	0.094	186	381	3.34
3	351	585	602	0.076	187	363	3.58
4	345	567	628	0.08	181	382	3.42

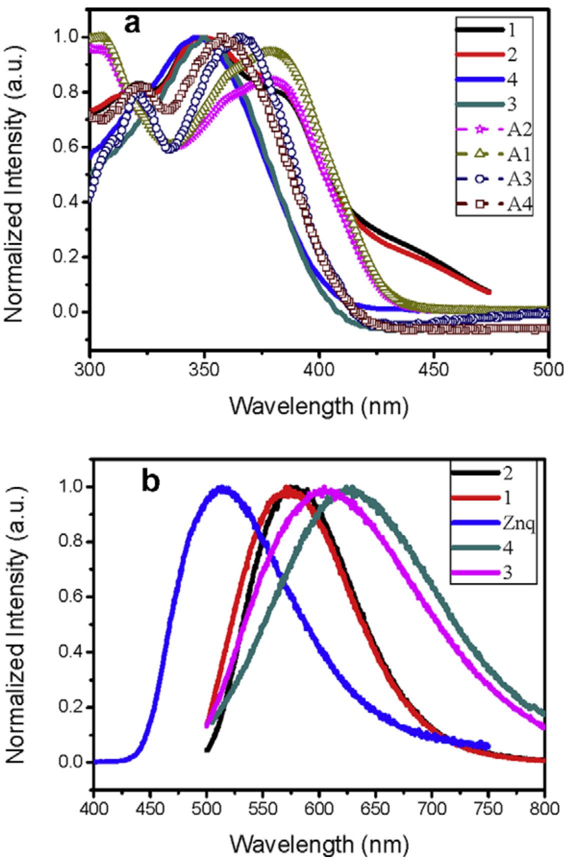

Fig. 1. (a) The absorptive spectra of samples 1, 2, 3 and 4 in DMF; (b) the PL spectra of samples 1, 2, 3, 4 and Znq in solid states.