



Achieving NIR emission for tetradentate platinum (II) salophen complexes by attaching dual donor-accepter frameworks in the heads of salophen



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ABSTRACT

Two novel tetradentate platinum (II) salophen complexes A and B, respectively substituted by dual donor-accepter frameworks of phenazine-triphenylamine in the heads and waists of salophen, were synthesized and characterized. By changing the substituted positions of dual phenazine-triphenylamine units, different optophysical, electrochemical and electroluminescent properties were remarkably observed for the both platinum (II) salophen complexes. Using a blend of poly(vinyl-carbazole) (PVK) and 1,3-bis(5-(4-(*tert*-butyl) phenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7) as host matrix, the platinum (II) salophen complexes A and B exhibited a deep red emission at 653 nm and a near-infrared (NIR) emission at 695 nm in the single-emissive-layer polymer light-emitting devices, respectively. The maximum external quantum efficiency (EQE) of 1.36% and highest radiant intensity (*R*) of 45 $\mu\text{W cm}^{-2}$ were obtained in the complex B-doped devices, which are 13.6 and 2.6 times of those corresponding values in the complex A-doped devices. It indicates that appending dual donor-accepter frameworks in the heads of salophen is an efficient strategy to achieve NIR emission for their tetradentate platinum (II) complexes.

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1. Introduction

Near-infrared (NIR) luminescent organic compounds are an emerging class of materials with potential applications in night-vision displays, sensors, optical communication, and offering superior biocompatibility for medical systems [1–5]. The materials that are able to display detectable NIR electroluminescence (EL) include mainly boron-dipyrromethene dyes, fluorescent materials with a donor-acceptor (D-A) structure, rare-earth (lanthanide) complexes and transition-metal complexes [6–9]. Among these

materials, transition-metal complexes are available to exhibit higher emission efficiency due to their strong spin-orbit coupling and fast intersystem crossing in the presence of heavy metals, which leads to an internal quantum efficiency as high as 100% [10–16]. However, this category of emitters suffers from some intrinsic obstacles: the decreased luminescence quantum yields with increasing emission wavelength and the triplet-triplet annihilation (TTA) with conjugated molecular packing [17,18].

Up to now, the most efficient NIR phosphorescent materials were platinum (II) emitters. For example, in an organic light-emitting device with a sophisticated configuration, platinum (II) emitters based on N[−]C[−]N ligands realized an unusually high external quantum efficiency (EQE) of up to 14.5% at ~700 nm, which is the highest value for these organic NIR-emitting devices to date [19]. Metalloporphyrin complexes exhibited an EQE maximum of 3.0% for polymer light-emitting devices (PLEDs) and 9.2% for organic light-emitting devices (OLEDs) with a NIR emission in the 760–780 nm range [20]. However, all of these platinum (II) emitters with square-planar structure commonly unfolded a gradient

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efficiency roll-off at high current densities, which could be attributed to the triplet-triplet exciton annihilation aggravated by long excited-state lifetimes [21].

In contrast to platinum (II) complexes, most NIR-emitting organic and polymeric fluorescent dyes are built with electron-donating (D) units and electron-accepting (A) units. Their bandgap levels and photo-electronic properties can be readily tuned through a systematic variation between D and A units [22–28]. For example, Wang et al. reported a class of D-A type fluorescent dyes, which extended the emission region to above 1000 nm successfully [7,29]. Reynolds et al. reported a kind of D-A-D telechelic conjugated oligomers, which display an emission ranges from 651 to 1088 nm [30]. Be inspired, platinum (II) complexes with the D-A framework are expected to present NIR electrophosphorescent emission.

Platinum (II) Schiff base complexes were an important class of platinum (II) complexes and used as dopant for high-performance OLEDs [31–36]. However, most of them give visible emissions from blue, yellow, red and even white [37–43]. The NIR-emitting platinum (II) Schiff base complexes has been still unreported. In order to develop their application in NIR-emitting materials and study structure-properties relationship, specially the effect of D-A frameworks on photophysical and EL properties, in this contribution, we report two novel platinum (II) salophen complexes A and B, in which dual triphenylamine (TPA)-phenazine (PZ) units are used as the D-A frameworks and attached in the heads and waists of salophen ligand. The molecular structures of complexes A and B are shown in Fig. 1. By changing the positions of the dual D-A frameworks in the salophen, the resulting platinum (II) Schiff base complexes exhibited significantly different optical and electrochemical properties, as well as electroluminescent (EL) properties. Using both platinum (II) complexes as a single dopant and a blend of poly(vinylcarbazole) (PVK) and 1,3-bis(5-(4-(*tert*-butyl) phenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7) as a host matrix, the single-emissive-layer PLEDs were made by solution process. A near-infrared emission at 695 nm with a *EQE* of 1.36% and a radiant intensity (*R*) of $45 \mu\text{W cm}^{-2}$ was observed in the complex B doped devices, while the complex A doped devices exhibited a deep red emission at 653 nm with a low *EQE* of 0.1% and *R* of $17 \mu\text{W cm}^{-2}$. This work demonstrates that appending the dual D-A frameworks into the heads of the Schiff base core of salophen can tune the emissive wavelength to NIR region and further improve the EL properties for its resulting platinum (II) salophen complexes in PLEDs.

2. Results and discussion

2.1. Measurements and materials

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF. Thermogravimetric analysis (TGA) was conducted under a dry nitrogen gas flow at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ on a Perkin-Elmer TGA 7. UV–Vis absorption spectra were recorded on a HP-8453 UV visible system. Cyclic voltammetry was carried out on a CHI660A electrochemical work-station in a three-electrode cell dipped in a 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution under nitrogen protection at a scan rate of 100 mV s^{-1} at room temperature (RT). In this three-electrode cell, a platinum rod, platinum wire and saturated Ag/AgCl electrode were used as a working electrode, counter electrode and reference electrode, respectively. All solvents were carefully dried and distilled prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were performed under nitrogen atmosphere and monitored by thin-layer chromatography.

As shown in Scheme 1, compounds **2**, **5** and **8** are commercially available reagents and used without further purification. Intermediate **1**, **6** and **10** were synthesized by referring to the reported procedure [34,44,45]. Compounds **3** and **4** were synthesized through an amine aldehyde condensation and a coordination reaction with a mediate yield of 61% and 41%, respectively. Compound **9** was obtained via boric acid esterification reaction using $\text{PdCl}_2(\text{dppf})_2$ as a catalyst with a yield of 62%. Compounds **7**, platinum complexes A and B were prepared through Suzuki coupling reaction, respectively. Both substituted platinum (II) salophen complexes were characterized by ^1H NMR, MALDI-TOF mass spectra and elemental analyses, which confirmed the well-defined chemical structures. The thermogravimetric analyses (TGA) curves of two platinum (II) salophen complexes A and B under N_2 atmosphere are depicted in Fig. S1 (see electronic supporting information, ESI), and the corresponding data are summarized in Table 1. The decomposition temperature (T_d) level of $351 \text{ }^\circ\text{C}$ for complex A and $358 \text{ }^\circ\text{C}$ for complex B are observed at a 5% weight loss, respectively. It indicates that both substituted platinum (II) salophen complexes have high thermal stability.

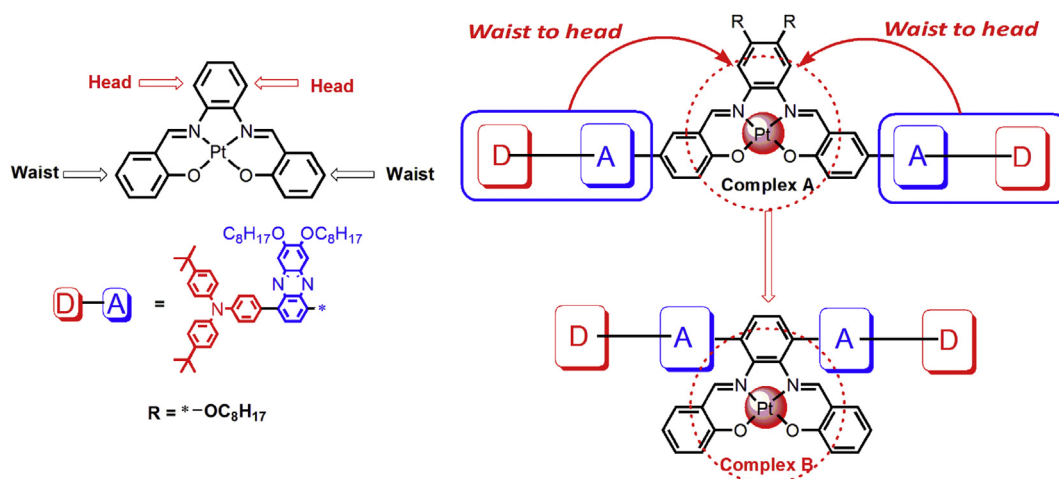


Fig. 1. Molecular structures of two platinum (II) salophen complexes A and B.

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