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A novel near-infrared-emitting cyclometalated platinum (II) complex with donor–acceptor–acceptor chromophores

Junting Yu [a], Keqi He [a], Yanhu Li [b], Hua Tan [a], Meixiang Zhu [a], Yafei Wang [a], Yu Liu [a], Weiguo Zhu [a,*], Hongbin Wu [b,*]

[a] College of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in the Ministry of Education, Xiangtan University, Xiangtan 411105, PR China

[b] Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, PR China

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ABSTRACT

A novel near-infrared-emitting cyclometalated platinum (II) complex of (TPA-BT-Q)Ptpic with a donor–acceptor–acceptor (D–A–A) chromophores was synthesized and characterized, in which the TPA-BT-Q unit is a cyclometalated ligand of N,N-di(4-octyloxyphenyl)-4-(7-(quinolin-2-yl)-benzo[c][1,2,5]thiadiazol-4-yl)-phenylamine and pic is picolinate anion. Its optophysical, electrochemical and electroluminescent characteristics were primarily studied. An intense UV–vis absorption peak at 540 nm and a strong near-infrared emission peak at 759 nm were observed for (TPA-BT-Q)Ptpic in dichloromethane. Using (TPA-BT-Q)Ptpic as a single dopant and a blend of poly(vinylcarbazole) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole as a host matrix, the single-emissive-layer polymer light-emitting devices exhibited a near-infrared emission peaked at 760 nm with the maximum external quantum efficiency of 0.12% at 16.6 mA cm^{-2} and a radiance intensity of 112 μW cm^{-2} at 11.7 mA cm^{-2} at the doping concentrations of 2.0 wt%. This work provides an efficient approach to realize near-infrared electrophosphorescent emission with high radiance intensity by employing platinum (II) complex with the D–A–A structure.

1. Introduction

Recently, the research on near-infrared (NIR) organic luminescent materials has gained great attentions due to their diverse potential applications in night-vision displays, sensors, optical communication, and offering superior biocompatibility for medical systems [1]. The developed NIR-emitting materials mostly contain lanthanide complexes [2], fluorescent materials with a donor–acceptor (D–A) structure [3], boron dipyrromethene dyes [4] and transition-metal complexes [5]. Among these materials, transition-metal complexes are available to exhibit higher emission efficiency due to their strong spin-orbit coupling in the presence of heavy metals, which leads to an internal quantum efficiency as high as 100% [6]. Metalloporphyrin is the most typical class in the reported transition-metal complexes and has recorded an external quantum efficiency (EQE) maximum of 2.49% for polymer light-emitting devices (PLEDs) and 9.2% for organic light-emitting devices (OLEDs) with NIR emission in the 760–780 nm range. However, these EQE levels were typically obtained at very low current densities [7]. It is well known that squareplanar platinum (II) complexes have rapidly developed in OLEDs with high-efficiency red, green, blue and even white emission by tuning their molecular structures [8]. But, few platinum (II) complexes besides Pt-porphyrin complexes have displayed satisfactory EQE level in NIR emission. In order to develop new NIR-emitting platinum (II) complexes, Gao et al. reported a platinum complex of ppyPtq, which displayed an EL emission peaked at 730 nm without EQE datum [5b]. Che et al. reported a series of neutral platinum complexes containing substituted 8-hydroxyquinoline, which gave a deep-red emission peak from 650 to 695 nm with another weak NIR emission peak from 705 to 755 nm in the device with an EQE of 1.7% [5e]. Recently, some NIR-emitting organic and polymeric fluorescent materials with donor (D) and acceptor (A) chromophores were developed because the band gap levels and photoelectronic properties can be readily tuned through a systematic variation between the D and A units [1,9]. For example, Wang et al. reported a class of fluorescent materials with D–π–A–π–D type chromophore,

* Corresponding authors. Tel.: +86 731 58298280; fax: +86 731 58292251.
E-mail addresses: zhuwg18@126.com (W. Zhu), hbwu@scut.edu.cn (H. Wu).

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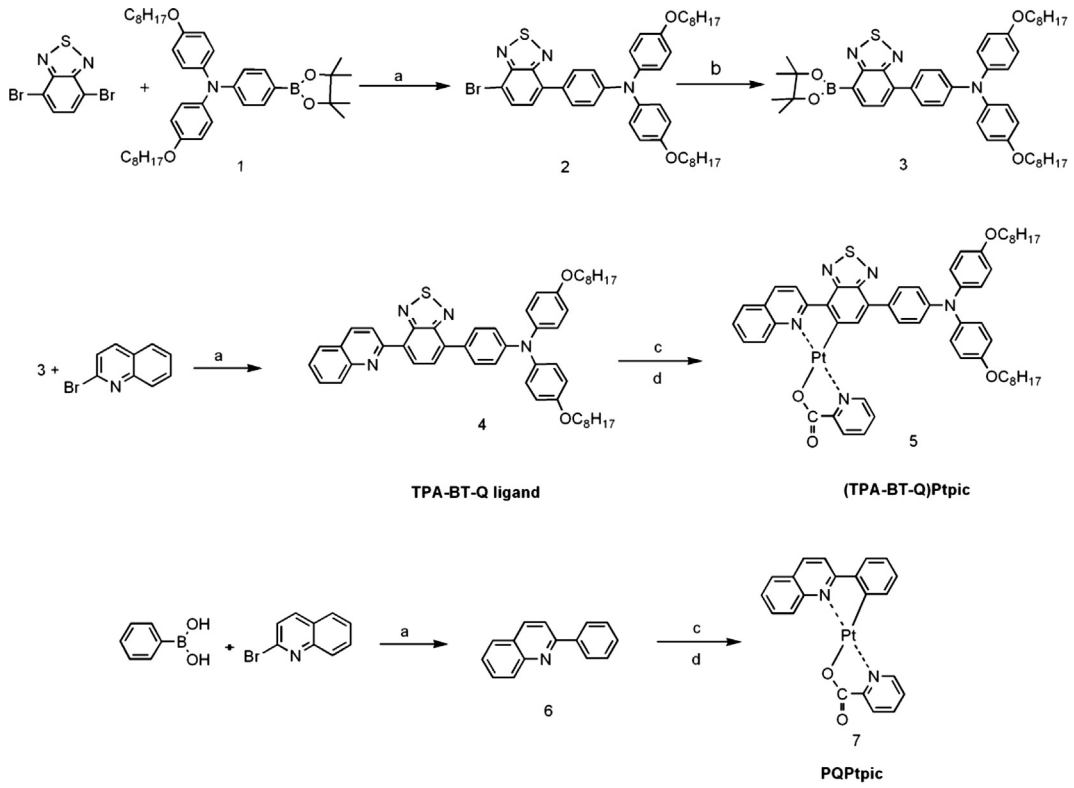
which displayed emission exclusively at 1080 nm with an EQE of 0.28% in the OLEDs [10]. Reynolds et al. reported a family of conjugated oligomers with a multi-heterocycle D–A–D structure, which displayed emission ranging from 651 to 1088 nm with an EQE of 0.87% in the PLEDs [3a].

As phosphorescent materials have exhibited higher external quantum efficiency than fluorescent materials in OLEDs, it was always interesting in developing NIR-emitting platinum complexes. In order to study effect of molecular structure of platinum complexes on NIR-emitting property, a type of platinum complexes of (Piq-G)Pt(acac) with D–A chromophores was obtained in our previous work, which exhibited an emission with a peak at 640 nm and a shoulder at 700 nm [11]. There was about 40–60 nm red-shift compared to that from the non-functionalized platinum (II) complex of (Piq)Pt(acac). Based on this findings, we here designed another novel platinum (II) complex of (TPA-BT-Q)Ptpic with D–A–A type chromophores, in which a triphenylamine (TPA) was used as an electron donor unit, a benzothiadiazole (BT) and a quinoline (Q) were simultaneously employed as strong electron acceptor units. In this (TPA-BT-Q)Ptpic, the non-planar TPA unit is available to improve carrier-transporting properties and suppress aggregations, the BT unit is a good class of luminescence units in OLEDs and acceptor units in organic solar cells (OSCs) reported in recent years [12], two alkoxy groups are benefit to improve solubility. Therefore, the (TPA-BT-Q)Ptpic with D–A–A units should provide low-energy near-infrared emission more easily than those counterparts with D–A units. The synthetic route of (TPA-BT-Q)Ptpic is shown in Scheme 1. For comparison, the counterpart of PQPtpic was made. Using (TPA-BT-Q)Ptpic as a single dopant and a blend of poly(vinylcarbazole) (PVK) and 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) as the host matrix, we fabricated the single-emissive-layer (SEL) PLEDs by solution process and studied the device performances. A NIR emission peaked at 760 nm with a maximum EQE of 0.12% at 16.6 mA cm^{-2} and an irradiance intensity of 112 μW cm^{-2} (obtained at an applied current density of 11.7 mA cm^{-2}) were observed in the device at 2.0 wt% dopant concentration. This work indicates that introducing D–A–A structure is an efficient approach to constructure NIR-emitting platinum (II) complex and obtained high-efficiency NIR-emitting PLEDs with high radiance intensity.

2. Experimental

2.1. General information

The solvents were carefully dried and distilled by standard procedures before use. All chemicals, unless otherwise stated were obtained from commercial sources and used as received. The Suzuki coupling and cyclometalated reactions were carried out in inert gas atmosphere and monitored by thin-layer chromatography (TLC). ^{1}H NMR spectra was recorded with a Bruker Dex-400 NMR instrument using $CDCl_3$ as a solvent. Elemental analysis was carried out with a Harrios elemental analysis instrument. Mass spectrum was recorded on a Voyager Depro MALDI-TOF spectrometer. UV–vis absorption and photoluminescent spectra were recorded with a Shimadzu UV-265 spectrophotometer and a Perkin–Elmer LS-50 luminescence spectrometer, respectively. Thermogravimetric analysis (TGA) was conducted under a dry nitrogen gas flow at a heating rate of 20 °C min^{-1} on a Perkin–Elmer TGA 7 instruments. Surface morphologies were recorded by AFM on a Veeco, DI



Scheme 1. Synthetic route of (TPA-BT-Q)Ptpic and PQPtpic.