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Effect of the bipyridine ligand substituents on the emission properties of phosphorescent Ir(III) compounds

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ABSTRACT

To investigate the effect of bipyridine ligand substituents on the emission properties of Ir(III) compounds, four homoleptic iridium(III) compounds, specifically, *mer*-Ir(**Mepypy**)$_3$ (**1**), *mer*-Ir(**Me$_2$pypy**)$_3$ (**2**), *fac*-Ir(**OMe$_2$pypy**)$_3$ (**3**) and Ir(**OMe$_2$Bupypy**)$_3$ (4), where **Mepypy** = 2'-methyl-2,3'-bipyridine, **Me$_2$pypy** = 2′,6'-dimethyl-2,3'-bipyridine, **OMe$_2$pypy** = 2′,6'-dimethoxy-2,3'-bipyridine and **OMe$_2$ Bupypy** = 2′,6'-dimethoxy-4-*tert*-butyl-2,3'-bipyridine, were prepared via a one-pot reaction of the corresponding methyl- or methoxy-substituted ligand with Ir[(COD)]BF$_4$ as the starting material. Under the same reaction conditions, the major isolated products differed depending on the substituent used. The methyl substituents resulted in Ir(III) compounds with a meridional geometry, while methoxy-substituted Ir(III) compounds with a facial geometry were isolated in high yields when the methoxy substituent was used. Compounds **1** and **2** emit a green phosphorescence ($\Phi_{PL} = 0.3$) with a $\lambda_{max} = 459$–463 nm, while **3** and **4** show a bright, sky-blue emission ($\Phi_{PL} = 0.5$). The dimethoxy-substituted bipyridine ligand was advantageous in terms of yield, thermal stability and quantum efficiency, and its iridium compound is a good candidate for triplet emitters in phosphorescence organic light-emitting diodes (PHOLEDs).

1. Introduction

Bipyridine ligands, such as 2,3'-bipyridine, have C,N chelating modes with heavy transition metals, and they have recently attracted attention because of their high triplet energy (T_1) [1–6]. In particular, iridium(III) compounds bearing the 2,3'-bipyridine ligand have been shown to be suitable blue emitting-phosphors in phosphorescence organic light-emitting diodes (PHOLEDs) due to their excellent external quantum efficiency (EQE ~20%) [7]. The phosphorescent emission for bipyridine(pypy)-based iridium compounds is thought to originate from both the ligand-centered triplet (^{3}LC) transition and the metal-to-ligand charge transfer transition (MLCT) [8]. Moreover, the emission energy can be tuned via the introduction of substituents, such as electron-donating or withdrawing groups, into the main ligand [9]. Therefore, the judicious selection of both the C,N chelate ligand and the substituents on the chelate ligand is necessary to control the phosphorescent emission of a compound. Although tuning the emission energy for bipyridine(pypy)-based iridium compounds can be achieved by incorporating an ancillary ligand into the ligand framework, the effect of the bipyridine ligand substituent in homoleptic iridium(III) has not been investigated thus far [10]. We recently developed blue triplet emitters, Ir(dfpypy)$_3$ [8] and Ir(OMe$_3$pypy)$_3$ [11], using the fluorine- and methoxy-functionalized bipyridine ligands, 2′,6′-difluoro-2,3′-bipyridine (dfpypy) and 2′,6′,4-trimethoxy-2,3′-bipyridine (OMe$_3$pypy), respectively. Based on our observations, the triplet energies of the bipyridine derivatives with substituents appeared in the region of 2.70–2.82 eV, as shown in Fig. 1. The bipyridine ligand has a greater triplet energy than phenylpyridine (ppy), thus, it is a very promising ligand candidate for the development of blue phosphorescent iridium(III) compounds. However, because of the high reactivity and low selectivity of the pyridine ring, incorporating the proper substituents into a bipyridine ligand is usually problematic in regard to the yields and reaction conditions [10].

Therefore, we performed a systematic investigation on the effect of bipyridine ligand substituents on iridium(III) compounds. In our

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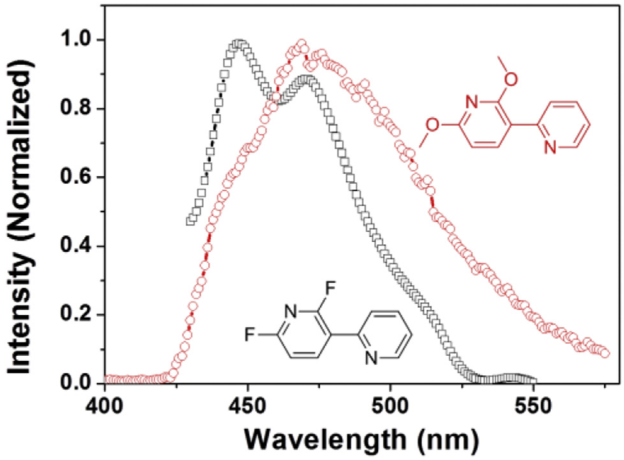


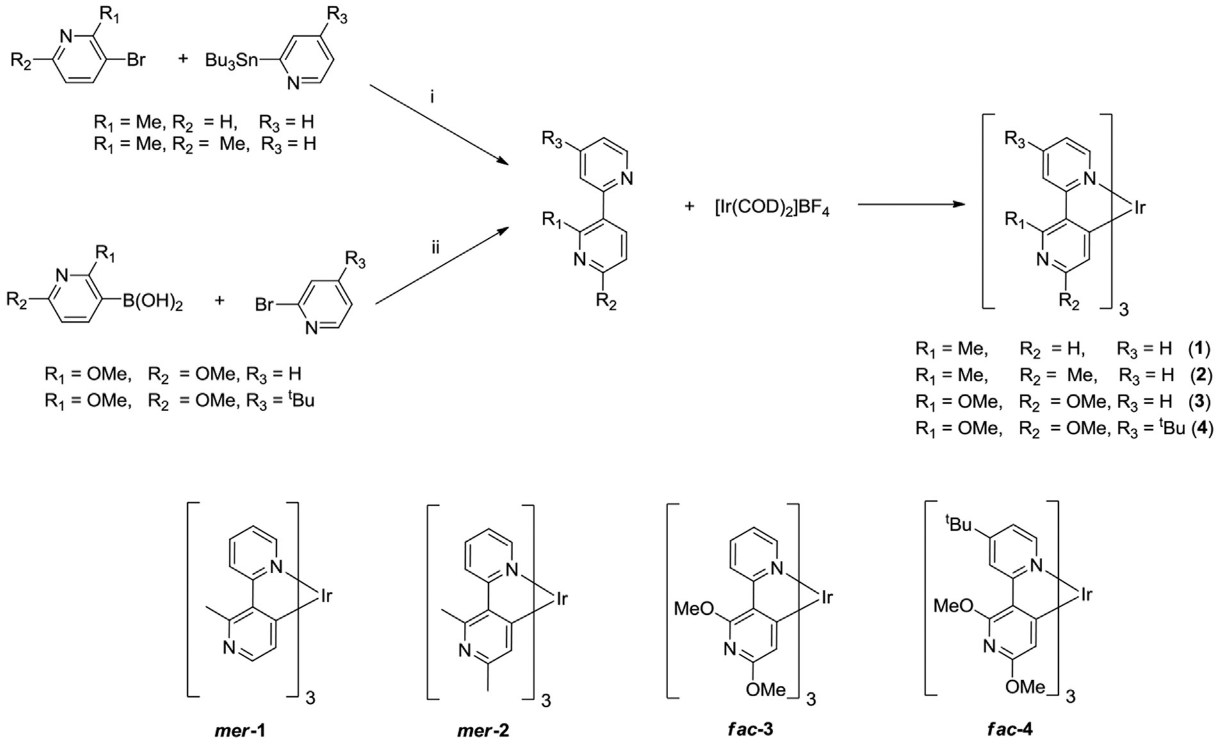
Fig. 1. Phosphorescence of dfpypy (black, T_1: 2.82 eV) and OMe_2pypy (red, T_1: 2.70 eV). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ongoing investigation of homoleptic Ir(III) compounds using $[Ir(COD)_2]BF_4$ as the starting material, we observed that homoleptic *fac*-Ir(C^N)$_3$ derivatives were obtained with a high selectivity [11]. For example, *fac*-Ir(OMe_3pypy)$_3$, without the meridional isomer, was obtained via a one-pot reaction of $[Ir(COD)_2]BF_4$ and 2′,6′,4-trimethoxy-2,3′-bipyridine (OMe_3pypy) under mild conditions. This provides a potentially simple and selective synthetic pathway for blue phosphorescent *fac*-Ir(III) compounds with substituted bipyridine ligands. Herein, we report an efficient synthesis of homoleptic Ir(III) compounds possessing dimethyl- and dimethoxy-substituted bipyridine (pypy) ligands and their photophysical and electrochemical properties.

2. Result and discussion

The synthetic details for compounds (**1**–**4**) are shown in Scheme 1. The four different ligands were prepared via typical cross-coupling reactions using the corresponding boronic acid or tin reagent. The procedure to produce the Ir(C^N)$_3$ compounds uses reactive Ir(I) and reacts it with the substituted bipyridine ligand in 1,2-propandiol at a high temperature (~180 °C) [11]. Based on our previous reports, the use of an Ir(I) compound as the starting material and this reaction condition usually result in iridium compounds with facial geometry. Compounds **3** and **4**, bearing the dimethoxy and *tert*-butyl substituents on the bipyridine ligand, were obtained in the facial form in moderate yields. However, when using the dimethyl-substituted bipyridine ligand, the iridium compounds **1** and **2** were mainly isolated in the meridional form [12]. Moreover, the yields (<20%) for both **1** and **2** were much lower than those for **3** and **4**. The molecular structures of **1**–**4** were confirmed using various spectroscopic methods, including X-ray analysis on **2**. The molecular structure and crystal data of **2** are shown in Fig. 2 and Table 1, respectively. Based on the NMR and crystal structure data, both **1** and **2** have meridional geometries. The facial geometry was observed in **3** and **4**, as shown in Figure S8 and S10, respectively.

The normalized emission spectra of **1**–**4** in CH_2Cl_2 at ambient temperature are shown in Fig. 3. The emission energy can be tuned from blue (462 nm) to green (511 nm) depending on the ligand substituents. Compounds **3** and **4** with the dimethoxy substituents have a shoulder peak (vibronic structure) in the emission spectra, indicating a mostly MLCT emission [13], whereas **1** and **2** exhibit broad emission bands without the vibronic structure. In addition, the emission maxima of **1** and **2** appear at 509 and 511 nm, respectively, which are remarkably redshifted compared to the emission maxima of **3** and **4**. These results indicate that the ligand



Scheme 1. Synthetic routes and structures of **1**–**4**.