



The intramolecular π – π stacking interaction does not always work for improving the stabilities of light-emitting electrochemical cells

Fuli Zhang, Lian Duan*, Juan Qiao, Guifang Dong, Liduo Wang, Yong Qiu*

Key Lab of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

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ABSTRACT

Recently, the stabilities of light-emitting electrochemical cells (LECs) based on cationic iridium(III) complexes with controlled intramolecular π – π stacking interactions by adopting pendant phenyl rings have been dramatically enhanced compared with those of the complexes without π – π stacking interactions within the molecule. Herein, a novel cationic iridium complex $[\text{Ir}(\text{ppy})_2(\text{pyphmi})]\text{PF}_6$ [ppy = 2-phenylpyridine, pyphmi = 1-pyridyl-3-phenylimidazolin-2-ylidene- $\text{C},\text{C}^{2'}$] which exhibits intramolecular π -stacking interaction has been prepared and its X-ray crystal structure has been investigated. Unexpectedly, however, the corresponding LECs based on $[\text{Ir}(\text{ppy})_2(\text{pyphmi})]\text{PF}_6$ do not show significantly enhanced stabilities compared to the LECs based on $[\text{Ir}(\text{ppy})_2(\text{pymi})]\text{PF}_6$ [pymi = 1-pyridyl-3-methylimidazolin-2-ylidene- $\text{C},\text{C}^{2'}$] without pendant phenyl rings within the molecule. This phenomenon is attributed to the very long centroid–centroid distance between the π -stacked phenyl rings, which results from the larger tension of substituted five-membered ring moiety (imidazolin-2-ylidene). In addition, irreversible oxidation and reduction processes would also decrease the electrochemical stability of $[\text{Ir}(\text{ppy})_2(\text{pyphmi})]\text{PF}_6$. Thus, intramolecular π – π stacking interaction using pendant phenyl rings is not always effective to improve the stability of LECs.

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1. Introduction

Light-emitting electrochemical cells (LECs) are an exciting alternative to organic light-emitting diodes (OLEDs) due to their promising advantages such as simple architecture, solution processing, air-stable electrodes [1–4]. Compared with polymer-based LECs, ionic transition metal complexes (iTMCs)-based LECs have drawn extensive attention due to no additional inorganic salts or ion conducting polymers required, easy purification [5] and high efficiency by harvesting both singlet and triplet states [6,7]. However, the LECs still suffer from slow response and severe excited-state quenching in the active layers compared with conventional OLEDs [6,8]. In particular, the limited stability of the LECs is the most challenging

problem [9–11], which mainly originates from the breakdown of the iTMCs facilitating the nucleophilic attack by water and other nucleophiles.

Iridium(III) complexes are the best candidates among iTMCs in terms of their short excited-state lifetimes, color tuning and high photoluminescence quantum yields. Recently, the stabilities of LECs based on cationic iridium(III) complexes bearing pbpy, dpbpy, pphen and phpzpy (pbpy = 6-phenyl-2,2'-bipyridine, dpbpy = 6,6'-diphenyl-2,2'-bipyridine, pphen = 2-phenyl-1,10-phenanthroline and phpzpy = 2-(1-phenyl-1H-pyrazol-3-yl)pyridine) as the ancillary ligands have been dramatically enhanced by adopting intramolecular face-to-face π -stacking between the pendant phenyl rings of the ancillary ligands and the phenyl rings of the cyclometalated ligands [12–15]. This interaction makes both ground and excited states of the complexes more robust and reduces the possibility for nucleophilic attack at the central iridium(III) ions, which would lead to the degradation of the complexes. The long

* Corresponding authors. Tel.: +86 10 62779988; fax: +86 10 62795137.

E-mail addresses: duanl@mail.tsinghua.edu.cn (L. Duan), qiuy@mail.tsinghua.edu.cn (Y. Qiu).

lifetimes of these LECs are achieved thousands of hours. In the past 2 years, LECs based on cationic iridium complexes with *N*-heterocyclic carbene ancillary ligands, which show blue to orange electroluminescence, have been reported [16,17]. However, some of them exhibit short lifetimes of several to 50 min. Lately, we have reported the electroluminescence properties of OLEDs based on cationic iridium complexes with pyridine–carbene ancillary ligand [18]. In order to improve the stability of the LECs based on carbene based cationic iridium complexes, we attempt to adopt the above-mentioned strategy by introduction of intramolecular π – π stacking interaction to these complexes.

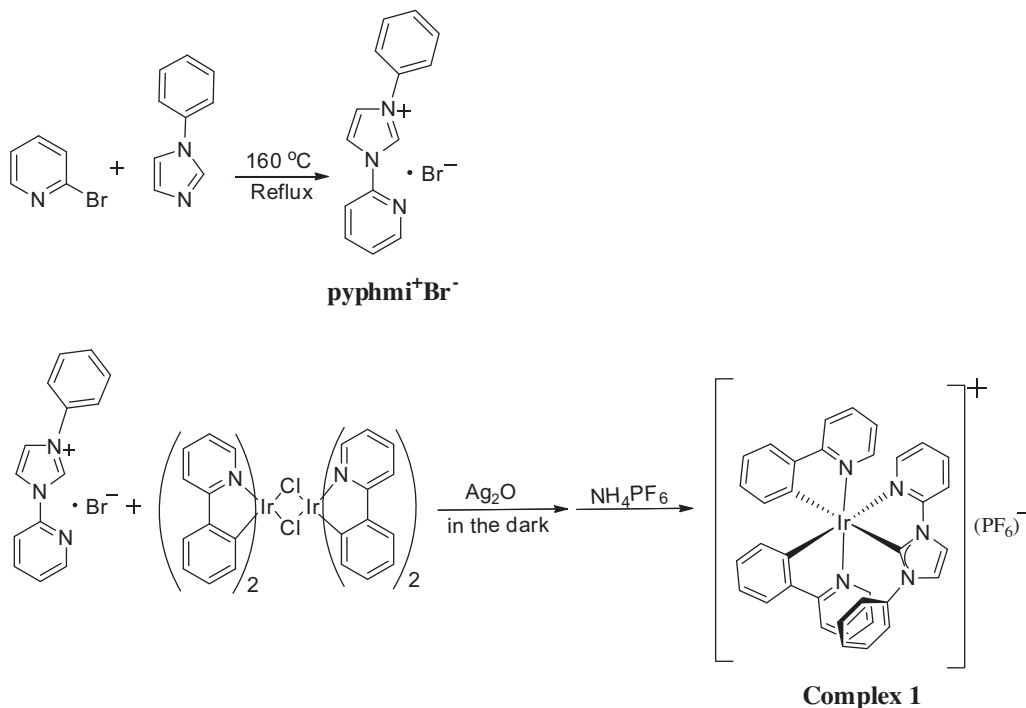
Herein, we report a novel cationic iridium complex $[\text{Ir}(\text{ppy})_2(\text{pyphmi})]\text{PF}_6$ (**1**) (ppy = 2-phenylpyridine, pyphmi = 3-phenyl-1-(2-pyridyl)imidazolin-2-ylidene- C_2) (Scheme 1) with ppy as the cyclometalated ligand, pyphmi as the ancillary ligand. In complex **1**, the pendant phenyl group of pyphmi forms a weak face-to-face π -stacking with ppy plane because of (1) a large dihedral angle of 22.72° between the pendant phenyl ring of pyphmi and its neighboring ppy plane and (2) a long centroid-to-centroid distance of 3.71 \AA between the π -stacking phenyl rings. Electrochemical measurements showed that the added phenyl group makes the oxidation potential of **1** more irreversible than that of the complex $[\text{Ir}(\text{ppy})_2(\text{pymi})]\text{PF}_6$ (**2**) [pymi = 1-pyridyl-3-methylimidazolin-2-ylidene- C_2] (Scheme 1) without pendant phenyl rings within the molecule [18]. As mentioned above, we applied complex **1** as active component in LECs to explore the effect of intramolecular π – π stacking interactions on the performances of the devices. Different from previous reports where intramolecular π – π stacking interaction significantly enhanced the stability of LECs [12–14], the

LECs based on complex **1** do not show significantly enhanced stabilities compared to the LECs based on complex **2**. Our work suggests that intramolecular π – π stacking interaction using pendant phenyl rings is not always effective to improve the stability of LECs.

2. Experimental

2.1. Characterization

^1H NMR spectra were recorded on a JOEL JNM-ECA600 NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectrometry was performed with an Esquire-LC_00136 mass spectrometer. Elemental analysis for carbon, hydrogen and nitrogen were determined on an Exeter Analytical CE-440 Elemental Analyzer. UV absorption spectra were obtained from CH_3CN solutions were recorded with a UV–vis spectrophotometer (Agilent 8453). PL spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). The PL decay lifetimes were recorded on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920) with a time-correlated single-photon counting technique. The photoluminescent quantum yields (PLQYs) of the complexes were measured in degassed CH_3CN solutions with quinine sulfate ($\Phi_p = 0.545$ in $1 \text{ M H}_2\text{SO}_4$) as the standard [19]. The solutions were degassed by three freeze-pump-thaw circles before measurements. The PLQYs in thin films were measured with an integrating sphere on a fluorospectrophotometer (Jobin Yvon, FluoroMax-3) according to a reported procedure [20]. Cyclic voltammetry was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in CH_3CN



Scheme 1. The synthetic protocols for the proligand $\text{pyphmi}^+\text{Br}^-$ and complex **1**.

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