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Iridium (III) complexes with 5,5-dimethyl-3-(pyridin-2-yl)cyclohex-2-enone ligands as sensitizer for dye-sensitized solar cells



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ABSTRACT

The three iridium complexes based on 5,5-dimethyl-3-(pyridine-2-yl)cyclohex-2-enone ligand and pyridine-2,4-dicarboxyl acid (**5b**) or 2,2'-bipyridine-4,4'-dicarboxyl acid (**5c**) as ancillary anchoring ligands were synthesized and characterized as potential photosensitizer for dye-sensitized solar cells (DSSC). Using of cyclohexenone derivatives as ligands extended the absorption response of the iridium complex to low energy band near 550 nm and shifted the maximum emission peak to deep red (near the 680 nm). The theoretical molecular orbital calculations shows that the HOMO orbitals of all the complexes are contributed by the combination of orbitals on Ir atom (about 50%) and π orbitals located on 5,5-dimethyl-3-(pyridine-2-yl)cyclohex-2-enone. While auxiliary ligands with anchoring group exclusively contribute to electron density of the LUMO orbital, accounting for 96.33% in **5b** and 95.51% in **5c**. It is beneficial for electron injection in DSSC application. Applying them to DSSC, the IPCE response of the DSSCs covered a wide visible spectral range from 350 to 675 nm and the cells presented an open-circuit voltage of 645 mV, a power conversion efficiency of 1.03%.

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1. Introduction

Dye-sensitized solar cells (DSSCs) continuously have attracted great attention because of easy fabrication and cost-effectiveness compared with silica-based photovoltaic device since pioneering research by O'Regan B. and Gratzel M. in 1991 [1]. As one of the crucial parts in DSSCs, the photosensitizers (PS) have been well developed over the past two decades and many different PS including metal complexes, porphyrins, phthalocyanines and metal-free organic dyes have been designed and applied to DSSCs.

The metal complexes, in particularly ruthenium complexes [2–6], have been intensively investigated because of their broad absorption spectrum and favorable photovoltaic properties. So far, the best conversion efficiencies have been achieved with ruthenium-based sensitizers except for recently reported the best efficiency of 12.7% with donor- π -bridge-acceptor zinc porphyrin dye [7]. The light absorption of this type of complexes in visible part of solar spectrum is mainly due to MLCT (metal-to-ligand charge transfer) process, which is very sensitive to the spatial separation (r) with electrode surface. Upon optical excitation, the electrons in TiO₂ film injected from dyes are inclined to recombination with a redox couple presented in electrolyte. Also, isothiocyanate ligand (–NCS) usually includes the most of Ru-based complexes using for raise the HOMO energy of the complex, and the monodentate ligand

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appears to be unfavorable to the stability of the materials [8,9]. Thus, the dilemma for Ru-based cells is that their conversion efficiency fluctuated at a range of 11–12% in recent years [4,10].

Iridium complexes have been widely investigated in the past two decades for their practical applications in organic light-emitting devices because of high photoluminescence quantum yields and excellent color tunability [11–14]. In 2006, it has been first demonstrated as sensitizer in DSSC to produce current by LLCT (ligand to ligand charge transfer) process [15], which is favorable to the suppress of charge recombination. Up to now, there are only few published papers on iridium complexes as sensitizer in DSSC [16,17] and cell parameters reported in these papers are not very good. However, despite poor characteristics of these cells compared with the usually used Ru-based cells, iridium complexes have been suggested to have great promising application in DSSC due to several advantages such as having the possibility for dual sensitization through LLCT and MLCT process, less accessible MC (metal-centered) state and thus higher stability [18]. Unfortunately, the development of iridium complex for this purpose is in their infancy for a main barrier that their absorption response is exclusively located at a UV or blue region, little overlapping with the radiant energy of sun light. So, improving their absorption responses in visible light range is a top concern for iridium complex to be applied to DSSC fields.

Recently, several strategies performed intended to improve the absorption response of iridium complexes, such as modifying phenylpyridine ligand with oligothiophene pendants [19], oligofluorene segment [20] or using 7-diet-hyaminocoumarine auxiliary ligand [21]. These endeavors only induced significantly enhanced absorption response in wavelength range from 400 to 500 nm. Just recently, we demonstrated that introducing of dicyanovinyl unit into phenyl *meta*-position of ppy (phenylpyridine) in iridium (III) bis(phenylpyridinato)picolinate can induced a significantly enhanced absorption capacity in the visible light range from 400 to 500 nm and used them as co-sensitizer with N719, notably improved cell parameters have been observed. In addition, we noticed that alkenylpyridines-based iridium complexes showed a more wide absorption response than 2-arylpyridine or 2-arylquinolines and -isoquinolines did in visible light range [22–24].

In this paper, we report three new iridium complexes using 5,5-dimethyl-3-(pyridin-2-yl)cyclohex-2-enone as cyclometalation ligands for DSSC (Fig. 1). The newly

designed iridium complexes are expected to have a wide absorption response in visible light range and suppressed triplet–triplet (T–T) annihilation when anchored on TiO₂ film because of using rigid and bulky cyclohexenone ligands.

2. Results and discussion

2.1. Synthesis, UV and emission spectra

The synthesis route of the three complexes is shown in Scheme 1. The ligand (3) was prepared by treating 2-bromopyridine with *n*-butyllithium at –78 °C, and then by 5,5-dimethyl-3-Ethoxy-cyclohex-2-enone (2) in 28% yields. Here, the intermediate (2) was prepared by etherifying enol of 5,5-dimethyl-1,3-cyclohexanedione with ethanol in the presence of *p*-toluenesulfonic acid. The desired complex **5a**, **5b** and **5c** were prepared according to our previously published procedure [25]. Typically, the chloro-bridged iridium(III) dimer directly reacted with sorts of auxiliary ligands 2,2'-bipyridine-4,4'-dicarboxylic acid or picolinic acid/pyridine-2,4-dicarboxylic acid in proper solvent to provide the desired final product.

The UV-vis absorption and photoluminescence spectra of **5a–5c** measured in CH₃CN solution are presented in Fig. 2, as well as absorption spectra of **5b** and **5c** on TiO₂ film, and corresponding spectra data are summarized in Table 1. Fig. 2(a) indicates that the three iridium complexes own wide absorption response in visible light range and absorption bands with significant intensity extend to about 550 nm, which is very interesting for DSSC application. A slight blue-shifted absorption response was observed in the spectra of complex **5c** compared with that of the complex **5a** and **5b**. These phenomenons have been ever observed in several iridium complexes when auxiliary ligands picolinic acid/pyridine-2,4-dicarboxylic acid was replaced by 2,2'-bipyridine-4,4'-dicarboxylic acid in our research. The UV-region, 250–350 nm, shows a strong absorption band, that can be assigned to $\pi-\pi^*$ intra ligand absorption for 5,5-dimethyl-3-(pyridin-2-yl)cyclohex-2-enone and sorts of auxiliary ligands. The near-visible and visible region between 350 and 550 nm was occupied by a flat absorption band with considerably intensive extinction coefficient. This could be attributed to MLCT transition (metal-to-ligand charge transfer) or LLCT transition. The absorption spectra of **5b** and **5c** on TiO₂ film are similar with that in CH₃CN.

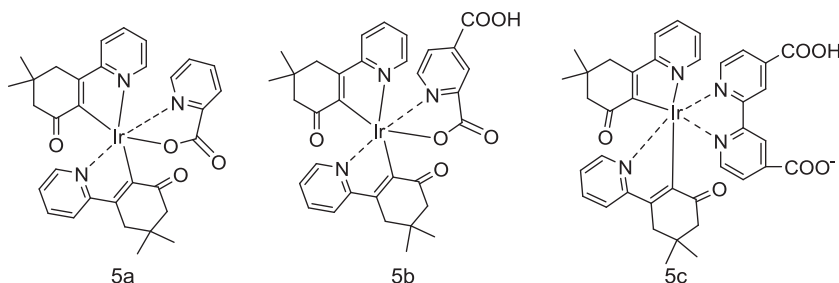


Fig. 1. Schematic structure of the synthesized iridium complexes.

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