



Synthesis, photo- and electro-luminescence of dinuclear Ir(III) complexes containing bis- β -diketonate carbazole ligand

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ARTICLE INFO

Article history:

Received 26 August 2018

Received in revised form

22 September 2018

Accepted 25 September 2018

Available online 27 September 2018

Keywords:

Dinuclear iridium complex

Bis- β -diketonate ligand

Photoluminescence

Electroluminescence

ABSTRACT

A carbazole-functionalized bis- β -diketonate as ancillary ligand, 1,1'-(9-(heptan-3-yl)-9H-carbazole-3,6-diyl)bis(4,4,4-trifluorobutane-1,3-dione) (**H₂L**), which contains two trifluorinated alkyl groups, has been prepared for the synthesis of two green and red emitting dinuclear Ir(III) complexes with the general formula Ir₂(C⁻N)₄L [C⁻N = 3-(pyridine-2-yl)coumarinato (**¹L**) and 2-(1-naphthyl)benzothiazole (**²L**)]. The photophysical and electrochemical properties and thermal stabilities of two dinuclear Ir(III) complexes were investigated systematically. The results showed that two dinuclear Ir(III) complexes not only exhibit excellent thermal stabilities, but also emit stronger green and red emissions, respectively. Furthermore, based on two dinuclear Ir(III) complexes, the solution-processed organic light-emitting devices have been successfully fabricated, in which the devices fabricated from the green emissive Ir(III) complex exhibited a maximum brightness of 6057 cd/m² and a maximum luminous efficiencies of 16.39 cd/A and the devices fabricated from the red emissive Ir(III) complex displayed a maximum brightness of 1949 cd/m² and a maximum luminous efficiencies of 2.52 cd/A.

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1. Introduction

Since the Ir atom has a large spin-orbit coupling effect, the cyclometalated iridium(III) complexes have unique advantages, such as high quantum yield, brightness, relatively short excited-state lifetime, and tunable emission wavelength across the visible light spectrum, the phosphorescent Ir(III) complexes have been the subject of ever-increasing attention owing to the widespread applications in organic light-emitting devices (OLEDs), light-emitting electrochemical cells, chemosensors and biological labeling [1–12]. During the past decade, considerable efforts have been made in terms of the highly efficient Ir(III) complexes with variable emissions from the blue light to the near-IR light by modulating the cyclometalating and ancillary ligands [5,13–16]. Up to now, blue, green and orange OLEDs with external quantum efficiencies (EQEs) used Ir(III) complexes as emitters have exceeded 30% [17–21], and EQEs of over 25% for red phosphorescent Ir(III) complexes have

been reported [22–25].

Generally, the neutral phosphorescent Ir(III) complexes include one core Ir atom and three monoanionic bidentate ligands, and these complexes can be divided into homoleptic and heteroleptic Ir(III) complexes. The homoleptic Ir(III) complexes contain three identical cyclometalating ligands, whereas the heteroleptic Ir(III) ones contain two identical cyclometalating ligands and an ancillary ligand. Usually, for homoleptic Ir(III) complexes, the atoms of the cyclometalating ligand bonded to the Ir atom are C and N, where C has a formal negative charge. The representative ancillary ligands are picolinate and β -diketonate derivatives. For example, Lamansky et al. [26] reported a series of the Ir(III) complexes forming with two cyclometalated ligands (C⁻N) and a single monoanionic, bidentate ancillary ligand (LX), and found that these Ir(III) complexes exhibit highly efficient emission and the emission colors from these Ir(III) complexes are strongly dependent on the choice of cyclometalated ligand. Lamansky et al. [27] also investigated the effect of the non-chromophoric and chromophoric β -diketonate ancillary ligands, such as acetylacetonate (acac), benzoylacetonate (bza) and dibenzoylmethane (dbm), on the luminescence efficiency of the Ir(III) complexes, and found that the phosphorescence quantum

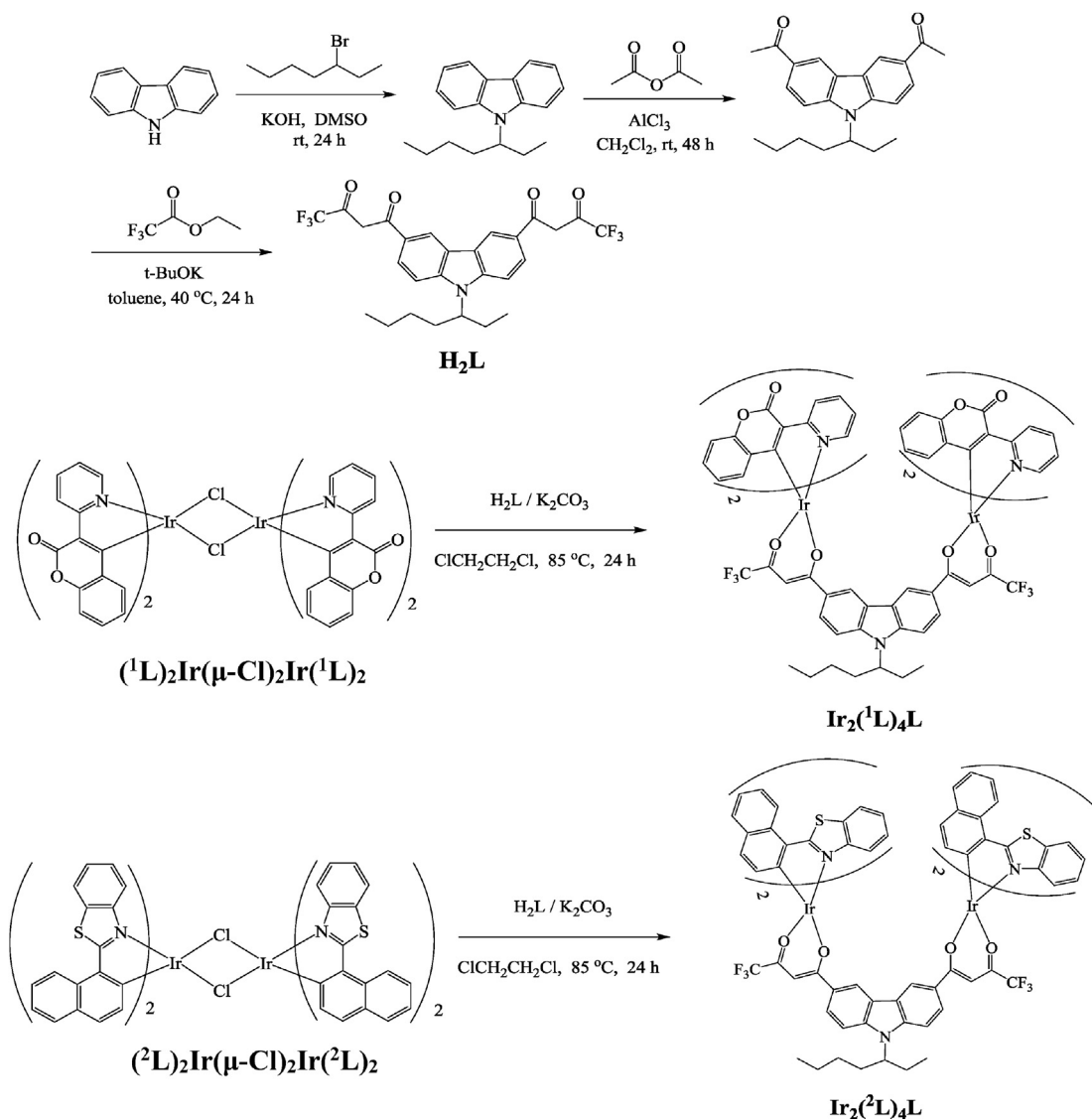
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efficiency (Φ_p) was strongly dependent upon changing the ancillary ligand structures. Recently, our group has also reported some luminescent heteroleptic Ir(III) complexes formed from different cyclometalating ligands and functionalized β -diketonate ancillary ligands for OLEDs [28–33]. As far as we know, the small molecule Ir(III) complexes for OLEDs are mainly mononuclear Ir(III) complexes, but the dinuclear Ir(III) complexes used in OLEDs are rarely reported [34–36]. In general, compared with mononuclear Ir(III) complexes, dinuclear Ir(III) complexes usually give low luminescence quantum efficiencies and are not suitable for highly efficient OLEDs. Hao et al. [34] reported two dinuclear Ir(III) complexes with carbazole-hole or oxadiazole-electron transporting bridging unit and their analogue mononuclear Ir(III) complexes, they found that the dinuclear Ir(III) complexes present lower Φ_p and relatively lower EQEs. However, Yang et al. [36] used 2-phenylpyrimidine-type ligands as the cyclometalating ligands and acetylacetonate (acac) as the ancillary ligand to synthesized two highly emissive 2-phenylpyrimidine-based mononuclear Ir(III) complexes and their corresponding dinuclear Ir(III) complexes, although the Φ_p value of the dinuclear Ir(III) complex containing F atomic substituent (0.68) were lower than that of the corresponding mononuclear Ir(III)

complex (0.99), the device performance of the solution-processed device based on the dinuclear Ir(III) complex exhibits better than that of the vacuum-deposited device on the corresponding mononuclear Ir(III) complex except for the brightness.

Bis- β -diketonate ligands have more negatively charged binding sites, which are often used to synthesize stable dinuclear metal complexes. Moreover, bis- β -diketonate ligands can effectively transfer the intramolecular energy to the central metal ion, contributing to bringing characteristic luminescence properties [37]. Bis- β -diketonate ligands have been used for sensitizing Eu^{3+} luminescence [38,39]. As part of our continuous research interests in extending the luminescence studies to new Ir(III) complexes based on β -diketonate ancillary ligands, in this paper, a carbazole-functionalized bis- β -diketonate containing two trifluorinated alkyl groups was prepared for the synthesis of two green and red emitting dinuclear Ir(III) complexes with the general formula $\text{Ir}_2(\text{C}^*\text{N})_4\text{L}$ [$\text{C}^*\text{N} = 3\text{-(pyridine-2-yl)coumarinato} (^1\text{L})$ and $2\text{-(1-naphthyl)benzothiazole} (^2\text{L})$]. The photophysical, electrochemical properties and thermal stabilities of these dinuclear Ir(III) complexes were reported, and solution processed light-emitting devices were fabricated to investigate their electroluminescence properties.



Scheme 1. Synthetic routes to the bis- β -diketonate ligand and its Ir(III) complexes.

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