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Synthesis, characterization and photophysical properties of new cyclometallated platinum(II) complexes with pyrazolonate ancillary ligand

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ABSTRACT

New cyclometalated platinum(II) complexes with pyrazolonate ancillary ligand (ppy)Pt(pmip) (**1**) and (dfppy)Pt(pmip) (**2**) (ppy = 2-phenylpyridine, dfppy = (4,6-difluorophenyl)pyridine, Hpmip = 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone) were synthesized and structurally characterized. Both compounds revealed square-planar geometry. The crystal cell of **1** was found to contain the monomer molecules of platinum compound whereas dimer molecules of **2** with short Pt···Pt contacts of 3.2217(3) Å were observed in the crystal cell of **2**. Photophysical properties of **1** and **2** were investigated in detail. The highly resolved photoluminesence spectra of the platinum complexes in solution contain emission bands in the region of 470–550 nm attributed to monomer compounds **1** and **2**. The triplet-state energies of **1** and **2** obtained from DFT calculations agree very well with the experimental data. In the crystalline state complex **2** revealed excimer emission as a structureless broad band at ca. 584 nm related to dimer molecules of platinum compound presented in the crystals.

1. Introduction

Cyclometalated platinum(II) complexes are widely used as efficient emitters in OLEDs [1,2]. The high efficiency of platinum based emitters is due to strong spin-orbit coupling of the heavy metal atom which allows for the facile intersystem crossing from the singlet to the triplet exited state. Thus both singlet and triplet excitons can be utilized in the platinum complexes and as a result their internal quantum efficiency can theoretically approach 100%. Square-planar platinum(II) luminescent complexes have a tendency to form aggregates in the solid state or in concentrated solution and can produce both high energy monomer emission and red-shifted broad-band excimer emission [1,3,4]. The relative intensity of monomer and aggregate emissions can be regulated by either dopant concentration of platinum complex in host matrix or by variation of the ligand environment around the platinum center [3–5]. Using these strategies the efficient single dopant white OLEDs (WOLEDs) have been successfully developed [2,6,7].

One of the most exploring type of platinum emitters comprises the complexes with cyclometalating arylpyridine ligands and ancillary β-diketonate ligands [1,2]. In a series of works a large number of platinum complexes with the same β-diketonate ligand (mostly acac ligand) and different substituted arylpyridine ligands were synthesized and the relations between their luminescent properties and the nature of arylpyridine ligands were explored [4,8–11]. The other representative works were devoted to synthesis and luminescent properties of platinum complexes with phenylpyridine or (4,6-difluorophenyl)pyridine ligands and different β-diketonate ancillary ligands [3,5,12–15]. The luminescent efficiency and ability to form aggregates and produce excimer emission were shown to depend both on the nature of cyclometalating arylpyridine ligands and ancillary β-diketonate ligands.

The preparation and efficient PL and EL properties of the platinum(II) complex with cyclometalating 1-phenylisoquinoline ligand and fluorine substituted pyrazolonate ancillary ligand have been recently described [16].

Herein we report the synthesis, characterization and photophysical properties of the new cyclometalated platinum(II) complexes **1** and **2** with arylpyridine and 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonate ligands.

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