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Construction and characterization on composite electrospinning fibers doped with iridium complex owing fluorine atoms in its auxiliary ligand

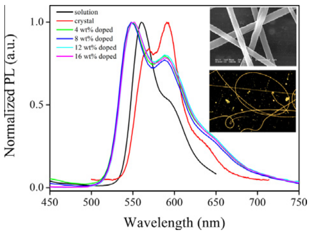
Gao Yu-qian [a,b], Zhang Shimin [a,b], Wang Pengju [a,b], Xu Shuxia [a,b], Wu Kun [a,b,*], Mou Wanzhi [c]

[a] College of Life Sciences, Henan Agricultural University, 95 Wenhua Road, Zhengzhou 450002, China
[b] Key Laboratory of Enzyme Engineering of Agricultural Microbiology, Ministry of Agriculture, Henan Agriculture University, Henan 450002, China
[c] College of Chemistry and Molecular Engineering, Tsinghua University, Beijing 100871, China

HIGHLIGHTS

- A fluorine-containing ligand and its Ir(III) complex were synthesized and studied.
- Electrospinning composite fibers with this complex as dopant were constructed.
- The photophysical features of bulk and composite samples were compared.
- Composite fibers had improved performance by repressing geometric relaxation.

GRAPHICAL ABSTRACT



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ABSTRACT

The authors synthesized a fluorine-containing Ir(III) complex Ir(PTZ)$_2$(HFD) and the corresponding composite electrospinning fibers PVP@Ir(PTZ)$_2$(HFD), where PTZ, HFD and PVP stood for 2-phenylbenzo[d]thiazole, 1,1,1,5,5,5-hexafluoropentane-2,4-dione and poly(vinylpyrrolidone), respectively. The molecular structure of the Ir(III) complex was confirmed by its single crystal analysis, which suggested that Ir(PTZ)$_2$(HFD) molecules crystallized as monoclinic system with two molecules in each unit cell. Density functional theory calculation on the crystal revealed that the onset electronic transitions possessed a mixed character of metal-to-ligand-charge-transfer (MLCT) and ligand-to-ligand-charge-transfer (LLCT). Ir(PTZ)$_2$(HFD) was then doped into electrospinning fibers so that the photophysical comparison between bulk Ir(PTZ)$_2$(HFD) and composite samples could be performed. It was found that both face-to-face π–π attraction in crystal and the immobilization in PVP host could improve photoluminescence performance by restraining the geometric relaxation of MLCT excited state, showing emission blue shift, longer excited state lifetime and improved photostability.

Introduction

Recently, research efforts have been devoted to the development of one-dimensional nanostructures, focusing on their possible applications in nanodevices of charming optoelectronic, electrochemical and mechanical features [1]. Electrospinning, owing to its virtues such as simple procedures and low cost, has been proved to be attractive [2–4]. By using electric force, fibers with diameters ranging from nanometer to micrometer can be constructed with controllable morphology, porous structure, high surface-to-volume ratio and applicable mechanical strength, serving as potential hosts in optoelectronic field [2,3,5,6].

Aiming at desired optical features for practical applications, emitting dopants, including organic compounds and transition

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* Corresponding author at: College of Life Sciences, Henan Agricultural University, 95 Wenhua Road, Zhengzhou 450002, China.
E-mail address: wukun218@163.com (K. Wu).

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metal complexes, are usually doped into those electrospinning fibers to yield composite ones [7,8]. Of all the proposed candidates, phosphorescent transition metal complexes, especially Ir(III)-based ones, have attracted much attention due to their high emission efficiency, thermal stability and good photophysical characters [9,11]. Then a series of phosphorescent Ir(III) complexes have been reported and investigated [6–11]. The correlation between their molecular structure and photophysical features, such as substituent effect, electronic effect and steric hindrance effect, has been analyzed. It has been suggested by theoretical calculations and then proved by experiment results that the occupied frontier molecular orbitals (MOs) are dominant by metal ion while the unoccupied ones are ligand π^* in nature [12]. The onset electronic transitions correspond to the transitions from HOMO to LUMO and thus are assigned as a character of metal-to-ligand-charge-transfer [d(Ir) → π^*(ligand)]. Such transitions usually play an important role in photoinduced optoelectronic procedures [13]. In addition, due to its slim participation, the photophysical features are largely immune to auxiliary ligand variations. In other words, the auxiliary ligand is free to be changed or modified to superimpose or improve desired functions.

Above hypothesis has been proved by the results reported by Petrov and Wang, which suggests that the emission features of phosphorescent Ir(III) complexes can be finely adjusted by changing the molecular structures and substituents. In addition, it is proved that the introduction of fluorine atoms into ligands is positive to improve emission performance, showing better emission yield and shorter excited state lifetime [14].

Guided by above considerations, we decide to incorporate fluorine substituents into the auxiliary ligand, hoping to construct an excellent phosphorescent emitter without compromising its emission features. By doping this fluorine-containing Ir(III) complex into the electrospinning fibers, the emission features are expected to be further improved since the host may provide a rigid matrix to depress the structural relaxation of excited state [15].

Experimental details

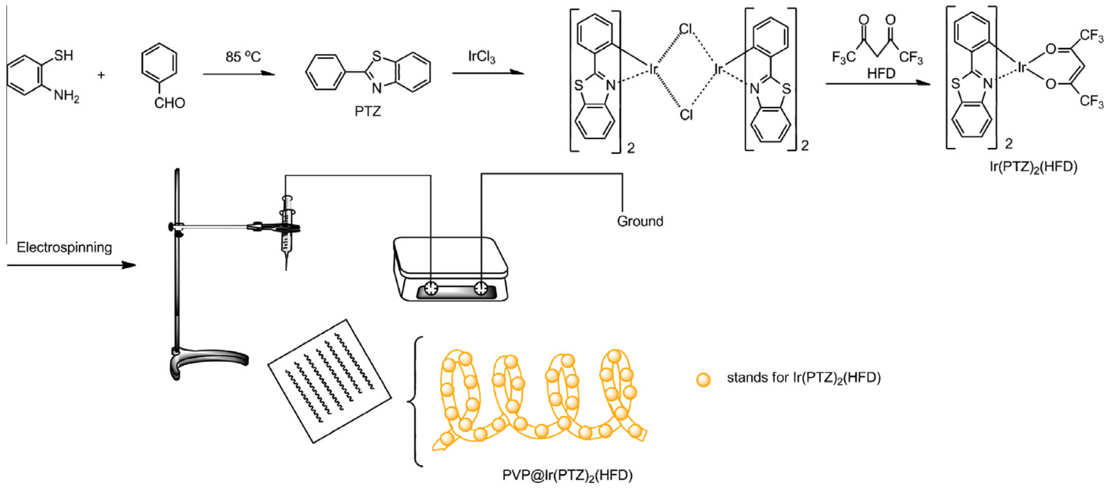
Scheme 1 depicts the construction route for the ligand 2-phenylbenzo[d]thiazole (referred to as PTZ), the fluorine-containing Ir(III) complex Ir(PTZ)$_2$(HFD) and the corresponding composite electrospinning fibers PVP@Ir(PTZ)$_2$(HFD), where HFD and PVP stand for 1,1,1,5,5,5-hexafluoropentane-2,4-dione and poly(vinylpyrrolidone), respectively. Some staring chemicals and materials, including benzaldehyde, 2-aminathiophenol, 1,1,1,5,5,5-hexafluoropentane-2,4-dione, *p*-toluenesulfonic acid monohydrate, $IrCl_3 \cdot 3H_2O$ and PVP (K30), were bought from Alfresa Pharma Corporation and used with no further purifications. The organic chemicals and solvents, including 1,2-dichloroethane, 2-ethoxyethanol, ethanol, CH_2Cl_2 and $CHCl_3$, were bought from Shanghai Chemical Company (Shanghai, China) and purified through standard operations before use. The solvent water in this work was deionzied.

Synthetic procedure for ligand PTZ

PTZ was synthesized according to a procedure described as follows. The solution of 10 mmol of benzaldehyde, 10 mmol of 2-aminathiophenol and 1 mmol of *p*-toluenesulfonic acid monohydrate in 30 mL of $CHCl_3$ was heated to reflux for a whole day under N_2 protection. After cooling, the solution was mixed with 300 mL of cold water. The mixture was extracted with 30 mL of CH_2Cl_2. After the evaporation of organic solvent, the resulting solid was further purified in ethanol/water (V:V = 1:2) to give the desired product as light yellow powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.32 (d, J = 7.5 Hz, 1 H), 7.38 (d, J = 7.0 Hz, 1 H), 7.54 (d, J = 8.5 Hz, 1 H), 7.61 (m, 1 H), 7.94 (d, J = 8.5 Hz, 1 H), 8.13 (m, 2 H), 8.24 (m, 2 H).

Synthetic procedure for Ir(III) complex Ir(PTZ)$_2$(HFD)

The detailed synthetic procedure for the fluorine-containing Ir(III) complex Ir(PTZ)$_2$(HFD) can be described as follows. The mixed solution of 1 mmol of $IrCl_3 \cdot 3H_2O$, 2 mmol of PTZ, 20 mL of 2-ethoxyethanol and 5 mL of water was heated to reflux for 40 h under N_2 atmosphere. Then the solution was cooled and mixed with 5 mL of water. The resulting solid product was filtered off and washed with ethanol. After drying in vacuum at 50 °C, the solid was dissolved in 30 mL of 2-ethoxyethanol. 5 mmol of anhydrous sodium carbonate and 1 mmol of HFD were also added into this solution which was heated to reflux under N_2 protection for 20 h. Then the solution was cooled and mixed with 5 mL of water. The resulting solid product was filtered off and further purified by a silica column to give the desired Ir(PTZ)$_2$(HFD) as orange yellow powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 5.47 (s, 1H), 6.18 (d, J = 7.5 Hz, 2 H), 6.61 (d, J = 10 Hz, 2H), 6.70 (d, J = 7.0 Hz, 2 H), 7.55 (m, 4 H), 7.89 (m, 4 H), 8.22 (m, 2 H). Anal. Calcd. for $C_{31}H_{17}F_6IrN_2O_2S_2$: C 45.42, H 2.09, N 3.42. Found: C 45.55, H 1.90, N 3.36. Its single crystal XRD will be later discussed.



Scheme 1. The construction route for PTZ, Ir(PTZ)$_2$(HFD) and the composite electrospinning fibers PVP@Ir(PTZ)$_2$(HFD).