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Electrospinning composite fibers doped with rhenium complex: Preparation, characterization and photophysical feature comparison

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ABSTRACT

In the present paper, a diamine ligand possessing an electron-pulling group 2-phenyl-5-(pyridin-2-yl)-1,3,4-oxadiazole (denoted as PPYO) and its corresponding Re(I) complex $Re(CO)_3(PPYO)Br$ were synthesized and carefully characterized. The geometric structure of $Re(CO)_3(PPYO)Br$ was analyzed by its single crystal XRD. Theoretical calculation on the crystal suggested that the first few electronic excitations owned a mixed character of metal-to-ligand-charge-transfer (MLCT) and ligand-to-ligand-charge-transfer (LLCT). By doping $Re(CO)_3(PPYO)Br$ into a polymer host of poly(vinylpyrrolidone) with electrospinning technique, composite fibers were yielded. The photophysical feature comparison between bulk samples and composite fibers was performed, which suggested that both face-to-face π–π attraction in crystal and the immobilization in PVP matrix could repress the MLCT excited state geometric relaxation, leading to improved emissive parameters including emission blue shift, longer excited state lifetime and better photostability.

1. Introduction

Aiming at structures and materials with fascinating optoelectronic and mechanical characters, researchers have devoted their efforts to the exploration of one-dimensional nanostructures [1]. Among the numerous proposed strategies for constructing such nanostructures, electrospinning has been considered as a promising one due to its advantage of simple, straightforward and economic preparation technique [2–4]. The resulting fibers can offer a porous structure with large surface-to-volume ratio, along with adjustable morphology and proper mechanical strength, making them a shining supporting host for optoelectronic dopants [2,3,5,6].

Photo-active dopants are usually doped into those fibers to generate desired photophysical features. These dopants include organic dyes and transition metal complexes [7,8]. Of all the proposed transition metal complexes, phosphorescent Re(I) complexes are considered as attractive ones owing to their high photoluminescence (PL) efficiency, adjustable emissive energy and good stability [9–11]. A class of representative phosphorescent Re(I) complexes $Re(CO)_3(N–N)X$, where N–N and X mean diamine ligand and halogen atom, respectively, has been studied in detail. It is found that the photoinduced excitations correspond to electronic transitions from occupied frontier molecular ortbitals (MOs) to unoccupied ones. The involved occupied frontier MOs consist of atomic contributions from metal ions and halogen atoms, while the unoccupied frontier MOs are essentially π^* of N–N ligands. The phosphorescence is generated by the radiative decay of the lowest triplet excited state, showing a character of metal-to-ligand-charge-transfer ^{3}MLCT [$d(Re)\rightarrow\pi^*(N–N)$].

Further analysis on such MLCT excited states suggests that they lose their energy mainly through geometric relaxation. The corresponding emissive energy and emission quantum yield depend on the effective restraint of the geometric relaxation and are thus vulnerable to surrounding variations [12–15]. It is then reasonable to expect that the PL performance of MLCT excited states can be improved if the molecules are immobilized in solid matrix, favoring various applications. In addition, it has been proved that electron-pulling groups in N–N ligand are positive to improve the PL performance of corresponding Re(I) complexes [12–15].

Enlightened by above considerations, we decide to synthesize a diamine ligand possessing an electron-pulling group and construct the composite electrospinning fibers using the corresponding phosphorescent Re(I) complex as the dopant. By doing this, the complex molecules are diluted and immobilized by the polymer matrix, so that the geometric relaxation of MLCT excited states can be repressed, showing improved PL performance.

2. Experimental details

The preparation strategy for the diamine ligand of 2-phenyl-5-(pyridin-2-yl)-1,3,4-oxadiazole (denoted as PPYO), its corresponding

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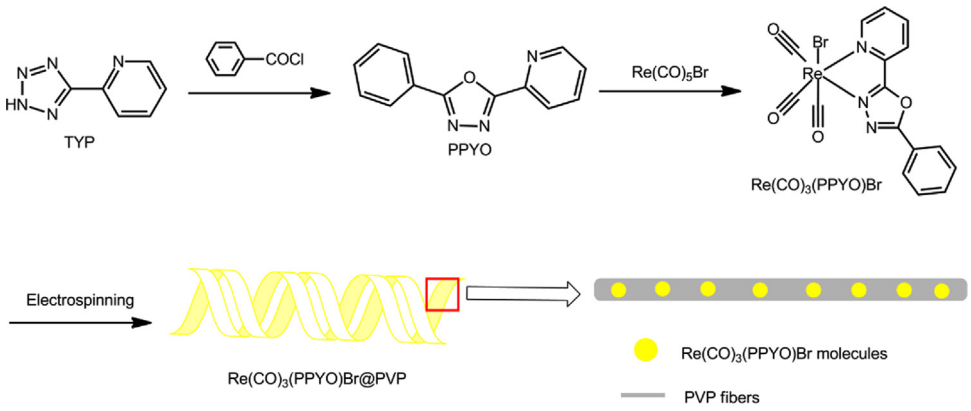

Scheme 1. The preparation strategy for PPYO, $Re(CO)_3(PPYO)Br$ and $Re(CO)_3(PPYO)Br@PVP$.

Re(I) complex of $Re(CO)_3(PPYO)Br$ and the final composite electropinning fibers of $Re(CO)_3(PPYO)Br@PVP$ is depicted in Scheme 1. The starting compound of 2-(2*H*-tetrazol-5-yl)pyridine (denoted as TYP) was synthesized according to a literature procedure [16]. The other chemicals and reagents such as benzoyl chloride, sodium azide, poly (vinylpyrrolidone) (PVP, K30), zinc bromide and $Re(CO)_5Br$ were bought from Alfresa Pharma Corporation and used with no further purifications. The organic solvents such as *N*,*N*′-dimethyl formamide (DMF), ethanol, CH_2Cl_2 and $CHCl_3$ were purified using standard procedures and redistilled before usage. The solvent water was deionized in this work.

2.1. Synthesis of PPYO diamine ligand

The diamine ligand of PPYO processing an electron-pulling group was synthesized according to a simple procedure described as follows. A 10 mmol of TYP and 11 mmol of benzoyl chloride were dissolved in 20 mL of anhydrous pyridine which was then heated to reflux under N_2 protection for 48 h. Then the solution was cooled and poured into 500 mL of cold water. The resulting solid product was collected and dried. The crude product was further purified on a silica column. Yield: 58%. ^{1}HNMR (300 MHz, $CDCl_3$): δ 7.46 (1*H*, m), 7.58 (3*H*, m), 7.87 (1*H*, m), 8.26 (1*H*, t), 8.32 (1*H*, t), 8.39 (1*H*, d, *J*=6.0), 8.79 (1*H*, d, *J*=3.5). Anal. Calcd. For $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.76; H, 4.13; N, 18.74.

2.2. Synthesis of $Re(CO)_3(PPYO)Br$

PPYO's corresponding Re(I) complex $Re(CO)_3(PPYO)Br$ was synthesized according to a simple procedure described as follows. A 0.21 mmol of PPYO and 0.2 mmol of $Re(CO)_5Br$ were dissolved in 20 mL of anhydrous toluene. The solution was heated to reflux under N_2 protection for 10 h and then cooled to room temperature. The solvent was removed under reduced pressure. The obtained crude product was purified first by recrystallization from mixed solvent of *n*-hexane:CH_3Cl=1:1 (*V*:*V*) and then on a silica column. Yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (1*H*, m), 7.65 (3*H*, m), 7.91 (1*H*, m), 8.32 (1*H*, t), 8.39 (1*H*, t), 8.48 (1*H*, d, *J*=6.0), 8.75 (1*H*, d, *J*=4.0). Anal. Calcd. for $C_{16}H_9BrN_3O_4Re$: C, 33.52, H, 1.58, N, 7.33. Found: C, 33.64, H, 1.72, N, 7.23. This molecular composition was further confirmed by single crystal XRD analysis.

2.3. Construction of $Re(CO)_3(PPYO)Br@PVP$ composite fibers

The $Re(CO)_3(PPYO)Br@PVP$ composite fibers were constructed by an electrospinning method described as follows. First, PVP was dissolved in DMF to get a 22 wt% homogeous solution. Then quantified $Re(CO)_3(PPYO)Br$ was added into the solution under stirring. The resulting solution was transferred into a 5 mL glass syringe, with a plastic needle (inner diameter=0.6 mm) connected to the opening end [17]. The anode terminal of a high-voltage generator was wired to the solution through a copper wire. An Al foil which was connected to the grounding electrode was placed under the plastic needle to be the collecting plate, with tip-to-plate distance of 25 cm and driving voltage as high as 18 kV.

2.4. Methods and measurements

The single crystal data of $Re(CO)_3(PPYO)Br$ was measured at 298 K through a Siemens P4 single-crystal X-ray diffractometer loaded with a Smart CCD-1000 detector, using graphite-monochromated Mo *K*α radiation. All hydrogen atoms were calculated. The composition of frontier MOs and the first 10 singlet excitations was analyzed by time dependent density functional theory (TD-DFT) at RB3PW91/SBKJC level in vacuum, using the single crystal structure as the initial structure. All DFT calculations were done by GAMESS. The graphical presentation for the frontier MOs was plotted by wxmacmolplt software package, with contour value of 0.025. ^{1}H NMR spectra were measured on a Varian INOVA 300 spectrometer. The elemental analysis data were collected on a Carlo Erba 1106 elemental analyzer. The PL and absorption spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer and a HP 8453 UV–vis–NIR diode array spectrophotometer, respectively. Luminescence intensity decay dynamics were measured with a 355 nm light generated from the third-harmonic-generator pump, using pulsed Nd:yttrium aluminium garnet (YAG) laser as the excitation source. A two-channel TEKTRONIX TDS-3052 oscilloscope was used to store the emission decay data. Scanning electron microscopy (SEM) and fluorescence microscopy images were taken by a Hitachi S-4800 microscope and a Nikon TE2000-U fluorescence microscopy using a mercury lamp as the power supply, respectively. All measurements were carried out in the air at room temperature without specific notes.

3. Results and discussion

3.1. Single crystal structure of $Re(CO)_3(PPYO)Br$

The single crystal structure shown in Fig. 1a confirms that the Re(I) complex $Re(CO)_3(PPYO)Br$ has been successfully synthesized. The selective geometric parameters are also summarized in Table 1. It can be observed that the central Re(I) ion is surrounded by three CO groups, two N atoms from one PPYO ligand and a Br atom, showing a distorted octahedral coordination sphere. Although these values are comparable with literature values of similar complexes [18], the three Re–C bond length values are slightly different with each other. Re–C (1) bond is shorter than the other two Re–C bonds, suggesting that the