

Synthesis and Optoelectronic Properties of An Electrically Stimulated Phosphorescent Iridium Complex

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In order to better describe and verify the mechanism of electrophosphor discoloration, an ionic iridium complex with different counterions is designed and synthesized. It is found that the luminescent properties of the phosphor not only show the concentration and acid / base induced phosphorescence, but also show the phosphorescence change induced by electrical stimulation. The hydrogen bond acceptor (-NH) is introduced into the ionic iridium complex to modulate the emission wavelength of the complex by different counterions. In order to further control the emission wavelength of the complexes, a series of ionic iridium complexes with different counterions are designed and synthesized by selecting the auxiliary ligands containing two hydrogen bond acceptors (-NH). It is proved that there is not only electrostatic interaction between the cations and counterions, but also interesting hydrogen bonds. In addition, because the hydrogen bond strength formed by complex anions and different counter anions is different, it can effectively control the photophysical properties of complexes and adjust the emission wavelength from 493 nm to 591 nm. In conclusion, the phosphorescence change induced by electric field can be realized by applying the electric field to change the hydrogen bonding intensity. At the same time, the construction of quasi solid-state information storage devices is beneficial to the development of phosphorescent materials in information optoelectronic devices.

1. Introduction

In recent years, phosphorescent transition metal complexes have attracted much interest due to their excellent photoelectric properties and wide application prospects (Shi et al., 2015). Compared with the traditional fluorescent dyes (singlet emission), phosphorescent transition metal complexes (triplet emission) can increase the yield of phosphorescence by simultaneously using singlet and triplet excitons via heavy metal induced spin orbit coupling (Moon, et al., 2015). Theoretically, the internal quantum efficiency is up to 100%, so it is widely used in organic light emitting diodes (Shiu et al., 2017). In addition to the high quantum efficiency at room temperature, phosphorescent transition metal complexes also have excellent photophysical properties such as easily modulated emission wavelength, long emission lifetime, large Stoke shift, and good optical stability (Cho and Ha, 2017). Therefore, the application of phosphorescent materials in the fields of biosensing and imaging has attracted extensive attention of researchers (Zhang et al., 2016). Since used as light-emitting materials in organic light-emitting diodes, a lot of researches about phosphorescent transition metal complexes have been reported. The application is from the organic light emitting diode field of traditional extended to other areas, such as chemical sensing, biological imaging, photoelectron-chemical cell, organic solar cells and organic storage fields. Because phosphorescent iridium complexes have complex excited state properties, the results of these regulatory methods are often difficult to predict. Therefore, it limits the further development of phosphorescent iridium complexes and even the whole phosphorescent transition metal complexes. Therefore, it is very important to develop a new, easy- to- implement and universal regulation strategy photophysical properties.

In order to further control the emission wavelength of complexes, a series of ionic iridium complexes with different counterions are designed and synthesized by selecting the auxiliary ligands containing two hydrogen bond acceptors (-NH) (Park et al., 2016). In addition, the photophysical properties of phosphorescent iridium complexes and their applications under the electric field are studied due to the sensitivity of the hydrogen bonding acceptor to the electric field (Liu et al., 2016).

2. Method

2.1 Experimental drugs and reagents

Carbazole, CP, China Pharmaceutical Group (Shanghai) Chemical Reagent Company; 1-bromoethane, 98%, China Pharmaceutical Group (Shanghai) Chemical Reagent Company; N-bromobutanamide, AR, Aldrich; potassium hexafluorophosphate, 99%, Aldrich; Bis(pinacolato)diboron, 98%, Perimed; Tetrakis (triphenylphosphine) palladium, 99%, Perimed; Potassium acetate, 99 %, Perimed; 2- bromopyridine, 99%, Perimed; polyphosphoric acid, 84%, Perimed; iridous chloride ($\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$), 95%, Shanghai Jiushan Chemical Co., Ltd.; 95% sodium chloride, NanJing WanQing Chemical Glassware Instrument Co., Ltd; Sodium bromide, 95%, NanJing WanQing Chemical Glassware Instrument Co., Ltd; tetrabutylammonium bromide (TBAB), 99%, Aladdin reagent; potassium iodide, 95%, Aladdin reagent.

2.2 Experimental instrument

The nuclear magnetic resonance (NMR) spectra of the complexes are determined by Bruker Ultra Shield Plus 400 MHz NMR spectrometer. The luminescence spectra of the complexes are measured by Edinburgh LFS920 luminoscope. Taking diode laser (379 nm excitation wavelength) as excitation light source, the phosphorescence lifetime is measured on Edinburgh LFS920 luminoscope, and the phosphorescence lifetime data are fitted by Edinburgh software package. Mass spectrometry is determined by matrix assisted laser desorption ionization time-flight mass spectrometer Bruker autoflex MALDI-TOF/TOF. Fluorescence microscopy imaging is determined by inverted fluorescence microscopy Olympus IX81. Fluorescence lifetime imaging is determined by Olympus IX81 confocal microscopy. Time-resolved signals are measured by time-dependent single photon counting techniques. Time gated imaging is obtained by the software package of the fluorescence lifetime microscope imaging provided by PicoQuant Company.

2.3 Synthesis and characterization of ligands

Without special instructions, all drugs and reagents are no longer purified before use. For sensitive reactions in air, reagents are usually carried out in a nitrogen atmosphere.

Synthesis of 3- boric acid ester carbazole: 5g (29.9 mmol) carbazole is added to the 2-neck reaction bottle, and 60 mL DMF is injected into the reaction bottle with syringe. 5.32g (29.9 mmol) N- bromobutanamide (NBS) the is dissolved in 20 mL DMF, and the reaction bottle is cooled to -5°C in the ice bath. The DMF used to dissolve NBS is installed into a constant pressure drop funnel, and then slowly dripped into the reaction bottle. The whole reaction system is protected from light. After stirring for 12 hours at room temperature, the reaction liquid is poured into 300 mL deionized water, and white precipitate is generated. The crude product is obtained by the filter funnel, and the product is recrystallized with ethanol to obtain pure 3- carbazole bromide. The product is purified by column chromatography and the yield is 82%.

Synthesis of 3- pyridyl carbazole: 117 mg (0.38 mmol) 3- boric acid ester-carbazole, 45 mg (0.38 mmol) NBS and 10 mg (0.38 mmol) 4-triphenylphosphine-palladium are added to the 2-neck reaction bottle. After sealing the condenser tube, evacuation and nitrogen aeration are carried out in three times. 60 mg (0.38 mmol) 2-bromopyridine, 1 mL saturated sodium carbonate solution and 3 mL toluene are injected into the reaction bottle with a syringe. After the reaction was heated to 80°C for 24 hours, the reaction was stopped and cooled to room temperature. The solvent was removed by steaming. The product is purified by column chromatography and the yield is 85%.

Synthesis of 3-pyridyl-9-hexylcarbazole: 276mg (1.2 mmol) 3-pyridyl-9-hexylcarbazole and 150 mg (0.8 mmol) tetrabutylammonium bromide (TBAB) are added to the 2-neck reaction bottle. 20 mL dimethyl sulfoxide (DMSO) is injected into the reaction bottle with a syringe, and the reactants are dissolved by stirring. Then, 100 mg (5 mmol) sodium hydride is dissolved in 5 mL deionized water and added to the reaction bottle. After stirring for 2 hours at room temperature, 360 mg (2.2 mmol) bromide is added to react for 10 hours and then stopped. The reaction liquid is extracted with dichloromethane and water. The organic phase is collected and concentrated to obtain the crude liquid product. The product is purified by column chromatography and the yield is 90%.

3. Results and discussion

3.1 Luminescent properties of complexes

The photoluminescence properties of complex 1-4 in acetonitrile are studied in detail. The specific data are shown in Table 1. The luminescence spectra of complex 1-4 are shown in Figure 1. As shown in the figure, the maximum emission wavelength of the complex exhibits an obvious blue shift with the change of the counterion from hexafluorophosphate ion to chloride ion. The phosphorescence lifetime has also undergone

some changes. In addition, the broad emission peaks of complexes 1 and 2 exhibit obvious MLCT transition properties, while the fine structure emission of complexes 3 and 4 has mixed LLCT and MLCT transition properties. It is concluded that this emission wavelength has a certain regularity with the change of counter anion, that is, it shifts blue with the decrease of the counterion radius. The four counterions we selected are negative valence and are spherical ions (Li et al., 2016). Therefore, the decrease of the counterion radius will increase the surface charge density of the ion (Giridhar et al., 2015). The change of the surface charge density of the anion will affect the luminescent properties of the complexes by hydrogen bonds formed with the iridium cation centers (Jang et al, 2016).

Table 1: Photophysical properties of complex 1-4

Complex	λ_{em}/nm	ζ/ns
1	591	45.5
2	551	47.6
3	493,522	64.0
4	493,522	38.3

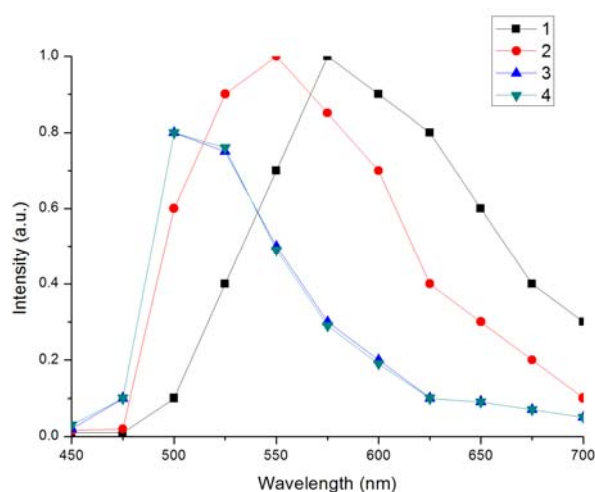


Figure 1: Photoluminescence spectra of complex 1-4 ($\lambda_{ex}=365\text{ nm}$, $C=0.1\text{ mM}$)

3.2 Acid / base titration of complexes

As shown in Figure 3, when the trifluoroacetic acid is added into the solution of the complex 4, the maximum emission wavelength obviously has a red shift. When adding trifluoroacetic acid (strong hydrogen bond acceptor), counterions (chlorine ions) of complex 4 can form strong hydrogen bonds with trifluoroacetic acid, which weaken the hydrogen bond effect of chlorine ion and cationic center and change the emission wavelength. At the same time, the emission spectrum of the acid titration endpoint of the complexes is similar to the emission spectrum of the complex 1. After adding trifluoroacetic acid (strong hydrogen bond acceptor), the counterion (chlorine ions) of the complex 4 mainly forms strong hydrogen bonds with trifluoroacetic acid, and weakens the hydrogen bond interaction between the cation center and the chloride ion. Therefore, at the end of acid titration, the complex 4 exhibits emission spectra similar to that of complex 1. When trifluoroacetic acid is added to the solution of complex 4, the emission spectrum remains unchanged. The strong hydrogen bonds are formed between the cations of the complexes and the counterions (chlorine ions), and the hydrogen bond donor (triethylamine) has little effect on the hydrogen bonds. Therefore, the emission spectra of the complexes do not change with the addition of triethylamine.

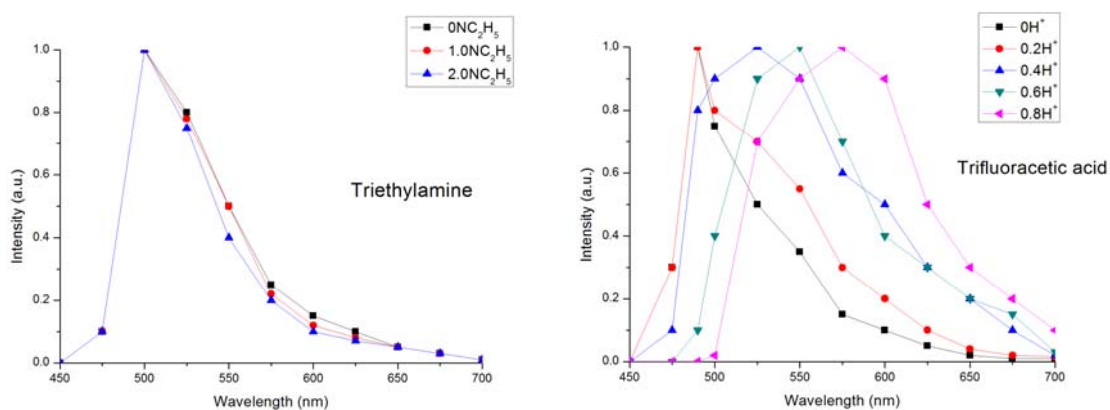


Figure 2: Spectra of complex 1 (0.1 mM) titrated with triethylamine and trifluoroacetic acid

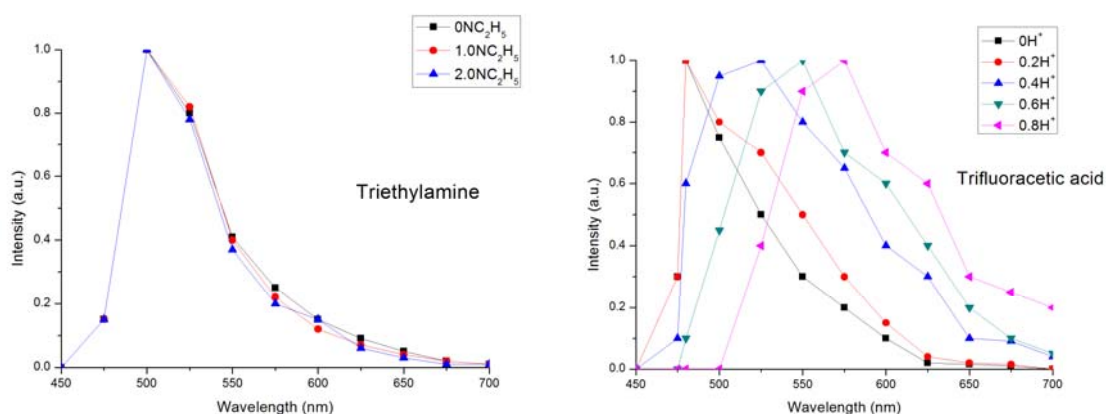


Figure 3: Spectra of complex 4 (0.1 mM) titrated with triethylamine and trifluoroacetic acid

3.3 Phosphorescent discoloration of complexes

Because hydrogen bond is a weak force between atoms, hydrogen bonding strength is easily affected by external stimuli. Thus, we further studied the luminescence properties of the complexes under the electric field (Adeloye, et al., 2017). Specific experiments are as follows: The two pieces of tinfoil are taken as the acetonitrile solution immersed into the complex 1 through the electrode, and the distance between the two electrodes is about 20 mm. In the absence of applied electric field, the complex solution shows orange light emission under ultraviolet light. When the 10V voltage is applied at both ends of the electrode, the luminous color of solution near the anode remains unchanged.

However, the solution near the cathode shows green emission. Subsequently, the green luminescent solution gradually expands to the middle of the solution and reaches equilibrium. Then, when the reverse voltage is applied to the electrode, the green light emitting solution gradually restores to orange light emission, while the orange light emitting solution gradually changes to green emission (Liang, et al., 2016). Furthermore, when the positive voltage is applied to both ends of the electrode, the state of the luminous color of the solution is restored to the original applied voltage. In addition, as shown in figure 4, the emission spectra of the solution near the anode and cathode are measured. The maximum emission wavelength of the complex near the anode remains almost unchanged, while the maximum emission wavelength of the complex near the cathode exhibits an obvious blue shift (from 611 to 508nm).

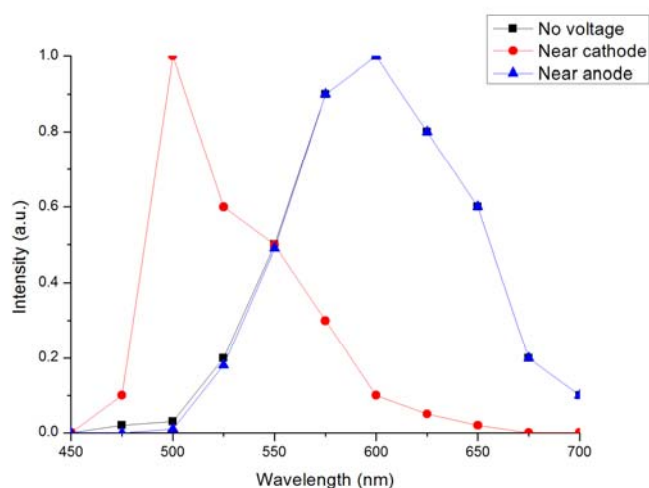


Figure 4: Luminescence spectra of complex 1 before and after power up

4. Conclusions

In this paper, a series of ionic iridium complexes with different counterions are designed and synthesized by introducing ligands containing hydrogen bond receptors into the complexes. It is found that there is not only electrostatic interaction but also interesting hydrogen bonding between cations and counterions in the complexes. The photophysical properties of the complexes are effectively controlled by the hydrogen bond strength of the cations and the different counterions, and the emission wavelength is adjusted from 493 nm to 591 nm (-100 nm). Because the added acid or base will affect the hydrogen bonding interaction between the complex ions, the emission wavelength of the complexes shows acid / alkali dependence. Theoretical calculations show that the change of the emission wavelength is due to the electron transfer effect induced by hydrogen bonding, leading to the change of the frontier orbital energy level of the complex, thus changing with the change of hydrogen bond strength. In addition, due to the hydrogen bond sensitivity to the electric field, the complex exhibits phosphorescence discoloration under the electric field and is used for information recording and storage.

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