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Influence of alkyl chain lengths on the properties of iridium(III)-based piezochromic luminescent dyes with triazole-pyridine type ancillary ligands

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ABSTRACT

To investigate the relationship between structures and piezochromic luminescence behavior and to develop excellent materials for efficient light-emitting electrochemical cells, a series of iridium(III) complexes with different length of alkyl chains have been designed and synthesized. The results show that all complexes exhibit not only naked-eye visible and reversible piezochromic behavior, but chain length-dependent emission properties: the shorter the alkyl chain is, the more remarkable mechanochromic behavior and higher recrystallization temperature will be. In light of powder X-ray diffractometry and differential scanning calorimetric data, the interconversion between crystalline and amorphous states upon external stimuli is response for the present piezochromism. Additionally, these complexes show high quantum yields of 55–65% in neat films as well as excellent redox reversibility. Despite changed alkyl chains are introduced into these complexes, the negligible effect on emitting colors and excited-state characters of them in both solutions and neat films have been observed. Such photophysical properties are also interpreted with the help of theoretical calculations. Moreover, the theoretical results suggest that the intrinsic intramolecular π–π stacking confirmed by the crystal structures can effectively restrict the opening of the structures in metal-centered excited-state, demonstrating their stability. The structure–property relationships and the results demonstrated here will help researchers develop and design more promising iridium(III)-based piezochromic materials and attractive phosphors for optical devices.

1. Introduction

Organic luminophores that exhibit clear and vivid luminescence in the solid states have attracted tremendous attention due to their great potential in various photofunctional applications [1,2]. The photophysical properties of these solid-state organic luminophores, for example emission color, strongly depend on the mode of molecular stacking and the intermolecular interactions [3,4]. Accordingly, dynamic tuning and switching of solid-state luminescence can be achieved by means of the external stimulus that triggers the alteration of molecular arrangement motif [5–7]. Recently, the organic luminophores undergo a significant pressure-induced change in the emission color, termed piezochromic luminescent (PCL) materials, are growing rapidly [8–18]. Such materials exhibit reversible and obvious color change upon external mechanical forces but without chemical reactions, making them highly attractive alternative for both fundamental research and practical application. To this date, PCL behaviors for a few materials have been observed, including organic and inorganic complexes, liquid crystal materials, and polymer-based assemblies [19–27]. However, the number of such materials is still rare, especially for metal-contained complexes. To develop excellent PCL materials and establish clear structure–property relationship, the in-depth understanding of PCL phenomena at molecular level are essential. Thereby, it remains a great challenge to design new PCL materials and investigate the relationship between molecular packing and piezochromic behavior.

Organometallic iridium(III) complexes exhibiting high phosphorescence efficiency and rich photophysical properties as well as superior optical stability, have emerged as promising candidates for high-tech applications such as organic light-emitting diodes (OLED), light-emitting electrochemical cells (LECs), chemical sensor, and biological probes, etc [28–32]. Recently, our group and others have developed a series of cationic iridium(III) complexes

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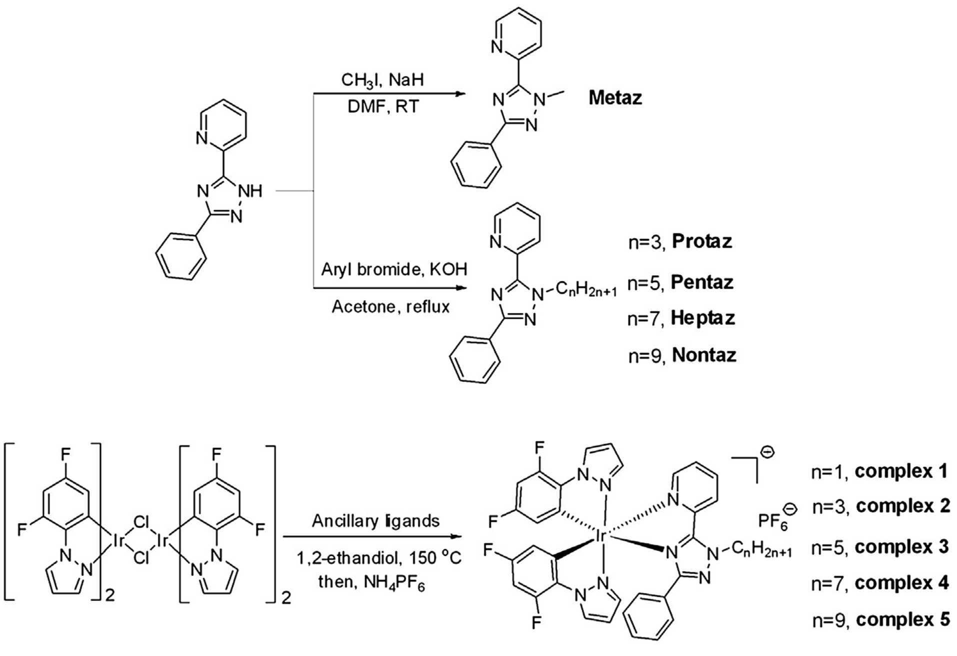
showing an interesting piezochromic behavior, and found that their emission color switch is generally attributed to a crystalline–amorphous phase transformation [33–36]. Based on this mechanistic proposal, the PCL behavior can be ingeniously switched by simply adjusting the substitution on ancillary ligands of the iridium(III) complexes [37]. In addition, iridium(III) complexes can provide a better structural control on excited-state properties and the optical output in different medias. Very recently, the multifunctional iridium(III) complexes simultaneously exhibiting aggregation-induced emission (AIE) and PCL properties have been realized by attaching the dendritic group into complexes or modifying ancillary ligand with carbazole unit [37,38]. Despite these advances in iridium(III)-based PCL material, such materials are still in their infancy and more clear structure–property relationship has not been well addressed. Recent works on organic fluorescent PCL materials demonstrates that different long alkyl chains grafted on the materials not only can construct a series of new PCL materials with comparable molecular structure, but also provide an efficient way to study the relationship between the structure and PCL behavior [39–41]. Whereas, such great successes obtained through the flexible strategy in organic fluorescent PCL materials are still limited for metal complexes.

On the other hand, to realize efficient and long-lifetime light-emitting electrochemical cells (LECs), cationic iridium(III) complexes with fascinating characteristics, such as high quantum efficiency especially in the neat film, excellent stability and redox reversibility, are highly desired [42–45]. And the exploitation of novel cationic iridium(III) complexes for the efficient and stable LECs is also rising significant interest in recent years [46–50]. If the different length of alkyl chains are attached to the ligands to construct a series of comparable molecular PCL cationic iridium(III) complexes that can meet the above-mentioned requirement for efficient LECs, which may be a "one stone two bird" design strategy. Keeping this in mind, we herein designed and prepared a new cationic iridium(III) complex $[(dfppz)_2(L1)]PF_6$ (complex **1**) as shown in Scheme 1 and its analogues **2**, **3**, **4**, and **5** with different length of alkyls. Their photophysical properties in the solid-states as well as solution have been investigated systematically. The results indicate that all complexes exhibit naked-eye visible PCL behavior with a color change from sky-blue to blue-green emitting and alkyl chain length dependent PCL properties. The emission color can be easily switched by grinding and heating. Comprehensive density functional theory (DFT) approach has been performed to gain insights into their photophysical properties in solutions as well as to evaluate the stability accommodated by intramolecular π–π stacking. The theoretical results suggest that the intrinsic intramolecular π-stacking in the complexes can effectively restrict opening of the structure in the ^{3}MC state, indicative of their good stability. Combining with the high quantum efficiency in neat film and excellent redox reversibility, it is anticipated that these complexes are also attractive candidates for LECs.

2. Experimental section

2.1. Materials and measurements

All reagents and solvents employed were commercially available and used as received without further purification. The solvents for syntheses were freshly distilled over appropriate drying reagents. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. ^{1}H NMR spectra were measured on Bruker Avance 500 MHz with tetramethylsilane as the internal standard. The molecular weights of ligands and complexes were tested by using electrospray-ionization mass spectroscopy and matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry, respectively. UV–vis absorption spectra were recorded on Hitachi U3030 spectrometer. The emission spectra were recorded using the F-4600 FL spectrophotometer. The excited-state lifetime were measured on a transient spectrofluorimeter (Edinburgh FLS920) with time-correlated single-photon counting technique. The photoluminescence quantum yields (PLQYs) of the neat film were measured in an integrating sphere. Cyclic voltammetry was performed on a BAS 100 W instrument with a scan rate of 100 mV s^{-1} in CH_3CN solutions with the three-electrode configuration: a glassy-carbon electrode as the working electrode, an aqueous saturated calomel electrode as the



Scheme 1. Synthetic procedure and the chemical structures of complexes **1**–**5**.