DOCTORAL THESIS

Photofunctional molecular materials for chemical sensing, bioimaging and electrochromic applications

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Date of Award:
2015

ABSTRACT

This thesis is dedicated to developing novel photofunctional molecular materials for the applications in chemical sensing, bioimaging and electrochromic.

To begin with, a brief introduction of photofunctional molecular materials and an overview of their applications in chemical sensing, bioimaging and electrochromic were presented in Chapter 1.

In chapter 2, we have synthesized a series of water-soluble phosphorescent cationic iridium(III) solvato complexes (**1**-**7**) as multicolor cellular probes for imaging in living cells. All of these complexes can be dissolved in PBS. The emission of complexes can be tuned from green to red by changing the chemical structure of cyclomedtalating ligands. All complexes exhibit low cytotoxicity to living cells and exhibit cell membrane permeability and specific staining of cytoplasm. They enter the cells by the mechanism of energy-independent passive diffusion mechanisms. More importantly, complex **7** can act as a two-photon phosphorescent cellular probe, and fluorescence lifetime imaging microscopy is successfully applied for bioimaging in the presence of short-lived background fluorescence.

We developed two excellent optical probes for CO_2 detection in Chapter 3. The first one for the CO_2 detection is a phosphorescent probe based on an iridium(III) complex with 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline. After bubbling CO_2 into the detection solution, the quenched phosphorescence by the addition of CH_3COO^- can

be recovered. Photobleaching experiment demonstrates that this phosphorescent CO_2 probe shows higher photostability than some of the reported organic probes. More importantly, the time-resolved PL experiment demonstrates that this probe can be used to detect CO_2 in the presence of strong background fluorescence, which improves the sensitivity and signal-to-noise ratio of the sensor in complicated media. The second one is a water-soluble fluorescent probe based on tetraphenylethene derivative. After bubbling CO_2 into the detection solution, remarkable color change and fluorescence enhancement could be observed. The response of this probe to CO_2 in aqueous solution is fast and the detection limit is about 2.4×10^{-6} M. To emphasize the practical application of this probe, a porous film was successfully fabricated by mixing the dye with sodium carboxymethyl cellulose in water, which can serve as an efficient CO_2 gas sensor. More importantly, this probe exhibits low cytotoxicity towards live cells and has the ability to monitor the external CO_2 concentration changes of living cells.

Chapter 4 focused on the development of novel soft salt based phosphorescent probe. This type of probe consists of two oppositely charged ionic complexes with two distinguishable emission colors, which makes it a perfect candidate as a ratiometric probe. The emission color of **10** changes from blue to red with increasing pH value. **10** is cell-permeable and exhibits low cytotoxicity, and it has been successfully applied for ratiometric pH imaging with the use of confocal microscopy, demonstrating its great potential for intracellular environment monitoring. Furthermore, phosphorescence lifetime imaging experiments can detect intracellular

pH variations by photoluminescence lifetime measurements, which allowed for eliminating background fluorescence and selecting long-lived phosphorescence images. Quantitative measurement of intracellular pH fluctuations caused by oxidative stress has been successfully carried out for **10** based on the pH-dependent calibration curve.

A series of cationic Zn(II) complexes has been designed and synthesized in chapter 5. The photophysical properties of these Zn(II) complexes are affected by the counterions. By altering the counterions, the emission peak can be changed from 549 nm to 622 nm. Interestingly, the CIE coordinate and the emission colors can be simply tuned by adjusting the concentration of **11d** in the polyether. Under an electric field of about 15 V applied onto the electrodes, the emission color of the solution of **11b-11d** near the cathode changed its original emission color to sky blue. Based on this interesting electrochromic fluorescence of **11d**, a quasi-solid information recording device has been successfully designed. Furthermore, data encryption has been realized by combining **1d** with BODIPY, and information decoding processed has been accomplished, for the first time, by employing TPA excitation techniques, in which the large TPA cross section of **11d** is differentiated from small TPA cross section of common organic dyes.

Finally, Chapters 6 and 7 present the concluding remarksand the experimental details of the work described in Chapters 2–5.

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