Abstract

The structural design, synthesis and characterization of luminogens with aggregation-induced emission (AIE) properties are studied in this thesis. The remarkable emission properties, thermal stability and biocompatibility of the AIE-active materials demonstrate the promising applications in bioimaging and organic light-emitting diodes (OLEDs).

Chapter 1 introduces the existence of aggregation-caused quenching (ACQ) effect in most conventional organic dyes as well as phosphorescent transitional metal complexes. Discovery of AIE and its mechanical study allow further exploration of usage in organic luminescent materials. This chapter also gives some examples and the applications these AIE-active compounds.

In Chapter 2, a series of cyanostilbenes with simple electron donor (D)-π-electron acceptor (A) structure are presented and synthesized. They exhibit remarkable AIE effect as well as deep red emission peak in 95 % water fraction in THF. These results indicate that attachment of these electron acceptors provides alternative strategy for designing highly emissive AIE-active materials.

In Chapter 3, strongly emissive cyanostilbenes with phenothiazine unit are designed and synthesized. This chapter also investigates the effect of substituents in phenothiazine and terminal cyanostilbene on the photophysical properties and
AIE effect. The results suggest that they are AIE-active with different sizes in nano-aggregates. Furthermore, these dyes exhibit clear and strong fluorescence in live cell imaging with excellent biocompatibility.

In Chapter 4, a series of AIE-active phosphorescent Pt(II) complexes made up of C^N^C tridentate ligands are designed and synthesized. They exhibit different morphologies and emission properties upon aggregation in 90 % water in acetonitrile although similar tridentate ligands are applied. One of the complexes in this chapter show nano-rod formation with the highest quantum efficiency in aggregated state, suggesting that rapid self-assembly process occurs to prevent non-radiative decay and oxygen quenching.

In Chapter 5, a series of bis-cyanostyryl fluorophores are designed and synthesized. They are emissive in solid state with colour range from orange to NIR region. Furthermore, they are AIE-active and some of them may contain hybridized local and charge transfer (HLCT) excited state to achieve highly efficient emission upon solvatochromic investigation. Some bis-cyanostyryl thiophenes are fabricated in OLED devices show deep-red to NIR emission, indicative of a promising way to design solid-state NIR-emissive compounds using bis-cyanostyryl derivatives.

Finally, Chapter 6 and 7 present the concluding remarks and the experimental details of the work in Chapters 2 to 5, respectively.
Table of Contents

DECLARATION i
Abstract ii
Acknowledgements iv
Table of Contents vi
List of Tables ix
List of Figures xi
List of Schemes xx
List of Abbreviations and Symbols xxi
Formula Index xxv

Chapter 1 Introduction 1
1.1 Introduction 1
1.2 Aggregation-Caused Quenching 2
1.3 Aggregation Induced Emission 5
1.3.1 Phenomena 5
1.3.2 Mechanism of AIE 7
1.4 Types of AIE-active Compounds 9
1.4.1 Hydrocarbons 10
1.4.2 Heteroatoms 14
1.4.3 Polymer 23
1.4.4 Metal Complexes 24
1.5 Applications 30
1.5.1 Optoelectronics 31
1.5.2 Sensors 34
1.5.3 Biological Applications 38
1.5.4 Mechanochromic Materials 43
1.6 Scope of Thesis 44
References 48

Chapter 2 Synthesis and Characterization of D-π-A Based Cyanostilbenes with Aggregation-Induced Emission Properties 57
Chapter 3 The Effect of $N$-substituents and Terminal Functional Groups in Phenothiazine-Based Cyanostilbenes in Photophysical and Aggregation-Induced Emission Properties

3.1 Introduction 91
3.2 Synthesis of Phenothiazine-Based Cyanostilbenes 95
3.3 Spectroscopic and Structural Characterization of Phenothiazine-Based Cyanostilbenes 98
3.4 Photophysical Properties of Phenothiazine-Based Cyanostilbenes 111
3.4.1 Absorption and emission properties 111
3.4.2 Solvent effect 113
3.4.3 AIE effect 117
3.4.4 pH effect 125
3.5 Electrochemical Properties of Phenothiazine-Based Cyanostilbenes 127
3.6 Biological Imaging using Phenothiazine-Based Cyanostilbenes 131
3.7 Concluding Remarks 137
References 138

Chapter 4 Synthesis and Characterization of Neutral Cyclometalated Platinum(II) Complexes with Aggregation-Induced Emission and Self-Assembly Properties 141
4.1 Introduction 141
4.2 Synthesis of Platinum(II) Complexes 146
4.3 Spectroscopic and Structural Characterization of Platinum(II) Complexes 151
4.4 Photophysical Properties of Platinum(II) Complexes 163
4.4.1 Absorption and Emission Properties 163