

## DOCTORAL THESIS

# Synthesis, characterization and application studies of cyanostilbene-based molecular materials with aggregation-induced emission (AIE) characteristics

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*Date of Award:*  
2014

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## Abstract

The molecular design, synthesis, spectroscopic and photophysical characterization of a series of cyanostilbene-based compounds are studied in this thesis. The thermal, electrochemical and aggregation induced emission (AIE) properties of these cyanostilbene-based compounds, as well as their application in organic lighting-emitting diodes, live cell imaging, chemical vapor sensor were investigated.

Chapter 1 gives a brief introduction on the aggregation-caused quenching (ACQ) behavior of the conventional organic luminogens and the discovery and proposed mechanism of AIE phenomenon. Furthermore, some examples and the applications of these AIE compounds will be discussed.

In Chapter 2, triphenylamine- and carbazole-containing cyanostilbene-based derivatives are presented. From the examination of the emission profile, they are all AIE-active through comparison of the photoluminescence intensity in dissolved and in aggregated states. Additionally, the calculation of the enhancement ratio ( $I/I_0 - 1$ ) of each fluorophore was performed in order to quantify its AIE effect. One of our cyanostilbene-based luminogens has achieved an enhancement ratio with a value of 1128. This cyanostilbene-based luminogens has also shown good performance in OLED investigation. In addition to the OLEDs application, the selected

cyanostilbene-based luminogens with solid-state emission, cell-permeability and reversible switch-on/off capability have illustrated the positive result in live-cell imaging and chemical vapor sensing.

Conjugated polymer with high molecular weight is the superior option by overcoming the weaknesses of low-molecular-weight luminogens with excellent thin-film form ability and comparatively simple and inexpensive fabrication processes. The design and synthesis of the cyanostilbene-based polymeric chromophores are described in Chapter 3. The polymerization of the AIE-active diacetylene ligands by connection of *trans*-[Pt(PBu<sub>3</sub>)<sub>2</sub>] unit at both ends has successfully retained their AIE behavior. In contrast, the ACQ problem has occurred on the polymers with organic spacers and the AIE-active ligands. From the DFT calculation on the Pt polymers and the blue shift of emission spectra in high water content suggested that the AIE phenomenon of Pt polymers is probably originated from the elimination of the non-radiative intramolecular charge transfer (ICT) process.

Owing to the high demand in red-emitting materials in the applications of electroluminescent devices, fluorescent sensing and bio-imaging, effort has been made to design a system with the new chromophores with donor (D) – acceptor (A) system and thus to synthesize phenothiazine (D)-containing cyanostilbene (A)-based derivatives which are depicted in Chapter 4. Consistent with the conventional

AIE-active luminogens with a successively climb of photoluminescence intensities in response to the increase of water proportion, phenothiazine-containing cyanostilbene-based derivatives has exhibited a V-shape fashion of emission intensity. It suggests that the emission of chromophores started to be quenched due to the increase of solvent polarity, overriding that of the molecular aggregation when a “small” volume of water is being introduced. While aggregate formation was dominant from the addition of a “large” amount of poor solvent, less polar local environment was created which suppressed the non-radiative transition to the ICT state and intensified the emission efficiency. Phenothiazine (D) – cyanostilbene (A) system has created a series of red-emitting chromophores with great tunability for the sake of achieving the desired emission color and better emission efficiency.

To functionalize these AIE-active cyanostilbene-based chromophores, pyridine group was attached to the compounds to take the advantage of its metal-chelating capability, which is discussed in Chapter 5. The AIE features of cyanostilbene-based compounds can be preserved after the introduction of the pyridyl unit. Even it possessed a weak photoluminescence in its dilute solution which suggest that the high electron delocalization within the molecule has rigidified the structure to some extent, it is transformed to a highly emissive state with a high proportion of water. The exclusive variation of emission behavior with obvious bathochromic shift and boost

of emission spectrum in the presence of cadmium-(II) ion has demonstrated its potential metal ion sensing ability.

Chapter 6 and 7 present the concluding remarks and the experimental data of the compounds of Chapter 2 to 5, respectively.

## Acknowledgements

I would like to express my deepest gratitude and sincere thanks to my supervisor Prof. Raymond W.-Y. Wong for his invaluable advice, encouragement and fruitful discussion throughout my research project. His precious opinions and comments in the thesis preparation are gratefully acknowledged. His erudite advice has opened up new horizons for me. Without his generous guidance and suggestion, this thesis will not be possible.

Wordless thanks also go to Prof. Zhiyuan Xie at Changchun Institute of Applied Chemistry for the fabrication and testing of OLEDs; Prof. Wei Huang and Prof. Qiang Zhao at Nanjing University of Posts and Telecommunications for the preparation and testing in two-photon cell imaging; Prof. Jianzhang Zhao at Dalian University of Technology for the DFT calculations.

Moreover, I would like to show my kind gratitude to our research group members, Dr. C. L. Ho, Dr. Y. Zeng, Dr. G. P. Tan, Dr. X. L. Liu, Dr. Q. Liu, Dr. L. F. Lai, Miss H. Wu, Mr. S. H. Siu, Mr. C. H. Cui, Ms. N. Y. Chau, Mr. Y. Ma, Mr. P. Y. Ho, Ms. J. Xiang, Mr. Z. G. Meng, Mr. S. C. Yiu and Ms. Y. J. Dong for their sincere care, guidance, support and encouragement. In addition, I would like to give special thanks to scientific and clerical officers in the Department of Chemistry for their genuine guidance and support. Especially, I would like to thank Dr. C. L. Ho for her

kind assistance and helpful suggestions in my research.

I would like to show my kind gratitude to my co-supervisor, Dr. H. W. Li.

I would like to acknowledge the receipt of a postgraduate studentship from Hong Kong Baptist University and Hong Kong Research Grants Council (HKBU 2024/0 and HKUST2/CRF/10) for financial support of this work.

Finally, I would like to record my sincere indebtedness to my family, in particular, to my grandmother and mother, for their care and continuous encouragement and to my boyfriend for his endless love and personal support during my course of study.

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