

DOCTORAL THESIS

Organic and metallated aryeneethynyls: synthesis, characterization and photovoltaic application

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Date of Award:
2014

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Abstract

Photovoltaic (PV) technology using organic solar cells have attracted much attention, as it is a simple and efficient way to convert solar energy into usable electricity. At present, bulk-heterojunction (BHJ) organic solar cells, which are based on conjugated p-type polymers and n-type fullerene derivatives, have been intensively investigated in both academia and industry. Organic and metallated conjugated small molecules (SM) represent an intriguing and promising class of materials. Atomic-thick 2D nanosheets have attracted tremendous attention recently because of their novel electronic structures and physical properties. This thesis describes the synthesis and characterization of some series of organic and metallated aryleneethynylenes and their applications in BHJ solar cells.

To begin with, a brief overview on the background of organic solar cells (OSCs) and two-dimensional (2D) nanomaterials was presented in Chapter 1.

In Chapter 2, a new series of multichromophoric small molecular systems of ruthenium(II)-bis(aryleneethynylene) compounds containing triphenylamine and/or thiophene as the donor and benzothiadiazole as the acceptor were designed and obtained by straightforward synthesis and purification procedures with reasonable yields. These ruthenium complexes absorb strongly in the visible region which are

potentially attractive materials for photovoltaic cell applications. The best power conversion efficiency (PCE) of 0.66% was achieved for **D1** with the open-circuit voltage (V_{oc}) of 0.51 V, short-circuit current density (J_{sc}) of 4.24 mA cm⁻² and fill factor (FF) of 0.31 under illumination of an AM 1.5 solar-cell simulator.

Furthermore, in Chapter 3, a new series of small molecular systems of platinum-containing organometallic conjugated molecules containing different donating groups (such as thiophene, BDT, carbazole, and bithiazole), benzothiadiazole and/or dimesitylborane as the acceptors were successfully designed and obtained. Among all the BHJ devices based on these platinum complexes, PT5-based device, which we introduced strong donor group carbazole in the molecule, showed the highest PCE of 1.46% with high V_{oc} of 0.70 V, J_{sc} of 6.17 mA cm⁻² and FF of 0.33 at the optimized active layer thickness of 60 nm, which indicates that the photovoltaic performance can be significantly improved by introducing a strong D group in the molecule.

Besides, a new series of organic small molecules **M1-M16** of D-A-spacer-A-D structure were successfully designed and obtained. Intramolecular charge transfer (ICT) effect could be observed due to the strong electron-withdrawing units (such as benzothiadiazole, DPP, triazole and dimesitylborane) and strong electron-donating units (such as triphenylamine, thiophene, BDT, carbazole, and bithiazole), and this

effect between the acceptor and donor units causes low bandgap. By introducing strong oligothiophene donor group in the molecule **M4**, which showed the highest PCE of 3.68% among all the devices with high V_{oc} of 0.95 V, J_{sc} of 7.76 mA cm⁻² and FF of 0.44 at the optimized active layer thickness of 75 nm, which also indicates that the photovoltaic performance can be significantly improved by introducing a strong D group in the molecule.

In Chapter 5, we designed and synthesized a new series of the “bottom-up” metal complex nanosheets: π -conjugated bis(dipyrinato) metal complex nanosheets, including monolayer and multilayer nanosheets. AFM, IR, XPS and SEM analyses have been applied to study the morphologies, chemical state and size or nanostructure of the as-prepared nanosheets, and the results indicated that the “bottom-up” method is useful for the construction of photoresponsive and semiconductive nanosheets. This work is going to enlarge the futurity of the “bottom-up” nanosheet as next-generation nanomaterials.

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

Acknowledgements

I would like to express my profound gratitude and sincere thanks to my supervisor Prof. Raymond W. Y. Wong for his invaluable advice, encouragement and uninterrupted support throughout my study. His precious comments and opinion in the preparation of this thesis at the time he was very busy are gratefully acknowledged. He has been supporting me not only by providing precious comments and opinion, but also provided me academic and spiritual support for three years. Thank him for giving me an opportunity to have excellent exchange study experience in the University of Tokyo. His erudite advices always open up new horizons for me and his devoted attitude in research has influenced me a lot and made my study a truly rewarding experience.

Special thanks are given to Prof. H. Nishihara, Dr. R. Sakamoto, Mr. K. Hoshiko and Miss J. Kakinuma (Department of Chemistry, Graduate School of Science, The University of Tokyo, Japan) for giving me an opportunity to do an exchange program in his group.

Wordless thanks also go to Prof. Z. Y. Xie and Dr. Y. Y. Fu (State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry Chinese Academy of Sciences, Changchun, China), Prof. H. B. Wu (Institute of

Polymer Optoelectronic Materials and Devices, Key Lab of Specially Functional Materials, Ministry of Education, South China University of Technology, Guangzhou, China), Prof. F. R. Zhu and Mr. E. Tam (Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Hong Kong) for the fabrication and testing of BHJ solar cell; Prof. F. Yan and Dr. J. H. Li (Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong) for the calculation of hole-carrier mobilities; Prof. P. D. Harvey (Department of Chemistry, University of Sherbrooke, Canada) and Dr. S.-P. Huang (Institute for Materials Chemistry and Engineering and International Research Center for Molecular Systems, Kyushu University, Japan) for TD-DFT of calculation.

I would like to show my kind gratitude to our research group members, Dr. C. L. Ho, Miss L. F. Lan, Miss Hao Wu, Dr. H. M. Zhan, Dr. F. R. Dai, Dr. G. P. Tan, Dr. Q. C. Dong, Dr. Q. W. Wang, Dr. L. Li, Dr. X. L. Liu, Dr. Z. Xie, Mr. Z. H. Siu, Miss W. S. Lau Mr. C. H. Cui, and others, for their genuine care, guidance, support and encouragement. I am indebted to all clerical and scientific officers of the Department of Chemistry.

I would like to give special thanks to scientific officers in the Department of Chemistry for their sincere guidance and support.

I would like to acknowledge the financial support from the Hong Kong Baptist

University (FRG2/10-11/101), Hong Kong Research Grants Council (HKBU203011) and Areas of Excellence Scheme, University Grants Committee of HKSAR (project No. [AoE/P-03/08]) and the National Natural Science Foundation of China (project number 21029001) for financial support of this work.

Last but not least, my wordless and wholehearted gratitude must be dedicated to my parents and brothers for care, comfort and unconditional supporting during my study of course.

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