DOCTORAL THESIS

Organic and metallated aryleneethynylenes: synthesis, characterization and photovoltaic application

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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, trizaole 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(dipyrrinato) 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.

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