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Tuning the fluorescence lifetime of donor polymers containing different proportion of electron withdrawing groups inhybrid solar cells

Manman Li^a, Yuancheng Qin^{a,*}, Chun Yan^b, Weili Dai^a, Xubiao Luo^{a,*}, Xiao Jin^a, Qinghua Li^a

^a Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, PR China ^b Technical Center for Dangerous Goods Testing of Guangxi Entry-Exit Inspection and Quarantine Bureau, Beihai, 536000, PR China

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ABSTRACT

Photoluminescence (PL) lifetime of the D-A polymer can ensure that there is enough time for the exciton to reach the interface of donor-acceptor and separate it into free charges. Also, the introduction of electrons withdrawing groups in D-A polymer can effectively adjust the band gap, molecular self-assembly, electron mobility, fluorescence lifetime, and optoelectronic properties. Herein, we use 2,1,3-benzothiadiazole (BT) as an acceptor unit, and indole and benzodithiophene (BDT) as the electron acceptors in the D-A copolymers with different proportions of BT and indole. The ratio of the monomers affect not only the electrochemical structure but also the PL lifetime. Results show that the PL lifetime is obviously changed with the increase of BT. The polymer, possessing a long PL lifetime and outstanding charge transfer capability, exhibits a high power conversion efficiency of hybrid solar cells.

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1. Introduction

Organic/inorganic hybrid solar cells (HSCs) have become more and more popular for scientists to explore, because they not only possess a high electrical conductivity, thermal stability and chemical stability of crystalline inorganic semiconductor material, but also can overcome the problems of traditional organic bulk heterojunction [1–4]. Conceptually, HSCs are related to the both dye-sensitized solar cells (DSCs) and organic solar cells (OSCs), which are acted as the technologies with the potential to become low-cost alternatives to inorganic photovoltaic devices [5,6]. HSCs have diversified structure of organic electronic material, high optical absorption rate, fast electronic mobility, good mechanical, and high stability. These advantages have important theoretical significance and potential value for development of new type of solar cells [7]. Despite the many advantages of HSCs, it is necessary to further improve the power conversion efficiency (PCE) to achieve commercialization.

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At present, the conjugated structure photovoltaic material of electron donating group electron accepting group (D-A) is one of the most widely used organic photovoltaic material [8,9]. The D-A alternately link is a kind of polymer structure which can effectively regulate the electronic bang gap [10,11]. At the same time, this kind of structure can promote the transfer of electrons in the molecule, which leads to the absorption of light in the long-wave direction. In the different kinds of conjugated polymers, D-A copolymers based on BT or indole have been studied carefully for photovoltaic properties [12,13]. Including a six element benzene rings and a five element nitrogen containing pyrrole ringindole is an aromatic heterocyclic organic compounds. Due to the lone pair of nitrogen atom, its chemical properties are different from the conventional amine, thus which has an important influence on the chemical and optical properties. Since the BT has stronger electron withdrawing ability and stable in the air, it has served as acceptor unit in the acceptor-donor polymer solar cells of the donor material. As a result, the higher PCE can be achieved with the polymer that obtained by polymerization with different donor units.

In the current study, most of the researchers are committed to narrow the band gap of polymer to obtain a higher PCE. The indoles polymer is a new type of organic photovoltaic material, and there are only few studies on the indoles polymer solar cells so far. Therefore, we started from the basic molecular engineering point







^{*} Corresponding authors.

E-mail addresses: qinyuancheng@hotmail.com (Y. Qin), luoxubiao@126.com (X. Luo).

 Table 1

 Molecular weight and the distribution of polymer P1–P5.

	Polymer	M_n (g/mol)	M_w (g/mol)	PDI	T_d (°C)
Ī	P1	4541	5555	1.22	304
	P2	3989	5317	1.33	308
	P3	5900	7957	1.34	309
	P4	7646	9171	1.19	316
	P5	2256	3007	1.33	295

of view. By using the BDT as donor material group, different proportion of the indole and the BT fgroup were polymerized by the Stille coupling, and five novel polymers were designed and synthesized [13]. By means of the characterization, the relationship between the photoelectric properties of five polymers and the change of proportion of the indole and BT was carefully investigated. Also, the relationship among the molecular structure of the material. PL lifetime, and the performance of the device was studied. On the other hand, we made an in-depth investigation on the effects of monomer ratio on the PL lifetime and device performance of the polymer. In the transient fluorescence, after the sample is excited, the thermal relaxation (the excess energy in the form of heat dissipation) of electrons will be occurred before the transition from highly-excited state energy level to the low-excited state level, then to emit the fluorescence transition to the ground state. In solar cells, the absorption of light by donor material, the formation of exciton, the decay process of exciton, and the dissociation of exciton are the critical factors which affect the PCE of solar cells [14,15]. So it is necessary to study the formation and decay of the exciton in donor material which are very important to improve the PCE of solar cells in the future.

2. Result and discussion

Table 1 shows the weight-average molecular weight (M_w) , the dispersion index (M_w/M_n) , and decomposition temperature (T_d) of the polymer P1–P5. Through the above synthesis on five kinds of polymer P1–P5 in tetrahydrofuran solubility are all well, the polymer molecular weight of P1–P5 five kings were tested by gel penetration chromatography (GPC) using THF (HPLC grade) as solvent.



Fig. 2. UV-vis absorption spectra of polymer P1-P5 in solution.

From the TGA curves, P3, P4 polymer began to lose weight at about 300 °C, and P1,P2,P5 began to lose their weight at about 200 °C. The 5% weight loss temperature of P1–P5 polymers were at 304, 308, 309, 316, and 295 °C, respectively. At the weight loss of 5%, the molecular weight of the sample was severely reduced and unable to achieve the desired performance indicators, suggesting that the thermal stability of these polymers is satisfied with the basic conditions of the battery device (Fig. 1).

UV-vis absorption spectroscopy can be implemented to characterize the absorption capacity of solar light [16]. The UV-vis absorption spectra of polymer P1–P5 in chloroform were shown in Fig. 2. It can be seen that the polymer P1–P5 has obvious absorption peaks in the UV-vis region and a wide absorption band, which means all samples have different degrees of absorption intensity and absorption peak in the 300–600 nm. In P1 and P2, each of polymers has three absorption peaks. P4 and P5 have four absorption peaks from 300 to 650 nm. Compared to other four polymers, P3 has an obvious absorption peak at 335 nm and a weak peak at 522 nm. This result suggests that the electron donor containing the electron-donation indole groups can promote the



Fig. 1. TGA curves of polymer P1-P5.

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