

A performance model of six new organic small molecule photovoltaic materials

This article in view of the Compound 1 to Compound 6 (six) kinds of organic small molecule photovoltaic material preparation, thermal properties, UV-vis absorption spectroscopy, fluorescence spectroscopy, electrochemical properties and its ontology with PC60BM heterostructure of solar cell device is analyzed, in order to explore the performance differences of different organic small molecules, provide theoretical guidance for the preparation and development of photovoltaic materials. The results show that increase in the compound rigid structure helps to improve its thermal stability. The UV absorption spectra and fluorescence spectra of organic photovoltaic small molecules are mainly determined by receptor units, when the receptor cell contains three different kinds of donor cells of organic small molecule optical performance difference is not very big, and the UV absorption spectrum of DPP series is wider than that of the benzothiadiazole series. The bandgap size of the six compounds containing triphenylamine depends mainly on the narrow band gap in the small molecule; the triphenylamine is stronger than the carbazole hole transport capacity and fluorene, but its solubility is relatively poor; the DPP series of optical performance and benzothiadiazole is better, but the PV performance is not as benzothiadiazole series.

Keywords: Performance model, organic small molecule, photovoltaic materials, photochemical properties, electrochemical properties.

Introduction

Using solar cell obtain energy from the sun directly, is an world recognized and important way to solve the increasingly serious energy crisis and environmental pollution, organic solar cells have the advantages of low cost, light quality, can make the large area, has become a hotspot in the field of solar cells. The basic structure of organic solar cells including positive and negative electrodes and light between the active layer, its working principle includes: shock

zichan, exciton diffusion, exciton in the donor dissociation and charge transfer and collect four process. (Chen, 2014) pointed out that, as the core part of the battery, the photoactive layer formed by organic semiconductor heterostructure electron donor and acceptor materials, light absorption of light energy by active layer electron transition after exciton moving, exciton diffusion to occur at the body by dissociation, namely electronic donor molecules to the receptor molecules and the formation of transfer charge separated state, resulting in the formation of holes and electrons to the anode and the cathode current migration, formation of light. Due to poor solubility of organic photovoltaic material and low light absorption efficiency, it has played a limiting role in the popularization and application of solar cells, in order to reduce the constraints, many scientists have made many attempts on the new materials. On the one hand, based on polymer as electron, fullerene derivatives as receptor of organic solar cell energy conversion efficiency of 8.13%. Now, polymer solar cells to some extent can realize commercialization; on the other hand, small molecules to body and fullerene derivatives receptors of organic solar cells due to the uncertainty of the small molecule structure and its high purity, has attracted more and more people's attention, through the method of vacuum evaporation device is made after the efficiency reached 5.6% (Sreedhar and Reddy, 2007).

Many researchers have made efforts to study new types of organic photovoltaic materials. Among them Motahari, et al., 2013 introduced the structures and properties of various derivatives, their receptors used as organic photovoltaic materials were reviewed, including small molecule diimide materials, including diimide receptor cell donor/receptor double unit and functional molecules containing diimide receptors to the body. In order to study and develop the organic photovoltaic materials and to improve the efficiency of photoelectric conversion of organic photovoltaic devices, the design of the new hybrid of the thiophene derivatives was designed. Mishra and uerlp, 2012 designed and synthesized successfully with key, three key for the bridge, benzene and thiamethoxam receptor (A) unit of 1,2 hexyl fluorene as donor (D) units of D-A-type D small molecule FLEBT photovoltaic materials, using nuclear magnetic, high resolution mass

Messrs. Ai-Min Yang, Shan-Shan Li, Xiao-Jun Men, Feiyu Cheng and Yue Wang, Hebei Key Laboratory of Data Science and Applications, North China University of Science and Technology, Tangshan, 063000, China. Email: aiminyangtujian@163.com

spectrometry to the structure characterization of the compounds, optical properties and electrochemical performance of FLEBT respectively by ultraviolet-visible spectroscopy and cyclic voltammetry were used, the results showed that FLEBT has good solubility in organic solvent and film forming, strong intramolecular charge transfer (ICT) features, the ultraviolet-visible absorption with wider range, and material with receptor PCompound - 61 nm matching electronic level.

In this paper, the use of narrow band unit benzodiazole, DPP as the receptor (A) element, with hole transport group triarylamine as a donor material (D), designed and synthesized a series of D-A-D type organic photovoltaic materials, and using the test equipment in the corresponding test conditions

to analyze the performance of the new type of organic photovoltaic materials.

Experimental

There are six compounds to be prepared in this paper. The reagents and preparation processes needed are shown in Table 1.

In order to study the properties of Compound-1 to Compound-6 photovoltaic material, this paper studied the thermal performance, UV-visible absorption spectra and fluorescence spectra, electrochemical properties and pv properties of organic small molecules. The instrument for the experimental data acquisition of the product is as follows.

Using thermal gravimetric test (TGA) to test the thermal

TABLE I: THE MAIN RAW MATERIALS OF THE EXPERIMENT

symbol	The name of the product	The preparation process
Compound-1	4, 7-2 (5 - (9, 9-dioctyl - 2-fluoro) - 2 - thiophenyl) - 1, 2, 5, - benzoyl triazole	add compound 3 (0.50g, 0.1 mmol) in the 50ml single bottle, compound 10 (0.2g, 0.04 mmol), Pd (PPh ₃) 4(0.03g), toluene 20mL, anhydrous ethanol 10mL, K ₂ CO ₃ (2M) 10mL. put the mixed solution in the single-mouthed bottle on the magnetic stirrer, and under the protection of nitrogen, the constant temperature of 80°C will reflect 24h, and the mixing solution will gradually change from dark red to bright red as the reaction is carried out. Stop reaction, cool to room temperature, methylene chloride extraction, combined organic phase washed with water, using anhydrous MgSO ₄ dry overnight, filtration, distillation solvent, coarse product: PE DCM (came) as developing agent, using column chromatography separation and purification, red solid 0.25g, is the product of Compound 1.
Compound-2	4, 7-2 (5 - (4-n, n-diphenylaniline) - 2 - thiophenyl) - 1, 2, 5 - benzoyl, and diazole	The preparation process and the Compound - 1 are as follows: Compound 4 (0.60g, 1.6 mmol), compound 10 (0.30g, 0.7 mmol), Pd (PPh ₃) 4 (0.04g), toluene 20mL, no water ethanol 10mL, K ₂ CO ₃ (2M) 10mL. The crude products are based on PE: DCM (3:1), which is separated by column chromatography, and the deep red solid is 0.26g, which is the product Compound 2.
Compound-3	4, 7-2 (5 - (9-octyl-3-3 -carbazolyl) - 2-thiophene) - 1, 2, 5 - benzoyl, and diazole	The preparation process and the Compound-1 are as follows: Compound-7 (0.70g, 1.7 mmol), compound-10 (0.30g, 0.7 mmol), Pd (PPh ₃) 4 (0.03g), toluene 20mL, anhydrous ethanol 10mL, K ₂ CO ₃ (2M) 10mL. The crude products are separated by column chromatography and separated by the column chromatography, which is the product Compound.
Compound-4	3, 6-2 (5 - (9, 9-dioctyl -2-fluorene) - 2-thiophene) - 2, 5 - dioctyl - 1, 4 - pyrrole and pyrrolidone	The preparation process and the Compound-1 are as follows: Compound-3 (0.25g, 0.5 mmol), compound-13 (0.15g, 0.2 mmol), Pd(PPh ₃) 4(0.02g), toluene 20mL, anhydrous ethanol 10mL, K ₂ CO ₃ (2M) 10mL. The crude products are based on PE: DCM (4:1), which is separated by column chromatography, and the dark blue solid 0.13g is obtained, which is the product Compound-4.
Compound-5	3, 6-2 (5 - (4-n, n-dioctyl - 1, 4-pyrrole and pyrrolidone)	The preparation process and the Compound-1 are as follows: Compound 4 (0.38g, 1.0 mmol), compound 13 (0.30g, 0.4 mmol), Pd (PPh ₃) 4 (0.02g), toluene 20mL, anhydrous ethanol 10mL, K ₂ CO ₃ (2M) 10mL. The crude products are based on PE: DCM (2:1) and separated by column chromatography, and the dark blue solid 0.23g is obtained, i.e. the product Compound-5.
Compound-6	3, 6-2 (5 - (9-octyl-3-carbazole) - 2, 5-dioctyl - 1, 4-pyrropryrrole	The preparation process and the Compound-1 are as follows: Compound-7 (0.70g, 1.7 mmol), compound 13(0.30g, 0.7 mmol), Pd (PPh ₃) 4(0.03g), toluene 20mL, anhydrous ethanol 10mL, K ₂ CO ₃ (2M) 10mL. The crude products were developed with PE: DCM (1:1), separated by column chromatography, and obtained dark blue solid 0.28g, which is the product Compound-5.

Note: compound 1~13 are: 2-bromo fluorene; 2-bromo-9, 9-dioctyl fluorene; 2 - (9, 9-dioctyl) - 4, 4, 5, 5-tetramethyl-1, 3, 2-dioxane; N, n-diphenyl - 4 - (4, 4, 5, 5, 5-tetramethyl-1, 3, 2 - dioxygen-2-boron) aniline; 3-bromo-9-hydrocarbazole; 3-bromo-9-octyl carbazole; 3 - (9-octyl carbazole) - 4, 4, 5, 5-tetramethyl-1, 3, 2-dioxane; 2-3 (tert-butyl) tin thiophene; 4, 7-2 (2 - thiophene) - 1, 2, 5 - benzothiazole; 4, 7-2 (5-bromo-2-thiophene) - 1, 2, 5 - benzothiazole; 3, 6-2 (2-thiophene) - 2, 5-dihydro-1, 4-pyrrolidone; 3, 6-2 (2-thiophene) - 2, 5 - dioctyl - 1, 4 - pyrrole and pyrrolidone; 3, 6-2 (5-bromo-2-thiophene) - 2, 5-dioctyl - 1, 4-pyrrole and pyrrolidone.

properties of organic small molecules, the instrument for the domestic WRT-3P analyzer analyzer, N2 protection, heating rate of 20°C/min.

Ultraviolet absorption spectra (UV-vis) using Himadzu UV-265 spectrophotometer was used to measure the sample solution with dichloromethane as the solvent and the droplets on quartz films.

The fluorescence spectrum (PL) was measured by Pekin-Elmer LS50B spectrometer. The sample solution was prepared by dropping methylene chloride into a quartz film.

Electrochemical performance-cyclic voltammograms (CV) using CHI 660A measure electrochemical workstation, organic small molecule film platinum, nano-sno2 electrode was covered by metal foil as the electrode, saturated calomel reference electrode was, in 0.1mol/L tetrabutyl six fluorine phosphoric acid amine (Bu4NPF6) in acetonitrile solution as electrolyte solution, scanning speed is 100 mv/s.

The photovoltaic performance test is used as a white light source simulating the sunlight with a 500W xenon lamp and AM 1.5 filter combination. The light intensity measured on the device is 100mW/cm².

Result and discussion

The TGA curve of Compound-1 to Compound-6 (six) D-A-D type photovoltaic material molecules as shown in Fig.1, the temperature range of 2 measurement is 0-700°C, weight variation of the six compounds is corresponding to its own weight of 5%.

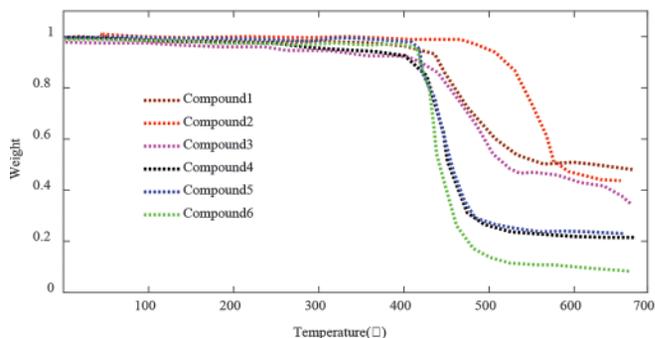


Fig.1 The TAF curve of six D-A-D type photovoltaic material molecules

By testing the thermal stability of Compound-1 to Compound-6 TGA, the data can be obtained from the D-A-D type small molecule organic compound has good thermal stability, which corresponds to the Compound-2 5% weight loss temperature value is the highest, this means that the 4,7-two (5- (4-N, N- two Diphenyl aniline) -2- Thienyl) -1,2,5-benzene and with stage two has the highest thermal stability, show an increase in rigidity of the compound structure can improve the thermal stability of promotion. UV-vis absorption spectra of Compound-1 - Compound-3 in CH₂Cl₂ solution and solid film are shown in Fig.2.

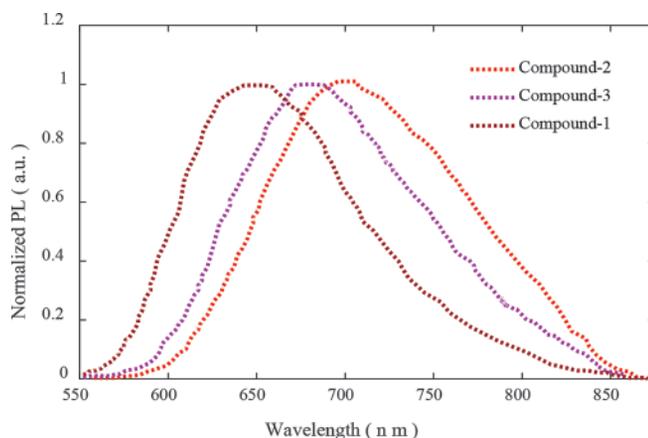


Fig.2 UV-vis absorption spectra of Compound-1~Compound-3 in CH₂Cl₂ solution and solid film

As can be seen from Fig.2, the ultraviolet absorption spectrum of Compound-1~Compound-3 in CH₂Cl₂ solution is basically the same, and there is a strong absorption peak at about 360nm and 520nm. Among them, the absorption peak at 360nm is the donor cell in the compound; the absorption peak at 520nm is the acceptor cell and the absorption of electrons between the D-A chains. The fluorescence spectra of Compound-1~Compound-3 in CH₂Cl₂ solution is shown in Fig.3.

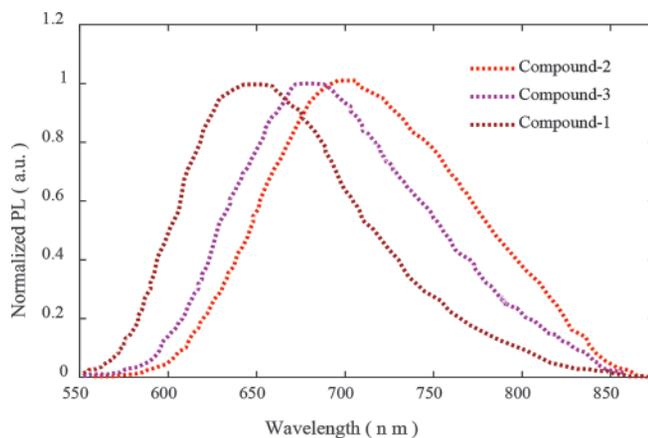


Fig.3 Fluorescence spectra of Compound-1~Compound-3 in CH₂Cl₂ solution

We can see from Fig.3, fluorescence spectra of Compound-1~Compound-3 in CH₂Cl₂ solution is roughly the same, and the maximum emission peak of Compound-1 occurred at 647nm, the maximum emission peak of Compound-2 occurred at 699nm, the maximum emission peak of Compound-3 occurred at 680nm, the three compounds emission peak may be due to the different degree of resonance. UV-vis absorption spectra of Compound-4~Compound-6 in CH₂Cl₂ solution and solid film are shown in Fig.4.

We can see from Fig.4, Compound-4~Compound-6 UV absorption spectra in CH₂Cl₂ solution are basically the same,

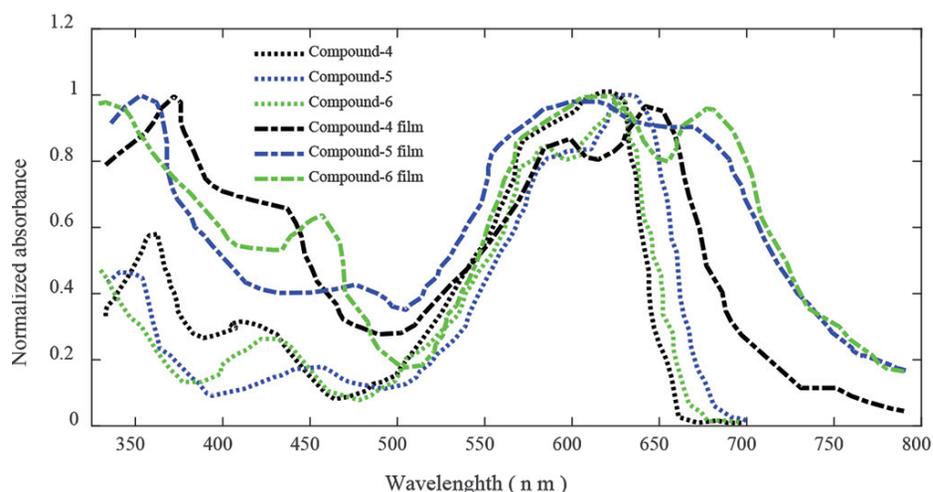


Fig.4 UV-vis absorption spectra of Compound-4~Compound-6 in CH₂Cl₂ solution and solid film

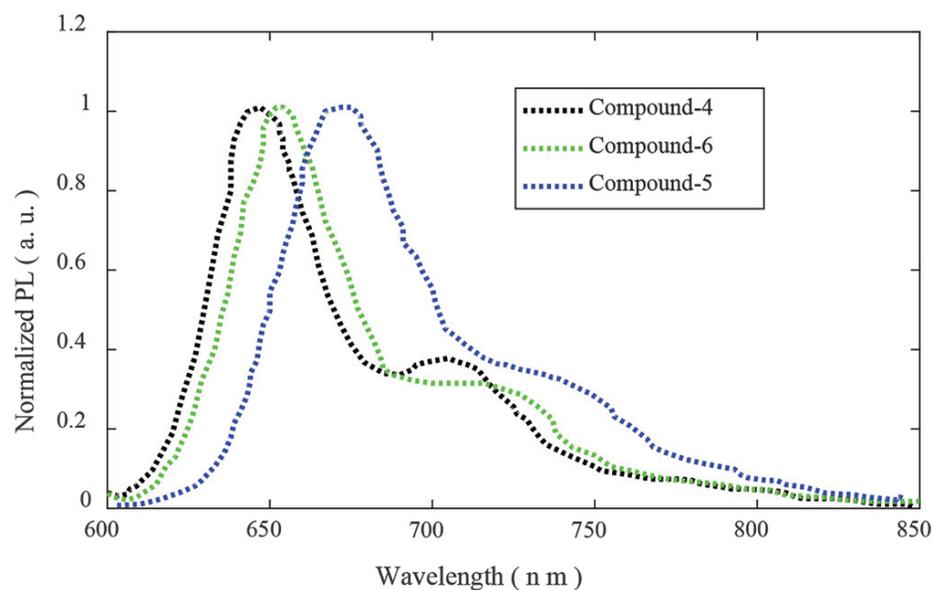


Fig.5 The fluorescence spectra of Compound-4~Compound-6 in CH₂Cl₂ solution

investigated by UV vis spectroscopy (UV-vis) and fluorescence spectroscopy (PL), and the data of UV-vis and PL for the six materials were shown in Table 2.

As shown in Fig.5, the fluorescence spectra of Compound-4~Compound-6 in CH₂Cl₂ solution, and the corresponding fluorescence data, can be queried in Table 2. As you can see from Fig.5, the PL spectra of the compounds based on the DPP series are approximately the same shape. The emission peak of Compound-4 occurred at 646nm, the maximum emission peak of Compound-5 occurred at 671nm, the maximum emission peak of Compound-6 occurred at 653nm, the three compounds emission peak may be due to the different degree of resonance.

This paper uses cyclic voltammetry analysis of electrochemical properties of Compound-1~Compound-6, small organic molecules dissolved in CH₂Cl₂ solution, drop on the platinum electrode is formed on the thin film, and as a working electrode, metal foil as the counter electrode and saturated calomel electrode as the reference electrode, with 0.1mol/L (BU4NPF6) in acetonitrile solution as electrolyte the solution, the scanning speed is

in the absorption peak of 360nm belongs to the donor element in the compound, in 520nm, 580nm and 620nm peaks belong to the electron acceptor unit and D-A chain absorption.

In this paper, the optical properties of organic photovoltaic materials Compound-1 ~ Compound-6 were

100mV/s, under the protection of nitrogen by cyclic voltammetry, and then from the CV curve record that reduction potential or oxidation potential, HOMO and LUMO level calculation compounds in the empirical formula according to the following formula.

TABLE 2: THE COMPOUND-1~COMPOUND-6 DATA ON PHOTOCHEMICAL PROPERTIES AND ELECTROCHEMICAL PROPERTIES

Compound-X		X=1	X=2	X=3	X=4	X=5	X=6
$\lambda_{\max}^{abs} (nm)$	Solution	365,509	373,528	357,525	411,580,622	450,593,633	427,583,625
	Film	370,525	385,561	382,571	422,592,646	467,609,668	452,614,680
$\lambda_{\max}^{em} (nm)$	Solution	647	699	680	646,706	671,736	653,715
HOMO(eV)		-5.24	-5.91	-5.82	-5.05	-5.42	-5.51
LUMO(eV)		-3.20	-3.94	-3.83	-3.19	-3.63	-3.67
$E_g(eV)$		2.04	1.97	1.99	1.86	1.79	1.84

TABLE 3: LIST OF PHOTOVOLTAIC PERFORMANCE PARAMETERS OF D-A-D TYPE COMPOUND-1~COMPOUND-6 SOLAR CELLS

Compound-X	X=1	X=2	X=3	X=4	X=5	X=6
Compound/PC ₆₀ BM (w/w ratio)	1:4	1:4	1:4	1:4	1:4	1:4
V _{oc} (V)	0.74	0.16	0.61	0.66	0.64	0.02
I _{sc} (mA/cm ²)	6.18	6.62	4.42	2.12	6.17	0.99
FF (%)	0.30	0.71	0.32	0.27	0.30	0.20
PCE (%)	1.39	0.75	0.84	0.38	1.18	0.004

$$\begin{cases} E_{HOMO} = -(E_{OX} + 4.38) (eV) \\ E_{LUMO} = -(E_{red} + 4.38) (eV) \\ E_g = 1214 / \lambda \end{cases}$$

The electronic energy levels of the compounds are obtained by their maximum absorption of the ultraviolet spectrum and the formula, and their electrochemical performance data are shown in Table 2. We can learn from the data shown in Table 2, with two of Dibenzothiophene as the core of the D-A-D type compounds Compound-1~Compound-3, with donor group electron mobility increases, LUMO decreases, the gap becomes smaller, containing three aniline in the energy gap of Compound-2 is smaller than that of Compound-1 and Compound-3, but have little difference at about 2.0eV. D-A-D and Compound-4~Compound-6 with DPP as the core, with donor groups the electron mobility increases, LUMO decreases, the energy gap is smaller, containing three aniline in the energy gap of Compound-5 is smaller than that of Compound-4 and Compound-6, but the difference is not large, about 1.8eV. Thus, the energy gap size of Compound-1~Compound-6 depends mainly on the narrow band gap in small molecules.

The bulk heterojunction solar cell device /PC60BM with six organic small molecules Compound-1~Compound-6 [10] is used to analyze the photovoltaic properties of D-A-D organic small molecules. The structure of the device is ITO/PEDOT (50nm)/Sample(70nm)/LiF(0.5)/Al(150nm).

Simulation of solar radiation in AM1.5100mW/cm², and the corresponding photovoltaic performance parameters are shown in Table 3, table PCE and FF 4 values were calculated according to the formula.

$$\begin{cases} PCE = V_{oc} J_{sc} FF / V_{oc} J_{sc} FF \\ FF = V_{oc} J_{sc} FF / V_{oc} J_{sc} FF \end{cases}$$

As illustrated, solar cells fabricated with compounds Compound-1/PC60BM (1:4 w/w) exhibit the best photovoltaic performance. The PCE values of the devices made from the benzothiadiazole series were in the order of compound - 2<Compound-3<Compound-1 and the corresponding PCE values are 0.75%, 0.84% and 1.39%. Although the transport capacity of triphenylamine and carbazole is stronger than that of fluorene, but the efficiency of Compound-1 is the best due to the problem of solubility, followed by carbazole with flexible chain.

Conclusions

This efficiency is not completely consistent with the photophysical properties, and the reason for this phenomenon is likely to be related to the dispersion of compounds in PCBM. In the fabrication of DPP series compounds PCE value according to the sequence of Compound-6<Compound-4<Compound-5, the corresponding PCE values are 0.004%, 0.38% and 1.18%, with triphenylamine Compound-5 has better PV performance, the reason and the dispersion properties in PCBM and film-forming properties and UV absorption properties related to better comprehensive performance. Although the photochemical properties of the DPP series are better than those of the benzothiadiazole series, the PV performance is not as good as that of the benzothiadiazole series. The reason for this phenomenon is likely to be that its solubility and film-forming properties The conditions and other related.

Acknowledgments

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