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Donor - Acceptor Type Conjugated Polymers Containing Carbazole and Fluorene for Organic Photovoltaic Applications

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1. Introduction

Conjugated polymers have attracted considerable interest for their properties such as electrical conductivity, electroluminescence, nonlinear optical properties and potential applications in photoelectronic devices.[1~2, 4]

The synthesis of new conjugated polymers for applications in photovoltaic cells has been of great interest. Promising performances have been obtained from devices using the bulk heterojunction architecture and using PCBM as the acceptor. A few conjugated polymers have emerged as good electron donor, among them, poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylenevinylene](MDMO-PPV) and regioregular poly(3-hexylthiophene)(P3HT) reached efficiencies(3~5%). [1]

Fluoene have been used as a blue light emitter in light emitting diodes. However, the light emitted and hence the band gap of polyfluorene could be tuned with addition of different electron donating or electron accepting units in the back bone of the polymer. [2, 4]

Carbazole moiety is in contrast with the fluorene unit the fully aromatic, providing a better chemical and environmental stability. [3]

In this study, we report the preparation of novel carbazole & fluorene containing conjugated polymers by Suzuki cross coupling reaction and fabricated bulk heterojunction solar cell for high efficiency solar cells.

2. Experimental section

Characterization

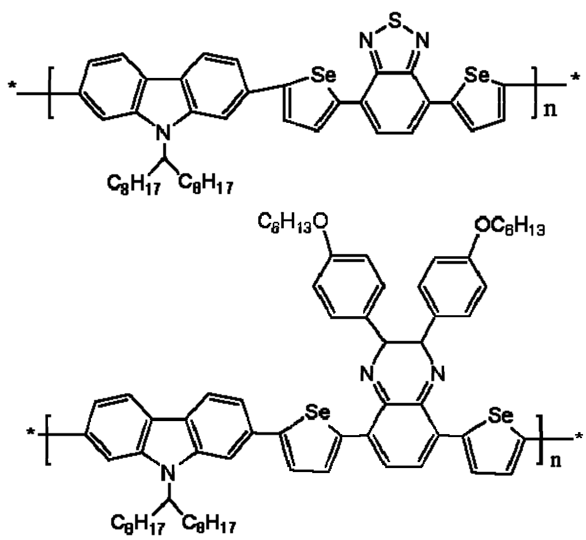
Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-400 mesh, Merck) as the stationary phase. ^{1}H-NMR spectra were performed in a Bruker ARX 400 spectrometer using solutions in $CDCl_3$ and chemical were recorded in ppm units with TMS as the internal standard. Electronic absorption spectra were measured in chloroform using a HP Agilent 8453 UV-Vis spectrophotometer. Cyclic voltammetry experiments were performed with a Princeton Applied Research Model 273A Potentionstat/Galvanostat. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a nonaqueous Ag/AgCl reference electrode at the scan rate of 50mV/s. The solvent in all experiments was acetonitrile and the supporting electrolyte was 0.1 M tetrabutyl ammonium-tetrafluoroborate. TGA measurements were performed on NETZSCH TG 209 F3 thermogravimetric analyzer. All GPC analyses were made using THF as eluant and polystyrene standard as reference.

Polymerization

All the polymerizations were carried out by Suzuki cross coupling reaction of the two monomers in an inert atmosphere. Monomer 1 and 2 were dissolved in toluene. $Pd(PPh_3)_4$ (1.5 mol%)was added and the mixture was stirring for 10 min. After addition of K_2CO_3 aqueous solution and Aliquate 336(2~3 drops), the reaction mixture was vigorously stirred at 85^{o}C. After 40h, bromobenzene(2~3 drops) was added to the reaction. The solution was then cooled to room temp., and the mixture was poured into a large amount of methanol to precipitate a polymer, which was collected by filtration and washed on Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform fraction was remove the solvent, precipitated in methanol-chloroform.

Photovoltaic device fabrication

Photovoltaic solar cells were fabricated by spin coating a chlorobenzene solution made from a mixture of [60]PCBM or [70]PCBM and polymer. Films obtained using this method was uniformly deposited onto an ITO/glass substrate coated with PEDOT/PSS. Aluminium was evaporated for the cathode and on Ba and BaF_2 was used between the cathode and the active layer.



Scheme 1. P1(upper) and P2(lower)

3. Results & discussion

Optical properties

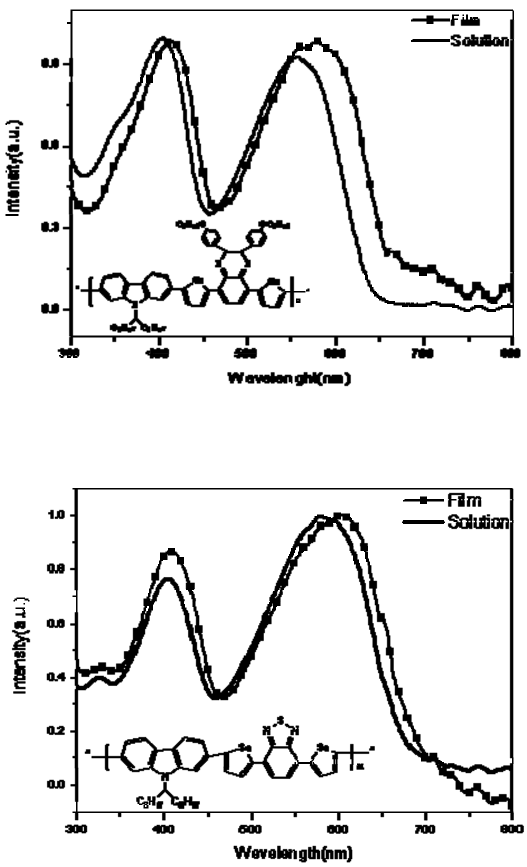


Fig.1 UV-bis absorption spectroscopy of polymers

As show in Fig 1, two absorption peaks were observed in chloroform solutions and in films. The absorption peaks of P1 and P2 in films red shifts maximum 27nm as compared with that in chloroform solution, indicating that a strong intermolecular interaction occurred in solid state. The optical band gap of P1 and P2 deduced from its absorption edge in solid state are 1.80, 1.87, respectively. HOMO energy levels are calculated from these electrochemical cyclic voltammetry. HOMO levels of P1 and P2 were 5.70, 5.30, respectively. LUMO levels are calculated from difference between optical band gap and HOMO energy levels.

Table I. optical properties and energy levels

Polymer	UV-vis		E_g^{opt}	HOMO	LUMO
	Solution	Film			
P1	430, 578	408, 605	1.80	5.70	3.90
P2	402, 558	409, 571	1.87	5.30	3.41

Device performances

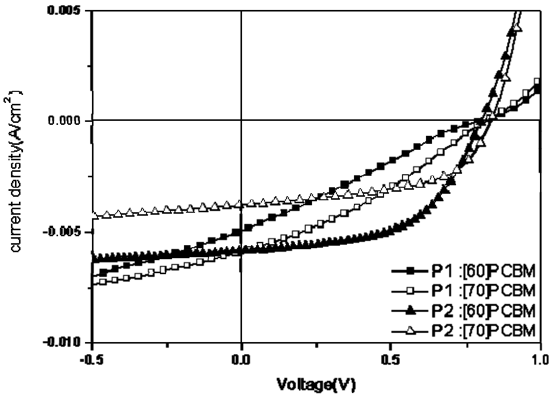


Fig. 2 *J-V* curves of polymers

Table II. Performances of solar cells

Polymer:Acceptor	V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE(%)
P1 : [60]PCBM	0.788	4.81	26.4	1.00
P1 : [70]PCBM	0.828	5.81	31.7	1.52
P2 : [60]PCBM	0.798	5.83	55.2	2.57
P2 : [70]PCBM	0.838	3.78	54.1	1.71

4. Conclusions

We successfully synthesized new conjugated polymers based on fluorene & carbazole units. The polymers have good solubility, relatively high molecular weight(about ~100,000), and thermal stability(5% weight loss temp. up to 280^{o}C). Photovoltaic cells based on these polymers blended with PCBM have revealed a power conversion efficiency of 2.57%. It is believed that further improvements from device fabrication should lead to even better performances.

References

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