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Efficient Bulk Heterojunction Photovoltaic Cells using Sublimable Transition Metal Complex as Photosensitizers

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ABSTRACT

Multilayer bulk heterojunction photovoltaic cells using chlorotricarbonyl rhenium (I) bis(phenylimino)acenaphthene (Re-DIAN) complex as photosensitizer were studied. The complex is sublimable, has lower band gap, good thermal stability and good processibility. It has broad absorption in UV-visible region. Therefore, Re-DIAN exhibits good photosensitising property for photovoltaic cells. Multilayer bulk heterojunction photovoltaic cells with simple structures were fabricated base on Re-DIAN complex. The active layer consists of a blend of Re-DIAN and fullerene that were co-deposited in the same layer by vacuum deposition. The photovoltaic properties of the devices were studied by irradiaton under AM1.5 simulated solar light. The effects of changing the co-deposition film thickness, amount of Re-DIAN photosensitizer, and hole transporting materials were studied.

INTRODUCTION

Many scientists are increasingly interested in high power and efficient solar cells based on both small organic molecules and conjugated polymers. It is because of the advantages of organic materials such as low fabrication costs, lightweight, tunability of the electronic band gap by chemical synthesis, and simple fabrication into flexible and thin film panels. However, many studies showed that organic solar cells in general exhibit much lower efficiencies of energy conversion compared to current inorganic silicon solar cells. One of the major barriers to fabricate efficient organic photovoltaic cells is the insufficient exciton dissociation at low bias and the low charge carrier mobility. In order to design an efficient organic photovoltaic cell, the efficiency for dissociation of excitons and the charge transport process should be improved.

A typical organic photovoltaic device consists of multilayer organic thin films. The photovoltaic performances in multilayer bulk heterojunction devices can be greatly improved compared to that in multilayer heterojunction devices [1]. The bulk heterojunction consists of a blend of two materials, which form interpenetrating networks that one of the materials serve as the electron donor and the other one serve as the electron acceptor. After Re-DIAN is excited, it transfers an electron to C_{60} immediately so that a pair of free hole and electron is generated. Then, these charges are transported to the corresponding electrodes, which results in the generation of photocurrent.

EXPERIMENTAL DETAILS

Synthesis of photosensitizer

Chlorotricarbonyl rhenium (I) bis(phenylimino)acenaphthene (Re-DIAN) complex [2] was used as the photosensitizer to fabricate photovoltaic cells [3]. DIAN was synthesized according to literature procedure [4]. The synthesis of Re-DIAN was carried out in the following procedure. A mixture of DIAN (1 g, 1 mmol) and rhenium pentacarbonyl chloride (0.92 g, 1 mmol) in 40 ml toluene was refluxed at 140 °C under nitrogen atmosphere for overnight. The mixture was cooled to room temperature and filtered off. The solid was washed with toluene and dried in vacuum. The structure of the Re-DIAN is shown in Figure 1. The complex can be conveniently purified by sublimation under high vacuum (280 °C at 10^{-5} mbar) [1].

Fabrication of photovoltaic devices

Photovoltaic devices with multilayer bulk heterojunction structure ITO/CuPc/Re-DIAN:C_{60}/C_{60}/Al were fabricated by vacuum sublimation. Copper phthalocyanine (CuPc) and fullerene (C_{60}) were used as the hole and electron transport materials, respectively. The thickness of both CuPc and C_{60} layers were kept at 10 nm. The active layer was fabricated by co-deposition of Re-DIAN and C_{60}. C_{60} can capture electrons more efficiently once excitons are formed. The thickness of Re-DIAN:C_{60} mixed layer was varied from 25 to 100 nm. Aluminium (thickness = 40 nm) was used as the cathode. The photovoltaic properties of the devices were studied by irradation under AM 1.5 simulated solar light (100 mW/cm^2) .The device active area is 0.13 cm^2.

RESULTS AND DISCUSSION

Photovoltaic performances with different thickness of co-deposition film and amount of Re-DIAN photosensitizer in mixed layer in the device structure ITO/CuPc(10 nm)/Re-DIAN:C_{60} [1:1] (25, 50, 75, 100 nm)/C_{60}(10 nm)/Al(40 nm) were studied. Their current-voltage (*I-V*) characteristics are summarized in Table I. When the thickness of the mixed layer was 25 nm, highest power conversion efficiency (η_p) was observed in the device with 30% photosensitizer in mixed layer. For devices with active layer thickness 50 nm, 75 nm and 100 nm, maxima η_p were observed when the amount of photosensitizer were 50%. These results clearly show that the amount of photosensitizer and electron transport molecules may strongly affect the balance between the photon absorption, exciton formation, dissociation, and charge transport processes. In order to improve the devices performance, determining exciton diffusion length and optimising the thickness of each layer should be achieved.

Table I. Effect of different thickness of mixed layer and amount of photosensitizer in mixed layer in device structure ITO/CuPc(10 nm)/Re-DIAN:C_{60}(25, 50, 75, 100 nm)/C_{60}(10 nm)/Al(40 nm) irradiated with AM1.5 simulated solar light.

Thickness of mixed layer (nm)	Amount of photosensitizer in mixed layer (%)	I_{sc} [a] (mA/cm^2)	V_{oc} [b] (V)	FF [c]	η_p [d] (%)
25	10	4.13	0.37	0.49	0.74
	30	4.03	0.42	0.45	0.76
	50	3.02	0.47	0.33	0.46
50	10	2.67	0.37	0.40	0.40
	30	2.72	0.44	0.52	0.62
	50	5.07	0.51	0.51	1.29
75	10	1.48	0.30	0.39	0.17
	30	2.93	0.46	0.43	0.58
	50	4.34	0.42	0.42	0.76
100	10	2.29	0.30	0.46	0.31
	30	0.03	0.30	0.12	0.001
	50	3.23	0.46	0.32	0.47

[a] Short circuit current

[b] Open circuit voltage

[c] Fill factor = $(I_{max} \times V_{max})/(I_{sc} \times V_{oc})$, where I_{max} and V_{max} corresponding to the point of maximum power output

[d] Power conversion efficiency = $(I_{sc} \times V_{oc} \times FF)/P$, where P is the incident light power.

The effect of changing the hole transporting materials (HTMs) is summaried in Table II. The structure of multilayer bulk heterojunction device is ITO/HTM(10 nm)/Re-DIAN:C_{60}[1:1](50 nm)/C_{60}(10 nm)/Al(60 nm). When (N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine) (NPB), 1,1'-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), N,N'-diphenyl-N,N'-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (TPD) and 4,4',N,N'-dicarbazolyo biphenyl (CBP) were used as HTMs, the η_p of these devices were 0.08%, 0.05%, 0.03%, and 0.001%, respectively. It is well-known that the oxidation potential or ionization potential of HTM can be varied by modifying the chemical structures. The ionization potentials of HTMs reported in the literature are: NPB (5.1-5.4 eV) [5], TAPC (5.4 eV) [5], TPD (5.3-5.5 eV) [5], CBP (6.0-6.3 eV) [6-7], CuPc(5.0 eV) [8], ZnPc(4.7 eV) [8]. Thus, different HTMs will yield different energy barriers at ITO/HTM interface [5]. Also, the hole carrier mobility may strongly affect the photovoltaic performance. When copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) were used as HTMs, the η_p were 1.29% and 0.59%, respectively. These two photovoltaic cells show greatly improved performance compared to the devices mentioned above. The metallophthalocyanines may strongly affect the photon absorption and exciton diffusion in photovoltaic devices.

The external quantum efficiency (η_q) is given by the ratio of the number of electrons flowing through external circuit to the number of incident photons. The η_q is given by $\eta_q = (1240 \times J_\lambda[\mu A/cm^2]) / (\lambda[nm] \times P_\lambda[W/m^2])$. This shows that the quantum efficiency can be calculated from a measurement of the short circuit current at a given wavelength with input radiant power

P_λ [9]. Figures 1 and 2 show the absorbance and η_q of Device 3 and 5. Figure 1 shows the photocurrent response of device structure ITO / TPD(10 nm)/ Re-DIAN:C_{60}[1:1](50 nm) / C_{60}(10 nm) / Al(60 nm) at different wavelength. The absorption spectrum of the device is shown for comparison. This device has the maximum η_q (1.9%) at 510 nm. The photocurrent action spectrum agrees well with the corresponding Re-DIAN absorption spectrum. The UV-visible absorption spectrum of Re-DIAN thin film shows broad absorption band that covers most of the visible region in the range between 430 and 600 nm. The maximum absorption peak at around 500 nm is assigned to be the MLCT [d_π(Re) to π^*(DIAN)] electronic transition. Therefore, Re-DIAN may be a promising candidate as photosensitizer in photovoltaic cells. Figure 2 shows the photocurrent response of the device structure ITO / CuPc(10 nm) / Re-DIAN:C_{60}[1:1] (50 nm) / C_{60}(10 nm) / Al(60 nm) at different wavelength. This device has the maximum η_q (25%) at 620 nm. The photocurrent action spectrum agrees well with the corresponding CuPc absorption spectrum. This result clearly shows that the CuPc:C_{60} junction also contributes to the photovoltaic process.

Table II. Effect of different hole transporting materials (HTMs) in device structure ITO/HTM(10 nm)/Re-DIAN:C_{60}[1:1](50 nm)/C_{60}(10 nm)/Al(60 nm) irradiated with AM1.5 simulated solar light.

Device	HTM	I_{sc} (uA/cm^2)	V_{oc} (V)	*FF*	η_p (%)	η_q at 510nm (%)
1	NPB	384	0.72	0.29	0.08	3.50
2	TAPC	297	0.58	0.31	0.05	1.52
3	TPD	203	0.48	0.36	0.03	1.89
4	CBP	14	0.34	0.26	0.001	0.45
5	CuPc	5067	0.51	0.51	1.29	5.42
6	ZnPc	2412	0.48	0.51	0.59	4.31

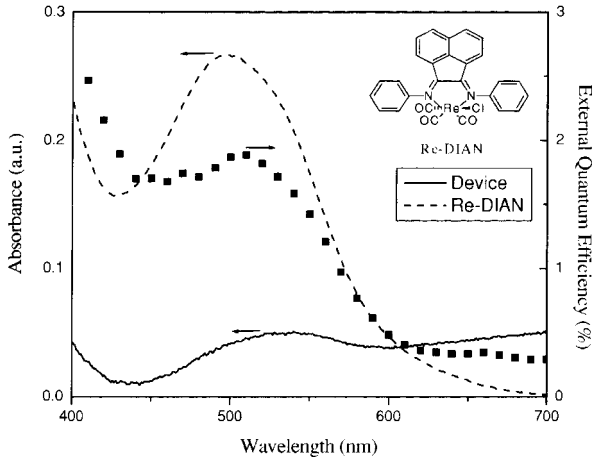

Figure 1. Structure of Re-DIAN and plot of external quantum efficiency and the absorbance of the device ITO/TPD(10 nm)/Re-DIAN:C_{60}[1:1](50 nm)/C_{60}(10 nm)/Al(60 nm) and Re-DIAN thin film at different wavelength.

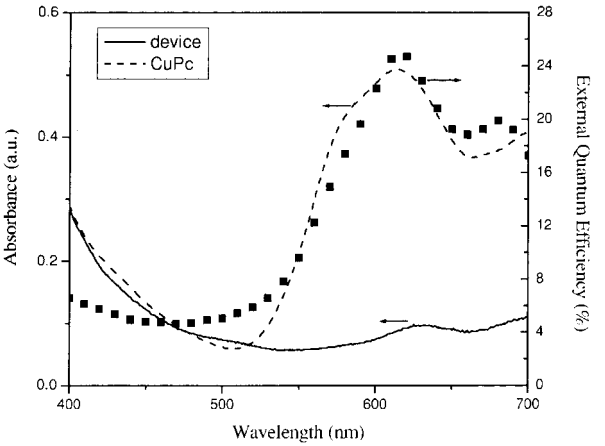

Figure 2. Plot of external quantum efficiency and the absorbance of the device ITO/CuPc(10 nm)/Re-DIAN:C_{60}[1:1](50 nm)/C_{60}(10 nm)/Al(60 nm) and CuPc thin film at different wavelength.

CONCLUSIONS

Chlorotricarbonyl rhenium (I) bis(phenylimino)acenaphthene (Re-DIAN) complex was synthesized. The complex was used as the photosensitizers to fabricate photovoltaic cells. Efficient multilayer bulk heterojunction photovoltaic devices were fabricated based on Re-DIAN complex by vacuum sublimation. Their photovoltaic properties were studied under AM 1.5 simulated solar light illumination respectively. The amount of photosensitizer and electron transport molecules may strongly affect the balance between the photon absorption, exciton formation, dissociation, and charge transport processes. Photovoltaic performances with different HTMs were studied. Different energy barriers at ITO/HTM interface and the hole carrier mobility may strongly affect the photovoltaic properties.

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