Study of Photovoltaic Performance of Host-Guest System Comprising Photoluminescent Polyurethane and Rhodamine B Dye

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ABSTRACT: The photovoltaic property of Rhodamine B dye embedded into Poly(tolyl-1,1'-binaphthyl carbamate) (PU_1) and poly(hexamethylene-1,1'-binaphthyl carbamate) (PU_2) matrices have been evaluated using host-guest approach. The photoactive layer comprising photoluminescent polymer matrix (PU_1 or PU_2), Rhodamine B and TiO_2 nanoparticles were prepared by spin casting method. The power conversion efficiency (PCE) the photovoltaic devices based on PU_1 and PU_2 matrices were found to be 0.043% and 0.029%, respectively. PCE of the photovoltaic devices were limited due to low lying highest occupied molecular orbital of PU_1 and PU_2 polymers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3316–3321, 2011

Key words: host-guest; polyurethanes; spin coating; power conversion efficiency; conjugated polymers; rhodamine B

INTRODUCTION

The use of photovoltaic technology to harvest the energy directly from sunlight is considered to be one of the most convenient ways to address growing global energy needs. Polymeric solar cells hold a great promise as an economically and environmentally friendly technology to use solar energy because of their simple fabrication processes and minimal material usage.[1–5] Initially, single layer photovoltaic devices based on dyes or polymers resulted limited power conversion efficiency (PCE) below 0.1%.[6] In 1986, a major breakthrough was realized by Tang, who introduced a double-layer structure of a p-and n-type organic semiconductor and PCE of 1% was achieved for the device.[7] This concept paved the way for many efficient donor-acceptor solar cells, including dye/dye, polymer/dye, polymer/polymer, polymer/fullerene, and polymer/inorganic semiconductor blends.[6,8–16] Notably, the improvements in device performance are strongly related to the balance between use of novel acceptor, donor, interface materials, and the processing conditions.[17–28] Polymeric solar cells have witnessed different model architectures and approaches, one of which includes the host-guest system. The basic idea is to form a system composed of three components: donor component, acceptor component, and the polymeric matrix. The host-guest approach has been used with success for various applications compared to other approaches for the following reasons: less interchain interaction, possibility of ordering in the matrix, increase in stability of the photoactive polymer, possibility of tuning of charge transfer by changing intermolecular distance, or dielectric permittivity of the host matrix.[29–31] A set of systems based on conjugated polymer-methanofullerene networks in polystyrene matrix may serve as an example. Photovoltaic behavior of soluble derivative of p-phenylene vinylene (MDMO-PPV), and a highly soluble methanofullerene, [6,6']-phenyl C_{61}-butyric acid methyl ester (PCBM), embedded into a polystyrene was studied and it exhibited PCE of 1.5%.[29] Luhman and Holmes reported a composite electron donor layer with host-guest approach consisting of a N,N'- bis-(naphthalene-1-yl)- N,N'-bis(phenyl)-benzidine (NPD) host doped with the phosphorescent guest fac-tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] where the presence of phosphor allows increase in exciton diffusion length. This leads to ∼ 80% improvement in PCE relative to devices containing an undoped donor layer.[32] The use of small molecules in organic solar cell is also growing rapidly although there possesses stability issue and dye molecules are one of the widely studied organic compounds in solar cells.[33] The formation of active photovoltaic interface between the elctropolymerized polypyrrole or

poly(N-methylpyrrole) and the Rhodamine B dye was studied by Uehara et al. and found PCE of $5.8 \times 10^{-3}\%$ only.[34] Ruankham et al. studied performance of ZnO dye sensitized solar cells (DSSC) with Eosin-Y, Rhodamine B, and crystal violet dyes as sensitizer.[35] It was reported that ZnO DSSC with Eosin-Y exhibited the best photoelectrochemical characteristics with an energy conversion efficiency of 0.42% compared to those with Rhodamine B and crystal violet that exhibited an energy conversion efficiency of 0.18 and 0.08%, respectively. Wu et al. studied surface morphology of TiO_2 films using ethylene glycol and ethylene glycol monomethyl ether and observed crack free microstructure for the film.[36] These films with binder possessed stronger ability to adsorb dye molecules and hence exhibited good photoelectrochemical properties. Syrrokostas et al. also demonstrated the dye-sensitized solar cells using TiO_2-thin films and Rhodamine B dye as sensitizer and studied the effect of paste storage on the photovoltaic properties of nanostructured thin films.[37] Many other reports give an account on the dye and TiO_2 based solar cells to achieve improvement in PCE.[6,20,38–40] In some earlier works, Chang et al. showed the utility of Rhodamine B dye doped polyurethane thin films in light amplification and this gives an idea of utility of such films in electronic applications.[41] But host-guest approach with photoluminescent host material and small molecule, that is, dye as guest is not properly addressed for solar cell applications. In our approach, we have tried to use photoluminescent polyurethane as host material and Rhodamine

B dye as guest for solar cells performance so that combination of both would offer easy way of fabricating solar cell by solution processing. Polyurethanes possess good film forming ability, which in turn provide ample opportunities of macroscopic ordering by mechanical stretching of host polymer. Moreover, polyurethanes offer good environmental stability to small organic molecules like Rhodamine B dye and improves overall photoactive sample quality.

In this article, we have studied photovoltaic characteristics of donor host-guest system of photoluminescent polyurethane and Rhodamine B composite using TiO_2 nanoparticles as acceptors. This system gives PCE of 0.043% and 0.029% for the system based on Poly(tolyl-1,1'-binaphthyl carbamate) (PU₁) and poly(hexamethylene-1,1'-binaphthyl carbamate) (PU₂).

EXPERIMENTAL

Chemicals and measurements

PU₁ and PU₂ were synthesized by the process reported elsewhere.[42] These two polymers were used as host materials in solar cell and photovoltaic properties of the same were studied.
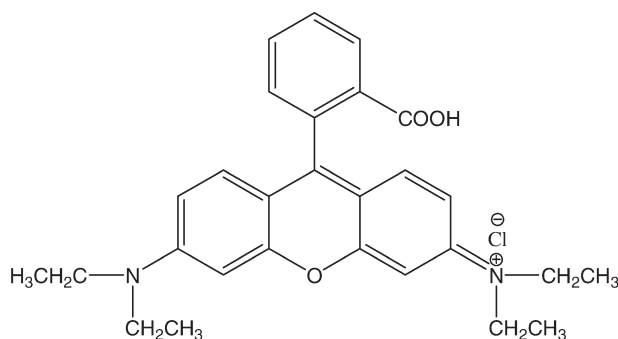
Poly(ethylene-dioxy-thiophene) : poly(styrene sulfonate), PEDOT : PSS, (Aldrich), Rhodamine B (Aldrich) TiO_2 nanoparticles, avg. size 5 nm, (Aldrich) were commercial products and used as received. All the solvents were properly purified before use by standard methods.
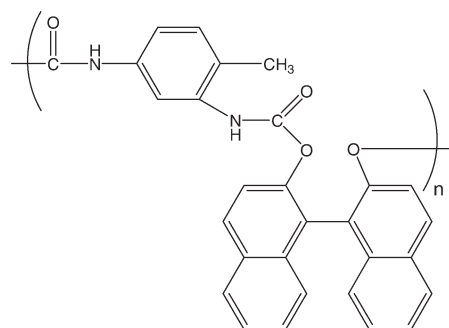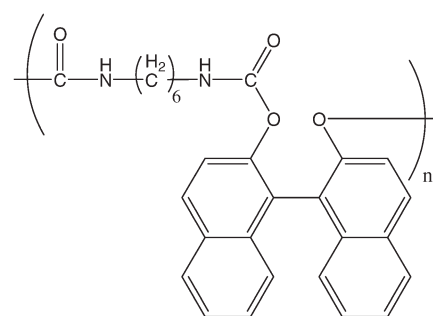
Poly(tolyl-1,1'-binaphthyl carbamate) (PU₁) poly(hexamethylene-1,1'-binaphthyl carbamate) (PU₂)

Rhodamine B (Rh B)

TABLE I
Physical Properties of PU_1 and PU_2

Polymer	Yield (%)	η_{inh} (dLg^{-1})	M_n	M_w	M_w/M_n	Degree of Polymerization (DP)
PU_1	86	0.24	14,563	32,798	2.25	33
PU_2	84	0.26	17,647	37,891	2.14	39

UV–visible absorption spectra were taken on a Shimadzu UV-2500 spectrophotometer. Photoluminescence (PL) spectra were recorded using Hitachi F-2500 FL Spectrophotometer. The inherent viscosity (η_{inh}) was determined using an Ubbelohde viscometer in N,N-dimethylacetamide (DMAc) at 30 ± 0.1°C with 0.5 g/dL polymer solution. The electrochemical cyclic voltammetry was conducted on a Sycopel AE-W2-10 electrochemical workstation with indium tin oxide (ITO) coated glass, Pt and Ag/Ag$^+$ as working electrode, counter electrode, and reference electrode, respectively, in a 0.1M lithiumperchlorate (LiClO$_4$) acetonitrile solution. Thermal analysis was performed using Universal V4.2E TA instrument with heating rate of 10°C per minute in nitrogen atmosphere. Molecular weights of polymers were measured by gel permeation chromatography (GPC) using 410 Waters differential refractometer with the Flow rate of 1 mL/min. The solvent used in GPC was tetrahydrofuran (THF) and polystyrene was used as standard.

Fabrication and characterization of polymer solar cell

Solar cells were fabricated with the structure of ITO/PEDOT : PSS/PU_1 or PU_2 + Rhodamine B : TiO$_2$ nanoparticles/Al. A thin layer PEDOT : PSS was spin cast on precleaned ITO coated glass from a PEDOT : PSS (Aldrich) aqueous solution and dried in vacuum oven at 120°C for 20 min. The thickness of PEDOT : PSS layer was about 60 nm. The photosensitive blend layer comprising polyurethane and Rhodamine B as host-guest mixture as well as dispersed TiO$_2$ nanoparticles in THF was spin-coated on the ITO/PEDOT : PSS electrode and dried at 75°C for 30 min. Polyurethane and Rhodamine B, the host-guest mixture were taken in 3 : 1 (w/w) ratio whereas TiO$_2$ nanoparticles was taken in 2 : 1

(w/w) ratio to the composite weight of host-guest mixture. This composition gives stable film when 2% (w/v) host-guest mixture in THF is spin coated onto anode. The thickness of the photosensitive layer was about 90 nm, which was spin cast at the rotating speed of 1200 rpm for 60 s. Then the metal cathode of Al was deposited on the polymer layer by vacuum evaporation under (4×10^{-5} Pa). The effective area of one cell is about 3 mm^2. The current-voltage (I–V) measurements of the device were conducted on a computer-controlled Keithley 2420 Source Measure Unit. A Xenon lamp with AM1.5 filter (Newport oriel 150 W) was used as the white light source, and the optical power at the sample was 100 mW/cm^2.

RESULTS AND DISCUSSION

Synthesis, characterization, and study of the thermal and electrochemical properties of PU_1 and PU_2 are reported elsewhere.[42] The racemic 1,1'-binaphthol was used for preparation of host polyurethane because of high stability and ease of synthesis compared to its R- or S-enantiomers. Polyurethanes are generally insulator materials but presence of conjugated binaphthyl group imparts semiconducting property to PU_1 and PU_2. Physical properties of the polymers are summarized in Table I. The electrochemical band gap, highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) energy levels obtained from cyclic voltammetry analysis, are listed in Table II. The nearly similar onset oxidation potential and band gap observed for PU_1 and PU_2 are resulted due to presence of same binaphthyl chromophore with similar donor ability and band gap. The electrochemical band gap for PU_1 and PU_2 found to be 3.19 and 3.17 eV nearly matching the optical band gap values. The

TABLE II
Electrochemical Onset Potentials and Band-Gap of the Polymer Films

Polymers	φ_{ox} (V vs. Ag/Ag$^+$)/ E_{HOMO} (eV)	φ_{red} (V vs. Ag/Ag$^+$)/ E_{LUMO} (eV)	E_g^{ec} (eV)	E_g^{opt} (eV)[a]
PU_1	1.31/−6.02	−1.88/−2.83	3.19	3.40
PU_2	1.41/−6.12	−1.76/−2.95	3.17	3.39

[a] The optical band gap was obtained from empirical formula, $E_g = 1240/\lambda_{edge}$, in which λ_{edge} is the onset value of the absorption spectrum in the longer wavelength direction.
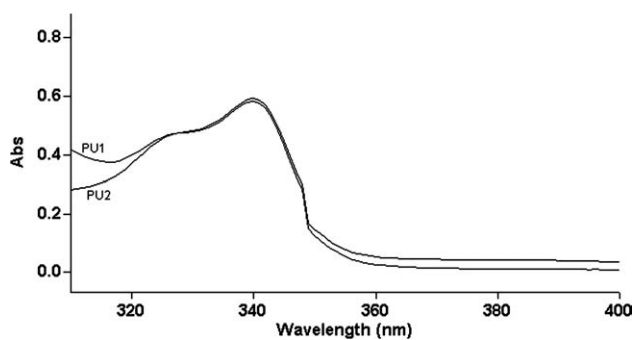
Figure 1 UV–visible absorption spectra of PU$_1$ and PU$_2$ in solution.

optical properties of PU$_1$, PU$_2$, and Rhodamine B as well are discussed and photovoltaic performance of the polymer/Rhodamine B (host-guest approach) based solar cell devices are reported herein.

Optical properties

UV-visible absorption

The UV–vis absorption spectra of the polymers, PU$_1$ and PU$_2$ for 0.05% solution in THF are reported in Figure 1. The spectra display the maximum absorption for PU$_1$ and PU$_2$ at the wavelength of 339 and 340 nm, respectively, that is due to π-π^* transition originating from the binaphthyl moieties. However, π-π^* transition results the maximum absorption of Rhodamine B to be 554 nm as shown in UV–vis absorption spectra (Fig. 2).

Photoluminescence

PL spectra provide good deal of information on the electronic structure of the conjugated polymers. The fluorescence spectra of the polymers in THF (0.05%) solution exhibited emission maxima at 379 nm with
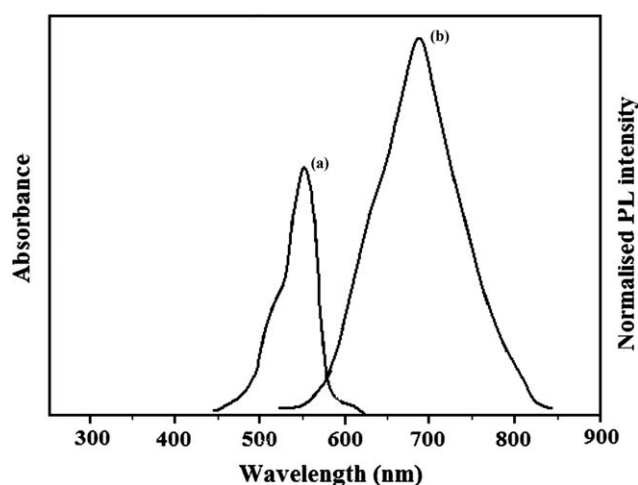

Figure 2 (a) UV–visible absorption spectrum and (b) PL spectrum of Rhodamine B in solution.
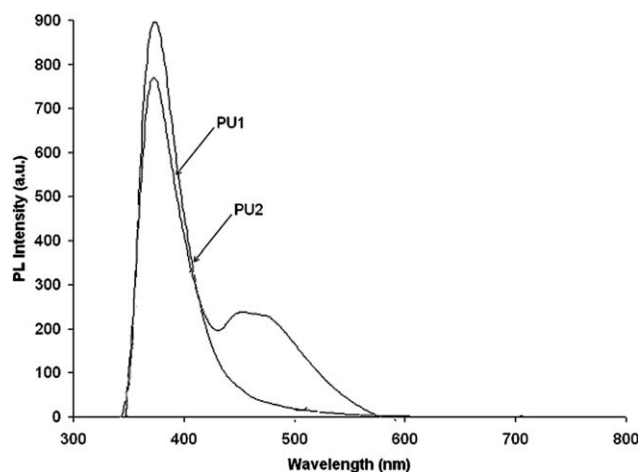

Figure 3 PL spectra of PU$_1$ and PU$_2$ in 0.05% THF solution.

a shoulder peak at 435 nm for PU$_1$ and 380 nm for PU$_2$, showing emission at nearly blue region. This may be attributed to the recombination of the excitons in the main chains with binaphthyl unit being present as the π-conjugated component in the polymers. All the spectra of the polymers are shown in Figure 3. The PL emission maximum found for Rhodamine B is 690 nm when excited at λ_{max}, that is, 554 nm (Fig. 2).

Photovoltaic properties

The photovoltaic properties of the host-guest system have been studied by fabricating the device with the bulk heterojunction structure using polyurethane and Rhodamine B dye composite as active material and TiO$_2$ as acceptor. This hybrid polymer-inorganic solar cells give rise to photovoltaic current via following processes.[43] On photon absorption by the conjugated polymer, an electron is excited from the HOMO to the LUMO. This electron hole pair relaxes with a binding energy between 0.1 and 1.4 eV, which is known as an exciton. The bound excitons
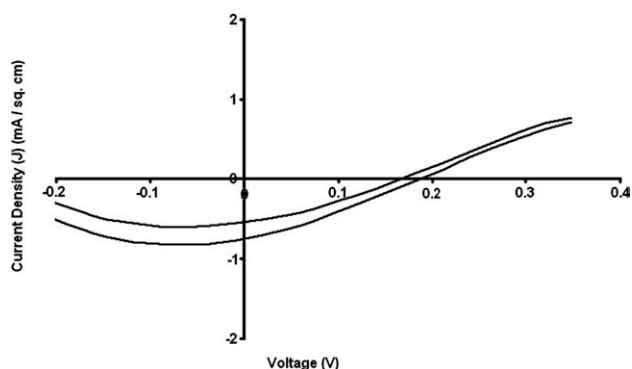

Figure 4 J-V Characteristics of (a) PU$_1$ + Rhodamine B (b) PU$_2$ + Rhodamine B based photovoltaic devices.

Photovoltaic Parameters of Devices based on PU$_1$ and PU$_2$ with Rhodamine B

Host-guest system	V_{OC} (V)	I_{SC} (mA/cm^2)	FF	PCE, η_e (%)
PU$_1$ + Rhodamine B	0.19	0.81	0.28	0.043
PU$_2$ + Rhodamine B	0.17	0.56	0.30	0.029

migrate to an interface across the donor and acceptor and get dissociated at the interface due to the effect of internal field. Thus electrons are collected at Al electrode through acceptor and holes are collected at ITO via hole injecting PEDOT : PSS layer causing voltage difference in two electrodes. The charges are transported primarily by drift caused by the built-in-field. The current that reaches the electrodes with no applied field is known as the short-circuit current and the maximum potential generated by the device is known as the open-circuit voltage. Figure 4 shows the *J-V* Characteristic curve of the fabricated solar cells under the illumination of AM 1.5, 100 mW/cm^2, and photovoltaic properties obtained from the curve are listed in Table III. The device parameters were calculated using the following equations:

$$FF = I_p \cdot V_p / I_{SC} \cdot V_{OC} \qquad (1)$$

$$\eta \ (\%) = FF \cdot I_{SC} \cdot V_{OC} / P_{in} \times 100 \qquad (2)$$

where V_{OC} is the open-circuit voltage, I_{SC} is the short-circuit current, FF is the fill factor (FF), η_e is the PCE, P_{in} is the intensity of the white light and V_P, and I_P are the voltage and the current at the maximum power point of the *J-V* curve.

The hybrid polymer-inorganic solar cells based on the host-guest system with the structure ITO/PEDOT : PSS/PU$_1$ + Rhodamine B : TiO$_2$ nanoparticles/Al exhibited PCE (η_e) of 0.043% with short circuit current I_{SC} = 0.81 mA/cm^2 and open circuit voltage V_{OC} = 0.19 V. The FF of the device was calculated to be 0.28. Whereas PCE for the device structure ITO/PEDOT : PSS/PU$_2$ + Rhodamine B : TiO$_2$ nanoparticles/Al was calculated to be 0.029%, with I_{SC}, V_{OC}, and FF being 0.56 mA/cm^2, 0.17 V, and 0.30, respectively.

The photovoltaic devices based on polyurethanes, namely, PU$_1$ and PU$_2$ as host and Rhodamine B dye as guest were fabricated so that the host molecules gets well dispersed in polymer matrix to give uniform films. Simple physical mixing of polyurethane and dye does not ensure significant change in physicochemical properties but offers better stability to the film by noncovalent interaction, that is, hydrogen bonding or vander waal's force between host and guest molecules. Generally, small organic molecules bear stability issue compared to polymers as their low thermal stability may cause recrystallizion

or diffusion into one another, owing to repeated heating, and cooling condition.[44] The Rhodamine B dye thus will receive better thermal stability when embedded into polyurethane matrix. Moreover, the combination of optically active photoluminescent host polymer with dye molecule (guest) ensures wide range of absorption ability by the active host-guest material over the solar spectrum thereby providing good option to choose photoluminescent host material to fabricate a solar cell device. Thus efficient photon absorption as well as increase in PCE in such devices is desired. However, power conversion efficiencies shown by both the host-guest system devices are very low. The reason can be explained with the help of energy level diagram shown in the Figure 5 The collection of holes at the anode is limited due to high energy barrier (> 0.82 eV) between low lying HOMO level of polyurethanes and hole injecting PEDOT : PSS level. This will restrict the charge separation and migration to the two opposite electrodes and results in decrease of V_{OC} and PCE as well.[21,33] Moreover, it is apparent that the PCE of the device based on PU$_1$ matrix showed improvement in PCE compared to that of PU$_2$ although all the other parameters for the fabricated devices were the same. This could also be explained from energy level diagram as HOMO of PU$_2$ is lying 0.1 eV lower to that of PU$_1$ thereby causing relatively hindered hole migration to hole injecting layer. This shortfall of inefficient charge collection at the anode could be solved by incorporating intermediate energy level between the
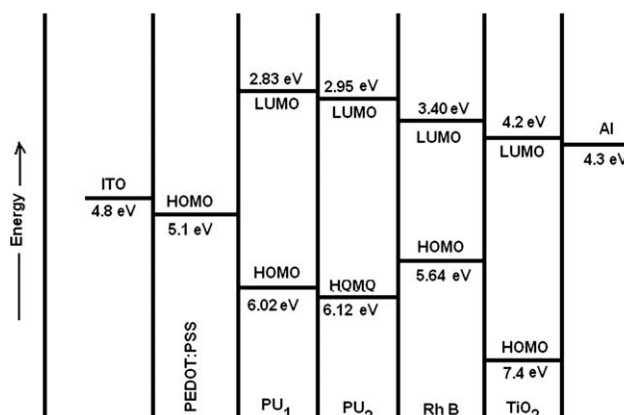

Figure 5 Schematic energy level diagram for photovoltaic devices, with energy levels in eV relative to vacuum.

polymer and PEDOT : PSS layer. The PCE solar cell may be increased manifold by optimization. Polymer purity, polymer to acceptor ratio, use of processing additives, solvent annealing are the some of the factors, which affects the efficiency (η_e) of the PSC.[45–48]

CONCLUSIONS

Polymer-inorganic bulk heterojunction photovoltaic devices using host-guest approach were fabricated with photoluminescent polyurethanes (PU_1 and PU_2) as host and Rhodamine B dye as guest. The wide range of absorption ability of the composite system is the basis of taking this host-guest system for the device application. TiO_2 nanoparticles dispersed within the host-guest system were used as the electron acceptor material. The device performance of the solar cell based on PU_1 polymer matrix showed better PCE of 0.043% compared to that of PU_2 based cell with PCE 0.029%, which is attributed to difference in their respective HOMO energy levels. The overall PCE of the devices have been found low due to low lying HOMO levels of polyurethanes (host polymer) hindering the efficient charge collection at cathode. The device performance could be improved by multiparametric optimization so that polymeric solar cells find the new realm of application for clean and renewable energy.

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