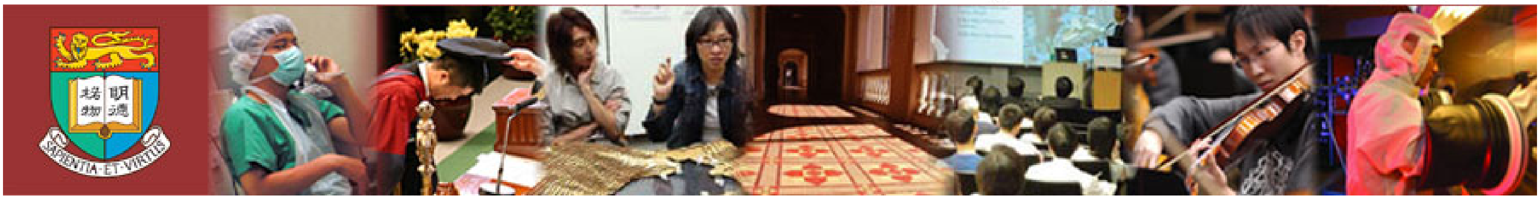

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| **Author(s)** | **Hui, CS; Wong, HL; Kwong, CY; Chan, WK; Djuriši, AB** |
| **Citation** | **Organic photovoltaics IV, San Diego, California, USA, 7-8 August 2003, v. 5215, p. 254-261** |
| **Issued Date** | **2004** |
| **URL** | **http://hdl.handle.net/10722/45703** |
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# Fabrication of Photovoltaic Cell From Rhenium Containing Polymer

Ching Sum Hui[1], Hei Ling Wong[1], Chung Yin Kwong[2], Wai Kin Chan[1]*,
Aleksandra B. Djurišić[2,3]
[1]Department of Chemistry, the University of Hong Kong, Pokfulam Road,
Hong Kong
[2] Department of Electrical and Electronic Engineering, the University of Hong Kong,
Pokfulam Road, Hong Kong
[3] Department of Physics, the University of Hong Kong, Pokfulam Road, Hong Kong

## ABSTRACT

Photovoltaic devices were fabricated using rhenium bis(arylimino)acenaphthene (DIAN) complex containing poly(*p*-phenylenevinylene). These polymers absorb strongly in the visible region at ca. 440-550 nm. In addition, this type of transition metal based polymers have been shown to exhibit large photo-sensitivity due to the presence of the rhenium complex, which has a relatively long-lived Metal-to-Ligand Charge Transfer (MLCT) character. By using this type of polymers, the metal content can be adjusted easily by simply changing the monomer feed ratio. Moreover, the excited state properties and electronic absorption properties can be modified by varying the structure of the diimine ligand coordinated to the metal. This approach allows us to fine-tune the absorption spectra of the polymers by employing different types of rhenium complex derivatives. PEDOT:PSS and PTCDI were used as the hole and electron transport layers, respectively. The ITO/PEDOT:PSS/DIAN-PPV/PTCDI/Al devices were found to exhibit photovoltaic response under the illumination of AM1 solar radiation. The short-circuit current $I_{sc}$, open-circuit voltage $V_{oc}$, and the fill factor $FF$ were measured to be 38 μA/cm$^2$, 0.93 V and 0.21 respectively. Another photovoltaic device was prepared with the structure ITO/PEDOT:PSS/DIAN-PPV:$TiO_2$/PTCDI/Al and its photovoltaic properties were studied. The presence of $TiO_2$ will assist the electron transport of the DIAN-PPV to the PTCDI, in which the electrons can be collected at the aluminium electrode. The short-circuit current $I_{sc}$, open-circuit voltage $V_{oc}$, and the fill factor $FF$ were measured to be 51 μA/cm$^2$, 1.18 V and 0.12 respectively. It was observed that the power conversion efficiency of photovoltaic devices related closely to the rhenium content and the structure of the rhenium complex used.

**Keywords**: poly(*p*-phenylenevinylene), rhenium, bis(arylimino)acenaphthene, photovoltaic

## 1. INTRODUCTION

Poly(*p*-phenylenevinylene)s (PPV) and its derivatives are among one of the most studied conjugated polymers because of their potential applications of optoelectronic devices[1,2]. Poly(*p*-phenylenevinylene) was the first conjugated polymer that shows electroluminescence (EL) activities[3,4] which emits light in the green–yellow region of the visible region. Besides, the colour can be modified by incorporating electron donating and electron withdrawing substituents on the polymer backbone or by limiting the conjugated length of the chromophore. Today, PPV and its derivatives play an important role in light-emitting diodes (LEDs) as they have good film forming properties, high photoluminescence and electroluminescence efficiencies. Recently, they served as the active materials in photodiodes[5,6], photodetectors, and light-emitting electrochemical cells[7,8]. The use of d$^6$ transition metal complexes incorporated in poly(*p*-phenylvinylene)s has been gaining more attention because of the flexibility in structure design and modification. The light emitting properties can be fine tuned by using different transition metals and ligands[9].

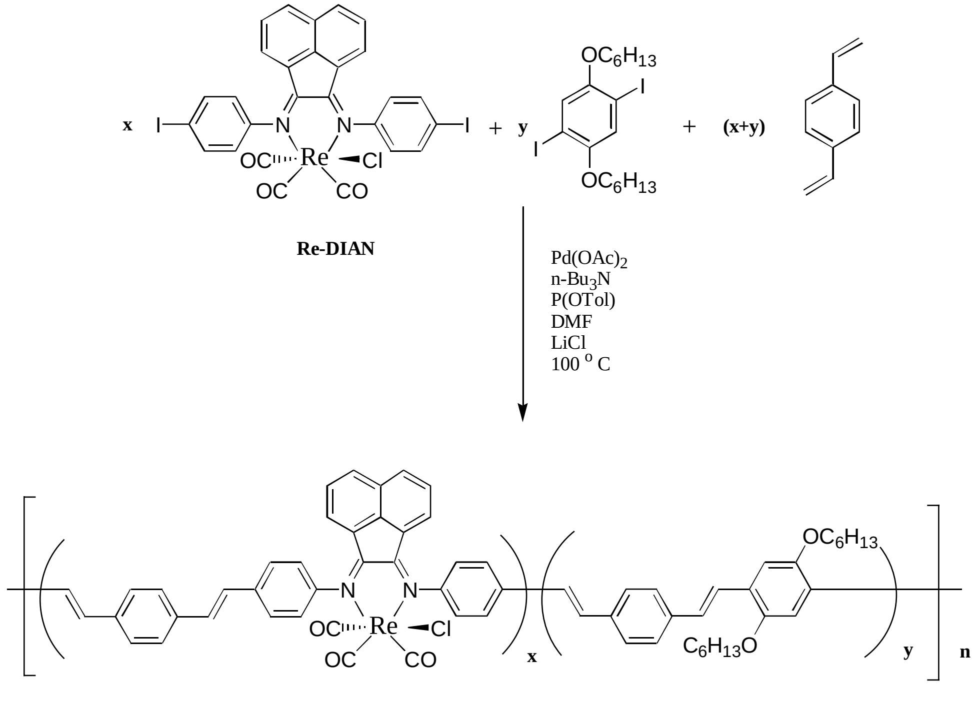
Our group has developed a series of poly(*p*-phenylenevinylene) (PPV) incorporated with rhenium DIAN complex. Rhenium DIAN complex shows a rhenium(I) d$\pi$ to $\pi^*$ (diimine) metal-to-ligand charge transfer (MLCT)

Organic Photovoltaics IV, edited by Zakya H. Kafafi, Paul A. Lane, Proceedings of SPIE
Vol. 5215 (SPIE, Bellingham, WA, 2004) · 0277-786X/04/$15 · doi: 10.1117/12.505328

transition in the visible spectral region at ca. 440-550 nm. It is expected that PPV functionalized with rhenium DIAN complex will show interesting photosensitization properties and the polymer main chain may act as charge transport units. Therefore, no external charge carrying species is needed for the photosensitization process. The photoconductivity of DIAN-PPV can be facilitated by the rhenium diimine complex moiety. A three layered photovoltaic device based on DIAN-PPV with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) as hole transporting layer and 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) as the electron transporting layer was prepared and its photovoltaic properties were studied. The polymer doped with titanium oxide ($TiO_2$) nanoparticles was also used as the active material in the device.

## 2. RESULTS AND DISCUSSIONS

The rhenium containing PPVs were synthesized by the palladium catalyzed Heck coupling reaction[10]. Scheme 1 shows the synthetic route of DIAN-PPV **1-3**. *p*-Divinylbenzene was copolymerized with different proportions of monomer **Re-DIAN** and 1,4-dihexoxy-2,5-diiodobenzene to produce DIAN-PPV **1-3**. Excess lithium chloride (LiCl) was used the spectator ions in the reaction mixture to suppress the displacement of chloride by iodine. LiCl was chosen as it showed no interference on other palladium catalyzed reactions. Distilled DMF was used as the solvent. Palladium (II) acetate, tri-*n*-butylamine and tri-*o*-tolylphosphine were used the catalysts for the reaction. The incorporation of 1,4-dihexoxy-2,5-diiodobenzene into the PPV main chain is to enhance the solubility of the resulting polymers. Table 1 summarizes the physical properties of DIAN-PPV **1-3**.



DIAN-PPV **1-3**

**Scheme 1**. Synthesis of DIAN-PPV **1-3**.

**Table 1**. Physical properties of the DIAN-PPV **1-3**.

| **DIAN-PPV** | x | y | Yield (%)[a] | $T_d$ (°C )[b] | $M_w$[c] (GPC) | PD[d] |
|---|---|---|---|---|---|---|
| **1** | 0.1 | 0.9 | 40.4 | 446 | 9196 | 1.55 |
| **2** | 0.3 | 0.7 | 56.0 | 450 | 96392 | 2.43 |
| **3** | 0.5 | 0.5 | 81.4 | 319 | 79147 | 1.66 |

[a] The yield was calculated on the basis of the polymer obtained after washing with methanol.
[b] The decomposition temperatures were measured under a nitrogen atmosphere.
[c] NMP was used as the eluent and the molecular weight was calculated against polystyrene narrow standards.
[d] Polydispersity.

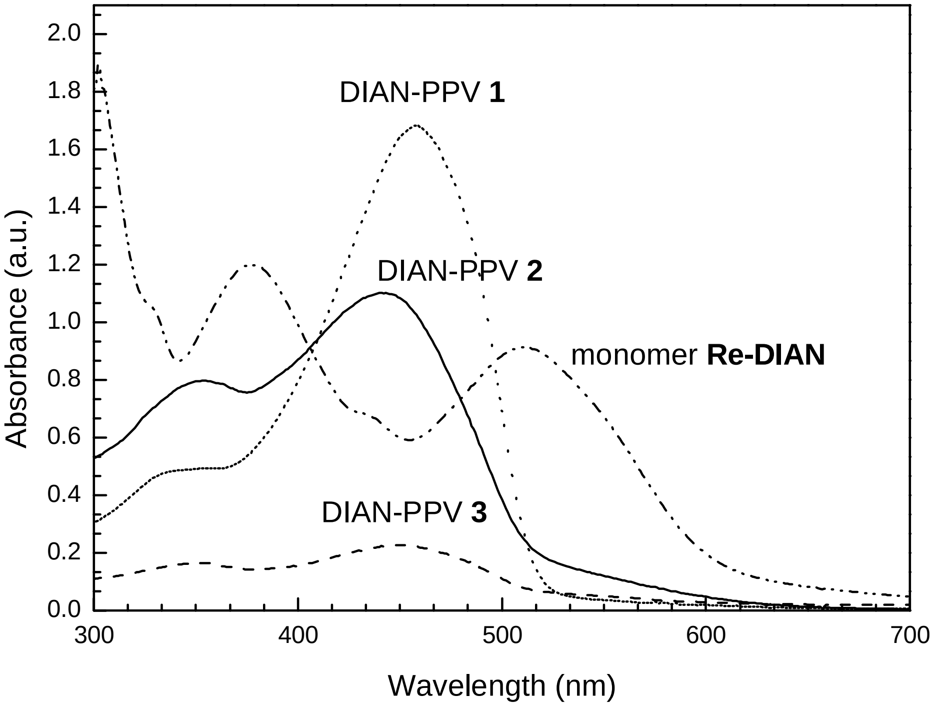


**Figure 1**. UV-vis absorption spectra of monomer and DIAN-PPV **1-3** in $CHCl_3$ solution.

Figure 1 shows the UV-vis spectra of monomer and DIAN-PPV **1-3** in $CHCl_3$ solution. The UV-vis spectrum of monomer shows two absorption peaks centered at 376 and 510 nm, which are assigned to the intraligand $\pi \rightarrow \pi^*$ transition the diimine ligand and the MLCT [$d\pi$ (Re) $\rightarrow \pi^*$ (diimine ligand)] transition of rhenium complex. The extinction coefficient of monomer is 5260 $dm^3mol^{-1}$ $cm^{-1}$, which is a typical value for MLCT transition. The UV-vis spectra of DIAN-PPV **1-3** also show strong MLCT absorption bands at about 440-460 nm. In general, it was observed that the absorption maxima of these bands shifted to shorter wavelengths when the metal content was increased. This is because the bulky metal complexes on the main chain may inhibit an efficient overlapping of the π-orbitals and thus increase the energy of the conjugated system. When the rhenium content in the polymer is increased, the absorption intensity between MLCT band and $\pi \rightarrow \pi^*$ band of PPV become more comparable. In addition, all the polymers show absorption bands at about 360 nm, which is attributed to the $\pi \rightarrow \pi^*$ electronic transition of the conjugated PPV backbone.

The photoconducting properties of DIAN-PPV **1-3** were studied by using an argon laser (488 nm) as the light source. The thin films were prepared by dissolving DIAN-PPV into chloroform and casting on ITO coated glass slide. The typical thickness of the polymer film was 0.5-1 μm. Rhenium(I) diimine was shown to be a good photosensitizer as it processes the MLCT character[11]. Moreover, the conjugated systems in PPV backbone will assist the charge carrying processes. The effect of metal complex in the PPV main chain on the photoconductivity was investigated. A plot of quantum yield as the function of the electric field strength for DIAN-PPV **1-3** is shown in Figure 2. DIAN-PPV **2** had the highest quantum yield because there was a balance in the amount of rhenium complex moiety and the distribution and effectiveness of PPV conjugated units. It was proved that the amount of photosensitizing rhenium complexes was not the sole factor to determine the photosensitivity. The presence of charge transporting species was also essential to the photogeneration process.

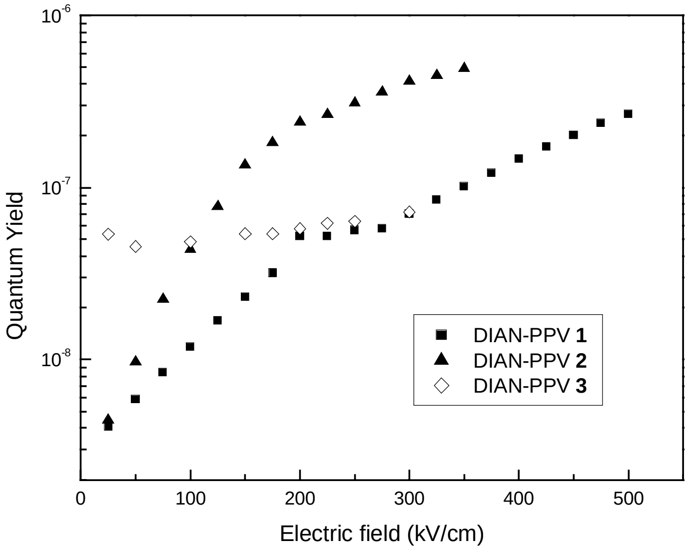


**Figure 2**. Plot of the quantum yield as the function of the electric field strength for DIAN-PPV **1-3**.

DIAN-PPV **1-3** were used as the polymeric materials in photovoltaic experiments with the structure ITO/PEDOT:PSS/DIAN-PPV/PTCDI/Al and their photovoltaic properties were studied. The ITO glass slides were treated by ozone to remove the remaining organic residue. PEDOT:PSS (25 nm) was spin-coated on ITO glass slide[12] and baked for 5 mins. The DIAN-PPV (40 nm) was dissolved in chloroform and spin-coated on PEDOT:PSS surface. A thin layer of PTCDI (25 nm) was evaporated on the polymer, which was followed by a layer of aluminium electrode (130 nm). The structure of the device is shown in Figure 3.

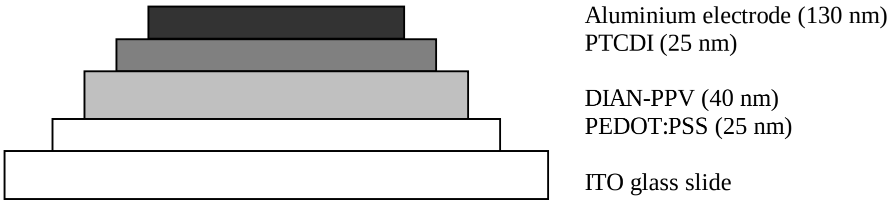
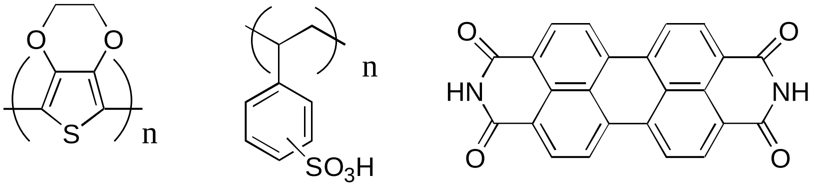


**Figure 3**. Structure of device for photovoltaic measurement.

Poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) and 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) in these devices were used as hole and electron transporting layer, respectively. The structures of PEDOT:PSS and PTCDI are shown in Figure 4. PEDOT:PSS[13,14] is widely used as a hole injection polymer atop the transparent indium tin oxide (ITO). It smoothens the anode surface and prevents the direct contact between ITO and the polymer in which the work function of ITO varies considerably with surface treatment[15]. PEDOT:PSS can provide high work function (5.1 eV) for hole injection to match the position of the valence band edge in the polymer. Previous studies showed that PEDOT:PSS/PPV device could improve the exciton dissociation[16] because when the device was illuminated through the PEDOT:PSS electrode, charges were collected independently of where in the device the incident light was absorbed. This facilitates the transport of electrons through PEDOT:PSS/PPV film to the aluminium electrode. 3,4,9,10-Perylenetetracarboxylic diimide (PTCDI) is an organic pigment which is used as the n-type transporting layer in the photovoltaic device[17]. It exhibits an absorption at 540 nm and it is usually used accompany with copper phthalocyanine (CuPc) to form the interface where the exciton dissociates and the electrons are transported in PTCDI layer. The photovoltaic properties of DIAN-PPV **1-3** are given in Table 2. Figure 5 shows the current-voltage characteristics of the ITO/PEDOT:PSS/DIAN-PPV **2**/PTCDI/Al in the dark and under 100 mW/cm$^2$ AM 1 irradiation.



**(a)** **(b)** **(c)**

**Figure 4.** The structure of **(a)** PEDOT, **(b)** PSS and **(c)** PTCDI .

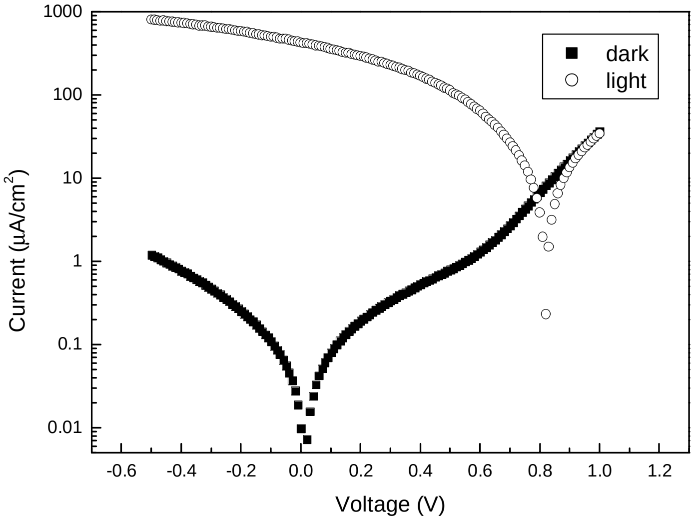


**Figure 5**. Current-voltage characteristics of the ITO/PEDOT:PSS/DIAN-PPV **2**/PTCDI/Al in the dark and under 100 mW/cm$^2$ AM 1 irradiation.

**Table 2**. Photovoltaic properties of DIAN-PPV **1-3**.

| **DIAN-PPV** | $I_{sc}$ (μA/cm$^2$) | $V_{oc}$ (V) | Fill Factor | Power Conversion efficiency (%) |
|---|---|---|---|---|
| **1** | 37.5 | 0.93 | 0.21 | $4.50 \times 10^{-3}$ |
| **2** | 426.5 | 0.86 | 0.21 | $6.06 \times 10^{-2}$ |
| **3** | 102.2 | 0.76 | 0.23 | $1.22 \times 10^{-2}$ |

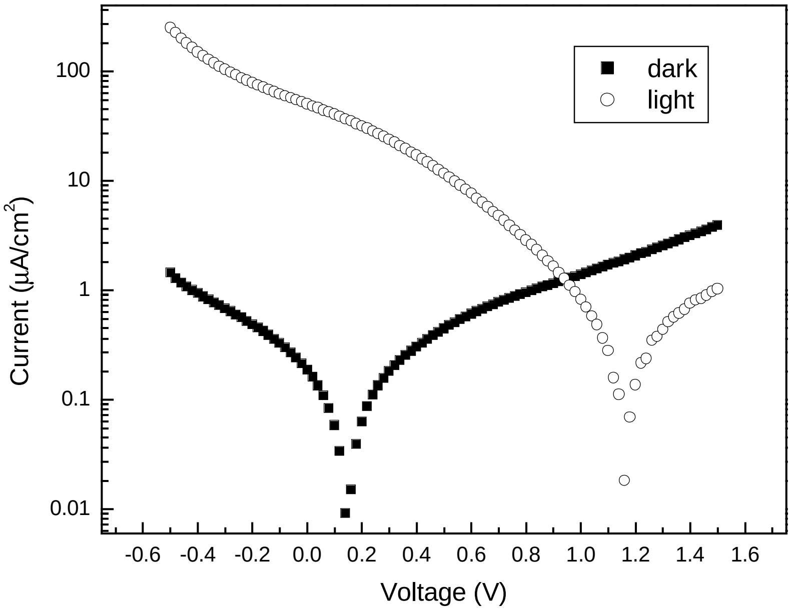


**Figure 6**. Current-voltage characteristics of the ITO/PEDOT:PSS/DIAN-PPV **2**:$TiO_2$/PTCDI/Al in the dark and under 100 mW/cm$^2$ AM 1 irradiation.

Since DIAN-PPV **2** has shown the highest power conversion among the polymers under studied. Another photovoltaic device using DIAN-PPV **2** as the polymeric material was prepared with the structure ITO/PEDOT:PSS/DIAN-PPV **2**:$TiO_2$/PTCDI/Al and their photovoltaic properties were studied. Figure 6 shows the current-voltage characteristics of the ITO/PEDOT:PSS/DIAN-PPV **2**:$TiO_2$/PTCDI/Al in the dark and under 100 mW/cm$^2$ AM 1 irradiation. Titanium oxide ($TiO_2$) nanoparticles were mixed with DIAN-PPV **2** in 3:1 ratio (by weight) in chloroform and the mixture was spin coated to provide thin film with thickness of approximately 40 nm. For this system, the initial step in the photosensitization process is the absorption of visible light by DIAN-PPV. The electrons will be captured by $TiO_2$ matrix. The presence of $TiO_2$ will assist the electron transport of the DIAN-PPV **2** to the PTCDI, in which the electrons can be collected at the aluminium electrode. In addition, $TiO_2$ does not absorb visible light because of the large bandgap (3.2 eV) which will not affect the visible light absorption of DIAN-PPV[18,19]. The $V_{oc}$ and $I_{sc}$ were found to be 1.18 V and 51 μA/cm$^2$, respectively. It was shown that the fill factor was 0.12 with the power conversion efficiency of $4.37 \times 10^{-3}$ %. As compared the results with the ones with the structure ITO/PEDOT:PSS/DIAN-PPV **2**/PTCDI/Al, there was a reduction in the fill factor and power conversion efficiency of the ones with $TiO_2$. It might be due to the limitation of charge transport (incomplete filling) in the polymer/$TiO_2$ photovoltaic devices. The loading of $TiO_2$ could be adjusted to ensure that the majority of photoexcited charge carriers in the polymer reach the $TiO_2$ interface where charge separation occurs. Moreover, the reduction in fill factor and conversion efficiency may be due to the high contact resistance and nonohmic contact between the interfaces[20].

## 3. CONCLUSIONS

A series of rhenium containing poly(*p*-phenylenevinylene) using chlorotricarbonylrhenium(I) bis(iodophenylimino)acenahthene as the monomer was synthesized by Heck reaction. Lithium chloride was used as to suppress the halide exchange. The photoconductivity of DIAN-PPV **1-3** was investigated and DIAN-PPV **2** was found to have the highest quantum yield in photocurrent measurements. The photovoltaic devices based on DIAN-PPV using PEDOT:PSS and PTCDI as hole and electron transporting layers were prepared and the photovoltaic properties were studied. It was found that DIAN-PPV **2** had the highest power conversion efficiency ($\eta_e = 6.06 \times 10^{-2}$ %). The balance in the amount of rhenium complex moiety and charge transport species in conjugated polymers was essential to the photosensitation process. In addition, photovoltaic properties of device based on DIAN-PPV **2** doped with $TiO_2$ as polymeric material were also investigated ($\eta_e = 4.37 \times 10^{-3}$ %).

## 4. ACKNOWLEDGEMENT

This work was supported by a grant from the Research Grants councils of The Hong Kong Special Administrative Region, China (Project Nos. HKU 7096/00P and 7395/00E). Partial financial support from the Committee on Research and Conference Grant (University of Hong Kong) is also acknowledged.

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