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Low-band-gap, sublimable rhenium(I) diimine complex for efficient bulk heterojunction photovoltaic devices

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The use of chlorotricarbonyl rhenium(I) diimine complex as photosensitizing molecule in photovoltaic cells is demonstrated. Unlike other transition-metal-based sensitizers, the complex is sublimable and has low band gap. It also exhibits bipolar charge transport character with relatively high carrier mobilities on the order of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. Multilayer heterojunction and bulk heterojunction devices with fullerene as the electron accepting molecule were prepared. For the bulk heterojunction devices, the fill factor and power conversion efficiency under simulated solar light illumination were 0.56 and 0.48%, respectively. Atomic force microscopic images showed that the complex dispersed evenly with fullerene molecules in solid state. © 2004 American Institute of Physics.

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The transient photocurrent profiles showed typical non-Gaussian charge transport characteristics that were dispersive in nature. The electron and hole carrier mobilities of the complex were determined to be 2.5 and 2.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, respectively. These results are in line with our previously reported rhenium complexes that exhibited bipolar charge transport character.\(^4\) The electron deficient DIAN ligand and the rhenium metal center may act as hopping sites for electron and hole transport, respectively.

Two types of multilayer photovoltaic devices were fabricated. The first type was multilayer heterojunction device ITO/CuPc/Re-DIAN:C\(_{60}\)/Al in which copper phthalocyanine (CuPc) and fullerene were used as the hole and electron transport molecules, respectively. The second type of device consists of multilayer bulk heterojunctions ITO/CuPc/Re-DIAN:C\(_{60}\)/C\(_{60}\)/Al in which Re-DIAN and C\(_{60}\) were co-deposited together in the same layer (Fig. 1). In this type of device, C\(_{60}\) molecules are able to capture electrons more efficiently once excitons are formed.\(^5\) The thickness of CuPc, Re-DIAN (or Re-DIAN:C\(_{60}\) mixed layer), and C\(_{60}\) layers was kept at 10, 50, and 10 nm, respectively. ITO glass slide with a sheet resistance of 20 \\Omega/sq was used as the anode and aluminum (thickness=40 nm) was used as the cathode. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the Re-DIAN were estimated by cyclic voltammetry using ferrocene as the internal standard and they were determined to be \(-5.9\) and \(-3.7\) eV, respectively, which gives rise to a HUMO–LUMO gap \(E_{\text{gap}}\) of 2.2 eV. In order for an exciton to dissociate in a photo voltaic process, the band offset of donor and acceptor material must be larger than the exciton binding energy.\(^6\)

From the band edge in the absorption spectrum, the optical band gap \(E_{\text{opt}}\) of Re-DIAN is measured to be 2.0 eV. The exciton binding energy is estimated to be \(E_{\text{gap}}-E_{\text{opt}}=0.2\) eV.\(^1\) In addition, it was shown that rapid electron transfer could occur in rhenium complex with fullerene substituted bipyridine ligand.\(^2\) The lowest triplet MLCT excited state of the complex was quenched by the C\(_{60}\) moieties with a rate constant of \(10^8\) s\(^{-1}\). Therefore, both the small exciton binding energy and rapid electron transfer may facilitate the subsequent exciton dissociation once excitons are formed.

The current–voltage (\(I-V\)) characteristics under AM 1.5 illumination (100 mW/cm\(^2\)) of different photovoltaic devices are shown in Fig. 2, and their performance data are summarized in Table I. In the multilayer heterojunction device, the open circuit voltage \(V_{\text{oc}}\), short circuit current \(I_{\text{sc}}\), and fill factor FF were measured to be 0.58 V, 0.18 mA/cm\(^2\), and 0.28, respectively. The overall conversion efficiency of the power of the incident light into electrical power is given by the \(\eta_p\), which is calculated according to the equation \(\eta_p=(I_{\text{sc}}V_{\text{oc}}FF)/P\), where \(P\) is the incident light power. The \(\eta_p\) of this device was calculated to be 0.03%. The relatively poor performance may be attributed to the limitation of exciton dissociation at the Re-DIAN/C\(_{60}\) junction and the lower absorption by Re-DIAN than C\(_{60}\). On the other hand, the photovoltaic responses were greatly improved in the cases of bulk heterojunction devices. The \(V_{\text{oc}}, I_{\text{sc}},\) FF, and \(\eta_p\) of the device with Re-DIAN:C\(_{60}\) ratio=1:1 (device 3 in Table I) were 0.45 V, 1.9 mA/cm\(^2\), 0.56, and 0.48%, respectively. The simple three-layered Re-DIAN sensitized photovoltaic cells show improved performance compared to previously reported CuPc/C\(_{60}\) heterojunction devices.\(^3\) It has been shown that a LiF/Al electrode may improve the photovoltaic device efficiency by providing a good ohmic contact.\(^4\) In our case, the device with a thin layer (0.3 nm) of LiF showed no significant improvement (device 4).

The amount of photosensitizer and electron transport molecules may strongly influence the balance between the exciton formation, dissociation, and charge transport processes. The effect of changing the Re-DIAN/C\(_{60}\) ratio was studied. For the device with Re-DIAN:C\(_{60}\)=1:9 (device 5), \(V_{\text{oc}}\) and \(I_{\text{sc}}\) values are similar, but the measured FF and \(\eta_p\) are poorer (0.32 and 0.28%) compared to the device with 1:1 Re-DIAN:C\(_{60}\) ratio. In general, low fill factor can be induced by high series resistance or by small shunt resistance. The device with Re-DIAN:C\(_{60}\)=9:1 shows the poorest performance among all the bulk heterojunction devices. The FF was 0.21 and its \(I-V\) curve shows a concave instead of a convex shape.
convex shape. These results clearly demonstrate the importance of C₆₀ in the exciton dissociation process. Although Re-DIAN itself is also a good hole and electron carrier, the electron transport process is still dominated by the C₆₀ molecules, which has an electron carrier mobility of 1.3 cm² V⁻¹ s⁻¹.

Efficient charge separation and transport strongly rely on even dispersion of Re-DIAN and C₆₀. Figure 3 shows the tapping mode atomic force microscopy (AFM) images of different Re-DIAN:C₆₀ blends (50 nm) coated on ITO substrates. All the samples were prepared by vacuum deposition on unheated substrate, and it is expected that there is no significant difference between bulk and surface morphologies. Phase contrast AFM image provides information on the change in viscoelasticity between materials. It was used to study the miscibility of blends in polymer photovoltaic cells. The thin film with 1:1 ratio [Fig. 3(a)] exhibits features of approximately 30 nm in size, and its phase image clearly indicates that the “peaks” are of different chemical nature from the surrounding “valleys.” Since the exciton diffusion length in organic materials is typically small, such small feature size would facilitate exciton separation and subsequently yield higher efficiency. All samples have relatively small roughness and the height and phase images show clearly that no significant aggregation is formed by either one type of molecules. These observations suggest that the rhenium complex and fullerene molecules are highly compatible with each other.

In conclusion, efficient multilayer bulk heterojunction photovoltaic devices with simple structures were fabricated based on a chlorotricarbonyl rhenium diimine complex with low band gap and good processibility. The active layer consists of a blend of rhenium complex and fullerene that were co-deposited by vacuum sublimation. The rhenium complex acts as both photosensitizer and exhibits bipolar charge transport character. Improved performance can also be achieved by optimizing the thickness of each layer and fabrication of more sophisticated devices.

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