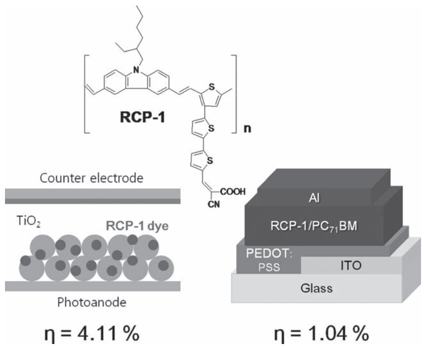
Multifunctional Conjugated Polymers with Main-Chain Donors and Side-Chain Acceptors for Dye Sensitized Solar Cells (DSSCs) and Organic Photovoltaic Cells (OPVs)

Dong Wook Chang, Seo-Jin Ko, Jin Young Kim, Su-Moon Park,
Hyo Joong Lee,* Liming Dai,* Jong-Beom Baek*

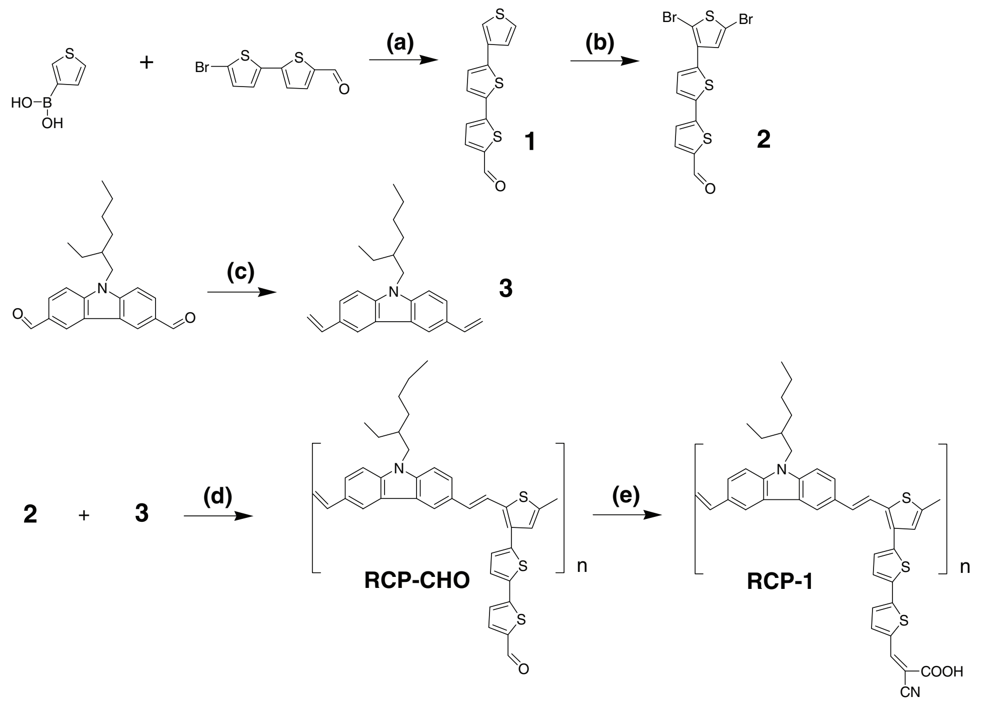
A novel multifunctional conjugated polymer (RCP-1) composed of an electron-donating backbone (carbazole) and an electron-accepting side chain (cyanoacetic acid) connected through conjugated vinylene and terthiophene has been synthesized and tested as a photosensitizer in two major molecule-based solar cells, namely dye sensitized solar cells (DSSCs) and organic photovoltaic cells (OPVs). Promising initial results on overall power conversion efficiencies of 4.11% and 1.04% are obtained from the basic structure of DSSCs and OPVs based on RCP-1, respectively. The well-defined donor (D)-acceptor (A) structure of RCP-1 has made it possible, for the first time, to reach over 4% of power conversion efficiency in DSSCs with an organic polymer sensitizer and good operation stability.



1. Introduction

Due to increasing energy demands and environmental issues, considerable research interest has been directed to green and renewable energy resources, including solar light and other natural sources, over the past two decades.[1] As a result, various types of photovoltaic cells, typically classified as the 1st (silicon-based),[2] 2nd (thin film of CIGS and CdTe)[3] and 3rd (organic and organic/inorganic hybrid materials)[4–6] generation devices, have been intensively developed for efficient conversion of solar light to electricity. Although the 1st and 2nd generation devices have been successfully commercialized and are dominating the current market shares, they still suffer from some intrinsic drawbacks, such as heavy weight, high manufacturing cost and lack of flexibility. To overcome these limitations and further improve solar cell performance, dye-sensitized solar cells (DSSCs)[5] and bulk-heterojunction (BHJ)[6] organic photovoltaic cells (OPVs) have been devised and tested as the most promising alternatives due to their low-cost fabrication and easy molecular engineering of key elements for obtaining high efficiencies. Recently, some metal-free organic materials from small molecules to polymers have been widely investigated as photoactive layers for both DSSCs and OPVs and have many advantages, including their high molar extinction coefficient and cost-effective structural modification.[5,6] Although various conjugated polymers have been developed for light-harvesting and charge-transporting in BHJ OPVs,[6]

Dr. D. W. Chang, S.-J. Ko, Prof. J. Y. Kim,
Prof. S.-M. Park, Prof. J.-B. Baek
Interdisciplinary School of Green Energy/Institute of Advanced Materials and Devices, Ulsan National Institute of Science and Technology,
Ulsan, 689-798, South Korea
E-mail: jbbaek@unist.ac.kr
Prof. H. J. Lee
Department of Chemistry,
Chonbuk National University,
Chonbuk, 561-756, South Korea
E-mail: solarlee@jbnu.ac.kr
Prof. L. Dai
Department of Macromolecular Science and Engineering,
Case Western Reserve University,
Cleveland, Ohio, 44106, USA
E-mail: limig.dai@case.edu



Scheme 1. The synthetic scheme of RCP-1: (a) Pd(PPh$_3$)$_4$, THF, 2 M K$_2$CO$_3$, 70 °C, 24 h; (b) *N*-bromosuccinimide, THF, r.t., overnight; (c) Methyltriphenylphosphonium iodide, potassium *t*-butoxide, THF, r.t., 2 h; (d) Pd(OAc)$_2$, *p*-(tolyl)phosphine, triethylamine, DMF/NMP, 130 °C, 48 h; (e) Cyanoacetic acid, chloroform/acetonitrile, reflux, overnight.

their utilization in DSSCs as a sensitizer is much less discussed.[7,8] Owing to their excellent structural stability and unique structure-dependent optoelectronic properties, however, conjugated polymers should still hold a promising position as a sensitizer in DSSCs as well as in OPVs. In particular, many good characteristics of conjugated polymers could be incorporated into DSSCs if we can design and anchor polymeric dyes to the TiO$_2$ surface in a DSSC. In this context, the same conjugated polymer sensitizers can be used in both DSSCs and OPVs for synergistic device integration to produce systems (modulus) with an overall good flexibility and high efficiency. Among the few studies reported so far on the application of conjugated polymers as organic sensitizers in DSSCs,[7,8] the first trial involving simple polymers such as polythiophene modified with a COOH anchoring group gave relatively low power conversion efficiencies (<2%), due probably to the lack of a directional charge flow.[7] More recent efforts led to new polymer sensitizers with a conjugated donor (D)-acceptor (A) structure, which enhanced efficiencies up to about 3% under simulated AM 1.5 condition.[8,9] In addition to DSSCs, various conjugated polymers with the main chain donor (D) and side chain acceptor (A) architecture have been successfully utilized in OPVs[10] with high power conversion efficiency due to the expected directional charge flows. Therefore, it should be interesting to design a new D-A type polymer sensitizer that can be simultaneously used in both conventional DSSC and OPV devices.[11] By doing so, it will be possible to generalize the D-A architecture concept for sensitizers and gain new insights into synergistic integration of DSSCs and OPVs.

In DSSCs, it is highly desirable to design a dye that can work stably on the surface of metal oxides under operation conditions. Compared with small molecular dyes, polymeric dyes will be attached onto the metal oxide surface more stably through multiple anchoring interactions along a long macromolecular chain, and hence a higher overall stability. In addition, the large body of molecular engineering knowledge accumulated from various polymer-based OPVs could be used to guide the design of polymeric dyes for improving not only their operation stability in DSSCs but also overall power conversion efficiencies in both DSSCs and BHJ OPVs.[10] The efficient sequential charge transfer in conjugated polymeric dyes from the electron donating main chain via the electron accepting side chain to PCBM is responsible for their high OPV efficiencies.

Herein, we report the synthesis of a multifunctional polymer, RCP-1, with a carbazole donor in the main chain and a cyanoacrylic acid acceptor in the side chain connected through π–π conjugation of vinylene and terthiophene, along with their device performances in both DSSCs and OPVs. Our results showed a relatively high power conversion efficiency of 4.11% (the highest value for DSSCs using organic polymer sensitizers)[8,9] for DSSCs with the RCP-1 dye sensitizer, and a moderate efficiency of 1.04% was also achieved in BHJ OPVs based on RCP-1 (Scheme 1) and [6,6]-phenyl-C71-butyric acid methyl ester

($PC_{71}BM$). Thus, the newly-synthesized RCP-1 is promising as a polymeric sensitizer in DSSCs and a photovoltaic active layer in OPVs.

2. Experimental Section

Detailed synthetic procedures and characterization of all compounds are described in the Supporting Information. ^1H and ^{13}C NMR spectra were recorded on a Varian VNMRS 600 spectrometer. UV-vis and photoluminescent spectra were measured using a Perkin-Elmer Lambda 35 and LS 35, respectively. The MALDI-TOF MS analyses were conducted on a Bruker UltraFlex III TOF/TOF mass spectrometer using a 2,3-dihydroxybenzoic acid (DHB) matrix. Differential pulse voltammetry (DPV) measurements were performed in DMF containing 0.1 M $TBAPF_6$ and RCP-1 using an EG&G 263 potentiostat/galvanostat in a three-electrode configuration. A platinum disk electrode and a platinum gauze were used as a working and counter electrode, respectively. A silver (Ag) wire was used as a pseudo-reference electrode with a ferrocene internal standard. Thermal gravimetric analysis (TGA) was performed using a Q600 from TA instruments.

2.1. Fabrication and Analysis of Dye Sensitized Solar Cells (DSSCs)

Photoelectrodes composed of nanocrystalline TiO_2 layers were prepared following a typical procedure reported in the literature.[12] FTO glass plates (Solaronix, TCO22-15) were used as the transparent conducting electrodes. After $TiCl_4$ treatment, a paste composed of 20 nm anatase TiO_2 particles (Solaronix, Ti-Nanoxide T/SP) for the transparent nanocrystalline layer was coated on the FTO glass plate by screen printing to produce a ~11 μm thick film. The scattering layer (~3 μm) was applied over the transparent layer by screen printing, and then gradually heated to 500 °C for sintering. The resulting TiO_2 electrodes were treated by $TiCl_4$ and sintered again at 500 °C for 30 min. After cooling to about 80 °C, the TiO_2 electrodes were immersed into the RCP-1 solutions (3 mg of RCP-1 in 10 mL chlorobenzene) with 0.3×10^{-3} M 3a,7a-dihydroxy-5b-cholic acid (Cheno) and kept at room temperature overnight. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate (Solaronix, TCO22-15) and heating at 400 °C for 15 min. The dye-stained TiO_2 electrode and Pt counter electrode were assembled into a sealed sandwich-type cell by hot-pressing with a 50 μm thick transparent hot-melt film (Himilan® of Mitsui-DuPont poly chemical). An electrolyte solution (1.0 M 1,3-dimethylimidiazolium iodide, 0.03 M iodine, 0.05 M LiI, 0.10 M guanidinium thiocyanate and 0.50 M *tert*-butylpyridine in a 15/85 (v/v) mixture of valeronitrile and acetonitrile) was prepared and injected into the inter-electrode space from the counter electrode side through a pre-drilled hole, which was then sealed with a Himilan® sheet and a thin glass slide cover by heating. In order to reduce scattered light from the edge of the glass electrodes of the dyed-TiO_2 layer, light shading metal masks were used on the DSSCs, so that the active area of DSSCs was fixed to 0.159 cm^2.

A class A solar simulator (Model, 91195A) from Newport (USA), which has a 450 W xenon lamp with an irradiance of 100 $mW\cdot cm^{-2}$ (equivalent to one sun at AM 1.5) at the surface of the solar cell, was used. The spectral output of the lamp was calibrated using a standard silicon solar cell (PV Measurements, Inc). The current–voltage characteristics of the cell were then obtained by applying an external bias potential to the cell and measuring the photocurrent with a Keithley model 2636A digital source meter (Keithley, USA). The incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 300 to 800 nm using a Model QEX7 system (PV Measurements Inc.).

2.2. Fabrication and Analysis of Organic Photovoltaic Cells (OPVs)

The poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) (AI 4083) was purchased from H. C. Starck (Germany). [6,6]-Phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) was purchased from Electronic Materials (EM) Index Co. Ltd. The device structure of the solar cells was glass/indium-tin-oxide (ITO)/PEDOT:PSS/RCP-1:$PC_{71}BM$/Al. The devices were fabricated according to the following procedures. First, the ITO-coated glass substrates were cleaned with detergent, then sonicated in acetone and isopropyl alcohol in a regular sequence, and subsequently dried in an oven overnight at 100 °C. The PEDOT:PSS layer was spin-coated (after passing through a 0.45 μm filter) at 5000 rpm for 40 s on top of the ITO-coated glass, then baked at 140 °C for 10 min in air and then moved into a glove box. A mixed solution of RCP-1 and [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) (1:1 ~ 1:4, 0.8 wt%) in chlorobenzene (CB) was spin-coated at 800 ~ 4000 rpm for 60 s on top of PEDOT:PSS layers. The device was pumped down in vacuum ($<10^{-6}$ torr; 1 torr ~ 133 Pa) and a 100 nm thick Al electrode was deposited on top of the active layer. The deposited Al electrode area defined the active area of the devices as 13.5 mm^2. The sample was then annealed at 90 °C for 10 min inside the glove box filled with nitrogen gas. Measurements were carried out with the solar cells inside the glove box using a high quality optical fiber to guide the light from the solar simulator equipped with a Keithley 2635A source measurement unit. The *J*–*V* curves for devices were measured under AM 1.5G illumination at 100 $mW\cdot cm^{-2}$ with mask. EQE measurements were also conducted using an EQE system (Model QEX7) by PV Measurements Inc. (Boulder, Colorado). After collecting the EQE data, the software also integrated the data with the AM 1.5 G spectrum and reported the calculated J_{SC} value.

3. Results and Discussion

While the synthetic route to RCP-1 is shown in Scheme 1, the experimental details and structural characterization are given in the Supporting Information. Briefly, the dibromothiophene monomer with dithiophene-carbaldehyde (**2**) was first prepared by a Suzuki coupling reaction followed by bromination with *N*-bromosuccinimide (NBS). Then **2** was polymerized with (2-ethylhexyl)-3,6-divinyl-9H-carbazole (**3**) via a Heck coupling reaction to produce aldehyde-functionalized polymer (RCP-CHO). Finally, RCP-1

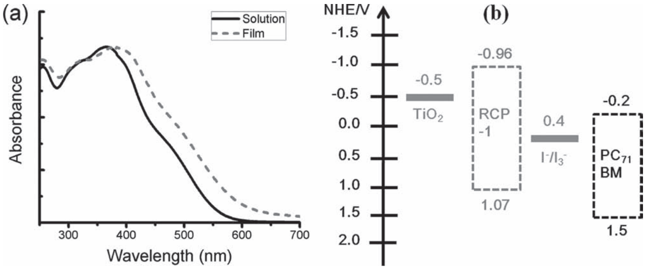


Figure 1. (a) Normalized UV-vis spectra of RCP-1 in THF and on film and (b) energy level diagram vs. a normal hydrogen electrode (NHE) of TiO_2, RCP-1, I^-/I_3^- and $PC_{71}BM$.

was synthesized by a Knoevenagel reaction between RCP-CHO and cyanoacetic acid. The weight average molecular weight ($\overline{M}_W$) and polydispersity index (PDI) determined by GPC with a polystyrene standard and THF as an eluent for RCP-1 were 4600 $g{\cdot}mol^{-1}$ and 1.49, respectively. RCP-1 exhibited a good thermal stability with a 5% weight-loss temperature ($T_{d5\%}$) of 259 °C (see Figure S1 in the Supporting Information).

Figure 1(a) shows the UV-vis absorption spectra for RCP-1 in a THF solution and as a spin-coated film on a quartz plate. As can be seen, RCP-1 showed a characteristic broad absorption band in the UV-visible region with the onset wavelength at about 600 nm. A red-shift of about 15 nm was also observed for optical absorption of the solid film with respect to the corresponding solution spectrum, probably due to the strong intermolecular interactions between polymer chains in the film. The optical band gap (E_g) of RCP-1 was estimated from the absorption edge of the film to be 2.03 eV using the relation $E_g = 1240/\lambda$. The oxidative energy level of RCP-1 was analyzed by differential pulse voltammetry (DPV) in DMF. Ag wire was used as a quasi-reference electrode with ferrocene as an internal standard. The oxidation potential (E_{ox}) of RCP-1, corresponding to the highest occupied molecular orbital (HOMO), was found to be located at 1.07 V vs. a normal hydrogen electrode (NHE). That was more positive than the redox couple (I^-/I_3^-, ~0.4 V), ensuring that there is a sufficient driving force for the dye regeneration. The lowest unoccupied molecular orbital (LUMO) level of RCP-1 (–0.96 V) was obtained by adding E_g to HOMO, and was also found to be more negative than the TiO_2 conduction band (~–0.5 V vs. NHE) for efficient electron injection. Therefore, this new polymer dye has proper electronic energy levels as a promising sensitizer in DSSCs. The electrochemical properties of RCP-1 and the energy level diagram of TiO_2, RCP-1, I^-/I_3^- and $PC_{71}BM$ vs. NHE are summarized in Table 1 and Figure 1(b), respectively.

Table 1. Electrochemical properties of RCP-1.

Dye	λ_{ab} [nm]	HOMO [V]	LUMO [V]	E_g [eV]
RCP-1	360	1.07	–0.96	2.03

Nanostructured TiO_2-films sensitized with RCP-1 were prepared on fluorine doped SnO_2/glass following the typical procedures reported in the literature (see Experimental Section).[12] The photocurrent density-voltage (*J-V*) curve and incident photon to current conversion efficiency (IPCE) spectrum measured from RCP-1 sensitized cells are shown in Figure 2 and the data summarized in Table 2. The DSSC with RCP-1 as a sensitizer displayed a short-circuit current (J_{sc}) of 8.43 $mA{\cdot}cm^{-2}$, an open-circuit voltage (V_{oc}) of 0.67 V and a fill factor (*FF*) of 0.73, thus leading to an overall efficiency (η) of 4.11%. To the best of our knowledge, this is the first result showing over 4% power conversion efficiency in DSSCs using a polymer sensitizer.[7–9] This relatively high performance can be ascribed to the well-defined D-A structure of the repeating unit in the polymer, which is very similar to a typical

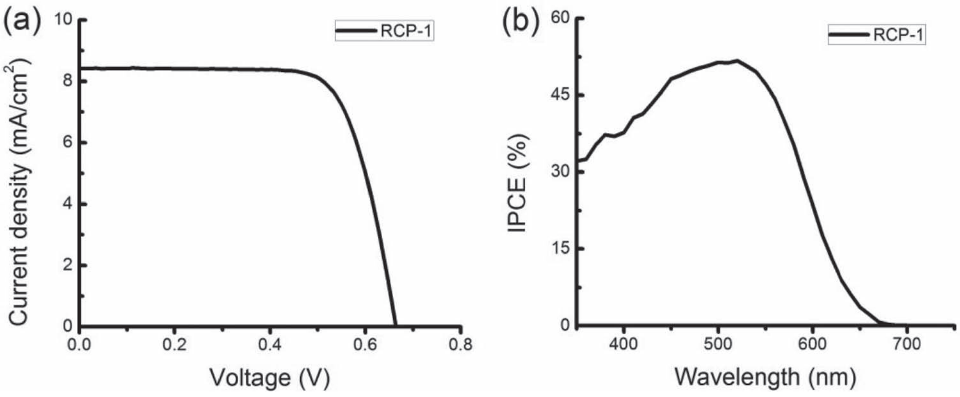


Figure 2. (a) J-V characteristics, (b) IPCE.

Table 2. Photovoltaic properties of RCP-1 in DSSCs and OPVs.

Device	RCP-1: $PC_{71}BM$	J_{sc} [$mA \cdot cm^{-2}$]	$J_{sc,IPCE}$ [$mA \cdot cm^{-2}$]	V_{oc} [V]	*FF* [%]	PCE [%]
DSSCs	-	8.43	-	0.67	0.73	4.11
OPVs	1:1	3.07	3.13	0.76	0.32	0.74
	1:2	3.61	3.87	0.77	0.33	0.92
	1:3	4.14	4.25	0.77	0.32	1.04
	1:4	3.51	3.71	0.77	0.34	0.92

organic dye that gives a good result based on directional charge flows in DSSCs.

The IPCE spectrum of the RCP-1 sensitized DSSC showed a wide range of photoactive regions from 350 to 700 nm with the highest peak value of 51% at around 520 nm. In terms of stability, the RCP-1 sensitized cell maintained its initial power conversion efficiency for 3 months until leakage of the volatile solvents used occurred. Further studies are currently underway to address the general stability issue of organic polymer dyes in DSSCs.

In addition to DSSCs, the use of RCP-1 in BHJ OPVs with the device structure indium tin oxide (ITO) glass/PEDOT:PSS/RCP-1:$PC_{71}BM$/Al was investigated. Figure 3(a) shows the photocurrent density-voltage (*J-V*) curves for the devices with various ratios of RCP-1 to $PC_{71}BM$ (from 1:1 to 1:4), with the corresponding numerical results summarized in Table 2. Among all the RCP-1:$PC_{71}BM$ weight ratios investigated in this study, 1:3 demonstrated the highest efficiency of 1.04% with a short circuit current (J_{sc}) of 4.14 $mA \cdot cm^{-2}$, an open-circuit voltage (V_{oc}) of 0.77 V and fill factor (*FF*) of 0.32. The relatively larger band gap of RCP-1 (~2.03 eV) is considered to be one of limiting factors for higher efficiency in OPVs, which can be solved by future structural modifications for lower band gaps. All devices showed a relatively high V_{oc} of 0.77 V, which is higher than the V_{oc} of typical P3HT-based devices,[13] and this value is correlated with the energy gap between the HOMO level of RCP-1 and the LUMO level of $PC_{71}BM$ (~ -0.2 V shown in Figure 1(b)).[14] The IPCE spectra of all devices are shown in Figure 3(b), which exhibit efficient photoresponse in the broad range of 350–700 nm. The J_{SC} values estimated from IPCE ($J_{sc,IPCE}$) curves for devices with various ratios of PCP-1:$PC_{71}BM$ are 3.13 (1:1), 3.87 (1:2), 4.25 (1:3) and 3.71 (1:4) $mA \cdot cm^{-2}$, respectively. These values agreed well with the J_{sc} measured from the devices (Table 2).

Further insight into the molecular electron distributions and energy levels of dyes was obtained from density functional theory (DFT) calculations at the B3LP/6-31G ** level in the Gaussian 09 program.[15] The electron distribution of the HOMO and LUMO of dyes with calculated energy levels is shown in Figure 4. In RCP-1, the HOMO shows the highest electron density near the electron-donating carbazole, while it is located near electron-withdrawing cyanoacrylic acid units in the LUMO. Thus the efficient photo-excited electron transfer from the LUMO of dyes to the conduction band of TiO_2 is expected through the close position of LUMO to the anchoring group in the excited-state.[16] Furthermore, the efficient charge separation through sequential electron transfer from the main chain donor to the side chain acceptor and then finally to $PC_{71}BM$ is possible in RCP-1 based BHJ OPVs.[10]

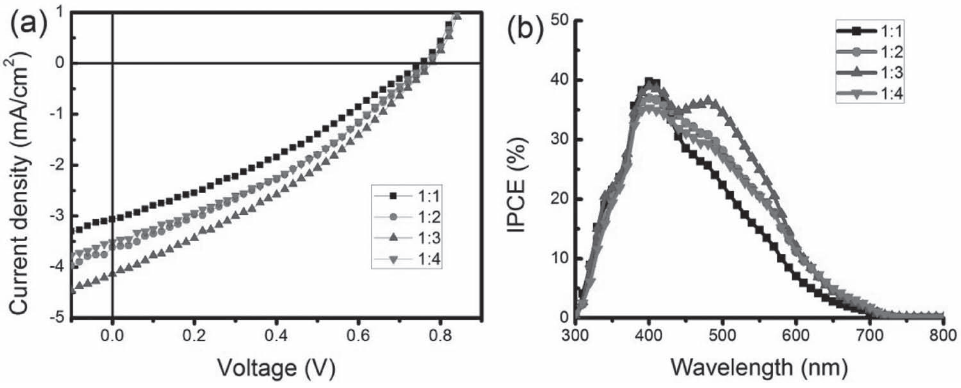


Figure 3. (a) *J–V* characteristic; (b) IPCE of RCP-1 based OPVs.

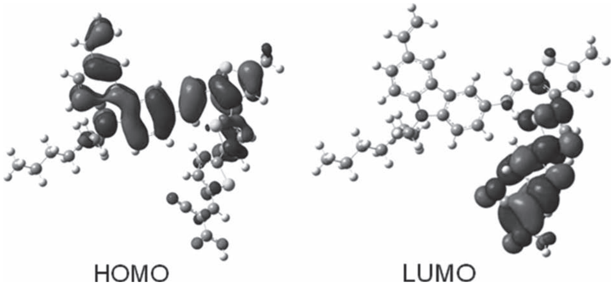


Figure 4. The frontier molecular orbitals of RCP-1 calculated at the B3LYP/6-31G** level: (a) HOMO; (b) LUMO level.

4. Conclusion

In summary, a novel multifunctional conjugated polymer, RCP-1, with carbazole donor in the main chain and a side chain cyanoacrylic acid acceptor (Scheme 1) has been synthesized and tested as a light-harvesting sensitizer in dye sensitized solar cells (DSSCs) and a photoactive layer in organic photovoltaic cells (OPVs). The well-defined donor (D)-acceptor (A) structure of RCP-1 has made it possible, for the first time, to reach over 4% of power conversion efficiency in DSSCs with an organic polymer sensitizer and good operation stability. Meanwhile, a moderate efficiency of 1.04% was also achieved in BHJ OPVs based on RCP-1 and [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$). Although high efficiencies in DSSCs and OPVs have been observed, the device performance of RCP-1 may be further improved by increasing its molecular weight, and thus a systematic approach to preparing higher molecular weights is currently underway. We believe that the well-organized D-A type of polymer dye developed in this study will open up a new avenue in designing sensitizers satisfying simultaneously two important criteria in DSSCs, namely high efficiency and long-term stability, as well as serving as a photovoltaic active material in BHJ OPVS for synergistic device integration of DSSCs and OPVs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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