

Solution Processable Rhodanine-Based Small Molecule Organic Photovoltaic Cells with a Power Conversion Efficiency of 6.1%

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In the past few years, great progress has been made in organic photovoltaic (OPV) cells for an alternate of silicon semiconductor-based solar cells. OPV has the advantages of clean, low-cost, flexibility, and the possibility of roll-to-roll production.^[1–4] Currently, most of the works have been focused on polymer donor molecules using bulk heterojunction (BHJ) architecture and [6,6]-phenyl-C61-butyrac acid methyl ester (PC₆₁BM) as the acceptor.^[5,6] Indeed, in addition to the currently better OPV performance than small molecules, polymers have the advantages for such as better film forming quality and so on.^[7] However, it cannot be denied that there are disadvantages for polymer-based OPV, such as batch to batch reproducibility, difficulty of purification, and so on. In contrast, small molecules intrinsically do not have such flaws;^[8] additionally, their band structures could be tuned easily with much more choices of chemical modification. Furthermore, small molecules generally have higher charge mobility and open voltages.^[9,10] However, even with these advantages, small-molecule-based OPV cells have not been investigated as intensively as that of their polymer counterparts because one of the major problems for small molecules is their generally poor film quality when using the simple solution spinning process.^[11] This has been hampering their performance, and indeed their power conversion efficiencies (PCEs) (4%–5%)^[12–18] are still significantly lower compared with that (>7%)^[19–25] from polymers. It is thus expected that better PCE could be achieved when their intrinsic bad film quality and morphology in BHJ architecture could be improved combining with their other advantages. But to achieve this, careful molecule design has to be carried out to address many factors collectively, including their molar absorption, morphology compatibility with the acceptors for a better film quality, and so on.

Previously, we have reported a small molecule (DCAO7T, **Scheme 1**), which gives rather high quality of solution spin-coated film and a high 5.08% PCE.^[12] But this molecule comes with an end unit of cyanoacetate group, which could not contribute too much for the overall solar absorption. So, we thought that the current density J_{sc} might be able to be enhanced if structures with stronger molar absorption is used to replace such an end unit, in the conditions that overall molecular backbone and morphology will not be affected too much. Considering the generally high absorption coefficients and good OPV performance of many dye molecules, such as triarylaminines,^[16,26] acenaphthoquinoline,^[27] diketopyrrolopyrroles (DPP),^[17] squaraines,^[18,28,29] merocyanine,^[30,31] isoindigo,^[32] phthalocyanine,^[33] and dipyrromethene boron difluoride (BODIPY),^[34–36] we thus introduce a new dye unit, 3-ethylrhodanine, into the targeted OPV molecule named as DERHD7T (**Scheme 1**) with a conjugated thiophene backbone. With such a design, DERHD7T is expected to have a stronger solar absorption to improve J_{sc} , and hopefully also combine the generally good high fill factor (FF) and open voltage (V_{oc}) from the previous molecules.^[12,37] As expected, this material indeed shows a stronger solar absorption in addition to good film quality from solution process. Using the simple solution spin-coating fabrication process, a record high PCE of 6.10% was obtained by using a blend of DERHD7T and PC₆₁BM as the active layer, with a high V_{oc} of 0.92 V and a remarkable J_{sc} of 13.98 mA cm⁻². As far as we know, this is the first PCE passing the landmark of 6% for any BHJ OPV devices based on small molecules.

The synthesis of DERHD7T is shown in **Scheme 1** with details described in the Supporting Information. Compound DF7T (diformylseptithiophene) was obtained through a reaction of 7T (septithiophene) with the Vilsmeier reagent prepared by POCl₃ and DMF. By the Knoevenagel condensation of compound DF7T with 3-ethylrhodanine, DERHD7T was afforded with a high yield of 90%. Thermogravimetric analysis (TGA) has been carried out to study the thermal stability of DERHD7T, which shows that it is stable up to 377 °C (**Figure S1**, Supporting Information).

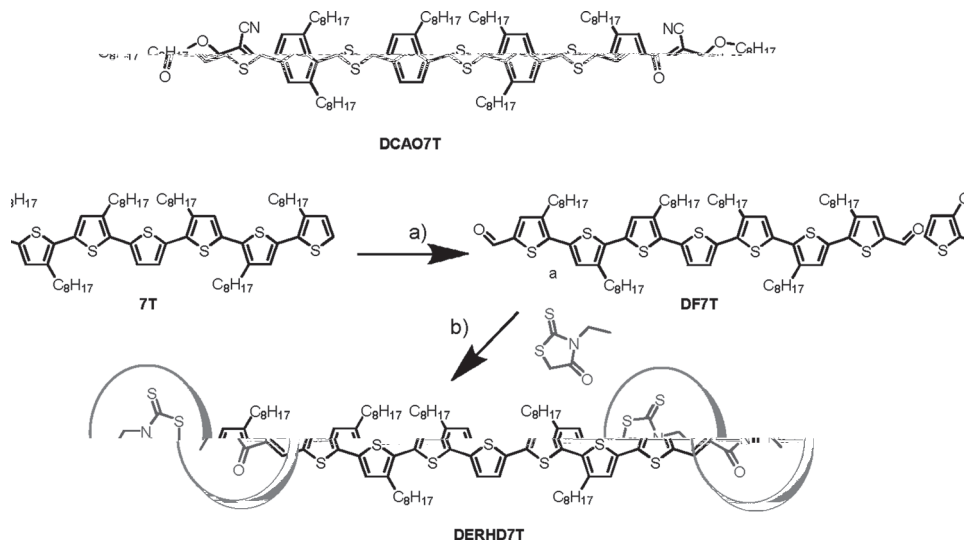
UV/Vis absorption spectra of compound 7T, as the model compound for the backbone of DERHD7T for comparison, and DERHD7T are shown in **Figure 1**. The solution absorption maximum of DERHD7T is red-shifted by approximately 100 nm to a value of 508 nm compared with that of the model compound 7T ($\lambda_{max} = 407$ nm), indicating the existence of strong intramolecular charge transfer between the end dye units and the conjugated backbone. This is consistent with the efficient quench of fluorescence of DERHD7T (see **Figure S2**,

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Scheme 1. Structures of DERHD7T and DCAO7T; synthesis of DERHD7T. (a) POCl_3 , dimethylformamide (DMF), dichloroethane; (b) AcONH_4 , AcOH .

Supporting Information). Indeed, DERHD7T has a rather high molar absorption coefficient of $9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ in solution, which is almost double that of 7T ($5.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and much larger than those of DCAE7T, DCAO7T, and DCAEH7T in our previous works.^[14] The DERHD7T film cast from CHCl_3 shows a broad absorption from 450 to 750 nm and an absorption maximum at 618 nm, which is red-shifted by 110 nm in comparison with that in solution, along with a shoulder peak at 700 nm. This indicates a strong π - π packing between the molecular backbones.^[38] The film also has a high molar absorption coefficient of $7.2 \times 10^4 \text{ cm}^{-1}$. This strong absorption echoes our thought in the design. The optical band gap of DERHD7T thin films was estimated from the onset of the absorption spectra to be 1.69 eV. Cyclic voltammograms (CV) (Figure S3a, Supporting Information) of DERHD7T in CH_2Cl_2 solution shows two reversible oxidation waves and one irreversible reduction wave. From the CV curve, the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of DERHD7T are estimated to be -5.00 and

-3.28 eV, respectively, with a band gap of 1.72 eV, which is consistent with the optical band gap. The cyclic voltammogram of DERHD7T film shows only one irreversible oxidation wave due to stacking in solid state. The HOMO, LUMO, and band gap of DERHD7T are -5.21 , -3.68 , and 1.53 eV, respectively (Figure S3b, Supporting Information).

High crystallinity and ordered structure of donor molecules generally offer high hole mobility, which is essential for high-performance OPV. The structural ordering of pristine DERH7T and blend of DERHD7T:PC₆₁BM was investigated by X-ray diffraction (XRD) analysis for the films spin-coated from CHCl_3 solutions onto glass substrates, and the results are shown in Figure S4, with key d-spacing values summarized in Table S1. The pristine DERHD7T film exhibited a strong first-order diffraction peak (100) at $2\theta = 4.6^\circ$, corresponding to a d100-spacing value of 19.3 Å for the distance between the planes of the main conjugation chains of these molecules, which is similar to that observed for P3OT (20.1 Å).^[39] The diffraction peaks at $2\theta = 9.2^\circ$ and 13.9° corresponding to d-spacing of 9.6 and 6.4 Å for second and third order are also observed. These XRD results of pristine DERHD7T indicate a highly organized assembly and crystallinity of this π -conjugated molecule at solid state which could be explained by the planar structure supported by the density functional theory (DFT) calculation result at the B3LYP/6-31G(d) model (see Figure S5, Supporting Information).^[40] The crystallinity of DERHD7T blending with PC₆₁BM in a ratio of w:w 1:0.5 still exists in spite of decayed first-order diffraction. However, the second-order diffraction peaks (200) and the third-order diffraction peaks (300) have vanished. This can be explained by the interruption of DERHD7T network from PC₆₁BM and the forming of small BHJ hole and electron transporting domains^[13] which is supported by the AFM images (Figure S6, Supporting Information). From the AFM images, rather smooth surface with a root mean square (rms) roughness of 0.38 nm is exhibited in the height profile image (Figure S6a, Supporting Information). Also, as shown in Figure S6b, the phase images reveal two distinct feature types, which we

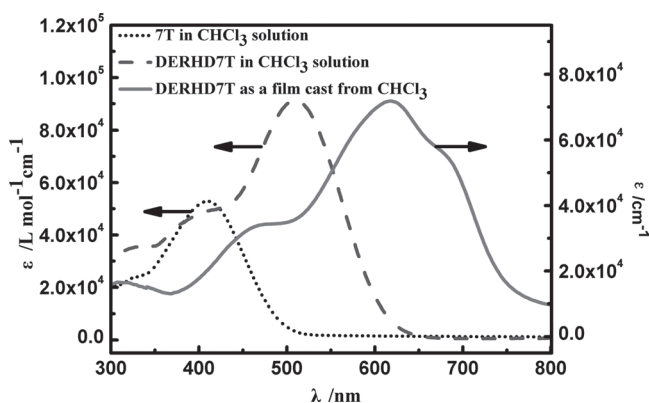


Figure 1. Absorption spectra of the backbone unit compound 7T in chloroform (dotted line), DERHD7T in chloroform (dashed line), and as a thin film (solid line).

assign to the acceptor-rich and donor-rich domains with size of $\approx 10\text{--}20$ nm. These AFM image features indicate that the donor material has a good miscibility with PC₆₁BM molecules in the blend film, and an optimized donor/acceptor interpenetrating network has formed. The interpenetrating network of the blend films indicates that efficient percolation channels are formed, thus improving the carrier collection efficiency and leading to a high short-circuit current.^[17]

On the basis of the confirmation of crystallinity and ordered structure of DERHD7T, the hole mobility of the pristine DERHD7T was measured by the space charge limited current (SCLC) method.^[41] Pristine DERHD7T film shows a hole mobility of $1.50 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (shown in Figure S8, Supporting Information), similar with that of P3HT for $(1.4\text{--}3.0) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[42] and DCAO7T of our previous work.^[12]

BHJ OPV cells were fabricated using DERHD7T as the electron donor with a general device structure of ITO/PEDOT:PSS/DERHD7T:acceptor/LiF/Al using the conventional solution spin-coating process. Detailed studies for BHJ device performance of these materials for systematic investigation were presented in Supporting Information. The best result was observed for a donor/acceptor weight ratio of 1:0.5 from chloroform solutions with donor concentration of 8 mg mL^{-1} using PC₆₁BM as the acceptor. The current density versus voltage ($J\text{--}V$) curves are shown in Figure 2a. The device with highest PCE (DERHD7T/PC₆₁BM w:w 1:0.5) shows a $V_{\text{oc}} = 0.92 \text{ V}$, $J_{\text{sc}} = 13.98 \text{ mA cm}^{-2}$, fill factor (FF) = 47.4%, and PCE = 6.10% (data demonstrated in Table 1) which is slightly larger than the average PCE of 5.88%. We note that the device performance is generally lower when other solvents, such as chlorobenzene, were used, which gave a PCE of 3.72% and poor film quality was observed. An optimized thickness of active layer has been found to be ≈ 80 nm. Furthermore, it is important to note that the optimized devices have a high donor:acceptor ratio (1:0.5) in the active layer, compared with a generally lower donor content (20%–50% donor content corresponding to donor: acceptor ratios of 1:4 to 1:1) for most polymer-based devices.^[4] The high donor concentration is expected to absorb solar light more efficiently and give more balanced charge carrier transport for donor and acceptor,^[17] which could improve FF and PCE.

Table 1. Photovoltaic performance of DERHD7T/PC₆₁BM bulk heterojunction (BHJ) solar cells with w:w = 1:0.5 using chloroform solutions.

Ratio	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1:0.5	13.98	0.92	47.4	6.10

Ca/Al instead of LiF/Al as the cathode was also tested for improving the FF. However, the devices at similar conditions generally gave poorer results, indicating that the interfacial contact issue between active layer and electrode may be much more complicated than expected.^[43,44] Furthermore, similar devices using [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) as the acceptor were also fabricated and tested. Though intensive optimization has been performed, generally lower PCEs and FF were obtained so far due to poor film quality clearly observed in AFM images (Figure S7, Supporting Information). And it is believed that the feeble compatibility between PC₇₁BM and oligothiophenes may cause poor film quality, resulting in lower performance. This is also consistent with our previous small molecules with the similar main chain.^[12] Also, no clear improvement was observed by thermal annealing.

It is important to note that both the values of PCE and J_{sc} for optimized devices using this material are the highest for all solution-processed small molecule solar cells so far and comparable with that of the best polymer solar cells.^[19,22,24] The higher J_{sc} , compared with that of DCAO7T with similar backbone structure but different end unit, is believed due to the high molar absorption enhanced by the end dye unit ethylrhodanine.

The incident photon to current efficiency (IPCE) curve of the BHJ devices based on this small molecule under monochromatic light is shown in Figure 2b. The IPCE curve exhibits a broad response covering 350–750 nm, with monochromatic IPCE maximum of 70%. These high values indicate that the photoresponse of this molecule is very efficient in the BHJ devices. The integration through the whole EQE (External Quantum Efficiency) spectrum has been carried out to give a J_{sc} of 13.10 mA cm^{-2} , which is in agreement with the photocurrent obtained by the $J\text{--}V$ measurements (within 6.3% error).

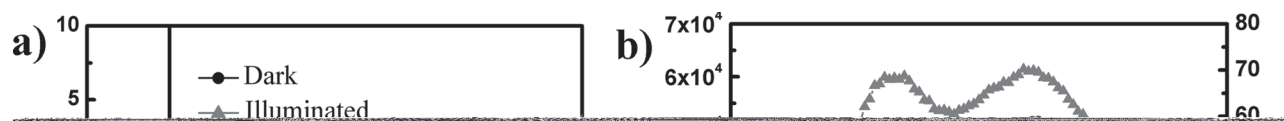


Figure 2. (a) Characteristic current density versus voltage ($J\text{--}V$) curves for the bulk heterojunction (BHJ) solar cells derived from DERHD7T/PC₆₁BM with w:w = 1:0.5. (b) The incident photon to current efficiency (IPCE) and absorption spectra for the BHJ devices derived from the blend of DERHD7T/PC₆₁BM with w:w = 1:0.5.

Note, the typical FF values for the devices are still low, which may indicate further optimization is needed to have even better performance.^[9]

In summary, a novel small molecule for OPV, with high absorption coefficient and high mobility, has been designed and synthesized with a dye end unit. This molecule gives a higher PCE than the landmark of 6% for the first time for any small-molecule-based BHJ OPV cells. This result demonstrates that the strategy, designing the molecules with balanced molecular band structure and morphology from the backbone part, together with a tunable end unit using a dye structure with a high molar absorption coefficient, should give rather promising OPV performance for small molecules by the simple solution process. These exciting results prompt us to believe strongly that further optimization for both the structure modification and device fabrication, which is currently underway at our group, should make small molecules to offer comparable, if not better, OPV performance as their polymer counterparts. This is obviously an exciting development when combined with the advantages of small molecules.

Supporting Information

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

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