Rhodanine dye-based small molecule acceptors for organic photovoltaic cells

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Rhodanine dye-based small molecule acceptors for organic photovoltaic cells

Yujeong Kim,[a] Chang Eun Song,[b] Sang-Jin Moon[c] and Eunhee Lim[*a]

The solution-processable small molecules based on carbazole or fluorene containing rhodanine dye at both ends were synthesized and introduced as acceptors in organic photovoltaic cells. The high energy levels of their lowest unoccupied molecular orbitals resulted in a power conversion efficiency of 3.08% and an open circuit voltage up to 1.03 V.

Organic photovoltaic cells (OPVs) have attracted attention as promising candidates for the production of renewable energy. Nowadays, solution-processed bulk-heterojunction (BHJ) solar cells have been developed to make interpenetrating networks with large donor–acceptor (D–A) interfacial areas. The importance of the flexible and large-area solar cells with long term stability is also emphasized for the commercial viability.[1] Currently, a power conversion efficiency (PCE) of 9.2% has been reported in solution-processed OPVs using a polymeric donor and a fullerene acceptor.[2] The development and synthesis of new donor and acceptor materials for use in the active layer are considered essential, together with technical progress on device fabrication to achieve high-performance BHJ solar cells. While advancements in donor materials have been actively progressing, the development of new acceptor materials has lagged behind. The fullerene derivatives of [6,6]-phenyl-C_{61} butyric acid methylester (PCBM) and [6,6]-phenyl-C_{71} butyric acid methyl ester ($PC_{71}BM$) have been widely used as representative acceptor materials because of their good electron mobility, adequate band gaps, and good interaction with donor materials in OPVs. However, they also have some disadvantages such as weak absorption in the visible region and difficult synthesis and purification. To solve these problems, new non-fullerene electron acceptor materials with high absorbance in the solar spectrum, facile synthesis, and controllable frontier orbital energy levels are needed for OPV applications.[3] The non-fullerene acceptor materials that have been introduced recently are mainly based on strong electron-withdrawing units such as rylene imide, vinazene, and diketopyrrolopyrrole. Although the PCE for OPVs employing non-fullerene small molecule acceptors has very recently reached 4.03%,[3d] the device efficiencies are still relatively low

compared to those of the corresponding PCBM devices, and few non-fullerene acceptors have PCEs over 3%.

Meanwhile, a series of dye building blocks including 3-ethylrhodanine (RH), 1,3-indandione, and 1,3-dimethylbarbituric acid (DMBA) have been introduced as electron-withdrawing units to be used in conjunction with the electron-rich units of oligothiophenes and/or benzo[1,2-b:4,5-b']dithiophene (BDT) to provide low band-gap small molecule donor materials.[4] The introduction of various dye end units effectively improved the light absorption and electron affinities and consequently resulted in a high performance as an electron acceptor. PCEs over 8% were obtained, and the device performances varied depending on the types of terminal dye units according to their different electron-withdrawing abilities.[4a] For example, a small molecule donor with 3-ethylrhodanine dye end units and a BDT central building block achieved a high PCE of 8.12%,[4b] which was the best PCE using a small molecule donor to date, and nearly reached the record performance of 9.2% in solution-processed OPVs based on a polymeric donor. In addition, small molecules having dye end units recently showed their potential for use as acceptors, with PCEs up to 2.56%.[5] In this case, 1,3-indandione was used as an electron-withdrawing unit in small molecule acceptors.

In this communication, we synthesized two small molecule acceptors by introducing rhodanine dye end groups to carbazole and fluorene cores for use in solution-processable OPVs. The simple syntheses and general properties of the rhodanine dye-based oligomers, including their thermal, optical, and electrochemical properties, were investigated. A PCE of over 3% is demonstrated in OPV cells (active area of 0.09 cm^2) fabricated with P3HT and our non-fullerene oligomer as donor and acceptor, respectively.
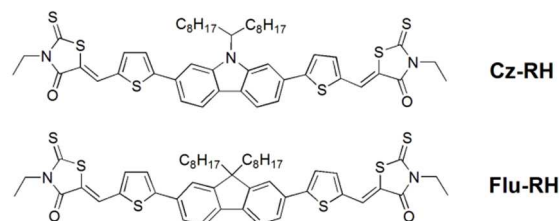

Fig. 1 Molecular structures of Cz-RH and Flu-RH.

Two small molecules (Cz-RH and Flu-RH), based on carbazole and fluorene, respectively, were synthesized with 3-ethylrhodanine dyes at both ends (Fig. 1). 2,7-Diboronic esters of carbazole and fluorene, whose syntheses are well-documented,[6] were reacted with 5-bromothiophene-2-aldehyde by a Suzuki coupling reaction. (see ESI†) Then, Cz-RH and Flu-RH were obtained in yields up to 70% by the Knoevenagel condensation of the diformyl compounds and 3-ethylrhodanine. The two oligomers show good solubility in common organic solvents such as chloroform, chlorobenzene (CB), and o-dichlorobenzene (o-DCB). The synthetic scheme and all the synthetic and characteristic details including ^{1}H and ^{13}C NMR spectroscopy and elemental analyses are shown in the ESI†. The thermal characteristics of the oligomers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, see ESI†). The two oligomers were sufficiently thermally stable for use in OPV applications, showing weight losses lower than 5% up to 420 °C.

The UV-visible absorption spectra of the two oligomers in solution are similar (Fig. 2). The absorption spectra of both oligomers in chloroform and o-DCB showed maxima at around 500 nm. While the Cz-RH and Flu-RH films spin-coated from chloroform exhibited slightly broadened absorption bands compared to the spectra of the solutions, the oligomer films prepared from o-DCB showed much broader absorption bands that extended up to 800 nm (λ_{max}(Cz-RH) = 525, 568 nm and λ_{max}(Flu-RH) = 510, 550 nm), providing favorable light-harvesting properties.[7] Such a broad absorption suggested that improved molecular aggregation exists in the films prepared from o-DCB.

The electrochemical properties of the oligomers were studied by cyclic voltammetry (CV) (Fig. 3a). The films were prepared by dip-coating the oligomer solution onto Pt wire and the measurements were calibrated using the ferrocene value of –4.8 eV as the standard. The anodic/cathodic scans showed that the onsets of oxidation/reduction for Cz-RH and Flu-RH occurred at 1.14/–0.89 V and 1.19/–0.86 V (vs SCE), respectively. The highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy levels of Cz-RH and Flu-RH were estimated as –5.53/–3.50 eV and –5.58/ –3.53 eV, respectively, according to the empirical relationship proposed by Leeuw et al. (I_p(HOMO) = –($E_{onset,ox}$ + 4.39) (eV) and I_p(LUMO) = –($E_{onset,red}$ + 4.39) (eV), where $E_{onset,ox}$ and $E_{onset,red}$ are the onset potentials of oxidation and reduction, respectively).[8] The high-lying LUMO levels of Cz-RH and Flu-RH compared to PCBM (–3.82 eV) could be responsible for the increased open-circuit voltage (V_{OC}) and high OPV efficiency.[9] The electrochemical energy band gaps (E_{elec}) for Cz-RH and Flu-RH are 2.03 and 2.05 eV, respectively, which are comparable to the optical band gaps (E_{opt}) of Cz-RH and Flu-RH estimated from the absorption onset wavelength of the oligomer films (E_{opt} = 2.05 eV and 2.10 eV in Cz-RH and Flu-RH films, respectively). The band diagram for the oligomers is shown in Fig. 3b, together with the energy levels of P3HT for comparison.[10]
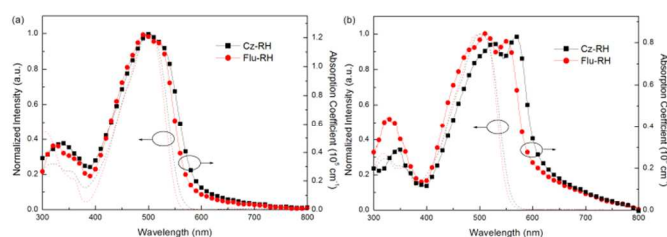

Fig. 2 UV-vis absorption spectra of Cz-RH (black) and Flu-RH (red) in (a) chloroform and (b) o-DCB. Normalized intensity (in dotted lines) and absorption coefficient (with symbols) were used for the spectra in solution and film, respectively.)
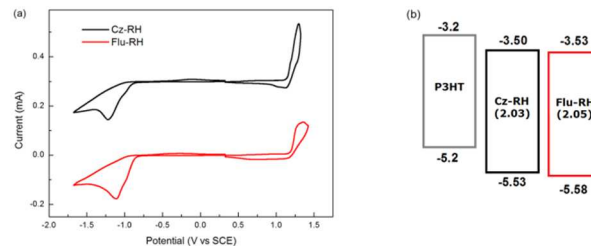

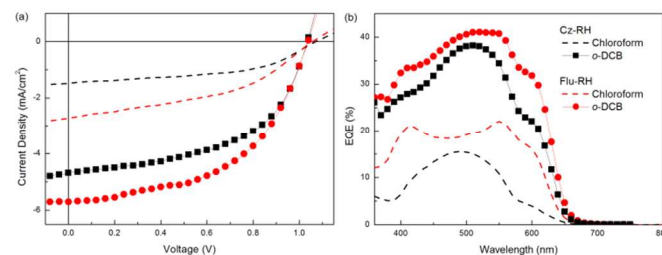Fig. 3 (a) CV and (b) energy diagram of Cz-RH (black) and Flu-RH (red) together with P3HT.

Fig. 4 (a) J–V curves and (b) EQE of P3HT:Cz-RH (black) and P3HT:Flu-RH (red) devices fabricated using chloroform (in dashed lines) and o-DCB (with symbols).

Table 1. Optimized photovoltaic properties of OPV devices

Acceptor	D–A ratio	Solvent	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Cz-RH	1:0.5	CHCl$_3$^{a}	1.07	1.48	50	0.79
	1:1	CB^a	1.05	2.20	41	0.94
	1:1.5	o-DCB^b	1.03	4.69	53	2.56
Flu-RH	1:2	CHCl$_3$^{a}	1.06	2.73	43	1.25
	1:1	CB^a	1.06	3.49	35	1.30
	1:1.5	o-DCB^b	1.03	5.70	52	3.08
PCBM	1:1	o-DCB^a	0.60	9.08	61	3.34

^{a} Annealed at 150°C for 10 min. ^{b} Annealed at 100 °C for 10 min.

OPV cells were fabricated with the configuration ITO/PEDOT:PSS/P3HT:oligomer/LiF/Al. Fig. 4 shows plots of the current-density versus voltage (J–V) and the external quantum efficiency (EQE) curves measured in air under white light AM 1.5 illumination (100 mW/cm^2), and the representative photovoltaic properties of the films are summarized in Table 1. P3HT:PCBM devices were also fabricated as a control for comparison. In addition, the oligomer:PCBM devices showed no photovoltaic characteristics. More detailed characteristics of devices fabricated with various blend ratios (D:A = 1:0.5, 1:1, and 1:2), annealing temperatures (pristine, 90 °C, 120 °C, and 150 °C), and solvents (chloroform, CB, and o-DCB) are provided in Tables S1–S2 and Figs S6–S12 in the ESI†. The optimized blending ratios and annealing temperatures were varied according to the acceptor and solvent. The small amount (0.5–3 wt%) of diiodooctane was also introduced as additive into the active layer but no noticeable improvement of performance was achieved. Under the same conditions, the highest performance was obtained with the device using o-DCB, and the devices using CB were superior to those from chloroform. For example, the Cz-RH device from o-DCB (2.56%) showed a PCE ca. 3 times higher than the PCEs obtained from chloroform (0.79%) and CB (0.94%). The difference caused by the solvent was mostly attributed to the J_{SC}, which probably originated from the differences in the degree of molecular aggregation. It is well-known that the molecular aggregation of the polymeric donor P3HT is dependent on the solvent used.[11] Our P3HT:PCBM device fabricated from o-DCB also exhibited a higher PCE (3.34%) than those from chloroform (3.01%)

and CB (1.44%, Table S2). More interestingly, the increase of J_{SC} from chloroform to *o*-DCB in the P3HT:Cz-RH and P3HT:Flu-RH devices is more enhanced than in the case of P3HT:PCBM. This can be explained by the solvent dependence of the molecular aggregation of the acceptors, which is seen in UV absorption spectra of the films.

Among the two acceptors, the PCE of Flu-RH was higher than that of Cz-RH mainly because of the better J_{SC} values of Flu-RH, which could be explained by the higher EQE intensity in Fig. 4b. The EQE intensity of Flu-RH is clearly higher than that of Cz-RH in the full wavelength region of 350–800 nm. The maximum EQE intensity of 40% was achieved in the P3HT:Flu-RH device. The higher EQE intensities of the films from *o*-DCB compared to the films from chloroform agreed well with the higher J_{SC} values obtained when using *o*-DCB. In this work, the P3HT:Flu-RH device using a blend ratio of 1:1.5 and *o*-DCB showed the best PCE of 3.08%, which is comparable to the PCE value (3.34%) obtained from the control P3HT:PCBM device fabricated under the same conditions. Such a good PCE was attributed to the considerably high V_{OC} of 1.03 V with a moderate J_{SC} and fill factor. The high V_{OC} values for the devices using both acceptors of Cz-RH and Flu-RH can be readily explained by the high-lying LUMO energy level (Fig. 3b). A similarly high V_{OC} value of 0.95 V was also reported with another fluorene-based non-fullerene acceptor and is a major advantage for these fluorene- and carbazole-based non-fullerene acceptors. It is worth noting that, despite the high-lying LUMO levels of the acceptors (Cz-RH and Flu-RH), a sufficient offset exists between the LUMOs of the P3HT and the acceptors, for efficient charge generation.[12] A photoluminescence (PL) quenching experiment was also performed to investigate the charge transfer characteristics between P3HT and the acceptors. A relatively high PL quenching efficiencies (PLQE) were obtained from P3HT:acceptor films (Fig S13, ESI†). In particular, higher PLQE of P3HT:Flu-RH film (86.7%) than P3HT:Cz-RH film (77.0%) indicates more efficient charge transfer from P3HT to Flu-RH than Cz-RH, supporting higher EQE intensity of P3HT:Flu-RH device.

Atomic force microscopy (AFM) images were measured to examine the morphology of the active layers (Fig S14, ESI†). For comparison, the exact same films of the OPV devices were used in the AFM measurements. The film morphologies of P3HT:Flu-RH and P3HT:Cz-RH using *o*-DCB are similar to the morphology in the P3HT:PCBM device. Such crystalline domains with a rough morphology are observed in annealed P3HT films due to the high degree of P3HT self-organization.[11,13] In addition, the values of the surface root-mean-square (rms) roughness of the P3HT:Flu-RH films increased from 0.70 nm (chloroform) to 14.97 nm (o-DCB). The films from *o*-DCB are rougher than those from chloroform, which matches well with the red-shifted UV absorption and efficient PL quenching observed in films from *o*-DCB. Further development of small molecule acceptor materials is in progress, including the replacement of the rhodanine end groups by various dye groups such as DMBA and [1,2']-biindenylidene-3,1',3'-trione.

Conclusions

In conclusion, we synthesized new small molecules, Cz-RH and Flu-RH, for use as acceptors in solution-processable OPVs. These two non-fullerene acceptors showed high PCEs up to 3.08% (active area of 0.09 cm^2) owing to the high V_{OC} and high-lying LUMO energy levels. The device performances were dependent on the solvent used, and better device performance was obtained using *o*-DCB. The improved UV absorption and good PL quenching (or film morphology) indicate the good molecular aggregation of the films from *o*-DCB. This work demonstrated that the introduction of dye units in small molecules based on carbazole and fluorene is a good strategy for developing new non-fullerene acceptors with high OPV devices performance.

Notes and references

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1 (a) D. Gupta, M. Bag and K. S. Narayan, *Appl. Phys. Lett.*, 2008, **93**, 163301; (b) A. K. Pandey, J. M. Nunzi, B. Ratier and A. Moliton, *Phys. Lett. A*, 2008, **372**, 1333; (c) J. U. Lee, J. W. Jung, J. W. Jo and W. H. Jo, *J. Mater. Chem.*, 2012, **22**, 24265.

2 Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photon.*, 2012, **6**, 591.

3 (a) A. Mishra and P. Bäuerle, *Angew. Chem. Int. Ed.*, 2012, **51**, 2020; (b) Y. Fang, A. K. Pandey, A. M. Nardes, N. Kopidakis, P. L. Burn and P. Meredith, *Adv. Energ. Mater.*, 2013, **3**, 54; (c) P. E. Schwenn, K. Gui, A. M. Nardes, K. B. Krueger, K. H. Lee, K. Mutkins, H. Rubinstein-Dunlop, P. E. Shaw, N. Kopidakis, P. L. Burn and P. Meredith, *Adv. Energ. Mater.*, 2011, **1**, 73; (d) X. Zhang, Z. Lu, L. Ye, C. Zhan, J. Hou, S. Zhang, B. Jiang, Y. Zhao, J. Huang, S. Zhang, Y. Liu, Q. Shi, Y. Liu and J. Yao, *Adv. Mater.*, 2013, **25**, 5791.

4 (a) Y. Chen, X. Wan and G. Long, *Accounts. Chem. Res.*, 2013, **46**, 2645; (b) J. Zhou, Y. Zuo, X. Wan, G. Long, Q. Zhang, W. Ni, Y.Liu, Z. Li, G. He, C. Li, B. Kan, M. Li and Y. Chen, *J. Am. Chem. Soc.*, 2013, **135**, 8484.

5 K. N. Winzenberg, P. Kemppinen, F. H. Scholes, G. E. Collis, Y. Shu, T. B. Singh, A. Bilic, C. M. Forsyth and S. E. Watkins, *Chem. Commun.*, 2013, **49**, 6307.

6 (a) J.-S. Wu, Y.-J. Cheng, M. Dubosc, C.-H. Hsieh, C.-Y. Chang and C.-S. Hsu, *Chem. Commun.*, 2010, **46**, 3259; (b) E. Lim, B.-J. Jung and H.-K. Shim, *Macromolecules*, 2003, **36**, 4288.

7 J. Hou, Z. A. Tan, Y. He, C. Yang and Y. Li, *Macromolecules*, 2006, **39**, 4657.

8 D. M. de Leeuw, M. M. J. Simenon, A. R. Brown and R. E. F. Einerhand, *Synthetic Met.*, 1997, **87**, 53.

9 M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789.

10 P. P. Khlyabich, B. Burkhart and B. C. Thompson, *J. Am. Chem. Soc.* 2011, **133**, 14534.

11 G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864.

12 T. V. Pho, F. M. Toma, B. J. Tremolet de Villers, S. Wang, N. D. Treat, N. D. Eisenmenger, G. M. Su, R. C. Coffin, J. D. Douglas, J. M. J. Fréchet, G. C. Bazan, F. Wudl and M. L. Chabinyc, *Adv. Energy Mater.*, 2013, DOI: 10.1002/aenm.201301007.

13 Y. Lin, P. Cheng, Y. Li and X. Zhan, *Chem. Commun.*, 2012, **48**, 4773.