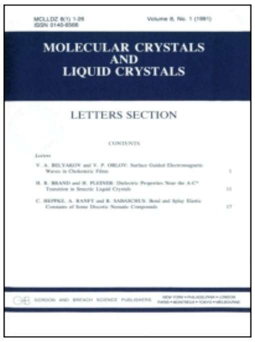


Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Solution-processed small-molecule organic solar cells based on diketopyrrolopyrrole and perlyene derivatives with coplanar structures

Woong Shin, Gyeong Eun Lim, Nadhila Sylvianti, Mutia Anissa Marsya, Devi Saskia Putri, Youn Whan Kim, Tae-Dong Kim, Hee Lack Choi, Bong Lee & Joo Hyun Kim

To cite this article: Woong Shin, Gyeong Eun Lim, Nadhila Sylvianti, Mutia Anissa Marsya, Devi Saskia Putri, Youn Whan Kim, Tae-Dong Kim, Hee Lack Choi, Bong Lee & Joo Hyun Kim (2016) Solution-processed small-molecule organic solar cells based on diketopyrrolopyrrole and perlyene derivatives with coplanar structures, Molecular Crystals and Liquid Crystals, 635:1, 40-44, DOI: 10.1080/15421406.2016.1199998

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1199998

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 635, 40–44
http://dx.doi.org/10.1080/15421406.2016.1199998

Solution-processed small-molecule organic solar cells based on diketopyrrolopyrrole and perlyene derivatives with coplanar structures

Woong Shin[a], Gyeong Eun Lim[a], Nadhila Sylvianti[a], Mutia Anissa Marsya[a], Devi Saskia Putri[a], Youn Whan Kim[a], Tae-Dong Kim[b], Hee Lack Choi[c], Bong Lee[a], and Joo Hyun Kim[a]

[a]Department of Polymer Engineering, Pukyong National University, Busan, Korea; [b]Department of Advanced Materials, Hannam University, Daejeon, Korea; [c]Department of Materials Science, Pukyong National University, Busan, Korea

ABSTRACT
A series of small-molecules (SMs) based on coplanar perylene unit coupled with diketopyrrolopyrrole chromophoric core exhibit broad absorption in the range of 500–800 nm and low bandgap energise of 1.6–1.7 eV. The power conversion efficiency approximately reach at 0.4% under 1.5 G illumination is achieved for organic solar cells based on a small-molecule bulk heterojunction system consisting of SMs as a donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as an acceptor.

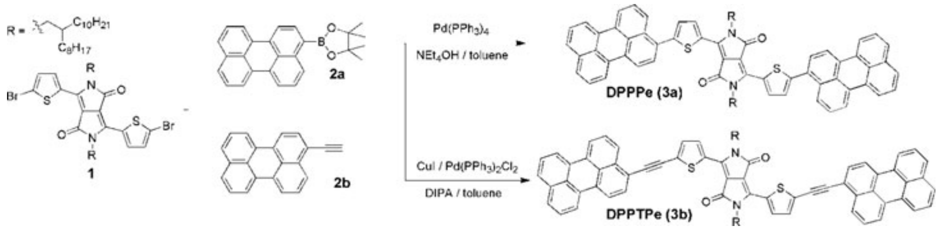
KEYWORDS
Organic solar cells; small-molecule; diketopyrrolopyrrole; perylene; coplanar structure

1. Introduction

Bulk hetero-junction (BHJ) organic solar cells (OSCs) based on low band gap π-conjugated polymers as a donor and fullerene derivatives as an acceptor have been intensively researched in recent years for developing and renewable clean energy [1–3]. Compare to the polymer solar cells (PSCs), small-molecule (SM)-based OSCs have made vast studies as polymeric counterparts, offering several unique advantages such as well-defined structure, monodispersity, easy purification, and better reproducibility [4, 5]. Even through tremendous high performance SM OSCs have been reported, the number of results are still lower than PSCs. The main problems of small-molecular system are relatively narrower absorption ability and poor film quality than polymeric system. To overcome these problems, well-reorganizing donor (D)-π-acceptor (A)-π-D or A-π-D-π-A core frameworks-based SMs with coplanar structures have been proposed and reported for SM OSCs with high performance approaching PSCs [6, 7]. Recently, diketopyrrolopyrrole (DPP) derivatives have been focused on efficient electron deficient unit in small-molecular systems, due to well conjugated rigid and coplanar backbone with electron withdrawing effect [8]. Especially, coplanar electron rich units, including benzofuran, benzene, and pyrene units coupled with central DPP chromophoric core-based SMs show high performances [9–11]. In this research, we describe the design, optoelectronic and photovoltaic properties of low bandgap π-conjugated D-π-A-π-D

CONTACT Joo Hyun Kim ✉ jkim@pknu.ac.kr 🖃 Department of Polymer Engineering, Pukyong National University, Yongdang-Dong, Nam-Gu, Busan 608-739, Korea (ROK).

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.



Scheme 1. Synthesis of small-molecules (DPPPe and DPPTPe).

type SMs (Scheme 1), 2,5-bis-(2-octyl-dodecyl)-3,6-bis-(5-perylen-3-yl-thiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPPPe) and 2,5-bis-(2-octyl-dodecyl)-3,6-bis-(5-perylen-3-ylethynyl-thiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPPTPe). In DPPTPe, electron rich ethynyl group were introduced inter-thienyl and Pe units for giving the more improved absorption ability into small-molecular backbone.

2. Experimental

2.1. Synthesis of 2,5-Bis-(2-octyl-tetradecyl)-3,6-bis-(5-perylen-3-yl-thiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPPPe) (3a)

To a mixture of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (**1**)[12] (0.24 g, 0.24 mmol) and 4,4,5,5-tetramethyl-2-perylen-3-yl-[1,3,2]dioxaborolane (**2a**)[13] (0.19 g, 0.51 mmol) in dry toluene (5 mL) was added $Pd(PPh_3)_4$ (13.9 mg, 12.0 μmol). The mixture was stirred for 10 min at 90°C. Tetraethylammonium hydroxide solution (TEA, 0.7 mL, 20 wt.% in water, 1.0 mmol) was then added, and the mixture was stirred for 6 h under reflux condition. After cooling to room temperature, the reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **3a** as a dark green solid (yield = 0.26 g, 76%). MS: [M^+], *m/z* 1417. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.12–9.11 (d, $J = 4.04$ Hz, 2H), 8.23–8.10 (m, 10H), 7.69–7.67 (d, $J = 8.04$ Hz, 4H), 7.56–7.57 (d, $J = 7.68$ Hz, 2H), 7.53–7.46 (m, 8H), 4.10–4.07 (d, $J = 7.68$ Hz, 4H), 1.23–1.19 (m, 70H), 0.87–0.85 (m, 16H), $C_{98}H_{116}N_2O_2S_2$: C, 83.00; H, 8.24; N, 1.98; O, 2.26; S, 4.52. Found: C, 83.01; H, 8.21; N, 1.96; O, 2.25; S, 4.51.

2.2. Synthesis of 2,5-Bis-(2-octyl-dodecyl)-3,6-bis-(5-perylen-3-ylethynyl-thiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (PPTPe) (3b)

To a stirred solution of **1** (0.13 g, 0.13 mmol) in diisopropylamine (DIPA):toluene blending solution (15 mL, 1:2, v/v) was added dry toluene (5 mL) was added $Pd(PPh_3)_2Cl_2$ (7.5 mg, 10 μmol) and cupper iodide (CuI, 2.0 mg, 10.0 μmol) at room temperature. The mixture was allowed to react for 30 min at room temperature. 3-Ethynyl-perylene (**2b**)[14] (0.25 g, 0.91mmol) was then added, and the mixture was stirred for 6 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After

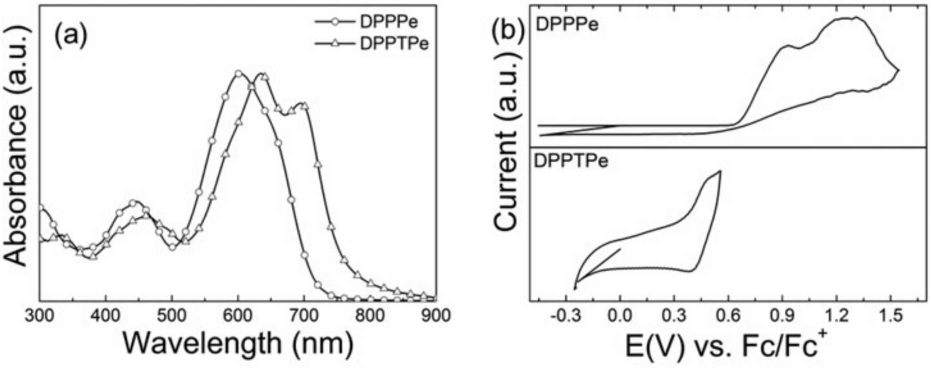


Figure 1. (a) UV/vis spectra of the small-molecule in thin films and (b) cyclic voltammograms of the small-molecules.

filtration and evaporation, the product was purified by silica gel column chromatography (eluent: chloroform), recrystallized from chloroform/methanol, and dried under vacuum to afford **3b** as a dark violet solid (yield = 0.13 g, 69%). MS: [M$^+$], *m/z* 1410. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.91–8.90 (d,*J* = 4.04 Hz, 2H), 8.20–8.18 (d, *J* = 7.32 Hz, 2H), 8.15–8.13 (d,*J* = 8.44 Hz, 2H), 8.10–8.08 (d, *J* = 7.36 Hz, 2H), 8.05–8.03 (d, *J* = 8.4 Hz, 2H), 7.66–7.62 (t, *J* = 8.43 Hz, 8H), 7.59–7.55 (t, *J* = 7.88 Hz, 2H), 7.44–7.41 (m, 6H), 4.02–4.00 (d, *J* = 7.32 Hz, 4H), 1.24–1.20 (m, 58H), 0.84–0.81 (m, 20H). Anal. Calcd. for $C_{98}H_{108}N_2O_2S_2$: C, 83.48; H, 7.72; N, 1.99; O, 2.27; S, 4.55. Found: C, 83.46; H, 7.71; N, 1.97; O, 2.25; S, 4.53.

3. Results and discussion

DPPPe and DPPTPe were synthesized from DPP precursor (**1**) and perylene (Pe) with or without ethynyl group, as shown in Scheme 1. SMs are soluble in organic solvents owing to their multiple solubilizing alkyl chain into DPP central core. Glass transition temperature of DPPPe and DPPTPe showed at 101 and 110°C, respectively. Melting behavior of DPPPe and DPPTPe appeared at 140 and 151°C, respectively. However, both materials did not show any crystallization behavior up to 200°C.

To investigate the optical properties of SMs, UV/vis absorption spectra and cyclic voltammetry (CV)[15] have been measured, and depicted in Figure 1. The UV-Vis absorption spectrum of DPPPe film shows broad absorption with a maximum absorption (λ_{max}) at 605 nm, as a result of strong intramolecular charge transfer (ICT). In DPPTPe film also shows broad absorption and red-shifted spectrum with the λ_{max} at 636. In addition, a vibronic shoulder peak at 697 nm was observed, which indicates stronger π-π stacking between molecular backbones attributed to existence of triple bonded ethynyl group between DPP and Pe backbones [16]. Compared to DPPPe with single bonding inter-thienyl and Pe units, ethynyl group with strong electron donating property in DPPTPe are caused by improving the ICT ability and having a more coplanar structures. The optical band gaps of DPPPe and DPPTPe are estimated to be 1.7 and 1.6 eV, respectably, from the absorption edge. The HOMO energies of SMs were calculated from the measured onset potential of oxidation by assuming the energy level of ferroccene (Fc) as − 4.8 eV by CV and figured out from the oxidation onset potentials of DPPPe and DPPTPe was – 5.2 eV (Figure 1b). The LUMO energy levels of DPPPe (– 3.5 eV) and DPPTPe (– 3.6 eV) were estimated from the HOMO energy level and the

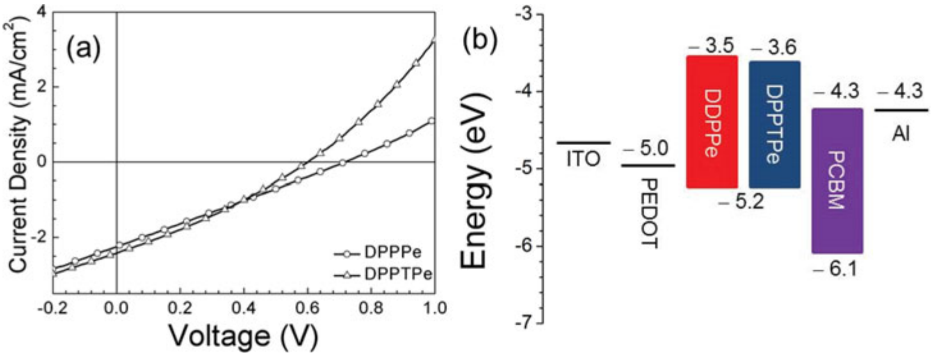


Figure 2. (a) Current density-voltage (*J-V*) characteristics under one sun illumination and (b) energy diagram for solar cells based on SM:PC_{61}BM (1:2, w/w) BHJ blends.

optical band gap energy. Energy level diagram of SM-based OSC are shown in Figure 2b, and SMs could be applied to BHJ OSCs as the donor, due to higher LUMO energy values above 0.3 eV than the that of PC_{61}BM [17].

Solution-processed BHJ OSCs were fabricated using SMs as the donor and PC_{61}BM as the electron acceptor with a device structure of ITO/PEDOT:PSS/SM:PC_{61}BM/Al. Figure 2a shows the current density-voltage (*J-V*) characteristics of the optimized BHJ OSCs based on SM:PC_{61}BM (1:2, w/w) blend. The DPPP:PC_{61}BM blend-based OSCs showed the power conversion efficiency (PCE) of 0.41% with a short-circuit current density (J_{sc}) of – 2.24 mA/cm^2, V_{oc} of 0.72 V, and fill factor (FF) of 0.26. In the DPPTPe:PC_{61}BM blend-based OSCs showed similar performance with a J_{sc} of – 2.42 mA/cm^2, V_{oc} of 0.60 V, and FF of 0.40 yielding a PCE of 0.43%. Thermal and solvent annealing also additive technique were tried to improve the device performance, but any improvement of PCEs could not be observed. Despite the linkage between DPP and Pe units with coplanar structures, branched octyldodecyl chain in DPP central core seems to prevent the well-ordered orientation, due to amorphous characteristics, and thus SMs are unable to an appropriate chromophore packing structure after any treatments.

4. Conclusions

We have synthesized and characterized a series of diketopyrrolopyrrole and perylene-based small-molecules (SMs). The SMs show broad absorption in the range of 500–800 nm and low bandgap energise of 1.6–1.7 eV, as a result of intermolecular charge transfer. DPPTPe with ethynyl group shows broader absorption characteristic than DPPPe without ethynyl group. The use of these molecules as donors has been demonstrated in solution-processed organic solar cells with PC_{61}BM as the acceptor. The photovoltaic performances approximately 0.4% is achieved for OSCs based on a bulk-hetero-junction system consisting of SMs as the donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM) as an acceptor.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2015015683) and Ministry of Education, Science and Technology (MEST) and by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (20153010140030).

References

[1] Yu, G., Gao, J., Hummelen, J. C., Wudl, F., & Heeger, A. J. (1995). *Science*, *270*, 1789.

[2] Peumans, P., Yakimov, A., & Forrest, S. R. (2003). *J. Appl. Phys.*, *93*, 3693.

[3] Service, R. F. (2011). *Science*, *332*, 293.

[4] He, Z., Zhong, C., Su, S., Xu, M., Wu, H., & Cao, Y. (2012). *Nat. Photon.*, *6*, 593.

[5] Sun, K., Xiao, Z., Lu, S., Zajaczkowski, W., Pisula, W., Hanssen, E., White, J. M., Williamson, R. M., Subbiah, J., Ouyang, J., Holmes, A. B., Wong, W. W. H., & Jones, D. J. (2015). *Nat. Commun.*, *6*, 6013.

[6] Kan, B., Li, M., Zhang, Q., Liu, F., Wan, X., Wang, Y., Ni, W., Long, G., Yang, X., Feng, H., Zuo, Y., Zhang, M., Huang, F., Cao, Y., Russell, T. P., & Chen, Y. (2015). *J. Am. Chem. Soc.*, *137*, 3886.

[7] Shin, W., Yasuda, T., Hidaka, Y., Watanabe, G., Arai, R., Nasu, K., Yamaguchi, T., Murakami, W., Makita, K., & Adachi, C. (2014). *Adv. Energy Mater.*, *4*, 1400875.

[8] (a) Qu, S., & Tian, H. (2012). *Chem. Commun.*, *48*, 3039. (b) Kim, J.-H., Song, C. E., Kang, I.-N., Shin, W. S., & Hwang, D.-H. (2013). *Chem. Commun.*, *49*, 3248.

[9] Walker, B., Tamayo, A. B., Dang, X. D., Zalar, P., Seo, J. H., Garcia, A., Tantiwiwat, M., & Nguyen, T.-Q. (2009). *Adv. Funct. Mater.*, *19*, 3063.

[10] Shin, W., Yasuda, T., Watanabe, G., Yang, Y. S., & Adachi, C. (2013). *Chem. Mater.*, *25*, 2549.

[11] Lee, O. P., Yiu, A. T., Beaujuge, P. M., Woo, C. H., Holcombe, T. W., Millstone, J. E., Douglas, J. D., Chen, M. S., & Fréchet, J. M. J. (2011). *Adv. Mater.*, *23*, 5359.

[12] Stas, S., Sergeyev, S., & Geerts, Y. (2010). *Tetrahedron*, *66*, 1837.

[13] Brown, K. E., Veldkamp, B. S., Co, D. T., & Wasielewski, M. R. (2012). *J. Phys. Chem. Lett.*, *3*, 2362.

[14] Yamaji, M., Maeda, H., Nanai, Y., & Mizuno, K. (2012). *Chem. Phys. Lett.*, *536*, 72.

[15] Shin, W., Jo, M. Y., You, D. S., Jeong, Y. S., Yoon, D. Y., Kang, J. W., Cho, J. H., Lee, G. D., Hong, S. S., & Kim, J. H. (2012). *Synth. Met.*, *162*, 768.

[16] Kan, B., Zhang, Q., Li, M., Wan, X., Ni, W., Long, G., Wang, Y., Yang, X., Feng, H., & Chen, Y. (2014). *J. Am. Chem. Soc.*, *136*, 15529.

[17] Walker, B., Tamayo, A. B., Dang, X., Zalar, P., Seo, J. H., Garcia, A., Tantiwiwat, M., & Nguyen, T. Q. (2009). *Adv. Funct. Mater.*, *19*, 3063.