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Graphical Abstract



TEXT

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Synthesis of promising new constituted low bandgap small molecules based on the *push-pull* (Donor-Acceptor) system and obtained power conversion efficiency up to 3.24%.

Paper

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A Facile method to synthesize [A`(D`AD)₂]-based push-pull small molecules for organic photovoltaics

Mohamed Shaker, Jong-Hoon Lee, Cuc Kim Trinh, Wonbin Kim, Kwanghee Lee, and Jae-Suk Lee*

An efficient route to synthesize, for the first time, a series of small molecules based on the [A`(D`AD)₂] architecture was developed using selective direct heteroarylation of the C-H bond with a Pd(AcO)₂/Bu₄NBr simple catalytic system. The C-H arylation of the unsymmetrical compound 4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(thiophen-2yl)benzo[c][1,2,5] thiadiazole (5), showed that, the (C5) in the ethyldioxythiophene moiety is more reactive towards C-H arylation than its counterpart in the thiophene unit. The new small molecules bear two different acceptors and/or donors which led to decrease the electron band gap and improve the strength of push-pull system as well as the amount of intramolecular charge transfer from donor to acceptor units. Lactams and imide containing acceptors are used as second electron withdrawing units due to their well-conjugated structure, strong π - π interaction and the lactam and high electron affinity as well as their potential as electron withdrawing units in photovoltaics conjugated materials. All small molecules showed broad absorption spectra with the optical band gaps which were estimated to be in the range of 1.72-1.29 eV. From the Cyclic voltammetry, the high occupied molecular orbital (HOMO) energy level could be tuned with the changing of the second acceptor, suggesting high open circuit voltage (V_{oc}). The EHID(EDBTT)₂:PC₇₁BM-based solar cells reached a maximum PCE of 3.24%.

Introduction

Recently, much focus has been on the solution processing of organic solar cells development. The organic small molecules have unique advantages, such as, low cost, flexibility, lightweight, and large-area device fabrication.¹⁻⁴ Moreover, small molecules offer potential advantages over the conjugated polymer, such as, their defined molecular structure, high purity, easy purification, easy mass-scale production and good batch-to-batch reproducibility. The previous advantages encouraged many scientists to dear their challenges to design the perfect small molecule chemical structure to improve the optical and electrical properties, as well as the power conversion efficiency 5-8 that recently achieved up to 10%. The the first bulk heterojunction solar cell was realized in 1995.⁹ This design improved the charge extraction and enhanced both of light absorption and the photocurrent density. Ten years later, the first solutionprocessed small molecules were introduced as donor material in the molecular bulk heterojunction (BHJ). That materials based on the oligothiophenes which investigated as the novel

electron donors and blended with PCBM, and showed in a power conversion efficiency of in the range of $0.2 \sim 0.8\%$.^{10,11}

Recently, a series of conjugated donor-acceptor (push-pull) chemical structures were developed. That helps to broad the absorption window, increase the efficiency of intramolecular charge transfer (ICT)^{12a,b} along the backbone structure, and enhance the net short circuit current $(J_{sc})^{12c-15}$ in device applications. Among these structures, a series of conjugated (D-A-D) and (A-D-A) small molecules based on 2,1,3benzothiadiazole.¹⁶⁻¹⁹ Thieno[3,4-c]pyrrole-4,6-dione,²⁰ diketopyrrolo-pyrrole,²¹⁻²⁴ and isoindigo²⁵⁻²⁷ as electron accepting units were integrated into two low-energy gap oligothiophenes. These materials showed broad absorption bands. Insertion of second donor into (D-A-D) small molecule structure offered a variety of architectures, such as [A(D-D`)₂]²⁸ and [D`(D-A-D)2]²⁹⁻³¹ building blocks.

In parallel, most of organic small molecules are synthesized via Stille and/or Suzuki cross-coupling reactions.^{32,33} Despite the high selectivity of these synthesis methodologies, they have some disadvantages, such as, contamination by organometallic intermediates. Recently, we succeeded in the synthesis of isoindigo based small molecules³⁴ via Stille and Suzuki cross-coupling methodologies, which needed organometallic monomer derivatives that contaminated several byproducts in the net product. To avoid the difficulty that faced during the synthesis of some stannyl and/or boronic esters, catalyzed C-H direct heteroarylation was preferred.

In this work, Pd(OAc)₂ catalyzed C-H direct arylation methodology³⁵⁻³⁷ was used to synthesize a new series of

Page 2 of 9

School of Materials Science & Engineering and Research Institute for Solar and Sustainable Energies (RISE), Heeger Center for Advanced Materials (HCAM), Gwangju Institute of Science and Technology, Gwangju 500-712, Korea.

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[A`(D`AD)₂] conistituted small molecules. Compound 4-(2,3dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(thiophen-2yl)benzo[c] [1,2,5]thiadiazole (EDBTT) (5) was the key structure of this class of materials (Scheme 1), which contain ethylene dioxythiophene (EDOT) and thiophene as electron rich cores which offered strong (ICT) with acceptors and extended the low energy optical transitions.³⁶ In addition, 2,1,3benzothiadiazole (BT) afforded high electron affinity, which increased across the backbone structure through the introduction of another electron accepting core such as 2,5bis(2-ethylhexyl)-3,6-di(thien-2-yl)pyrrolo[3,4-c]pyrrole-1,4-

(2H,5H)-dione (DTDPP) (7), N,N'-bis(2-ethylhexyl)isoindigo (EHID) (9) and\or 5-hexylthieno[3,4-c]pyrrole-4,6-dione (HTPD) (11) between the two arms of (EDBTT) to obtain our targets A`(EDBTT)₂ (Scheme 1) and showed the success of CH-arylation methodology in the synthesis of much complicated small molecules in minimal steps.

All of the previous acceptors have high electron affinities that help to low-lying the HOMO levels and maintain high oxidation potentials. In addition, the attached aliphatic chains to these acceptor moieties induced solubility of the obtained small molecules in the most of organic solvents,² which helps the solution processable solar cells.



Synthesis of monomers and small molecules

4-bromo-7-(thiophen-2-yl)-2,1,3-Synthesis of benzothiadiazole (3). 4,7-Dibromo-2,1,3-benzothiadiazole (1.00 g, 3.40 mmol) and tributyl(thiophen-2-yl)-stannane (1.39 g, 3.70

Pd(PPh₃)₂Cl₂/ Tolue Pd(PPh₃)₂Cl₂/ Toluene (EDBTT) P(EDBTT) HID(EDBTT) HTPD(EDBTT)

(12) C-H arylation = $Pd(AcO)_2$ / AcOK / (Bu)₄NBr / DMF / 80°C, 24hr

Scheme 1 Synthetic route of DTDPP(EDBTT)2, EHID(EDBTT)2 and HTPD(EDBTT)2 via C-H arylation reaction.

Experimental

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Materials

3,4-ethylenedioxythiophene (Sigma-Aldrich, 97%), thiophene-3,4dicarboxylic acid (Frontier Scientific), 2,1,3-benzothiadiazole (Sigma-Aldrich, 98%), 2-(tributylstannyl)- thiophene (Sigma-Aldrich, 97%) are used as received. The materials 4,7-dibromo-2,1,3benzothiadiazole (1),^{38,39} 2,5-bis(2-ethylhexyl)-3,6-di(5-bromothien-2-yl)pyrrolo[3,4-c]- pyrrole-1,4-(2H,5H)-dione (7),40 6,6'-dibromoN,N'-bis(2-ethylhexyl)-isoindigo (9),⁴¹ 2-tributylstannyl-3,4-ethylenedioxythiophene (4),⁴² 1,3-dibromo-5-hexylthieno[3,4-c]pyrrole-4,6dione (HTPD) (11)⁴³ were synthesized by literature procedures.

Characterization

¹H and ¹³C NMR spectra were measured with a Varian spectrometer (400 and/or 300MHz). The UV/Vis absorption spectra were obtained with a Varian Cary UV/Vis/NIR-5000 spectrophotometer on the pure samples. Differential scanning calorimetry (DSC) was performed with a TA instrument (DSC-TA Q-20) under nitrogen at a heating rate of 10 °C/min. Cyclic voltammetry (CV) measurements performed with B-class were а solar simulator: Potentiostate/Galvanostate (SP-150 OMA company); the supporting electrolvte was tetrabutylammonium-hexafluorophosphate (Bu_4NPF_6) in acetonitrile (0.1 M) and the scan rate was 50 mV/s. A three-electrode cell was used; a Pt wire and silver/silver chloride [Ag in KCl (0.1 M)] were used as the counter and reference electrodes, respectively. The HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO}) of the materials were determined from the following relationships: $E_{HOMO} = -E_{ox} - 4.71$ and $E_{LUMO} = -E_{red} - 4.71$ (in eV), where E_{ox} and E_{red} are the onset oxidation and reduction potentials, respectively, of the material vs. the Ag/AgCl reference electrode. The small molecules thin films for electrochemical measurements were drop-coated from a materials/chloroform solution on ITO glass slides, 10 mg/mL. XRD experiments were performed with a Bruker D8 advanced model diffractometer and with Cu-Kα radiation $(\lambda = 1.54 \text{ Å})$ at a generator voltage of 40 kV and a current of 40 mA.

Fabrication and characterization of photovoltaic devices

The bulk heterojunction organic photovoltaic devices were

fabricated with a structure of ITO/PEDOT:PSS/organic material:PC71BM/Ca/Al. The ITO substrates were sequentially cleaned by ultrasonication using a detergent, deionized water, acetone and isopropyl alcohol. Surface treatment was performed by exposing the ITO to UV/ozone treatment. PEDOT:PSS (Clevios P VP AI4083) solution was spin coated at 5000 rpm for 20 s on an ITO substrate, serving as an anode. The coated substrate was dried at 150 °C for 10 min in air and was transferred into a glove box filled with N₂. The small molecule: $PC_{71}BM$ (1:1, w/w), dissolved in chlorobenzene with a concentration of 20 mg/mL, was spin cast on the PEDOT:PSS layer and dried at 100 °C for 5 min except for (first small molecule). The cathode, Ca (10 nm) and Al (100 nm), was deposited in a vacuum chamber (10⁻⁶ Torr). The active area was 4.64 mm². The current–voltage (J–V) characteristics were measured under air mass (AM) 1.5 G illumination with light-source operation at 100 mW/cm². The incident photon-to-current efficiency (IPCE) measurements were performed using a QE-IPCE 3000 spectral response/QE/IPCE measurement system (Titan Electro-Optics Co. Ltd.).



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mmol) were dissolved in anhydrous Toluene (50 ml) and dichlorobis(triphenylphosphine)-palladium(II) (0.120 g, 0.170 mmol) was added at room temperature and degassed with argon for 20 min. The mixture was refluxed at 110 °C for 24 hr under nitrogen atmosphere. After have been allowed to cool to room temperature, the reaction mixture was extracted with EtOAc and the organic layers were separated, washed thoroughly with water, and finally dried with anhydrous Na₂SO₄. The solvent was evaporated under vacuum and the crude product was purified by neutralized silica gel flash column chromatography (hexane) to generate a yellow solid (0.670 g, 66% yield) of **3**. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.99 (d, J = 4.03 Hz, 1H, CH, thiophene), 7.75 (d, 1H, CH, benzothiadiazole), 7.60 (d, 1H, CH, benzothiadiazole), 7.38 (d, J = 4.03 Hz, 1H, CH, thiophene), 7.12 (dd, 1H, CH, thiophene); ¹³C NMR (100 MHz, CDCl3), δ (ppm): 153.68, 151.90, 138.41, 128.08, 127.99, 127.23, 127.00, 125.76, 112.28; MALDI TOF [M+1]⁺ found: 297.17 (calcd: 297.19); Anal. Calcd for C₁₀H₅BrN₂S₂: C, 40.41; H, 1.70; Br, 26.89; N, 9.43; S, 21.58; Found: C, 40.39; H, 1.70; Br, 26.77; N, 9.49; S, 21.51.

Synthesis of 4-(3,4-ethylenedioxythiophene-7`-yl)-7-(thiophen-2-yl)-2,1,3-benzothiadiazole (5)(EDBTT). A mixture of 3 (3.00 g, 10.0 mmol), 2-tributylstannyl-3,4-ethylenedioxythiophene (4) (4.50 g, 11.0 mmol) and Pd(PPh₃)₂Cl₂ (0.350 g, 0.500 mmol) was dissolved in THF (50 mL) and degassed with nitrogen for 20 min. The reaction mixture was stirred and heated under reflux at 73 °C for 16 h. After having been allowed to cool to room temperature, the reaction mixture was extracted with ethyl acetate and the organic layers were separated, washed thoroughly with water, and finally dried with anhydrous Na2SO4. The solvent was evaporated under vacuum and the crude product was purified by silica gel flash column chromatography (n-hexane/ EtOAc 10:1) to generate 5 (1.25 g, 34% yield) as an orange red solid. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.33 (d, J = 4.00 Hz, 1H, CH, thiophene), 8.07 (s, 1H, CH, benzothiadiazole), 7.86 (s, 1H, CH, benzothiadiazole), 7.41 (d, J = 4.00 Hz, 1H, CH, thiophene), 7.19 (dd, 1H, CH, thiophene), 6.57 (s, 1H, CH, EDOT-thiophene), 4.38 (t, J = 12.00 Hz, 2H, CH₂, EDOT), 4.30 (t, J = 12.00 Hz, 2H, CH₂, EDOT); 13 C NMR (100 MHz, CDCl3), δ (ppm): 152.46, 152.28, 141.60, 140.46, 139.56, 127.90, 127.12, 126.11, 113.44, 102.39, 64.99, 64.28; MALDI TOF [M+1]⁺ found: 358.44 (calcd: 358.46); Anal. Calcd for C₁₆H₁₀N₂O₂S₃: C, 53.61; H, 2.81; N, 7.81; O, 8.93; S, 26.84; found: C, 53.60; H, 2.80; N, 7.79; O, 8.90; S, 26.87.

General Procedure for Thermal direct Pd catalyzed CHarylation Cross-Coupling. Under dry condition, a mixture of 5 (0.360 g, 1.00 mmol), desired dibromo-derivative (7, 9 and/or 11) (0.480 mmol), potassium acetate (0.590 g, 6.00 mmol), tetrabutylammonium bromide (TBAB) (0.640 g, 2.00 mmol) and palladium acetate (0.040 g, 0.200 mmol) in dry DMF (15 ml) was degassed with nitrogen for 20 min then heated under reflux for 24 h at 80 C. The reaction mixture was cooled to room temperature followed by adding a mixture of CH_2CI_2 (50 ml) and water (25 ml). The organic layer was separated and dried with anhydrous Na_2SO_4 , then filtered and concentrated under reduced pressure. The crud product was purified by flash chromatography on silica gel eluted by n-hexane/EtOAc (10:3) to give the corresponding product derivative.

Synthesis of DTDPP(EDBTT)2. Compound 5 (0.186 g, 0.520 mmol). 2,5-bis(2-octyldodecyl)-3,6-di(5-bromothien-2-yl)pyrrolo-[3,4-c]pyrrole-1,4-(2H,5H)-dione (7) (0.143 g, 0.21 mmol), to afford 8 (0.148 g, 60% yield), as a deep violet solid. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.17 (d, J = 3.30 Hz, 2H, 2xCH, DPP-thiophene), 8.40 (d, J = 5.1 Hz, 2 H, 2xCH, benzothiadiazole), 8.06 (s, 2 H, 2xCH, benzothiadiazole), 7.83(d, 2H, 2xCH, thiophene), 7.36 (d, 2H, 2xCH, DPP-thiophene), 7.12 (d, J = 4.66, Hz 2H, 2xCH, thiophene), 6.89(d, J = 4.30 Hz, 2H, 2xCH, thiophene), 4.91-4.82 (m, 8H, 4xCH₂, EDOT), 3.05 (m, 4 H, 2xCH₂-, hexyl-C1), 1.68 (m, 2H, 2xCH-, hexyl-C2), 1.19-1.33 (m, 16H, 2x(CH₂)₃, hexyl-C3-C5 & 2xCH₂, ethyl-), 0.740-0.790 (m, 12H, 4xCH₃-, ethylhexyl-); MALDI TOF [M+1]⁺ found: 1237.65 (calcd: 1237.66); Anal. Calcd for C₆₂H₅₆N₆O₆S₈: C, 60.17; H, 4.56; N, 6.79; O, 7.76; S, 20.73 found: C, 60.11; H, 4.50; N, 6.78; O, 7.69; S, 20.67.

Synthesis of EHID(EDBTT)₂. Compound **5** (0.186 g, 0.520 mmol), reacted with 6,6⁻dibromo-N,N⁻bis(2-ethylhexyl)-isoindigo 9 (0.152 g, 0.230 mmol), to afford 10 (0.101 g, 57% yield), as a dark blue solid. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.10 (d, *J* = 8.40 Hz, 1H, indole), 9.02 (d, *J* = 8.40 Hz, 1H, indole), 8.41 (d, *J* = 4.60 Hz, 2H, 2xCH, thiophene), 8.10 (s, 2H, 2xCH, benzothiadiazole), 7.86 (s, 2H, 2xCH, benzothiadiazole), 7,43 (dd, 2H, 2xCH, thiophene) 7.31 (d, *J* = 4.00 Hz, 2H, 2xCH, thiophene), 7.26 (dd, *J*₁ = 7.55 Hz, *J*₂ = 2.30 Hz, 2H, 2xCH, indole), 6.83 (d, *J* = 1.87 Hz, 2H, 2xCH, indole), 4.49-4.45 (m, 8H, 4xCH₂, EDOT), 3.66 (m, 4 H, 2xCH₂-, hexyl-C1), 1.84(m, 2H, 2xCH-, hexyl-C2), 1.35-1,32 (m, 16H, 2x(CH₂)₃, hexyl-C3-C5 & 2xCH₂, ethyl-), 0.920-0.890 (m, 12H, 4xCH₃-, ethylhexyl-); MALDI TOF [M+1]⁺ found: 1199.56 (calcd: 1199.57); Anal. Calcd for C₆₄H₅₈N₆O₆S₆: C, 64.08; H, 4.87; N, 7.01; O, 8.00; S, 16.04; found: C, 64.06; H, 4.87; N, 6.99; O, 8.01; S, 15.91.

Synthesis of HTPD(EDBTT)₂. Compound **5** (0.186 g, 0.520 mmol), reacted with 1,3-dibromo-5-hexyl-5H-thieno[3,4-c]pyrrole-4,6-dione 11 (0.093 g, 0.230 mmol), to afford 12 (0.128 g, 37% yield), as a dark brown solid. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.45 (d, *J* = 4.05 Hz, 2 H, 2xCH, thiophene), 8.14 (s, 2 H, 2xCH, benzothiadiazole), 7.91 (s, 2 H, 2xCH, benzothiadiazole), 7.68 (d, *J* = 4.00 Hz, 2H, 2xCH, thiophene), 7.45 (dd, 2H, 2xCH, thiophene), 4.53-4.51 (m, 8H, 4xCH₂, EDOT), 3.66 (m, 2 H, CH₂-, hexyl-C1), 1.55 (m, 2 H, CH₂-, hexyl-C2), 1.31 (m, 6 H, 3xCH₂, hexyl-C3-C5), 0.870 (t, 3H, CH₃-, hexyl-C6); MALDI TOF [M+1]⁺ found: 950.07 (calcd: 950.20); Anal. Calcd for C₄₄H₃₁N₅O₆S₇: C, 55.62; H, 3.29; N, 7.37; O, 10.10; S, 23.62; found: C, 55.98; H, 3.29; N, 7.37; O, 10.13; S, 23.55.

Results and discussion

Synthesis and characterization

As shown in Scheme 1, 4,7-dibromo-2,1,3-benzothiadiazole (1) was coupled with 2-(tributylstannyl)thiophene (2) under Stille coupling conditions to afford 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3) in a good yield. Compound 3 was then reacted with 2-tributylstannyl-3,4-ethylenedioxy-thiophene (4) to obtain co-monomer 5. To optimize the synthesis of new small molecules using direct C-H arylation, several reaction conditions were utilized as shown in (Table S1, ESI⁺). The optimal reaction condition was achieved by using Pd(OAc)₂ as a catalyst, terabutylammonium bromide (TBAB)

ARTICLE

and KOAc as a base. The temperature, solvent, and concentration were held constant for this work, based on general procedures was reported in the literature.^{13a,b} Furthermore, $Pd(OAc_2)(O-Tol)^{33}$ catalyst was not sufficient for this reaction, even combined with TBAB and/or tris(2-methoxyphenyl)phosphine (L2), (Table S1. ESI⁺). By using one step, highly selective, Pd-catalyzed direct arylation coupling reaction, compound **5** coupled with a series of electron withdrawing moieties, **7**, **9** and/or **11**, to afford DTDPP(EDBTT)₂ (**8**), EHID(EDBTT)₂ (**10**) and HTPD(EDBTT)₂ (**12**), respectively, (Scheme 1).

The selectivity resulted from the difference in reactivity between (C5) in the EDOT moiety and its counterpart in the thiophene unit. The (C5) in the EDOT moiety is more active due to the effect of the cyclic ether oxygen atom, which acts as a directing group. This cyclic ether oxygen attracted the Pd catalyst by coordination bond and makes the catalyst much nearby position of (C5) in the EDOT moiety, see the proposed reaction mechanism pathway (Scheme S1, ESI⁺). This simple catalytic system decreases the obtained by-products and avoids the use of organometallic reagents, as well as helps to obtain a reasonable product yield.³³



Fig. 1 (a) TGA thermograms of DTDPP(EDBTT)₂, EHID(EDBTT)₂ and HTPD(EDBTT)₂ and (b) Differential scanning calorimetry (DSC) curves of DTDPP(EDBTT)₂, EHID(EDBTT)₂ and HTPD(EDBTT)₂ under nitrogen at a heating rate of 10 °C/min.

All of the new materials structures were thermally stable and were confirmed with NMR spectroscopy, FT-IR and elemental analysis. The FT-IR spectra provided an evidence for the presence of the lactam and imide groups by showing two peaks assigned to free carbonyl (-C=O) stretching vibration in the range of 1682–1800 cm⁻¹ (Fig. S1, ESI[†]).

Thermal stability

The DSC curve exhibited clear melting peaks and phase transitions of crystallization of the A'(D'AD)2 based small molecules, DTDPP(EDBTT)₂, EHID(EDBTT)₂ and HTPD(EDBTT)₂ (Fig. 1b). The melting (T_m), crystallization (T_c) and decomposition (T_d) temperatures are summarized in (Table S2, ESI[†]). As known, the molecular weights, intermolecular interactions and the alkyl chain affected the thermal properties. The melting point of DTDPP(EDBTT)₂ the due to the high planar structure and rigidity of isoindigo unit. Furthermore, DTDPP(EDBTT)₂ showed slightly phase transition signal observed at around 101°C supposed to be a result of twisted structure for the present molecule, due to the steric hindrance at the linkage between EDOT and benzothiadiazole unit.⁴⁴

The HTPD(EDBTT)₂ showed low T_m at 85 °C due to the attachment of the hexyl- chain to the small size TPD unit. The thermal stability of all the small molecules was observed by TGA at a heating rate of 100 °C/min under nitrogen (Fig. 1a). When the threshold for the thermal decomposition was defined at a mass loss of 5%, all the materials possess good thermal stability with decomposition temperatures above 350 °C.

X-ray diffraction analysis

To the study the crystalline structure and the planarity of the obtained materials 8, 10 and 12, X-ray diffraction (XRD) measurements were obtained (Fig. S2, ESI⁺). New small molecules exhibited two important diffraction peaks, the first one at approximately $2\theta = 5.79^{\circ}$ (DTDPP(EDBTT)₂), 6.64° (EHID(EDBTT)₂) and 5.45° (HTPD(EDBTT)₂), which corresponds to a d-spacing of 15.4, 14.0 and 17.1 Å, respectively, These spacing referred to the interchain spacing between the planes of the main conjugated backbone of these small molecule separated by the corresponding ethylhexyl- and/or hexylchains. The high intensities observed in the diffraction peaks of DTDPP(EDBTT)₂ and EHID(EDBTT)₂ proved a better ordering in solid state, which would led to good film morphology for BHJ solar cells. The second peak assigned at 2θ = 21.46° (DTDPP(EDBTT)₂) and 21.30° (HTPD(EDBTT)₂) with a *d*-spacing of 4.1 and 4.3 Å, respectively, demonstrated the π - π stacking between the small molecule backbones and implied the long range ordering and highly organized assembled structure in solid state. Fig. S3 (ESI⁺) showed the proposed packed structures in solid stat for DTDPP(EDBTT)₂, EHID(EDBTT)₂ and HTPD(EDBTT)₂.

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UV/Vis absorption Cvclic voltammetry Solution^a Materials Flim Eg^{elc} Еномо **E**_{LUMO} Eg^{op} λ_{max} λ_{max} λonset (eV) (eV) (eV)^c (eV)^b (nm) (nm) (nm) DTDPP(EDBTT)₂ -5.49 -3.80(-4.20)⁶ (630)(704) 836 962 1.29 1 69 $-3.89(-4.01)^{d}$ EHID(EDBTT)₂ 641 822 -5.52 586 1.51 1.63

524

^aMeasured in CHCl₃. ^bEstimated using the onset of the UV-vis spectrum ($Eg^{op} = 1240/\lambda_{onset}$). ^cCalculated from $Eg^{elc} = E_{LUMO} - E_{HOMO}$. ^dCalculated by the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$

1.72

721

Optical properties

HTPD(EDBTT)₂

The optical properties were investigated using UV-visible absorption spectroscopy (Fig. 2), and the data are summarized in Table 1. Considering that, the EDBTT unit is fixed, the changes in maximum absorption depends on the active conjugated length induced by the introduced of second acceptors. In general, absorption in range of 423-468 nm ascribed to ICT between the EDOT and thiophene donors with the acceptors. In film, In case of DTDPP, small molecule 8 exhibited a broad absorption with onset absorption (λ_{onset}) at 962 nm. The DTDPP is considered as (D-A-D) unit due to the presence of two thiophene units around the DPP core, which effective extended the conjugation length and bathochromically shifted the wide absorption band associated with the DPP core and thiophene rings.³⁴

Table 1 Optical and electrochemical properties of all of the materials in this study.

496



Fig. 2 UV-vis spectra of small molecules (a) in \mbox{CHCl}_3 solution and (b) in films.

EHID(EDBTT)₂ showed λ_{max} values of 641 nm. The lowest λ max value was 524 nm in the case of HTPD(EDBTT)₂, which was expected to have the lowest ICT. In contrast, DTDPP(EDBTT)₂ showed two λ max peaks in solution at 630 and 704 nm, which combined into one peak at 836 nm in the film. All of small molecules have two different high-energy absorption bands in the range of 300 to 450 nm which have been attributed to a more localized π - π * transition due to the presence of two different electron accepting units along the backbone structure.

-5.55

-3.87(-3.83)^d

In particular, when the donor is highly electropositive, the polarizability of the acceptor unit becomes a critical factor to determine the amount of ICT.^{12a} So that, using strong electron donor and strong electron acceptor units along the conjugated materials backbone decreases the electron band gap and improves the strength of push-pull system as well as the performance of organic solar cells by controlling the photo-induced ICT from donor to acceptor units.^{12b} Confirming the previous deduction, all the new synthesized A'(D'AD)₂ based small molecules showed more narrow optical band gaps than their counterparts of small molecules with (D-A-D) building block which have same number of building units and also based on the same electron withdrawing units (DTDPP²¹⁻²⁴, ID^{25-27,34a} and TPD²⁰), see Table 1.

Electrochemical properties

Cyclic voltammetry (CV) measurements were obtained for all materials (Fig. 3a). The HOMO and low unoccupied molecular orbitals (LUMO) energy levels were derived from the onset of oxidation (E_{ox}) and reduction potentials (E_{red}) of the CV curves of the drop-cast films, using a platinum electrode in 0.1 M of Bu₄NPF₆ acetonitrile solution at a scan rate of 50 mV/s versus a Ag/AgCl reference electrode. According to the equations HOMO = $-(E_{ox} + 4.71)$ eV and LUMO = $-(E_{red} + 4.71)$ eV. The interface barrier present between the small molecule film and the electrode surface made the estimated electronic E_{σ} values are quite higher than the optical E_g estimated in thin films. All of the materials have low-lying (LUMO) because of the increased electron defficiency by the addition of one more acceptor. DTDPP(EDBTT)₂, EHID(EDBTT)₂ and HTPD(EDBTT)₂ showed LUMO energy levels at -3.80, -3.89 and -3.87 eV, respectively (Fig. 3b).

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Fig. 3 (a) Cyclic voltammograms of all small molecules in 0.1 M solution of TBAPF₆ in acetonitrile at room temperature and (b) HOMO and LUMO energy levels diagram.

DTDPP(EDBTT)₂ not only exhibited highest-lying LUMO (-3.80 eV) among the materials under study, but also showed the highest-lying HOMO energy level at -5.49 eV because the presence of four thiophene units which increased the electron donating properties as well as increase the HOMO energy level. EHID(EDBTT)₂ and HTPD(EDBTT)₂ showed low-lying HOMO energy levels at -5.52 and -5.55 eV, respectively (Fig. 3b). The E_{HOMO}, E_{LUMO} and the electrochemical band gaps (Eg^{elc}) are summarized in Table 1.

Photovoltaic properties

To estimate the photovoltaic performances of the new synthesized small molecules, BHJ solar cells, conventional devices structure ITO/PEDOT:PSS/organic material:PC₇₁BM /Ca/Al were fabricated. The optimized results were obtained by varying the small molecule:PC₇₁BM weight ratios, active layer thicknesses, and annealing temperature.³⁴ The optimized active layer thickness was around 80 nm for all the small molecule:PC₇₁BM blend layers.

Table 2 Photovoltaic Parameters of the Solar Cells

Materials:PC ₇₁ BM (1:1)	V _{oc} (V)	J _{sc} mA/cm 2	FF	PCE (%)
DTDPP(EDBTT) ₂	0.75	6.87	0.49	2.52
EHID(EDBTT) ₂	0.83	8.13	0.48	3.24
HTPD(EDBTT) ₂	0.88	3.51	0.26	0.80



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Fig. 4 (a) Current density-voltage (J-V) characteristics of the small molecules:PC₇₁BM solar cells and (b) Corresponding external quantum efficiency (EQE) spectra measured under illumination of monochromatic light.

All the device parameters are summarized in Table 2. The photovoltaic performances were significantly affected by the changing of the lactam and/or imide containing acceptor core the small molecules structures and in the EHID(EDBTT)2:PC71BM based solar cells reached a maximum PCE of 3.24%, with a V_{oc} of 0.83 V, J_{sc} of 8.13 mA/cm², and fill factor (FF) of 0.48. The Voc values of each optimized device decreased gradually from 0.88 to 0.75 V as the electron withdrawing ability of the accepting units TPD, DPP and ID decreased. As confirmed by the CV results, The HTPD(EDBTT)₂ has the HOMO level of -5.65 eV and exhibited a high V_{ac} value of 0.88 V. Thus EHID(EDBTT)₂ and DTDPP(EDBTT)₂ showed V_{oc} values of 0.83 and 0.75 V, respectively.

Unlike the V_{oc} trend, EHID(EDBTT)₂ exhibited a high J_{sc} value of 8.13 mA/cm², while HTPD(EDBTT)₂ showed low J_{sc} value of 3.51 mA/cm², due to its narrow light absorption window as well as low ICT. The J_{sc} value of DTDPP(EDBTT)₂ was 6.87 mA/cm² (Fig. 4a). To examine the accuracy of the J_{sc} from the *J*-*V* measurements, the corresponding external quantum efficiencies of the fabricated solar cells were measured under the illumination of monochromatic light (Fig. 4b). All the J_{sc} results calculated from integrating the EQE with an AM 1.5G reference spectrum matched with the J_{sc} obtained from the *J*-V measurements. As shown in Fig. 4b, the EHID(EDBTT)₂ showed

much higher EQE values up to 45% in the broad wavelength range of 400–750 nm, compared to those of HTPD(EDBTT)₂ and DTDPP(EDBTT)₂. Moreover, in spite of the broad absorption of DTDPP(EDBTT)₂, it showed low external quantum efficiencies around 34% (Fig.4b) reflected some leakage in the number of charge carriers.

Morphology analysis

In order to imply the effect of the active layer morphology on the device performance, the morphologies of all the small molecule: $PC_{71}BM$ blend films were studied by atomic force microscopy (AFM), as shown in Fig. 5).



Fig. 5 AFM images (5x5 μ m²) of (small molecules:PC₇₁BM) (1: 1) active layers.

HTPD(EDBTT)₂:PC₇₁BM film showed low (rms), around 4.16 nm compared with the other small molecules active layer, but the low melting point of HTPD(EDBTT)₂ small molecule and the incompitability with PC₇₁BM, drop the J_{sc} to 3.51 mA/cm² as well as drop the net PCE to 0.80%. In spite of the high root mean-square (rms) roughness of EHID(EDBTT)₂:PC₇₁BM and DTDPP(EDBTT)₂:PC₇₁BM, which founded to be 5.38 and 11.53 nm, respectively, they exhibited somewhat different AFM topology compared with the HTPD(EDBTT)₂:PC₇₁BM film. They showed continuous network which is good for obtaining high J_{sc} around 8.13 and 6.87 mA/cm², respectively, Thus, the EHID(EDBTT)₂:PC₇₁BM based solar cell exhibited the highest photovoltaic performance among the solution-processed small molecules solar cells under this study.

Conclusions

In summary, a series of new constituted small molecules based on the [A`(D`AD)₂] constitution were synthesized via Pd(OAc)₂/Bu₄NBr catalytic system. All of the new materials, DTDPP(EDBTT)₂, EHID(EDBTT)₂ and HTPD(EDBTT)₂, included two different strong acceptors and two different strong donors to induce an efficient push-pull donor-acceptor system. This new system offered high intramolecular charge transfer (ICT) and high short circuit current (J_{sc}) in organic photovoltaic (OPV) applications. Due to the broad absorption window, the optical band gaps of the materials were in the range of 1.29-1.72 eV, this result closely matched the ideal low band gap of small molecules, which is suggested in the design criteria for organic solar cells. The EHID(EDBTT)₂:PC₇₁BM-based solar cells reached a maximum power conversion efficiency (PCE) of 3.24%, with open circuit voltage (V_{oc}) of 0.83 V, large short circuit current J_{sc} of 8.13 mA/cm², and exhibited a low fill factor (FF) of 0.48.

New photovoltaic devices and a number of additives will be further studied to improve the FF as well as the PCE.

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