Synthesis, Characterization of Two Novel Diphenylpyranylidene Molecules and their Application in Organic Solar Cells

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Abstract. Two novel D-A and A-D-A structural small molecule based on diphenyl pyran donor and dicyanovinylene acceptor unit have been designed, prepared, and studied for the application of organic solar cells. The UV-vis absorption spectra showed that D-A structural molecule has more extended light-harvesting ability than the A-D-A molecule and can complement with P3HT in the wavelength of 300-500 nm and 600-800 nm.

Keywords: Organic solar cells, diphenylpyranlidene, UV-vis absorption.

1. Introduction
In the field of academic and industry, researchers concerned extensively about the global energy shortage and focused on sustainable clean energy source such as solar power. With dominance of low cost, pliability, lightweight and easy preparation, organic solar cells (OSCs) are superior to their inorganic rivals in aspect of assembling large-scale bendable optoelectronic commodities [1,2]. In the device structure of OSCs, active layers consisted of electron donor and acceptor materials influence the photovoltaic performances of the cells to great extent. Besides of traditional polymer donors [3] such as poly(3-hexylthiophene) or P3HT, small molecules of donor materials holding merits of well-defined structure, high purity and no batch difference, play a key role in the application of OSCs in recent years [4,5]. Specially, small molecules with conjugated symmetrical A-D-A or D-A-D structures of and unsymmetrical D-A ones are generally researched by the chemists in the field. Diphenylpyranylidene (DP) derivatives with an extended π-conjugation system that absorbs light intensively within the ultraviolet and visible region, have already presented impressive performance in the application of organic field-effect transistors (OFETs) and dye-sensitized solar cells (DSCs) [6, 7]. DP units with the favourable molecular alignment provide good hole charge carrier mobilities of 0.05-0.1 cm²V⁻¹s⁻¹ in OFET devices due to their high crystallinity and densely packed thin-film morphology, which are also desirable for the utilization of OSCs. In this paper, two novel D-A and A-D-A structural small molecule DP1 and DP2 with diphenyl pyran donor unit and dicyanovinylene acceptor unit have been designed, prepared, and studied for the application of organic solar cells.
2. Experimental

All reagents were purchased from Sigma-Aldrich, Shanghai Macklin and ACROS and used without further purification unless stated otherwise. All reactions were carried out under an argon atmosphere. The PEDOT: PSS (AI 4083) aqueous solution was purchased from H. C. Starcks. The P3HT was purchased from Luminescence Technology Corporation.

Figure 1. Synthetic routes of DP1, DP2. (a) Malononitrile, piperidine, CH₂Cl₂, 40°C.

2.1. Synthesis

4-(5-((2,6-diphenyl-4H-pyran-4-ylidene) methyl) thiophen-2-yl) benzaldehyde (D1-1) and 4,4’-(3-((2,6-diphenyl-4H-pyran-4-ylidene) methyl) thiophene-2,5-diyl) benzaldehyde (D2-1) was prepared following the literature procedures [8]. DP1: Malononitrile (90 mg, 1.37 mmol) and piperidine (0.13 mL, 1.37 mmol) were added to a solution of D1-1 (0.3 g, 0.68 mmol) in anhydrous CH₂Cl₂ at room temperature. The mixture was heated 40°C for 24 h. Concentration and purification of the residue by flash column chromatography (CH₂Cl₂: Hexane = 1:1, volume ratio) gave the product 0.18 g. Yield: 55%. Mp: 243.7-245.6°C. 1H NMR (600 MHz, THF) d/ppm = 8.11 (s, 1H), 8.03 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 7.3 Hz, 2H), 7.91-7.88 (m, 4H), 7.63 (d, J = 3.9 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.49 (t, J = 7.7 Hz, 3H), 7.43 (s, 1H), 7.29 (d, J = 1.3 Hz, 1H), 7.09 (d, J = 3.9 Hz, 1H), 6.73 (d, J = 1.5 Hz, 1H), 6.25 (s, 1H). HRMS (ESI, m/z): [M+H]+ Calcd. for C₃₂H₂₁N₂O₅S: 481.1369. Found 481.1374.

DP2: Malononitrile (50 mg, 0.75 mmol) and piperidine (0.08 mL, 0.75 mmol) were added to a solution of D2-1 (0.1 g, 0.19 mmol) in anhydrous CH₂Cl₂ at room temperature. The mixture was heated 40°C for 24 h. Concentration and purification of the residue by flash column chromatography (100% CH₂Cl₂) gave the product 0.048 g. Yield: 41%. Mp: 275.2-275.5°C. 1H NMR (600 MHz, CDCl₃) d/ppm = 7.97 (t, J = 8.6 Hz, 8H), 7.84 (d, J = 8.5 Hz, 4H), 7.70 (d, J = 8.5 Hz, 5H), 7.75 (s, 2H), 7.72 (s, 2H), 7.68 (s, 3H). HRMS (ESI, m/z): [M+H]+ Calcd. for C₄₂H₂₅N₄O₅S: 633.1744. Found 633.1746.

2.2. Fabrication and characterization of devices

The device structure is indium tin oxide (ITO)/PEDOT: PSS/DP: P3HT: ITIC/aluminum (Al). The ITO-coated glass substrates (15 Ωcm⁻²) were washed in an ultrasonic bath with distilled water, acetone, detergent, distilled water (5 times) and isopropyl alcohol for 10 min each. These substrates were dried in N₂ atmosphere and then UV-ozone treated for 20 min. PEDOT: PSS was ultra-sonicated for 10 min and submerged for 10 min, then deposited by spin-coating at 4000 rpm for 60 s on top of the ITO substrates and dried subsequently at 150°C for 20 min in air. The solution of active layer with different weight ratio were dissolved in chlorobenzene (CB) organic solvent (total concentration: 20 mg/ml) with stirring and heating at 70°C for 2h. The blend solution was spin-coated onto the PEDOT: PSS layer under a spin-coating rate of 1000 rpm to form a film thickness of 80~110 nm. Next, the film was dried for 3 h in glove box, followed by thermal annealing at 100°C for 10 min. After the active spin coating, solvent annealing was used to tune the morphology of the blend film. For solvent annealing, the films were placed in a glass petri-dish, containing 40 μL CB for 3h and followed by thermal annealing at 100°C for 10 min. Subsequently, the Al (100 nm) electrode was evaporated onto the top of active layer under vacuum at 3×10⁻⁴ Pa with an active area of 0.03 cm².
3. Results and discussion

3.1. Theoretical studies
Density functional theory (DFT) calculation using Gaussian 09W at B3LYP/6-31G* program was carried out to understand geometrical configurations and molecular energy level for the small molecules and both of them show a linear coplanar molecular skeleton conformation from the side view, which is beneficial for π-π stacking and improve the hole mobility. In addition, the calculated highest occupied molecular orbital (HOMO) level and lowest unoccupied molecule orbital (LUMO) energy level of DP1 are -4.94 eV and -2.78 eV, and those of DP2 are -5.31 eV and -3.31 eV, respectively.

Table 1. Photo-physical and electrochemical properties of the donor molecules.

| Molecule | $\lambda_{max}^1$/ nm | $\lambda_{max}^2$/ nm | $E_{ox}^3$/ V | $E_{g}^4$/ eV | $E_{HOMO}^5$/ eV | $E_{LUMO}^6$/ eV |
|----------|----------------------|----------------------|---------------|--------------|----------------|------------------|
| DP1      | 535                  | 655                  | 0.77          | 1.45         | -5.23          | -3.78            |
| DP2      | 396                  | 480                  | 0.94          | 1.56         | -5.40          | -3.84            |

$^1$Absorption maximum in solution. $^2$Absorption maximum on film. $^3$Oxidation potential obtained from CV and calibrated to V (vs. NHE). $^4$Energy gap obtained from absorption onset. $^5$HOMO levels were calculated from $E_{HOMO} = -[4.46 + E_{ox} (V vs. NHE)]$ eV. $^6$LUMO levels were calculated from $E_{LUMO} = (E_{HOMO} + E_{g})$ eV.

Figure 2. Absorption spectra of DP1 and DP2 (a) in solution, (b) on thin film and (c) comparison with P3HT.
3.2. Photo-physical and Electrochemical properties

The UV-vis absorption spectra in DMF solution and the thin film of DP1 and DP2 were presented in Fig. 2(a), and the correlation data are summarized in Table 1. As shown in Fig. 2a, for DP1, the maximum absorption wavelength ($\lambda_{\text{max}}$) at 535 nm (corresponding molar extinction coefficient $\varepsilon$ is $4.0 \times 10^4$ M$^{-1}$ cm$^{-1}$) with 420-670 nm absorption wavelength region. DP2 have two main absorption bands at 396 nm ($\varepsilon = 3.6 \times 10^4$ M$^{-1}$ cm$^{-1}$) and 480 nm ($\varepsilon = 1.4 \times 10^4$ M$^{-1}$ cm$^{-1}$) with 310-630 nm absorption wavelength region. Besides, $\varepsilon_{\text{max}}$ of DP1 is higher than that of DP2, indicating a better light-harvesting ability of DP1. The normalized UV-vis absorption spectra of DP1 and DP2 on thin films are shown in Fig. 2(b). DP2 showed a 42nm red-shifted absorption maximum on film compared to that in solution, indicating DP2 have strong intermolecular π-π interaction in solid state. The absorption edge ($\lambda_{\text{edge}}$) of DP1 and DP2 film are at 855 nm and 795 nm, corresponding to an optical bandgap of 1.45 eV and 1.56 eV, respectively. It is worth noting that the absorption of DP1 thin films is nearly always strong in the 350-750 nm wavelength region, which is beneficial for achieving a higher $J_{\text{sc}}$ in the OSCs devices. Their absorption spectra compared with that of P3HT are presented in Fig. 2 (c). DP1 can complement the with P3HT in the wavelength of 300-500 nm and 600-800 nm for a better light-harvest efficiency. The HOMO energy levels of DP1 and DP2 as determined from the oxidation potentials of cyclic voltammetry (CV) are -5.23 eV and -5.40 eV, respectively. While the LUMO energy levels are determined by adding the optical bandgap to the HOMO energy level, leading to the DP1 and DP2 LUMO energy levels of -3.78 eV and -3.84 eV, respectively.

![Figure 3. OSCs device structure and energy levels of materials used in active layer.](image)

| entry | P3HT:PC$_{61}$BM: DP1 | $J_{\text{sc}}$ (mA/cm$^2$) | $V_{\text{oc}}$ (V) | $FF$ (%) | PCE (%) |
|-------|----------------------|-----------------|-----------------|--------|--------|
| A     | 1:0:8:0              | 6.62            | 0.59            | 59.4   | 2.32   |
| B     | 0.95:0.8:0.05        | 5.56            | 0.45            | 26.5   | 0.66   |
| C     | 0.9:0.8:0.1          | 5.15            | 0.48            | 27.7   | 0.69   |

3.3. Performance of the Organic solar cells

According to the absorption spectra and energy levels, DP1 donor was used as complementary materials in the structure of OSCs devices. A preliminary characterization of the OSCs fabricated with DP1/P3HT donor and PC$_{61}$BM acceptor were conducted and the related parameters are summarized in Table 2. Due to the low solubility, the introduction of DP1 donor in the system effected the film morphology significantly, leading to a decreased photovoltaic performance. As the DP1 amount increased from 0.05 to 0.1 ratio, short-circuit current $J_{\text{sc}}$ decreased slightly while open-circuit voltage $V_{\text{oc}}$ and fill-factor $FF$ improved.
4. Conclusion

To sum up, we presented the synthesis of two novel structural small molecule DP1 and DP2, and their photo-physical and electrochemical properties and DSC performance were also investigated. The D-A structural DP1 holding a thiophene ring introduced between diphenyl pyran unit and phenyl conjugated bridge linked with dicyanovinylene, has more extended absorption spectrum than its A-D-A structural analogue DP2. The OSC devices based on P3HT:PC$_{61}$BM: DP1 showed a decreased photovoltaic performance as compared to the reference cells, resulting from the poor solubility of the DP1 molecules that hold no solubilizing long side chain functional group. Further molecule modification and device optimization for enhancing OSC efficiency is in progress.

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