Solar Cells

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An Organic Dyad Composed of Diathiafulvalene-Functionalized Diketopyrrolopyrrole–Fullerene for Single-Component High-Efficiency Organic Solar Cells

*K. Narayanaswamy, A. Venkateswararao, P. Nagarjuna, Swati Bishnoi, Vinay Gupta, Suresh Chand, and Surya Prakash Singh**

Abstract: *A new low-band gap dyad DPP-Ful, which consists of covalently linked dithiafulvalene-functionalized diketopyrrolopyrrole as donor and fullerene (C_{60}) as the acceptor, has been designed and synthesized. Organic solar cells were successfully constructed using the DPP-Ful dyad as an active layer. This system has a record power-conversion efficiency (PCE) of 2.2 %, which is the highest value when compared to reported single-component organic solar cells.*

Solution-processable organic solar cells (OSC) have attracted immense attention in both academia and industry owing to their light weight, mechanical flexibility, easy device fabrication, high transparency, and cost-effectiveness over the market-dominant silicon-based solar cells.[1] At present, the state-of-the-art power-conversion efficiency (PCE) of solution-processable OSCs achieved more than 10 % by blending π-conjugated polymers[2] or small-molecule[3] donors with commonly used fullerene acceptors.[4] The PCE of OSC mainly depends on interpenetrating the nano-sized structured network formed at the interface of the donor and acceptor of the blend film and serves as an efficient charge-transporting carrier.[4a,5] The nano-sized structured network of the active layer can be efficiently controlled by tedious optimizing fabrication process by choosing various donor–acceptor ratios and different solvents, solvent/thermal annealing, layer thickness, and pinhole-free deposition of the active layer.[1,6] However, these processes severely deteriorate the performance and stability of OSC and retard its commercialization at lower production costs.

In an active layer, the aggregate formation of fullerene, which is prone to aggregation, also decreases the donor–acceptor interface to form nano-sized network, resulting in a poor PCE.[4,7] However, the aggregated fullerene has unique properties, such as a strong accepting nature/high electron affinity, and it possesses suitable HOMO and LUMO levels relative to the donor molecule; good charge-transporting properties make it as a potential candidate for electronic applications.[7]

Integration of the donor and acceptor in a single molecule by a covalent linkage, termed as a dyad or triad, is a promising design for suppressing phase segregation and higher charge separation, resulting in a higher J_{SC}, which is attributed to the close proximity of the donor and acceptor.[8] Earlier, dyads based on fullerene-azothiophene produced a PCE of 0.37 %.[9] An another dyad based on cyanine–fullerene achieved a PCE of 0.1 %.[10] However, fullerene–oligophenylene ethynylene dyad achieved a poor spectral response; owing to its incorporation of a weak donor it showed a lower absorption ($<$ 450 nm).[11] Several dyads and triads based on diketopyrrolopyrrole (DPP)-containing oligothiophene and fullerene have been reported with a PCE ranging from 0.5 % to more than 1 %.[12] A triad with dumbbell-like structure containing a dithienosilole–benzothiadiazole conjugate donor and two fullerene acceptors achieved a PCE of 0.4 %.[13] Also, oligo(*p*-phenylene vinylene)-based dyads were demonstrated as potential candidates owing to the crystalline nature of oligo(*p*-phenylene vinylene) unit, which improves the transporting property and fill factor and PCE (up to 1.28 %).[14] Moreover, highest PCE of single component OSC can be further achieved through molecular designing of donor unit to improve the spectral response and fill factor.[8,11]

In this context, we have designed and synthesized DPP-Ful by covalent linkage of dithiafulvalene (DTF)-functionalized DPP containing oligothiophene and *N*-methyl fulleropyrrolidine to achieve a broad spectral response, and it achieved the highest PCE of 2.2 % among reported single-component organic dyads. DPP-Ful displayed red-shifted absorption in the solid state when compared to reported fullerene-based dyads owing to strong intermolecular interactions and aggregate formation. Recently we reported a small molecule (DPP-DTF) for OSC produced a PCE of 4.3 %.[15] The incorporation of DTF improves donating strength and charge transporting property, which is crucial to obtain high PCE. The alkyl chains at 2,5 positions of DPP and 4,5 positions of dithiafulvalene increases solubility for a solution-processable device and enhanced the PCE of the solar cell devices.[15,16] DPP-Ful is synthesized (Scheme 1) by refluxing C_{60}-fullerene, *N*-methyl glycene, and DPP-ald[17] in

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[*] K. Narayanaswamy, A. Venkateswararao, P. Nagarjuna,
Dr. S. P. Singh
Inorganic & Physical Chemistry Division
CSIR–Indian Institute of Chemical Technology
Uppal Road, Tarnaka, Hyderabad-500007 (India)
E-mail: spsingh@iict.res.in

S. Bishnoi, V. Gupta, S. Chand
Physics of Energy Harvesting Division, CSIR-National Physical Laboratory, New Delhi (India)

K. Narayanaswamy, P. Nagarjuna, S. Bishnoi, V. Gupta, S. Chand,
Dr. S. P. Singh
Network Institute of Solar Energy (CSIR-NISE) and Academy of Scientific and Innovative Research (AcSIR)
New Delhi (India)

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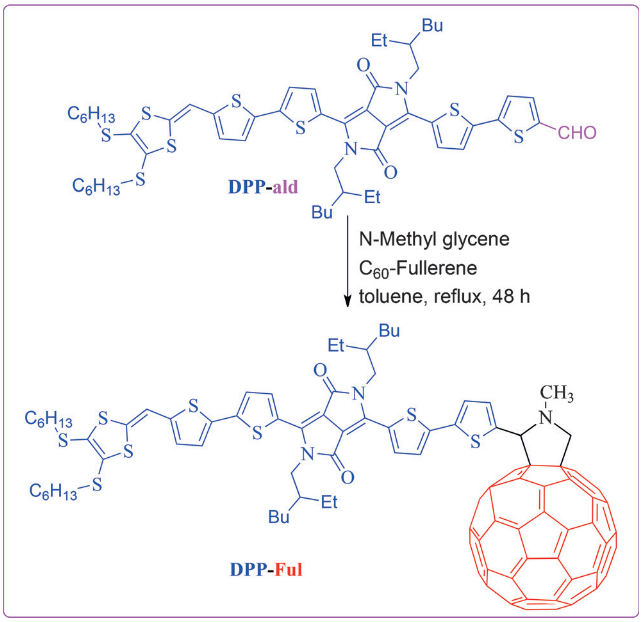

Scheme 1. Synthetic route to prepare the DPP-Ful dyad.

toluene solvent and yields a blue solid. It was thoroughly characterized by NMR and MALDI-TOF-MS; synthetic details and spectroscopic data are given in the Supporting Information. DPP-Ful showed good solubility in common organic solvents and good thermal stability up to 282 °C (Supporting Information, Figure S7).

The absorption spectra of the dyad DPP-Ful was recorded in dichloromethane (DCM; Figure 1), and it showed three types of transition peaks at ca. 330, 380, and 653 nm; absorption spectra of fullerene and DPP-ald were also recorded for comparison.[15,17] The peak in the higher-energy region at 330 nm arises from the fullerene unit, and the peak at 380 nm arises from the oligothiophene-containing DPP unit. The absorption peak in the lower-energy region at 653 nm is attributed to the conjugated back-bone of DPP unit. Thin film absorption of DPP-Ful exhibits a red-shift with a broad pattern and tailing up to 1000 nm when compared to solution spectra owing to intermolecular stacking interactions or close-packing of the molecule in the solid film, which is useful for broader light-harvesting properties.[15,18] DPP-Ful showed positive solvatochromism (Supporting Information, Figure S3) from non-polar to polar solvents owing to the solvation of dipolar compounds in more polar solvents, and we observed a linear correlation for the Reichardt polarity index ($E_T(30)$ parameter;[19] Supporting Information, Figure S3 b), and this dipolar nature facilitates better charge separation under photoinduced light.[5]

To ascertain redox potentials, we have measured the cyclic voltammogram of DPP-Ful (Supporting Information, Figure S5) in DCM, and it showed two oxidation couples corresponding to the DTF and DPP containing oligothiophene,[15] respectively, and two reduction couples corresponding to the fullerene and DPP unit, respectively. HOMO and LUMO energy levels of DPP-Ful were −4.95 eV and −3.23 eV relative to the vacuum.[20] The HOMO of DPP-Ful became high-lying owing to the electron-rich DTF-DPP-oligothiophene unit covalently attached to the fullerene.

To gain deeper insight into the HOMO and LUMO energy levels, we performed the quantum-chemical calculations by B3LYP/6-31g (d,p)[21] and BMK/DGDZVP[22] using the PCM[23] model (DCM phase) and best correlation for optical properties obtained from the later method. The HOMO is mainly located on DTF-DPP containing oligothiophene, and the LUMO is mainly located on the fullerene unit (Figure 2), indicating photoinduced charge transfer from the DTF-DPP core to the fullerene acceptor.

Suitable HOMO and LUMO energy levels of DPP-Ful are adequate to construct single-component organic solar cells with a device configuration of ITO/MoOx/DPP-Ful/Ca(20 nm)/Al(100 nm) (Figure 2 b) to evaluate the performance of DPP-Ful, and the energy-level diagram (Figure 2 c) is given for a better understanding. The detailed procedure of the device fabrication is given in the Supporting Information.

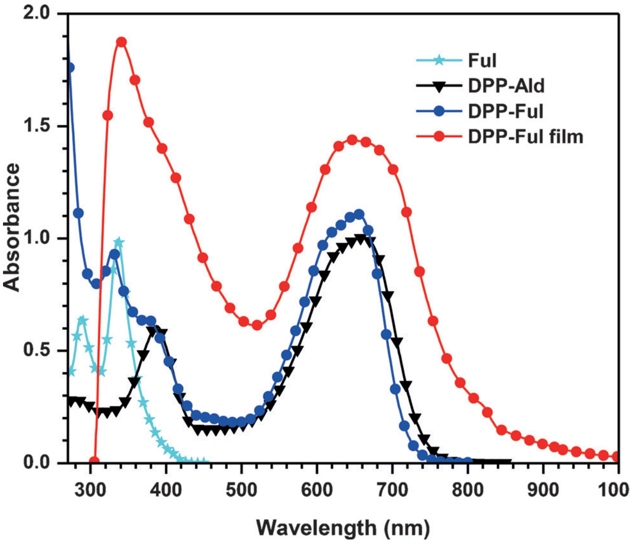

Figure 1. Absorption spectra of Ful, DPP-ald, and DPP-Ful in DCM and of the DPP-Ful thin film.

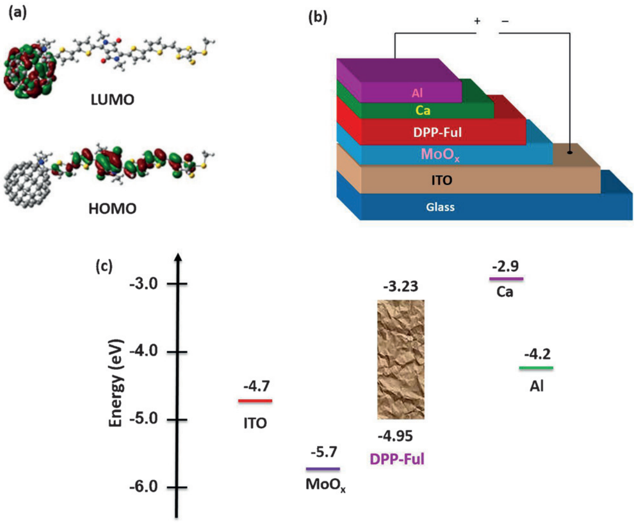

Figure 2. a) Frontier molecular orbitals, b) device configuration, and c) the energy level diagram of DPP-Ful.

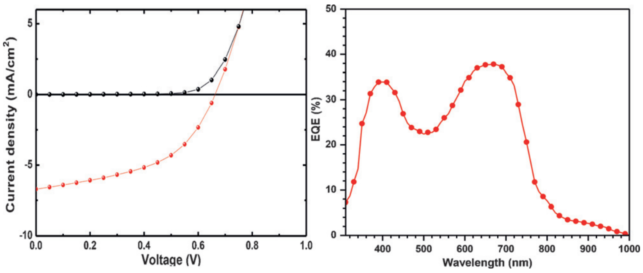

Figure 3. *J*–*V* characteristics and EQE of the DPP-Ful dyad.

Figure 3 illustrate the *J*–*V* characteristics and EQE of the photovoltaic device based on DPP-Ful. Preliminary results produced a PCE of 2.167 % with J_{SC} of 6.708 mA cm^{-2}, V_{OC} of 0.663 V, and fill factor (FF) of 0.488. The average performance values from the evaluation of multiple devices are presented in the Supporting Information, Table S2. The average PCE of the optimized devices is 2.02 ± 0.15 %. The measurements are based on data of over 25 devices. The device based on DPP-Ful showed highest J_{SC} when compared to reported single-component OSCs based on DPP and other organic dyads owing to its red-shifted absorption with a tailing up to 1000 nm.[8–13] Incorporation of DTF as the terminal donor to the oligothiophene-DPP core helps to red-shift the absorption and give a high J_{SC}, which led to record PCE. DTF strongly influences the J_{SC} owing to tuning of the energy level of the dye and facilitates strong donor–acceptor interactions.[24] The device based on DPP-Ful showed an EQE from 400 to 800 nm with the highest EQE (38 %) at 670 nm and tailing up to 1000 nm; it is well-matched with film absorption spectra.

We performed two-dimensional grazing incident X-ray diffraction (2D-GIXRD) to investigate the microstructure and its effect on the morphology and photovoltaic performance of DPP-Ful. The XRD diffractogram of the DPP-Ful film (Figure 4) show peaks at $2\theta = 5.07°$ and 4.37°, corresponding to an inter-plane spacing of 1.74 nm and 2.02 nm, respectively. The inter-plane spacing of 1.74 nm in DPP-Ful is higher than the inter-plane spacing of 1.4–1.5 nm of pure DPP, observed in previous studies[25–27] and similar to 1.78–2.07 nm for DPP blended with PCBM.[28,29] The peak at 1.97° corresponds to an in-plane spacing of 4.48 nm, which is also close to the molecular length of DPP-Ful. There is no π–π stacking diffraction near $2\theta = 24°$, which means that there is direct edge-on orientation between DPP molecules.[29] The weak peak at $2\theta = 19.01°$ (0.466 nm) is due to the C_{60} molecule.[29] The striking feature in the case of DPP-Ful film is the crystalline size which is 24.4 nm and 41.5 nm for inter-plane and in-plane directions, respectively. Such a large fibril volume with long range ordering is the key factor for efficient exciton dissociation and charge transport in the DPP-Ful film and hence high PCE.

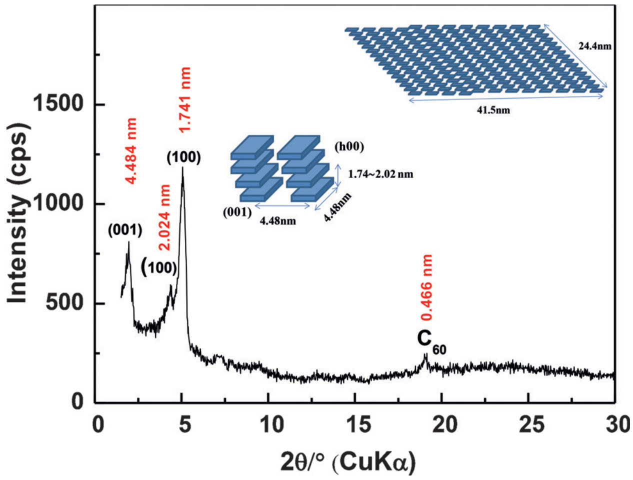

Figure 4. 2D-GIXRD pattern of DPP-Ful. Lower inset: intermolecular and intramolecular distances; upper inset: crystalline size.

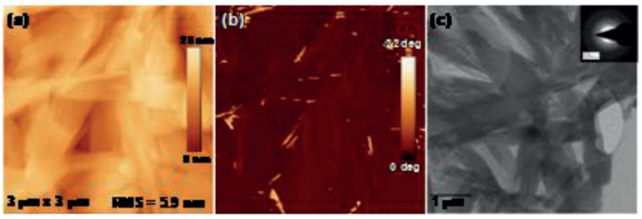

Figure 5. a) AFM height and b) phase images and c) TEM images of the DPP-Ful based device.

The fibril structure is further supported by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Figure 5 a,b shows AFM height and phase images of the DPP-Ful active layer surface with the root mean square roughness (RMS) of 5.9 nm, where the fibril structure of the DPP-Ful is evident. Figure 5 c displays TEM images of the DPP-Ful active layer, which also confirms the fibril structure. The 2D-GIXRD shows strong peaks at high d-values; therefore, the crystalline features are too close to the central beam to be observed in the selected-area electron diffraction (SAED) pattern (inset of Figure 5 c). The SCLC hole mobility and electron mobility of DPP-Ful are 1.3×10^{-4} and 1.1×10^{-4}, respectively (Supporting Information, Figure S9 and S10). DPP-Ful gives higher mobility owing to its continuous morphology.

In summary, we have designed and synthesized a new organic dyad containing dithiafulvalene-functionalized diketopyrrolopyrole as a donor and C_{60} (fullerene) as an acceptor, which were connected together by a covalent linkage. The PCE of 2.2 % achieved here using DPP-Ful as an active layer is the highest reported so far based on single-component organic solar cells. This study demonstrates dithiafulvalene-functionalized DPP as a new donor attached to fullerene to form better dyads with long-range ordering and pave the way to develop future dyads and triads to produce a high PCE. The balanced hole and electron mobility of the device are responsible for highest J_{SC} and FF. AFM and TEM analysis demonstrated the nanophase separation of the active layer. Furthermore we are optimizing the energy levels of the dyad to improve the J_{SC} and V_{OC} and balancing the charge carriers to improve the FF via molecular engineering on the dyad.

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Keywords: diketopyrrolopyrroles · dithiafulvalenes · organic dyads · power conversion efficiency · single-component solar cells

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