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New cyclopentadithiophene (CDT) linked porphyrin donors with different end-capping acceptors for efficient small molecule organic solar cells

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The synthesis of two new A- π -D-A molecules bearing a Zn-porphyrin core donor linked through cyclopenta[2,1-b:3,4-b']dithiophene bridges to the electron-acceptor rhodanine (SA1) or dicyanovinylene (SA2) groups is described. The optical and electrochemical properties of these compounds are investigated. The horizontal conjugation of cyclopentadithiophene between the porphyrin core and the end-capping acceptor not only effectively increases the light harvesting between the Soret and Q bands of the porphyrin unit, but also optimizes the molecular packing through linear π -conjugated backbones. Compounds SA1 and SA2 are employed as donors along with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as an acceptor in organic bulk heterojunction organic solar cells. After optimizing the processing of the active layer (a solvent additive and subsequent solvent vapor annealing), overall power conversion efficiencies of 6.94% and 8.19% (with low energy loss of 0.55 eV) are obtained for the organic solar cells. The use of a solvent additive and subsequent solvent vapor annealing provide enhanced nanoscale morphology and the bi-continuous interpenetrating networks in the active layer required for efficient exciton dissociation into free charge carriers and their subsequent transportation towards electrodes. This change led to higher PCE values when compared to devices based on as-cast active layers.

Introduction

Organic solar cells (OSCs) have received considerable attention owing to their potential in flexible, lightweight and low cost solar energy conversion devices.¹ The most widely used active layer architecture for efficient OSCs is the bulk heterojunction (BHJ), which consists of a mixture of a polymer or small molecule as a donor and fullerene as an acceptor to form a nanoscale interpenetrating network morphology for efficient exciton dissociation and charge transport.² A great deal of effort has been focused on polymer-based OSCs and power conversion efficiencies (PCEs) of nearly 12% have been achieved for a single BHJ active layer and greater than 13% for multijunction cells by integrating state of the art technologies.^{3,4} These approaches include the synthesis of organic semiconducting donor and acceptor materials,

optimization of BHJ active layers and interface engineering.

The design of efficient small molecules (SMs) as donor components for OSC devices involves the optimization of several parameters, including the nature of the donor and acceptor moieties to give appropriate frontier molecular orbitals for two reasons: (a) to lower the optical band gap and thus broaden the absorption of light, which leads to an increase in the short circuit current, and (b) to obtain as low a HOMO level as possible to achieve a high open circuit voltage. Furthermore, the solubility must be high enough for processing and extended conjugation is required to favor π -stacking to enhance intramolecular charge transfer.⁵ In recent years, SMs have attracted attention because of their ever increasing PCE values, which have reached levels of around 10% on employing single BHJ active layers.⁶ The increasing interest in SMs as donors in BHJ OSCs is also inspired by several potential advantages over their polymeric counterparts. These possible advantages include more reproducible synthesis, relative ease of purification and control over the energy levels and absorption profiles. The rapid advances in small molecule-based OSCs can be largely attributed to the sensible design of molecular structures. The mainstream design motifs for these small molecules involve a combination of an electron-rich donor (D) and an electron-deficient acceptor (A) units linked by a π -spacer in symmetrical manner, e.g., A- π -D and D- π -A, to produce a small molecule

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with strong light harvesting ability, suitable energy levels and desirable film forming capability through solution processing.⁷ The push-pull effect of donor- π -acceptor (D- π -A) systems depends on the strength of the donor and acceptor groups. However, this effect also depends on the conjugated π -system connecting the two units and a zwitterionic resonance structure should contribute to this.⁸ As the push-pull effect has a strong influence on the long-wavelength absorption in these systems (and therefore on the current of the device if used in photovoltaics), the nature of the π -conjugated bridge is very important for the efficiency of bulk heterojunction (BHJ) solar cells. Although many combinations of different donors and acceptors have been investigated,⁹ less attention has been paid to the role of the π -conjugated connector between D and A units. In this respect, we recently described the application as donor molecules in BHJ solar cells of different A- π -D- π -A molecules in which thienylenevinylene (TVs) were used as wires between the donors and acceptors.^{10,11,12} The exceptionally low values of the attenuation factor shown by TVs ($\beta = 0.016 \text{ \AA}^{-1}$) favor excellent electronic coupling between the donor and acceptor moieties.¹³ In this sense, the semiconducting properties of cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) based materials have attracted significant attention recently as they display extended conjugation, low bandgaps and high electrical conductivities.¹⁴ Comparison of rigidified spacers with their open chain analogues has shown that the bridging of double bonds significantly improves the intramolecular charge transfer and makes this kind of compound a potential candidate for organic electronics.¹⁵

Natural photosynthetic systems utilize chlorophylls to absorb light and carry out photochemical charge separation to store light energy. Porphyrins exhibit large absorption coefficients and their electrochemical and optical properties can be tuned by modification of the central metal and/or the introduction of suitable substituents at peripheral positions on the macrocycle. Porphyrins and their derivatives have been explored for a long time as sensitizers in dye-sensitized solar cells, with the highest PCE value of 13% achieved.¹⁶ However, disappointing results were obtained in porphyrin-based BHJ solar cells before 2012 with only modest values obtained (below 1%).¹⁷ Nevertheless, in the last four years impressive progress has been made in the field of solution-processed BHJ OSC porphyrin-based small molecules due to the use of the meso-ethynyl-linkages to enable maximum conjugation.¹⁸ Since this breakthrough remarkable efficiencies as high as 8.20% and 9.06% have been obtained.^{19,20} Our group recently prepared new A- π -D- π -A and D- π -A- π -D porphyrin-based donors that gave outstanding efficiencies of 7.63% and 8.03%, respectively.^{21,22}

The work described here concerns the synthesis and properties of two novel A- π -D- π -A molecules, **SA1** and **SA2**, based on Zn-porphyrin as a donor moiety linked through cyclopenta[2,1-b:3,4-b']dithiophene with dicyanovinylene or rhodanine acceptor groups (Scheme 1).

The electrochemical and optical properties of the molecules were investigated and it was found that **SA1** and **SA2** can be

employed as donors for BHJ OSCs. These new Zn-porphyrin-based molecules were used as donors for the fabrication of solution-processed BHJ OSCs in combination with PC₇₁BM as the electron acceptor. The processing techniques for the active layer were optimized and included solvent addition followed by solvent vapor annealing. The resulting devices gave overall PCEs of 6.94% and 8.19% for **SA1** and **SA2**, respectively.

Scheme 1 Chemical structures of the new Zn-porphyrin-based molecules **SA1** and **SA2**

Results and discussion

Theoretical Calculations

The most stable theoretical geometries, electronic density contours and energy levels of the frontier molecular orbitals of **SA1** and **SA2** were initially calculated by density functional theory (DFT) at the B3LYP 6-31G* level *in vacuo* using Gaussian 09W. As depicted in Fig. S18 (Supporting information), the π -conjugated system, i.e., the porphyrin ring-cyclopentadithiophene-acceptor, is completely flat according to the values of the dihedral angles ($\theta < 0.5^\circ$) calculated for both structures. This structure favors the conjugation between the porphyrin macrocycle and the electron acceptor moieties, thus allowing better electronic delocalization – as shown in the theoretical electronic density contours of the frontier molecular orbitals (Fig. S19), which are delocalized over the entire molecule.

The HOMO and LUMO levels (Fig. S19) are higher in **SA1** than those in **SA2** (**SA1**: HOMO = -5.00 eV; LUMO = -3.21 eV; **SA2**: HOMO = -5.17 eV; LUMO = -3.40 eV) and this difference is attributed to the higher withdrawing electron ability of the dicyanovinylene group with respect to the rhodanine moiety. Although high V_{oc} values are expected in photovoltaic devices with PC₇₁BM, a higher V_{oc} should be expected for devices based on **SA2**, which has a lower HOMO energy.

Given the low HOMO-LUMO gap found for **SA1** and **SA2** (1.79 eV and 1.77 eV respectively) one would expect good absorption of light and, consequently, an excellent current in devices. Finally, efficient exciton dissociations at the D/A interface would be expected due to the offset between the

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Scheme 2 Synthesis of compounds **SA1** and **SA2**

LUMO of the donors and the LUMO of PC_{71}BM (**SA1**: 0.79 eV; **SA2**: 0.60 eV).

Synthesis and characterization of **SA1** and **SA2**

The synthesis of **SA1** and **SA2** is outlined in Scheme 2. Firstly, iodoaldehyde **2** was prepared in 92% yield by reaction of **1** with iodine and bistrifluoroacetoxyiodobenzene in CCl_4 at room temperature.^{23,24}

Zn-porphyrin **3** was reacted with **2** under Pd-catalyzed copper-free Sonogashira coupling conditions, using triphenylarsine and $\text{Pd}_2(\text{dba})_3$ as the catalyst, to afford bisaldehyde **4** in 75% yield after purification by column chromatography (silica gel, hexane: CH_2Cl_2 , 1:1). The target compounds were obtained by Knoevenagel condensation of **4** with 3-ethylrhodanine (**SA1**) or malononitrile (**SA2**) using piperidine or triethylamine as base, respectively. The compounds were purified by column chromatography and recrystallization from CH_2Cl_2 :MeOH and both were obtained in excellent yields (**SA1**: 91% and **SA2**: 86%). All new compounds were satisfactorily characterized by ^1H and ^{13}C NMR, FT-IR and MALDI-TOF MS (for characterization details see supporting information).

The thermal properties of **SA1** and **SA2** were studied by thermogravimetric analysis (TGA). The TGA results for the studied compounds are shown in Fig. S14 and it can be seen

that both have very high thermal stability, with decomposition observed at 387 °C and 400 °C, respectively.

Optical and electrochemical properties

The absorption spectra of **SA1** and **SA2** in the 350–850 nm region are shown in Fig. 1 and the optical data are summarized in Table 1.

Table 1 UV-Vis absorption^a and OSWV^b data for compounds **SA1** and **SA2**

	$\lambda_{\text{max soln}}$ (nm)	Log (ϵ)	E_{ox}^1 ^{b, c} (V)	E_{red}^1 (V)	E_{HOMO}^d (eV)	E_{LUMO}^e (eV)	E_g^f (eV)
SA1	530 722	5.08 4.96	0.20	-1.53	-5.30	-3.57	1.73
SA2	539 725	5.55 5.47	0.26	-1.42	-5.36	-3.68	1.68

^a 10^{-5} M, in dichloromethane; ^b 10^{-3} M in ODCB-acetonitrile (4:1) versus Fc/Fc^+ ($E_{\text{ox}} = 0.04$ V) glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu_4NClO_4 , scan rate = 100 mV s^{-1} ; ^c reversible processes; ^d calculated with respect to ferrocene, $E_{\text{HOMO}}: -5.1$ eV; ^e estimated from E_{red}^1 ; ^f $E_g = E_{\text{HOMO}} - E_{\text{LUMO}}$

In dichloromethane solution, the absorption spectra of both molecules are similar and they exhibit two broad peaks. The

higher energy peak at around 530-540 nm corresponds to the Soret band, which is red-shifted with respect to the Soret band of pristine porphyrin ($\lambda_{\text{max}} = 435$ nm) due to the extended conjugation. The lower energy band at around 725 nm is ascribed to the intramolecular charge transfer (ICT) transition. It is worth noting that **SA2** shows a broader ICT absorption band than **SA1** and this can be attributed to the stronger electron-withdrawing character of the dicyanovinylene group when compared to 3-ethylrhodanine.

Fig. 1 UV-Vis absorption spectra of **SA1** (red) and **SA2** (blue) in (a) CH_2Cl_2 solution (10^{-5} M) and (b) spin-coated thin film

On comparing the spectra from solution to film, both compounds show a significant red shift in the absorption contours, which indicates strong intermolecular interactions leading to aggregation in the solid state (Fig. 1b). The conjugation of CDT can effectively increase the solar flux between the Soret and Q bands of porphyrin. This phenomenon may be associated with the end capping acceptors on both the porphyrin core and the CDT backbone promoting much stronger intermolecular self-assembly in the solid state.²⁵ The optical bandgaps estimated from the onset absorption edge observed in the absorption spectra of **SA1** and **SA2** are 1.53 eV and 1.45 eV, respectively.

The optical absorption spectra of the **SA2**:PC₇₁BM active layer cast from CB, DIO/CB and after subsequent SVA are shown in

Fig. 2. Similar absorption spectra were obtained for **SA1**:PC₇₁BM blended films.

Fig. 2 Optical absorption spectra of **SA2**:PC₇₁BM thin films processed under different conditions

It can be seen from Fig. 2 that the absorption spectra of blended films show a broad band response covering the range 350-850 nm. This band consisted of the absorption bands corresponding to the porphyrin and PC₇₁BM, indicating that both the porphyrin donor and PC₇₁BM contribute to the exciton generation and therefore the photocurrent generation in the OSCs.

The electrochemical properties of **SA1** and **SA2** were investigated by Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV) in *o*-DCB-acetonitrile (4:1) solution (See Table 1 and Fig. S15-S17). The results obtained indicate that both molecules show comparable electrochemical behavior. In the anodic window, both molecules show two consecutive and reversible steps, with the first oxidation potential of **SA1** lower than that of **SA2** by 60 mV (0.20 V vs. 0.26 mV respectively). This difference can be attributed to the lower electron-withdrawing strength of the rhodanine moiety with respect to the cyanovinylene group. The reductions also proceed in a similar way and **SA2** is easier to reduce (-1.42 V vs. -1.53 for **SA1**) for the reason given above. The HOMO and LUMO energy levels of both molecules were estimated from the CV data (Table 1). The calculated energies of the HOMOs are -5.30 eV (**SA1**) and -5.35 eV (**SA2**); overall, high open circuit voltage (V_{oc}) values are expected for devices constructed with these molecules. Finally, the HOMO-LUMO gaps, as determined from the electrochemical data, are as narrow as 1.73 and 1.68 eV for **SA1** and **SA2**, respectively, suggesting a good absorption of light in the visible region. The lower energy bandgap of **SA2** relative to **SA1** may be due to the end capping CN unit, which has stronger electron-withdrawing characteristics that lead to slight deepening of both the HOMO and LUMO energy levels of **SA2** when compared to **SA1**. The HOMO and LUMO energy levels of these porphyrins are compatible with PC₇₁BM for efficient photo-induced charge transfer.

Photovoltaic properties

OSCs were fabricated with solution processed BHJ active layers using either **SA1** or **SA2** as donor materials and PC₇₁BM as the acceptor material in a conventional architecture device structure (ITO/PEDOT:PSS/active layer/PFN/Au). Chlorobenzene (CB) was used as the solvent for film deposition since CB has a high boiling point and slow evaporation of CB can facilitate the molecular assembly and formation of interpenetrated networks with good crystallinity. The weight ratio between donor and acceptor was optimized at 1:2 for both **SA1** and **SA2** devices and the thickness of the active layer was around 90 nm ± 5 nm. The current-voltage characteristics of the OSCs based on the optimized active layers processed with CB are shown in Fig. 3 (Fig. 3a). The photovoltaic device parameters are displayed in Table 2.

Fig. 3 (a) Current-voltage characteristics of OSCs under illumination and, (b) IPCE spectra of the OSCs.

It can be seen from the results in Table 2 that the overall PCE for the **SA2** (3.61%) device is higher than that for the device based on **SA1** (2.81%). Having optimized the weight ratio in the active layer processed with CB, we proceeded to optimize the concentration of solvent additive (DIO) (3 v%) in the host solvent. This change gave rise to PCE values of 6.04% and 7.16% for **SA1** and **SA2**, respectively, with significant improvements in both J_{sc} and FF (Table 2).

Table 2 Photovoltaic parameters of OSCs based on **SA1**:PC₇₁BM and **SA2**:PC₇₁BM active layers processed under different conditions

Donor	Processing conditions	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
SA1	As cast	7.61	0.90	0.41	2.81 (2.74) ^a
	DIO/CB	12.46	0.85	0.57	6.04 (5.93) ^a
	DIO/CB/SVA	13.38	0.85	0.61	6.94 (6.84) ^a
SA2	As cast	8.56	0.98	0.43	3.61 (3.55) ^a
	DIO/CB	13.12	0.91	0.60	7.16 (7.07) ^a
	DIO/CB/SVA	13.84	0.91	0.65	8.19 (8.11) ^a

^a) Average of 10 devices

In order to improve the PCE further, the active layers were exposed to chloroform vapour for 60 s. The current-voltage (J - V) characteristics under illumination intensity (AM1.5G, 100 mW/cm²) of the optimized devices, i.e., DIO/CB/SVA, are shown in Fig. 3. The PCE of the device based on **SA1** after the addition of 3 v% of DIO and subsequent chloroform solvent vapor annealing (SVA) showed a significantly improved value of 6.94% for **SA1** with a J_{sc} of 13.38 mA/cm², V_{oc} of 0.85 and FF of 0.61. Similarly, an improved value of 8.19% was obtained for **SA2** with a J_{sc} of 13.84 mA/cm², V_{oc} of 0.91 V and FF of 0.65. It can be seen from Fig. 3a that the intensity of the absorption band, which corresponds to the longer wavelength region, increased after the addition of DIO and SVA treatment. This indicates that such treatment effectively improves the self-assembly of the donor (porphyrins) and the crystallinity of the active layer and leads to enhancements in J_{sc} and FF. It can be seen from the results in Table 2 that all OSCs based on **SA2**, fabricated under different processing conditions, showed higher V_{oc} values than those for **SA1**. This difference may be due to the deeper HOMO energy level caused by the stronger CN withdrawing unit, since the V_{oc} of OSCs based on a BHJ active layer is directly related to the difference in the HOMO energy level of the donor and LUMO energy level of the acceptor. Moreover, the energy loss (E_{loss}) defined as $E_{loss} = E_g - qV_{oc}$, where E_g is the optical bandgap of the donor, for optimized **SA2**:PC₇₁BM is as low as 0.55 eV and this may also be responsible for high the V_{oc} .²⁶

The incident photon-to-current conversion efficiency (IPCE) values of the optimized devices are shown in Fig. 3b. It can be seen that IPCE values up to 66.5% were obtained from 350–850 nm under optimal conditions for an **SA2**:PC₇₁BM-based device, which are higher than those for **SA1**:PC₇₁BM under identical conditions. The J_{sc} values obtained from the integration of the IPCE spectra of the devices are around 13.25 mA/cm² and 13.72 mA/cm² for **SA1**:PC₇₁BM and **SA2**:PC₇₁BM devices, respectively, and these values are consistent with those obtained in the J - V characteristics under illumination. The IPCE spectrum of the **SA2**-based device is slightly broader than that for **SA1** and this finding is consistent with the absorption spectra of the respective blends (Fig. 2).

In order to obtain information about the differences in the J_{sc} and FF values of the devices, we fabricated hole-only devices with the structure ITO/PEDOT:PSS/active layer/Au. The dark J - V characteristics were measured to estimate the hole mobility

of the active layer (Fig. 4) and the curves were fitted to the space charge limited current (SCLC) model to give estimated values of $2.31 \times 10^{-5} \text{ cm}^2/\text{Vs}$ and $3.12 \times 10^{-5} \text{ cm}^2/\text{Vs}$ for as-cast blends of **SA1**:PC₇₁BM and **SA2**:PC₇₁BM, respectively.

Fig. 4 Current-voltage characteristics of hole only devices based on active layers processed under different conditions (a) **SA1**:PC₇₁BM and (b) **SA2**:PC₇₁BM

The hole mobilities increased up to $9.95 \times 10^{-5} \text{ cm}^2/\text{Vs}$ and $9.13 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for **SA1**:PC₇₁BM and **SA2**:PC₇₁BM active layers, respectively, upon the addition of DIO and up to $0.95 \times 10^{-4} \text{ cm}^2/\text{Vs}$ and $1.18 \times 10^{-4} \text{ cm}^2/\text{Vs}$ after SVA under optimal conditions. The increase in the hole mobility upon either solvent addition or subsequent SVA treatment results in a more balanced charge transport in the active layer. These results are consistent with higher J_{sc} and FF values for the **SA2**:PC₇₁BM-based device.

We proceeded to investigate the variation in the photocurrent (J_{ph}) with effective voltage (V_{eff}) for the devices (Fig. 5) in an effort to evaluate the charge carrier transport and

photocurrent extraction properties.²⁷ J_{ph} is defined as $J_{ph} = J_L - J_D$, where J_L and J_D are the current densities under illumination and dark, whereas V_{eff} is defined as $V_{eff} = V_o - V_{appl}$, where V_{appl} is the external applied voltage and V_o is the voltage at which J_{ph} is zero.

The V_{eff} value determines the electric field in the BHJ active layer and thereby can reflect the carrier transport and photocurrent extraction properties. When the V_{eff} is sufficiently high, the J_{ph} saturates and this suggests that all of the photogenerated excitons are dissociated into free charge carriers and subsequently collected by the electrodes.

Fig. 5 Variation of photocurrent density (J_{ph}) with effective voltage (V_{eff}) for the OSCs

In this case, the saturation photocurrent (J_{phsat}) is only limited by the total amount of absorbed incident photons and the ratio J_{sc}/J_{phsat} provides information about the product of exciton dissociation efficiency and charge collection efficiency.²⁸ It can be seen in Fig. 5 that at high V_{eff} , the J_{ph} values for both of the optimal devices based on **SA1** and **SA2** reach very similar values of J_{phsat} . The values of J_{sc}/J_{phsat} at short circuit conditions are about 0.89 and 0.91 for **SA1** and **SA2** devices, respectively, and this suggests that both devices show high dissociation efficiency or charge collection efficiency. The higher value of J_{sc}/J_{phsat} for the **SA2**-based device indicates either a higher exciton dissociation efficiency or charge collection efficiency for the **SA2** device relative to the **SA1** counterpart. The exciton dissociation efficiency is related to the absorption profile of the active layer and, as can be seen from the absorption spectra of the active layers, **SA2**:PC₇₁BM has a broader absorption profile compared to **SA1**:PC₇₁BM – a finding that also confirms the higher generation of excitons in **SA2**-based devices. The higher charge collection efficiency for the **SA2**:PC₇₁BM-based device also suggests that a lower bimolecular recombination is responsible for improved FF.²⁹ However, the J_{ph} - V_{eff} characteristics for the devices are significantly different at low V_{eff} values. At maximum output conditions, J_{ph}/J_{sat} values are 0.72 and 0.81 for **SA1** and **SA2** devices, respectively, indicating suppressed bimolecular

recombination in the latter device. The devices based on active layers processed with CB only show stronger field dependence across a large bias range and this becomes slightly saturated at 2.8 V, indicating dominant bimolecular recombination and leading to low FF.³⁰ However, the J_{ph} values of the devices fabricated from DIO/CB or DIO/CB/SVA became saturated at much lower V_{eff} values, which suggests that the photogenerated excitons can be efficiently dissociated into free charge carriers and subsequently collected at the electrode with suppressed bimolecular recombination, thus leading to enhanced FF values.³¹ The maximum exciton generation rate (G_{max}) was estimated using $J_{phsat} = qLG_{max}$ (where q is the electronic charge and L is the thickness of the active layer). The values obtained are 6.23×10^{27} , 7.42×10^{27} and $8.67 \times 10^{27} \text{ m}^3/\text{s}$ for CB, DIO/CB and DIO/CB/SVA treated **SA1**:PC₇₁BM layers, respectively, and 7.27×10^{27} , 7.58×10^{27} and $9.56 \times 10^{27} \text{ m}^3/\text{s}$ for CB, DIO/CB and DIO/CB/SVA treated **SA2**:PC₇₁BM layers, respectively. The steady increase in G_{max} values with DIO/CB and subsequent SVA treatment can be attributed to the more ordered self-assembly of the porphyrin donor and the enhanced film morphology upon addition of DIO and SVA.

The structural ordering and crystallinity of the active layer also play an important role in exciton dissociation, charge transport and subsequent collection by electrodes, thereby affecting the overall PCE of the OSCs. As a consequence, the active layers were investigated by X-ray diffraction (XRD) (see Fig. 6 for the **SA2**:PC₇₁BM film).

Fig. 6 X-ray diffraction patterns of **SA2**:PC₇₁BM thin film processed under different conditions

Similar XRD patterns were observed for **SA1**:PC₇₁BM films. As-cast **SA1** blended film showed a diffraction peak at $2\theta = 4.82^\circ$ corresponding to a d-interspacing distance of 2.14 nm and crystal size of 11.2 nm. The **SA1** blended film processed with DIO showed a reduced spacing of 2.09 nm with an increased crystal size of 11.56 nm. The d-spacing was further reduced to 2.01 nm and the crystal size increased to 11.72 nm when the blend was processed with DIO/CB/SVA. The as cast **SA2** blended film showed a diffraction peak at $2\theta = 4.98^\circ$ with a d-interspacing distance of 2.02 nm and a crystal size of 11.43 nm, whereas the DIO/CB and DIO/CB/SVA processed **SA2** blended film showed d-interspacing/crystal sizes of 1.96 nm/11.58 nm

and 1.89 nm/11.86 nm, respectively. Moreover, the diffraction peak intensities are much stronger for DIO/CB and DIO/CB/SVA processed blended films, thus demonstrating the more ordered self-organization and increased crystallinity of the blended film. It can be seen from Fig. 6 that the π - π stacking peaks at $2\theta = 24.26^\circ$ in these molecules are weak and broad and these correspond to a distance of 0.34 nm. The broad band may be due to the interference of the diffraction peak of PC₇₁BM in the blended film. This value is quite small, which is beneficial for the strong intermolecular interactions and reduced steric effect with the less bulky alkyl chain substituents. The small π - π stacking distance is favorable for charge transport and this results in a higher FF value.³²

Conclusions

In summary, two new porphyrin small molecules with the same Zn-porphyrin donor core and different end-capping acceptors, i.e., rhodanine (**SA1**) or dicyanovinylene (**SA2**), linked through cyclopenta[2,1-b:3,4-b']dithiophene bridges have been designed and synthesized. The optical and electrochemical properties of these materials were investigated for their potential application as donors in conjunction with PC₇₁BM as an electron acceptor for solution processed bulk heterojunction OSCs. Both **SA1** and **SA2** showed absorption profiles from the visible to near infrared region and they had suitable frontier energy levels for exciton dissociation and charge transfer from donor to acceptor and vice-versa in the BHJ active layer employed in OSCs. After optimizing the weight ratio between the donor (**SA1** or **SA2**) and PC₇₁BM, solvent addition and subsequent solvent vapor annealing, PCE values of 6.94% and 8.19% (with low energy loss of 0.55 eV) were achieved for **SA1** and **SA2** OSCs, respectively. The improvement in the PCE of OSCs based on an active layer processed with the addition of DIO and subsequent SVA is related to the efficient photogenerated exciton dissociation and charge collection due to the favorable nanoscale morphology induced by the external treatments.

Experimental Section

Synthetic Details

4,4-Dihexyl-6-iodo-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (2). 4,4-Dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (**1**) (1.2 mmol, 450 mg) was reacted with PhI(OCOCF₃)₂ (0.65 mmol, 280 mg) and I₂ (0.59 mmol, 152 mg) in CCl₄ (1.5 mL). The mixture was stirred at room temperature overnight. The reaction was quenched with saturated aqueous sodium thiosulfate, stirred for 15 min and extracted with CH₂Cl₂. The combined organic phases were dried over anhydrous MgSO₄ and filtered. The solvent was removed under reduced pressure. The product was purified by column chromatography (silica gel, hexane:CHCl₃, 7:3) to give compound **2** as a yellow oil (450 mg, 1.11 mmol, 92% yield). ¹H NMR (400 MHz, CDCl₃, δ): 9.84 (s, 1H), 7.57 (s, 1H), 7.17 (s, 1H), 1.84 (m, 4H), 1.14 (m, 12H), 0.92 (m, 4H), 0.82 (m, 6H); ¹³C

NMR (100 MHz, CDCl_3 , δ): 182.5, 161.0, 157.1, 146.7, 143.4, 135.8, 129.8, 124.9, 124.3, 116.8, 54.5, 37.4, 31.5, 29.2, 24.4, 22.5, 13.9.

Synthesis of 4. A solution of freshly distilled Et_3N (45 mL/mmol, 16 mL) in dried and degassed THF (81 mL, 230 mL/mmol) was added to solution of porphyrin **3**^{11a} (0.35 mmol, 230 mg), **2** (1.05 mmol, 525 mg), $\text{Pd}_2(\text{dba})_3$ (0.6 eq, 0.21 mmol, 192 mg) and AsPh_3 (4 eq, 1.40 mmol, 428 mg) under argon. The reaction mixture was heated under reflux for 18 h. The solvent was removed under reduced pressure. The product **4** was purified by column chromatography (silica gel, hexane: CH_2Cl_2 , 1:1) to give a green solid (0.28 mmol, 404 mg, 82%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.79 (s, 2H), 9.64 (d, 4H, J = 4.5 Hz), 8.74 (d, 4H, J = 4.5 Hz), 7.62 (s, 2H), 7.57 (s, 2H), 7.33 (s, 4H), 2.67 (m, 4H), 2.00 (t, 6H, J = 7.9 Hz), 1.87 (m, 13H), 1.53 (m, 10H), 1.25–1.22 (m, 22H), 1.08 (m, 6H), 0.89–0.83 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 182.7, 162.3, 159.4, 151.8, 150.1, 147.4, 144.0, 139.2, 138.4, 138.0, 137.4, 131.9, 131.4, 130.1, 128.4, 128.0, 126.3, 121.9, 100.8, 99.7, 91.1, 54.5, 38.0, 32.1, 31.8, 29.9, 29.9, 29.6, 24.9, 22.9, 22.9, 21.8, 21.7, 14.3, 14.2; FT-IR (KBr): ν = 2931, 2915, 2850, 2811, 2140, 2059, 1650, 1500, 1423, 1396, 1334, 1288, 1226, 1149, 1130, 1076, 998, 852, 802, 713 cm^{-1} ; MALDI-TOF MS m/z : [M^+] calculated for $\text{C}_{86}\text{H}_{88}\text{N}_4\text{O}_2\text{S}_4\text{Zn}$: 1400.51; found: 1401.40.

Synthesis of SA1. 3-Ethylrhodanine (1.06 mmol, 175 mg) and 3 drops of piperidine were added to a solution of **4** (0.10 mmol, 150 mg) in dry CHCl_3 (5 mL, 25 mL/mmol) under argon. The reaction mixture was stirred and heated under reflux for 18 h and quenched by the addition of water. The product was extracted with CHCl_3 (3x150 mL). The combined organic extracts were dried over anhydrous MgSO_4 and filtered. The solvent was removed under reduced pressure and the solid was purified by column chromatography (silica gel, hexane: CHCl_3 , 1:1) and recrystallized from CH_2Cl_2 :MeOH. **SA1** was obtained as a green solid (137 mg, 0.09 mmol, 91% yield). mp >300 °C; ^1H NMR (400 MHz, $\text{THF}-d_8$, δ): 9.57 (d, 4H, J = 4.4 Hz), 8.65 (d, 4H, J = 4.4 Hz), 8.01 (s, 2H), 7.76 (s, 2H), 7.59 (s, 2H), 7.34 (s, 4H), 4.18 (m, 4H), 2.64 (m, 6H), 2.51 (m, 9H), 2.09 (t, 6H, J = 7.67 Hz), 1.90 (m, 12H), 1.28–1.23 (m, 28H), 1.11 (m, 6H), 0.83 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 192.5, 167.7, 162.0, 161.6, 152.5, 150.8, 146.6, 140.9, 140.0, 139.9, 138.8, 131.9, 129.5, 128.8, 127.4, 126.9, 122.3, 119.3, 101.1, 92.0, 55.4, 40.6, 38.9, 32.7, 30.8, 23.7, 22.0, 21.7, 14.5, 12.5; FT-IR (KBr): ν = 2931, 2854, 2368, 2321, 1700, 1577, 1504, 1488, 1415, 1373, 1315, 1234, 1126, 1103, 998, 879, 829, 790, 732, 709 cm^{-1} ; MALDI-TOF MS m/z : [M^+] calculated for $\text{C}_{96}\text{H}_{98}\text{N}_6\text{O}_2\text{S}_8\text{Zn}$: 1686.48; found: 1687.05.

Synthesis of SA2. Under an argon atmosphere malonitrile (0.10 mmol, 7 mg) was added to a solution of **4** (0.03 mmol, 50 mg) and triethylamine as base in dry CHCl_3 (2 mL). The reaction mixture was stirred and quenched by the addition of water. The product was extracted with CHCl_3 (3x150 mL). The combined organic extracts were dried over anhydrous MgSO_4 and filtered. The solvent was removed under reduced pressure and the solid was purified by column chromatography (silica gel, CHCl_3) and recrystallized from CH_2Cl_2 :MeOH. **SA2** was obtained as a green solid (46 mg, 0.02 mmol, 88% yield). mp: >

300 °C; ^1H NMR (400 MHz, CDCl_3 , δ): 9.65 (d, 4H, J = 4.5 Hz), 8.79 (d, 4H, J = 4.5 Hz), 7.72 (s, 2H), 7.58 (s, 4H), 7.32 (s, 4H), 2.67 (m, 4H), 2.00 (t, 6H), 1.87 (m, 13H), 1.53 (m, 10H), 1.26–1.22 (m, 22H), 1.17–1.05 (m, 6H), 0.87–0.83 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 164.1, 160.1, 151.8, 150.9, 150.5, 150.2, 139.2, 138.3, 138.1, 136.8, 136.5, 132.1, 131.4, 130.8, 128.0, 126.3, 122.3, 115.1, 114.4, 101.4, 100.5, 91.1, 72.5, 54.7, 38.0, 31.8, 29.8, 24.8, 22.8, 21.7, 14.2; FT-IR (KBr): ν = 2919, 2850, 2360, 1727, 1562, 1457, 1407, 1380, 1276, 1130, 1079, 968, 890, 794, 740, 717, 709 cm^{-1} ; MALDI-TOF MS m/z : [M^+] calculated for $\text{C}_{92}\text{H}_{88}\text{N}_8\text{S}_4\text{Zn}$: 1496.53; found: 1497.23.

Device fabrication and characterization

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 10–12 $\Omega \text{ cm}^{-2}$ were thoroughly cleaned prior to device fabrication by soaking in detergent solution followed by ultrasonication in deionized water, acetone and isopropyl alcohol sequentially for 15 min. The substrates were dried in vacuum overnight and a 40 nm thick poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) layer was spin-coated on the ITO-coated glass substrates at 2500 rpm for 30 s. The substrates were dried at 110 °C for 10 min in air. The active layers were spun from solutions of **SA1** or **SA2**:PC₇₁BM at different weight ratios of 1:1, 1:1.5, 1:2 and 1:2.5 with an overall concentration of 16 mg/mL from CB or DIO/CB as solvents. Solvent vapour annealing (SVA) of active layers spin coated from solution in a blend of DIO/CB with weight ratio of 1:2 was carried out by placing the substrate in a glass petri dish containing 0.3 mL CHCl_3 for 60 s. The thin PFN layer was spin coated from solution at a concentration of 1.5 mg/mL on top of the active layer at 3000 rpm for 30 s. Finally, the aluminum (Al) top electrode was thermally deposited on the active layer in a vacuum of 10^{-5} Torr through a shadow mask area of 20 mm^2 . All devices were fabricated and tested in an ambient atmosphere without encapsulation. The hole-only devices with architectures of ITO/PEDOT:PSS/active layer/Au were also fabricated in a similar way in order to measure the hole mobility. The current-voltage (J-V) characteristics of the BHJ organic solar cells were measured using a computer-controlled Keithley 2400 source meter in the dark and under simulated AM1.5G illumination of 100 mW/cm^2 . A xenon light source coupled with an optical filter was used to provide stimulated irradiance at the surface of the devices. The incident photon-to-current efficiency (IPCE) of the devices was measured by illuminating the devices through the light source and a monochromator and the resulting current was measured using a Keithley electrometer under short-circuit conditions.

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Supporting Information

New cyclopentadithiophene (CDT) linked porphyrin donors with different end capping acceptors for efficient small molecule organic solar cells

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1. Materials and methods

Synthetic procedures were performed under Argon atmosphere, in dry solvent unless otherwise noted. All reagents and solvents were reagent grade and were used without further purification. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040-0.063 mm). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. ^1H NMR spectra were obtained on Bruker TopSpin AV-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl_3 , 7.27 ppm). ^{13}C NMR chemical shifts (δ) are reported relative to the solvent residual peak (CDCl_3 , 77.0 ppm). Fourier transform infrared spectrophotometer (FT-IR) Thermo Nicolet AVATAR 370 was used. UV-Vis measurements were carried out on a Shimadzu UV 3600 spectrophotometer. For extinction coefficient determination, solutions of different concentration were prepared in CH_2Cl_2 (HPLC grade) with absorption between 0.1-1 of absorbance using a 1 cm UV cuvette. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. Mass spectra (MALDI-TOF) were recorded on a VOYAGER DETM STR mass spectrometer using dithranol as matrix. Melting points are uncorrected. The molecular geometries and frontier molecular orbitals of these new dyes have been optimized by density functional theory (DFT) calculations at the B3LYP/6-31G* level using Gaussian09W.^{S1} Cyclic voltammetry was performed in ODCB-acetonitrile (4:1)

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solutions. Tetrabutylammonium perchlorate (0.1 M as supporting electrolyte) were purchased from Acros and used without purification. Solutions were deoxygenated by argon bubbling prior to each experiment, which was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode ($\varnothing = 2$ mm) and a platinum wire counter electrode. An Ag/AgNO₃ (0.01 M in CH₃CN) electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc⁺) before and after each experiment.

The thermal stability was evaluated by TGA on a Mettler Toledo TGA/DSC Starte System under nitrogen, with a heating rate of 10 °C/min. Heating of crystalline samples leads to melting of the solids, but no recrystallization was observed.

2. ^1H NMR, ^{13}C NMR, FT-IR and MALDI-TOF MS spectra **Figure S1.** ^1H NMR spectrum (400 MHz, CDCl_3) of **2**. **Figure S2.** ^1H NMR spectrum (400 MHz, CDCl_3) of **4**.

Figure S3. ¹³C NMR spectrum (100 MHz, CDCl₃) of **4**.

Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃) of **SA1**.

Figure S5. ¹³C NMR spectrum (100 MHz, CDCl₃) of SA1.

Figure S6. ¹H NMR spectrum (400 MHz, CDCl₃) of SA2.

Figure S7. ^{13}C NMR spectrum (100 MHz, CDCl_3) of SA2.

Figure S8. FT-IR spectrum of compound **4** (NaCl window)

Figure S9. FT-IR spectrum of compound **SA1** (NaCl window).

Figure S10. FT-IR spectrum of **SA2** (NaCl window).

Figure S11. MALDI-TOF MS spectrum of compound **4** (Matrix: Dithranol).

Figure S12. MALDI-TOF MS spectrum of compound **SA1** (Matrix: Dithranol).

Figure S13. MALDI-TOF MS spectrum of compound **SA2** (Matrix: Dithranol).

3. Thermogravimetric analysis of compounds SA1 and SA2.

Figure S14. Thermogravimetric analysis of **SA1** (up) and **SA2** (down).

4. Electrochemical studies

Figure S15. Cyclic voltammetries (anodic window) of **SA1** (up) and **SA2** (down) (referred to Fc/Fc^+).

Figure S16. OSWV voltammetries (anodic window) of **SA1** (up) and **SA2** (down) (referred to Fc/Fc^+).

Figure S17. OSWV voltammetries (cathodic window) of **SA1** and **SA2** (referred to Fc/Fc^+).

5. Theoretical Calculations.

Figure S18. Theoretical optimized geometries and dihedral angles of **SA1** and **SA2**.

Figure S19. Electronic density contours and energy levels for HOMO and LUMO calculated for SA1 (left) and SA2 (right).