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An all-small-molecule organic solar cell derived from naphthalimide for solution-processed high-efficiency nonfullerene acceptors[†]

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Two small molecules **BYG-1** and **BYG-2** with fluorene donor and benzothiadiazole acceptor units connected to the terminal naphthamide group *via* ethyne linker were designed and synthesized. In this work we have discussed the effect of fluorine atoms connected with electron withdrawing benzothiadiazole unit to the fluorene core (**BYG-1**). In this study, we have fabricated solar cells with small-molecular donor and acceptor materials in the device architecture of bulk-heterojunction, using highly conjugated **BYG-1** and **BYG-2** as electron acceptors along with an appropriate small molecule donor (**SMD**). After improving the device architecture of the active layer using a suitable donor-to-acceptor weight ratio with solvent vapour annealing, we achieved power conversion efficiencies of 8.67% and 7.12% for **BYG-1** and **BYG-2**, respectively. The superior photovoltaic performance of the fluorine-substituted **BYG-1** can be attributed to its higher crystallinity, more balanced charge transport mobilities and efficient exciton dissociation.

Introduction

Organic solar cells (OSCs) have various fascinating advantages such as being light weight, flexible and low-cost photovoltaic devices fabricated through solution-processing on a large scale.¹⁻⁵ In OSC devices, active layer materials play a major role; fullerene derivatives are used as electron acceptors whereas a variety of polymers and small-molecule organic materials are used as electron donors with power conversion efficiencies (PCEs) of over 11%.⁶⁻¹⁴ Recently, a record PCE of above 14% has been reported for ternary active layer-based OSCs.15 However, due to some disadvantages of the fullerene derivatives, such as low absorption range, high cost of synthesis, no scope for tuning the energy levels and high voltage loss, the PCE cannot be further improved.^{16,17} In order to overcome these obstacles, during the last few years a large amount of work has been dedicated towards the design and development of non-fullerene small molecule acceptors (NFAs).^{18–23} Remarkably high PCEs in the range of 11–13% have been reported for OSCs based on NFAs,^{24,25} surpassing the fullerene-based counterparts, representing immense future for NFA-based OSCs.

Small molecule donors (**SMD**s) have diverse advantages and potential applications compared to their polymer counterparts, such as known chemical structures, good photovoltaic performance, less synthetic cost, and easy and reproducible purification process.^{26–30} Considering the above-mentioned advantages, the investigation of NFAs has become a very hot topic in the research area of OSCs, which may pave the way for potential large-area devices. Recently, OSCs based on **SMD** and SMA BHJ active layers have shown remarkable PCEs in the range of 9–11%.^{31,32}

In most of the non-fullerene-based OSCs, the electron mobility of the acceptor is generally lower compared to the hole mobility of the donor.³³ This mismatched charge mobility leads to charge recombination and results in poor short-circuit current as well as poor fill factor. Therefore, in order to employ non-fullerene acceptors in the OSCs, it is necessary to design a non-fullerene with high electron mobility. Small molecule nonfullerene acceptors consisting of a strong electron-withdrawing moiety like perylenediimide have high electron mobilities.³⁴ The incorporation of additional electron-withdrawing units like cyano into the small molecule non-fullerene acceptor has also been found to increase the electron mobility.35-38 Furthermore, these strategies also lead to a lower LUMO energy level of the acceptor.³⁹ When such an acceptor is employed in BHJ OSCs that have a donor with high-lying LUMO energy levels, it leads to a reduction in the V_{oc} value and also the PCE of the device

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due to the large offset between LUMO of the donor and the acceptor, which causes great energy loss.⁴⁰ Therefore, in order to increase the PCE of the OSC devices, exploring new widebandgap non-fullerene molecules with appropriate redox potentials and high electron mobilities is also necessary.

We have designed, synthesized and characterized two small molecule non-fullerene acceptors 6,6'-((7,7'-(9,9-didecyl-9H-fluorene-2,7-diyl)bis(6-fluorobenzo[c][1,2,5]thiadiazole-7,4-diyl))bis(ethyne-2,1-diyl))bis(2-(2-ethylhexyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione) (BYG-1) and 6,6'-((7,7'-(9,9-didecyl-9H-fluorene-2,7-diyl)bis(benzo[c]-[1,2,5]thiadiazole-7,4-diyl))bis(ethyne-2,1-diyl))bis(2-(2-ethylhexyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione) (BYG-2), see Fig. 1. The BYG-1 and BYG-2 compounds were molecularly engineered by using the electron-donating fluorene unit as the central core, connected on both the sides to the strong electron-withdrawing 2-ethylhexyl naphthamide group via the strong electron acceptor linking groups 5-fluorobenzo[c][1,2,5]thiadiazole and benzo[c]-[1,2,5]thiadiazole. The central fluorine core is a well-known highly planar and electron-rich moiety, with a major advantage of a low-lying HOMO energy level. The attachment of two n-decyl chains at the C-9 position of the fluorine unit improves the solubility and aggregation behaviour of the calamitic-type NFAs.⁴¹ This is also helpful for high charge carrier ability and enhances the open-circuit voltage (V_{oc}) of the devices. In addition to the electron-withdrawing properties of the benzo [c][1,2,5]thiadiazoles in BYG-1 and BYG-2, which lowers the LUMO energy levels, these hetero-aromatic groups extend the conjugated systems and increase the planarity of compounds, which results in stronger light absorption and better charge transport.^{41,42}

Among the designs of n-type molecules for organic solar cell applications, 1,8-naphthalimide (NAI) is a gifted candidate. The NAI molecules generally own a LUMO energy level that can match well with small molecular donors and some of the polymer donors.^{43,44} Further, the presence of NAI groups in the terminal positions of the designed molecules can influence the molecular self-assembly tendencies. Due to the bulkiness of the NAI moiety, intermolecular interactions can be weakened, which can be used for the control of aggregation. In addition, the solubility of molecules with NAI groups can notably increase by introducing an alkyl chain at the N-position of the NAI moiety. In the present study, we have explored these NFSMAs for their application in all small molecule OSCs along

with an asymmetrical D1–D2–A small molecule donor, which consists of a phenothiazine (D2) core and the terminal groups of TPA (D1) and 1,3-indandione (A), denoted as **SMD**.⁴⁵ The chemical structure of the present NFSMA along with the **SMD** are shown in Fig. 1. After the optimization of the BHJ active layer, we achieved overall PCEs of about 8.67% and 7.12%, respectively, for the **BYG-1** and **BYG-2** OSCs.

Results and discussion

Material synthesis and optoelectronic properties

The synthetic procedure of BYG-1 and BYG-2 non-fullerene acceptors is described below (Scheme 1). The amide formation of 4-bromo-1,8-naphthalic anhydride afforded intermediate 1 in a good yield. The Sonogashira coupling reaction between intermediate 1 and 2-methylbut-3-yn-2-ol gave intermediate 2, which after de-protection using NaOH resulted in intermediate 3 in a good yield. Intermediates 4 and 5 were prepared by using 3 and 4,7-dibromobenzo[c][1,2,5]thiadiazole, and 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole substrates in the Sonogashira coupling reaction, respectively. Alkylation of 2,7-dibromo-9H-fluorene resulted in intermediate 6 and the Miyaura borylation reaction of 6 yielded 2,2'-(9,9-didecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (intermediate 7). Finally, Suzuki coupling of intermediate 7 with 4 and 5 yielded the small molecules BYG-2 and BYG-1, respectively. Column chromatography using silica gel was applied for the purification of both the molecules and they were characterized by ¹H-NMR, ¹³C-NMR and mass spectrometry. Details of these analyses are reported in the supporting information. The synthesis and structural characterization of SMD was reported in our earlier study.⁴⁵ BYG-1 and BYG-2 are highly soluble in dichloromethane (DCM), ethyl acetate (EtOAc), chloroform (CHCl₃), dimethylsulfoxide (DMSO) and dimethylformamide (DMF).

UV-visible absorption

UV-vis absorption spectra of the **BYG** molecules were obtained in dilute chloroform solution and as well as in thin films. The absorption spectra of **BYG-1** and **BYG-2** showed similar absorptions in dilute solution (Fig. 2), where both molecules exhibited a broad absorption range in the region from 300 nm to 500 nm

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Scheme 1 Synthetic procedure of BYG-1 and BYG-2 non-fullerene acceptors.

with strong absorptions at 443 nm and 458 nm due to intramolecular charge transfer (ICT) transitions and weak absorptions at 375 nm and 378 nm due to π - π transitions, respectively. The molecular molar extinction coefficients (ε) of **BYG-1** and **BYG-2** (Fig. 2b) were determined to be $8.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $7.97 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The absorption spectrum of BYG-1 and BYG-2 in thin films extends up to 456 nm and 470 nm, respectively (Fig. 2a). This suggests that they are effectively aggregated in the thin film state due to the existence of strong intermolecular π - π interactions derived from the conjugated backbone structure. The optical band gaps (E_{α}^{opt}) of BYG-1 and BYG-2 as thin films were determined to be 2.49 eV and 2.45 eV, respectively. It is likely that the broader absorption of BYG-2 compared to BYG-1 can result in more efficient exciton generation and higher short-circuit current density $(J_{\rm SC})$, and lead to a better photovoltaic performance in BHJ OSCs. The absorption spectra of SMD in the thin film is also shown in Fig. 2a, and exhibits a strong absorption band in the wavelength 500–750 nm with an optical band gap of 1.74 eV, which is similar for **BYG-1** and **BYG-2**.

Herein, both BYG molecules have similar molecular structure and show similar absorption spectra. The main difference between **BYG-1** and **BYG-2** is that the incorporation of F atom in the benzo[c][1,2,5]thiadiazole (BT) group increases the interaction and enhances the push–pull effect among the donor and acceptor units due to the strong electron-withdrawing effect of F atom, which increases the molar extinction coefficient, and hence, enhances the light harvesting capacity and J_{sc} .

Cyclic voltammetry

The frontier molecular orbital HOMO and LUMO values of **BYG-1** and **BYG-2** were calculated by cyclic voltammetry in anhydrous DCM by using 0.1 M tetrabutyl ammonium perchlorate (TBAF) as the supporting electrolyte. The cyclic voltammograms were consistent using a ferrocene/ferrocinium (Fc/Fc^+) redox couple. Both **BYG-1** and **BYG-2** showed multiple reduction waves with



Fig. 2 (a) UV-visible absorption spectra of compounds BYG-1, BYG-2 and SMD in solution and in the thin film. (b) Molar extinction coefficient plots of BYG-1 and BYG-2.



Fig. 3 Cyclic voltammograms of **BYG-1** and **BYG-2** recorded in dichloromethane with 0.1 M TBAP.

similar structure within the potential window of the solvent. The CV plots of **BYG-1** and **BYG-2** are represented in Fig. 3 and the relevant data are presented in Table 1. The HOMO energy levels of **BYG-1** and **BYG-2** were determined to be -5.89 eV and -5.84 eV, respectively, calculated using the equation $E_{\text{HOMO}} = -e[E_{\text{ox}} + 4.80 - E_{(\text{Fc/Fc+})}]$. The LUMO energy levels of **BYG-1** and **BYG-2** were determined to be -3.40 eV and -3.39 eV, respectively, from the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{o-o}}$. The reason for the lower HOMO and LUMO energy levels for **BYG-1** is evidently due to the high electronegativity of the F atom in the benzodithiazole ring.

The LUMO energy level of both **BYG-1** and **BYG-2** are quite high compared to that of $PC_{71}BM$, and this should be beneficial for achieving high V_{oc} values for the corresponding OSCs. The HOMO and LUMO energy levels of **SMD** are -5.28 eV and -3.26 eV, respectively. Hence, the HOMO energy offsets

Table 1	Optical and electrochemical parameters BYG-1 and BYG-2					
Material	$\lambda_{\max, solution} (nm) \ (\epsilon, M^{-1} cm^{-1})$	$\lambda_{ m max, film}$ (nm)	E_{0-0} (eV)	HOMO (eV)	LUMO (eV)	
BYG-1 BYG-2	443 (81 103) 458 (79 737)	456 470	2.49 2.45	$\begin{array}{c} -5.89 \\ -5.84 \end{array}$	$-3.40 \\ -3.39$	

for **SMD/BYG-1** and **SMD/BYG-1** are 0.61 eV and 0.56 eV, respectively. This is sufficient for efficient hole transfer from the **BYG-1** or **BYG-2** to **SMD**. The LUMO offset in **SMD/BYG-1** and **SMD/BYG-2** is about 0.12 eV, which is lower than the generally accepted empirical threshold value of 0.3 eV.⁴⁶ The optical and electrochemical properties of **BYG-1**, **BYG-2** and **SMD** indicate that **BYG-1** and **BYG-2** can be suitable as acceptors along with **SMD** as donor for the all small molecule OSCs.

Photoluminescence (PL) spectra

In order to get high PCE for the OSCs, high values of both I_{sc} and Voc are required, and it is necessary to minimize the LUMO offset among the donors and acceptors used in the BHJ active layer of OSCs and maintain a well-organized charge transfer from the donor to the acceptor. In order to get the details about the exciton separation and charge transfer in the BHJ active layer, PL spectra of the pristine donor, pristine acceptor and the blend film were studied. Fig. 4 demonstrates the PL spectra of SMD, BYG-1 and their blend films. From the properties of the absorption spectra of SMD and BYG-1 in thin film, both molecules, BYG-1 and SMD, were selected and excited at 450 nm and 580 nm, respectively, in pure form as well as in blend. The PL intensity of BYG-1 was notably quenched when compared to that of SMD:BYG-1 blend at 450 nm excitation, indicating favourable hole transfer from BYG-1 to SMD. Importantly, PL emission of SMD was also quenched at 580 nm during the addition of BYG-1, which can be ascribed to the well-organized electron transfer from SMD to BYG-1. A Similar PL spectrum was also observed for SMD:BYG-2 thin film. An effective PL quenching behaviour was observed in these active layers indicating that the appropriate nano-scale phase separation of the blend film morphology is favourable for efficient exciton dissociation.⁴⁷⁻⁴⁹ The efficient exciton dissociation and charge transfer in these blends explained the advantage of effective photocurrent generation for the resulting OSCs.

Charge carrier mobility

The electron mobilities of pristine **BYG-1** and **BYG-2** were calculated by the space charge limited current (SCLC) measurement



Fig. 4 (a) PL spectra of BYG-1 and BYG-2 in DCM solution. (b) PL spectra of BYG-1 and SMD: BYG-1 blend in a thin film at different wavelengths of light.

with device structures ITO/Al/**BYG-1** and **BYG-2**/Al. The **BYG-1** showed higher electron mobility $(3.64 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ than that of **BYG-2** $(2.18 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$. The high electron mobility of **BYG-1** may be related to the fact that the incorporation of F atom in the BT improves the intermolecular interaction through C-F···S and C-F···H interactions. The enhanced electron mobility of **BYG-1** benefits the balanced charge transport and reduces the probability of charge recombination during their transport in the active layer towards the electrode when acting as an electron acceptor in the blend.

XRD patterns of the BYG-1 and BYG-2 thin films

To understand the difference in molecular ordering and crystallinity of pristine **BYG-1** and **BYG-2**, we recorded the X-ray diffraction patterns, shown in Fig. 5. Both the SMAs showed a (100) diffraction peak at $2\theta = 4.72$ corresponding to the lamellar stacking distance of 1.72 nm. Moreover, the (100) diffraction peak of **BYG-1** was significantly stronger than that of **BYG-2**. The (010) diffraction peaks were found at $2\theta = 23.02$ and 22.64 for **BYG-1** and **BYG-2**, respectively, which can be attributed to the π - π stacking. The π - π stacking distance extracted from the (010) diffraction peak was 0.37 nm and 0.40 nm for **BYG-1** and **BYG-2**, respectively. The stronger lamellar and π - π stacking properties and compact intermolecular packing of **BYG-1** indicated that **BYG-1** had a higher crystallinity than **BYG-2**, which is beneficial for high electron mobility, as confirmed from the



Fig. 5 XRD patterns of the BYG-1 and BYG-2 thin films.

SCLC measurement, and responsible for the improvement of J_{sc} and FF of the corresponding OSCs.

Photovoltaic properties

The performance of the OSCs was based on BYG-1 and BYG-2 as electron acceptors along with SMD as the donor using the conventional configuration of ITO/PEDOT:PSS/SMD:BYG-1 or BYG-2/PFN/Al. SMD was selected as a donor due to its complementary absorption spectra to that of both BYG-1 and BYG-2 and suitable HOMO and LUMO energy levels of -5.28 eV and -3.26 eV, respectively. Initially, we optimized the donor and acceptor weight ratio using chloroform solution and observed that the optimized weight ratio of 1:2 showed the best PCEs of 3.12% (J_{sc} = 7.34 mA cm⁻², V_{oc} = 1.12 eV and FF = 0.38) and 2.73% (J_{sc} = 7.03 mA cm⁻², V_{oc} = 1.08 eV and FF = 0.36) for BYG-1- and BYG-2-based OSCs, respectively. The fabrication of OSCs and their characterization are reported in the supplementary information. For the implementation of these device PCEs, we performed SVA treatment of the active layer (in THF for 60 s) to improve the phase separation and morphology. The *I-V* characteristics of the SVA-based devices are shown in Fig. 6a and their photovoltaic values are displayed in Table 2. The optimized devices presented overall PCEs of 8.67% and 7.12%. It was observed that the $V_{\rm oc}$ of these devices was fairly high (more than 1.0 V), which might be due to the higher values of LUMO energy levels of both BYG-1 and BYG-2.⁵⁰⁻⁵³ We also constructed the devices based on PC71BM as acceptor under identical conditions for comparison, and the data are presented in Table 2. Although, the Isc and FF values of OSC based on PC71BM are comparable to that for the non-fullerene acceptors, the difference in the values of $V_{\rm oc}$ is quite significant, due to the different LUMO energy levels of non-fullerene acceptors and PC71BM. This indicates that our design for the new wide-bandgap acceptor with a higher value of LUMO energy level is effective to improve the $V_{\rm oc}$.

In order to know the different J_{sc} values of the OSCs using **BYG-1** and **BYG-2** as acceptors, the incident photon to current conversion efficiency (IPCE) responses of the OSCs are displayed in Fig. 6b. Both the OSCs exhibit a broad response ranging from 350 nm to 750 nm, and it resembles the optical absorption spectra of the blend active layers (as shown in Fig. S3, ESI†) suggesting that both the donor and acceptors employed in the



Fig. 6 (a) Characteristic *J*–*V* curves of the optimised **SMD:BYG-1**- and **SMD:BYG-2**-based BHJ photovoltaic devices measured under AM 1.5G illumination at 1 sun intensity. (b) IPCE spectra of **BYG-1** and **BYG-2** molecules.

Table 2 Photovoltaic parameters of OSCs based on **BYG-1** and **BYG-2** as acceptors

Acceptor	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}$ (V)	FF	PCE (%)	$E_{\rm loss}$ (eV)
BYG1 (as cast)	7.34	1.12	0.38	$3.12(3.05)^a$	
BYG2 (as cast)	7.03	1.08	0.36	$2.73(2.67)^{a}$	
BYG1 (SVA)	12.95	1.08	0.62	$8.67(8.61)^{a}$	0.66
BYG2 (SVA)	11.84	1.02	0.59	$7.12(7.05)^{a}$	0.72
PC ₇₁ BM	12.06	0.82	0.63	6.23	0.92
^{<i>a</i>} Average of 8 d	levices.				

active layer are responsible for the photocurrent generation. The maximum values of EQE for the **BYG-1**- and **BYG-2**-based devices are about 68.4% and 63.5%, respectively. The EQE response in the 350–500 nm wavelength regions corresponds to the exciton dissociation generated in **BYG-1** or **BYG-2** with the electron hole transfer from the HOMO of **BYG-1** or **BYG-2** to that of **SMD**. Moreover, the EQE response in the wavelength range of 550–750 nm corresponds to the exciton generation in the **SMD** and electron transfer from the LUMO level of **SMD** to that of **BYG-1** or **BYG-2**. The J_{sc} values estimated from the integration of EQE response are about 12.84 mA cm⁻² and 11.76 mA cm⁻² for **BYG-1** and **BYG-2**, respectively, which are in good agreement with the values observed in the J-V characteristics under illumination.

We have performed the variation of photocurrent density $(J_{\rm ph}, i.e. J_{\rm ph} = J_{\rm L} - J_{\rm D}$, where $J_{\rm L}$ and $J_{\rm D}$ are the current densities in the presence of light and in dark, respectively) with effective voltage ($V_{\rm eff}$, defined as $V_{\rm eff} = V_{\rm o} - V_{\rm app}$, where $V_{\rm o}$ is the voltage when $J_{\rm ph}$ is zero and $V_{\rm app}$ is the applied voltage) (Fig. 7). In both the OSCs, the $J_{\rm ph}$, after linear variation with $V_{\rm eff}$ at less voltages, reached saturation quickly (saturation photocurrent ($J_{\rm phsat}$)) at 0.73 V and 0.96 V for **BYG-1** and **BYG-2**, respectively, indicating that all the photogenerated excitons were dissociated into free charge carriers and subsequently collected at the electrodes very efficiently.⁵⁴ The overall exciton dissociation efficiency and charge collection efficiency ($P_{\rm diss}$) are estimated from the ratio of $J_{\rm phsat}/J_{\rm ph}$ under short-circuit environment and the values are 0.95 and 0.91 for the OSCs based on the optimized **SMD:BYG-1** and **SMD:BYG-2** active layers, respectively.



Fig. 7 Photocurrent density variation with effective voltage plots of BYG-1 and BYG-2 molecules.

To better understand the charge transport we measured the electron and hole mobilities in the optimized active layers using the dark *J*–*V* characteristics and fitting these with the SCLC model (as shown in Fig. 8 only for electron-only devices).



Fig. 8 Dark current-voltage characteristics of electron-only devices using optimized **BYG-1BYG-1**:SMD and **BYG-2**:SMD active layers. Straight lines are SCLC fitting.



Fig. 9 TEM images of BYG-1:SMD and BYG-2:SMD in optimized active layers. Scale bar is 200 nm.

The hole mobility in both the blends was about 9.93 × 10^{-5} cm² V⁻¹ s⁻¹, but the electron mobility was 2.87 × 10^{-4} cm² V⁻¹ s⁻¹ and 1.9×10^{-4} cm² V⁻¹ s⁻¹, for **BYG-1:SMD** and **BYG-2:SMD**, respectively. The higher value of electron mobility for **BYG-1:SMD** leads to an increase in both J_{sc} and FF, thereby resulting in higher PCE of the OSC based on **BYG-1:SMD**.

Active layer morphology

To study the phase separation and morphology of the active layers, we carried out transmission electron microscopy (TEM) measurements, as shown in Fig. 9, for the optimized active layers. The TEM images of the as-cast active layers are shown in Fig. S4 (ESI[†]), which show poor phase separation that hinders charge transport. However, when the active layers were subjected to SVA treatment, they showed much better phase separation, which is beneficial for charge transport. As can be seen from Fig. 9, the **BYG-1:SMD** active layer showed more phase separation (15–20 nm) than the **BYG-1:SMD** (12–15 nm) counterpart. Phase separation is useful for charge transport, which leads to the enhancement of the overall PCE of the OSCs.

In OSCs, one of the important factors is the voltage energy loss ($E_{\rm loss}$), which is defined as $E_{\rm loss} = E_{\rm g} - V_{\rm oc}$, where $E_{\rm g}$ represents the optical band gap of the donor or the acceptor.⁵⁰ The values of $E_{\rm loss}$ for optimized OSCs based on **BYG-1**, **BYG-2** and PC₇₁BM are 0.66 eV, 0.72 eV and 0.92 eV, respectively. The lower value of $E_{\rm loss}$ for the non-fullerene acceptor than that for PC₇₁BM may be attributed to the higher values of $V_{\rm oc}$ for our devices, leading to the higher values of PCE for our non-fullerene OSCs.

Theoretical study

The theoretical studies of **BYG-1** and **BYG-2** molecules were conducted using the B3LYP exchange correlation functional with 6-311g(d,p) as the basis set in Gaussian 09 program. To know the solvation effect from DCM on both the molecules, we performed the self-consistent reaction field (SCRF) calculation



using the conductor-like polarizable continuum model (CPCM). The optimized geometric structures of **BYG-1** and **BYG-2** molecules are shown in Fig. 10.

TDDFT for BYG-1 and BYG-2

We used the time-dependent density functional theory (TDDFT) method to study the correlation of the experimental absorption results with the theoretical absorption results of both the molecules using similar exchange correlation functional and basis set in Gaussian 09 program. The geometric parameters of both the molecules in the singlet state reproduced the experimental values. We performed several excitations to cover the visible and ultraviolet regions of the dyes from 300 nm to 600 nm. Herein, we have mainly focused on the visible region to observe the charge transfer property. The theoretical absorption spectra of both molecules were well aligned with the experimental absorption spectra, as shown in Fig. 11. The frontier molecular orbital energies calculated at the B3LYP/6-311g(d,p) level of theory compared with the experimental values are shown in Table 3, and also, the major allowed transitions in the range of 290-450 nm of BYG-1 and BYG-2 were calculated by using B3LYP/6-311g(d,p) level of theory in DCM solvent, which is briefly explained in the supporting information (Fig. S1, S2 and Tables S1, S2, ESI[†]).



Fig. 11 Normalized plots of experimental and simulated absorption spectra of BYG-1 (a) and BYG-2 (b) molecules

 Table 3
 The comparison of frontier molecular orbital energies (theoretical and experimental values) of both the molecules

	Experimental			Theoretical			
Compound	$E_{\rm HOMO}^{a}$	E_{LUMO}^{b}	E ₀₋₀	E _{HOMO}	E_{LUMO}	HLG	
BYG-1 BYG-2	$\begin{array}{c} -5.89 \\ -5.84 \end{array}$	$-3.40 \\ -3.39$	2.49 2.45	$-5.91 \\ -5.89$	$-3.37 \\ -3.28$	2.54 2.61	

 a Obtained by adding 4.8 to $E_{\rm oxd}.$ b Obtained by adding 4.8 to LUMO values. c HOMO–LUMO gap.

Conclusion

Two wide-bandgap small molecule non-fullerene acceptors **BYG-1** and **BYG-2** were synthesized and their photophysical properties were investigated. The optical and electrochemical properties indicated that both **BYG-1** and **BYG-2** were suitable as acceptors along with an appropriate donor with complementary absorption spectra and similar HOMO and LUMO energy levels. We used a small molecule donor (**SMD**) along with these non-fullerene acceptors for the construction of the all small OSCs devices. Upon optimization of the active layer phase separation, we achieved overall PCEs of 8.67% and 7.12% for **BYG-1** and **BYG-2** acceptors, respectively, which were higher than that for the PC₇₁BM acceptor. The increase in the PCEs for the non-fullerene acceptors may be attributed to their higher LUMO energies and low voltage losses.

Conflicts of interest

The authors declare no competing financial interest.

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