Non-fullerene all small molecule OBHJSCs with profound device characteristics

Manohar Reddy Busireddy¹,²,³ | Ejjurothu Appalanaidu¹,³ | Dyaga Bharath¹ | Narendra Reddy Chereddy¹,³ | Balaiah Shanigaram² | Ganesh Datt Sharma⁴ | Jayathirtha Rao Vaidya¹,³

¹ Fluoro-Agro Chemicals Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana, India
² Catalysis and Fine Chemicals Department, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana, India
³ Academy of Scientific and Innovative Research, CSIR-Indian Institute of Chemical Technology, Sector 19, Kamla Nehru Nagar, Ghaziabad, Uttar Pradesh 201002, India
⁴ Department of Physics, The LNM Institute of Information Technology, Jamdoli, Jaipur, Rajasthan, India

Correspondence
Jayathirtha Rao Vaidya, Fluoro-Agro Chemicals Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana 500007, India.
Email: vaidya.ooip@gmail.com
Ganesh Datt Sharma, The LNM Institute of Information Technology, Jamdoli, Jaipur, Rajasthan, India.
Email: gdsharma273@gmail.com

Abstract
In this work, we have reported two donor materials ONAF and SNAF that complement the widely used non-fullerene acceptor ITIC, with the aim to develop non-fullerene all small molecule organic bulk heterojunction solar cells (NF-ASM-OBHJSCs). Two small molecule donors A-D-D’-D-A architecture, namely ONAF and SNAF are synthesized and explored their ability to act as donor material along with the ITIC acceptor. Benzodithiophene (BDT) is used as central donor unit (dialkoxy-BDT for ONAF and Dialkylthiophene-BDT for SNAF) along with novel naphthodithiophene (NDT) terminal donor to improve light harvesting and charge conducting ability of the donor materials. N-Butylrhodanine is employed as terminal acceptor to enhance the intramolecular charge transfer (ICT) and to place energy level of the donor materials. Both the small molecule donor materials have good thermal stability, broad and intense absorption displayed in the UV-vis region with energy levels suitable for ITIC acceptor. NF-ASM-OBHJSCs are fabricated by using all small molecules (ONAF & SNAF) as donors and ITIC as acceptor. OBHJSCs based on SNAF displayed superior photovoltaic properties with power conversion efficiency (PCE) as 9.94 % (J_sc = 15.93 mA cm⁻², V_oc = 0.96 V and FF = 0.65) compared to ONAF based devices with PCE as 7.48 % (J_sc = 14.93 mA cm⁻², V_oc = 0.82 V and FF = 0.61). The substantial high PCE of SANF is attributed to the broad absorption, relatively well-matched HOMO-LUMO energy levels between SNAF – ITIC acceptor, better film morphology for efficient charge transport and exciton dissociation at donor/acceptor (D-A) junction. The observed PCE is one of the best reported for the NDT-BDT-based all small molecule non-fullerene OBHJSCs. Moreover, simplicity in the device fabrication procedures and low energy loss associated are added advantages with the SNAF based devices. We predict that the HOMO-LUMO levels (CV) of D/A falling in this category, as in
INTRODUCTION

In recent years, solution processed organic bulk heterojunction solar cells (OBHJSCs) have been emerged as one of the forefront and promising renewable energy technologies to meet the future energy demands worldwide.\cite{1-5} This is because of the low cost, light weight, good flexibility, simple device framework, and easy fabrication of OBHJSCs and attained great interest. Over the past few decades great progresses in the research on organic solar cells (OSCs) is observed.\cite{6-9} Because of the limitations associated with the fullerene acceptors (PC\textsubscript{61}BM and PC\textsubscript{71}BM), many researchers started making OBHJSCs involving non fullerene acceptors. Specially, small molecule non-fullerene acceptors (SM-NFAs) have gained utmost importance and extensive investigation has been taking place to develop simple and efficient SM-NFAs.\cite{10-15} Unlike the intrinsic limitations of weak absorption, high synthetic cost, and purification difficulty of fullerene based acceptors (PC\textsubscript{61}BM and PC\textsubscript{71}BM),\cite{16,17} SM-NFAs have several unique advantages, such as near-infrared absorption, tuneable energy levels and easy synthesis which allow better photon absorption and morphology modulation.  

Owing to the endless efforts, increase in the PCE from 10% to over 18% reported for the OBHJSCs with non-fullerene acceptors (NFAs) and polymer-based donor materials.\cite{18-24} However, the drawbacks like batch-to-batch variation in the molecular weight and polydispersity associated with the polymer donors limit their widespread applications and paving way for the development of small molecular donor materials suitable for all SM-NFAs. The combination of SM-NFAs with small molecular donors provides various advantages like tuning the blend absorption, frontier molecular orbital energy levels, and crystallization characteristics. These advantages greatly attracted the researchers and the research area of NF-ASM-OBHJSCs has been rapidly growing.\cite{25-29} Nevertheless, the best power conversion efficiency (PCE) reported for the NF-ASM-OBHJSCs is around 14% which is still lagging far behind their polymer donor counterparts. Hence it is worthy to develop new organic small molecular D/A materials with reinforcing characteristics to improve the PCE of NF-ASM-OBHJSCs.\cite{30-32} Among the donor materials reported for NF-ASM-OBHJSCs, most part are based on benzothiophene (BDT) internal core due to fused benzene ring with two peripheral thiophene rings of BDT induces strong intra and intermolecular interactions in its thin film state and improves charge carrier mobility in the OBHJ.\cite{30,33,34} Extensive research has already done to improve the efficiency of BDT based materials by adopting various combinations, like alkyl chain modification, and incorporating various substituents on the BDT core.\cite{35-38} This indicates the necessity to develop new and efficient donor materials for NF-ASM-OBHJSCs. Naphthodiophene (NDT), a structural analogue of BDT, has been explored recently for photovoltaic applications. Polymeric materials using NDT as donor core are utilized for solar cell and thin film transistor applications.\cite{39,40} These materials showed high hole carrier mobility due to their unique properties like coplanarity, highly ordered \textpi -stacked structures and high charge density of the NDT core. However, small molecule donor materials with NDT core are very few.\cite{41}

Prominent structural and charge transport characteristics of NDT core motivated us to develop new small molecule donor materials for NF-ASM-OBHJSCs using \textit{ITIC} as non-fullerene acceptor. Backbone structure is fixed from one of our recently reported, efficient donor material with replacement of dithienopyrrole (DTP) units with NDT core. Such modifications resulted in hypsochromic shift in the absorption spectrum leading to complementary absorption with \textit{ITIC} acceptor. Moreover, HOMO energy level is well stabilized and is an additional advantage to provide high \textvoc values. Marks and co-workers was first reported NDT based donor material.\cite{42,40} NDT  exhibits their unique properties like rigid, coplanar molecular structure and facilitating the charge carrier transport. Further, two linear 2-ethylhexyloxy chains on the NDT units at the 5- and 6-position increased the solubility of the resulting donor materials and also minimized the formation of molecular aggregates which can cause the charge recombination in the OBHJSCs.\cite{43-49}  

OBHJSCs are fabricated using the synthesized donors and \textit{ITIC} acceptor materials by adopting simple fabrication procedures. The devices with \textit{SNAF}/\textit{ITIC} photoactive blend showed superior photovoltaic performance with
PCE of 9.94% and energy loss of 0.56 eV over the device with ONAF/ITIC photoactive blend (PCE = 7.48% with energy loss of 0.70 eV). Reason for the observed superiority of SNAF/ITIC based device (compare to ONAF/ITIC device), could be the better matched energy levels of D/A materials leading to ease of formation of hole (radical cation) and electron (radical anion). These results revealed the scope to develop new NDT based donor materials for NF-ASM-OBHJSCs with various kinds of organic all SM-NFAs.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and thermal properties

The chemical structures of all three small molecules (ONAF, SNAF & ITIC) are displayed in Figure 1. All the target compounds were synthesized for previous modified literature procedures as displayed in Scheme 1 [33,47,50] and their synthetic procedures are provided in experimental section. ITIC was synthesized by previous modified literature procedure [16]. The reported small molecules ONAF and SNAF were synthesized Knoevenagel condensation pathway by treating with corresponding bis-aldehyde intermediates (ONp-CHO & SNp-CHO, respectively for ONAF & SNAF) with n-butylrhodanine. The prefinal bis-aldehyde derivatives ONp-CHO and SNp-CHO were obtained by reacting with the corresponding di-stannilated derivatives (7 and 8, respectively for ONp-CHO and SNp-CHO) with compound 6 using palladium catalyzed Stille cross-coupling reaction. Intermediates 7 and 8 were synthesized as per our previously reported procedures [9,51]. The key intermediate 6 was obtained by reacting compound 5 with NBS. The compound 5 was synthesized by reacting 4 with Vilsmeier formylation pathway in the presence of POCl₃ and DMF. Compound 4 was obtained by treating with 3 in presence of anhydrous FeCl₃ and CH₃NO₂. Intermediate 3 was synthesized by reacting the tributyl(thiophen-3-yl)stannane and compound 2 using palladium catalyzed Stille cross-coupling reaction. Compound 2 was obtained from catechol by reacting with
2-ethylhexylbromide in presence of base. All the synthesized small molecules and intermediates were confirmed by using $^1$H NMR, $^{13}$C NMR and Mass spectral (MALDI-TOF) analysis and their spectra’s were depicted in ESI (Figures S10-S37). All Small molecules (ONAF, SNAF & ITIC) are soluble in common organic solvents (up to 30 mg/mL).

The thermal properties of ONAF and SNAF were measured by using TG Analyzer and DSC instruments. As depicted in Table 1 and Figure 2, both the compounds exhibited excellent thermal stability with insignificant weight loss over wide range of temperature ($T_d$ 346°C & 394°C, respectively for, ONAF & SNAF). Both the small molecule donors are significantly differed in their melting temperature ($T_m$) and crystallization temperature ($T_{cr}$) behavior studied through DSC analysis. Both the compounds showed endothermic peaks corresponding to their

| Material | Decomposition temperature ($T_d$)°C | Melting temperature ($T_m$)°C | Crystallization temperature ($T_{cr}$)°C |
|----------|------------------------------------|------------------------------|----------------------------------------|
| ONAF     | 346                                | 194                          | –                                      |
| SNAF     | 394                                | 333                          | 305                                    |

$T_m$. The SNAF molecule shows $T_{cr}$ on its first cooling cycle, which is not observed for ONAF. This indicates better intermolecular aggregation of SNAF induced by alkylthiophene substituent on BDT donor unit.[52] The observed thermal properties of these compounds demonstrated their potential for various optoelectronic device applications.
2.2 Optical and electrochemical properties

Optical properties of ONAF, SNAF, and ITIC were measured in dilute CHCl₃ solution and in thin film cast from chloroform shown in Figure 3A and B, respectively, and corresponding data is provided in Table 2. Both the compounds displayed broad and intense absorption in UV-vis region in the range of 300–580 nm and it is complementary to the absorption of ITIC. The absorption bands located at shorter wavelength corresponds to localized aromatic π-π* transition of the A-D-D′-D-A system, while the bands at longer wavelength is mainly attributed to an ICT transition from donor to the terminal acceptor units.[7–9,53] In CHCl₃ solution SNAF displayed absorption maxima as 554 nm (molar extinction coefficient is $0.86 \times 10^5$ Mol⁻¹ cm⁻¹) at longer wavelength region and multiple absorption bands were observed in shorter wavelength region with good molar extinction coefficients, whereas, absorption maxima for ONAF was 548 nm (molar extinction coefficient was $0.71 \times 10^5$ Mol⁻¹ cm⁻¹). Compared to solution, the absorption spectra of these molecules were significantly red-shifted and got broadened. This is attributed to the better intermolecular π-π stacking in solid state (Figure 3B), due to their planer structure. The absorption peak in thin film are located at 600 nm (absorption coefficient of $2.2 \times 10^4$ Mol⁻¹ cm⁻¹) and 616 nm (absorption coefficient of $1.67 \times 10^4$ Mol⁻¹ cm⁻¹) for ONAF and SNAF,
TABLE 2  Photo-physical and electrochemical data of ONAF, SANF & ITIC

| Material | UV-vis absorption | Electrochemical properties |
|----------|-------------------|---------------------------|
|          | Solution          | Film                      | CV                          |
|          | $\lambda_{\text{max}}$ (nm)$^a$ | $\xi$ ($\times 10^4$ mol$^{-1}$ cm$^{-1}$)$^a$ | $E_{\text{opt}}$ (eV)$^b$ | $E_{\text{onset}}$ (V) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) |
| ONAF     | 548               | 0.71                      | 2.12                       | 600                      | 1.89                      | 0.15 | -5.25 | -3.51 |
| SANF     | 554               | 0.86                      | 2.11                       | 616                      | 1.81                      | 0.33 | -5.43 | -3.54 |
| ITIC     | 677               | 1.77                      | 739                        | 1.57                     |                           | 0.68 | -5.78 | -3.95 |

$^a$In dilute chloroform solution (10 $\mu$M).
$^b$Estimated from intersection of absorption and emission spectra in chloroform solution.
$^c$Estimated from $E_{\text{opt}} = 1240/\lambda_{\text{onset}}$, $\lambda_{\text{onset}}$ is onset absorption wavelength in thin film.

FIGURE 4  (A) Cyclic voltammograms of ONAF, SANF & ITIC from electrochemical cyclic voltammetry; (B) energy level diagram of all materials

respectively. The optical bandgap of these two molecules estimated from the onset absorption edge observed in the thin film absorption spectra is 1.87 and 1.78 eV, for ONAF and SANF, respectively. The estimated optical bandgap of ITIC is about 1.52 eV, which are well matched with the value reported in literature. In Figure 3, that absorption profile of ONAF or SANF showed complementary absorption with ITIC, indicating that blend of these small molecule donors with ITIC can show the absorption ranging from 300 to 850 nm, which is beneficial for the light harvesting efficiency of the OSCs.

In order to get information about the exciton dissociation and charge transfer between the donors and ITIC acceptor in the BHJ active layers, we have investigated the photoluminescence (PL) spectra of pristine SANF, ONAF, and ITIC thin films and SANF:ITIC and ONAF:ITIC blended films excited at the wavelength corresponding to the absorption peak of the donors and ITIC acceptor and shown in Figure S6a and S6b. As shown in Figure S6, SANF and ONAF showed a strong PL peak around 670–680 nm, which was quenched when blended with ITIC, but the quenching in more for SANF:ITIC blend, suggesting the photoinduced electron transfer from SANF to ITIC was more effective in the SANF:ITIC blend. The pristine ITIC showed a strong PL peak around which was quenched in both SANF:ITIC and ONAF:ITIC, indicating the efficient electron transfer from SANF or ONAF to ITIC (Figure S6). This is an interesting situation that absorption of light by either donor or acceptor results in electron transfer from donor to acceptor. Further the HOMO/LUMO energy levels of these donors (SANF & ONAF) and acceptor (ITIC) are very well matched (Figure S7). We predict that the HOMO/LUMO levels of D/A falling in this category (Figure S7) with further close energy levels will have implications on the efficiency of OBHJSCs.

Electrochemical properties of ONAF, SANF and ITIC were measured by using a standard three electrodes of cyclic voltammetry (CV) technique (Figure 4A and Table 2). The HOMO energy values of all small molecules were obtained from onset oxidation potential observed in CV and calculated from the empirical formula:
E_{HOMO} = -\epsilon[5.1 + E_{OX}] eV based on Fc/Fe^{+}\ energy level relative to vacuum. The first oxidation peak potential was used to calculate the HOMO and the values are -5.25, -5.43 and -5.78 eV for ONAF, SANF, and ITIC respectively. The LUMO values calculated from CV (onset reduction potential) and obtained values are -3.51, -3.54, and -3.95 eV for ONAF, SANF, and ITIC, respectively. The HOMO and LUMO energy levels of ONAF and SANF small molecules well matched with ITIC acceptor. The difference of LUMO level of acceptor and LUMO of donors are 0.44 and 0.41 eV for ONAF and SANF, respectively, which greater than the threshold value (0.3 eV) for exciton dissociation and subsequent electron transfer at D/A interface, efficient in both BHJ active layers (Figure 4B).\[^{[55]}\]

2.3 | Theoretical studies

We further tried to show the relationship between the structural variations optical and electrochemical properties using DFT and TD-DFT methods. Initial geometries of the molecules were optimizes using B3LYP, M06 and CAM-B3LYP functionals with a common 6–311G (d, p) basis set. Detailed DFT methodology followed is given in ESI. Degree of \(\pi\)-conjugation between the donor and acceptor segments is essential to analyze the extent of charge transfer via the overlap of orbital interactions. More planar is the molecule, greater the charge transport. In these molecules, NDT-BDT-NDT segment was found with a torsional distortion of \(\sim 3.02^\circ\) & \(7.67^\circ\) respectively for ONAF & SANF and terminal Rh-NDT units maintain almost 0\(^\circ\) torsion angle (Figure S1, ESI). We also computed the electron density population to predict the charge transfer transitions. Electron density of HOMO owns a well delocalized characteristic with dominant population on NDT-BDT-NDT segments. On the other hand, electron density population of LUMO prevailed on the acceptor parts with a considerable magnitude on NDT-BDT-NDT segments. This displacement of electron density all over the molecule indicates ICT character in the molecular backbone, direct visualization on the iso-density surface of frontier molecular orbitals (FMOs) appears to be nearly identical for both compounds (Figure S5). To examine contribution of individual units toward charge transfer transition for the A-D-D’-D-A framework, we have adapted the partial density of states (PDOS) analysis. For the purpose, we have parted the symmetrical A-D-D’-D-A framework into three segments such as D’ (BDT unit), D (two NDT units) and A (two terminal acceptor units). HOMO is majorly populated on NDT and BDT units and LUMO is located more on Rh and NDT moieties, it indicates the first excitation is high from HOMO to LUMO transition, moderate charge transfer from the BDT and NDT units to the Rh unit.

To understand the photo-physical behavior of ONAF and SANF, we looked at the absorption spectra using three various density functionals (B3LYP, M06 and CAM-B3LYP) with a 6–311G (d,p) basis set. CPCM model has been chosen to describe the solvation of the molecules to mimic the real environment and CHCl\(_3\) was used as solvent medium in this study. Of these, trend simulated by M06 functional was found to be in line with experimental observations albeit having a small overestimation (Figure S3, ESI) and CAM-B3LYP functional showed a small underestimation. The simulations predicted using other B3LYP functionals were highly deviated. The predicted oscillation strength was exceptionally high computed at the TD-DFT/CAM-B3LYP/6-311G(d,p)/CPCM (CHCl\(_3\)) level of theory. Nonetheless, B3LYP predicted HOMO-LUMO gap showed a difference of 0.1 eV, followed a consistent trend with the experimental band gap (solution state). A little underestimation was noticed in HOMO of ONAF but SANF showed a small overestimation, whereas, LUMO of ONAF showed almost same as experimental but for SANF, it was little underestimated. Electrostatic surface potential (ESP) of all the compounds displayed in Figure S4 (ESI). The red, green and blue colors represent negative, neutral, and positive charge population on the segments respectively. Positive charge sites were delocalized over the -NDT-BDT-NDT- framework except O-atoms of NDT-BDT and terminal acceptor units bearing negative charge population sites on both sides. The yellow color of S-C = S functionality of Rh bears a large but moderate negative electron density cloud due to weak electronegativity and strong polarizability of sulfur atoms.

2.4 | Photovoltaic properties

The photovoltaic properties of these two organic SM donor and ITIC as non-fullerene acceptor were investigated by fabricating the OSCs with conventional device structure of ITO/PEDOT:PSS/ONAF or SANF:ITIC/PFN/Al. The optimized OSCs were obtained by employing chloroform as processing solvent with donor/acceptor (D/A) weight ratio of 1:1.5 and subsequent the optimized as cast active layer showed overall PCE of 6.08 % and 4.57 % for SANF:ITIC and ONAF:ITIC, respectively. The current -voltage characteristics for optimized OSCs under
illumination (AM1.5G, 100 mW cm\(^{-2}\)) were displayed in Figure 5 and photovoltaic parameters were compiled in Table 3. The optimized OSC based on SNAF showed overall PCE of 9.94 % which a \(V_{oc}\) of 0.96 V, a \(J_{sc}\) of 15.93 mA cm\(^{-2}\) and FF of 0.65. In contrast, the optimized OSC based on ONAF showed lower PCE of 7.48 % with a \(V_{oc}\) of 0.82 V, a \(J_{sc}\) of 14.93 mA cm\(^{-2}\) and FF of 0.61. The higher PCE for SNAF based OSC as compared to ONAF counterpart is attributed to its higher \(J_{sc}\), FF and \(V_{oc}\). The relatively high value of \(V_{oc}\) in SNAF based OSC was in agreement with the deeper HOMO energy level of SNAF relative to ONAF (as shown in Figure 4B).

The incident photon to current conversion efficiency (IPCE) spectra of the optimized OSCs was shown in Figure 5. The SNAF based OSC exhibit a broader photo-response in the wavelength region of 300–850 nm, while ONAF based OSC showed a broad photo-response from 300 to 850 nm with a dip around 600 nm. Moreover, the maximum IPCE value of SNAF based OSC was higher than that of ONAF counterpart. The integrated value of \(J_{sc}\) from IPCE spectra of the OSCs were about 15.63 mA cm\(^{-2}\) and 14.75 mA cm\(^{-2}\) for SNAF and ONAF, respectively, and were consistent with the \(J_{sc}\) values obtained from the J-V characteristics under illumination. These results indicated that IPCE efficiency was higher in SNAF based OSC than that of ONAF.

The charge transport properties of the optimized SNAF:ITIC and ONAF:ITIC blended films were evaluated by space charge limited current model using the hole only and electron only devices (Figure 6). We have also measured the hole mobilities in the pristine small molecules and are about \(0.92 \times 10^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) and \(0.81 \times 10^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively for SNAF and ONAF. The electron/hole mobilities of SNAF:ITIC and ONAF:ITIC were determined to be \(1.25 \times 10^{-4}/2.12 \times 10^{-4}\) and \(1.02 \times 10^{-4}/2.19 \times 10^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively, which corresponded to \(\mu_{e}/\mu_{h}\) ratios of 1.67 and 2.15, respectively. These results indicate that SNAF:ITIC blend film showed higher hole mobility and a more balanced charge transport than that for ONAF:ITIC blend film, which is in agreement with the higher values of FF and \(J_{sc}\) observed in SNAF:ITIC based OSC.

In order to investigate the exciton dissociation and charge collection mechanisms, the variation of photocurrent density \((J_{ph})\) with effective voltage\(^{[56,57]}\) was employed and shown in Figure 7. As shown in Figure 7 that in both the OSCs, the \(J_{ph}\) increases linearly with \(V_{eff}\) and reached to a saturation value \((J_{sat})\) at high value \(V_{eff}\), indicating that all the photogenerated excitons after the absorption of light were dissociated into free charge carriers and collected by the electrodes. The \(J_{sat}\) value of the SNAF:ITIC OSC was about 16.56 mA cm\(^{-2}\), which is higher than that

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**TABLE 3** Photovoltaic performances of the all SM-NFAs based on ONAF:ITIC & SNAF:ITIC devices

| Material | \(J_{sc}\) (mA/cm\(^2\)) | \(V_{oc}\) (V) | FF | PCE (%) |
|----------|-----------------|----------------|----|--------|
| SNAF     | 15.93 (± 0.12)  | 0.96 (± 0.004) | 0.65 (± 0.006) | 9.94 (± 0.16) (9.72)\(^a\) |
| ONAF     | 14.83 (± 0.09)  | 0.82 (± 0.002) | 0.61 (± 0.002) | 7.42 (± 0.13) (7.25)\(^a\) |

\(^a\)Average of eight devices.
for ONAF:ITIC (~15.96 mA cm⁻²), indicating that the SNADF:ITIC based OSC exhibited enhanced charge generation and therefore, higher Jsc. The exciton dissociation rate (ηdiss) and charge collection efficiency (ηcoll) were estimated from the Jph/Jsat ratios under short circuit condition and maximum power points, respectively and were 0.96/0.74 and 0.93/0.69 for SNADF:ITIC and ONAF:ITIC based OSCs, respectively. Higher values of both ηdiss and ηcoll for the SNADF:ITIC than that for ONAF:ITIC indicates that former device had more efficient exciton dissociation and charge collections efficiency than that for later device.

In order to get more information about the charge carrier recombination behavior in the OSCs, we have measured the Jsc values at different illumination intensities (Pin) and shown in Figure 8. The relation between the Jsc and Pin can be described by the expression: Jsc ∝ (Pin)\(^\alpha\), where the exponent factor \(\alpha\) related to the extent of bimolecular recombination.\(^{[58]}\) The values of \(\alpha\) extracted from the Figure 8 are for SNADF and ONAF based OSCs, respectively, indicating that the bimolecular recombination in the SNADF based OSC is lower as compared to that of ONAF, and consistent with the balanced charge transport and resulting higher value of FF. The Voc follow a logarithmic relationship with illumination intensity as

\[V_{oc} = \frac{(nkT)}{q} \ln(P_{in}),\]

where k is Boltzmann constant, T is the temperature and q is the elementary charge.\(^{[59]}\) As shown in Figure 8, the slopes of fitting lines are 1.27 kT/q and 1.34 kT/q for SNADF and ONAF based OSCs, respectively, indicating there more trap-assisted recombination in ONAF based device.

The transient photovoltage (TPV) and transient photocurrent (TPC) measurements were carried out to get information about the carrier lifetime and charge extraction times of OSC based on ONAF:ITIC and SNADF:ITIC based active layers and shown in Figure 9. The carrier lifetime under open circuit conditions were extracted from TPV decay dynamics using mono-exponential fits.\(^{[60,61]}\)

In the assessment of TPV, the SNADF:ITIC based device shows a carrier lifetime of 4.58 µs which is higher than that for ONAF:ITIC counterpart (3.98 µs), which disclose that the charge recombination in the SNADF:ITIC based device is more effectively suppressed. The value of charge extraction time estimated from the TPC measurements for the device based on SNADF:ITIC is about 0.82 µs, which
is lower than that for ONAF:ITIC counterpart (0.93 μs) represents more effective charge extraction in SNAF:ITIC based device leading to higher value of J_sc and FF. These collective results revealed that SNAF:ITIC blend shows superior charge generation and charge transport characteristics leading to improved photovoltaic efficiency for the SNAF based OBHJSC devices.

The energy loss (E_loss) is an important factor and plays a crucial role in the overall PCE for OSCs. The E_loss is expressed as $E_{loss} = qV_{oc} - E_g$, where $E_g$ is the effective optical bandgap of the active layer and estimated from the onset of the IPCE spectra of the OSCs.\[62\] The values of $E_{loss}$ for the optimized OSCs based on optimized ONAF:ITIC and SNAF:ITIC active layers are 0.70 eV and 0.56 eV, respectively. The lower $E_{loss}$ for the SNAF:ITIC based OSCs may be due to the lower HOMO energy level of SNAF. The energy loss is divided into three parts: (i) radiative loss associated with the absorption bandgap, which unavoidable for any type of solar cells, (ii) additional radiative recombination originated from the absorption below the bandgap, and (iii) non-radiative loss, depends upon the LUMO and HOMO offsets between the donor and acceptor used in the active layer of BHJ OSCs. The low value of $E_{loss}$ for the SNAF:ITIC based OSCs may be due to the
suppressed non-radiative loss which is due to small value of HOMO and LUMO offsets for SNAF:ITIC than that for ONAF:ITIC [63,64].

The transmission electron microscopy (TEM) images were scanned to get information about the morphology and phase separation in the active layers and shown in Figure S8 (ESI). Both the active layers showed proper interpenetrating phase networks and the SNAF:ITIC showed more appropriate interpenetrating networks and compared to ONAF:ITIC, which is beneficial for charge transport and suppressed recombination leading to improvement in the both J_sc and FF values, resulting higher value of overall PCE of the OSCs.[65]

We have recorded the X-ray diffraction (XRD) pattern of the pristine SNAF and ONAF as well as their blend with ITIC and shown in Figure S9 (ESI). It can be seen from Figure S9 that the both the pristine SNAF and ONAF showed similar (100) diffraction peak (lamellar stacking) at 2θ = 4.96° and different (010) diffraction peaks (π–π stacking) at 2θ = 23.85° and 24.29° for ONAF and SNAF, respectively. The XRD diffraction of the blended ONAF:ITIC and SNAF:ITIC film showed same (100) diffraction peak located at 2θ = 5.38°, which is related to the combined lamellar diffraction of SM donor and ITIC, but different (010) diffraction peaks located at 2θ = 22.68° and 23.84°, for ONAF:ITIC and SNAF:ITIC, respectively, indicated different π–π stacking for the blended films. The π–π stacking distance for ONAF:ITIC and SNAF:ITIC is about 0.393 and 380 nm, respectively. Moreover, the higher intensity for both (100) and (010) diffraction peaks for SNAF:ITIC blend also indicate that the this blend is more crystalline. The compact π–π stacking and more crystalline nature of the active layer are beneficial for the charge transport and resulting the higher values of J_sc and FF for the OSCs based on SNAF:ITIC active layer.

3 | CONCLUSION

In summary, two organic small molecules namely ONAF & SNAF were synthesized and used as donors for SM-OSCs with small molecule acceptor ITIC and their thermal, optical, electrochemical, theoretical and photovoltaic properties were systematically evaluated. Both the small molecule donor shows broad absorption in UV-vis spectrum and complementary absorption with ITIC acceptor, there by covering almost complete solar spectrum. The HOMO/LUMO energy levels of both donor materials matched with acceptor ITIC. OBHJSC devices of ONAF:ITIC and SNAF:ITIC displayed PCEs 7.48 % and 9.94 % respectively. Compared to ONAF, SNAF showed higher PCE due to the broader absorption, improved hole mobility and high FF resulted from the efficient intermolecular packing of the active layer. The energy loss for the SNAF:ITIC based OSCs is about 0.56 eV, which is one of the lowest value for all small molecule OSCs. This efficiency is one of the best PCE for NDT-BDT based NF-ASM-OBHJSCs systems and ONAF & SNAF are a promising donor material for use in SM-OSCs. We predict that the HOMO/LUMO levels of D/A falling in this category, as in Figure S7, with further close energy levels will have implications on the efficiency of OBHJSCs.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

ORCID

Jayathirtha Rao Vaidya @ https://orcid.org/0000-0002-6173-3617

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