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# A new 2D-Naphtho[1,2-*b*:5,6-*b*']dithiophene Based Donor Small Molecules for Bulk-heterojunction Organic Solar Cells

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Research highlights:

- 1) 3 new small molecules based on new 2D-NDT donor core are explored for the bulkheterojunction organic solar cell.
- 2) Effect of intermolecular interaction in 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> was observed and affected the overall device performance.
- 3) Power conversion efficiency up to 1.22 % achieved for 2D-NDT(Ester)<sub>2</sub>.

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2	<b>Bulk-heterojunction Organic Solar Cell</b>
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Abstract: We present design and synthesis of three new symmetrical and linear A-D-A type  $\pi$ -11 conjugated donor small molecules (2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub>) 12 containing two dimensional naphthodithiophene (NDT) unit as the central donor core, end-13 capped with electron deficient unit such as thieno[3,4c]pyrrole-4,6-dione (TPD), 2-ethylhexyl 2-14 cyanoacetate (Ester) and 2-cyano-N-(2-ethylhexyl)acetamide (Amide) group respectively. We 15 16 characterized these small molecules and further investigated the optical, electrochemical, morphological and photovoltaic properties. When solution-processed bulk heterojunction 17 organic solar cells are fabricated using these small molecules, the morphology of 2D-18 19 NDT(Ester)<sub>2</sub> or 2D-NDT(Amide)<sub>2</sub> and [6,6]-PhenylC<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) blend film was optimized using 1,8 Diiodooctane (DIO) additive. DIO additive promotes the 20 formation of nanoscopically well-connected molecular domains in the active blend film. A 21 device based on (1%DIO, 1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM exhibited highest the efficiency of 22 1.22% with a short-circuit density ( $J_{sc}$ ) of 3.75 mA/cm<sup>2</sup>, an open circuit voltage ( $V_{oc}$ ) of 0.91 V 23 and fill factor (FF) of 35.50. Similarly for (1% DIO, 1:3,) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM device 24 efficiency of 0.55%, with  $J_{sc}$  of 2.36 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.64 V and FF of 36.95 was observed. 25 Whereas for (1:2) 2D-NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM device, due to the improper blending and phase 26 separation between donor and acceptor efficiency restricted to 0.33% with  $J_{sc}$  of 1.66 mA/cm<sup>2</sup>, 27  $V_{oc}$  of 0.73V and FF of 27.2. 28

29 Keywords: 2D-NDT, Small Molecules, Organic solar cell, Intermolecular interactions.

#### 1 1. Introduction

Organic solar cells (OSCs) have emerged as one of the finest ways of technology for production 2 3 of electricity through the abundant and eternal resource of sunlight to fulfill the energy demand of the growing world [1-2]. OSCs have numerous advantages such as low production cost, high 4 flexibility and light weight with ease of solution-processability [3-4]. Bulk heterojunction (BHJ) 5 OSCs, where active layer typically composed of donor materials such as D-A conjugated 6 polymers or small molecules (SM) and fullerene acceptor (PCBM) have delivered high power 7 conversion efficiencies (PCE) as a result of meticulous development in device engineering 8 (interface modification by Interfacial modifiers or by using interlayers) and molecular energy 9 levels alignments through structure modification [5-7]. Undoubtedly SM possesses advantages 10 over polymers [8], also shows potential to deliver the high PCEs than polymeric solar cells, 11 which have opened new pathways for research and development for SM OSCs. 12

Current enhancement in PCE of SM OSCs is mainly influenced by rational design and synthesis 13 of novel SM as photoactive materials. At glance, SM designs of linear analogs are generally 14 comprised of either D- $\pi$ -A- $\pi$ -D or A- $\pi$ -D- $\pi$ -A skeleton, [9-12] being as most effective molecular 15 motifs, where donor (D) and acceptor (A) are separated by  $\pi$ -conjugated spacer units. Among 16 17 these two strategies, A- $\pi$ -D- $\pi$ -A is appeared to be the effective one for obtaining the highperformance photovoltaic material. In the recent years, a new class of two-dimensional (2D) 18 photovoltaic materials are developed, where along the vertical axis of molecular framework, 19 20 thienyl conjugated side chains are introduced to broaden the spectral coverage (for high  $J_{sc}$ ), and to enhance charge transport ability (high hole mobility) for improving the device 21 22 performance[13]. Similar 2D conjugation concept is applied and explored for BDT molecular framework. For instance, an alkylthienyl-substituted benzo(1,2-b:4,5-b')dithiophene (BDT-TH) 23 donor unit has emerged as an efficient 2D conjugated donor block for small molecules. Chen et 24 al. have demonstrated the excellent utility of 2D-BDT core for DR3TBDTT-HD and 25 DR3TBDTT donor small molecules in OSCs applications [14]. Similarly Sun et al. have 26 prepared new 2D nematic liquid crystalline BTR small molecule, where higher thickness of 400 27 28 nm active layer, shows PCE around 8% with fill factor up to 70%, which is quite appreciable [15]. Furthermore, Liu. et al. showed an application of SMPV1, 2D small molecules in the single 29 junction and tandem solar cells, where PCE around 8 and 10% were recorded respectively [16]. 30

These results also assure the future mass scale production of 2D materials for commercial
 applications.

Among the rigidly fused polycyclic aromatic systems, naphthodithiophene (NDT) shows 3 desirable OSC properties, which have linear (INDT) [17] and zigzag shape isomers (zNDT) [18]. 4 zNDT unit shows unique properties, such as ideal HOMO energy level, balance charge transport 5 6 ability, and high space utilization than BDT [19]. Considering the vertical expansion of NDT 7 using alkyl thienyl moieties could expand the conjugation framework and increase the charge transport ability due to improved  $\pi$ - $\pi$  intermolecular interactions. Such example of an expansion 8 of zNDT based molecules are rarely studied and explored for SM [20]. Here in, we present a new 9 10 2D NDT donor core, coupled with strong acceptor thieno[3,4c]pyrrole-4,6-dione (TPD) to obtain new small molecule 2D-NDT(TPD)<sub>2</sub>. TPD is one the successful acceptor in polymeric solar cells 11 due to its excellent photovoltaic properties [21-23] and rarely used with 2D NDT based small 12 molecules for photovoltaic applications. 13

14 The resultant small molecule, 2D-NDT(TPD)<sub>2</sub> show limited solubility in common organic solvents. To improve the solubility we replaced the TPD acceptor group with 2-ethylhexyl 2-15 cyanoacetate (Ester) and 2-cyano-N-(2-ethylhexyl)acetamide (Amide) to obtain 2D-NDT(Ester)<sub>2</sub> 16 and 2D-NDT(Amide)<sub>2</sub> respectively. The structural variation of ester and amide acceptor end 17 group can influence the photoactive layer by the intermolecular interactions between donor and 18 19 acceptor [24]. These intermolecular interactions (hydrogen (H)-bonding,  $\pi$ - $\pi$  stacking and dipoledipole interactions) determine the molecular packing and orientation of molecules, also affect the 20 optical and electrical properties of the photoactive layer, thus relates to device performance. 21 22 Fused thiophene based D-A conjugated small molecules containing ester and amide acceptor units have recently gained considerable attention due to their efficient light harvesting, effective 23  $\pi$ - $\pi$  stacking, superior charge transfer behavior and solar cell performance. For instance, Kim et 24 al. developed donors comprised of dithioenosilole (DTS) central core and  $\pi$ -conjugated spacers 25 end-capped with different acceptors, such as 2-ethylhexyl 2-cyanoacetate and 2-cyano-N-(2-26 27 ethylhexyl)acetamide acceptor units, where the latter molecule is capable of forming strong Hbonding [25]. A similar type of small molecules with dithieno thiophene (DTT) core was 28 synthesized by Xiao et al [26]. Furthermore, Stupp et al. synthesized DPP core based symmetric 29 30 and asymmetric donor molecules end-capped with ester and amide end groups respectively [27].

So far small molecules based on 2D NDT donor coupled with ester and amide acceptor group are rarely studied and explored for OSCs applications. In order to evaluate the effect of ester and amide acceptor group on molecular interactions and photovoltaic performance in 2D NDT based small molecules, we synthesized a new 2D NDT based small molecules as 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> with ester and amide end group respectively.

In this contribution, we explored the use of new 2D NDT donor moiety to construct 2D small 6 7 molecules. Combining 2D NDT with TPD, ester and amide acceptor obtained new 2D small molecules as 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> respectively (Fig.1). 8 These small molecules were used to fabricate BHJ OSC devices, (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM 9 10 blend device were prepared using a 1,8-diiodooctane (DIO) additive, which proved to be effective and exhibited a PCE of 1.22%. Whereas for (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM blend 11 device with DIO additive PCE of 0.55% and for (1:2) 2D-NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM device, PCE of 12 0.33% was observed. Design, synthesis and photovoltaic properties of these three new small 13 molecules are studied and presented. 14



Fig. 1. Chemical structures of 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub>.

#### 1 2. Results and discussion

#### 2 2.1. Materials preparation and thermal properties

3 The synthesis of small molecules is shown in Scheme 1. 2-(2-Ethylhexyl)thiophene (1) was obtain by alkylating thiophene with 3-(bromomethyl)heptane, using n-butyl lithium, which was 4 further converted to (5-(2-Ethylhexyl)thiophen-2-yl) trimethylstannane derivative (2) and reacted 5 with 3-bromothiophene to obtain 5-(2-Ethylhexyl)-2,3'-bithiophene (3) in toluene by  $Pd(PPh_3)_4$ 6 7 catalyzed reaction. Compound 3 was selectively brominated using N- bromosuccinimide (NBS) to obtain bromine functionalized derivative 2'-Bromo-5-(2-ethylhexyl)-2,3'-bithiophene (4). 8 Compound 4 was reacted with compound 9 under Pd<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> catalyzed reaction in 9 chlorobenzene (CB) to obtain compound 10 which was further converted to stille derivative, 10 compound 11. The target compound 2D-NDT(TPD)<sub>2</sub> was synthesized via stille cross-coupling 11 reaction of compound 11 and compound 13 using Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tolyl)<sub>3</sub> as a catalyst. Further 12 compound 11 was treated with 5-bromothiophene-2-carbaldehyde under Pd(PPh<sub>3</sub>)<sub>4</sub> catalyzed 13 reaction in toluene to obtain compound 12, Then by Knoevenagel condensation, intermediate 12 14 was reacted with 2-ethylhexyl 2-cynoacetate acceptor in presence of catalytic triethyl amine in 15 chloroform to obtain 2D-NDT(Ester)<sub>2</sub>, whereas for acceptor 2-cyno-N-(2-16 dry ethylhexyl)acetamide strong base such as piperidine in catalytic amount under similar condition 17 was required to produce 2D-NDT(Amide)<sub>2</sub>. The molecular structures of small molecules were 18 confirmed by <sup>1</sup>H and <sup>13</sup>C NMR (Fig. S2-S9). The thermal properties of 2D-NDT(TPD)<sub>2</sub>, 2D-19 NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> were investigated by thermogravimetric analysis (TGA) and 20 differential scanning calorimetry (DSC) Fig. S1. The TGA curve reveals good thermal stability 21 22 with onset decomposition temperature, 5% weight loss (T<sub>d</sub>) occurring at 295 °C for 2D-NDT(TPD)<sub>2</sub>, whereas 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> shows decomposition temperature 23 at 331 °C and 350 °C respectively under a nitrogen atmosphere. DSC was performed at the ramp 24 rate of 10 °C/min, the melting endotherm for 2D-NDT(TPD)<sub>2</sub> occurs at 128.17 °C, and upon 25 cooling it exhibit crystallization exotherm at 76.71 °C, whereas for 2D-NDT(Ester)<sub>2</sub> shows 26 exothermic peak at 196 °C and sharp endothermic peak at 103 °C respectively, which indicates 27 the tendency to crystallize for 2D-NDT(TPD)<sub>2</sub> and 2D-NDT(Ester)<sub>2</sub>. 2D-NDT(TPD)<sub>2</sub> shows 28 lower exothermic and endothermic processes temperature, which could be assign to different 29 30 packing mode for this molecule. For 2D-NDT(Amide)<sub>2</sub> no prominent peaks were observed,

1 during heating and cooling cycle, which could be ascribed to the amorphous nature of 2D-2 NDT(Amide)<sub>2</sub>. The DSC results indicate, 2D-NDT(TPD)<sub>2</sub> and 2D-NDT(Ester)<sub>2</sub> molecules 3 shows higher crystalline nature as a result of closer intermolecular  $\pi$ - $\pi$  interaction. Varied 4 packing modes provide reasonable explanation for different DSC behavior for these small 5 molecules.





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#### 1 2.2. Optical and electrochemical properties

The absorption spectra of 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> in chloroform 2 and thin solid film are shown in Fig. 2a and b. and data is summarized in Table 1. In dilute 3 solution (10<sup>-5</sup> mol L<sup>-1</sup>) 2D-NDT(TPD)<sub>2</sub> shows absorption profile from 350–500 nm, with a 4 maximum absorption peak ( $\lambda_{max}$ ) at 443 nm ( $\epsilon = 108600 \text{ L M}^{-1}\text{cm}^{-1}$ ) whereas ester and amide 5 compounds shows broad absorptions range between 350-580 nm due to intramolecular charge 6 7 transfer (ICT) from donor NDT to acceptor either ester or amide. A closer observation of spectra showed vibronic shoulder around 360-380 nm. 2D-NDT(Ester)<sub>2</sub> shows maximum absorption at 8 478 nm ( $\epsilon = 236000 \text{ M}^{-1} \text{ cm}^{-1}$ ), while changing from ester to amide in 2D-NDT(Amide)<sub>2</sub> shows 9 maxima at 461 nm (105000 M<sup>-1</sup> cm<sup>-1</sup>). This hypochromic shift (~17nm) in the absorption 10 maxima could be the result of weak electron accepting tendency of amide than ester group. In 11 thin film state, 2D-NDT(TPD)<sub>2</sub> shows absorption peak at 480 nm with shoulder peak at 512 nm. 12 The red shift of 37 nm from solution to a thin film and prominent vibronic peak, indicate strong 13 14 intermolecular  $\pi$ - $\pi$  stacking of molecules in the thin film state. Effect of intermolecular interaction due to oxygen and nitrogen can be seen in thin film state spectra for ester and amide 15 compound. As both molecules have a different degree of intermolecular interaction, the 16 molecular ordering and stacking order is significantly altered. The maximum absorption of 2D-17 NDT(Ester)<sub>2</sub> was 519 nm which red-shifted by 41 nm, along with the intense vibronic peak in 18 lower energy region, could be the result of planner framework and enhanced intermolecular  $\pi$ - $\pi$ 19 stacking [28-29]. For 2D-NDT(Amide)<sub>2</sub> broad absorption (Peak maxima at 479) without any 20 significant vibronic peak was observed with red shift of a 18 nm. Probably 2-ethylhexyl side 21 chain disturbs the molecular planarity and thus,  $\pi$ - $\pi$  overlapping [30-31], which is strongly 22 influenced by hydrogen bonding in case of amide [25]. The optical band gaps were found to be 23 2.1, 1.9 and 2 for 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> respectively. To 24 estimate the molecular energy levels of 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> 25 cyclic voltammetry (CV) measurements were carried out using Ag/AgCl reference electrode in a 26 0.1 M solutions of Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile solution at room temperature under argon with scan 27 rate of 50 mV<sup>-1</sup> Fig. 2c. The CV instrument was calibrated using the ferrocene/ferrocenium 28  $(Fc/Fc^{+})$  redox couple as an external standard. The onset potential of the Fc/Fc<sup>+</sup> redox couple was 29 found to be 0.4 V relative to the Ag/AgCl reference electrode. HOMO/LUMO were calculated 30 from the onset oxidation and reduction potential according to the equations HOMO =  $-e(E_{ox}^{ox})$ 31

+ 4.4) and LUMO = -e(E<sup>red</sup><sub>onset</sub> + 4.4). From onset potential value, the HOMO energy level was
found to be -5.36, -5.46 and -5.4 eV, whereas LUMO was found to be -3.58, -3.61 and -3.57 eV
for 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> respectively. Optical band gap of
2.1, 1.9 and 2 eV was observed respectively.



Fig.2. (a) UV-vis absorption spectra of 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> in chloroform solution. (b) UV-vis absorption spectra of 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> in thin film state. (c) Cyclic voltammograms of UV-vis absorption spectra of 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> in chloroform. (d) Energy levels of small molecules with PC<sub>71</sub>BM.

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**Table 1**. Photophysical and electrochemical data for small molecules.

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Molecule	<sup>a</sup> λ <sub>max</sub> Sol (nm)	$\epsilon (\times 10^5  \text{M}^{-1}  \text{cm}^{-1})$	<sup>b</sup> λ <sub>max</sub> Film(nm)	$^{c} \lambda_{onset}$ (nm)	Eg <sup>(Opt)</sup> (eV)	E <sup>ox</sup> onset /HOMO (eV)	E <sup>red</sup> onset /LUMO (eV)	hole mobility (µ <sub>e</sub> )	electron mobility (µ <sub>e</sub> )
2D-NDT(TPD) <sub>2</sub>	443	1.08	480	570	2.1	0.86/-5.26	-0.82/-3.58	6.62×10 <sup>-9</sup>	5.07×10 <sup>-6</sup>
2D-NDT(Ester) <sub>2</sub>	478	2.36	519	624	1.9	1.06/-5.46	-0.79/-3.61	2.91×10 <sup>-6</sup>	8.08×10 <sup>-6</sup>
2D-NDT(Amide) <sub>2</sub>	461	1.05	479	609	2	1.0/-5.4	-0.83/-3.57	5.20×10 <sup>-8</sup>	7.04×10 <sup>-6</sup>

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4 <sup>a</sup> Measured in chloroform solution. <sup>b</sup> Spin-coated film from chloroform solution. <sup>c</sup> Optical band

5 gap,  $E_g^{opt} = 1240/(\lambda_{onset})$  film. <sup>d</sup> Potential determined by cyclic voltammetry in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>-

6 CH<sub>3</sub>CN. HOMO =-e( $E^{ox}_{onset}$ +4.4). LUMO = -e( $E^{ox}_{onset}$ +4.4). <sup>f</sup> hole mobilities ( $\mu_h$ ) and electron

7 mobility ( $\mu_e$ ) measured by SCLC technique.

#### 8 2.3. Photovoltaic properties

To check the utility of 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> in OSCs, 9 photovoltaic devices were fabricated using small molecules as donors and PC71BM as an 10 acceptor in chlorobenzene or chloroform solution using conventional device architecture of 11 ITO/PEDOT/small molecules:PC71BM/LiF/Al. Different weight ratios (D:A) of systems were 12 tested under a simulated AM 1.5 G illumination of 100 mW cm<sup>-2</sup>, to find the optimal device ratio 13 combination. The detailed Photovoltaic performance of small molecules is summarized in Table 14 2 and corresponding (J-V) curves are shown in Fig. 3a. For (1:1) 2D-NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM active 15 layer blend ratio PCE of 0.29 % with  $J_{sc}$  of 1.58 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.71 and FF of 25.61 was 16 observed. Further increasing the blend ratio to (1:2) delivered the highest PCE of 0.33% with 17 improved  $J_{sc}$  of 1.66 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.73 and FF of 27.20. This PCE enhancement is attributed 18 to the improved device parameters (Voc, Jsc and FF). Increasing the PCBM content to (1:3) and 19 (1:4) affected the  $\,J_{sc}\,$  and FF,  $\,J_{sc}$  dropped from 1.54 to 1.38 mA/cm^2 along with reduced FF of 20 27.01 and 26.02, thus PCE reduced to 0.3% & 0.26%; whereas Voc was nearly similar. For 2D-21 NDT(Ester)<sub>2</sub>, using (1:1) blend ratio gave highest PCE of 0.84% with J<sub>sc</sub> of 2.78 mA/cm<sup>2</sup>, V<sub>oc</sub> of 22 0.98 and FF of 30.72. Further increasing the blend ratio to (1:2), PCE changes to 0.64 %, with 23

 $V_{oc}$  of 0.98, FF of 31.69, and reduced  $J_{sc}$  of 2.05 mA/cm<sup>2</sup> was observed. Increasing the blend 1 ratio to (1:3) and (1:4), PCE dropped to 0.51 and 0.39% respectively with concomitant decrease 2 in J<sub>sc</sub> and V<sub>oc</sub>; whereas FF was nearly similar, which could be the result of high PCBM content. 3 Reduced PCE for these devices were attributed to the lower J<sub>sc</sub> values obtain for these devices. 4 Additive treatment was given to (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM to improve the efficiency. Using 5 0.5% DIO, PCE reaches to 0.97% with improved  $J_{sc}$  of 3.29 mA/cm<sup>2</sup> and FF of 31.22, with 6 reduced  $V_{oc}$  of 0.95V. Increasing to 1% DIO,  $J_{sc}$  and FF were elevated to 3.75 mA/cm<sup>2</sup> and 7 35.50, PCE reaches to a maximum of 1.22% with  $V_{oc}$  of 0.91. Further increasing DIO to 1.5 and 8 9 2%; J<sub>sc</sub> and FF were dropped with similar V<sub>oc</sub>, PCE changes to 1.07 and 0.81% respectively. For 2D-NDT(Amide)<sub>2</sub> system, (1:1) and (1:2) blend ratio system, shows average PCE of 0.25 and 10 0.30%. Further increasing the blend ratio to (1:3) highest PCE of 0.35 % with  $J_{sc}$  of 1.81 11 mA/cm<sup>2</sup>, V<sub>oc</sub> 0.64 and FF of 30.79 was obtained. For (1:4) blend ratio, PCE dropped to 0.33 % 12 as a result of reduced  $J_{sc}$  of 1.66 mA/cm<sup>2</sup> and  $V_{oc}$  0.62, whereas FF of 32.62 was observed. In 13 order to further improvise the device performance, DIO was used for optimized blend ratio of 14 (1:3). For 0.5 % DIO, (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM system, PCE was reached to 0.41%, 15 with improved J<sub>sc</sub> and FF. For 1% DIO, device parameters were improved and PCE elevated to 16 0.55% with higher  $J_{sc}$  of 2.36 mA/cm<sup>2</sup> and FF of 36.95, whereas  $V_{oc}$  remain unchanged to 0.64V. 17 Further increasing DIO to 2%, all the device parameters were reduced and PCE was dropped to 18 19 0.33%.

External quantum efficiency (EQE) Fig. 3b was measured for best devices, the observed 20 wavelength range for the EQE spectra of the devices were consistent with UV data (from 300-21 600 nm). For (1:2) 2D-NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM device shows a maximum value of 14% at 360 nm. 22 Whereas (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM device, shows EQE almost at every wavelength with 23 highest 23% at 380 nm. 1% DIO (1:1) 2D-NDT(Ester)<sub>2</sub>:PC71BM device system, shows improved 24 EQE of over 27% at 380 nm. For (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM device, 17% EQE at 380 nm 25 26 was observed which was improved to 21% at 380 nm, after addition of 1% DIO . Observed EQE explains the improved  $J_{sc}$  for additive processed devices. 27

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 Table 2. Photovoltaic performances of small molecules based solar cells.

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Active layer	$J_{sc}$ (mA/cm <sup>2</sup> )	Voc (V)	FF (%)	PCE (%)
(1:1) 2D-NDT(TPD) <sub>2</sub> :PC <sub>71</sub> BM_CB	1.58	0.71	25.61	0.29
(1:2) 2D-NDT(TPD) <sub>2</sub> :PC <sub>71</sub> BM_CB	1.66	0.73	27.20	0.33
(1:3) 2D-NDT(TPD) <sub>2</sub> :PC <sub>71</sub> BM_CB	1.54	0.73	27.01	0.30
(1:4) 2D-NDT(TPD) <sub>2</sub> :PC <sub>71</sub> BM_CB	1.38	0.72	26.02	0.26
(1:1) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM_CF	2.78	0.98	30.72	0.84
(1:2) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM_CF	2.05	0.98	31.69	0.64
(1:3) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM_CF	1.76	0.93	31.24	0.51
(1:4) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM_CF	1.55	0.80	31.30	0.39
0.5% DIO, (1:1) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM	3.29	0.95	31.22	0.97
1.0% DIO, (1:1) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM	3.75	0.91	35.50	1.22
1.5% DIO, (1:1) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM	3.63	0.92	32.01	1.07
2.0% DIO, (1:1) 2D-NDT(Ester) <sub>2</sub> :PC <sub>71</sub> BM	2.79	0.92	29.61	0.8
(1:1) 2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM _CF	1.49	0.63	26.84	0.25
(1:2) 2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM _CF	1.67	0.61	29.89	0.30
(1:3) 2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM _CF	1.81	0.64	30.79	0.35
(1:4) 2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM _CF	1.66	0.62	32.62	0.33
0.5% DIO,(1:3)2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM	1.83	0.64	35.04	0.4
1.0% DIO, (1:3) 2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM	2.36	0.64	36.95	0.55
1.5% DIO, (1:3) 2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM	2.13	0.65	35.90	0.50
2.0% DIO, (1:3) 2D-NDT(Amide) <sub>2</sub> :PC <sub>71</sub> BM	1.67	0.62	32.38	0.33

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To gain molecular ordering of the small molecules in a solid state, thin film-X-ray diffraction 1 (XRD) analysis on Si-wafer were performed and shown in Fig. 4. The pristine film display low 2 angle diffraction peak at  $2\theta = 4.58$  arising from the (100) plane, corresponding to the *d*-spacing 3 of 19.27 Å. The much stronger peak intensity of 2D-NDT(TPD)<sub>2</sub> indicate high crystallinity and 4 ordered molecular arrangement. The high crystallinity could be beneficial for carrier mobility, 5 which would lead to higher J<sub>sc</sub> and FF as consequence of effective transport and collection of 6 charge carrier in OSC devices. 2D-NDT(Ester)<sub>2</sub> pristine film shows low diffraction angled sharp 7 peak at  $2\theta = 5.18^{\circ}$  arising from the (100) plane, corresponding to the *d*-spacing of 17.05 Å, 8 whereas 2D-NDT(Amide)<sub>2</sub> show the broad peak with low intensity at  $2\theta = 4.066^{\circ}$  for the d-9 spacing of 21.070 Å. The stronger intensity and sharp peak of ester suggest high crystallinity 10 with ordered molecular domain compared to amorphous amine molecule. Peaks at the lower 11 12 angle are generally attributed to the main planes of small molecules segregated by alkyl chains. The *d* spacing calculated by Bragg equation for 2D-NDT(Ester)<sub>2</sub> (17.05 Å) is smaller than 2D-13 NDT(TPD)<sub>2</sub> (19.27 Å) 2D-NDT(Amine)<sub>2</sub> (21.070 Å), which indicate effective interdigitated 14 packing in ester, than amine and 2D-NDT(TPD)<sub>2</sub> molecules. 15



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#### 1 2.4. Morphology

To gain inside into photovoltaic performance details, atomic force microscopy (AFM) of the 2 3 optimized active layer was measured as shown in Fig. 5. For (1:2) 2D-NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM blend systems, small aggregates of PCBM domains can be seen with root mean square (RMS) 4 roughness values of 0.68. Higher crystallinity of 2D-NDT(TPD)<sub>2</sub> resulted in improper miscibility 5 of donor-acceptor at the nanoscale, which might have affected the PCE for 2D-NDT(TPD)<sub>2</sub> 6 device. For (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM device, good interpenetrating morphology with rms 7 of 2.71 nm was observed. Small domains size of around 10-20 nm were seen, generally required 8 9 for effective charge generation and transfer to respective electrodes [32]. It also explains the higher Jsc and Voc obtained for this device. Whereas in 1% DIO (1:1) 2D-NDT(Ester)2:PC71BM 10 device optimal rms of 0.98 nm, with nanoscale morphology and phase separation, which is 11 comparable to exciton diffusion length is observed. The increased roughness of the surface is an 12 indication of self-organization of small molecule and PCBM domains in the blend, promoted by 13 14 addition of DIO, which in turn enhances the ordered structure orientations in active layer film 15 state, essential for promoting exciton dissociation and charge separation towards respective electrodes. This nano-optimized, desired morphology improved J<sub>sc</sub> and FF of this device and 16 17 resulted in highest efficiency. For (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM device, higher rms of 3.47 nm and larger phase domains likely a result of the strong aggregation due to the intermolecular 18 hydrogen bonding of amide molecule was observed. Large aggregated domains of PCBM restrict 19 the charge generation and percolation towards the respective electrodes which restrict the J<sub>sc</sub> and 20 FF, thus lower PCE for these devices. In 1% DIO (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM device, after 21 22 addition of DIO, significantly reduced domain size and lower rms of 0.38 nm was observed; highly homogeneous system with optimized (D-A) interpenetrating network might have formed 23 for this system, which ensured the efficient percolation channels for charge transport. Thus 24 25 improved J<sub>sc</sub> was observed for this device.

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#### 1 2.5. Charge mobility

To evaluate the influence of charge carrier mobility on photovoltaic performance, hole and 2 3 electron mobility of (1:2) 2D-NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM, 1% DIO (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM and 1% DIO (1:3) 2D-NDT(Amide)<sub>2</sub>:PC71BM device, were measured by space-charge limited 4 current (SCLC) method, using the device architecture ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Ag 5 for holes and ITO/ZnO/active layer/LiF/Al for electrons, respectively. J-V Characteristics of 6 hole-only and electron only devices are shown in Fig. S10 and results are summarized in table 1. 7 (1:2) 2D-NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM device exhibits low hole mobility ( $\mu_h$ ) of  $6.62 \times 10^{-9}$  cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> 8 and electron mobility ( $\mu_e$ ) of 5.07 × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup>, with unbalanced electron to hole ratio ( $\mu_e/\mu_h$ 9 = 765.86), which explain the lower efficiency of this device. Higher ( $\mu_{\rm h}$ ) of 2.91 × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> 10  $S^{-1}$  and ( $\mu_e$ ) of 8.08 × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> was observed for 1% DIO (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM 11 device. The higher electron mobility could be attributed to the better planarity and improved 12 molecular packing of 2D-NDT(Ester)<sub>2</sub> molecule in the photoactive layer [33-34] Well-balanced 13 electron to hole ratio ( $\mu_e/\mu_h = 2.78$ ), an important pre-requisite for achieving high efficiency, 14 which also explains improved J<sub>sc</sub> and FF for this device [35] These mobility values are in 15 16 agreement with UV and XRD result. The UV absorption and XRD indicate 2D-NDT(Ester)<sub>2</sub> molecule shows stronger  $\pi$ - $\pi$  molecular stacking in the solid state. Closed molecular packing 17 favors better charge transport properties along with favorable film morphology, [26] explains the 18 higher performance for 2D-NDT(Ester)<sub>2</sub> device. For 1% DIO (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM 19 device, lower ( $\mu_{\rm h}$ ) of 5.20 × 10<sup>-8</sup> cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> and ( $\mu_{\rm e}$ ) of 7.04 × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> with unbalanced 20 ratio ( $\mu_e/\mu_h = 135.38$ ) was observed, than 2D-NDT(Ester)<sub>2</sub> molecule based device. The lower 21 charge carrier mobility for 2D-NDT(Amide)<sub>2</sub> molecule can be attributed to disturbed  $\pi$ - $\pi$ 22 stacking and random molecular ordering induced by strong intermolecular hydrogen bonding 23 24 between the amide molecules [25].

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#### 1 **3.** Conclusion

2 We developed, new 2D NDT donor based small molecules, 2D-NDT(TPD)<sub>2</sub>, 2D-NDT(Ester)<sub>2</sub> 3 and 2D-NDT(Amide)<sub>2</sub> comprise of A-D-A main framework, with 2D-NDT core end capped with TPD, ester and amide acceptor units. The molecules show good thermal stability, spectral 4 coverage, and sufficiently higher HOMO energy levels. For OSCs based on (1:2) 2D-5 NDT(TPD)<sub>2</sub>:PC<sub>71</sub>BM device, an improper blending of donor and acceptor component, has 6 limited the J<sub>sc</sub> and FF, also low and unbalanced charge mobility has restricted PCE to 0.33 %. In 7 case of ester molecules, 2D-NDT(Ester)<sub>2</sub> controlled molecular interaction, that maintain high 8 crystallinity, effective  $\pi$ - $\pi$  stacking along with the intermolecular compatibility with PCBM in 9 active blend were observed. For (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM device, PCE of 0.84% was 10 observed. Further treating with 1% DIO of (1:1) 2D-NDT(Ester)<sub>2</sub>:PC<sub>71</sub>BM device, highest PCE 11 of 1.22% was achieved, as a consequence of phase separated morphology and balanced charge 12 mobility. Whereas, in 2D-NDT(Amide)<sub>2</sub>, hydrogen bonding dominated the other intermolecular 13 interaction, also cause aggregations which give rise to unfavorable morphology, limits the charge 14 generation and charge transfer in active layer. For (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM device, PCE 15 16 of 0.35% was observed, further with 1% DIO (1:3) 2D-NDT(Amide)<sub>2</sub>:PC<sub>71</sub>BM devices PCE reached to 0.55%. This preliminary work demonstrates that this kind of two-dimensional small 17 molecules offers a good strategy to design new photovoltaic small molecule based donor 18 19 materials, further optimization of the morphology on an active layer would greatly improve the performance of the devices. 20

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#### 1 **4.** Experimental

#### 2 4.1 Materials and general methods

All the moisture sensitive reactions are carried in a dry vessel under nitrogen (N<sub>2</sub>) atmosphere, 3 unless stated otherwise, starting materials were obtained from Aldrich, across and used without 4 further purification. Anhydrous THF, toluene and chloroform were distilled over 5 Na/benzophenone prior to use. Chemical shifts were reported as  $\delta$  values (ppm) relative to the 6 7 internal standard tetramethylsilane (TMS). The UV-vis absorption spectra of films or solutions were obtained using a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra 8 9 of films were obtained using an FP-6500 (JASCO). Thermogravimetric analysis (TGA) was carried out with a TA Instrument Q-50 at a scanning rate of 10 <sup>0</sup>C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. 10 Differential scanning calorimetry (DSC) experiments were performed on a TA Instrument (DSC 11 2910) at a heating rate of 100  $^{0}$ C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. Cyclic voltammetry (CV) 12 measurements were made using a VersaSTAT3 (METEK) Electrochemical Analyzer under 13 argon at a scan rate of 50 mV s<sup>-1</sup> at room temperature, where a Pt wire and Ag/AgCl were used 14 as counter and reference electrodes, respectively. The reference electrode was calibrated with the 15 ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.4 eV below the vacuum level) as an external 16 17 standard. The samples were prepared in chloroform solution with 0.10 M tetrabutylammonium hexafluorophosphate  $(n-Bu_4NPF_6)$  as the electrolyte. The surface morphology was measured 18 using a Digital Instruments Multimode atomic force microscope (AFM) controlled by a 19 Nanoscope IIIa scanning probe microscope 20 controller. 20

# 21 **2-(2-Ethylhexyl)thiophene (1)**

22 Under the protection of N<sub>2</sub>, n-butyllithium (2.53 mL, 2.5 M), was added dropwise to the solution of the dry THF solution (20 mL) containing thiophene (1 gm, 11.8 mmol) at 0°C. After stirring it 23 for 30 mins, 3-(bromomethyl)heptane (2.53 mL, 14.2 mmol) was added and warm to room 24 temperature for overnight. The reaction was poured into water and extracted with 25 dichloromethane. The extracted organic phase was wash with brine, dried over MgSO<sub>4</sub> and 26 concentrated to get crude product as brown liquid, which was further vacuum distillate to obtain 27 pure compound 1 as colorless oil (0.750gm, 32%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.13 (d, 1H), 28 6.93 (d, 1H), 6.77 (d, 1H), 2.78 (d, 2H), 1.3 (m, 9H), 0.89 (t, 6H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 29

144.37, 126.52, 124.93, 122.89, 41.46, 33.82, 32.33, 28.84, 28.81, 25.48, 25.15, 22.98, 14.11,
 10.80.

#### 3 (5-(2-Ethylhexyl)thiophen-2-yl)trimethylstannane (2)

In a dried, 2-neck round bottom (100 mL) under the protection of N<sub>2</sub>, n-butyllithium (1.22 mL, 4 2.5M) was added dropwise to the dry THF (20 mL) solution of compound 1 (0.5 gm, 2.54 mmol) 5 at -78 °C for 0.5 hr. Then SnBu<sub>3</sub>Cl (3.31 ml, 3.3 mmol) was added to the reaction mixture at -78 6 °C . The reaction mixture was further stirred at -78 °C for 1 hr and then warm to room 7 temperature for overnight. Reaction was poured into water and extracted with dichloromethane. 8 9 Organic phase was wash with brine, dried over MgSO<sub>4</sub> and concentrated to obtain brown crude liquid (0.68 gm, 75 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.97 (d, 1H), 6.83 (d, 1H), 2.76 (d, 2H), 10 1.31-1.24 (m, 9H), 0.84 (t, 6H), 0.34 (s, 9H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 150.31, 134.87, 126.52, 11 124.92, 41.46, 32.89, 29.97, 28.88, 26.96, 23.82, 14.16, 10.80, -8.25. 12

## 13 **5-(2-Ethylhexyl)-2,3'-bithiophene (3)**

A mixture of compound 2 (0.5 gm, 1.39 mmol), 3-bromothiophene (0.2 gm, 1.25 mmol), 14 Pd(PPh<sub>3</sub>)<sub>4</sub> (0.08 mg, 5 mol%) were added to a 50 mL flame-dried two-neck flask and subjected 15 to three vacuum/argon fill cycles. N2 degassed dry Toulene (10 mL) was added and the mixture 16 was stirred for 15 min flushing N<sub>2</sub>. The reaction mixture was heated to reflux for 24 h. After 17 completion of the reaction, Toulene was removed under reduced pressure and the crude product 18 was purified by column using a hexane as an eluent afforded compound 3 as colorless liquid 19 (0.24 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.33 (m, 3H), 7.02 (d, 1H), 6.69 (s, 1H), 2.75(d, 20 2H), 1.31 (m, 9H), 0.9 (t,6H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 144.24, 136.74, 134.73, 128.75, 126.51, 21 22 125.61, 122.88, 122.40, 41.44, 34.17, 32.34, 28.86, 25.48, 22.99, 14.13, 10.82.

#### 23 2'-Bromo-5-(2-ethylhexyl)-2,3'-bithiophene (4)

Compound 3 (0.093 gm, 0.33 mmol) was dissolved in 10 mL of Chloroform: Acetic acid. NBS (0.059 gm, 0.33 mmol) was added in portion and reaction was allow to stir in dark at room temperature for overnight. The resultant brown solution was then diluted with 30 mL of water and extracted with dichloromethane. Organic phase was washed with brine solution and dried over anhydrous MgSO<sub>4</sub>, evaporated to obtain brown crude. Purification by column chromatography using silica gel with hexane as an eluent gave (0.065 gm, 55%) compound 4 as yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.22 (d, 1H), 7.17 (d, 2H), 6.66 (d, 1H), 2.69 (d,

2H), 1.32 (m, 1H), 1.27 (m, 8H), 0.84 (t, 3H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 145.44, 139, 129.67,
 128.46, 128.21, 127.82, 126.28, 112.53, 108.09, 41.40, 34.15, 32.38, 28.86, 25.61, 22.98, 14.09,
 10.82.

#### 4 2,7-bis(5-(2-ethylhexyl)-2,3'-bithiophene-2-yl)naphtho[1,2-b:5,6 b']dithiophene (10)

In a 100 mL two neck flask, Compound 9 (0.330 gm, 0.58 mmol), compound 4 (0.460 gm, 1.2 5 6 mmol, 2.2 eq) and dichlorobis-(triphenylphosphine)palladium(II) (0.020 gm, 0.029 mol) were 7 added and subjected to three vaccum/nitrogen fill cycles. Nitrogen degassed chlorobenzene (15 mL) were added and content were stirred for 15 min under nitrogen. The reaction mixture was 8 9 heated to reflux for 24 h. Further reaction was guenched with 30 mL of water and compound was extracted with dichloromethane. Organic layer was washed with brine, dried over MgSO4 and 10 concentrated under reduced pressure. The resulting brown crude was purified by column 11 chromatography eluting with hexane to afford compound to afford compound 10 as yellow solid 12 (0.310 gm, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.73 (dd, 2H), 7.75 (dd, 2H), 7.43 (d, 2H), 7.35 13 (d, 2H), 7.14 (d, 2H), 6.79 (s, 2H), 2.76 (t, 4H), 1.6 (m, 2H), 1.26 (m, 16H), 0.86 (t, 12H). <sup>13</sup>C 14 (100 MHz, CDCl<sub>3</sub>): δ 145.95, 138.74, 136.90, 135.64, 134.69, 130.94, 129.20, 128.17, 125.40, 15 123.95, 123.34, 120.95, 110.57, 40.79, 33.83, 31.92, 28.39, 25.03, 22.56, 13.71, 10.44. 16

# 17 2,7-bis(5-(2-ethylhexyl)-2,3'-bithiophene-2-yl)naphtho[1,2-b:5,6 b']dithiophene distanane 18 (11)

To solution of compound 10 (0.319 gm, 0.40 mmol) in THF (10 mL) at -78 °C, 2.5 M n-19 butyllithium in hexane (0.386 mL, 2.4 equ) was added dropwise under N<sub>2</sub> atmosphere. After 30 20 min, trimethyl tin chloride (0.965 mL, 2.4 equ) was added in one portion and stirred for 30 mins 21 22 at -78 °C. The reaction mixture was warmed to room temperature and stirred for overnight. The reaction was quenched with 20 mL of water and the compound was extracted with 23 Dichloromethane. The organic layer was washed with 10 mL brine and dried with anhydrous 24 MgSO<sub>4</sub>. Organic layer was concentrated under reduces pressure to obtain brown liquid, which 25 was used directly for next step 0.41 g (91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (d, 2H), 7.68 26 (d, 2H), 7.37 (s, 2H), 7.17 (d, 2H), 6.86 (s, 2H), 6.60 (s, 2H), 2.66 (d, 4H), 1.45 (m, 2H), 1.18 27 (m, 16H), 0.80 (t, 12H), 0.35 (s, 18H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 145.04, 138.37,137.11, 135.27, 28 134.76, 134.33, 126.63, 126.52, 125.66, 125.37, 125.22, 124.46, 122.51, 122.42, 121.20, 41.35, 29 34.12, 32.34, 28.81, 25.52, 22.98, 14.11, 10.85, -8.18. 30

#### 1 **2D-NDT(TPD)**<sub>2</sub>

In 100 mL flame dried flask, compound 11 (0.165 gm, 0.147mmol), compound 13 (0.121 gm, 2 0.353 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (7 mg, 5 mol %) and P(o-Tolyl)3 (5 mg, 10 mol %) were added and 3 subjected to three vacuum / N2 fill cycles. Previously N2 degassed chlorobenzene (10 mL) was 4 added and heated to reflux for 24 hr and was monitored by TLC. After completion of reaction, it 5 was quenched with water and organic layer was extracted with chloroform. Organic layer was 6 concentrated under reduced pressure. The resulting dark brown crude was purified by column 7 chromatography using (4:1) CF: hexane to obtain dark red solid compound. (80 mg, 42%). <sup>1</sup>H 8 9 NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (s, 2H), 7.74 (dd, 2H), 7.69 (dd, 2H), 7.56 (d, 2H), 7.48 (d, 2H), 6.95 (s, 2H), 6.67(s, 2H), 3.49 (d, 4H), 2.70 (d, 4H), 1.78 (m, 2H), 1.3-1.22 (m, 34H), 0.84 (t, 10 24H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 163.04, 162.57, 146.17, 138.86, 137.47, 137.23, 134.77, 133.99, 11 133.20, 132.43, 131.18, 127.70, 125.77, 125.57, 125.53, 122.58, 121.43, 42.58, 41.36, 38.18, 12 34.14, 32.34, 30.54, 28.80, 28.53, 25.51, 23.86, 23.04, 23.01, 14.12, 14.04, 10.86, 10.43. 13

#### 14 **2D-NDT-CHO** (12)

A solution of compound 11 (0.37 gm, 0.33 mmol) and 5-bromothiophene-2-carbaldehyde (0.176 15 gm, 0.92 mmol), PdPPh<sub>3</sub>)<sub>4</sub> (0.05 equiv) in dry toluene was refluxed and stirred for overnight. The 16 reaction mixture was cool to R.T. and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with 17 water and brine; dried over MgSO<sub>4</sub>; and concentrated in vacuum. The crude compound was 18 purified by flash column chromatography using the mixture of hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:1.5) as the 19 eluent to afford the corresponding product as a dark red solid (0.16 gm, 48% yield). <sup>1</sup>H (400 20 MHz, CDCl<sub>3</sub>): δ 8.9 (s, 2H), 7.78-7.74 (m, 2H), 7.72-7.67 (m, 3H), 7.43 (s, 2H), 7.31 (s, 2H), 21 22 7.21-7.18 (m, 3H), 6.92-6.91 (d, 2H), 6.66-6.65 (d, 2H), 2.28 (d, 4H), 1.4-1.1 (m, 18H), 0.89 (t, 12H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 182.42, 146.09, 146.01, 142.17, 139.30, 137.25, 137.19, 134.53, 23 134.06, 133.32, 133.04, 129.11, 128.12, 127.46, 125.74, 125.55, 125.32, 124.55, 122.58, 121.43, 24 41.36, 34.09, 32.33, 28.79, 25.51, 22.99, 14.11, 10.86. 25

## 26 **2D-NDT**(Ester)<sub>2</sub>

A solution of compound (12) (0.08 g, 1 equiv.) and 2-ethylhexyl 2-cyanoacetate (0.155 gm, 10 equiv.) in dry  $CHCl_3$  was refluxed overnight with catalytic amounts of triethylamine. The reaction mixture was cool to R.T. diluted with  $CH_2Cl_2$ . The organic layer was washed with water and brine; dried over MgSO<sub>4</sub>; and concentrated in vacuum. The crude compound was purified by

- 1 flash column chromatography using chloroform as the eluent to afford the corresponding product
- 2 as a dark red solid (0.075 gm, 69% yield). <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.1 (s, 2H), 7.76-7.61 (m,
- 3 6H), 7.45 (s, 2H), 7.36 (m, 2H), 7.22-7.21 (d, 2H), 6.93-6.92 (d, 2H), 6.67 (d, 2H), 4.06 (d, 4H),
- 4 2.7 (d, 4H), 1.6 (m, 4H), 1.25 (m, 32H), 0.89-0.79 (t, 24H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ 163.02,
- 5 146.22, 146.17, 145.92, 138.91, 137.29, 134.25, 134.20, 134.12, 133.44, 133.20, 129.49, 127.56,
- 6 125.77, 125.58, 125.34, 124.74, 122.61, 121.47, 115.83, 68.90, 41.40, 38.80, 34.14, 32.32, 28.92,
- 7 28.82, 25.52, 23.77, 23, 22.94, 14.13, 14.03, 11, 10.88.

#### 8 2D-NDT(Amide)<sub>2</sub>

9 A solution of compound (12) (0.08 gm, 1 equiv.) and 2-cyano-N-(2-ethylhexyl)acetamide (0.271 mg, 20 equiv.) in dry CHCl<sub>3</sub> was refluxed overnight with catalytic amounts of triethylamine. The 10 reaction mixture was cool to R.T. diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water 11 and brine; dried over MgSO<sub>4</sub>; and concentrated in vacuo. The crude compound was purified by 12 flash column chromatography using chloroform as the eluent to afford the corresponding product 13 as a dark red solid (0.035 gm, 37% yield). <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.8 (br, 2H), 8.2 (s, 2H), 14 7.79-7.69 (dd, 4H), 7.55-7.54 (m, 2H), 7.45 (d, 2H), 7.33 (d, 2H), 6.93 (d, 2H), 6.66 (d, 2H), 6.1 15 (d, 2H), 3.29 (d, 4H), 2.7 (d, 4H), 1.3-1.24 (m, 36H), 0.88-0.79 (t, 24H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): 16 δ 160.96, 146.51, 145.29, 144.42, 138.60, 135.54, 133.64, 127.89, 125.94, 125.59, 125, 121.79, 17 117.71, 99.92, 43.76, 41.64, 39.67, 34.36, 32.59, 31.20, 29.11, 29.05, 25.74, 23.20, 14.38, 14.29, 18 11.09. 19

#### 20 4.2 Solar cell fabrication and characterization

OSCs comprising a BHJ photoactive layer of small molecules: 6, 6- phenyl-C<sub>71</sub>-butyric acid 21 22 methyl ester (PC71BM) were prepared on a ITO-coated glass substrate with a structure of ITO/PEDOT: PSS/ NDT(TPD)<sub>2</sub> or NDT(TPDTT)<sub>2</sub>:PC<sub>71</sub>BM/ LiF/Al. Prior to use, the patterned 23 ITO-substrates were cleaned with deionized water, acetone, and isopropyl alcohol using 24 ultrasonication, followed by treatment with UV ozone. (PEDOT:PSS) (AI 4083, H. C. Starck) 25 was spin-coated (2600 rpm, 40 s) onto the cleaned ITO-glass at a thickness of 40 nm and dried at 26 140 °C for 20 min in atmosphere and then transferred into a glove box filled with N<sub>2</sub>. Blends of 27 NDT(TPD)<sub>2</sub> or NDT(TPDTT)<sub>2</sub> and PC<sub>71</sub>BM (Nano-C, USA) with different weight ratios (from 28 1:1 to 1:4 w/w) were solubilized overnight in chlorobenzene (20 mg mL<sup>-1</sup>) filtered through a 29 0.45 mm poly(tetrafluoroethylene) (PTFE)filter and subsequently spin-coated (thickness, 60-70 30

nm) onto the PEDOT:PSS layer of the ITO. The resulting films were dried at room temperature 1 for 20 min under N<sub>2</sub> and then under vacuum for 12 h. The devices were completed by deposition 2 of a 0.5 nm layer of LiF and a 120 nm Al layer. These layers were thermally evaporated at room 3 temperature under high vacuum at  $(10^{-6})$  Torr. The active area of every device was 9 mm<sup>2</sup>. The 4 current density-voltage (J-V) characteristics of the photovoltaic devices were measured in the 5 dark and under 1 sun illumination at AM 1.5G using a solar simulator (Newport) at 100 mW cm<sup>-</sup> 6 <sup>2</sup> adjusted with a standard PV reference  $(2 \times 2 \text{ cm}^2)$ , a mono-crystalline silicon solar cell 7 (calibrated at NREL, Colorado, USA) with a Keithley 2400 source-measure unit. The external 8 9 quantum efficiency (EQE) was determined using a Polaronix K3100 spectrometer.

#### 10 Acknowledgements

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1	Supporting Information (SI)
2	
3 4 5	A new 2D-Naphtho[1,2-b:5,6-b']dithiophene Donor Based Small Molecules for Bulk-heterojunction Organic Solar Cell
6 7	Sushil S. Bagde, Hanok Park, Van-Huong Tran, and Soo-Hyoung Lee*
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2	2,7-Bis(trimethylstannyl)naphtho[1,2-b:5,6-b']dithiophene (9) [1], 1-Bromo-5-(2-ethylhexyl)-
3	4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (13) [2], 2-Ethylhexyl 2-cyanoacetate [3], 2-Cyano-N-
4	(2-ethylhexyl)acetamide [3] and Thiophene-2,5-dicarbaldehyde [4] were synthesized according
5	to the procedures reported in the literature with slight modification.
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# 1 Material synthesis





**Fig. S2**. <sup>1</sup>H & <sup>13</sup>C NMR spectra of compound 11 in  $CDCl_{3}$ .



**Fig. S3.** <sup>1</sup>H & <sup>13</sup>C NMR spectra of TPD-Br in  $CDCl_{3.}$ 



**Fig. S4.** <sup>1</sup>H & <sup>13</sup>C NMR spectra of 2D-NDT(TPD)<sub>2</sub> in  $CDCl_{3.}$ 



**Fig. S5.** <sup>1</sup>H & <sup>13</sup>C NMR spectra of 2-ethylhexyl 2-cyanoacetate in CDCl<sub>3.</sub>



**Fig. S6**. <sup>1</sup>H & <sup>13</sup>C NMR spectra of 2-cyano-N-(2-ethylhexyl)acetamide in CDCl<sub>3</sub>.



**Fig. S7.** <sup>1</sup>H & <sup>13</sup>C NMR spectra of compound 12 in  $CDCl_{3.}$ 



**Fig. S8**. <sup>1</sup>H & <sup>13</sup>C NMR spectra of 2D-NDT(Ester)<sub>2</sub> in CDCl<sub>3</sub>.



**Fig. S9.** <sup>1</sup>H & <sup>13</sup>C NMR spectra of 2D-NDT(Amide)<sub>2</sub> in CDCl<sub>3.</sub>



**Fig. S10** Current density–voltage (*J-V*) characteristics of (a) hole- and (b) electron-only devices



 $<sup>26 \</sup>qquad 2D-NDT(Amide)_2:PC_{71}BM.$ 

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# **Research Highlights**

- 3 new small molecules based on new 2D-NDT donor core are explored for the bulkheterojunction organic solar cell.
- Effect of intermolecular interaction in 2D-NDT(Ester)<sub>2</sub> and 2D-NDT(Amide)<sub>2</sub> was observed and affected the overall device performance.
- Power conversion efficiency up to 1.22 % achieved for 2D-NDT(Ester)<sub>2</sub>.