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## Introduction

Conjugated polymers based on alternating electron donoracceptor (D–A) units have been extensively studied for use in the field of organic electronics. Diketopyrrolopyrrole (DPP)based polymers show high carrier mobility in organic fieldeffect transistors (OFETs) due to the strong intermolecular  $\pi$ – $\pi$ interactions and long-range order resulting from the coplanar nature of the conjugated backbone, short-contact oxygen– sulfur interactions, and cross-axis dipoles.<sup>1,2</sup>

In recent years, there has been rapid progress in the development of high-performance OFETs;<sup>3–7</sup> however, the commercial application of high-performance DPP-based polymers has been limited as they require processing in environmentally harmful halogenated

# Non-halogenated solution-processed ambipolar plastic transistors based on conjugated polymers prepared by asymmetric donor engineering<sup>†</sup>

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In addition to attaining strong charge transport capability, field-effect transistors based on conjugated polymer thin films should be processed using non-chlorinated solvents for device fabrication, to avoid adverse impacts on human health and the environment. Although many high-performance diketopyrrolopyrrole (DPP) based conjugated polymers have been studied, few DPP based polymers that can be processed in non-chlorinated solvents have been reported to date. In this work, ambipolar polymeric semiconductors based on a DPP backbone that can be solution-processed using non-chlorinated solvents are reported. The DPP backbone combined with asymmetric conjugated segments results in high solubility and processability in non-chlorinated solvents, such as toluene and *o*-xylene, without disruption in the conjugation and molecular ordering of the main backbone. The polymer films fabricated with a high-boiling-point additive show ambipolar charge transport characteristics and highly enhanced electrical performance due to greatly enhanced intermolecular interactions and the resulting aggregated nanostructures. The combination of non-chlorinated solution processing with the green additive, along with ambipolar characteristics, enables high-performance environmentally friendly complementary logic circuit integration to be achieved.

solvents (*e.g.*, chloroform, chlorobenzene (CB), trichlorobenzene and dichlorobenzene).<sup>8–10</sup> Chlorinated solvents are highly toxic, persistent and require large amounts of sodium hydroxide to scrub out of flue gases.<sup>11</sup> This has proved to be a major limitation for electronic device fabrication beyond the laboratory scale,<sup>12–15</sup> as well as with respect to compliance with stringent legal requirements to use these types of solvents within industry.<sup>16,17</sup> It is therefore necessary to develop high-performance DPP-based polymers that can be processed in non-chlorinated solvent systems for large-scale production.

Several studies have attempted to increase the solubility of conjugated polymers in less polar solvents, driven by a demand for processing in non-chlorinated solvents. Side-chain engineering is one strategy used to control the solubility of conjugated polymers. Numerous side-chain engineering studies on DPP-based polymers have been conducted,<sup>18–20</sup> focusing on the structure–property relationship. However, side-chain engineering proved to have little effect on the polarity and noncovalent interactions of DPP-based polymers; therefore, no significant increase of solubility in non-chlorinated solvents was achieved.<sup>21</sup> An alternative strategy, wherein the conjugated main backbone is varied, has been recently investigated. This strategy mainly introduced furan groups into conjugated polymers.<sup>22–24</sup> Furan-based conjugated polymers have accelerated the development of OFETs for non-chlorinated

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#### Paper

solution processing; however, their electrical performance remains lower than that of the analogous materials processed in chlorinated solvents. Another method for non-chlorinated processing is an irregular synthetic approach using random copolymerization, which makes the polymer backbone highly irregular so the polymer molecules become soluble in non-chlorinated solvents.<sup>25–27</sup> However, unlike the regular DPP-based polymers, these polymers display relatively poor electrical performances due to the disturbed intermolecular packing and band fluctuations in conjugated interchains.<sup>28–30</sup>

Recently, a novel irregular synthetic approach using structural asymmetry has been investigated.<sup>21,31</sup> When the DPP monomers with asymmetric donor segments were polymerized, the synthesized polymers lacked perfect translational symmetry in the main backbone and became soluble in non-chlorinated solvents. However, most studies on conjugated DPP-based polymers for non-chlorinated solvent processing have focused on hole-transporting p-type polymers;<sup>14,17,21,30,32–37</sup> therefore, n-type and ambipolar polymers remain relatively unexplored.<sup>25,38,39</sup> Ambipolar conjugated polymers are of great importance in fabricating organic p–n junctions, organic photovoltaic cells and complementary logic circuits. Such logic circuits offer desirable advantages, such as low power consumption, high operating speeds and device stability in electronic applications.<sup>40</sup>

In this work, we report two new DPP-based polymers prepared by asymmetric donor engineering which show ambipolar charge transport in non-chlorinated solvent systems. The newly developed asymmetric donor units, 2-(thiophen-2-vl)thieno[3,2-b]thiophene and 2-(selenophen-2-yl)thieno[3,2-b]thiophene, enhance the solubility of the polymers due to the randomly oriented irregular backbone. In addition, the well-regulated donor length optimizes the ambipolar character of the polymers and retains the intermolecular interaction between the donor and acceptor units, as well as their crystallinity. Both P29DPP-TTTh (poly[2,5-bis(7-decylnonadecyl)-3-(5-(5-(thiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5dihydropyrrolo[3,4-c]pyrrole-1,4-dione]) and P29DPP-TTSe (poly[2,5bis(7-decylnonadecyl)-3-(5-(5-(selenophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione]) display high solubility in non-chlorinated solvents, leading to fabrication of highly crystalline polymer films compared to those fabricated in chlorinated solution systems. With the addition of an eco-friendly additive, electrical performances of the P29DPP-TTSe polymer films processed in toluene were enhanced to have high hole  $(6.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$  and electron (0.71 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) mobilities according to the conventional gradual-channel approximation. Furthermore, we demonstrate onestep inverter applications as an example of complementary logic circuits by exploiting the ambipolar characteristics of non-chlorinated solution systems.

## **Experimental section**

#### Material preparation and polymer characterization

All solvents and reagents were purchased from Aldrich and Tokyo Chemical Industry Co (TCI). All solvents used were

further purified prior to use. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) and carbon-13 (<sup>13</sup>C)-NMR spectra were recorded using a Bruker Advance-300 and DRX-500 MHz spectrometer. High resolution mass spectrometry (HRMS) was conducted using a JMS-700 (MStation) spectrometer. Thermal analysis was performed on a Thermogravimetric analysis (TGA)-2100 thermogravimetric analyzer (TA Instruments) in a nitrogen atmosphere at a rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) was conducted in nitrogen on a 2100-DSC (TA Instruments) amplifier. The sample was heated at a rate of 10 °C min<sup>-1</sup> from 30 °C to 320 °C. Ultraviolet-visible (UV-Vis) absorption spectra were recorded by using a UV-1650PC spectrophotometer (Shimadzu). The molecular weight and polydispersity index of the copolymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration (Waters high-pressure GPC assembly model M515 pump, u-Styragel columns of HR4, HR4E, HR5E with 500 and 100 Å refractive index detectors, and tetrahydrofuran (THF) solvent). Cyclic voltammetry (CV) was performed on an EG & G Parc potentiostat/galvanostat system (model 273 Å) with a three-electrode cell in a solution of 0.1 M tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) in acetonitrile, at a scan rate of 50 mV s<sup>-1</sup>. The polymer films were coated on a square carbon electrode by dipping the electrode into appropriate solvents and then dried under nitrogen. A Pt wire was used as the counter electrode and an Ag/AgNO<sub>3</sub> (0.1 M) electrode was used as the reference electrode.

#### Thin film characterization

Tapping-mode atomic force microscopy (AFM) images of the polymer films were acquired using a VAIS AMT-045 vibration isolation platform. Grazing incidence X-ray diffraction (GIXD) measurements were conducted on the PLS-II 9A U-SAXS beamline at the Pohang Accelerator Laboratory in Korea. The X-rays emitted from the in-vacuum undulator (IVU) were monochromated at 11.025 keV (wavelength,  $\lambda = 1.12454$  Å) using a double crystal monochromator, and focused both horizontally and vertically (450  $\mu$ m (H)  $\times$  60  $\mu$ m (V) in the full width halfmaximum sample position) using K-B type mirrors. The GIXD sample stage was equipped with a 7-axis motorized stage for fine alignment of the sample, and the incidence angle of the X-ray beam was set to a range of  $0.12^{\circ}$ , which was close to the critical angle of the samples. GIXD patterns were recorded with a 2D charge-coupled device detector (SX165; Rayonix) and the X-ray irradiation time ranged from 30 s to 60 s, depending on the saturation level of the detector. Diffraction angles were calibrated using pre-calibrated sucrose (Monoclinic,  $P2_1$ , a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å,  $b = 102.938^{\circ}$ ) and the sample-to-detector distance was  $\sim 220.8$  mm.

#### **OFET fabrication and measurement**

Thermally grown SiO<sub>2</sub> gate dielectric ( $C_i = 11.5 \text{ nF cm}^{-2}$ ) highly n-doped (100) wafers, with a thickness of 300 nm, were used as substrates and gate dielectrics for OFETs with bottom-gate topcontact configuration to characterize the electrical performance of asymmetric DPP polymers. The SiO<sub>2</sub> surfaces were cleaned with a piranha solution for 30 min, followed by UV-ozone treatment. An n-octadecyltrimethoxysilane (OTS) self-assembled monolayer was applied to the wafers. The OTS solution (3 mM in trichloroethylene) was spin-coated onto the wafers at 1500 rpm for 30 s and the samples were exposed to ammonia vapor overnight in a vacuum desiccator. The wafers were then sonicated and washed with toluene, acetone and isopropyl alcohol, and dried in nitrogen. The DPP polymer thin films were spin-coated onto the OTS-treated substrates. The polymer solutions with and without the dimethyl sulfoxide (DMSO) additive were heated at 80 °C to fully dissolve the polymers prior to solution processing. The DPP solutions were placed onto the pre-heated substrates (60 °C) and spin-coated after 20-60 s, depending on the processing solvents. The samples were then thermally annealed at 250  $^\circ C$  for 30 mins in an inert atmosphere. Gold contacts (40 nm) were thermally evaporated onto the polymer films for source-drain electrodes with a channel length (L) of 50  $\mu$ m and a channel width (W) of 1000  $\mu$ m using a shadow mask. The electrical performances of OFETs were recorded in a N2-filled glove box using a Keithley 4200 semiconductor parametric analyzer.

### Results and discussion

#### Synthesis and characterization of conjugated polymers

The chemical structures of the conjugated polymers are presented in Scheme 1 and the synthetic procedures of monomers and polymers are shown in Scheme S1 (ESI<sup>†</sup>). The new asymmetric donor units, 2-(thiophen-2-yl)thieno[3,2-b]thiophene and 2-(selenophen-2-yl)thieno[3,2-b]thiophene, were obtained by the Stille reaction of 2-(thiophen-2-yl)thieno[3,2-b]thiophene with tributyl-(thiophen-2-yl)stannane and tributyl(selenophene-2-yl)stannane, respectively. The di(trimethylstannyl) asymmetric monomers were synthesized from n-BuLi and tetramethylethylenediamine (TMEDA) in THF and purified by recrystallization. P29DPP-TTTh and P29DPP-TTSe were also prepared using a palladium-catalyzed Stille coupling reaction. The polymers were purified by precipitation and successive Soxhlet extraction. The chemical structures of the monomers and polymers were characterized using various spectroscopic techniques, such as <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and HRMS (see Supplementary contents and Fig. S1-S11, ESI†). The average molecular weights of P29DPP-TTTh and P29DPP-TTSe were 40.6 kDa and 33.9 kDa, with a polydispersity index of 1.36 and 1.31, respectively; these were determined by GPC measurements

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#### P29DPP-TTTh P29DPP-TTSe Scheme 1 The molecular structures of P29DPP-TTTh and P29DPP-TTSe.

with polystyrene standards in THF solvent (Fig. S12 and S13, ESI†). The solubility was tested by checking the solution at a concentration of 0.5 wt% mL<sup>-1</sup> (see Table S1, ESI†). Both polymers with asymmetrically structured donor units showed good solubility in various solvents, including environmentally friendly solvents (*e.g.*, toluene and xylene), due to the irregularly oriented asymmetric backbone. TGA also showed them to be thermally stable up to 460–480 °C. DSC analysis up to 320 °C revealed that **P29DPP-TTTh** did not show transition to another phase, and **P29DPP-TTSe** showed a crystalline transition at around 310 °C (Fig. S14 and S15, ESI†).

The UV-Vis absorption spectra of P29DPP-TTTh and P29DPP-TTSe in toluene and a film state are presented in Fig. 1a and b and Table S2 (ESI<sup>†</sup>). The weak  $\pi \rightarrow \pi^*$  transition at 448 nm and the intramolecular charge transfer band at 788 nm are attributed to the toluene solvent. A 0-1 transition, the intermolecular interaction at 712 nm was observed in the film state for P29DPP-TTTh. The optical transitions of P29DPP-TTSe and P29DPP-TTTh were similar, *i.e.*,  $\pi \rightarrow \pi^*$  transition at 448 nm, an intramolecular charge transfer (ICT) band at 802 nm and intermolecular interaction at 723 nm. The optical band gaps of P29DPP-TTTh and P29DPP-TTSe calculated from the UV-Vis absorption edge were 1.36 eV and 1.33 eV, respectively. These results suggest that both polymers have a coplanar  $\pi$ -conjugated structure with a strong intramolecular charge transfer band from the donor to the acceptor, a strong intermolecular interaction without disruption of conjugation and molecular ordering, and an irregularly oriented asymmetric backbone for non-chlorinated solvent processing. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy level, calculated according to the electrochemical oxidation onset and the optical band gap, were -5.38 eV and -4.02 eV for P29DPP-TTTh and -5.37 eV and -4.04 eV for P29DPP-TTSe, respectively. The donor length also leads to ambipolar characteristics in OFET applications (Fig. 1c and Table S2, ESI<sup>†</sup>).

#### **Characterization of OFETs**

To investigate the impact of the non-chlorinated solvent on the charge transport properties of the synthesized materials, topcontact bottom-gate OFETs were initially fabricated using CB for comparison. The polymer solutions were spin-coated onto the OTS-modified SiO<sub>2</sub>/Si substrates and then thermally annealed at 250 °C. The experimental details of the OFET fabrication and measurements are included in the Experimental section. The two polymers exhibited hole-dominant ambipolar field-effect behaviors with typical V-shaped transfer curves (Fig. 2). These are likely due to the well-matched HOMO levels with respect to the work function ( $\sim 5.1 \text{ eV}$ ) of the gold electrodes, demonstrating lower injection barriers for positive charge carriers. Two non-chlorinated solvents, toluene and o-xylene, were used for the fabrication of OFETs. Fig. 2 presents the dependence of the representative transfer characteristics of the optimal OFETs on different processing solvents. Both polymer films exhibited typical V-shaped behaviors without chlorinated solvent processing, indicative of ambipolar charge transport, as well as the chlorinated references. The dependence of the output curves of the two

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**Fig. 1** UV-Vis-NIR absorption spectra of (a) **P29DPP-TTTh** and (b) **P29DPP-TTSe** in dilute toluene solution and solid thin-film states on a quartz plate. (c) Cyclic voltammograms of the polymer films on a square carbon electrode in a solution of 0.1 M tetrabutylammonium perchlorate ( $Bu_4NCIO_4$ ) in acetonitrile at a scan rate of 50 mV s<sup>-1</sup>.



Fig. 2 (a–c) Transfer characteristics of OFET based on **P29DPP-TTTh** polymer films using (a) chlorobenzene, (b) toluene, and (c) *o*-xylene solution after optimal thermal annealing at 250 °C. (d–f) Transfer characteristics of OFET based on **P29DPP-TTSe** polymer films using (d) chlorobenzene, (e) toluene, and (f) *o*-xylene solution after optimal thermal annealing at 250 °C. The left and right panels indicate the results of hole- and electron-enhancement operations with  $V_{DS} = -100$  and +150 V, respectively. Solid green, orange, and dotted grey fitting lines indicate the region for maximum mobility estimation, mobility at kinks, and the reliability factor (*r*), respectively.

polymer films on the processing solvent used is illustrated in Fig. S16 (ESI<sup>†</sup>). All output curves showed well-defined p-type dominant ambipolar behavior with a prominent transition to saturation behavior with increasing  $V_{\rm GS}$ .

The charge carrier mobility was calculated using the gradient from a plot of the square root of drain current ( $I_{\rm DS}$ ) against  $V_{\rm GS}$  in the transfer curve under the conventional gradualchannel approximation ( $\mu_{\rm h,gca}$  and  $\mu_{\rm e,gca}$ ). However, we observed non-linearity in  $|I_{DS}|^{1/2}$  at high  $V_{GS}$ , which was confirmed by the characteristics of other highly polar and electron-deficient DPP-based polymer films.<sup>4–6,18,19,30</sup> This is attributed to either carrier supersaturation in the conduction channel resulting in a reduction of the carrier velocity,<sup>41</sup> high electron affinity leading to electron injection in the hole-based conduction channel,<sup>42</sup> and reversible and rapid charge trapping in deep states during the  $V_{GS}$  sweep resulting in a change of the threshold voltage  $(V_{\rm T})$ ,<sup>43,44</sup> or a combination of these effects.<sup>30</sup> The undesirable transfer characteristics of OFETs due to such effects undermine the accurate determination of mobility using formulas derived from the gradual-channel approximation. Thus, the ambipolar charge mobility was estimated in accordance with recent studies.42,45 Initially, the charge mobilities in the additional  $V_{\rm GS}$  sweep region (*i.e.*, beyond the non-linear region) were extracted.42 The green and orange solid lines in the transfer curves display two regions for mobility extraction; one preceding the non-linear region (estimated by conventional gradual-channel approximation) and one after the non-linear region ( $\mu_{\text{gca}}$  and  $\mu_{\text{kink}}$ , respectively). Furthermore, we calculated the reliability factor r, defined as the ratio of the maximum channel conductivity experimentally achieved in the OFET to the maximum channel conductivity expected in an equivalent but ideal OFET.45 Initially, r was estimated for OFETs in the saturation regime using eqn (1).

$$r_{\rm sat} = \left(\frac{\sqrt{|I_{\rm DS}|^{\rm max}} - \sqrt{|I_{\rm DS}^0|}}{|V_{\rm GS}|^{\rm max}}\right)^2 / \left(\frac{\partial\sqrt{|I_{\rm DS}|}}{\partial V_{\rm GS}}\right)_{\rm claimed}^2 \tag{1}$$

where  $|I_{\rm DS}|^{\rm max}$  is the experimental maximum source-drain current at the maximum gate voltage,  $|V_{\rm GS}|^{\rm max}$ , and  $|I_{\rm DS}^0|$  denotes the source-drain current at  $V_{\rm GS} = 0$ .

Table 1 FET characteristics of **P29DPP-TTTh** and **P29DPP-TTSe** polymer films after optimal thermal annealing

A summary of the experimental results and estimated mobilities is presented in Table 1. Both DPP-based polymer films in all processing solvents are hole-dominant ambipolar  $\mu_{gca}$  ( $\mu_{h,gca}$ :  $2-5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $\mu_{e,\text{gca}}$ : 0.1–0.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), and displayed a non-linear mobility trend with a relatively low  $\mu_{kink}$  value. The annealed film of P29DPP-TTTh fabricated using non-chlorinated solvents displayed relatively reduced mobility compared to that using CB. The optimal **P29DPP-TTSe** polymer films exhibited comparable charge mobilities. The P29DPP-TTSe polymer films fabricated using toluene exhibited the best ambipolar mobilities, with high  $\mu_{\text{h,eff}}$  and  $\mu_{\text{e,eff}}$  values of 1.38 and 0.25 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. The comparable electrical performance in nonchlorinated solvent processing is attributed to their high solubility, which enabled a smooth and highly crystalline film coating to be applied. The gross irregularity of asymmetric segments in the conjugated backbone led to a breakdown in the perfect translational symmetry along the polymer chain, making them highly soluble even in non-chlorinated solvents.

A high-boiling-point additive was used to enhance the electrical performance. A small amount of DMSO was added to the nonchlorinated solution (Fig. 3, Fig. S17, ESI† and Table 1). DMSO was selected as an additive as it is less harmful to the environment and has a relatively high boiling point. When adding the additive, both hole and electron mobilities increased significantly. The **P29DPP-TTSe** polymer films fabricated using toluene and the DMSO additive showed increased mobilities of 1.92 and 0.33 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for  $\mu_{h,eff}$  and  $\mu_{e,eff}$ , respectively. The maximum  $\mu_{h,gca}$  value was 6.36 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which is comparable to those of the other DPP-based unipolar p-type polymer films processed in non-chlorinated solvents (Table S3, ESI†).<sup>14,17,21,25,30,32–39</sup> The **P29DPP-TTTh** polymer films using toluene and DMSO showed moderate ambipolar mobilities of 1.39 and 0.24 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for  $\mu_{h,eff}$  and  $\mu_{e,eff}$ , respectively. The maximum function of the polymer films using toluene and DMSO showed moderate ambipolar mobilities of 1.39 and 0.24 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for  $\mu_{h,eff}$  and  $\mu_{e,eff}$ , respectively. The solution of the polymer films using toluene and DMSO showed moderate ambipolar mobilities of 1.39 and 0.24 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for  $\mu_{h,eff}$  and  $\mu_{e,eff}$ , respectively. Hysteresis of both polymer films

|             |          |          |                 |                          |                 |                        |                            | 5                        |                             |                    |                     |
|-------------|----------|----------|-----------------|--------------------------|-----------------|------------------------|----------------------------|--------------------------|-----------------------------|--------------------|---------------------|
| Materials   | Solvent  | Additive | Transistor type | $I_{\rm on}/I_{\rm off}$ | $V_{\rm t}$ (V) | $\Delta V_{\rm t}$ (V) | $\mu_{ m gca,avg}{}^{a,b}$ | $\mu_{ m gca,max}^{a,b}$ | $\mu_{\mathrm{kink}}^{a,b}$ | r <sup>c</sup> (%) | $\mu_{\rm eff}^{a}$ |
| P29DPP-TTTh | CB       | _        | Р               | $> 10^{3}$               | -17.22          | 8.5                    | 5.74                       | 6.34                     | 0.58                        | 12                 | 0.76                |
|             |          |          | Ν               | $> 10^{3}$               | 70.35           | 12.6                   | 0.39                       | 0.47                     | 0.11                        | 10                 | 0.05                |
|             | Toluene  |          | Р               | $> 10^{3}$               | -17.13          | 5.8                    | 2.04                       | 2.40                     | 0.48                        | 21                 | 0.50                |
|             |          |          | Ν               | $> 10^{3}$               | 70.95           | 13.7                   | 0.22                       | 0.31                     | 0.050                       | 8                  | 0.03                |
|             |          | Additive | Р               | $> 10^{4}$               | -22.70          | 4.0                    | 3.68                       | 4.29                     | 0.57                        | 16                 | 0.69                |
|             |          |          | Ν               | $> 10^{4}$               | 70.95           | 13.1                   | 0.42                       | 0.57                     | 0.12                        | 11                 | 0.06                |
|             | o-Xylene |          | Р               | $> 10^{3}$               | -17.70          | 7.9                    | 2.14                       | 2.50                     | 0.60                        | 21                 | 0.52                |
|             |          |          | Ν               | $> 10^{3}$               | 73.19           | 19.8                   | 0.22                       | 0.29                     | 0.11                        | 11                 | 0.03                |
|             |          | Additive | Р               | $> 10^{3}$               | -12.09          | 4.3                    | 2.80                       | 3.50                     | 0.53                        | 17                 | 0.60                |
|             |          |          | Ν               | $> 10^{3}$               | 73.88           | 17.7                   | 0.30                       | 0.36                     | 0.36                        | 8                  | 0.03                |
| P29DPP-TTSe | CB       | _        | Р               | $> 10^{3}$               | -20.22          | 9.0                    | 4.18                       | 4.81                     | 0.71                        | 13                 | 0.63                |
|             |          |          | Ν               | $> 10^{3}$               | 63.66           | 16.4                   | 0.32                       | 0.46                     | 0.11                        | 12                 | 0.05                |
|             | Toluene  | —        | Р               | $> 10^{3}$               | -19.27          | 8.7                    | 4.48                       | 5.07                     | 0.77                        | 15                 | 0.76                |
|             |          |          | Ν               | $> 10^{3}$               | 71.18           | 16.9                   | 0.43                       | 0.52                     | 0.11                        | 8                  | 0.04                |
|             |          | Additive | Р               | $> 10^{5}$               | -27.90          | 5.6                    | 5.20                       | 6.36                     | 0.70                        | 14                 | 0.92                |
|             |          |          | Ν               | $> 10^{4}$               | 75.32           | 12.8                   | 0.58                       | 0.71                     | 0.11                        | 9                  | 0.07                |
|             | o-Xylene |          | Р               | $> 10^{3}$               | -18.30          | 8.8                    | 3.59                       | 3.85                     | 0.70                        | 20                 | 0.77                |
|             |          |          | Ν               | $> 10^{3}$               | 71.70           | 15.4                   | 0.33                       | 0.48                     | 0.17                        | 8                  | 0.04                |
|             |          | Additive | Р               | $> 10^{3}$               | -8.11           | 5.1                    | 4.15                       | 4.89                     | 0.74                        | 19                 | 0.90                |
|             |          |          | Ν               | $> 10^{3}$               | 79.00           | 13.9                   | 0.48                       | 0.62                     | 0.26                        | 7                  | 0.04                |
|             |          |          |                 |                          |                 |                        |                            |                          |                             |                    |                     |

<sup>*a*</sup> Unit: cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. <sup>*b*</sup> The average values obtained for at least six devices from more than two different batches. <sup>*c*</sup> Eqn (1) was used for estimating r values.



**Fig. 3** (a) Transfer characteristics and (b) output characteristics of OFET based on **P29DPP-TTSe** polymer films using toluene and DMSO additive after optimal thermal annealing at 250 °C. (c) Transfer characteristics and (d) output characteristics of OFET based on **P29DPP-TTSe** polymer films using *o*-xylene and DMSO additive after optimal thermal annealing at 250 °C. In transfer curves, the left and right panels indicate the results of hole- and electron-enhancement operations with  $V_{DS} = -100$  and +150 V, respectively. Solid green, orange, and dotted grey fitting lines indicate the region for maximum mobility estimation, mobility at kinks, and the reliability factor (*r*), respectively. In the output curves, the interval of the gate voltage was 10 V. (e) Schematic of the complementary inverter structure (left). CMOS-like inverter characteristics of **P29DPP-TTSe** inverters processed in toluene and DMSO additive solution (right;  $V_{DD} = 100$  V).

before and after DMSO additive treatment was confirmed (Table 1). The additive treatment gave rise to a reduction of hysteresis in both p- and n-type operation, irrespective of the processing solvents used, which exhibited better hysteresis stability than other non-chlorinated solvent processed polymer films using irregular backbone structures.<sup>25,30</sup> To exploit the advantages of ambipolar charge transport and electrical stability in nonchlorinated solvent processed films, the complementary metal oxide semiconductor (CMOS) inverter characteristics of P29DPP-TTSe were tested by connecting two identical ambipolar transistors in a single film deposition step (Fig. 3e). They exhibited high average gains of 139. The corresponding inverter voltage transfer characteristics for  $V_{\rm DD}$  = 100 V down to 25 V in steps of 25 V are shown in Fig. S18 (ESI<sup>+</sup>). It is noteworthy that the transition of the inverter is not located at  $V_{\rm DD}/2$  and there is a hysteresis in the voltage transfer characteristics. This result originated from the different threshold voltages and hysteresis characteristics in p- and n-operation.

#### Crystallinity and molecular orientation characterization

GIXD was carried out to further investigate how the processing solvent affects the crystallinity and molecular orientations of the polymer films. Fig. 4 and Fig. S19, S20 (ESI<sup>†</sup>) show the twodimensional (2D) GIXD images and the corresponding diffractogram profiles of polymer films with different processing solvents. Both polymer films processed in chlorinated solvents exhibited well-defined lamellar peaks up to the sixth order along the out-ofplane ( $q_z$ ) direction, showing that edge-on orientations relative to the substrate are dominant. **P29DPP-TITh** and **P29DPP-TTSe** had a similar intermolecular stacking structure along the alkyl side chains, with only a small difference (~0.2 Å) in the *d*-spacing of the (100) peaks. A well-defined in-plane diffraction peak at



**Fig. 4** 2D-GIXD images of **P29DPP-TTSe** polymer films using (a) chlorobenzene, (b) toluene, (c) o-xylene, and (d) toluene with DMSO additive after optimal thermal annealing at 250 °C. (e and f) The corresponding 1D-GIXD profiles of the (e) out-of-plane and (f) in-plane GIXD patterns of **P29DPP-TTSe** polymer films in different processing solvents. (g and h) The corresponding 1D-GIXD profiles of the (g) out-of-plane and (h) in-plane GIXD patterns of **P29DPP-TTSe** polymer films with DMSO additive treatment.

1.72  $\text{\AA}^{-1}$  for both polymer films was observed and attributed to an ordered  $\pi$ - $\pi$  packing (Table S4, ESI<sup>†</sup>). The two polymer films contained edge-on orientation with almost similar d-spacing and  $\pi$ - $\pi$  packing stacking distances, resulting in almost no difference in their electrical properties. Comparably high crystalline edge-on orientations were also obtained in polymer films spin-coated in non-chlorinated solvents with high-order out-of-plane diffraction peaks and a discernible in-plane diffraction peak at 1.73  $\text{\AA}^{-1}$ . The polymer films showed no change in the  $\pi$ - $\pi$  packing stacking distances with non-chlorinated solvent processing; however, they showed slightly shorter (100) layer distances, indicative of more tilted molecular plane or inter-digitated packing of linear alkyl side chains. Although shorter *d*-spacing of lamellar structures may be favorable for electrical charge transport, the number of layers more accurately reveals the combined effects of a layer distance and a crystallite size (i.e., the coherence length of the

layer).<sup>18,20</sup> The number of layers was estimated from  $L_{c,(100)}/d_{(100)}$ , allowing investigation of the crystallinity within well-ordered edge-on lamellae structures to be conducted. The  $L_{c,(100)}/d_{(100)}$ value of the **P29DPP-TTTh** polymer films processed in CB, toluene and *o*-xylene was estimated to be 7.7, 6.7 and 6.5 layers, respectively. This may account for the reduced electrical properties of the **P29DPP-TTTh** polymer films processed in non-chlorinated solvents. The estimated numbers of layers within **P29DPP-TTSe** polymer films in CB, toluene and *o*-xylene were 7.9, 7.7 and 7.4, respectively, showing the retention of edge-on lamella structures and high mobilities for polymer films processed within nonchlorinated solvents.

To investigate the effect of the additive on the crystallinity and molecular orientations of the polymer films, 2D GIXD analysis of the P29DPP-TTTh and P29DPP-TTSe polymer films after additive treatment was conducted. The DMSO treatment was shown not to affect the in-plane  $\pi$ - $\pi$  packing distances of both polymer films, but resulted in a reduction of the number of layers ( $\sim 1$  layer) along the out-of-plane directions, in turn reducing the crystallinity of edge-on lamella structures. Despite the reduced crystallinity along the out-of-plane directions, three different types of mobility estimations gave identical results, showing that the high-boiling-point additive treatment enhanced the charge mobilities of the polymer films. Hence, the reduction in the crystallinity of lamella structures may still facilitate charge transport in polymer films, as reported in amorphous conjugated polymer films,<sup>45,46</sup> and other factors could also compensate for the crystalline defects, judging from the morphological study using AFM (vide infra).

To determine whether the morphology and molecular packing characteristics could be the compensating factors, the morphologies of P29DPP-TTTh and P29DPP-TTSe thin films formed using different processing solvents, with and without DMSO treatment, were investigated using tapping-mode AFM. Fig. S21 (ESI<sup>†</sup>) presents the heights and phase images  $(2 \times 2 \mu m^2 \text{ scan})$  of the polymer thin films by AFM using different processing solvents. AFM analysis revealed that the optimally annealed polymer films of P29DPP-TTTh and P29DPP-TTSe consisted of large and densely packed nanofibrillar networks over the entire surface for both CB and non-chlorinated processing solvents with similar fibril sizes ( $\sim 80$  nm in diameter). The comparable charge mobilities of polymer films processed in non-chlorinated solvents is attributed to a similar morphology. The eco-friendly additive treatment for the non-chlorinated solvent-processed polymer films gave rise to the formation of much larger aggregates of nanofibrils  $(\sim 200 \text{ nm in diameter})$  as shown in Fig. 5. The introduction of high-boiling-point additive allows slow drying and evaporation of the processing solution, which gives the solvated polymer chains more time to aggregate prior to being fixed within the solid thin films. In addition, the driving force for interchain aggregation and strong intermolecular interactions increases as the fraction of the good solvent decreases due to the rule of the additive as the nonsolvent.<sup>47-50</sup> The significantly enlarged aggregates of nanofibrils are closely related to the enhanced charge transport capability that compensates for the reduced crystallinity of lamella structures found in GIXD results.



Fig. 5 AFM topography images of (a) P29DPP-TTTh and (b) P29DPP-TTSe polymer films made from different processing solvents after optimal thermal annealing at 250 °C (scale bar = 500 nm).

# Conclusions

This study presents the first examples of asymmetric ambipolar DPP-based polymers, which are highly soluble in non-chlorinated solvents, and their application as CMOS inverters with balanced electron and hole transport. OFET devices fabricated using these polymers dissolved in non-chlorinated solvents showed hole mobilities comparable to other DPP-based high-performance p-type polymers processed in non-chlorinated solvents. They also displayed moderate electron mobilities, resulting in ambipolar characteristics. Their high solubility in non-chlorinated solvents is a result of the introduction of asymmetric donor segments during polymerization, while still allowing the formation of highly crystalline edge-on structures without disruption in the conjugation and molecular ordering of the main backbone. In addition, when DMSO was used as an additive, the interchain aggregation and intermolecular interactions remarkably increased, resulting in enhanced ambipolar charge transport. Our results demonstrate a successful approach to the environmentally friendly solution processing of organic semiconducting materials, which may serve as a commercially viable practical solution for coating and printing processes, such as inkjet printing and roll-to-roll processes.

# Conflicts of interest

There are no conflicts to declare.

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