

Balancing sustainability and performance in ester-incorporated polymers for organic field-effect transistors via physical and chemical blending

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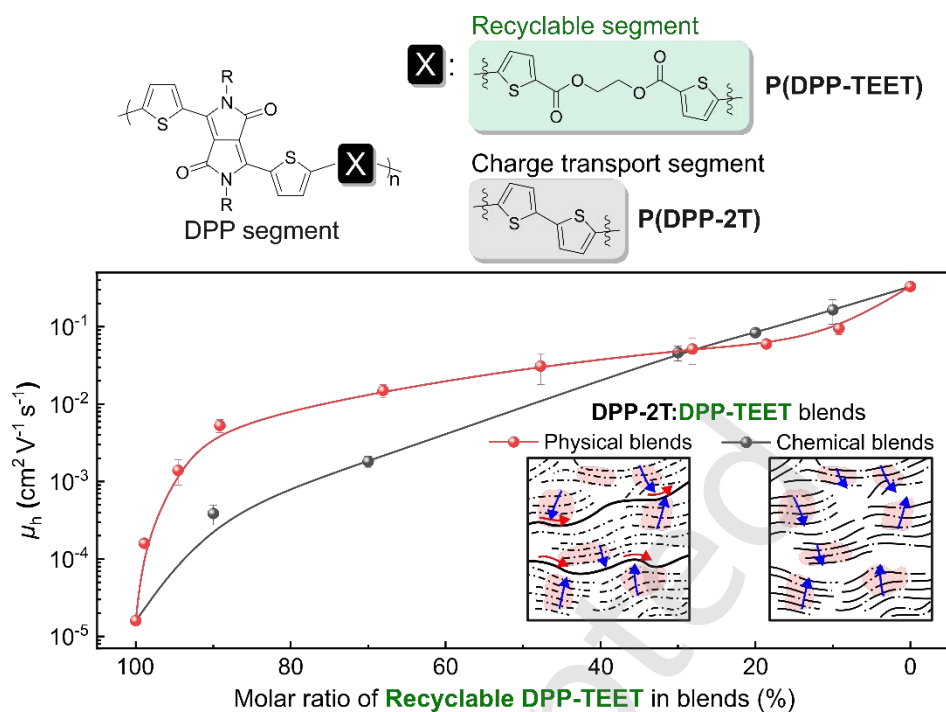
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Ester linkers demonstrate potential to achieve sustainability in organic semiconductors. However, ester incorporation weakens charge transport in DPP-based polymers. Physical blending demonstrates that by adding just 10 wt% of a fully conjugated polymer restores mobility dramatically while chemical blending requires much higher conjugated content to achieve similar performance.

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ABSTRACT: The sustainability of organic semiconductors has emerged as a critical challenge for reducing electronic waste, motivating the development of recyclable and degradable conjugated polymers. Incorporating ester linkages into polymer backbones enables depolymerization and repolymerization; however, these nonconjugated units disrupt the pi-conjugation and result in severe degradation of charge transport. Here, we address this fundamental trade-off between sustainability and device performance in diketopyrrolopyrrole (DPP)-based organic semiconductors by implementing two complementary strategies: *physical blending* and *chemical blending* of fully conjugated and ester-incorporated polymers. In the physical blending strategy, the introduction of only 10 wt% of a fully conjugated polymer, P(DPP-2T), into TEET- or TET-containing DPP polymers, in which the backbone esters are introduced as cleavable linkages, leads to dramatic enhancements in hole mobility – up to 330-fold and 380-fold, respectively – when compared to the corresponding neat polymer, while retaining 90 wt% of the ester-containing polymer in the film. By contrast, chemical blending via terpolymerization yields more limited mobility enhancement, as ester segments distributed along the backbone constrain intrachain charge transport, requiring substantially higher DPP-2T content to achieve appreciable electrical performance. Overall, these results demonstrate that physical blending can more efficiently restore charge transport in the ester-incorporated polymers at lower content of the corresponding fully conjugated polymer, while chemical blending requires higher content of conjugated segments to achieve comparable device performance. This work establishes a general framework for designing sustainable organic semiconductors that minimize electronic waste without sacrificing field-effect transistor performance.

KEYWORDS: organic field-effect transistors, physical blending, chemical blending (terpolymerization), ester-incorporated organic semiconductors

1 Introduction

π -Conjugated polymers continue to capture the interest of researchers, offering exciting possibilities in a wide range of electronic applications due to their semiconducting properties, tunable molecular structures, light weight, and sustainability [1-3]. Organic semiconductors have achieved impressive performance in devices such as organic field-effect transistors (OFETs), with charge carrier mobilities exceeding $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [4], and organic solar cells (OSCs) achieving power conversion efficiencies over 20% [5,6]. As

these materials advance closer to widespread commercialization, it becomes increasingly important to address their end-of-life implications. Unfortunately, the intrinsic stability of organic semiconductors, while beneficial for device durability, contributes to growing challenges of electronic waste (e-waste) [7,8]. While a ‘closed-loop’ recycling of organic semiconductors would be ideal, it is very challenging to design strategies to preserve the high device performance of such materials while imparting the recyclability.

Ongoing efforts to reduce e-waste from organic

semiconductors have focused on designing materials and strategies to achieve full degradation, recyclability, and minimizing the amount of e-waste generated [7,9,10]. Recently, the design of degradable and recyclable semiconductors has mainly focused on the incorporation of *conjugated/aromatic* linkers such as imines and 1,2,4-oxadiazole into the polymer backbones [7,11-19]. These linkers can maintain the extended conjugation of the parent polymer and largely retain the charge transport properties, yet can induce the degradation of such conjugated polymers under applied stimuli. Alternatively, blending high-performing organic semiconductors with biodegradable polymers (e.g., polycaprolactone and polylactide) have also been actively explored to maintain desirable device performance while minimizing waste [10]. This is because often only a small amount of the organic semiconductors is *truly* responsible for the intended application (e.g., a few nanometer thickness of organic semiconductor is sufficient for achieving high mobilities in OFETs) [20,21], and the bulk of the organic semiconductors generally serve as the support (e.g., mechanical) and can be replaced by other degradable nonconjugated polymers [22,23]. Combining these two strategies, Bao and coworkers accomplished a complete degradation of their materials for transient electronics by a synergistic incorporation of imine linkages into their conjugated polymers and further blending with polycaprolactone elastomers [24].

In our previous work, we achieved closed-loop recycling of an ester-incorporated organic semiconductor [25]. Our focus on ester linkages was motivated by the basis that mild decomposition conditions can selectively depolymerize ester-containing conjugated polymers without compromising the integrity of the resulting monomers, allowing the reuse of these recycled monomers for repolymerization. However, evenly incorporating esters into the building block of the conjugated backbone disrupts the conjugation, presenting a clear trade-off between sustainability and charge transport performance. Therefore, it is clear that new strategies are required to balance sustainability and performance in ester-incorporated organic semiconductors.

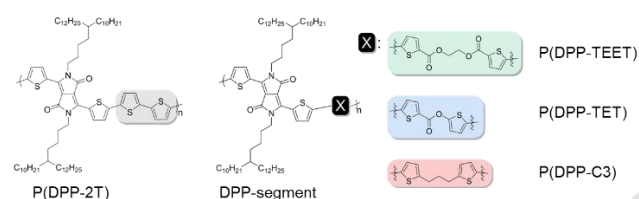
To address similar trade-offs between two or more desirable yet irreconcilable properties (e.g., stretchability and electronic performance), the community has attempted

different strategies to employ multiple components to balance material properties. The first approach is to physically blend of polymers of complementary properties. For example, Mei and co-workers blended a fully conjugated polymer having the desired charge transport properties with a semi-aromatic polymer and achieved melt processing [26-29]. The second approach involves terpolymerization, in which three monomers with distinct characteristics are combined at different molar ratios to modulate the desired properties. For example, this method has been employed to maintain charge transport properties of the original conjugated polymer while enhancing stretchability and processability [30-32]. To our knowledge, these strategies have not been applied with a focus on sustainability and, in particular, recyclability. Therefore, we adopted these techniques – referred throughout the article as *Physical Blending* for the polymer blends and *Chemical Blending* for the terpolymer approach – in our ester-incorporated polymers. Through the implementation of physical and chemical blending, we aim to strike a balance between sustainability and electronic performance.

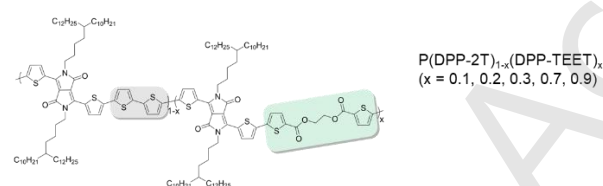
For the physical blending, two types of polymers are generally employed, namely, a matrix polymer and a tie-chain polymer. In our study, we used two matrix polymers, P(DPP-TEET), P(DPP-TET), and a reference polymer – P(DPP-C3); these three polymers feature disrupted conjugation along each individual backbone through the ester group or aliphatic carbons (**Scheme 1**). The tie-chain polymer, P(DPP-2T), is fully conjugated and serves to restore charge transport within the physical blend. On the other hand, the chemical blending explores terpolymers with the general composition $P(\text{DPP-2T})_{1-x}(\text{DPP-TEET})_x$ (where $x = 0, 0.1, 0.2, 0.3, 0.7, 0.9$, and 1), allowing for a systematic evaluation of the structure-property relationship with varying mol% of TEET and 2T monomers. With materials in hand, our objectives are to: 1) assess how esters influence OFET performance of DPP-based polymers; 2) evaluate how the difference in the physical blending and the chemical blending impact electronic properties in ester-incorporated polymers; and 3) establish a design framework to guide the development of future sustainable organic semiconducting systems. Our results show that while the incorporation of ester linkers (e.g., P(DPP-TEET) and P(DPP-TET)) led to decreased average hole mobilities by four and three orders

of magnitude, respectively, when compared to the parent P(DPP-2T) ($0.33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), the implementation of physical and chemical blending strategies were able to address the negative impact of esters on electronic performance. The addition of only 10 wt% of P(DPP-2T) to either P(DPP-TEET) or P(DPP-TET) enhanced mobilities by two orders of magnitude while retaining 90 wt% of the ester-containing polymer in the semiconducting film. On the other hand, the results from the chemical blending revealed a monotonic increase of the hole mobility with more incorporation of the DPP-2T monomer. Using morphological characterization via Atomic Force Microscopy (AFM) and Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS), we further elucidate the morphological factors underlying the charge-carrier mobility trends.

a) Physical Blending



b) Chemical Blending



Scheme 1. Overview of the polymer design explored in this study: a) Physical Blending, and b) Chemical Blending.

2 RESULTS AND DISCUSSION:

2.1 Design and Synthesis

Scheme 1a presents the four co-polymers utilized in the physical blending strategy. All polymers contain a thiophene-flanked diketopyrrolopyrrole (DPP) acceptor unit where the amide is functionalized with an alkyl side chain branched at the fifth carbon to promote solubility and π - π stacking [18]. We chose P(DPP-2T) as the starting point, where the DPP unit is connected by a bithiophene (2T) unit to afford a fully π -conjugated polymer. Because P(DPP-2T) has demonstrated high mobilities in OFETs [26,33], it serves as the tie-chain polymer in our physical blending study. We then designed an ester linker to be inserted between the thiophene units in the 2T moiety to afford Thiophene-Ester-Ethylene-Thiophene (TEET) and Thiophene-Ester-Thiophene (TET), respectively, as sites for selective chemical

cleavage at end of life. TEET yields an alternating co-polymer P(DPP-TEET) whose backbone esters are designed to be selectively cleaved, in principle allowing depolymerization to recoverable monomers; as discussed in Section 2.3.4, the extent to which this is realized in practice depends on the side chain. TET, on the other hand, forms a random copolymer P(DPP-TET) with extended conjugation relative to P(DPP-TEET), the cleavage of which would yield fragments rather than recoverable monomers and therefore offers degradability only [25]. We also synthesized a previously reported Thiophene-Propyl-Thiophene (C3) monomer to yield a non-degradable polymer (P(DPP-C3)) [26,32] as a reference. Having P(DPP-C3) in this study allows us to understand the impact of incorporating the ester linkers (versus the simple alkyl linker) on polymer microstructure and charge transport. Synthetic details and characterization for the ester-incorporated monomers can be found in the Supporting Information (SI).

As for the chemical blending, we focused on the TEET unit, given its recyclability and degradability, and thus synthesized terpolymers consisting of DPP, TEET and 2T monomers with varying molar ratios of 2T and TEET (from 9:1 to 1:9) to yield P(DPP-2T)_{0.9}(DPP-TEET)_{0.1}, P(DPP-2T)_{0.8}(DPP-TEET)_{0.2}, P(DPP-2T)_{0.7}(DPP-TEET)_{0.3}, P(DPP-2T)_{0.3}(DPP-TEET)_{0.7}, and P(DPP-2T)_{0.1}(DPP-TEET)_{0.9} (**Scheme 1b**), respectively. Synthetic details and characterization data can be found in the SI. We applied High-Temperature Gel Permeation Chromatography (HT-GPC) to estimate the molecular weights relative to polystyrene standards and the obtained data are summarized in **Table 1**.

We note that terpolymers containing 70 and 90 mol% of DPP-TEET, as well as the homopolymers P(DPP-TEET) and P(DPP-TET), show appreciably lower molecular weight when compared to other polymers in this study. This difference could, on its own, influence the measured mobilities of these conjugated polymers. However, the primary goal of this study is to evaluate the impact of the tie-chain polymer on mobility in the physical and chemical blending scenarios; since the tie-chain polymer P(DPP-2T) has sufficiently high molecular weight to ensure both high mobility and effective chain bridging, we conclude that the lower molecular weight of these aforementioned polymers would have minimal impact in achieving the primary goal of

this study.

Table 1. High-Temperature Gel Permeation Chromatography characterization.^a

Polymer	M_n (kg mol ⁻¹)	$\bar{D}$	DP ^b
P(DPP-2T)	26.9	2.1	44
P(DPP-TEET)	11.3	1.7	17
P(DPP-TET)	13.3	2.1	21
P(DPP-C3)	21.6	2.0	34
P(DPP-2T) _{0.9} (DPP-TEET) _{0.1}	30.2	1.7	49
P(DPP-2T) _{0.8} (DPP-TEET) _{0.2}	24.3	1.8	39
P(DPP-2T) _{0.7} (DPP-TEET) _{0.3}	29.9	1.7	48
P(DPP-2T) _{0.3} (DPP-TEET) _{0.7}	15.8	2.2	24
P(DPP-2T) _{0.1} (DPP-TEET) _{0.9}	12.4	2.4	19

^aPerformed in trichlorobenzene at 140 °C. ^bDegree of Polymerization (2 × repeating unit, n).

2.2 Optical and Electrochemical Properties

We next applied Ultraviolet-Visible (UV-Vis) absorption spectroscopy and cyclic voltammetry (CV) to investigate the effective conjugation, optical band gap, energy levels, and aggregation behavior of all polymers in this study. We collected UV-Vis absorption spectra of all polymers in both diluted solutions in chloroform and thin films spin-coated from concentrated chlorobenzene solution onto pre-treated glass substrates. All materials show similar trends with a slight redshift on the absorption onset (λ_{onset}) when comparing their solution to film spectra (Figure 1). However, there are some subtle differences between different polymers. Although P(DPP-TET) was expected to show a more red-shifted absorbance to P(DPP-TEET) or P(DPP-C3) due to its extended conjugation [25], which is indeed the case when comparing the absorption maxima for these three polymers (Figure 1a and 1b, Table 2), P(DPP-TEET) shows a pronounced tail to a longer wavelength in both film and solution spectra. We tentatively ascribe this observation to two possible factors. Compared with P(DPP-C3), P(DPP-TEET) has two additional ester units in the backbone, which can induce non-covalent interactions (e.g., S...O (in ester)) between the polymers, facilitated by the fact that DPP is known to have a strong tendency to aggregate [34]. On the other hand, P(DPP-TET) could also have such an

intermolecular interaction, yet it lacks the flexible ethylene linker in between the two ester units as in the case of P(DPP-TEET); this flexible linker could allow the conjugated units to use the conformational freedom to enable the intermolecular interaction. Because of the likely intermolecular interaction in P(DPP-TEET), its thin film absorption onset is almost identical to that of the fully conjugated polymer P(DPP-2T), resulting in an unusually small band gap. This observation is also evident in the thin film UV-Vis spectra of the terpolymers constructed from P(DPP-TEET) and P(DPP-2T) (Figure 1c and 1d); despite having disrupted conjugation due to the incorporation of TEET, all terpolymers exhibit a red-shifted absorption onset comparable to P(DPP-2T). However, their absorption maxima still show the expected increasing trend as the molar percent of 2T increases.

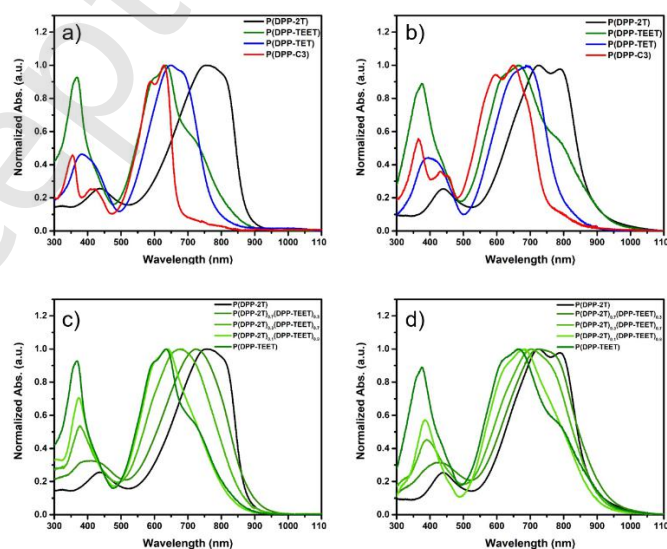


Figure 1. Normalized UV-Vis absorption spectra of Physical blending polymers (a. solution, b. film) and Chemical blending polymers (c. solution, d. film).

Table 2. Summary of the Optical and Electrochemical properties determined in Chloroform solution and film states cast from Chlorobenzene.

Polymer	Solution		Film				
	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	HOMO (eV) ^a	LUMO (eV) ^b
P(DPP-2T)	758	892	727	878	1.42	-5.15	-3.73
P(DPP-TEET)	635	845	662	918	1.35	-5.44	-4.08
P(DPP-TET)	650	780	687	802	1.55	-5.24	-3.69
P(DPP-C3)	628	670	650	757	1.64	-5.25	-3.61

P(DPP-2T) _{0.5} (DPP-TEET) _{0.5} 1	742	890	749	898	1.38	-5.15	-3.76
P(DPP-2T) _{0.5} (DPP-TEET) _{0.5} 2	734	889	726	896	1.39	-5.24	-3.85
P(DPP-2T) _{0.5} (DPP-TEET) _{0.5} 3	723	888	722	894	1.39	-5.27	-3.88
P(DPP-2T) _{0.5} (DPP-TEET) _{0.5} 7	680	866	705	896	1.39	-5.30	-3.91
P(DPP-2T) _{0.5} (DPP-TEET) _{0.5} 9	638	829	685	892	1.39	-5.30	-3.91

^aCalculated from the E_{ox} . ^bCalculated from the HOMO + E_g^{opt} . The E_{ox} was determined by employing a 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile solution as the supporting electrolyte.

We further conducted cyclic voltammetry (CV) to estimate the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for all polymers (**Figure S4**). The HOMO energy levels were calculated from the conversion of the oxidation onset (E_{ox}) through the ferrocene standard (E_{Fc}) using the equation $HOMO = -(4.8 + (E_{ox} - (E_{Fc})))$. Typically, LUMO energy levels are estimated by substituting the E_{ox} for the reduction onset (E_{red}); however, polymers containing an electron-poor DPP moiety often do not show clear reduction under this method [35-37]. For this reason, LUMO was estimated from the optical band gap ($E_g^{opt} = 1240/\lambda_{onset}$, where λ_{onset} is the film absorption onset) using the equation $LUMO = HOMO + E_g^{opt}$. Optical and electrochemical properties are summarized in **Table 2**. For both copolymers and terpolymers, a higher HOMO energy level is generally expected with an increased effective conjugation along the backbone. However, in spite of having similar broken conjugation by alkyl linkers, P(DPP-TEET) has a noticeably lower HOMO energy level (-5.44 eV) than that of P(DPP-C3) (-5.25 eV); we ascribe this to the incorporation of the electron-withdrawing esters in P(DPP-TEET), which can lower the HOMO energy level.

2.3 Charge Transport Properties in Organic Field-Effect Transistors

We next evaluated the charge transport properties of both physical and chemical blending approaches using OFETs. Devices were fabricated in a bottom-gate/top-

contact configuration on heavily doped Si substrates (gate electrode) covered with 300 nm of SiO₂ dielectrics treated with octadecyltrichlorosilane (OTS), with Au as the source and drain electrodes. For the organic semiconductor layers, physical blends were prepared by mixing stock solutions of P(DPP-2T) with either P(DPP-TEET), P(DPP-TET), or P(DPP-C3) at various weight fractions. Both physical blends and chemical blends (i.e., terpolymers) were then spin-coated onto the substrates and thermally annealed at 130 °C for 15 min prior to the electrical characterization.

2.3.1 Physical Blending

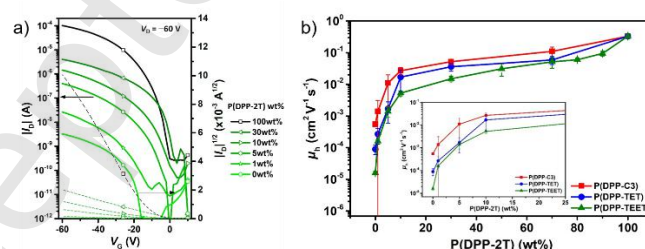


Figure 2. a) Representative transfer curves from field-effect transistors made with physical blends of P(DPP-2T) and P(DPP-TEET). Complete dataset with all weight percentages is included in the SI as **Figure S5a**. b) Hole mobility as a function of P(DPP-2T) weight percent in physical blends with P(DPP-C3) (red), P(DPP-TET) (blue), and P(DPP-TEET) (green).

We used transfer curves to quantify the charge transport properties of the physical blending approach. Using P(DPP-TEET) as the matrix and P(DPP-2T) as the tie-chain polymer, **Figure 2a** presents how the transfer curve changes as the weight percentage of P(DPP-2T) increases within the P(DPP-TEET) matrix (the complete dataset in **Figure S5a**). For comparison, we also obtained transfer curves for the P(DPP-TET) (**Figure S5b**) and P(DPP-C3) (**Figure S5c**) blends, with detailed charge transport properties for all three physical blending systems summarized in **Table S1**. To visualize the trend in mobility when blending different amounts of the tie-chain polymer, we plotted the calculated hole mobility values as a function of the P(DPP-2T) weight percentages for all these physical blending systems in **Figure 2b**.

The average hole mobilities of the individual polymers are 0.33, 1.6×10^{-5} , 9.0×10^{-5} , and $5.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for P(DPP-2T), P(DPP-TEET), P(DPP-TET), and P(DPP-C3), respectively. Notably, the obtained hole mobility of P(DPP-

2T) is comparable to literature values [37,38], whereas the other three matrix polymers show orders of magnitude lower mobilities (due to broken conjugation in their π -conjugated backbones). However, with the addition of 1 wt% P(DPP-2T), the average hole mobility in the case of P(DPP-TEET) is improved by an order of magnitude (from 1.6×10^{-5} to 1.6×10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) and by over two orders of magnitude at 10 wt% blending (to 6.8×10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) (see **Figure 2b** inset and **Table S1**), after which the mobility shows a more gradual increase with higher wt% of P(DPP-2T) (**Figure 2b**). The other two physical blending systems, P(DPP-TET) and P(DPP-C3), show similar trends, i.e., a rapid increase of mobility with the initial small amount of P(DPP-2T), followed by a rather slow improvement in the mobility as more tie-chain polymers are added. Our observed trends in mobilities of these three physical blending systems are similar to the previous reports [26]; however, Mei and co-workers achieved mobility values of the physical blend comparable to that of neat P(DPP-2T) within the 1-10 wt% of added P(DPP-2T) [26], whereas we were only able to achieve 2 orders of magnitude improvement. This discrepancy can be ascribed to the relatively lower molecular weight of the matrix polymers and the tie-chain polymer, as well as in the subtle difference in processing and device fabrication. It is worth noting that Mei and co-workers obtained this mobility enhancement likely because the neat mobility of their matrix polymer was just two orders of magnitude lower than that of the tie-chain polymer; by contrast, our system exhibits four orders of magnitude mobility gap between P(DPP-TEET) and P(DPP-2T).

2.3.2 Chemical Blending

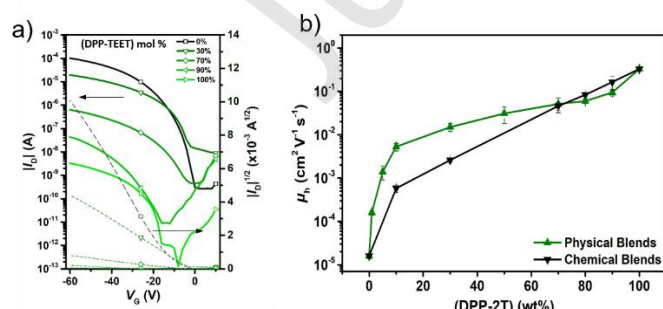


Figure 3. a) Transfer curves from field-effect transistors made with chemical blends. Complete dataset with all mole percentages is included in the SI as **Figure S7**. b) Hole mobility as a function of (DPP-2T) weight percent for Chemical Blending (Black) and Physical Blending (Green).

We applied similar characterization and analysis to the chemical blending system as well, with transfer curves summarized in **Figure 3a** (and **Figure S7**), and hole mobility

values calculated and plotted as a function of the (DPP-2T) weight percentage in the terpolymers (**Figure 3b**, black curve). A comprehensive summary of charge transport properties for the chemical blending system is provided in **Table S2**. Specifically, the average hole mobilities of the individual polymers are 0.33, 0.17, 8.4×10^{-2} , 4.6×10^{-2} , 1.8×10^{-3} , 3.9×10^{-4} , and 1.6×10^{-5} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for P(DPP-2T), P(DPP-2T)_{0.9}(DPP-TEET)_{0.1}, P(DPP-2T)_{0.8}(DPP-TEET)_{0.2}, P(DPP-2T)_{0.7}(DPP-TEET)_{0.3}, P(DPP-2T)_{0.3}(DPP-TEET)_{0.7}, P(DPP-2T)_{0.1}(DPP-TEET)_{0.9}, and P(DPP-TEET), respectively. When these values are plotted together in **Figure 3b**, we obtain an (almost) linear relationship on a semi-log scale between the mobility and the (DPP-2T) content, similar to what others observed in their own chemical blending studies [32]. As expected, increasing the (DPP-TEET) content leads to a decrease in hole mobility, primarily due to the reduced effective conjugation and limited intrachain charge transport pathways.

2.3.3 Comparing Physical vs. Chemical Blending

To compare the differences in OFET performance between the physical blending and the chemical blending systems, we plotted the mobility trend vs. wt.% P(DPP-2T) in P(DPP-TEET) of both systems together in **Figure 3b** (the mol% version in **Figure S8**). It is evident that the physical blending approach only needs a small amount of P(DPP-2T) to largely recover/improve the mobility of the system, whereas the chemical blend matches the mobility of the physical blend only at high wt% of P(DPP-2T) (e.g., 70 wt%). To examine whether the observed mobility enhancement originates from reduced trap density, we performed subthreshold-slope analysis and estimated the apparent trap density from the transfer characteristics. The apparent trap densities remain within the same order of magnitude across the series and do not monotonically follow the mobility trends (**Table S4** and **S5**, Supporting Information). In particular, the P(DPP-TEET):P(DPP-2T) physical blends show substantial mobility enhancement upon the addition of P(DPP-2T), yet the apparent trap density does not decrease accordingly. These results indicate that reduced trap density is not the primary origin of the mobility enhancement. Instead, the improved performance is more consistent with enhanced charge-transport connectivity and increased structural ordering upon incorporation of the fully conjugated P(DPP-2T) component, as further supported by

the morphological analysis below.

2.3.4 End-of-Life Behavior and Sustainability Assessment

It is important to distinguish three related but non-equivalent descriptors in this work. The ester-containing fraction refers to the weight (or mole) fraction of the film that carries cleavable ester linkages (either in the form of incorporated homopolymers or the form of the repeat unit in copolymers) and is a purely compositional quantity. Degradability (depolymerizability) refers to the demonstrated cleavage of those linkages under a defined set of conditions, and recyclability refers to the recovery of monomers in a form that can be repolymerized into the parent polymer. A high ester-containing fraction is a prerequisite for, but not evidence of, either of the latter two.

To assess the end-of-life behavior of the materials studied here, we subjected the P(DPP-TEET) used throughout this work to methanolysis and did not observe full depolymerization by ^1H NMR analysis. However, complete conversion to the desired dimethyl ester monomer was observed for a shortened side chain analogue, P(DPPC1-TEET), in which the spacer between the backbone and the branching point of the side chain is reduced from four carbons to one (**Figure S10**, Supporting Information). This difference in reactivity may stem from the polymer's tendency to aggregate in solution. Polymers having a relatively long straight chain before the branching point in the side chain design, such as the ones used in this study, are generally believed to aggregate more strongly due to enhanced backbone interactions, which in turn hinder the access to (and the reactivity of) the ester functionalities. Conversely, a shorter carbon chain to the branching point can create more steric hindrance and reduce backbone interactions, thereby allowing methanolysis to proceed more effectively. Accordingly, closed-loop recyclability is established here for P(DPPC1-TEET) rather than for the specific polymers used in the blending studies, and the ester-containing fraction of the blends should be read as the fraction of the film that is chemically addressable at end of life rather than as a demonstrated recyclable fraction.

From a sustainability standpoint, although ester-incorporated matrix polymers offer a more sustainable solution, they lack the necessary pathways for efficient intrachain charge transport. Physical blending offers a

compelling strategy to enhance the charge transport properties using small amounts of a non-degradable polymer and yields a semiconducting film in which 90 wt% of the material remains ester-containing and therefore chemically addressable at end of life, thereby reducing its contribution to electronic waste. By contrast, although chemical blending does not have mobility gain at low DPP-2T levels, at higher loading (up to 70%), it delivers reasonably good charge transport performance while retaining ester linkages distributed along the backbone. We note that the depolymerization behavior of these terpolymers has not been established experimentally in this work; because ester cleavage within a terpolymer backbone would generate oligomeric rather than monomeric fragments, any closed-loop recyclability would additionally require the repolymerization of those oligomers and therefore remains a design expectation rather than a demonstrated property. Finally, fully conjugated tie-chain polymers provide the highest mobility values but lack mechanisms to achieve sustainability through decomposition or recycling. **Figure 4** presents a comparative visualization of these key metrics, highlighting the balance between sustainability and charge transport performance.

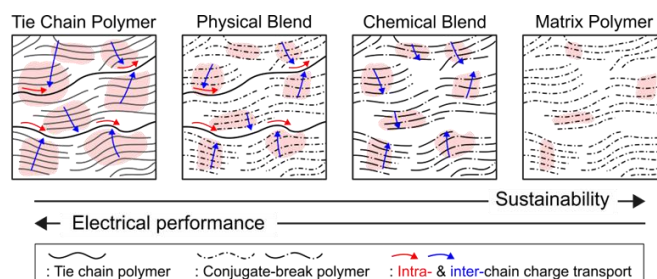


Figure 4. Comparative visualization of *Sustainability* and *Performance* across the polymer systems studied.

From the synthesis perspective, even though both physical and chemical blending approaches rely on shared monomeric units, their synthetic complexity differs. A full scale LCA (life cycle assessment) is needed to *comprehensively* compare these two different approaches, which should include the cost of raw materials and the degraded products as well as recycled monomers/oligomers/polymers. These exercises are beyond the scope of this work; nevertheless, we will offer some initial observations. For terpolymers, a key advantage

is the one-pot reaction, which reduces solvent use and catalyst consumption. By contrast, polymers prepared for physical blending require two separate polymer batches. Furthermore, because the two polymers may differ in polarity, phase separation can become a concern in thin film-based applications. Although phase separation-induced nanoconfinement has been shown to preserve performance in blends with insulating polymer, this effect has not yet been demonstrated for the type of polymers investigated in this work [39]. When looking into balancing sustainability and performance, polymer design strategies should not solely rely on the incorporation of degradable linkers; ideally, new strategies should also ensure efficient charge transport and reproducibility (i.e., consistent output). A holistic evaluation is needed for each new design strategy.

2.3.5 Morphological Characterization

As charge transport in OFET is heavily influenced by the thin film morphology, we next applied AFM and GIWAXS to investigate how morphological characteristics in representative polymer blends and terpolymers influence performance. We first employed AFM (**Figure 5**) to assess phase-separation behavior. Across all systems, including the physical blends of P(DPP-TEET) with P(DPP-2T) (**Figure 5a**), P(DPP-TET) with P(DPP-2T) (**Figure 5b**), and the chemical blends (**Figure 5c**), no fibrillar features or phase-segregated domains were observed. Instead, each system formed a uniform, miscible film. This indicates that nanoconfinement is unlikely to explain the dramatic mobility enhancement observed upon addition of P(DPP-2T) for both physical blends systems as well as the chemical blends (which are single component systems).

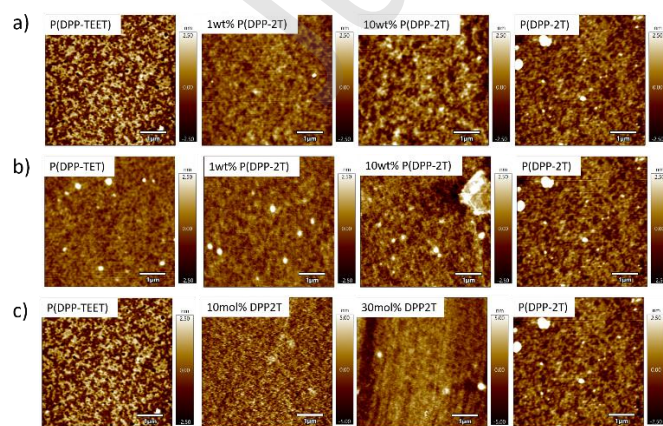


Figure 5. AFM images of a) Physical Blends made of P(DPP-TEET) and P(DPP-2T), b) Physical Blends made of P(DPP-TET) and P(DPP-2T), c) Chemical Blends.

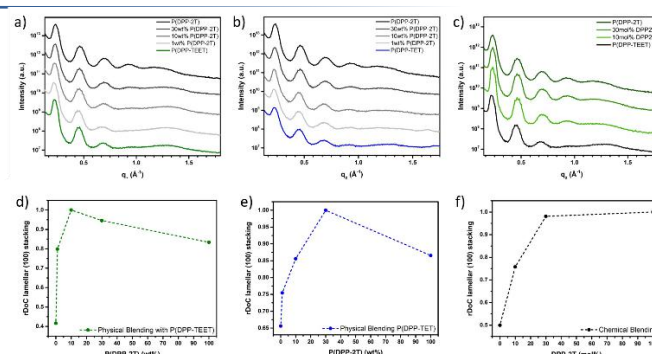


Figure 6. 1D GIWAXS diffraction patterns of a) Physical Blends of P(DPP-TEET) and P(DPP-2T) b) Physical Blends of P(DPP-TET) and P(DPP-2T), c) Chemical Blends. GIWAXS relative degree of crystallinity (100) stacking of d) Physical Blends of P(DPP-TEET) and P(DPP-2T), e) Physical Blends of P(DPP-TET) and P(DPP-2T), f) Chemical Blends.

To gain deeper insight into the morphological impact, we conducted solid-state structural characterization using GIWAXS. **Figure 6a-c** present the 1D diffraction profiles, while **Figures 6d-f** show the relative degree of crystallinity (rDoC) associated with the lamellar (100) stacking. The corresponding 2D diffraction patterns are provided in **Figure S9**. The 1D diffraction data consistently shows that, as the conjugated polymer content increases in both physical blends and chemical blends (terpolymers), the intensity near $0.9 \text{ \AA}^{-1}$ becomes stronger, indicating higher crystallinity across all systems. This trend is further supported by the rDoC analysis in **Figures 6d-f**. The matrix polymers, P(DPP-TEET) and P(DPP-TET), exhibit the lowest crystallinity which likely contributes to their poor charge-transport performance, as insufficient packing limits intermolecular transport on top of their disrupted conjugation along the polymer backbone. By contrast, the fully conjugated polymer P(DPP-2T) displays a significantly higher degree of crystallinity, consistent with its rigid conjugated structure and better aggregate formation.

For the physical blends, **Figure 6d** and **Figure 6e** illustrate how rDoC changes relative to increasing P(DPP-2T) weight percentage. In the P(DPP-TEET):P(DPP-2T) blends (**Figure 6d**), even the addition of just 1 wt% P(DPP-2T) leads to an increase in crystallinity relative to the neat P(DPP-TEET), with a further rise at 10 wt% and a slight decrease at 30 wt%. The corresponding improvements in hole mobility directly correlate with enhanced crystallinity. A similar trend was observed in the P(DPP-TET) blends (**Figure 6e**), where rDoC steadily increases with higher P(DPP-2T) loading. These results suggest that although the ester-incorporated polymers are inherently more

amorphous, blending them with a fully conjugated polymer promotes the formation of more crystalline domains, thereby improving charge transport. Finally, the terpolymers show a direct relationship between the amount of conjugated segment and overall crystallinity. This behavior likely arises from the increasingly rod-like polymer architecture at higher conjugated-segment content, which facilitates aggregation and ordered packing; by contrast, the more flexible saturated carbons in the DPP-TEET unit would introduce conformational freedom and suppress crystallinity.

3 CONCLUSIONS

Building off a high mobility conjugated polymer, P(DPP-2T), we introduced an ester linker into the polymer backbone to explore the degradability and recyclability of resulting polymers while retaining the charge carrier mobility. Our results show that conjugated polymers incorporating an ester linker into every repeat unit of the conjugated backbone (e.g., P(DPP-TEET) and P(DPP-TET)) only exhibit poor mobilities. However, physical blending of as little as 10 wt% of P(DPP-2T) as the tie-chain polymer increases the hole mobility of the ester-incorporated polymer-based blends by two orders of magnitude, while retaining 90 wt% of the ester-containing polymer in the film. We stress that this ester-containing fraction defines the portion of the film that is chemically addressable at end of life and should not be equated with a demonstrated recyclable or degradable fraction; under the conditions examined here, quantitative depolymerization to recoverable monomer was achieved only for the shortened side chain analogue P(DPPC1-TEET). On the other hand, chemical blending represents a modular strategy in which the ester content and the performance can be tuned in tandem, as reflected by the linear trend observed in the semi-log plot of hole mobility as a function of DPP-2T mol%.

Recently, imine linkers have been used to impart degradability and recyclability to conjugated polymers; however, these imine-incorporated conjugated polymers still cannot match the performance of their fully conjugated, all-carbon counterparts [13,15]. Taken together with our results in this work and previous report [25], these results indicate that new strategies enabling closed-loop recycling while maintaining high device performance are still required in the long term. In the meantime, strategic application of physical blending and chemical blending offers a promising

short-term solution.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909141>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

AMB and WY conceived the idea. AMB, SHK, SM acquired the data. All authors contributed to the data analysis. AMB, SHK and WY wrote the initial draft. All authors contributed to the writing of the revised manuscript. WY was responsible for the project administration and funding acquisition. HA was also responsible for funding acquisition. All the authors have approved the final manuscript.

Informed consent

"Not applicable"

Ethics statement

"Not applicable"

Use of AI statement

"None."

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Electronic Supplementary Material

Balancing sustainability and performance in ester-incorporated polymers for organic field-effect transistors via physical and chemical blending

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Materials and Methods

All chemicals were purchased from commercial sources (Sigma-Aldrich, Fisher, Ambeed, etc.) and were used as received. High temperature gel permeation chromatography (HT-GPC) measurements were performed on an Agilent 1260 HT-GPC instrument with TCB (1,2,4-trichlorobenzene) as the eluent at 140 °C. The obtained molar mass is relative to the polystyrene standard. ¹H nuclear magnetic resonance (NMR) measurements were recorded with Bruker DRX spectrometer (400 MHz) and Bruker Avance Neo (600 MHz) spectrometer. UV-visible absorption spectra were obtained with a JASCO V-770 spectrophotometer. CV measurements were conducted on thin films using a CH Instruments 600E potentiostat with a standard three-electrode configuration. A three-electrode cell of a glassy carbon working electrode, Ag/Ag⁺ reference electrode, and Pt counter electrode were used. Films were drop-cast onto the glassy carbon electrode from a hot chlorobenzene mixture (2 mg/mL, with tetrabutylammonium hexafluorophosphate added at 100 wt%). 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as a supporting electrolyte. Scans were conducted under an argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple.

Atomic force microscopy (AFM)

Tapping mode AFM images were collected on an Asylum MFP 3D system with silicon tips with a nominal resonant frequency of 300 kHz and a stiffness of 40 N/m. A scan rate of 0.75 Hz and a setpoint of 1V were used. Images were acquired in repulsive mode (phase less than 90 degrees) by adjusting the drive amplitude.

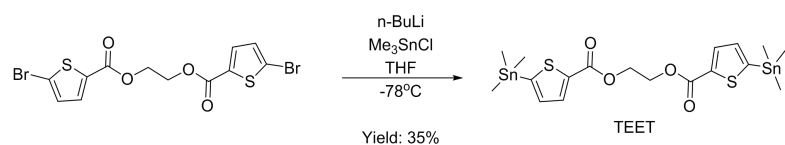
Grazing-Incidence Wide-Angle X-Ray Scattering (GIWAXS)

GIWAXS measurements were conducted using a laboratory based Xeuss 3.0 (Xenocs) system equipped with a Cu (8 keV) source. The samples were placed in a vacuum compartment during the measurements. Data were acquired at an incidence angle of 0.18° which is slightly above the critical angle of the film. The 2-D data were recorded with a Dectris Eiger2 1M detector with a pixel size of 75 μm and placed at a distance of 75 mm from the samples. The scattering data were analyzed using a custom Nika package for Igor Pro (Wavemetrics Inc.) [1].

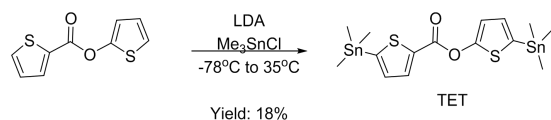
The one-dimensional in-plane (IP) and out-of-plane (OoP) profiles were extracted using 10° cake sectors. The π-π and lamellar stacking regions of the neat and blend profiles were analyzed by fitting multiple Gaussian peaks over a polynomial background. GIWAXS pole figures were generated from the missing-wedge-corrected 2D patterns by integrating the intensity at each detector azimuth over the *q*-range corresponding to the lamellar or π-π stacking peak of interest. A linear background, interpolated from the intensities at the two boundaries of the selected *q*-range, was then subtracted. Geometric correction of the intensity was performed by multiplying the background-subtracted intensity at each azimuthal angle by sinχ, where the detector azimuth, χ, is defined as the angle between the observed diffraction and the substrate normal. The relative degree of crystallinity (rDoC) was determined by integrating the geometry-corrected intensity over the detector azimuth, $rDoC = \int_0^{2/\pi} I(\chi) \sin\chi d\chi$, and normalizing the result by the illuminated sample volume, as determined from the sample length along the beam direction and the film thickness. Assuming similar structure factors the normalized rDoC calculated from the pole figure in the *q*-range 0.15–0.3 Å⁻¹ covering the lamellar stacking peaks and in the range 1.6–2 Å⁻¹ covering the π-π peaks. Because the contributions from DPP-2T and DPP-TEET/DPP-TET cannot be resolved owing to their overlapping peak positions, the rDoC values derived from the pole figures represent the overall degree of lamellar or π-π ordering in the blend films.

Synthetic scheme of ester-incorporated monomers

TEET Monomer:



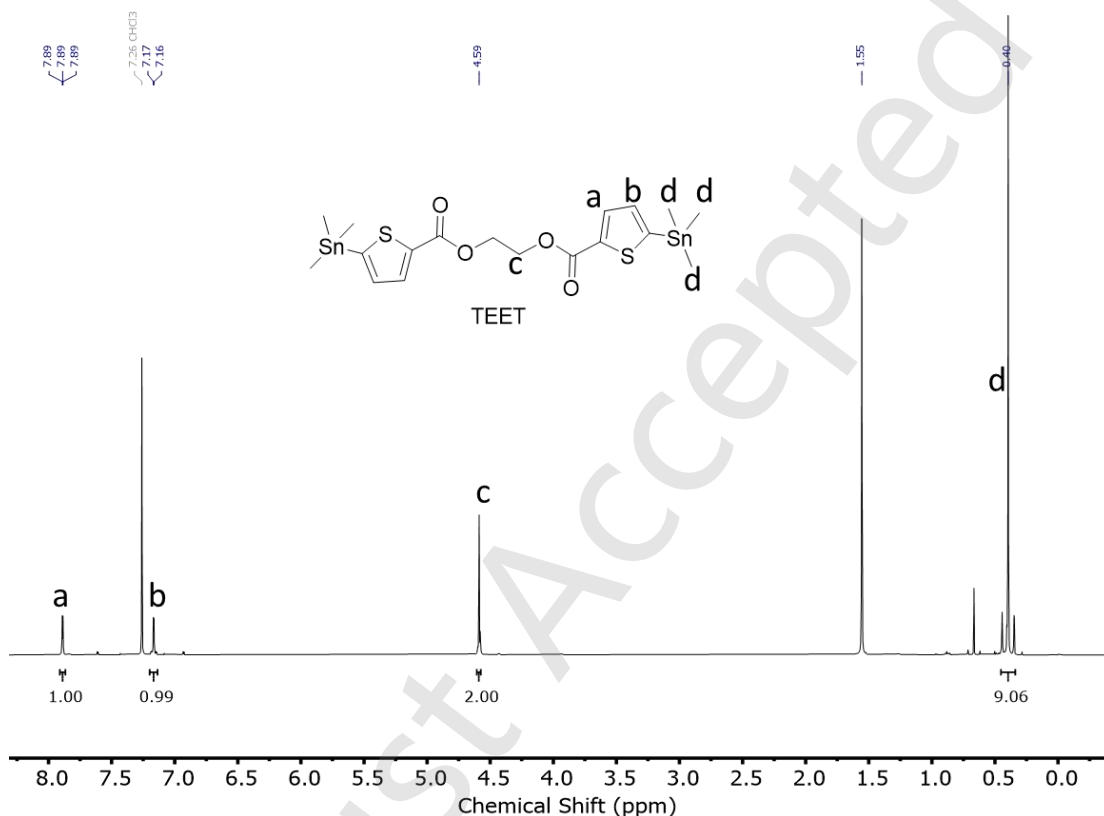
TET Monomer:

**Figure S1.** Representative synthetic scheme of ester-incorporated monomers (TEET and TET).

Detailed Synthetic Procedures and ^1H NMR data:**Synthesis of TEET: ethane-1,2-diyl bis(5-(trimethylstannyl)thiophene-2-carboxylate)**

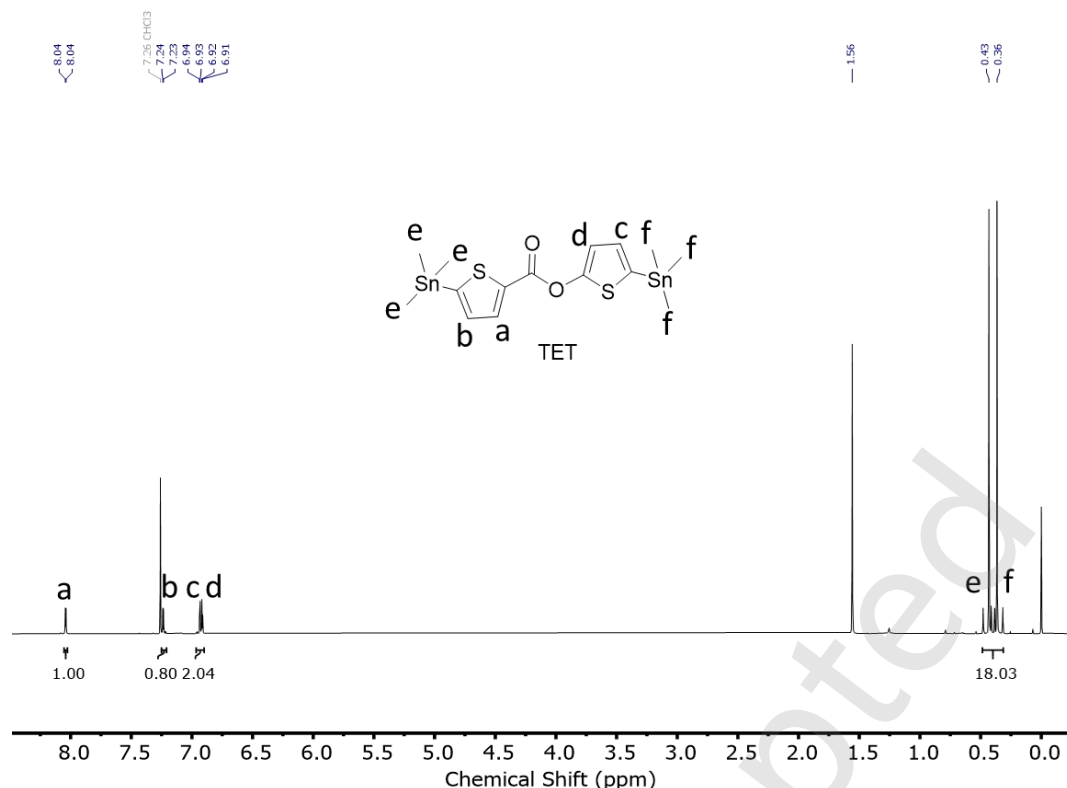
To a 250mL 2-neck round-bottom flask, ethane-1,2-diyl bis(5-bromothiophene-2-carboxylate) (602.5mg, 1 Eq, 1.369 mmol) was added. The mixture was evacuated and refilled with argon three times before addition of anhydrous tetrahydrofuran (THF) under argon stream. The reaction mixture was cooled to -78°C followed by the dropwise addition of butyllithium (0.18g, 1.1mL, 2.5 molar, 2.0 Eq, 2.8 mmol) which was left to react for 1 hour. Chlorotrimethylstannane (0.70 g, 3.5mL, 1 molar, 2.6 Eq, 3.5 mmol) was added slowly as the reaction turned from dark green to orange. The reaction was left to react to room temperature overnight. Ethyl acetate was added to the reaction mixture and washed using water, saturated KF aqueous solution and brine. The organic phase was dried over sodium sulfate, filtered and concentrated under reduced pressure. The resulting light-yellow viscous oil was dissolved in hexane and left on the fridge overnight to let impurity precipitate. Leaving yellow precipitate behind, the liquid was transferred to a clean vial and solvent was evaporated under reduced pressure and subsequently left overnight under vacuum. The yellow solid was washed one more time with hexane to obtain a faint yellow solid ethane-1,2-diyl bis(5-(trimethylstannyl)thiophene-2-carboxylate) (291.2 mg, 479.0 μmol , 34.99%).

^1H NMR (600 MHz, CDCl_3) δ : 7.89 (d, 2H), 7.16 (d, 2H), 4.59 (s, 4H), 0.40 (t, 18H)

**Synthesis of TET: 5-(trimethylstannyl)thiophen-2-yl 5-(trimethylstannyl)thiophene-2-carboxylate**

To a 100mL 3-neck round-bottom flask, thiophen-2-yl thiophene-2-carboxylate (292.3 mg, 1 Eq, 1.390 mmol) was added. The mixture was evacuated and refilled with argon three times before addition of anhydrous tetrahydrofuran (THF) under argon stream. The reaction mixture was cooled to -78°C followed by the dropwise addition of lithium diisopropylamide (0.30 g, 1.4mL, 2 molar, 2.0 Eq, 2.8 mmol) which was left to react for 1 hour. Chlorotrimethylstannane (0.64 g, 3.2mL, 1 molar, 2.3 Eq, 3.2 mmol) was added and left reacting for 30 minutes at -78°C and another 30 minutes at 35°C . Ethyl acetate was added to the reaction mixture and washed using water, saturated KF aqueous solution and brine. The organic phase was dried over sodium sulfate, filtered, concentrated under reduced pressure and left under vacuum overnight. The desired product was obtained through crystallization in methanol to yield a tan colored solid 5-(trimethylstannyl)thiophene-2-yl 5-(trimethylstannyl)thiophene-2-carboxylate (137.0 mg, 255.7 μmol , 18.39%).

^1H NMR (600 MHz, CDCl_3) δ : 8.04 (d, 1H), 7.24 (d, 1H), 6.94 (d, 1H), 6.92 (d, 1H), 0.43 (t, 9H), 0.36 (t, 9H)



General Synthetic Details for Polymers

Physical Blending Approach

DPP-based monomer (1.0 eq.), stannylated monomer (TEET, TET, C3, or 2T) (1.0 eq.), and Pd(PPh₃)₄ (0.04 eq.) were charged into a 10 mL microwave reactor vial. The mixture was evacuated and refilled with argon before addition of anhydrous toluene (1mL) and N,N-Dimethylmethanamide (0.1mL) under argon stream. The reaction was heated up to 190°C and held in a CEM microwave reactor (300 W) for 30 min. After the polymerization, the crude polymer was dissolved in hot chlorobenzene and precipitated into stirring methanol. The polymer was extracted via a Soxhlet extractor with hexanes, ethyl acetate, and finally collected in chloroform. The polymer solution was concentrated and re-precipitated in MeOH then collected via filtration and dried under vacuum.

P(DPP-2T); Yield: 93.8%

P(DPP-TEET); Yield: 51.9%

P(DPP-TET); Yield: 92.4%

P(DPP-C3); Yield: 64.0%

Chemical Blending Approach

DPP-based monomer (1.0 eq.), TEET monomer (x/100 eq.), 2T monomer ((100-x)/100 eq.) (where x = 10, 20, 30, 70, and 90), Pd₂dba₃·CHCl₃ (0.02eq.), and Tri(o-tolyl)phosphine (0.16eq.) were charged into a 10 mL microwave reactor vial. The mixture was evacuated and refilled with argon before addition of anhydrous toluene (1mL) and N,N-Dimethylmethanamide (0.1mL) under argon stream. The reaction was heated up to 190°C and held in a CEM microwave reactor (300 W) for 30 min. After the polymerization, the crude polymer was dissolved in hot chlorobenzene and precipitated into stirring methanol. The polymer was extracted via a Soxhlet extractor with hexanes, ethyl acetate, and finally collected in chloroform. The polymer solution was concentrated and re-precipitated in MeOH then collected via filtration and dried under vacuum.

P(DPP-2T)_{0.9}(DPP-TEET)_{0.1}; Yield: 81.0%

P(DPP-2T)_{0.8}(DPP-TEET)_{0.2}; Yield: 87.2%

P(DPP-2T)_{0.7}(DPP-TEET)_{0.3}; Yield: 91.9%

P(DPP-2T)_{0.3}(DPP-TEET)_{0.7}; Yield: 35.9%

P(DPP-2T)_{0.1}(DPP-TEET)_{0.9}; Yield: 24.1%

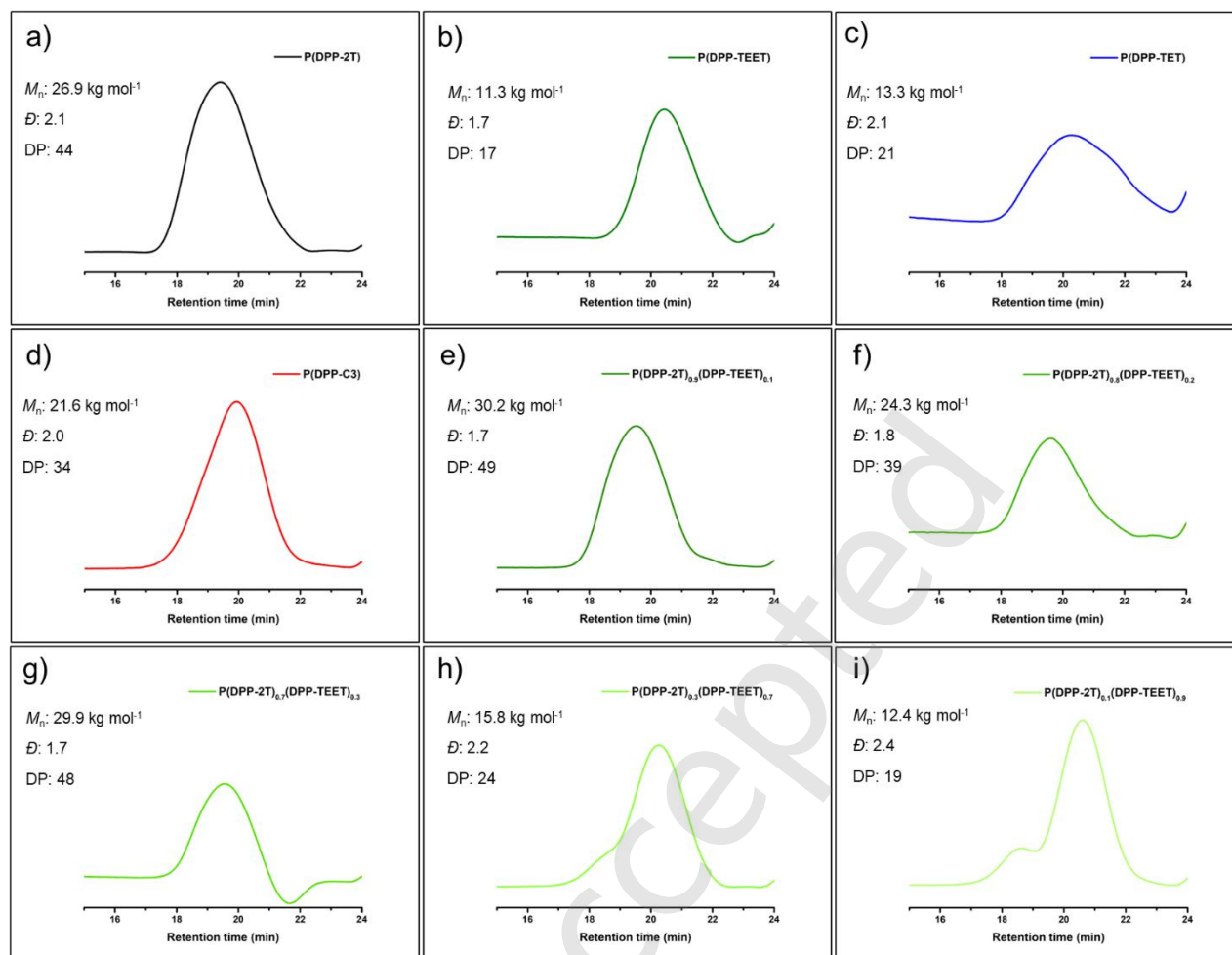


Figure S2. HT-GPC Chromatograms for a) P(DPP-2T), b) P(DPP-TEET), c) P(DPP-TET), d) P(DPP-C3), e) P(DPP-2T)_{0.9}(DPP-TEET)_{0.1}, f) P(DPP-2T)_{0.8}(DPP-TEET)_{0.2}, g) P(DPP-2T)_{0.7}(DPP-TEET)_{0.3}, h) P(DPP-2T)_{0.3}(DPP-TEET)_{0.7}, and i) P(DPP-2T)_{0.1}(DPP-TEET)_{0.9}.

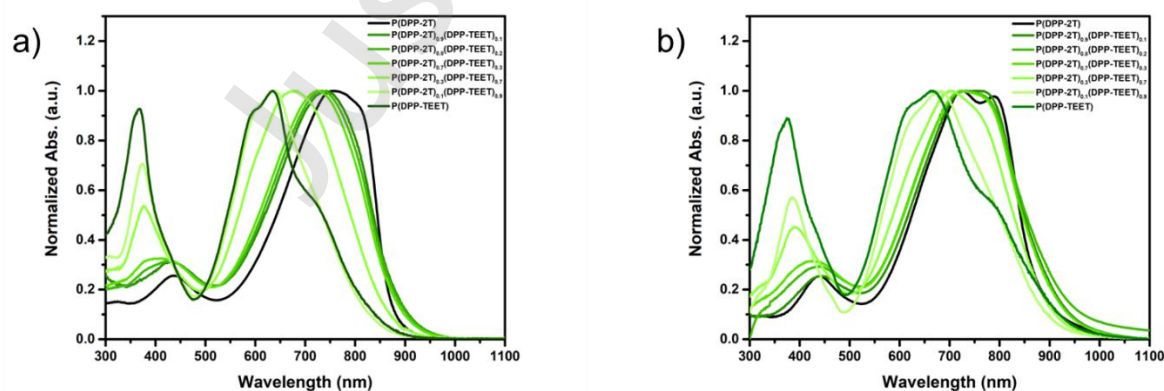


Figure S3. Normalized UV-Vis absorption spectra of Chemical blending polymers (a solution, b film).

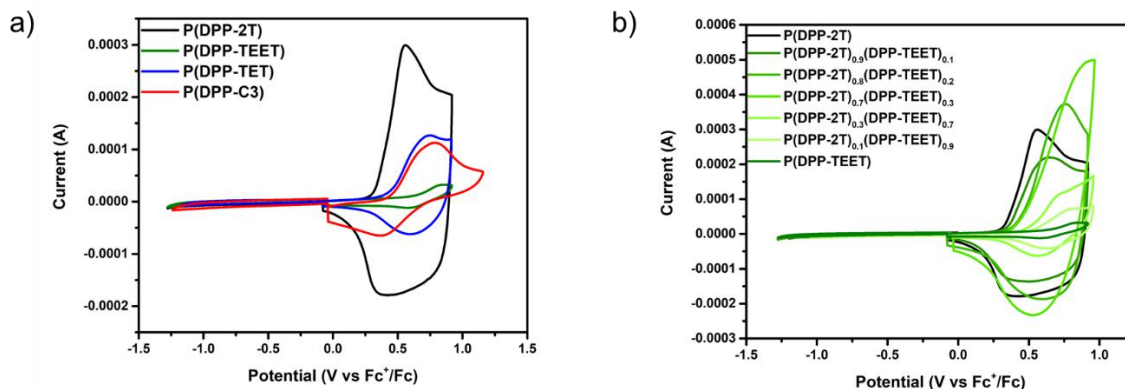


Figure S4. Superimposed cyclic voltammograms for a) Physical blending copolymers and b) Chemical blending terpolymers.

OFET Fabrication and Characterization

Bottom-gate top-contact OFETs were fabricated on heavily *n*-doped Si wafers with a 3000 Å SiO₂ dielectric layer (WaferPro), diced into 15 mm × 15 mm. The substrates were sequentially cleaned in DI water, acetone, and isopropanol for 15 min each. They were then dried in an oven at 60 °C for over 30 min to remove residual solvents, followed by surface activation using O₂ plasma for 30 min. After plasma treatment, the substrates were immersed in an octadecyltrichlorosilane (OTS) solution in toluene for 2 h to form a hydrophobic self-assembled monolayer on the SiO₂ surface. Following OTS modification, the substrates were rinsed thoroughly with toluene, ethanol, and isopropanol and subsequently dried in an oven at 60 °C.

For Physical Blending, P(DPP-2T) was dissolved in chlorobenzene (10 mg mL⁻¹) and stirred on a 60 °C hot plate for 3 h. P(DPP-C3), P(DPP-TET), and P(DPP-TEET) were each dissolved in chloroform (10 mg mL⁻¹) and stirred at 60 °C. After cooling the solutions to room temperature, they were mixed according to the desired weight ratios and stirred again at 60 °C for 30 min. For Chemical Blending, the polymers were dissolved in chloroform at 10 mg mL⁻¹ and stirred for 3 h at 60 °C.

The resulting solutions were spin coated onto the OTS-treated substrates at 2000 rpm for 60 s under ambient conditions. The films were subsequently thermally annealed at 130 °C for 15 min inside a nitrogen-filled glove box. Film thicknesses were measured using a KLA Tencor Alpha-Step® D-100 stylus profilometer. Films for thickness measurements were prepared under the same spin-coating and thermal annealing conditions as those used for OFET fabrication. Gold source and drain electrodes (50 nm) were then deposited through a shadow mask at a rate of 1.0 Å s⁻¹. The channel width (*W*) was defined as 1000 μm and channel lengths (*L*) were 25, 33, 50, and 100 μm.

Transfer and output characteristics were recorded under ambient conditions using a Keithley 2636B source meter. All measurements were carried out without encapsulation. The hole mobility (μ_h) was extracted using the saturation regime equation:

$$I_{D,sat} = \frac{W}{2L} C_i \mu (V_G - V_{th})^2,$$

where $I_{D,sat}$ is the drain current in the saturation regime, *W* and *L* are the channel width and length, respectively, and C_i is the capacitance per unit area of the SiO₂ dielectric ($C_i = 10.8$ nF cm⁻²). μ is the field-effect mobility, V_G is the gate voltage, and V_{th} is the threshold voltage.

The subthreshold slope (SS) was extracted from the linear region of the transfer curve using $SS = dV_G/d(\log_{10}|I_D|)$. The apparent trap density was estimated using $N_{trap} = (C_i/q)[SS/(k_B T \ln 10/q) - 1]$, q is the elementary charge, k_B is the Boltzmann constant, and T is the measurement temperature.

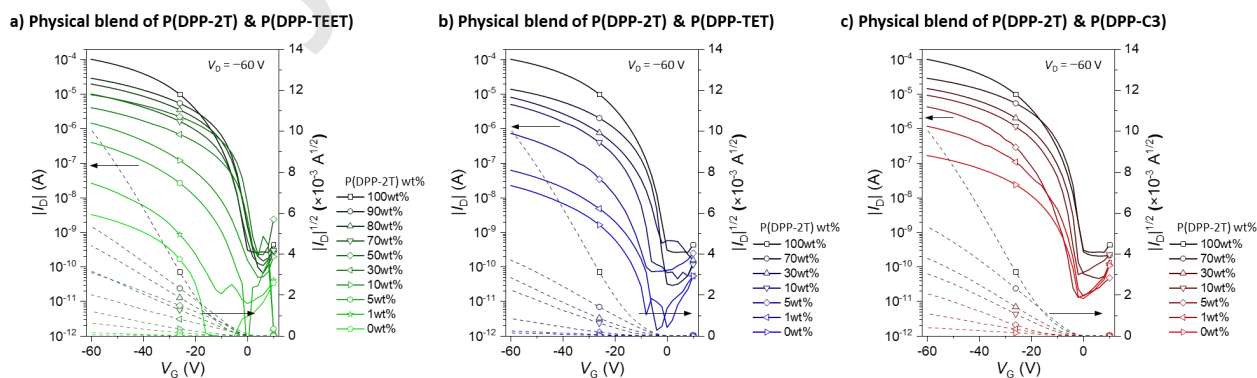


Figure S5. Transfer curves for physical blending strategy of a) P(DPP-TEET), b) P(DPP-TET), and c) P(DPP-C3) blends.

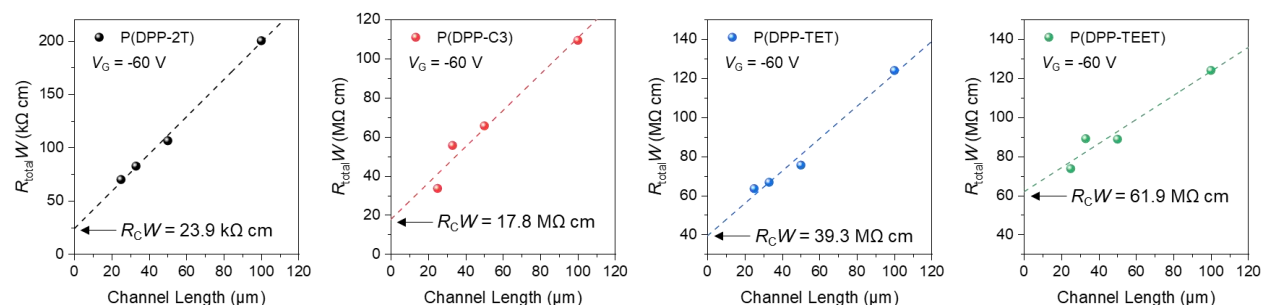


Figure S6. The transfer line method (TLM) plots for OFET devices based on P(DPP-2T), P(DPP-C3), P(DPP-TET), and P(DPP-TEET), respectively. The total resistance ($R_{\text{total}}W$) is plotted as a function of channel length (L) at $V_D = -0.2$ V with device width $W = 1000$ μm (0.1 cm). Linear extrapolation to $L = 0$ provides the contact resistance R_CW . The extracted R_CW values for the four polymer devices are 23.9 k Ω cm for P(DPP-2T), 17.8 M Ω cm for P(DPP-C3), 39.3 M Ω cm for P(DPP-TET), and 61.9 M Ω cm for P(DPP-TEET).

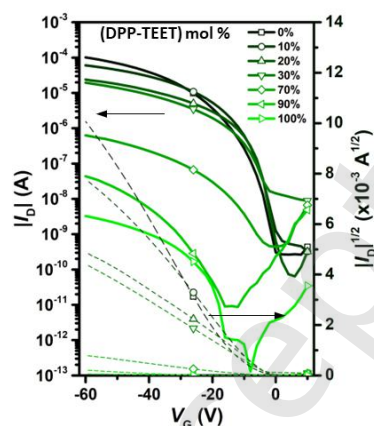


Figure S7. Transfer curves for chemical blending strategy.

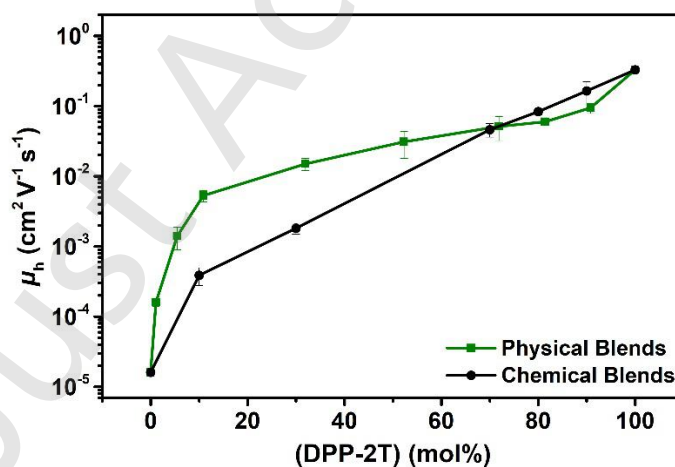


Figure S8. Comparison of the charge carrier mobility as a function of (DPP-2T) mol percent for Chemical Blending (Black) and Physical Blending (Green).

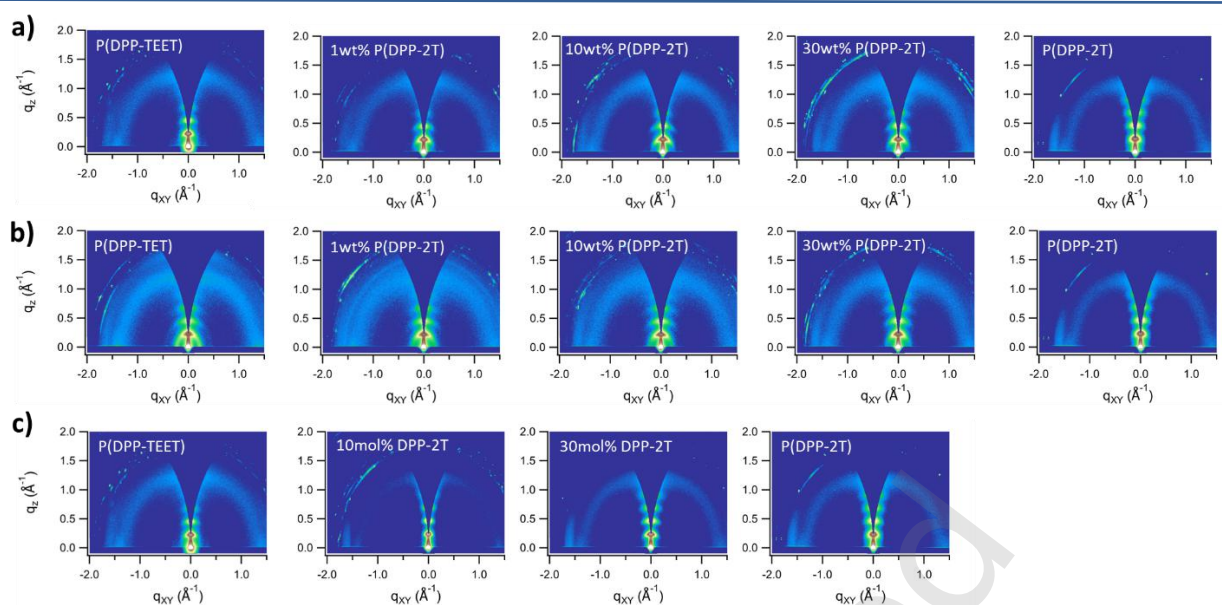


Figure S9. 2D GIWAXS diffraction patterns of a) Physical Blends made of P(DPP-TEET) and P(DPP-2T), b) Physical Blends made of P(DPP-TEET) and P(DPP-2T), c) Chemical Blends.

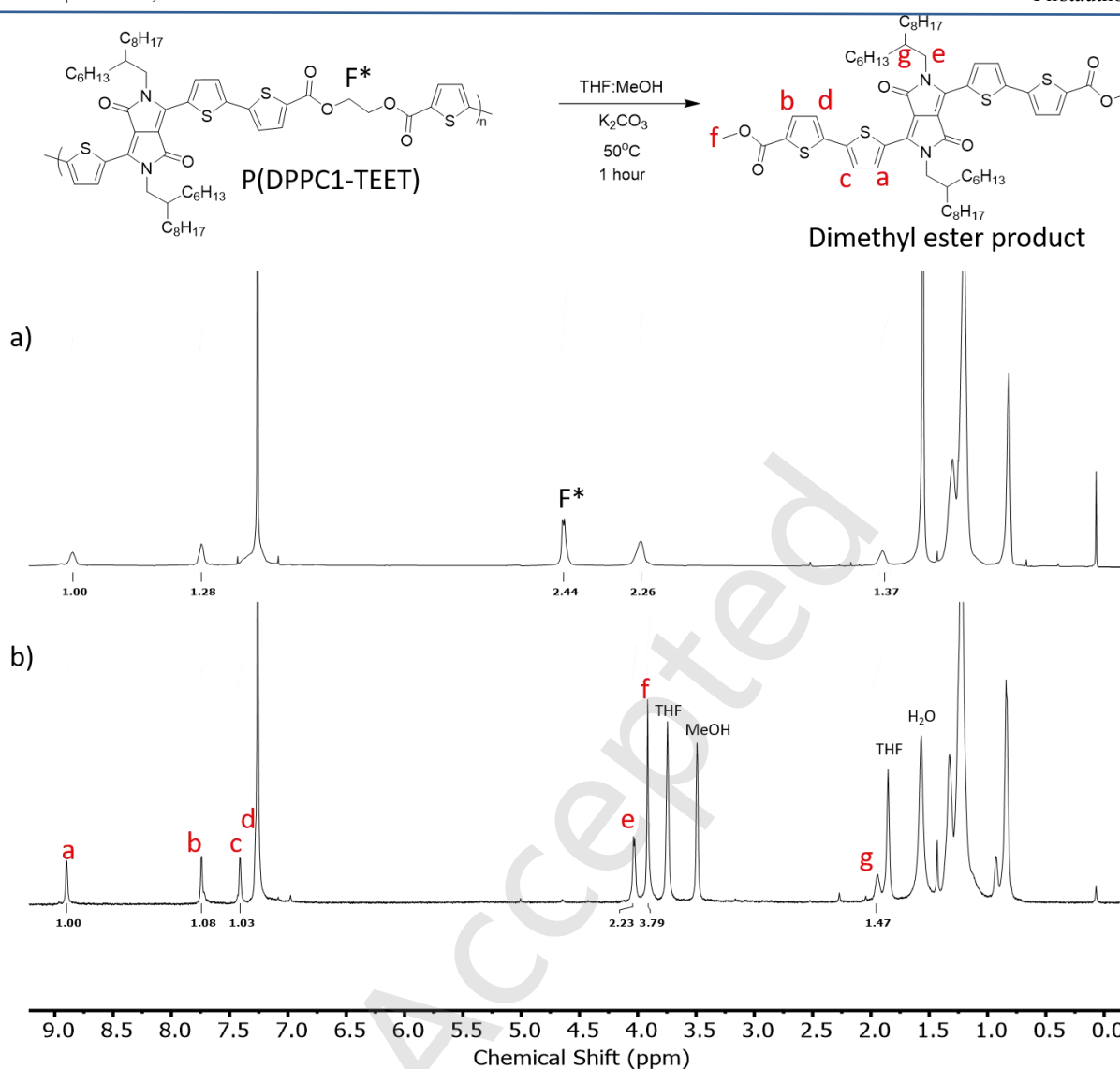


Figure S10. a) ^1H NMR of P(DPPC1-TEET). b) depolymerization product via methanolysis of P(DPPC1-TEET). Methanolysis was carried out as follows: To a 5mL scintillation vial, a stir bar, methanol (562 mg, 710 μL , 578 Eq, 17.6 mmol), tetrahydrofuran (1.2 g, 1.4 mL, 5.7×10^2 Eq, 17 mmol), and Potassium carbonate (8.7 mg, 2.1 Eq, 63 μmol) were added. P(DPPC1-TEET) (31.2 mg, 1 Eq, 30.4 μmol) was then added and left stirring at 50°C for 1 hour. Conversion to dimethyl 5',5'''-(2,5-bis(2-hexyldecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bithiophene]-5-carboxylate) was confirmed by ^1H NMR of the crude reaction mixture.

Table S1. Detailed charge transport characteristics for physical blending strategy.

P(DPP-2T) (wt%)	P(DPP-TEET)			P(DPP-TET)			P(DPP-C3)		
	$\mu_{h, \max} (\mu_{h, \text{avg}})$ [cm ² V ⁻¹ s ⁻¹]	V_{th} (V)	$I_{\text{on}}/I_{\text{off}}$	$\mu_{h, \max} (\mu_{h, \text{avg}})$ [cm ² V ⁻¹ s ⁻¹]	V_{th} (V)	$I_{\text{on}}/I_{\text{off}}$	$\mu_{h, \max} (\mu_{h, \text{avg}})$ [cm ² V ⁻¹ s ⁻¹]	V_{th} (V)	$I_{\text{on}}/I_{\text{off}}$
100	0.37 (0.33 ± 0.03)	-1.3 ± 0.9	6.4 × 10 ⁵	0.37 (0.33 ± 0.03)	-1.3 ± 0.9	6.4 × 10 ⁵	0.37 (0.33 ± 0.03)	-1.3 ± 0.9	6.4 × 10 ⁵
90	0.118 (0.095 ± 0.016)	-2.7 ± 0.9	1.5 × 10 ⁵	-	-	-	-	-	-
80	0.068 (0.060 ± 0.007)	-3.0 ± 2.0	6.8 × 10 ⁴	-	-	-	-	-	-
70	0.070 (0.051 ± 0.019)	-6.7 ± 2.2	5.0 × 10 ⁴	0.083 (0.059 ± 0.017)	-7.1 ± 2.8	2.1 × 10 ⁵	0.18 (0.11 ± 0.04)	-3.7 ± 0.2	3.6 × 10 ⁵
50	0.049 (0.031 ± 0.013)	0.8 ± 1.2	3.5 × 10 ⁴	-	-	-	-	-	-
30	0.018 (0.015 ± 0.003)	-4.6 ± 6.4	9.2 × 10 ⁵	0.056 (0.036 ± 0.010)	-14.0 ± 5.0	3.1 × 10 ⁵	0.067 (0.052 ± 0.010)	-6.7 ± 1.7	5.4 × 10 ⁵
10	0.0068 (0.0053 ± 0.0010)	-9.2 ± 5.2	2.3 × 10 ⁵	0.034 (0.017 ± 0.011)	-10.9 ± 4.5	7.4 × 10 ⁴	0.042 (0.027 ± 0.007)	-14.9 ± 3.6	3.6 × 10 ⁵
5	0.0021 (0.0014 ± 0.0005)	-10.9 ± 4.3	5.5 × 10 ⁵	0.0040 (0.0017 ± 0.0011)	-13.7 ± 3.9	7.8 × 10 ⁵	0.025 (0.011 ± 0.009)	-15.7 ± 4.4	1.3 × 10 ⁵
1	0.00019 (0.00016 ± 0.00002)	-19.2 ± 3.6	1.4 × 10 ⁵	0.00053 (0.00027 ± 0.00014)	-9.1 ± 10.4	3.1 × 10 ⁴	0.0048 (0.0014 ± 0.0017)	-13.9 ± 4.5	2.8 × 10 ⁴
0	0.000019 (0.000016 ± 0.000002)	-13.1 ± 2.5	7.8 × 10 ³	0.00014 (0.00009 ± 0.00003)	-14.3 ± 4.4	4.6 × 10 ⁵	0.00059 (0.00055 ± 0.00004)	-10.5 ± 5.1	2.3 × 10 ⁴

Statistical values were obtained from $N = 5$ independent devices. Uncertainties represent one standard deviation. The corresponding film thicknesses for each blend composition are summarized in Table S3.

Table S2. Charge transport characteristics of chemical blending strategy.

Polymer	$\mu_{h, \max} (\mu_{h, \text{avg}})$ [cm ² V ⁻¹ s ⁻¹]	V_{th} [V]	$I_{\text{on}}/I_{\text{off}}$
P(DPP-2T)	0.37 (0.33 ± 0.03)	-1.3 ± 0.9	6.4×10 ⁵
P(DPP-2T)_{0.9}(DPP-TEET)_{0.1}	0.25 (0.17 ± 0.06)	-4.2 ± 1.1	18×10 ⁵
P(DPP-2T)_{0.8}(DPP-TEET)_{0.2}	0.090 (0.084 ± 0.008)	-2.4 ± 0.2	4.3×10 ⁵
P(DPP-2T)_{0.7}(DPP-TEET)_{0.3}	0.058 (0.046 ± 0.010)	-2.6 ± 0.4	5.1×10 ⁵
P(DPP-2T)_{0.3}(DPP-TEET)_{0.7}	0.0026 (0.0018 ± 0.0003)	-13.6 ± 1.6	69.3×10 ³
P(DPP-2T)_{0.1}(DPP-TEET)_{0.9}	0.00058 (0.00039 ± 0.00011)	-30.5 ± 3.8	9.9×10 ³
P(DPP-TEET)	0.000019 (0.000016 ± 0.000002)	-13.1 ± 2.5	7.8×10 ³

Statistical values were obtained from $N = 5$ independent devices. Uncertainties represent one standard deviation. The corresponding film thicknesses for each blend composition are summarized in Table S3.

Table S3. Film thicknesses of physical and chemical blend films. Film thicknesses were measured by profilometry from 5 independently prepared films.

P(DPP-2T) content (%)	Physical 2T:TEET thickness (nm)	Physical 2T:TET thickness (nm)	Physical 2T:C3 thickness (nm)	Chemical 2T-co-TEET thickness (nm)
100	52.3 ± 1.0	52.3 ± 1.0	52.3 ± 1.0	52.3 ± 1.0
90	49.0 ± 1.4	-	-	38.8 ± 2.9
80	45.6 ± 1.8	-	-	41.2 ± 7.4
70	42.2 ± 2.2	66.0 ± 4.2	51.3 ± 1.8	53.2 ± 2.7
50	49.4 ± 3.0	-	-	-
30	43.3 ± 3.4	84.3 ± 8.4	57.9 ± 3.0	53.4 ± 3.2
10	53.3 ± 2.8	74.9 ± 10.6	54.3 ± 1.2	43.6 ± 3.5
5	46.7 ± 2.1	69.2 ± 8.0	55.4 ± 2.0	-
1	43.6 ± 2.3	83.9 ± 10.3	72.3 ± 2.6	-
0	38.6 ± 3.6	76.5 ± 8.7	70.2 ± 14.0	38.6 ± 3.6

Table S4. Subthreshold-slope analysis of physical blends.

P(DPP-2T) content (wt%)	P(DPP-TEET) blend		P(DPP-TET) blend		P(DPP-C3) blend	
	SS (V dec ⁻¹)	$N_{\text{trap}} (\times 10^{12} \text{ cm}^{-2})$	SS (V dec ⁻¹)	$N_{\text{trap}} (\times 10^{12} \text{ cm}^{-2})$	SS (V dec ⁻¹)	$N_{\text{trap}} (\times 10^{12} \text{ cm}^{-2})$
100	3.04	3.59	3.04	3.59	3.04	3.59
90	2.90	3.43	-	-	-	-
80	3.12	3.69	-	-	-	-
70	3.35	3.97	2.34	2.75	2.69	3.17
50	2.87	3.39	-	-	-	-
30	3.54	4.20	4.22	5.02	2.94	3.47
10	5.85	6.98	3.46	4.10	2.76	3.26
5	4.96	5.91	4.96	5.91	3.38	4.01
1	7.71	9.23	3.32	3.94	3.53	4.19
0	4.25	5.06	4.70	5.60	4.05	4.81

Table S5. Subthreshold-slope analysis of chemical blends.

(DPP-2T) ratio (mol%)	SS (V dec ⁻¹)	N_{trap} ($\times 10^{12}$ cm ⁻²)
100	3.04	3.59
90	3.31	3.92
80	2.65	3.12
70	5.74	6.85
30	7.62	9.12
10	6.41	7.66
0	4.25	5.06

Supplementary References

- [1] Ilavsky, J. Nika: software for two-dimensional data reduction. *Journal of Applied Crystallography* **2012**, 45, 324-328.

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