MATERIALS CHEMISTRY
FRONTIERS

REVIEW

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Cite this: DOI: 10.1039/d6qm00197a

Non-symmetric side chain engineering as a design strategy towards novel functional semiconducting polymers

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Received 13th March 2026,
Accepted 11th May 2026

DOI: 10.1039/d6qm00197a

rsc.li/frontiers-materials

Non-symmetric side-chain engineering has emerged as a promising strategy for tuning the mechanical and optoelectronic properties of π-conjugated polymers for applications in organic electronics. Most high-performance donor–acceptor semiconducting polymers, particularly those incorporating lactam-based acceptor units, rely on symmetrically substituted side chains to regulate solubility and solid-state packing. While effective, this design paradigm often restricts side chains to aliphatic motifs and limits opportunities to introduce additional functionality. In contrast, non-symmetric side chain architectures provide a versatile platform to move beyond conventional designs by enabling more functional and adaptive side-chain chemistries. Recent studies demonstrate that non-symmetric motifs can provide enhanced control over polymer self-assembly and structure–property relationships while helping decouple solubility from side chain functionality. In this review, we highlight recent advances in non-symmetric side chain engineering and discuss emerging synthetic strategies, design principles, and applications that illustrate the growing impact of this approach in the field of π-conjugated polymers.

1. Introduction

Organic electronics, which encompass electronic technologies fabricated from carbon-based active materials, have been a vibrant and transformative area of research for more than five decades.[1,2] From the seminal discovery of conducting polymers to the development of smart, functional sensors that can be seamlessly integrated with the human body, these technologies have continuously reshaped modern materials science.[3–5] Over the years, a wide range of advanced functional materials have been designed, synthesized, and implemented to enable increasingly high-performance organic electronic devices.

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Among these, carbon nanotubes, fullerene derivatives, and metal–organic hybrid materials are notable classes of materials that have been extensively explored for applications including photovoltaics, chemical and biological sensing, and light-emitting diodes.[6–8] While these material platforms have led to major technological advances and fundamental insights across materials science and materials chemistry, no class of materials has had a more profound and sustained impact on organic electronics than semiconducting π-conjugated polymers.[9–11] These polymers are characterized by alternating single and double carbon–carbon bonds, which give rise to extended π-electron delocalization along the backbone. This unique electronic structure provides them with several highly relevant properties in the context of organic electronics. Although their charge transport performance is generally lower than that of inorganic semiconductors used in conventional electronics, it is comparable to that of amorphous silicon, making them well suited for many emerging applications.[12] In addition, π-conjugated polymers are mechanically compliant and relatively soft, with Young's moduli typically ranging from tens of megapascals to a few gigapascals, and can be readily synthesized using robust palladium-catalyzed cross-coupling reactions.[13–15] Crucially, the incorporation of functional side chains provides an additional and powerful design handle, enabling precise synthetic tuning of electronic, mechanical, and solid-state properties while imparting solubility in common organic solvents.[16–18] This combination of tunability and solution processability underpins the exceptional printability of semiconducting polymers and positions them as key candidates for scalable, low cost manufacturing of next generation electronic technologies *via* solution based deposition techniques.[19]

Side-chain engineering has emerged as a powerful and widely exploited design strategy for tuning the properties of π-conjugated polymers across multiple length scales. Beyond imparting solubility in common organic solvents through modulation of polarity, side chains play a central role in dictating polymer self-assembly and packing in the solid-state.[20] Their specific structural attributes, such as length, branching, and bulkiness directly influence intermolecular interactions and packing motifs, which in turn have a profound impact on key thin film properties, including mechanical behaviour (Young's modulus, crack-onset strain, deformability) and electronic performance (crystallinity, effective conjugation length, and charge transport). Given these strong structure–property relationships, side chain engineering has been extensively leveraged to introduce new functionalities into conjugated polymers, ranging from non-covalent interaction motifs to molecular recognition units and dynamic chemical functionalities.[21–23] Most of these efforts have focused on the derivatization of well-established p-type backbones, such as diketopyrrolopyrrole, isoindigo, fluorene, and indacenodithiophene, as well as n-type systems including naphthalene diimide and perylene diimide derivatives.[11,24–27] A common feature of these materials is the presence of multiple, symmetrically distributed side chains on each repeating unit, with two or more chemically similar substituents per monomer. This symmetry is often critical for promoting ordered solid-state packing while simultaneously providing multiple synthetic handles for further functionalization. Notably, despite decades of intensive research and the demonstrated versatility of side chain engineering, the vast majority of conjugated polymers reported to date still rely on relatively simple hydrocarbon-based side chains (*e.g.*, linear or branched alkyl groups).[28] While effective for solubility and packing control, this limited chemical diversity underscores an important opportunity to move beyond conventional hydrocarbon motifs toward more functional, interactive, and adaptive side chain chemistries.

In contrast to the abundant symmetrical side chain architectures and related chemical designs that dominate the field of semiconducting polymers and organic electronics, non-symmetrical side chain engineering is a relatively novel approach that has emerged as a promising, yet comparatively underexplored, strategy for expanding the design space of π-conjugated polymers. By deliberately breaking side chain symmetry along the polymer backbone through the incorporation of chemically and structurally different side chains, this approach can enable decoupling of solubility, solid-state packing, mechanical compliance, and electronic performance, properties that are often intrinsically linked in conventional, symmetrically substituted systems. Additionally, non-symmetrical substitution can introduce controlled disorder, interfacial anisotropy, and spatially differentiated functionality, offering new opportunities to fine-tune microstructure formation, reduce crystallinity, and introduce directional or adaptive interactions without fundamentally altering the electronic backbone. Despite its clear conceptual appeal and growing number of isolated reports demonstrating enhanced mechanical robustness, improved processability, or unique structure–property relationships, non-symmetrical side chain engineering has not yet been systematically reviewed or unified under a common design framework.

This review article aims to address this gap by providing a comprehensive and critical overview of key literature examples that exploit non-symmetrical side chain engineering in semiconducting π-conjugated polymers. In the sections that follow, we will examine the synthetic strategies used to access non-symmetrical architectures, identify recurring design motifs, and analyze the pronounced effects of side chain non-symmetry on polymer aggregation, thin-film morphology, charge transport, and mechanical properties. Particular emphasis will be placed on exploring the contributions of side chain non-symmetry in polymer design, as well as on highlighting emerging opportunities enabled by functional, non-hydrocarbon side chains. Beyond covering existing knowledge, this review is intentionally structured to serve as a practical design toolbox for researchers interested in this rapidly evolving area. By consolidating and rationalizing key examples across semiconducting polymer systems, this review establishes non-symmetrical side chain engineering as a distinct and powerful design paradigm, while outlining future directions for the development of adaptive, biointegrated, and sustainable organic electronic materials poised to lead to novel exciting materials and devices across multiple fields of application.

2. Overview of common synthetic methods in side chain engineering

Side chain engineering is intrinsically synthetic in nature, and the choice of functionalization route strongly dictates not only the accessible chemical space but also the scalability, reproducibility, and structural precision of the resulting materials. A clear understanding of these foundational approaches is therefore essential for appreciating both the opportunities and the limitations associated with introducing non-symmetry along conjugated polymer backbones. To fully contextualize recent advances in non-symmetrical side chain engineering, it is, therefore, necessary to briefly review the conventional synthetic strategies that have historically underpinned side chain modification in π-conjugated polymers. This section will outline the most commonly employed methodologies for side chain engineering, beginning with the direct functionalization of monomeric building blocks prior to polymerization, which remains the dominant strategy for ensuring structural uniformity and precise placement of side chains. It will then discuss alternative approaches, including the use of masked or reactive side chain precursors and post-polymerization functionalization strategies that enable late-stage diversification of polymer properties.

2.1 Direct functionalization of monomeric units

For the vast majority of high-performance semiconducting polymers, side chains are designed to be symmetrical, possessing identical length and chemical structure along the entire polymer backbone. The installation of these side chains most commonly occurs at the monomer preparation stage, where simple alkylation reactions are employed to introduce solubilizing substituents onto π-conjugated cores. Typically proceeding through a nucleophilic substitution mechanism, halogenated alkyl side chain precursors are grafted onto the conjugated monomer using a strong base. This synthetic strategy is particularly attractive due to its high yields, excellent reproducibility, and scalability. In addition, it enables rapid and straightforward purification of the functionalized monomers, which are often highly aromatic and intrinsically insoluble, thereby making this approach the dominant route for side chain installation in semiconducting polymer synthesis. Beyond its traditional role in imparting solubility and controlling solid-state packing, alkylation chemistry, this synthetic approach has also been widely employed as a versatile entry point for introducing functionality into π-conjugated polymers. By precise selection of alkylating agents or protected side chain precursors, this approach has enabled the incorporation of chemically active, responsive, or interaction-driven moieties directly at the monomer stage, providing access to functional semiconducting polymers without disrupting backbone conjugation or polymerization efficiency. Such strategies have been successfully applied to a range of conjugated systems, allowing properties such as interfacial interactions, biological compatibility, mechanical compliance, and environmental responsiveness to be encoded through side chain design.[23,29]

In the context of non-symmetric semiconducting polymers, usual alkylation strategies for non-symmetric derivatives of organic dyes follow a similar ‘one-pot’ method where both desired side chains are added simultaneously to a basic alkylation condition.[30,31] While this method can enable the successful isolation of the targeted non-symmetrical monomer, it presents several inherent limitations. One of the most significant drawbacks is the formation of multiple side products, including symmetrically substituted isomers, which can lead to reduced overall yields, often below 30%, and necessitates extensive purification. These challenges are further exacerbated when the two side chains possess similar polarity or physicochemical characteristics, such as linear and branched aliphatic substituents, rendering chromatographic separation particularly difficult and limiting the practicality and scalability of this approach. A stepwise method has also been utilized in DPP based polymers where the monomer undergoes a basic alkylation with 1 equivalent of a side chain resulting in a mono-alkylated monomer. After purification, it is then subjected to a second basic alkylation with the second desired side chain.[32] In order to further probe for these limitations and to design a better synthetic route to non-symmetrical semiconducting polymers, our group explored a modular ‘‘Lego-like’’ method in isoindigo-based semiconducting polymers.[33] In this approach, selective alkylation of a halogenated isatin precursor is first employed to generate an alkylated intermediate, which is subsequently converted to the corresponding oxindole. Condensation of this alkylated oxindole with a second, independently functionalized isatin derivative then afforded a series of non-symmetric isoindigo monomers in moderate to good yields (typically 41–76%). Notably, this modular, stepwise strategy enabled precise control over side chain structure and position, while avoiding the statistical limitations associated with one-pot alkylation methods. Importantly, monomers prepared through this approach have been shown to afford high molecular-weight semiconducting polymers and enabled the incorporation of chemically complex or functionality rich side chains that would be difficult or inaccessible using conventional symmetric designs. As such, this methodology highlights how non-symmetrical side chain engineering can expand the accessible chemical space of π-conjugated polymers beyond the constraints imposed by traditional alkylation strategies.

2.2 Post functionalization of semiconducting polymer chains

Because the basic alkylation conditions commonly used to directly install side chains can be incompatible with chemically sensitive functional groups, alternative strategies for side chain engineering have been actively explored. Among these, post-functionalization of semiconducting polymers has emerged as a particularly powerful and versatile approach, enabling the introduction of a broad range of functionalities after polymer synthesis. Over the years, this strategy has been used to incorporate diverse side chain moieties, ranging from polar and biocompatible groups to bulky macromolecular structures, thereby opening direct pathways toward applications in bioelectronics, sensing, and responsive materials. A central methodology underpinning many post-functionalization strategies is the Cu-catalyzed azide–alkyne cycloaddition (CuAAC), a variant of the Huisgen 1,3-dipolar cycloaddition commonly referred as click chemistry, which has been widely adopted across the chemical sciences due to its efficiency, modularity, and functional-group tolerance.[34,35] In the context of semiconducting polymers, click reactions offer several key advantages: they are generally scalable, proceed under mild conditions, and avoid exposing sensitive functionalities to the harsh basic or catalytic environments often required during monomer synthesis and polymerization. Moreover, by decoupling backbone formation from side chain diversification, click chemistry enables the incorporation of bulky or structurally complex moieties that would be difficult or inaccessible through direct alkylation. A representative and influential example of this approach was reported by Li and co-workers, who developed a universal "click-to-polymer" strategy for the preparation of multifunctional conjugated polymers for human-integrated electronics.[36] In this work, conjugated polymer backbones bearing latent click handles were first synthesized and subsequently diversified *via* efficient post-polymerization click reactions to introduce functional groups such as photoreactive benzophenone and bioactive *N*-hydroxysuccinimide esters (Fig. 1a). Importantly, the resulting polymers retained good charge transport performance while gaining new functionalities, including high resolution photopatternability and enhanced biochemical sensing capabilities. This study elegantly demonstrates how post-functionalization can expand the functional landscape of conjugated polymers while preserving electronic performance. In another notable example of post-polymerization functionalization, Fong and co-workers reported the decoration of polyfluorene-wrapped single-walled carbon nanotube (SWNT) complexes *via* strain-promoted azide–alkyne cycloaddition (SPAAC). In this work, the authors specifically leveraged SPAAC, a copper-free variant of click chemistry, to enable efficient post-functionalization under exceptionally mild conditions.[37] Unlike the more commonly CuAAC, SPAAC proceeds without the need for a metal catalyst, eliminating concerns associated with metal contamination, catalyst removal, and potential degradation of optoelectronic properties. This

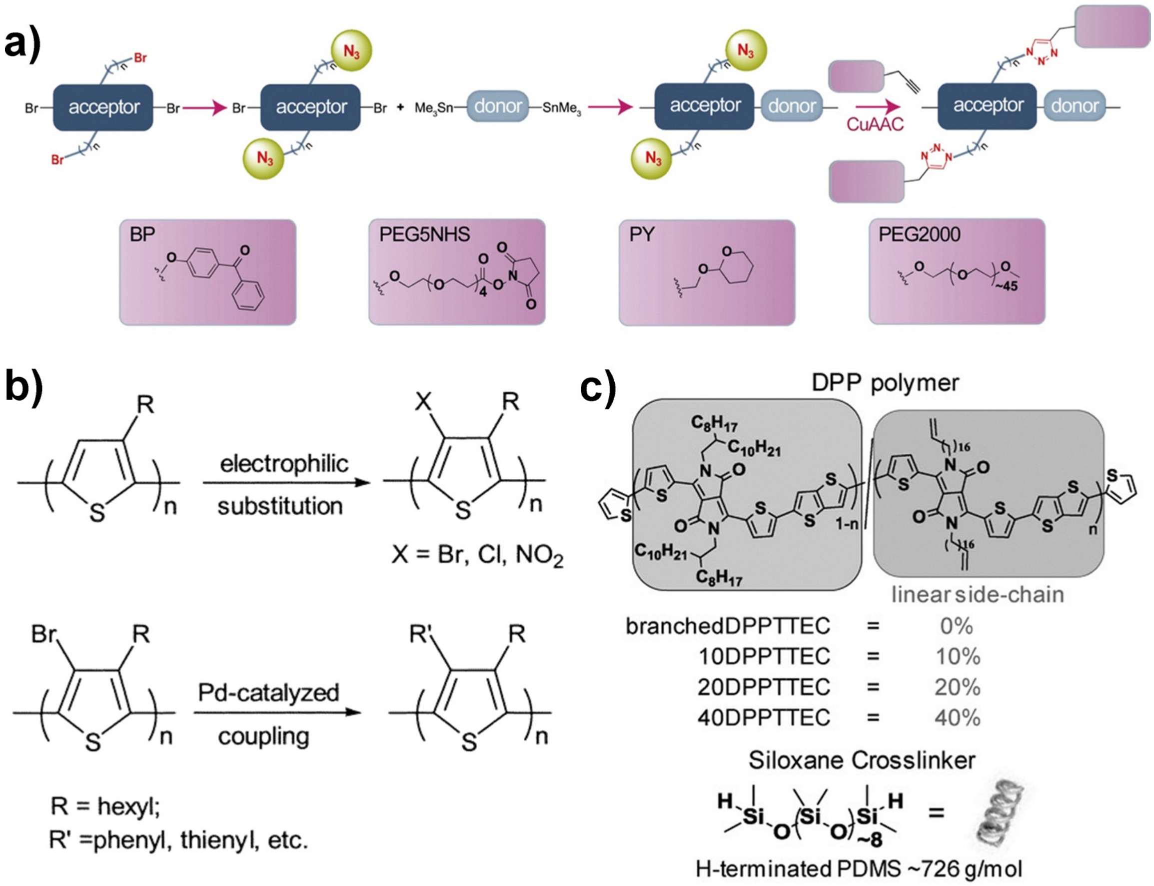

Fig. 1 Synthetic strategies for the post-functionalization of semiconducting polymers. (a) Click-to-polymer (CLIP) method of using CuAAC reaction to functionalize the side chains of conjugated polymers, as a post-polymerization step. Bottom: Chemical structures of four types of functional units used to functionalize conjugated polymers through the CLIP method; adapted with permission from ref. 36. Copyright 2021 Cell Press. (b) Post-functionalization of polythiophene through electrophilic substitution and Pd-catalyzed cross coupling. Adapted with permission from ref. 38. Copyright 2002 American Chemical Society; (c) DPP-based random co-polymer containing crosslinkable alkene-functionalized linear side chains for inter-molecular hydrosilylation. Adapted with permission from ref. 39. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

distinction is particularly important for semiconducting polymers and hybrid organic–inorganic systems, where residual metal ions can act as charge traps or quench excited states.

While click chemistry has emerged as a notable advance in the post-functionalization of donor–acceptor semiconducting polymers, it is still difficult to precisely control the incorporation ratio of functional groups. Therefore, a broader suite of chemical transformations has been developed to further expand the materials toolbox. In particular, direct chemical functionalization of conjugated backbones has been demonstrated as a versatile strategy for diversifying side chain functionality and tuning polymer properties. Among these, palladium-catalyzed cross-coupling reactions have proven especially effective in the context of polythiophene-based systems (Fig. 1b).[38] By leveraging well-established cross-coupling manifolds, such as Suzuki–Miyaura, Stille, and Negishi couplings, researchers have introduced a wide range of structurally diverse moieties onto thiophene backbones, enabling fine control over solubility, solid-state packing, and electronic structure without compromising the integrity of the conjugated framework. These approaches not only broaden the accessible chemical space beyond simple alkyl substituents but also facilitate the incorporation of functional groups that confer responsiveness, interfacial interaction, or processability. Complementary to cross-coupling strategies, polymer backbones bearing reactive alkene functionalities have been exploited as modular platforms for further post-polymerization modification. Alkenes can serve as versatile chemical handles for thiol–ene, ene, –yne, and hydrosilylation reactions, providing access to side chains and crosslinkers that are challenging to install *via* direct monomer synthesis. A particularly illustrative example of this concept is provided by work in which alkene functionalized conjugated polymers were functionalized with siloxane-based side chains and crosslinkers through hydrosilylation chemistry (Fig. 1c).[39] In this approach, pendant alkene units on the polymer backbone undergo efficient addition with silane derivatives under mild conditions, yielding well defined siloxane linkages that impart enhanced mechanical compliance and elastomeric behaviour while preserving electronic performance. Such alkene mediated post-functionalization strategies demonstrate the power of reactive backbone motifs to access side chain chemistries that extend beyond traditional synthetic limitations, providing a flexible route toward integrated mechanical and electronic functionality.

These examples illustrate the breadth and versatility of synthetic methodologies available for side chain engineering in semiconducting π-conjugated polymers, ranging from direct alkylation at the monomer stage to post-polymerization functionalization *via* click chemistry, cross-coupling reactions, and alkene mediated transformations. These approaches also have substantially expanded the functional landscape of conjugated polymers and enabled the incorporation of chemically diverse, responsive, and mechanically adaptive side chains while preserving electronic performance. However, despite these advances, the vast majority of reported systems continue to rely on symmetrical side chain architectures, largely due to synthetic convenience and the desire to maintain ordered solid-state packing. The following sections will therefore focus on non-symmetrical side chain strategies, critically examining their synthetic implementation, structure–property relationships, and emerging design rules, with the goal of establishing side chain non-symmetry as a powerful and generalizable paradigm in semiconducting polymer design.

3. Non-symmetric side chain engineering with hydrocarbon derivatives

Lactam-containing building blocks are particularly attractive platforms for side chain engineering in semiconducting polymers due to their strong electron withdrawing character, intrinsic planarity, and ability to engage in specific intermolecular interactions. The presence of the amide functionality often promotes enhanced backbone rigidity and dipolar interactions, which can strengthen intermolecular coupling and improve charge transport. Importantly, the lactam nitrogen provides a synthetically accessible site for side chain functionalization without disrupting the conjugated backbone, enabling systematic modulation of solubility, molecular packing, and solid-state morphology. As a result, conjugated lactam-based semiconductors offer an ideal model system to decouple and rationally investigate the role of side chain structure on optoelectronic and mechanical properties. Alkyl substitution at the lactam nitrogen is a widely employed strategy to achieve improved solubility in common organic solvents while enabling structural diversification and functional tuning. Although aliphatic side chains are generally thought of as insulating, they play a critical role in determining the intrinsic properties of the polymers, including the intermolecular interactions, molecular packing motifs, and crystallite orientation, all of which govern the solid-state morphology.[33,40–42] Consequently, side chain structures and symmetry affect the charge carrier mobility by modulating the π–π stacking distances, domain connectivity and structural disorder. In the case of branched aliphatic side chains, an odd–even effect has commonly been observed where polymers with even numbers of methylene units before the branching point typically display higher charge carrier mobilities, due to more favourable molecular packing and orientation, compared to their odd numbered counterparts.[40,41,43–47] When looking at processability through solution deposition techniques, polymers incorporating longer and highly branched alkyl side chains generally exhibit superior solubility in common organic solvents.[44,45,48] However, the increased steric bulk of these branched chains can hinder close backbone packing, reducing crystallinity and efficient charge transport pathways. In contrast, polymers functionalized with linear aliphatic side chains typically display higher degrees of crystallinity and molecular ordering, as the reduced steric hinderance at the backbone allows for closer packing.[32,33,49,50] Despite these advantages, linear side chains often result in poor solubility and limited processability which has restricted their use in device applications.

Non-symmetric side chain engineering offers a pathway to balance the competing advantages of linear and branched substituents allowing for simultaneously enhanced solubility and processability while promoting improved molecular ordering. In this respect, non-symmetric side chains offer a tunable trade-off between the higher crystallinity associated with linear chains and the enhanced solubility afforded by branched chains. Our recent work on the non-symmetric alkylation of isoindigo-based polymers addresses this through a systematic study of poly[isoindigo-*co*-thienothiophene] derivatives bearing exclusively aliphatic linear and branched side chains. In this series, a linear *n*-dodecyl chain remained constant on one of isoindigos' lactam nitrogen's, while the carbon spacer separating the backbone from the branching point on the second side chain was increased successively from one to four methylene units (Fig. 2a).[33] This controlled variation allowed for the discrimination of the effects of branching point position on the optoelectronic performance of the non-symmetric isoindigo polymer series. Notably, this structural modulation was found to have a pronounced influence on charge transport properties. Overall, increasing the carbon spacer length before the branching point was found to have a favourable impact on charge

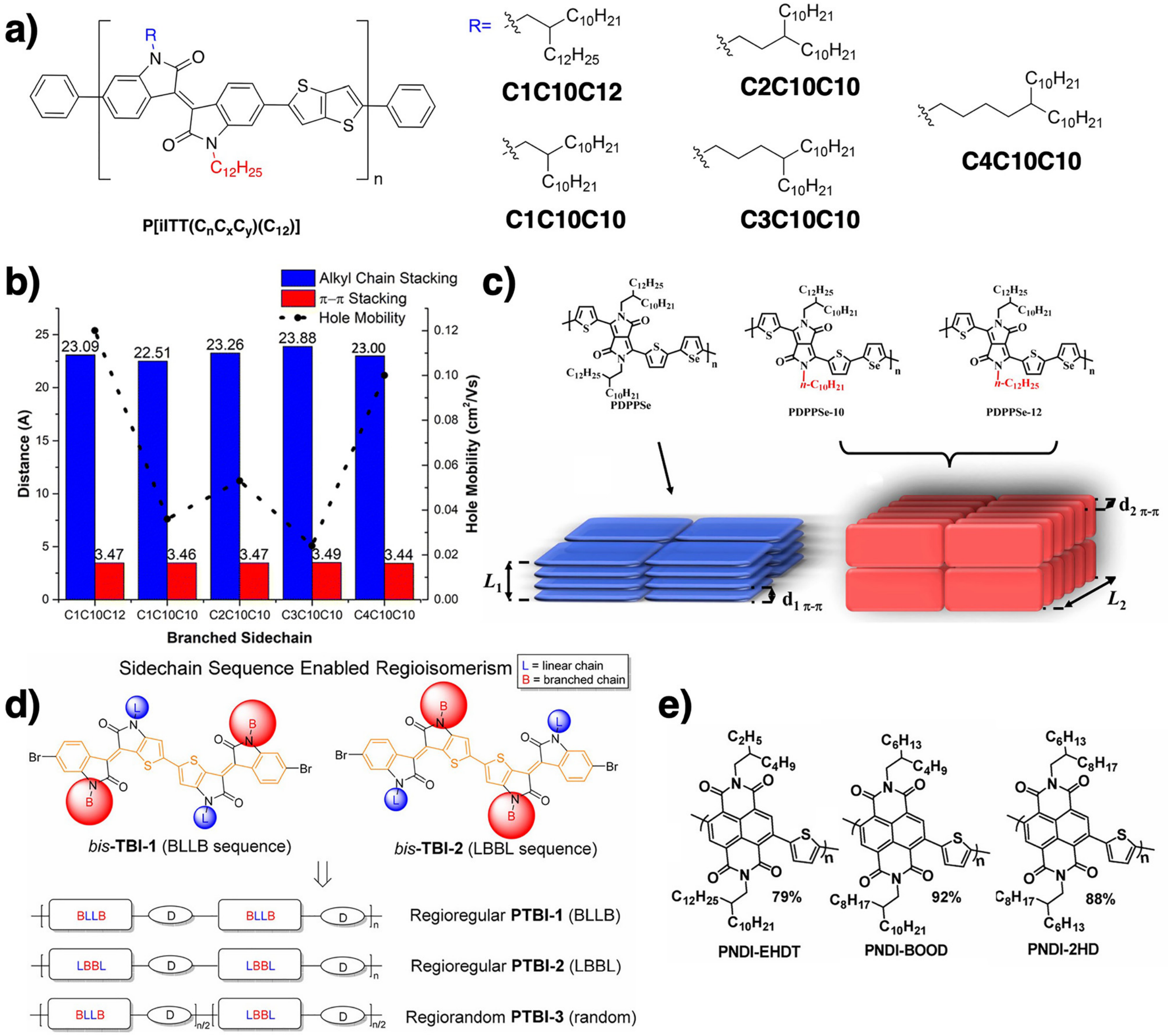

Fig. 2 Non-symmetric side chain engineering with aliphatic side chains. (a) Chemical structure of **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers; (b) summary of chain distances (alkyl packing distance and π–π stacking) and hole mobility *versus* branching point measured through the fabrication of organic field-effect transistors. Adapted with permission from ref. 33. Copyright 2025 Royal Society of Chemistry; (c) chemical structures of **PDPPSe**, **PDPPSe-10**, and **PDPPSe-12** (top) and schematic illustration for stacking orientation of **PDPPSe** (blue, face-on) and **PDPPSe-10**, **PDPPSe-12** (red, edge-on) (bottom). Adapted with permission from ref. 32. Copyright 2018 American Chemical Society; (d) chemical structures of regioregular **PTBI-1**, **PTBI-2**, and regiorandom **PBTI-3**. Adapted with permission from ref. 51. Copyright 2018 American Chemical Society (e) chemical structures of non-symmetric PNDI polymers. Adapted with permission from ref. 52. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

transport on the $\mathbf{C}_n\mathbf{C}_x\mathbf{C}_y$ series, with average hole mobilities of 0.12 $cm^2\ V^{-1}\ s^{-1}$ and 0.10 $cm^2\ V^{-1}\ s^{-1}$ reported for **P[iITT-($\mathbf{C_1C_{10}C_{12}}$)($\mathbf{C_{12}}$)]** and **P[iITT($\mathbf{C_4C_{10}C_{10}}$)($\mathbf{C_{12}}$)]** respectively (Fig. 2b). These values are comparable to those previously reported for symmetrically alkylated isoindigo-based polymers, suggesting that the incorporation of a linear dodecyl side chain does not adversely affect charge transport. Notably, increasing the distance of branching point from the conjugated backbone from the C1 position to the C4 position in the $\mathbf{C}_n\mathbf{C_{10}C_{10}}$ series generally led to improved charge mobility. This trend is consistent with reduced steric hinderance along the π-conjugated backbone, allowing for improved π–π stacking between adjacent polymer chains. An odd–even effect was also observed wherein polymers containing even numbered spacers prior to the branching point exhibit higher mobilities compared to their odd numbered counterparts, with the exception of the asymmetric $\mathbf{C_1C_{10}C_{12}}$ derivative. This deviation in the trend, may be attributed to the enhanced interdigitation of the asymmetric $\mathbf{C_1C_{10}C_{12}}$ branched chain compared to the symmetric $\mathbf{C}_n\mathbf{C_{10}C_{10}}$ derivatives. Collectively, these results underscore the critical role of branching point position in non-symmetric side chain designs and establish it as a powerful, tunable parameter for optimizing polymer architecture and charge transport performance. Pairing a linear dodecyl side chain with a branched counterpart enables favourable packing motifs with a high degree of structural order while mitigating steric hindrance. This non-symmetric side chain architecture promotes efficient intermolecular packing and provides a clear structural basis for the enhanced charge transport observed in these systems.

In another work, Wang and co-workers also investigated the incorporation of linear and branched aliphatic side chains in diketopyrrolepyrrole-selenophene polymers as a strategy to reduce steric hinderance and enhance intermolecular packing.[32] To promote the interdigitation of the linear alkyl chains, *n*-decyl and *n*-dodecyl were paired with a decyltetradecane ($C_{10}C_{12}$) **PDPPSe-10** and **PDPPSe-12** respectively (Fig. 2c). The non-symmetric polymers were compared with a symmetric **DPP-Se** reference polymer alkylated with bulky $C_{10}C_{12}$ side chains (**PDPPSe**). Molecular dynamic (MD) studies revealed that the conjugated backbones of the non-symmetric **PDPPSe-12** adopt a more planar conformation compared to the symmetric reference polymer, confirming that the replacement of one branched alkyl chain with a linear one leads to an increase in interchain π–π interactions and reduced steric hinderance along the backbone. Consistent with this finding, UV-vis spectroscopy revealed pronounced bathochromic shifts for both **PDPPSe-10** and **PDPPSe-12**, with an absorption maxima red-shifted in both solution and solid-state relative to PDPPSe. Raman spectroscopy, photothermal deflection (PDS) and theoretical calculations further corroborated the increased backbone planarity of the non-symmetrically alkylated DPP-Se polymers. GIWAXS measurements showed that non-symmetric **PDPPSe-10** and **PDPPSe-12** predominantly adopt an edge-on packing orientation, with higher intensity $n00$ reflections in the q_z directions indicating long range order of the crystallites. Compared to **PDPPSe**, which exhibited an alkyl packing distance of 23.5 Å, the non-symmetric derivatives showed significantly reduced packing distances of 21.9 Å and 21.2 Å for **PDPPSe-12** and **PDPPSe-10** respectively. The correlation lengths (L_C), the distance over which crystalline order is preserved along the conjugated backbone, along the π–π stacking direction extracted from the full width at half-maximum (fwhm) of the corresponding diffraction peaks lengths were estimated to be 3.74, 3.76, and 3.26 for **PDPPSe-10**, **PDPPSe-12**, **PDPPSe** respectively. These results indicate that the presence of a linear alkyl side chain enables more extended and coherent interchain π–π stacking in the non-symmetric polymer films. The reduced steric bulk and torsional strain achieved by replacing one branched side chain with a linear one translated directly into improved charge transport performance. OFETs fabricated from **PDPPSe-10** and **PDPPSe-12** thin films exhibited enhanced hole mobilities following thermal annealing at 180 °C, with maxima/average values of 8.1/5.8 $cm^2\ V^{-1}\ s^{-1}$ and 9.4/7.5 $cm^2\ V^{-1}\ s^{-1}$ respectively. In contrast, the symmetric **PDDPSe** reference polymer displayed substantially lower mobilities of 1.35/0.89 $cm^2\ V^{-1}\ s^{-1}$ under identical processing conditions. In a follow-up study, the Chen and coworkers investigated non-symmetric side chain engineering in vinyl-flanked DPP-selenophene polymers by fixing one branched side chain ($C_{10}C_{12}$) while systematically varying the second substituent from a linear dodecyl to a cyclohexyl group.[53] Materials characterization through optical spectroscopy, X-ray scattering and device fabrication revealed that polymers bearing linear side chains exhibit enhanced crystallinity, tighter π–π stacking, and a predominantly edge-on orientation, resulting in a high hole mobility of up to 6.76 $cm^2\ V^{-1}\ s^{-1}$. In contrast, the introduction of cyclic side chains led to increased steric hindrance, larger π–π stacking distances, reduced thin-film crystallinity, and a substantially lower mobility (0.83 $cm^2\ V^{-1}\ s^{-1}$). Collectively, these results highlight the effectiveness of non-symmetric side chain engineering of aliphatic side chains as a powerful approach to balance solubility, molecular ordering, and charge transport in high-performance conjugated polymers.

Luo and coworkers utilized non-symmetric linear and branched alkyl side chains in a bis-thieno-benzo-isoindigo (bis-TBI) acceptor–acceptor type building block to determine the effects of side chain non-symmetry in regioisomeric systems.[51] **Bis-TBI-1** possessed a branched-linear-linear-branched motif, while **bis-TBI-2** possessed a linear-branched-branched-linear side chain sequence and **PTBI-3** was a random co-polymer (Fig. 2d). The polymers exhibited similar frontier orbital energy levels, however, the polymer series displayed different aggregation patterns in thin films. The two isomeric monomers exhibited distinct absorption profiles in UV-Vis with **bis-TBI-1** exhibiting a large hypsochromic shift with a broad $\lambda_{\max}$ between 726 nm to 652 nm while **bis-TBI-2** displays a bathochromic shift with a $\lambda_{\max}$ of 815 nm. This difference can be attributed to their preferred packing motifs, with predominant H- and J-aggregates respectively, highlighting the importance of side chain engineering in inducing desired packing motifs. The polymers in thin films displayed similar absorption spectra, however a decrease in the 0-1/0-0 vibrational peaks were noticed in **PTBI-2** compared to **PTBI-1** and the regiorandom **PTBI-3**. AFM and 2D-GIXRD measurements displayed that **PTBI-2** displays a smooth fibrillar morphology and the largest ordered domains consistent with the highest achieved hole mobility of 2.22 $cm^2\ V^{-1}\ s^{-1}$.

Similarly, non-symmetric hydrocarbon side chain engineering has emerged as an effective strategy to enhance the efficiency of naphthalene diimide (NDI)-based systems in all-polymer solar cells (all-PSCs). In these systems, variations in side chain architecture strongly influence crystallinity, interchain packing, miscibility with donor polymers, and the resulting donor–acceptor blend morphology, ultimately governing device performance. In general, shortening alkyl side chains in NDI-based polymers effectively reduces lamellar and π–π stacking distances, thereby improving charge transport. However, this approach often comes at the expense of solubility and processability, limiting its practical implementation in solution-processed solar cell applications. To address this challenge, Jia and co-workers introduced non-symmetric alkyl side chains in which one long alkyl chain is replaced with a shorter counterpart while maintaining a constant total carbon number in each NDI unites (32 carbons total), as depicted in Fig. 2e.[52] Non-symmetric NDI polymers bearing 2-ethylhexyl/2-decyltetradecyl (**PNDI-EHDT**) or 2-butyloctyl/2-octyldecyl (**PNDI-BOOD**) sidechain pairs maintained a good solubility in common organic solvents used for deposition while also enabling closer intermolecular packing relative to symmetric NDI units substituted with two long alkyl sidechains. Copolymers blended with electron donating **PTB7-Th**, chosen for its light-absorbing ability and appropriate energy levels, markedly enhanced sidechain aggregation and increased crystallinity, reflecting more solid-state organization. Devices based on **PNDI-EHDT** and **PNDI-BOOD** blends showed impressive PCEs of 5.88% and 6.89%, respectively, both of which outperformed the 4.30% obtained from the device fabricated from **PNDI-2HD**. Morphological characterization by atomic force microscopy (AFM) and transmission electron microscopy (TEM) demonstrates that non-symmetric PNDIs maintain good miscibility with donor polymers while forming more distinct phase separated domains, a combination that is favourable for charge generation and transport.

As highlighted in the studies discussed above, non-symmetric hydrocarbon side chain engineering has proven effective in optimizing solid-state order and charge transport in thin-film transistors and photovoltaic devices. However, the impact of this design strategy in semiconducting polymers has remained largely confined to structural organization and packing effects. More recently, this concept has been extended to the incorporation of functional side chains, enabling the simultaneous tuning of electronic, interfacial, and processing properties. Across a broad range of organic electronic devices, functional side chains have been shown to impart additional capabilities, including enhanced miscibility with polar media, controlled ion transport, improved environmental stability, and more effective device integration. The following section highlights this shift from side chains as passive solubilizing groups toward active design elements that expand the performance envelope and application space of organic electronic materials, and illustrates how non-symmetric design principles can be leveraged to further tailor the properties of semiconducting polymers.

4. Side chain engineering with functional precursors

4.1 Non-symmetric silane- and siloxane-containing semiconducting polymers

Non-symmetric side chain engineering in semiconducting polymers is a powerful strategy to precisely control and fine-tune key material properties for organic electronic applications. As highlighted above, even subtle variations in hydrocarbon side chain structure or symmetry within lactam-based backbones can have a pronounced impact on both optoelectronic and thermomechanical performance. Beyond structural optimization, non-symmetric side chain engineering has also emerged as an effective approach to introduce new functionality into conjugated polymers, enabling unique and independent tuning of not only traditional optoelectronic properties, but also molecular stretchability, solubility in common organic solvents, and mixed ion-electron transport, among others. The following section surveys representative examples that demonstrate how symmetry breaking in these polymers can result in such significant changes in material performance and lead to emerging properties for next-generation organic electronics.

The growing demand for wearable and deformable electronics has intensified efforts to develop semiconducting polymers that combine efficient charge transport with intrinsic stretchability. Achieving this balance remains challenging, as high charge mobility typically relies on crystalline, co-planar chain packing, whereas mechanical compliance benefits from amorphous domains capable of dissipating strain. Traditional approaches to reconcile these competing requirements have often relied on backbone engineering through conjugation breaking units or crosslinking strategies to introduce amorphous character. In this specific context, non-symmetric side chain engineering offers an alternative and versatile pathway to modulate solid-state packing by introducing geometric disparities that simultaneously preserve ordered domains while promoting amorphous regions. Beyond mechanical considerations, such symmetry breaking can also influence molecular orientation and packing motifs, enabling mixed edge-on/face-on or bimodal orientations that may support more complex, three-dimensional charge-transport pathways. Xue and co-workers first explored non-symmetric side chain engineering towards intrinsically stretchable semiconductors by introducing a combination of a solubilizing branched alkyl chain paired with a siloxane-terminated side chain in a series of isoindigo-bithiophene polymers.[54] Specifically, **P1** (Fig. 3a, left), bearing a combination of branched and siloxane-terminated side chains exhibited enhanced bimodal orientation in thin films as revealed by GIXRD (Fig. 3b), compared to the symmetric reference polymers, which displayed predominantly edge-on orientations. This change in packing modes from the edge-on dominant orientation to the bimodal orientation can be explained by the

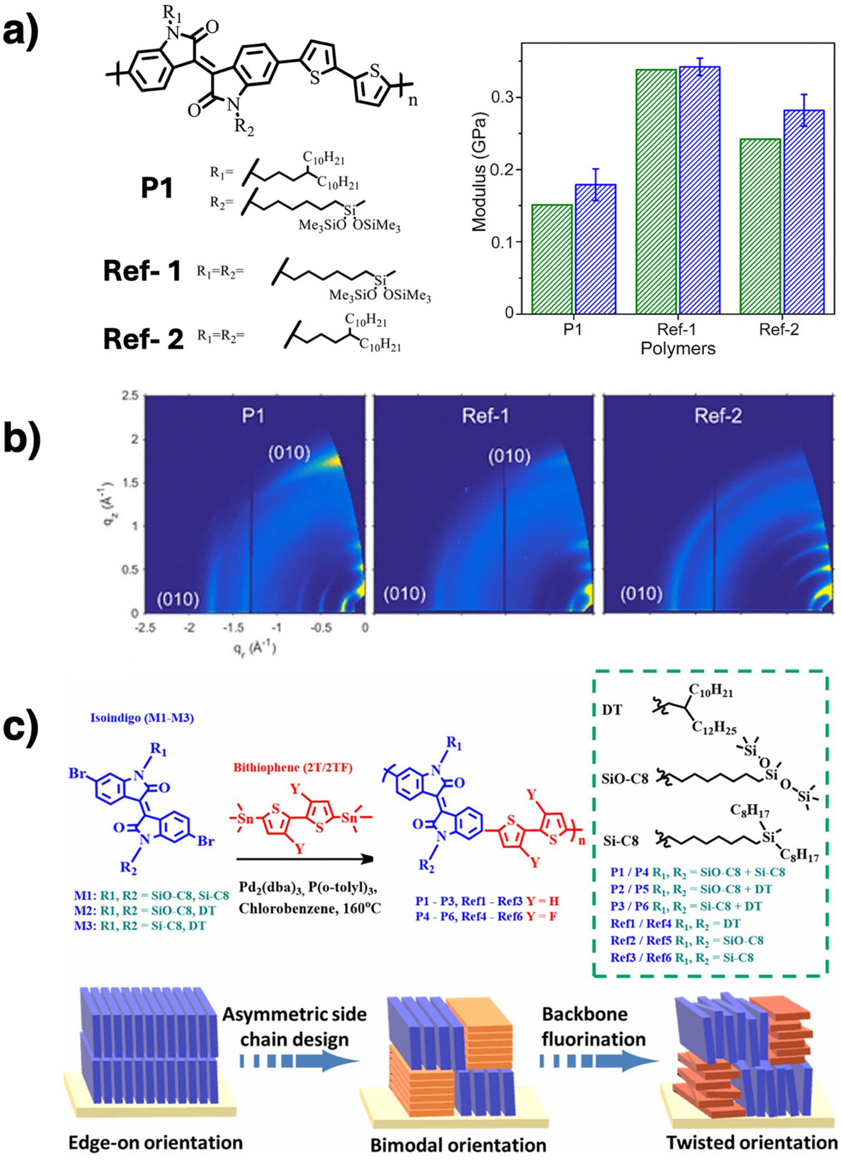

Fig. 3 Non-symmetric polymers bearing silane and siloxane terminated side chains. (a) Chemical structure (left) and mechanical properties (right) of non-symmetric isoindigo-bithiophene copolymers containing a combination of a solubilizing branched alkyl chain paired with a siloxane-terminated side chain in a series of isoindigo-bithiophene polymers. The data of the olive histogram are from buckling metrology and the data of the blue histogram are from nanoindentation measurement; (b) GIXRD pattern of annealed non-symmetric isoindigo-bithiophene copolymers. Adapted with permission from ref. 54. Copyright 2017 American Chemical Society; (c) (top) synthetic scheme of non-symmetric siloxane and silane containing polymers and (bottom) illustration of the effects of non-symmetrical side chains and backbone fluorination on the solid-state orientation; adapted with permission from ref. 55. Copyright 2019 American Chemical Society.

introduction of non-symmetric side chains which introduce a new interdigitation motif between the different side chains which in return is inducing differing packing in the solid-state. **P1** exhibited both superior charge mobility and the lowest tensile modulus among the compared polymers. Notably, the introduction of non-symmetric side chains promoted a well-defined bimodal orientation, increasing the fraction of face-on crystallites while preserving edge-on domains. Mechanical measurements (Fig. 3a, right) consistently showed a reduced modulus for **P1**, with values of 0.151 GPa (measured by buckling metrology) and 0.179 GPa (measured by nanoindentation), compared to 0.338 GPa (buckling metrology) and 0.342 GPa (nanoindentation) for **Ref-1**, and 0.242 GPa (buckling metrology) and 0.282 GPa (nanoindentation) for **Ref-2**. The coexistence of distinct molecular orientations in **P1** likely can generate mechanically softer interfacial regions between crystallites, reducing effective interchain π–π stacking and van der Waals interactions.

Lin and co-workers reported similar results for a non-symmetric isoindigo-biothiophene co-polymer systems utilizing non-symmetric siloxane terminated side chains (SiO-C8), carbosilane side chains (Si-C8), and a decyltetradecane (DT) side chain. Interestingly, the author also explored the impact of backbone fluorination on the thermomechanical and electronic properties of these polymers.[55] The authors found that the combination of SiO-C8/Si-C8 side chains induced the formation of bimodal orientation of the polymer chains (Fig. 3c), leading to enhanced charge mobility in thin film transistors. Far-branched hybrid siloxane-terminated side chains have also been demonstrated to increase the solubility of conjugated polymers in common organic solvents, without largely disturbing the intermolecular packing. However, the combination of SiO-C8/DT led to a decrease in charge mobility and in edge-on orientation revealed by GIWAXS. This result was attributed to the mismatch in methylene spacer units before the branching point; both Si-O-C8 and Si-C8 possess the same methylene spacer before the branching point, in contrast to DT which has a much shorter, one carbon, spacer unit. In this particular case the mismatch between the carbon spacer units causes more torsional strain on the backbone, interrupting the chain packing. However, this torsional strain was mitigated in Si-C8/DT despite the mismatch in branching point spacers and predominantly edge-on packing was achieved. The combination of a linear dodecyl chain with hybrid carbosilane (Si) and a hybrid siloxane (SiO) terminated chain have also been explored in a diketopyrrolopyrrole-thiophene copolymer system by Cheuh and co-workers, who reported differing degrees of bimodal packing orientation depending on the side chain combination.[56] Notably, **P(SiO-Si)** showed the highest degree of bimodal packing orientation compared to **P(SiO-C12)** and **P(Si-C12)** likely attributed to the linear alkyl side chain which promoted side chain indigitation and reduced steric hinderance leading to higher lamellar crystallinity in the out-of-plane direction in GIWAXS correlating to edge-on orientation. Surprisingly still, **P(SiO-Si)** displayed the highest average hole mobility of 0.465 $cm^2 V^{-1} s^{-1}$, compared to **P(SiO-C12)** and **P(Si-C12)** which displayed mobilities of 0.121 $cm^2 V^{-1} s^{-1}$ and 0.367 $cm^2 V^{-1} s^{-1}$ respectively. Although (300) peaks were observed for both **P(SiO-Si)** and **P(Si-C12)** in GIWAXS, indicative of long-range ordering, the combination of the branched silane and siloxane terminated side chains was found to enhance the bimodal stacking preferences leading to slightly enhanced charge transport ability. Additionally, after repeated stress–strain cycles, **P(SiO-Si)** was found to retain 57% of the initial charge mobility after 800 cycles of 60% strain. This contrast with **P(SiO-C12)** and **P(Si-C12)**, which only retained 2.4% and 4.1% respectively under the same strain. This example particularly highlights the benefit to the mismatch in side chain functionalization between the branched silane terminated side chain and the siloxane-terminated side chain, allowing for strain dissipation and retention of mobility after stretching. It is worth noting that complementary studies have also explored backbone heteroatom incorporation, such as fluorination, alongside non-symmetric side-chain designs, showing that fluorination can deepen frontier energy levels and enhance mechanical durability under strain, albeit often at the expense of reduced crystallinity and hole mobility.

In addition to the investigation of the impact of silane and siloxane-containing non-symmetric semiconducting polymers in stretchable thin film transistors, this design has also proven to be effective in optimizing bulk-heterojunction (BHJ) morphology in organic photovoltaics. For example, Tang and co-workers demonstrated that similar designs when paired with a non-fullerene acceptor (NFA) Y6, yielded more favourable nanoscale phase separation and power conversion efficiencies (PCEs) exceeding 14%.[57] These performance gains were attributed to the mismatch in side chain geometries that enhanced interchain packing and generated larger molecular dipole moments, reinforcing intermolecular interactions. Complimentary studies of isoindigo based polymers incorporating non-symmetric combinations of decyltetradecane (DT) and siloxane-terminated (SiO-C8) with and without backbone fluorination were paired with an NFA (ITIC-4F), revealed clear structure–property–performance correlations. Polymers with the non-symmetric side chains consistently outperformed their symmetric counterparts, delivering higher PCEs due to improved interchain packing and intermolecular interactions. However, backbone fluorination significantly narrowed the performance gap between the symmetric and non-symmetric architectures, an effect attributed to induced F–S interactions along the thiophene units which rigidify the polymer backbone, enhance crystallinity, and counteract side chain induced torsional disorder, diminishing the sensitivity of device performance due to side chain geometry. Optically, fluorinated polymers exhibited slightly red-shifted absorption maxima, reflecting increased backbone planarity. In inverted photovoltaic devices employing ITIC-4F as the acceptor, **P2** and **P5** with the non-symmetric SiO-C8/DT side chains, non-fluorinated and fluorinated backbone respectively, delivered the highest PCEs of 4.41% and 4.52%.

While branched siloxane side chains have been shown to improve the overall solubility and processability of non-symmetric polymers, linear siloxane side chains can further improve the intermolecular interactions between adjacent polymer chains. Yuan and co-workers investigated non-symmetric DPP architectures incorporating linear siloxane (Si) side chains paired with a branched decyltetradecyl (C) side chain, to improve the ductility of the polymer films (Fig. 4a).[58] Compared to its symmetric counterparts, non-symmetric **P(C-Si)** did not display any significant cracks even after 100% strain, as measured by film on elastomer. In contrast, the symmetric **P(C-C)** and **P(Si-Si)** showed significant cracking after 10% and 100% respectively, demonstrating the superior ductility of non-symmetric polymers to allow for better deformation tolerance. The optical dichroism ratio was measured using polarized UV-vis spectroscopy to quantify chain alignment and anisotropy within the polymer films under applied strain. The dichroic ratio at 100% strain was found to be the highest in the non-symmetric **P(Si-C)** (2.14), a value significantly higher than **P(Si-Si)** and **P(C-C)**, which were found to be 1.80 and 1.31 respectively (Fig. 4b). These results indicate that **P(Si-C)** has better chain alignment ability under elongation, caused by the lower crystallinity leading to higher ductility. Similarly, film-on-elastomer buckling metrology measured elastic moduli of 83.9, 225, and 388 MPa for **P(Si-C)**, **P(Si-Si)** and **P(C-C)** respectively.

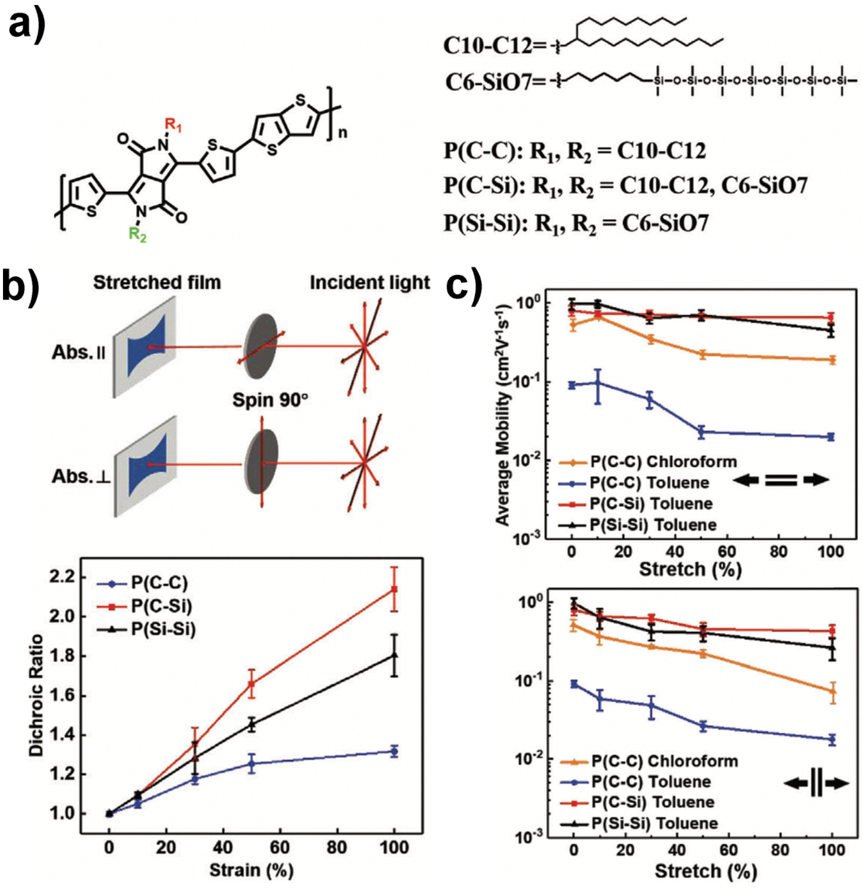

Fig. 4 Non-symmetric polymer bearing a linear siloxane side chain and a solubilizing branched aliphatic side chain. (a) Chemical structures of non-symmetric diketopyrrolopyrrole-thiophene copolymers with combinations of linear siloxane and branched aliphatic side chains; (b) schematic diagram of dichroism test and dichroic ratio of the polymer films in function of applied strain, ranging from 0 to 100%. Scale bar is 1 μm, and (c) average OFET charge mobility of the polymers in thin films under an applied strain from 0% to 100% elongation strain. Adapted with permission from ref. 58. Copyright 2022 Wiley-VCH Verlag GmbH & Co. KGaA.

The elastic moduli measured for the non-symmetric **P(Si-C)**, particularly low compared to other reported conjugated polymers that range between 250–800 MPa suggests that non-symmetry can increase the overall flexibility of the polymer chains. Finally, the authors probed the polymer performance upon deformation in OFETs. **P(Si-C)** showed an average mobility of 0.75 $cm^2\ V^{-1}\ s^{-1}$, and after applied strain at 100%, retained 86% of its initial mobility (0.65 $cm^2\ V^{-1}\ s^{-1}$) when strain was applied parallel to the channel direction, and 56% of the initial mobility (0.42 $cm^2\ V^{-1}\ s^{-1}$) with strain applied perpendicular to the channel. The stability of charge transport in the non-symmetric polymer was further tested with 400 stretch–release cycles, with the polymer retaining 53% of its initial mobility value in the vertical direction (Fig. 4c).

4.2 Non-symmetric glycolated and oligoether-containing semiconducting polymers

As discussed above, side chain engineering is a powerful strategy to control and fine-tune both the solid-state nanostructure and backbone conformation of semiconducting polymers. Beyond their traditional roles in solubilization and steric modulation, functionalized side chains provide a versatile platform for introducing targeted non-covalent interactions into conjugated polymer systems, enabling more precise control over molecular conformation, thin-film morphology, and solid-state organization. Naik and co-workers investigated the effect of non-symmetrically alkylated DPP derivatives utilizing a combination of either *n*-hexyl or 2-ethylhexyl with trietheylene glycol (TEG) in comparison to the symmetrical derivatives.[59] Variation in side chain structure has a pronounced effect on the solid-state behavior, a larger bathochromic shift relative to solution was exhibited for the symmetrically *n*-hexyl substituted derivative and the non-symmetrically substituted *n*-hexyl/TEG derivative, respectively. These red shifts were attributed stronger intermolecular interactions and increased planarity of the conjugated backbone in the solid-state. Linear alkyl chains favour more extended backbone conformations, promoting aggregation and resulting in broadened red shifted absorption features. In contrast, the polymer bearing the non-symmetric 2-ethylhexyl and TEG side chains, displayed a notably smaller red shift, consistent with reduced intermolecular interactions due to the bulky branched alkyl substituent. Further investigation with time-dependent density functional theory (TD-DFT) calculations determined that the nature of the alkyl side chain, whether branched or linear, played a critical role in determining the torsional angle between the central TDPP core and the adjacent thiophene rings.

In particular, the incorporation of polar or heteroatom-containing side chains, such as polyfluorinated, hydroxyl, and oligoether chains, can promote specific intermolecular interactions that enhance backbone planarity and interchain packing. Importantly, within non-symmetric polymer designs, these interactions can be selectively introduced without imposing excessive steric hindrance or severely compromising solubility, allowing functional groups that would otherwise render symmetric polymers insoluble to be effectively leveraged and investigated. Recent work by Mooney and co-workers utilized non-symmetric side chain engineering of a hydroxyl-terminated side chain paired with a solubilizing branched alkyl chain in an isoindigo-based copolymer system (Fig. 5a).[60] Notably, the hydroxyl moieties led to significantly improved processability in alcohol-based solvents without sacrificing the electronic performance in OFETs. Importantly, the presence of terminal hydroxyl groups also provides an accessible handle for post-functionalization, which can be performed directly on thin films, thus enabling the development of multifunctional OFETs through greener processing routes and allowing device properties to be tailored to specific applications *via* the rational selection of functional motifs. In this work, the non-symmetric polymer was post-functionalized with fluorescein isothiocyanate (FITC), a fluorescent probe commonly used for the detection of analytes such as phosphates, antibodies, and apoptotic cells. In another work, Singh and co-workers investigated boron dipyrromethene (BODIPY) containing non-symmetric isoindigo copolymers alkylated with a linear alkyl and ester terminated side chain (Fig. 5b).[61] Distinct self-assembly, aggregation and morphological differences in thin films were found with **P1** forming smooth films and **P2** forming porous films. Scanning electron microscopy (SEM) was employed to visually determine the influence side chain functionality on the aggregative behavior and film morphology of the BODIPY-based copolymers (Fig. 5c–f). Distinct morphological differences were noted between the

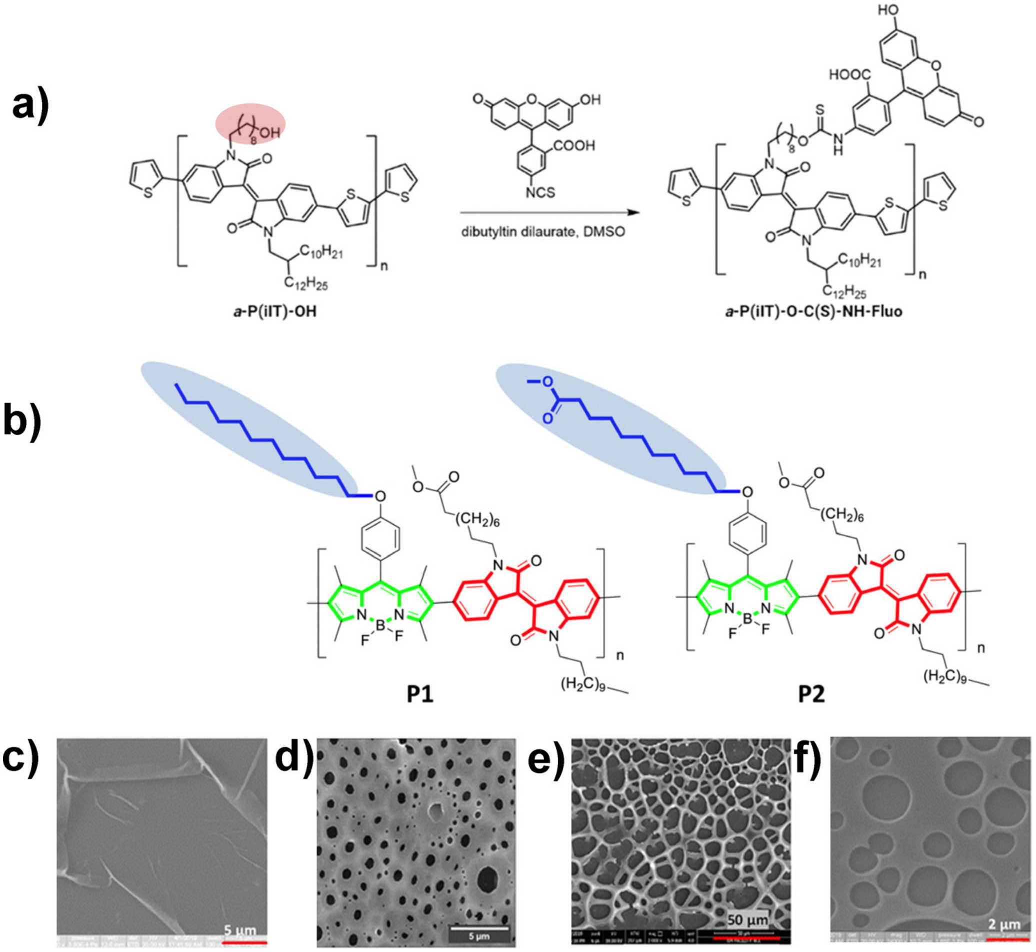

Fig. 5 Non-symmetric isoindigo-based polymers with functionalized side chains. (a) Post-functionalization of ***a*-P(iIT)-OH** (thin film) with fluorescein isothiocyanate to afford ***a*-P(iIT)-O-C(S)-NH-Fluo**. Adapted with permission from ref. 60. Copyright 2023 Royal Society of Chemistry. (b) BODIPY-*alt*-isondigo copolymers **P1** [poly(BDP12-*alt*-iI)] and **P2** [poly(BDPE-*alt*-iI)]; SEM images of 1 mg mL^{-1} of (c) copolymer **P1** and (d) copolymer **P2** in $CHCl_3$ at $t = 0$; (e) SEM images of 1 mg mL^{-1} of copolymers **P2** in 50% $CHCl_3$ at $t = 30$ min; (f) SEM images of 1 mg mL^{-1} of copolymers **P1** in 50% $CHCl_3$-THF. Adapted with permission from ref. 61. Copyright 2023 Royal Society of Chemistry.

non-functionalized alkyl side chains and the ester terminated side chain. In chloroform, the alkyl substituted copolymer (**P1**) formed a relatively uniform, sheet-like thin film, whereas the introduction of a terminal ester (**P2**) led to a porous film morphology with pore sizes averaging 557 nm. Prolonged exposure to the solvent further amplified this effect, with the surface pores of **P2** expanding to 8.6 μm after 30 minutes. The solvent composition was found to play a critical role in dictating the aggregation of the polymers, while uniform films were obtained in single solvent systems, mixed solvent systems such as 50% (v/v) chloroform-tetrahydrofuran promoted pore formation for **P1** which previously displayed a sheet like morphology in pure chloroform, highlighting the interplay between side chain functionality and solvent-polymer interactions. Finally, solvent titration studies were conducted to understand the relative contributions of the conjugated core as well as the non-symmetric side chain architecture to the film morphology and aggregation behaviour. By systematically varying the solvent polarity relative to chloroform, changes in UV-vis transitions associated with the polymer backbone (λ_{max} = 588 nm) and side chains (λ_{max} = 287 nm) respectively were monitored. Significant changes were noted in the intensity of the 287 nm peak when the polarity differences (ΔP) exceeded a threshold, indicating polarity driven reorganization of the polymer chains. However, minimal differences were noted for the peak at 588 nm, suggesting limited perturbation of the polymer conformation. Comparative titration experiments on the monomers revealed weaker and less systematic responses to solvent polarity than those observed for the copolymers. This distinction suggests that although the conjugated core does contribute to self-assembly, the dominant factor governing the aggregation behaviour and morphology is the side chains, reinforcing the importance of side chain engineering in self-assembly.

Non-covalent interactions introduced through functionalized side chains can play a decisive role in enhancing charge transport in OFETs by directing molecular aggregation and solid-state packing, thereby enabling clearer structure–property relationships. In this context, non-symmetric side chain engineering has emerged as an effective strategy to mitigate steric hindrance while promoting mixed molecular orientations, including bimodal edge-on and face-on packing that can support three-dimensional charge-transport pathways. At the same time, deliberate symmetry breaking can slightly reduce crystallinity while preserving long-range order, leading to improved ductility and processability without sacrificing electronic performance. Building on these concepts, Yen and co-workers systematically investigated a series of non-symmetric isoindigo-bithiophene copolymers incorporating three different side chains: a semifluorinated, a carbosilane, and an oligoether side chain.[62] **P(F-F)** and **P(F-O)** both displayed very low solubility due to a fluorophobic effect, and the symmetric **P(F-F)** was unable to afford a homogenous film for further study. In contrast, the non-symmetric siloxane-oligoethylene glycol polymer **P(Si-O)** displayed superior performance in OFET devices with average charge mobility values comparative to its symmetric **P(Si-Si)** counterpart (0.56 and 0.51 $cm^2\ V^{-1}\ s^{-1}$ respectively). This was attributed to the enhanced backbone aggregation and solid-state stacking (confirmed by GIWAXS) which shows long-range order, confirmed by the presence of (400) peaks in the q_z direction. The improved solid-state stacking of the polymer can be attributed to the favourable intermolecular interaction between the oligoether and siloxane side chains which mitigates the steric hindrance between the backbone and side chains. In contrast, the semifluorinated side chain combinations **P(Si-F)** and **P(F-O)** displayed lower mobilities of 0.14 $cm^2\ V^{-1}\ s^{-1}$ and 0.01 $cm^2\ V^{-1}\ s^{-1}$ respectively due to the irregular and disordered solid state attacking induced from the unfavourable side chain aggregates. Specifically, in **P(F-O)** the repulsion of the hydrophilic oligoether with the hydrophobic semifluorinated chain induced disordered conformation which is unfavourable for charge transport. Optical microscopy revealed that **P(Si-O)** and **P(O-O)** maintain largely pristine morphologies under 60% strain, while non-symmetric polyfluorinated polymers **P(Si-F)** and **P(F-O)** develop microcracks, indicative of reduced mechanical tolerance. Consistent with these observations, 2D-GIXD showed that **P(Si-O)** largely preserves its crystallinity under strain, attributed to the flexibility of the oligoether side chains. Dynamic mechanical testing further confirmed the superior compliance of **P(Si-O)**, which exhibits a markedly lower elastic modulus (0.45 GPa) compared to **P(Si-F)** (2.09 GPa), **P(F-O)** (2.79 GPa), **P(Si-Si)** (1.38 GPa), and **P(O-O)** (1.20 GPa). Polarized UV-vis measurements revealed increasing optical dichroic ratios with strain across the series, reflecting progressive chain alignment, with non-symmetric **P(Si-O)** showing the highest value (2.05 at 100% strain). This enhanced structural resilience translated into excellent device stability, with **P(Si-O)** retaining 92% ($\perp$) and 82% ($\parallel$) of its initial hole mobility at 100% strain and 95% after 1000 stretch–release cycles. In contrast, polyfluorinated **P(Si-F)** and **P(F-O)** displayed significantly lower dichroic ratios and mobility retention, underscoring their comparatively brittle behaviour.

In a follow-up study, Tsai and co-workers employed the same non-symmetric isoindigo-bithiophene copolymer series to investigate doping efficiency and thermoelectric performance by systematically tuning polymer hydrophilicity through side chain asymmetry.[63] Focusing on siloxane-terminated derivatives, the symmetric **P(Si-Si)** and the non-symmetric **P(Si-O)** and **P(Si-F)** polymers were chemically doped with $FeCl_3$ to evaluate their thermoelectric behaviour. The addition of oligoether side chains through non-symmetric side chain engineering has been shown to improve the dispersion of dopants in the polar environment of the oligoether side chains resulting in improved doping efficiency (η_d) and electrical conductivity (σ), increasing the presence of amorphous domains *via* the incorporation of bulky branched aliphatic side chains has also proven beneficial to increase the power factor. By modulating the hydrophilicity of the non-symmetric side chains, the relationship between polymer structure and thermoelectric performance can be observed. Non-symmetric sidechains can increase the prevalence of amorphous domains while still maintaining an extent of crystallinity. UV-vis-NIR was used to measure the p-doping of the polymer series, with doping efficiencies calculated to be 44.6%, 29.1%, and 21.8% for **P(Si-O)**, **P(Si-F)**, and **P(Si-Si)** respectively (Fig. 6a). **P(Si-O)** also displayed the highest power factor of 23.4 μW m^{-1} K^{-2}, attributed to the high polymer-dopant miscibility from the introduction of the hydrophilic oligoether side chain as well as the high degree of structural ordering (Fig. 6b). Additionally, X-ray photoelectron spectroscopy (XPS) showed a trend similar to the absorption spectra, with **P(Si-O)** demonstrating the highest proportion of dopants ionized by charge transfer to the backbone. Ultraviolet photoelectron spectroscopy (UPS), used to determine the work functions and changes in electronic structure of the films upon doping, showed the lowest thermal activation energy *via* integer charge transfer between $FeCl_3$ and **P(Si-O)**, implying that **P(Si-O)** is more likely to be doped by $FeCl_3$ and efficiently transport charge carriers. By using non-symmetric side chain engineering the polymer can create spacer domains to facilitate dopant diffusion into the side chains of the polymers, further enhancing doping efficiency.

Han and co-workers investigated the doping efficiency and thermoelectric performance of a series of non-symmetric oligoether DPP polymers.[64] Owing to their polar nature, the oligoether side chains enhance the miscibility with molecular dopants and promote a more homogeneous dopant dispersion and more efficient charge transfer. To further modulate the electronic structure, electron rich donor units; including thiophene (T), thienothiophene (TT), and bithiophene (2T) bearing electron donation alkoxy substituents were incorporated to elevate the HOMO energy level and increase the thermodynamic driving force for hole transfer to p-type dopants such as F4TCNQ and $AuCl_3$. This integrated design strategy aims not only to improve doping efficiency but also evaluate whether enhanced dopant–polymer interactions can be achieved without significantly disrupting molecular ordering. A structurally controlled series of D–A copolymers was synthesized to systematically probe the combined effects of non-symmetric side chains and donor strength. The reference polymer features

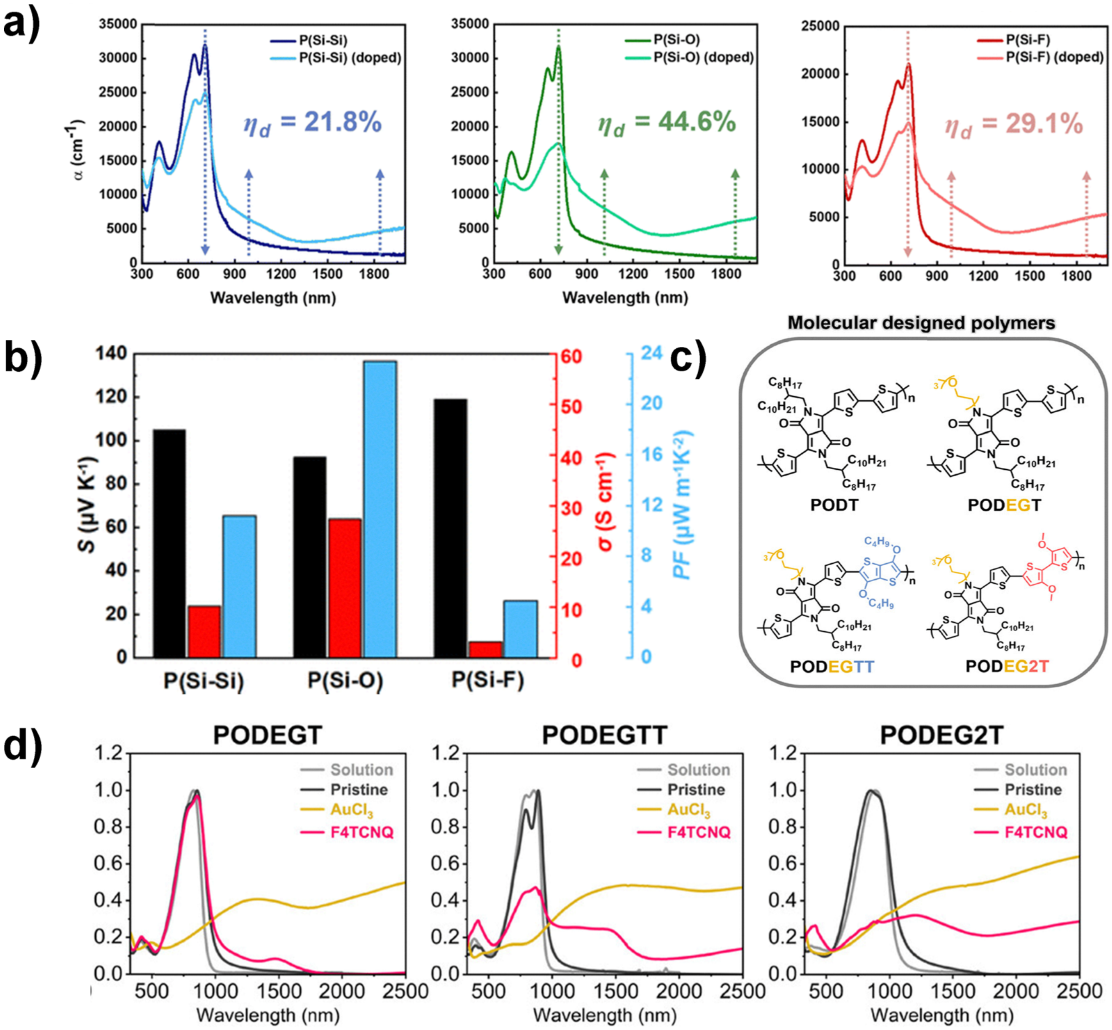

Fig. 6 Non-symmetric polymers with oligoethylene glycol side chains. (a) UV-vis-NIR absorption spectra for pristine and $FeCl_3$ doped polymer films; (b) thermoelectric properties of $FeCl_3$ doped polymer films; adapted with permission from ref. 63. Copyright 2023 Royal Society of Chemistry; (c) chemical structure of non-symmetric alkyl and oligoether polymers with electron rich donor units; (d) UV-Vis-NIR absorption spectra of pristine and $AuCl_3$ and F4TCNQ doped polymer films. Adapted with permission from ref. 64. Copyright 2025 Wiley-VCH Verlag GmbH & Co. KGaA.

symmetrically branched alkyl chains on the DPP core while the non-symmetric derivatives incorporate one branched alkyl (OD) and one oligoether (EG) side chain paired with progressively stronger donor units (Fig. 6c). The doping behaviours of the polymers was evaluated through solutions based sequential doping with F4TCNQ (molecular dopant) and $AuCl_3$ (Lewis Acid), as these dopants possess distinct redox potentials and molecular geometries enabling for a comparative assessment of polymer-dopant interactions across the non-symmetric series. Upon doping with $AuCl_3$, the polymers all exhibited significant structural changes in absorbance as shown by UV-vis. Bleaching of the absorbance band centered around 850 nm and the emergence of a broad polaronic absorption band in the 1000–2500 nm regain was observed. These features confirm successful doping of the polymers *via* charge transfer (Fig. 6d). In contrast, F4TCNQ doping induced clear polaronic absorption and bleaching of the neutral band at 850 nm in the non-symmetric **PODEGTT** and **PODEG2T**, however, the non-symmetric **PODEGT** and symmetric **PODT** showed negligible changes and limited doping efficiency, consistent with the relative energetic alignment of the HOMO levels of the polymers and LUMO level of the dopant. The relative alignment between the polymer HOMO and dopant LUMO plays a decisive role in determining the feasibility of charge transfer. In the case of **PODEGT**, although it displays an elevated HOMO level (−5.14 eV), only weak polaronic absorption features were observed in the NIR region, this behaviour likely arises from an insufficient driving force and limited dopant diffusion into the polymer matrix. By contrast, **PODGETT** and **PODEG2T** possess further elevated HOMO levels and enable more effective charge transfer characteristics, underscoring the importance of precise energy level tuning in enabling effective doping in conjugated polymers. Overall, the utilization of ethylene glycol side chains in a non-symmetric design facilitates more efficient p-doping not only through elevated HOMO levels but also by markedly improving the miscibility between the polymer matrix and the dopant. Additionally, a successive increase in doping efficiency was noticed with the incorporation of electron rich donors; thienothiophene and bithiophene, corroborating that the donor plays a cooperative role with more polar side chain substitution.

In thermoelectric devices non-symmetric oligoether side chains enhance doping efficiency, promote favourable microstructural organization, and balance charge carrier delocalization with controlled ionic interactions. Importantly, oligoether functionalities also facilitate ion transport and stabilize doped states through strong ion-dipole interactions. These same attributes are central to organic electrochemical transistors (OECTs), where non-symmetric polymer designs can enhance volumetric capacitance and facilitate ion diffusion, while preserving electronic conductivity by mitigating excessive swelling and disruption of π–π stacking. Yang and co-workers utilized a DPP-terthiophene based polymer with a non-symmetric side chain design incorporating a triethylene glycol chain paired with a branched octyldodecane side chain (**PDPP3T-1**) (Fig. 7a).[65] The non-symmetric polymer was shown to have enhanced spontaneous self-assembly into more ordered films compared to its statistical copolymer counterpart which possessed symmetrically substituted DPP bearing triethylene glycol and branched alkyl chains (**DPP3T-2**). The non-symmetric **DPP3T-1** had an average hole mobility of up to 2.6 $cm^2\ V^{-1}\ s^{-1}$ without post treatments when prepared as bottom-gate/bottom-contact field effect transistors. The charge carrier mobility of **PDPP3T-1** remains largely unchanged following thermal annealing at 100 °C, however, and only decreases upon subsequent annealing at 150 °C. This behavior contrasts with that of most conjugated polymers including **PDPP3T-2** and **PDPP3T**, where enhanced charge transport only occurs after annealing. In the case of the non-symmetric **PDPP3T-1**, thermal annealing appears unnecessary for achieving optimal charge transport, enabling more rapid device fabrication while minimizing the risk of thermally induced degradation. The presence of the triethylene glycol was also shown to impart the resulting FETs with sensitive and selective responses to ethanol vapor. The gaseous analytes were prepared by controllable dilution with air (15% humidity) with concentrations ranging from 0 ppb to 100 ppm. In particular, FETs fabricated with **PDPP3T-1** exhibited a sensitive response upon exposure to ethanol vapor, shown as a concentration-dependent decrease in the on-current (I_{DS}) (Fig. 7b and c). A measurable response is recorded at concentrations as low as 100 ppb with a 23% decrease observed at 1.0 ppm. Selectivity studies further reveal that the device response is minimal towards non-polar gaseous analytes including CO_2 and low polarity solvent vapors such as dichloromethane and hexanes even at elevated concentrations. Conversely, more polar solvent vapors such as ethyl acetate and acetone occur only at substantially higher concentrations, 1000 ppm and 100 ppm respectively. These findings highlight the potential of non-symmetric polar side chain engineering to impart multifunctional sensing capabilities in π-conjugated devices.

In OECTs, the conjugated polymer acts as the charge carrier channel in contact with an aqueous electrolyte layer. The electric field driven ions are transported though the aqueous layer into the electrolyte interface, thereby doping the polymer layer. Incorporating strategies to improve transistor performance, such as finetuning the hydrophilicity of the semiconducting polymer is critical to device performance. The incorporation of a non-symmetric oligoether and a solubilizing alkyl side chain design in isoindigo based polymers was investigated by Hu and co-workers (Fig. 7d).[66] When investigated through GIWAXS and AFM, the non-symmetric **P3** exhibited the longest-range order and improved thin film crystallinity, reflected in its performance in OFET devices. In OECTs the symmetric oligoether reference polymer **P2** demonstrated the highest performance and best device characteristics, confirming that oligoether side chains give sufficient swellability for aqueous electrolytes to allow ion conduction and bulk doping in OECTs. Despite this, the non-symmetric oligoether/alkyl side chain containing polymer also demonstrated the greatest cycling stability on select substrates attributed to its amphiphilic nature that balanced polymer adhesion to the non-polar

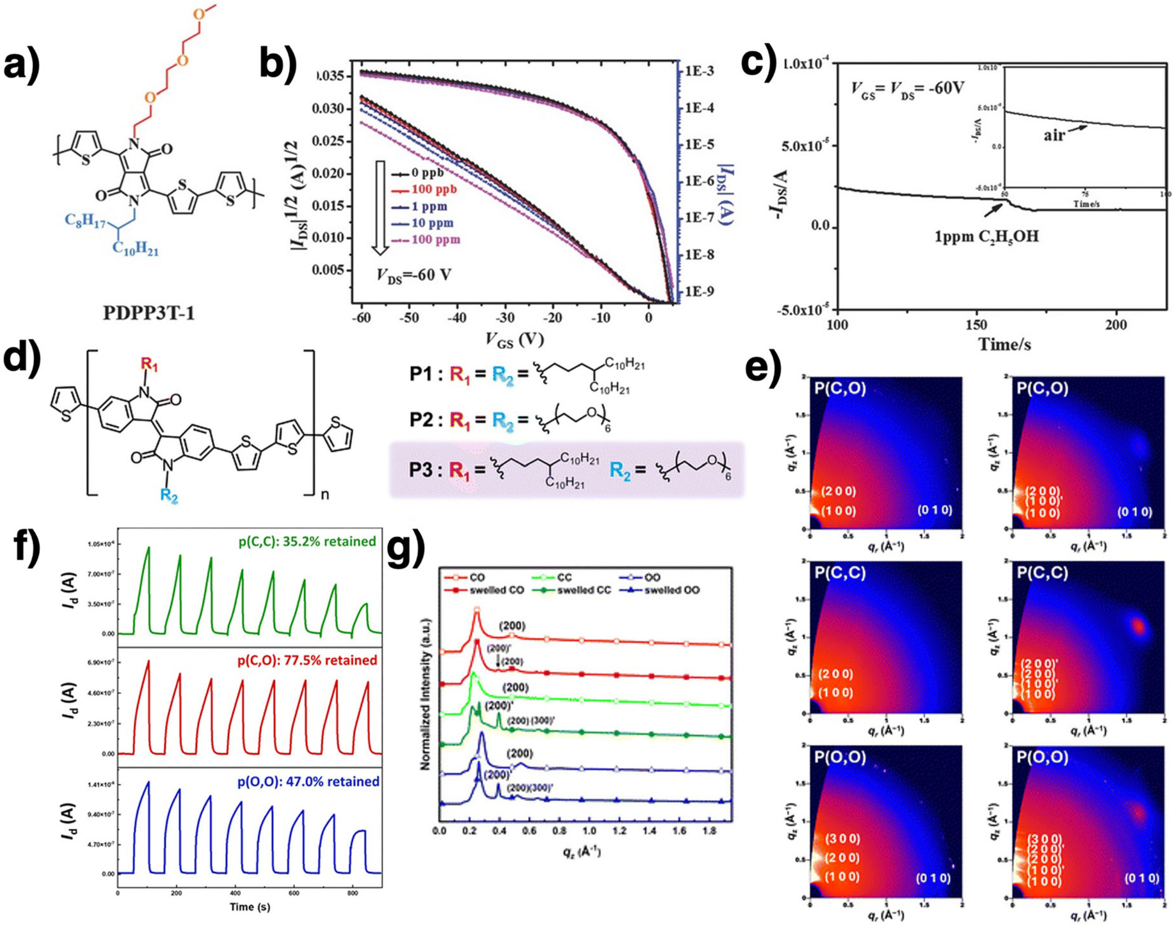

Fig. 7 Non-symmetric triethylene glycol side chains for applications in organic electrochemical transistors. (a) Chemical structure of non-symmetric **PDPP3T-1**; (b) transfer characteristics for devices fabricated with **PDPP3T-1** after exposure to differing concentrations (0–100 ppm) of ethanol vapour; (c) I_{DS} *verse* time under 1 ppm ethanol vapour and air. Adapted with permission from ref. 65. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA; (d) chemical structure of trethylene glycol and branched alkyl chain containing isoindigo-polymers; adapted with permission from ref. 66. Copyright 2023 Royal Society of Chemistry; (e) 2D GIXD patterns of (left) as cast and (right) electrolyte-swelled polymer films for **P(C,C)**, **P(C,O)**, and **P(O,O)**; (f) transient characteristics of **P(C,C)**, **P(C,O)**, and **P(O,O)**; polymer films; (g) 1D out-of-plane GIXD profiles for **P(C,C)**, **P(C,O)**, and **P(O,O)**. Adapted with permission from ref. 67. Copyright 2024 Royal Society of Chemistry.

substrate and ion interaction to the electrolyte solution. In electrochemical transistors, the key figures of merit are transconductance (g_m), mobility (μ) and volumetric charge storage capacitance (C^*). μC^* is considered the indicator for OECT performance. Similarly, Jiang and coworkers investigated a non-symmetric poly(isoindigo-*alt*-bithiophene) system utilizing branched octyl-decane and hydrophilic oligoether side chains in top-gate/bottom-contact OECT devices.[67] The oligoether side chains allowed for good wettability in aqueous electrolytes, and *in situ* electrochemical-optical microscopy measurement showed the non-symmetric **P(C,O)**, in addition to the symmetric oligoether polymer **P(O,O)**, exhibited strong electrochemical doping behaviours after 0.7 V again attributed to the polarity of the oligoether side chains. Notably, **P(O,O)** demonstrates poorer stability than **P(C,O)**, and its optical properties rapidly decreased after potential sweeping suggesting poorer electrochemical stability during OECT device operation compared to non-symmetric **P(C,O)**. Grazing-incidence X-ray diffraction (GIXD) was used to better understand the impact of side chain arrangement and electrolyte diffusion on morphology changes before and after being soaked in aqueous potassium chloride for 7 hours (Fig. 7e). The polymers initially exhibited a typical edge-on orientation as evidenced by the strong *n*00 lamellar and 010 π–π stacking reflections. Upon electrolyte swelling, structural rearrangements were noticed, in the out-of-plane direction, and electrolyte swelling slightly increased disorder in the symmetric **P(C,C)**, but improved crystallinity was observed for both symmetric **P(O,O)**, and non-symmetric **P(C,O)** reflected by increased crystalline coherence length ($L_{C,200}$) and a reduction in the disorder factor (g_{200}). Device characterization revealed an average C^* value of 8.72, 74.2, and 261 F cm^{-3} for **P(C,C)**, **P(C,O)**, and **P(O,O)** respectively, and an average hole mobility of 0.015, 0.78, and 0.35 cm^2 V^{-1} s^{-1} similarly. The introduction of the hydrophilic side chains does enhance the electrochemical doping as evidenced by the C^* value for the symmetric and non-symmetric oligoether containing polymers, however, **P(C,O)** which combines both hydrophilic and hydrophobic side chains displays good capacitance along with the highest retained mobility. Similarly, the response speed of the OECT devices was probed by single transient curve, and fitted with an exponential decay function, the non-symmetric **P(C,O)** was shown to have the lowest rise (t_r) and fall time (t_f) compared to its symmetric counterparts. Hydrophilic side chains such as oligoether moieties exhibit faster doping rates, while, hydrophobic side chains are shown to retain ions within the film, thus slowing the de-doping rates. Consequently combining both affinity side chains as in **P(C,O)** allows for the fastest t_r and t_f out of the polymer series. Non-symmetric **P(C,O)** also exhibits the fastest response rate and highest stability when measuring I_D in 8 continuous on/off cycles, with retention values of 35.2%, 77.5%, and 47.0% for **P(C,C)**, **P(C,O)**, and **P(O,O)** respectively (Fig. 7f). Supported by the GIRXD analysis (Fig. 7g), the combination of the alkyl and oligoether side chain promotes coplanarity and structural stability. Through the introduction of the non-symmetric polar side chain, the **P(C,O)** film was found to enhance orientation and crystallinity through swelling, this structural stability under swelling conditions ensures superior device performance and thus the best current retention.

5. Summary and perspective

Side chain engineering has long served as a central molecular design strategy in semiconducting π-conjugated polymers, enabling the simultaneous control of solubility, microstructure, and optoelectronic performance that underpins modern organic electronics. As this review article highlights, the deliberate introduction of non-symmetrical side chain architectures represents a significant conceptual and practical expansion of this design toolbox. By breaking the structural equivalence that has historically governed most conjugated polymer systems, non-symmetrical substitution can provide a powerful means to decouple and influence properties that are otherwise intrinsically interdependent in symmetrically substituted analogues. Across the growing body of literature surveyed here, this approach has been shown to modulate aggregation pathways, tune crystallinity and domain orientation, enhance mechanical compliance, and in several cases preserve (or even improve) charge transport characteristics in various organic electronics. These findings collectively establish side chain non-symmetry, not as a synthetic curiosity, but as a distinct structure–property design paradigm for next-generation organic electronic materials. At a fundamental level, non-symmetrical side chain engineering introduces new opportunities to manipulate disorder in a controlled and functional manner. Rather than viewing disorder as detrimental to electronic performance, this strategy enables its use as a tool for tailoring microstructure, reducing mechanical brittleness, and introducing spatially differentiated interactions that are often difficult to achieve in conventional systems. Such control is particularly relevant for emerging applications in which electronic performance must be balanced with mechanical deformability, environmental stability, and interfacial compatibility, including stretchable electronics, wearable and implantable sensors, and soft energy-harvesting devices. In this context, non-symmetrical side chains offer a molecular route to materials that are not only high performing, but also mechanically resilient and adaptive.

Despite these advances, the field remains at an early stage, and several important challenges must be addressed to fully realize the potential of this approach. First, synthetic accessibility and scalability remain non-trivial, as the preparation of regio-defined, non-symmetrical monomers often require multistep routes and careful control over substitution patterns. Importantly, while "lego-like" modular strategies are effective for isatin-based systems, their limited applicability to widely used acceptors such as NDI and DPP highlights a key synthetic gap and motivates the development of new methodologies enabling pre-functionalized, modular building blocks across broader conjugated polymer platforms. The development of more efficient, modular, and high-yielding synthetic methodologies will therefore be critical. Second, the lack of systematic, side chain focused structure–property studies make it difficult to disentangle the relative contributions of non-symmetry, side chain chemistry, and backbone structure. Standardized comparative studies, ideally across multiple device platforms, are needed to establish generalizable design rules. Third, deeper multiscale characterization and modeling will be essential to understand how molecular-level non-symmetry propagates into mesoscale morphology and macroscopic device behaviour. Predictive frameworks that link side chain sequence, packing frustration, and anisotropic interactions to electronic and mechanical performance would greatly accelerate rational materials discovery. Looking forward, some of the most exciting opportunities lie in moving beyond hydrocarbon-based substituents toward functional, interactive, and dynamic side chains. The integration of hydrogen-bonding motifs, ionic or zwitterionic groups, supramolecular recognition units, and stimuli-responsive chemistries within non-symmetrical architectures could enable polymers whose morphology and properties evolve in response to mechanical deformation, chemical environments, or biological interfaces. Such materials would be uniquely suited for bioelectronic and neuromorphic applications, where adaptive behaviour and long-term mechanical compatibility are essential. In parallel, incorporating sustainable and degradable side chain chemistries, as well as green synthetic and processing routes, will be important for aligning the field with broader environmental and manufacturing considerations. More broadly, non-symmetrical side chain engineering invites a shift in how conjugated polymers are conceptualized: from structurally uniform semiconductors toward sequence-defined, functionally heterogeneous soft electronic materials. This perspective opens connections to precision polymer synthesis, block and gradient architectures, and data-driven materials design, where non-symmetrical architectures and controlled heterogeneity are leveraged to encode function.

In summary, the body of work consolidated in this review demonstrates that non-symmetrical side chain design provides a versatile and underutilized molecular lever for tuning the complex and often competing requirements of organic electronic materials. Continued progress will depend on the convergence of synthetic innovation, advanced characterization, theoretical modeling, and device integration. As these efforts mature, non-symmetric side chain engineering is poised to play a central role in the development of adaptive, mechanically compliant, and sustainably manufactured organic electronic systems, ultimately enabling technologies that more seamlessly integrate with the dynamic and structurally complex environments in which they are intended to operate.

Author contributions

All authors contributed to the manuscript. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Acknowledgements

This work was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Discovery Grant (RGPIN-2022-04428).

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