

Modular hinge synthesis of linear conjugated polymer single crystals for intrinsic electronics

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Abstract

The intrinsic electronic properties of linear conjugated polymers have remained experimentally inaccessible for decades because growing single crystals and fabricating sub-micrometer devices from these materials have been considered impossible. Here, we overcome both barriers through a modular hinge synthesis strategy that enforces chain packing into two distinct crystalline architectures. Conventional synthesis yields non-porous parallel-linear conjugated polymers (P-LCPs), whereas sterically bulky backbone engineering forces orthogonal cross-stacking, generating a series of porous cross-linear conjugated polymers (C-LCPs)—a crystal topology never before observed in polymer science. Using continuous rotation electron diffraction, we unambiguously resolve the atomic structures of five C-LCPs and two P-LCPs. Furthermore, by implementing thermal scanning-probe lithography to circumvent electron-beam-induced damage and to achieve high-precision pattern alignment, we perform the first direct intrinsic conductivity measurements on individual sub-micrometer polymer crystals before and after chemical doping. Doped C-LCP-1 displays an 11-fold electrical conductivity enhancement—substantially outperforming P-LCP-1 (2.2-fold)—demonstrating the powerful synergy between porous framework architectures and redox-active motifs in promoting charge transport. These findings establish a general blueprint for custom-designing crystalline linear conjugated polymers and unlocking their fundamental transport limits in next-generation electronics.

Introduction

Linear conjugated polymers hold great promise for next-generation organic electronics and energy technologies owing to their solution processability, mechanical flexibility, tunable bandgaps, and efficient intrachain charge transport¹⁻¹². However, elucidating their fundamental electronic properties has long been hindered by two major bottlenecks. First, achieving precise control over the spatial arrangement of polymer chains and growing single crystals for atomic-structure determination remains exceptionally difficult. Because of their anisotropic nature and entropically driven disordered stacking, linear conjugated polymers typically adopt amorphous or semicrystalline, chain-entangled morphologies¹³⁻¹⁷. To date, fewer than ten directly synthesized single-crystal structures have been reported¹⁸⁻²³, with their linkages largely confined to reversible motifs such as boronate esters and imines that do not allow efficient charge transport. Overcoming this limitation requires new synthetic strategies that expand both the library and bond-type diversity of such crystals while affording atomic-level control over chain packing.

Second, probing the intrinsic physical properties of these materials, particularly charge transport, requires single-crystal devices at the sub-micrometer scale^{24,25}, which are notoriously difficult to fabricate. Organic polymer crystals are typically sub-micrometer-sized and highly susceptible to damage from electron-beam irradiation and chemical processing^{26,27}. Traditional photolithography lacks the requisite spatial resolution, whereas electron-beam lithography, despite its high resolution, degrades the fragile polymer and introduces alignment errors that severely compromise device yield²⁸. Consequently,

prior electrical characterization has relied almost exclusively on pressed pellets²⁹⁻³⁴ or polycrystalline³⁵⁻⁴⁰ thin films, where electrical conductivity measurements are convoluted by grain-boundary scattering, substrate interactions, and structural disorder, thereby obscuring intrinsic transport behavior.

Here, we address these dual challenges by introducing a modular hinge synthesis strategy that enables the controlled construction of linear conjugated polymers with two distinct packing architectures (Fig. 1b). Conventional synthesis affords non-porous parallel-linear conjugated polymers (P-LCP-1 and P-LCP-2). By contrast, incorporation of bulky substituents into the conjugated backbone enforces orthogonal cross-stacking and generates pores. This is realized in two series: first, condensation of anthracene-based dialdehydes with hydrazide monomers affords hydrazone-linked C-LCP-1 to C-LCP-3; second, condensation of aminophenyl-substituted tetraamines with dialdehydes yields imine-linked C-LCP-4 and C-LCP-5. Together, these two series constitute a family of porous cross-linear conjugated polymers (C-LCP-1 to C-LCP-5). Their atomic structures were unambiguously resolved by continuous rotation electron diffraction (cRED). Furthermore, to overcome the lithographic barrier for sub-micrometer crystals, we developed a fabrication technique based on thermal scanning-probe lithography (t-SPL). By performing nanoscale-resolution topographic imaging and patterning within an atomic force microscope (AFM) platform, t-SPL enables the fabrication of single-crystal devices without pattern misalignment or electron-beam-induced damage. This breakthrough facilitates the first direct, unambiguous measurements of the intrinsic electrical conductivity of sub-micrometer organic polymer crystals, both pristine and chemically doped.

Results and Discussion

Synthesis and characterization of C-LCPs-1-3. Growing single crystals of conventional linear conjugated polymers is exceptionally challenging, as chain entanglement and disordered stacking fundamentally hinder long-range crystalline order. Controlling polymer packing modes presents a further obstacle, as conventional synthetic strategies lack precise spatial control. To address these limitations, our molecular design relies on two key principles. First, bulky substituents—such as anthracene and aminophenyl groups—are incorporated into the polymer backbone to induce steric congestion, disrupting dense packing and expanding interchain space to form porous networks. Second, a hinge-like motif, stabilized by π - π stacking and interlayer hydrogen bonding, locks the polymer chains into a cross-stacked geometry. These cooperative non-covalent interactions enforce structural regularity while imparting conformational flexibility to tune pore angles. Together, these features direct anisotropic growth along a defined orientation, suppressing entanglement and disordered stacking to yield highly ordered, micrometer-sized single crystals of one-dimensional conjugated polymers. Crucially, this intrinsic permanent porosity provides accessible channels for chemical doping, enabling precise modulation of electrical conductivity through redox chemistry.

To demonstrate the proof of concept, C-LCP-1 was synthesized via a condensation reaction (Fig. 2a) between 4,4'-(anthracene-9,10-diyl)dibenzaldehyde (BFA) and 2,5-bis(benzyloxy)terephthalohydrazide (BZTH). To test the versatility of this approach, we extended the synthesis to analogues bearing different

alkoxy side chains, replacing BZTH with 2,5-diethoxyterephthalohydrazide (DETH) and 2,5-dibutoxyterephthalohydrazide (DBTH), which afforded C-LCP-2 and C-LCP-3, respectively. The formation of hydrazone linkages in C-LCP-1-3 was confirmed by Fourier transform infrared (FT-IR) spectroscopy (Supplementary Figs. S1-S3) and solid-state nuclear magnetic resonance (ssNMR) spectroscopy (Supplementary Figs. S4-S6). Compared with the reactants, the FT-IR spectra of C-LCPs showed a pronounced new peak at around 1606 cm^{-1} . The ^{13}C NMR spectra further confirmed the hydrazone-linkage formation, with characteristic C=N resonances at 150 ppm (the C=O resonance appeared at 160 ppm). For C-LCP-1, the benzylic methylene carbon of the benzyloxy group appeared at 73 ppm. In C-LCP-2 and C-LCP-3, the methylene carbons adjacent to oxygen in the alkoxy side chains resonated at 67 and 71 ppm, respectively, together with the alkyl-chain signals at 14 ppm for C-LCP-2 and at 16, 23 and 32 ppm for C-LCP-3. Thermogravimetric analysis (TGA) demonstrated that C-LCP-1 decomposed at approximately $330\text{ }^{\circ}\text{C}$, while C-LCP-2 and C-LCP-3 decomposed at approximately $360\text{ }^{\circ}\text{C}$ (Supplementary Fig. S7).

Characterization and structural details of C-LCP-1-3 crystals. Scanning electron microscopy (SEM) images revealed uniform strip-like crystals with typical lengths of $2\text{--}4\text{ }\mu\text{m}$ and widths of $0.2\text{--}0.3\text{ }\mu\text{m}$ (Fig. 2d and Supplementary Figs. S8-S9). To obtain detailed structural information, we performed continuous rotation electron diffraction (cRED) single-crystal analysis. Data for C-LCP-1, C-LCP-2 and C-LCP-3 were collected at resolutions of 1.02, 1.01 and $0.94\text{ }\text{\AA}$, respectively, allowing direct location of all non-hydrogen atoms (Supplementary Figs. S10-S12 and Tables S1-S3). After reconstructing the 3D reciprocal lattice (Fig. 2e and Supplementary Fig. S13), the unit-cell parameters were determined (Supplementary Table S4). Using Olex2, the crystal structures were solved under the **C2/c**, **I2/a** and **I2/a** space groups, respectively, and refined with the SHELXL package. The experimental PXRD patterns agreed well with the simulated patterns (Fig. 2f and Supplementary Figs. S14-S15). The crystal structures of C-LCP-1, C-LCP-2 and C-LCP-3 were determined by single-crystal analysis. Viewed along the crystallographic *c*-axis (Fig. 2b and Supplementary Figs. S16-S17), all three polymers exhibit a cross-stacked packing mode, which hints at the formation of open channels along the stacking direction. This structural feature was further corroborated by N_2 adsorption measurements (Supplementary Fig. S18). Viewed along the crystallographic *b*-axis (Fig. 2c and Supplementary Figs. S19-S20), long-range π - π stacking interactions are present between adjacent polymer chains in the interlayer region, which serve to stabilize the crystalline architecture and maintain long-range order. The interchain spacing (D_1), horizontal periodic length (L_1), interlayer distance (D_2) and intralayer chain intersection angle (α) were determined as follows: for C-LCP-1, $9.3\text{ }\text{\AA}$, $47.2\text{ }\text{\AA}$, $3.7\text{ }\text{\AA}$ and 23° ; for C-LCP-2, $8.8\text{ }\text{\AA}$, $43.9\text{ }\text{\AA}$, $3.5\text{ }\text{\AA}$ and 21.7° ; and for C-LCP-3, $9.0\text{ }\text{\AA}$, $45.1\text{ }\text{\AA}$, $3.6\text{ }\text{\AA}$ and 23.8° .

Design and synthesis of C-LCP-4 and C-LCP-5. To further test the versatility of our strategy, we replaced the previously employed bis(hydrazide) monomer with a tetraamine building block and substituted the anthracene moiety with the more conjugated pyrene unit. This monomer was reacted with dialdehyde linkers under analogous condensation conditions. Reaction between the tetraamine monomer 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline (PyTTA), which bears two unreacted amino-phenyl groups serving as

steric bulky units, and DMDA generates cross-stacked C-LCP-4 (Fig. 3a). In addition, replacing DMDA with 2',5'-dimethoxy-[1,1':4',1"-terphenyl]-4,4"-dicarbaldehyde (DMTDA) gave C-LCP-5, confirming that the bulky amino-phenyl groups on the tetraamine monomer alone are sufficient to enforce cross-stacking, independent of the substituents on the dialdehyde component. Compared with the reactants, the FT-IR spectra (Supplementary Figs. S21-S22) of the C-LCPs showed a pronounced new peak at around 1613 cm^{-1} stemming from the C=N stretch. The ^{13}C NMR spectra (Supplementary Figs. S23-S24) further confirmed the imine-linkage formation, with characteristic C=N resonances at 159 ppm. For C-LCP-4 and C-LCP-5, the methoxy carbon signal appeared at 54 ppm and 55 ppm, respectively. TGA demonstrated that C-LCP-4-5 decomposed at approximately $410\text{ }^{\circ}\text{C}$ (Supplementary Figs. S25). C-LCP-4 and C-LCP-5 exhibited the typical type-I N_2 isotherms. The Brunauer–Emmett–Teller (BET) specific surface areas were $533\text{ m}^2\text{ g}^{-1}$ for C-LCP-4 and $395\text{ m}^2\text{ g}^{-1}$ for C-LCP-5 (Fig. 3b), and the main pore widths centered around 0.8 nm for C-LCP-4, 0.7 nm for C-LCP-5 (Fig. 3c), consistent with the measured sizes from the single-crystal structures.

Characterization and structural details of C-LCP-4 and -5 crystals. SEM images revealed elongated rod-shaped crystals for both C-LCP-4 and the C-LCP-5, with typical lengths of 2-10 μm and widths of 0.2-0.5 μm (Fig. 3d and Supplementary Fig. S26). To obtain detailed structural information, we performed cRED single-crystal analysis on C-LCP-4 and C-LCP-5 using an XtaLAB Synergy-ED instrument. Data for C-LCP-4 and C-LCP-5 were collected at resolutions of 0.83 and 0.91 $\text{\AA}$, respectively, allowing direct location of all non-hydrogen atoms (Supplementary Figs. S27-S28 and Tables S5-S6). After reconstructing the three-dimensional reciprocal lattice (Fig. 3e and Supplementary Figs. S29), the unit-cell parameters were determined (Supplementary Tables S7). Using Olex2, the crystal structures of C-LCP-4 and C-LCP-5 were both solved in the *Pccm* space group, and refined with the SHELXL package. Based on the single-crystal structures, the experimental PXRD patterns of C-LCP-4 and C-LCP-5 match well with their simulated patterns (Fig. 3f and Supplementary Fig. S30). Viewed along the crystallographic *c*-axis (Figs. 3g and 3i), C-LCP-4 and C-LCP-5 also exhibit a cross-stacked packing mode. The in-layer chain intersection angle (α), interchain spacing (D_1), horizontal periodic length (L_1) and interlayer distance (D_2) of the C-LCPs were determined as follows: for C-LCP-4, 62.6° , 12.8 $\text{\AA}$, 24.6 $\text{\AA}$ and 3.7 $\text{\AA}$; for C-LCP-5, 53.6° , 13.2 $\text{\AA}$, 29.3 $\text{\AA}$ and 3.8 $\text{\AA}$ (Figs. 3h and 3j). Consistent with the hinge-like locking mechanism described above, both C-LCP-4 and C-LCP-5 adopt larger in-layer chain intersection angles than their shorter-linker counterparts (C-LCP-1, -2, and -3). Furthermore, from C-LCP-4 to C-LCP-5, elongation of the connecting monomer induces hinge rotation that alters the chain intersection angle by approximately 10° while essentially maintaining the interlayer spacing. These results demonstrate that the hinge angle can be systematically tuned by varying the linker length.

Design, synthesis and characterization of P-LCPs. To verify the structural uniqueness of the cross-stacked architecture and delineate the role of bulky backbone motifs, we designed two series of control experiments with parallel-stacked polymers. In the absence of bulky substituents, the polymer chains lose the steric constraint that enforces orthogonal chain orientation and instead adopt parallel stacking. In the first series, we condensed the anthracene-free analogue

[1,1'-biphenyl]-4,4'-dicarbaldehyde (BPDA) with BZTH, affording the parallel-stacked P-LCP-1 (Fig. 4a). In the second series, the pyrene diamine analogue without pendant bulky amino-phenyl units—4,4'-(pyrene-1,6-diyl)dianiline (PyDA) (Supplementary Figs. S31-S32)—was condensed with 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (DMDA) to give the parallel-stacked P-LCP-2 (Fig. 4b). Compared with the reactants, the FT-IR spectrum of P-LCP-1 (Supplementary Fig. S33) showed a new peak at around 1606 cm^{-1} , whereas P-LCP-2 (Supplementary Fig. S34) exhibited a characteristic imine peak at 1618 cm^{-1} , both of which are assigned to C=N stretches. ^{13}C NMR spectrum (Supplementary Figs. S35-S36) further confirmed the C=N bond formation: for P-LCP-1, the hydrazone C=N resonance appeared at 150 ppm (with C=O at 160 ppm) and the benzylic methylene carbon of the benzyloxy group at 70 ppm; for P-LCP-2, the imine C=N resonance appeared at 160 ppm and the methoxy carbon signal at 55 ppm. TGA demonstrated that P-LCP-1 decomposed at approximately $310\text{ }^{\circ}\text{C}$, while P-LCP-2 decomposed at approximately $410\text{ }^{\circ}\text{C}$. SEM images revealed uniform strip like crystals for P-LCPs (Supplementary Figs. S37-S38). cRED data for P-LCP-1 and P-LCP-2 were collected at resolutions of 1.01 and $0.90\text{ \AA}$ (Supplementary Figs. S39-S40 and Tables S8-S9), respectively. The 3D reciprocal lattices were reconstructed (Figs. 4c-4d and Supplementary Fig. S41), and the structures were solved in the **C2/c** and **P-1** space groups, respectively. Based on the single-crystal structures, the experimental PXRD patterns of P-LCP-1 and P-LCP-2 match well with their simulated patterns (Supplementary Figs. S42-S43). P-LCP-1 exhibits a parallel-stacked arrangement with an interchain spacing of approximately $10.0\text{ \AA}$ along the a- and c-axes (Figs. 4e-4f) and an interlayer distance of approximately $3.4\text{ \AA}$ (Fig. 4g). P-LCP-2 shows a similar parallel-stacked geometry with an interchain spacing of approximately $7.3\text{ \AA}$ (Fig. 4h) and an interlayer distance of approximately $3.7\text{ \AA}$ (Fig. 4i). Unlike the porous cross-stacked C-LCPs, the parallel-stacked P-LCPs show no porosity, consistent with their N_2 adsorption isotherms (Supplementary Fig. S44).

Single-crystal devices of C-LCP-1 and P-LCP-1. Single-crystal electronic devices eliminate interparticle junctions and ill-defined macroscopic conduction pathways and allow transport to be compared directly on the same device before and after chemical modification. Accordingly, we sought to fabricate two-probe single-crystal electrical devices with P-LCP-1 and C-LCP-1. Sonication-assisted exfoliation affords individual polymer crystals (Figs. 5b and 5c), but their sub-micrometer dimensions are incompatible with conventional lithography: photolithography lacks the necessary resolution, and e-beam lithography introduces electron-beam damage and alignment errors.

To overcome these limitations, we developed a fabrication technique based on t-SPL. t-SPL operates on an AFM platform equipped with a tip integrating a heater and a thermometer, which simultaneously achieves high-precision alignment as well as high-resolution patterning (Fig. 5a)⁴¹. Specifically, exfoliated crystals dispersed on SiO_2/Si are spin-coated with a layer of thermoresist, poly(phthalaldehyde) (PPA), atop a protective layer of poly(methyl methacrylate) (PMMA). The conformally coated bilayer retains a surface topographic signature of the underlying crystal under AFM imaging, allowing for determination of crystal location and orientation with nanoscale precision. Applying heat to PPA through the tip directly writes a pre-designed pattern within the same AFM

coordinate system, thereby eliminating coordinate transfer between separate instruments and avoiding electron-beam exposure. O₂-plasma treatment and ethanol development followed by metal deposition and subsequent lift-off produce electrodes on the target crystal while minimizing resist residues and process-induced perturbation. This procedure yields devices with 200-250 nm channel lengths for crystals slightly longer than 1 μm (Figs. 5d–f). Successful device fabrication of five C-LCP-1 and three P-LCP-1 crystals demonstrates the reproducibility of t-SPL (Supplementary Figs. S45–S46). To the best of our knowledge, this work represents the first demonstration of the deterministic integration of micrometer-scale polymer single crystals into devices with sub-micrometer channel lengths^{42,43}.

Compared with P-LCP-1, C-LCP-1 not only features redox-active anthracene moieties but also an open architecture that allows greater accessibility, offering additional handles to modulate charge density and conductivity. Motivated by this potential, we treated C-LCP-1 with a strong oxidant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄). We first measured pressed-pellet electrical conductivity in P-LCP-1 and C-LCP-1 as well as TCNQF₄-treated polymers at room temperature with a home-made *in situ* press setup (Supplementary Fig. S47c and Table S10). Both pristine polymers and TCNQF₄-treated P-LCP-1 exhibited exceptionally high electrical resistance, giving rise to ultralow current that prevents precise determination of their electrical conductivity. In contrast, TCNQF₄-treated C-LCP-1 showed significantly reduced electrical resistance likely as a result of enhanced charge density, yet its current–voltage characteristics is nonlinear, indicating Schottky-type barriers at the electrode–pellet interface (Supplementary Fig. S47a,b). As the pellet inevitably involves charge scattering at grain boundaries and masks anisotropy of charge transport, it prevents a reliable extraction of the intrinsic electrical conductivity.

Based on t-SPL technology fabricated devices, we conducted direct-current electrical characterization to measure electrical resistance of the same device before and after TCNQF₄ treatment (Supplementary Fig. S48 and Table S11). Whereas pristine P-LCP-1 ($\sigma = 9.6 \times 10^{-10} \text{ S}\cdot\text{cm}^{-1}$) and C-LCP-1 ($\sigma = 6.5 \times 10^{-10} \text{ S}\cdot\text{cm}^{-1}$) displayed comparable electrical conductivity values at room temperature, oxidation induces distinct amount of enhancement. Electrical conductivity increased by 2.2 times for P-LCP-1 ($\sigma = 2.2 \times 10^{-9} \text{ S}\cdot\text{cm}^{-1}$) (Supplementary Fig. S49). In contrast, it is enhanced by 11 folds on average in C-LCP-1 ($\sigma = 7.2 \times 10^{-9} \text{ S}\cdot\text{cm}^{-1}$) (Figs. 5g–5h and Supplementary Fig. S50); the enhancement ratio varies from 5.5 to 23.6 folds among individual devices, probably reflecting differences in the metal–crystal contacts, crystal quality, and doping level, but every device exhibits the same increasing trend. The distinct electrical responses to oxidants demonstrate a pronounced backbone dependence: the stronger response of C-LCP-1 should originate from its electron-rich anthracene units, which facilitate charge transfer to TCNQF₄ and increase the population of charge carriers available for transport along the conjugated chain^{44,45}. Together, these results establish backbone engineering as an effective chemical strategy for tuning the magnitude and redox responsiveness of electrical conductivity in LCPs.

Conclusion

In summary, we have established a modular hinge synthesis strategy that breaks the long-standing paradigm of parallel packing in linear conjugated polymers (P-LCPs), enforcing an orthogonal cross-stacked geometry (C-LCPs) with permanent microporosity. Atomic-resolution determination via cRED unambiguously confirms this fundamental geometric transition. By pairing this synthetic platform with non-destructive thermal scanning-probe lithography (t-SPL), we overcome the long-standing barrier of sub-micrometer single-crystal device integration, enabling the first direct tracking of intrinsic conductivity in individual polymer crystals upon doping. The remarkable 11-fold conductivity enhancement in C-LCP-1—far exceeding the 2.2-fold increase in its parallel counterpart—demonstrates that open porous channels facilitate dopant accessibility while redox-active backbones optimize intrachain and interchain charge transport. Beyond delivering a new class of porous organic semiconductors, this integrated synthetic and lithographic platform provides a universal methodology for custom-designing crystalline polymers, probing beam-sensitive organic single crystals, and advancing next-generation anisotropic electronic and optoelectronic technologies.

Methods

Chemicals. All reagents were purchased from commercial sources and used without further purification. AR-P 617.03 and poly(phthalaldehyde) (PPA) were purchased from Allresist GmbH.

Characterization. Solid-state ^{13}C NMR spectra were recorded on a Varian 300 MHz Solid State Infinityplus 300 spectrometer; powder X-ray diffraction patterns were collected on a D/Max-2500 diffractometer with Cu-K α radiation; gas adsorption isotherms were measured using a Micromeritics ASAP-2046; Fourier transform infrared spectra were obtained on a Nicolet iS 50 ATR-FTIR instrument; thermogravimetric analysis was performed on a NETZSCH TG209F3 Tarsus; scanning electron microscopy (SEM) images were taken with a GeminiSEM 450 field-emission scanning electron microscope (ZEISS) equipped with an InLens detector; electron diffraction was carried out on an XtaLAB Synergy-ED diffractometer equipped with a HyPix3000 detector at 200 keV; for device fabrication, single-crystal dispersions were prepared using a ZCPS-600 ultrasonic cell disruptor (Shanghai Zhichu); spin-coating was performed with a KW-4BC spin coater (SETCAS); substrate cleaning and residual removal were done with a VP-R3 O $_2$ plasma cleaner (SUNJUNE); baking and annealing were carried out on a MR Hei-Tec heated magnetic stirrer (Heidolph); all steps except lift-off were conducted in an anhydrous and oxygen-free glovebox (Mikrouna, Shanghai). Crystal mapping, AFM imaging, and thermal scanning-probe lithography were accomplished using a NanoFrazor Scholar system (Heidelberg Instruments Nano); metal deposition was performed by magnetron sputtering in an AMOD physical vapor deposition system (Angstrom Engineering Inc.); electrical characterization was carried out using a CRX-4K probe station (Lake Shore Cryotronics) and a Keithley 4200A-SCS parameter analyzer equipped with two 4200-PA preamplifiers.

The synthesis of C-LCP-1, C-LCP-2, and C-LCP-3 crystals. The synthesis of C-LCP-1 crystals was carried out in a 10 mL Pyrex tube charged with BFA (15.5 mg, 0.04 mmol), BZTH (16.2 mg, 0.04 mmol), 1,4-dioxane (0.7 mL), mesitylene (0.3 mL) and aqueous acetic acid (0.2 mL, 6 M). The tube was degassed

by three freeze-pump-thaw cycles, sealed under vacuum, and heated at 120 °C for 3 days. The precipitate was filtered, washed with DMF, soaked in DMF with several solvent exchanges, and finally rinsed with MeOH to replace DMF. After drying at 80 °C for 12 h, a light yellow powder was obtained in 73% yield (22 mg). C-LCP-2 and C-LCP-3 were prepared following the same procedure, except that BZTH was replaced by DETH (11.3 mg) for C-LCP-2 and by DBTH (13.5 mg) for C-LCP-3, and both reactions used o-dichlorobenzene (1.0 mL) as the organic solvent; their isolated yields were 79% (20 mg) and 69% (19 mg), respectively.

The synthesis of C-LCP-4 and C-LCP-5 crystals. The synthesis of C-LCP-4 crystals was carried out in a 10 mL Pyrex tube charged with DMDA monomer (10.8 mg, 0.04 mmol), PyTTA (11.3 mg, 0.02 mmol), n-butanol (1.0 mL), aniline (50 μ L) and aqueous acetic acid (0.1 mL, 6 M). The tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and heated at 120 °C for 3 days. The precipitate was filtered, washed with DMF, soaked in DMF with several solvent exchanges, and finally rinsed with MeOH to replace DMF. After drying at 80 °C for 12 h, a light-yellow powder was obtained in 88% yield (14.4 mg). C-LCP-5 was prepared following the similar procedure, except that DMDA was replaced by DMTDA (11.1 mg), the amount of aniline was 10 μ L and the reaction used mesitylene (1.0 mL) as the organic solvent (11.8 mg, 66% yield).

The synthesis of P-LCP-1 crystals. A Pyrex tube (10 mL) was charged with BPDA monomer (8.4 mg, 0.04 mmol), BZTH (16.2 mg, 0.04 mmol), 1,4-Dioxane (0.5 mL), Mesitylene (0.5 mL) and aqueous acetic acid (0.2 mL, 6 M). The tube was degassed by the freeze-pump-thaw technique three times and then sealed under a vacuum before being placed in an oven at 120 °C for 3 days. The resulting precipitate was filtered and then washed with DMF. The residue was soaked in DMF and refreshed with the solvent several times, then using MeOH in exchange for DMF. The solid was dried at 80 °C for 12 h to afford a light yellow powder (16 mg, 69% yield).

The synthesis of P-LCP-2 crystals. A Pyrex tube (10 mL) was charged with DMDA monomer (10.8 mg, 0.04 mmol), PyDA (11.3 mg, 0.02 mmol), n-butanol (1.0 mL), aniline (50 μ L) and aqueous acetic acid (0.1 mL, 6 M). The tube was degassed by the freeze-pump-thaw technique three times and then sealed under a vacuum before being placed in an oven at 120 °C for 3 days. The resulting precipitate was filtered and then washed with DMF. The residue was soaked in DMF and refreshed with the solvent several times, then using MeOH in exchange for DMF. The solid was dried at 80 °C for 12 h to afford a light yellow powder (14.4 mg, 88% yield).

Preparation and deposition of single crystals on SiO₂/Si substrates. Single-crystal dispersions were prepared by dispersing C-LCP-1 or P-LCP-1 crystals (10 mg) in isopropanol (30 mL) with ultrasonication (500 W, 1 h, ice bath). After standing undisturbed for 30–60 min, the supernatant was collected and spin-coated onto O₂-plasma-cleaned SiO₂/Si substrates (300 nm SiO₂) at 500 rpm (5 s, acceleration 250 rpm·s⁻¹) and then 5000 rpm (30 s, acceleration 10000 rpm·s⁻¹), followed by annealing at 120 °C for 20 min to obtain randomly dispersed single crystals.

Fabrication of two-probe single-crystal devices. All procedures except lift-off were conducted in an anhydrous glovebox. The crystals were coated with AR-P 617.03 (~130 nm) by spin-coating (1000 rpm, 5 s; 4000 rpm, 45 s), baked at 180 °C for 90 s, then overcoated with a 2 wt% PPA/anisole solution (~35 nm) and baked at 110 °C for 120 s. The buried crystals were located by AFM in Read-Layout mode, and electrode windows, interconnects and pads were patterned into the PPA layer by t-SPL (tip 950–1050 °C, depth 40 nm, electrode gap 200–250 nm). After O₂ plasma (135 W, 200 sccm, 90 s) to remove residual PPA and development in ethanol (60 s) to remove PMMA, Ni (5 nm) and Pd (55 nm) were deposited by magnetron sputtering (0.5 and 1 Å·s⁻¹). Lift-off in acetone (~5 min) yielded devices with a single crystal bridging two electrodes.

Electrical characterization. Electrical measurements were performed in air at room temperature using a probe station and parameter analyzer. With two-probe configuration, one electrode was swept from -2 to +2 V (0.1 V step, 0.5 s delay, compliance 1 pA) while the other was grounded. Resistance was extracted from linear fit of the full I–V curve. Conductivity was calculated as $\sigma = L/(R \cdot w \cdot h)$, where L (channel length) and w (width) were measured from SEM images, and h (thickness) from AFM height profiles.

Scanning electron microscopy. Scanning electron microscopic (SEM) images were acquired at an accelerating voltage of 1 kV using a GeminiSEM 450 field-emission scanning electron microscope (ZEISS) equipped with an InLens detector. The devices were imaged without an additional conductive coating. SEM imaging of the untreated devices was performed only after the initial electrical characterization. The images were used to assess electrode alignment and device morphology and to determine the channel length and width.

Chemical doping. For chemical doping, completed devices were immersed in saturated TCNQF₄/chlorobenzene for 2 h at room temperature, rinsed with chlorobenzene, acetone and isopropanol, dried under N₂, and re-measured. Powder samples of C-LCP-1 and P-LCP-1 were similarly treated with TCNQF₄ solution, filtered, washed with chlorobenzene and THF, and dried at 60 °C under vacuum.

Declarations

Data availability

All data are available in the main text or the supplementary materials. Crystallographic data for the P-LCPs and C-LCPs in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) (CCDC 2585791 for P-LCP-1, CCDC 2585792 for P-LCP-2 and CCDC 2585788 for C-LCP-1, CCDC 2585789 for C-LCP-2, CCDC 2585790 for C-LCP-3, CCDC 2584703 for C-LCP-4, CCDC 2584715 for C-LCP-5). Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

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Author contributions

Z.Z. and L.S. supervised the whole project. T.W. and Y.L. designed and synthesized the LCPs and performed most of the characterizations; Z.S. and Y.Y. carried out single-crystal device fabrication; J.Z., W.Z. and Y.Y. assisted in synthetic experiments and characterizations; T.W., Z.S. and Y.L. wrote the original draft, with input from all authors; T.W., Y.L., Z.S., M.J.Z., P.C., Y.C., L.S. and Z.Z. reviewed and edited the manuscript.

Competing interests

Westlake University and Nankai University have jointly filed a pending patent application (No. 2026113047437) related to devices fabrication described in this work. L.S., Z.Z., Z.S., Y.Y. and T.W. are named as inventors on this application. The remaining authors declare no competing financial interest.

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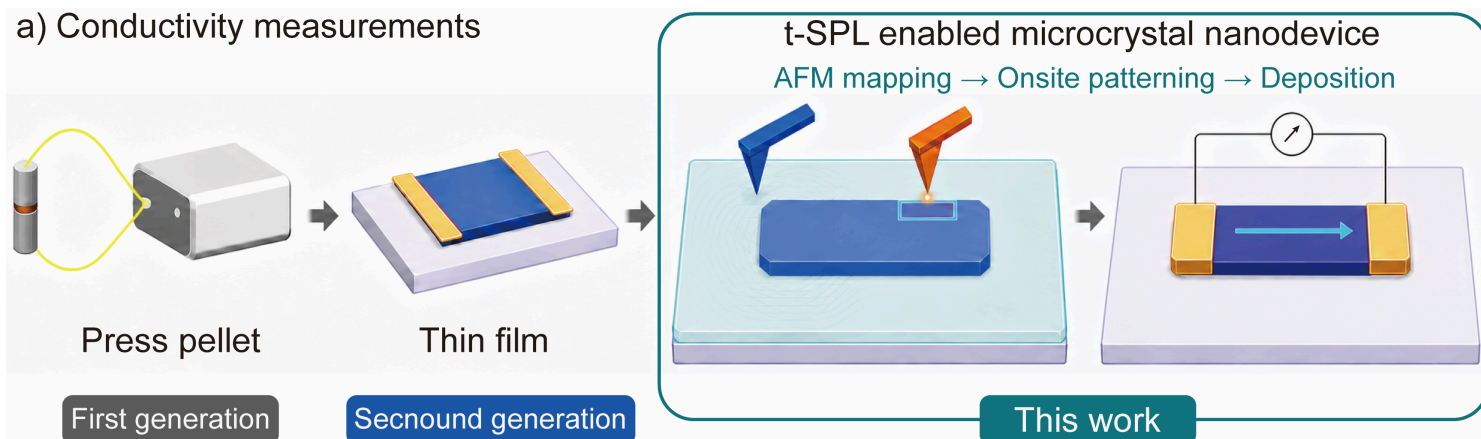
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Figures

a) Conductivity measurements



b) Modular hinge synthesis strategy

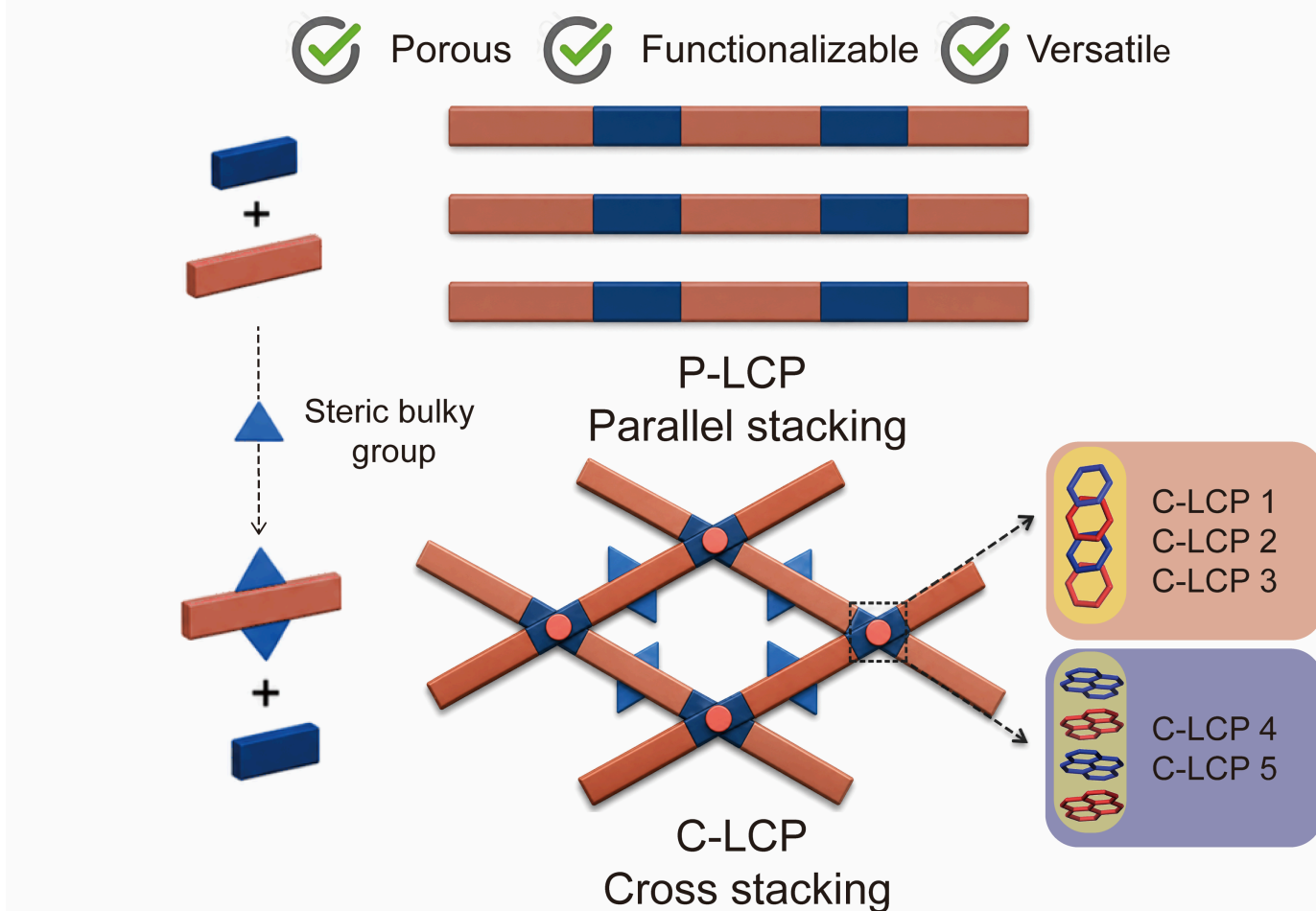


Figure 1

New-generation single-crystal devices and modular hinge synthesis strategy. a) Evolution of techniques for conductivity measurements for organic polymers. b) Schematic illustration of the

modular hinge synthesis strategy for controlling chain packing in linear conjugated polymers.

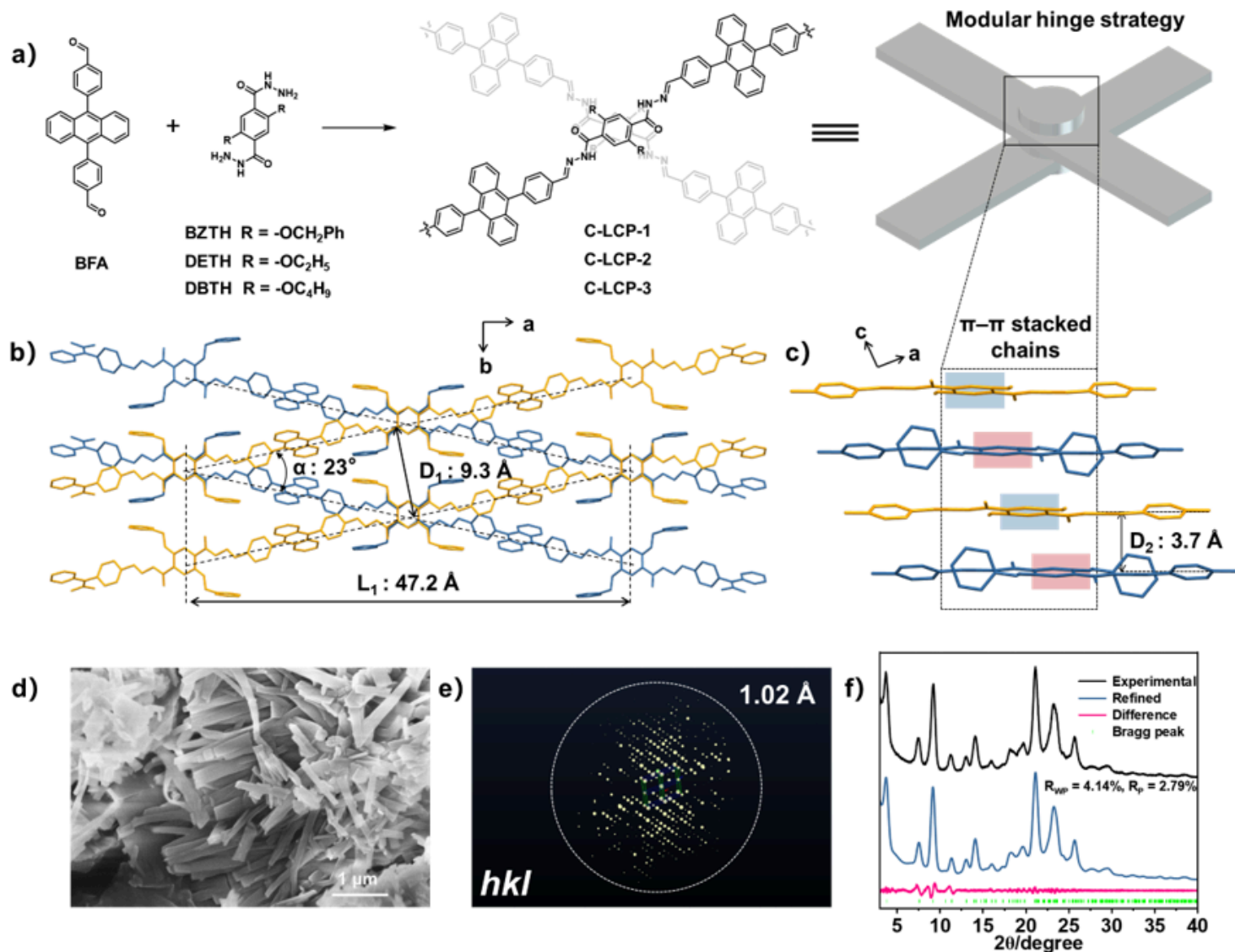


Figure 2

Synthesis, characterization and structure of C-LCP-1-3. a) Synthetic route of C-LCPs. b) The packing structure of C-LCP-1. c) The interlayer distance and π - π stacked chains of C-LCP-1 (hydrogen atoms and benzyl phenyl rings omitted for clarity). d) SEM image of C-LCP-1. e) 3D reciprocal lattice of C-LCP-1. f) The PXRD patterns of C-LCP-1.

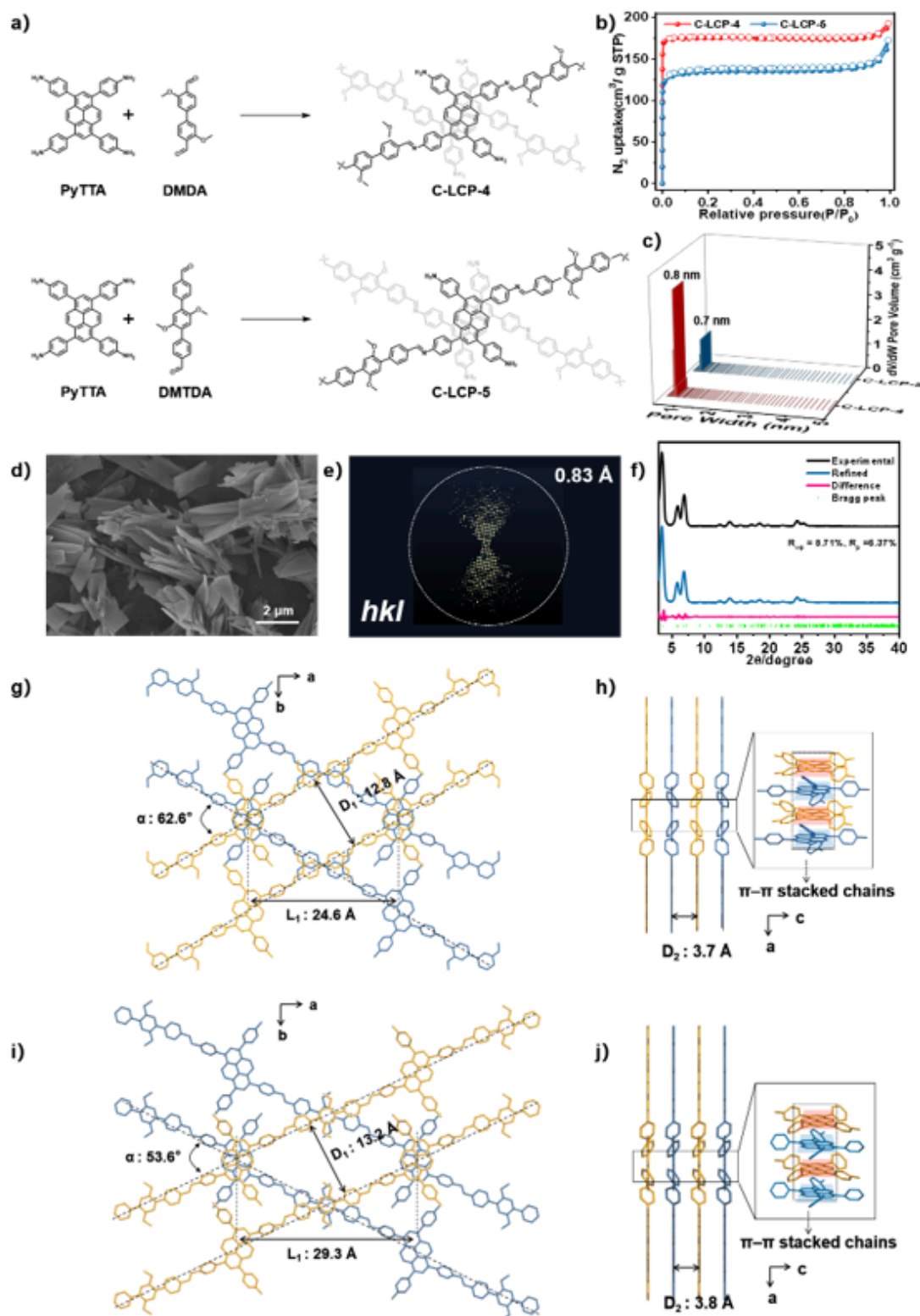


Figure 3

Synthesis, characterization and structure of C-LCP-4 and -5. a) Synthetic route of C-LCP-4. b) N_2 adsorption of C-LCP-4 and C-LCP-5. c) Pore width of C-LCP-4 and C-LCP-5. d) SEM image of C-LCP-4. e) 3D reciprocal lattice of C-LCP-4. f) The PXRD patterns of C-LCP-4. g) The packing structure of C-LCP-4. h) The interlayer distance and π - π stacked chains of C-LCP-4. i) The packing structure of C-LCP-5. j) The interlayer distance and π - π stacked chains of C-LCP-5.

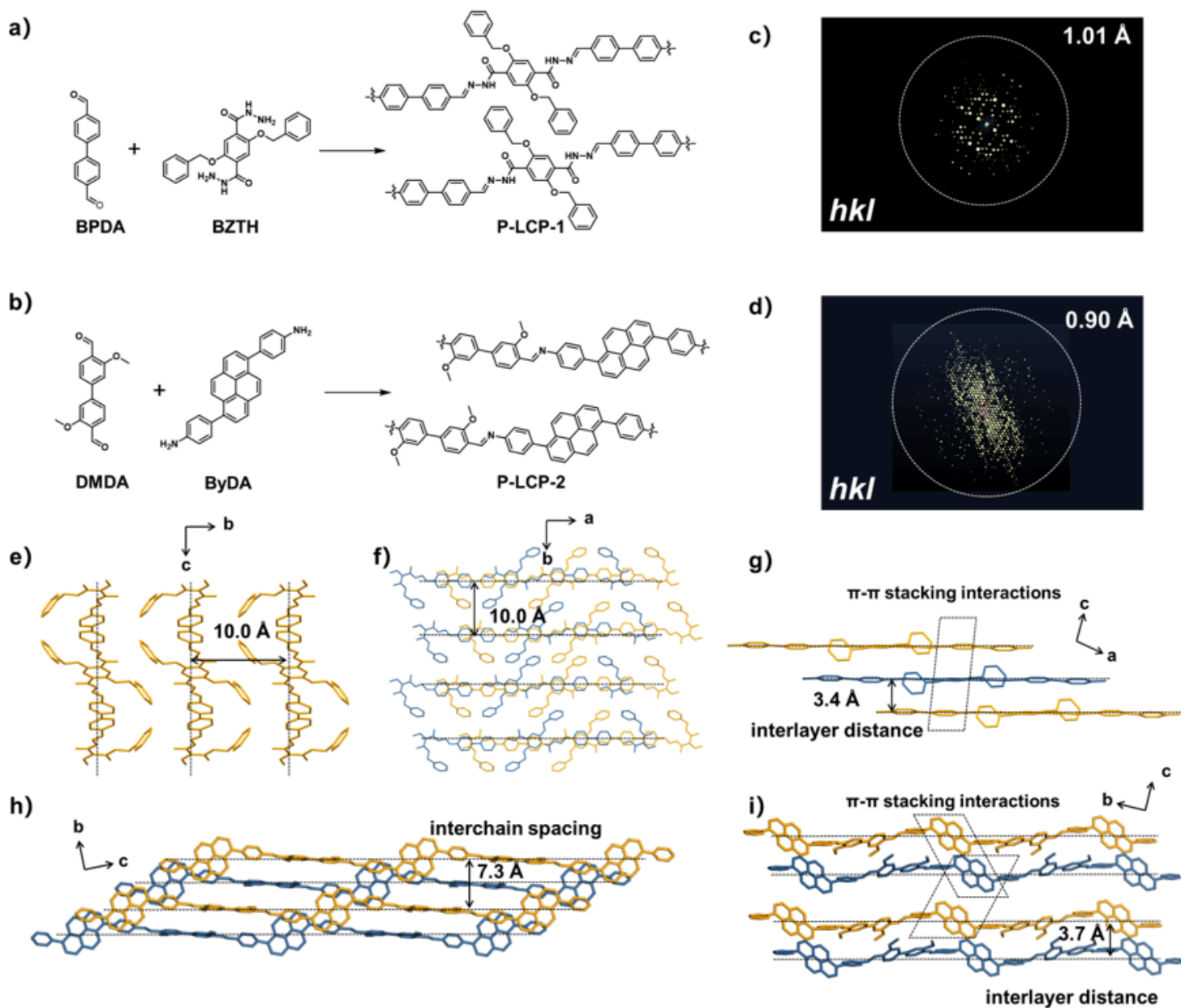


Figure 4

Synthesis, characterization and structure of P-LCPs. a) Synthetic route of P-LCP-1. b) Synthetic route of P-LCP-2. c) 3D reciprocal lattice of P-LCP-1. d) 3D reciprocal lattice of P-LCP-2. e) The interchain distance of P-LCP-1 along the a-axis. f) The interchain distance of P-LCP-1 along the c-axis. g) The interlayer distance of P-LCP-1. h) The interchain distance of P-LCP-2. i) The interlayer distance of P-LCP-2.

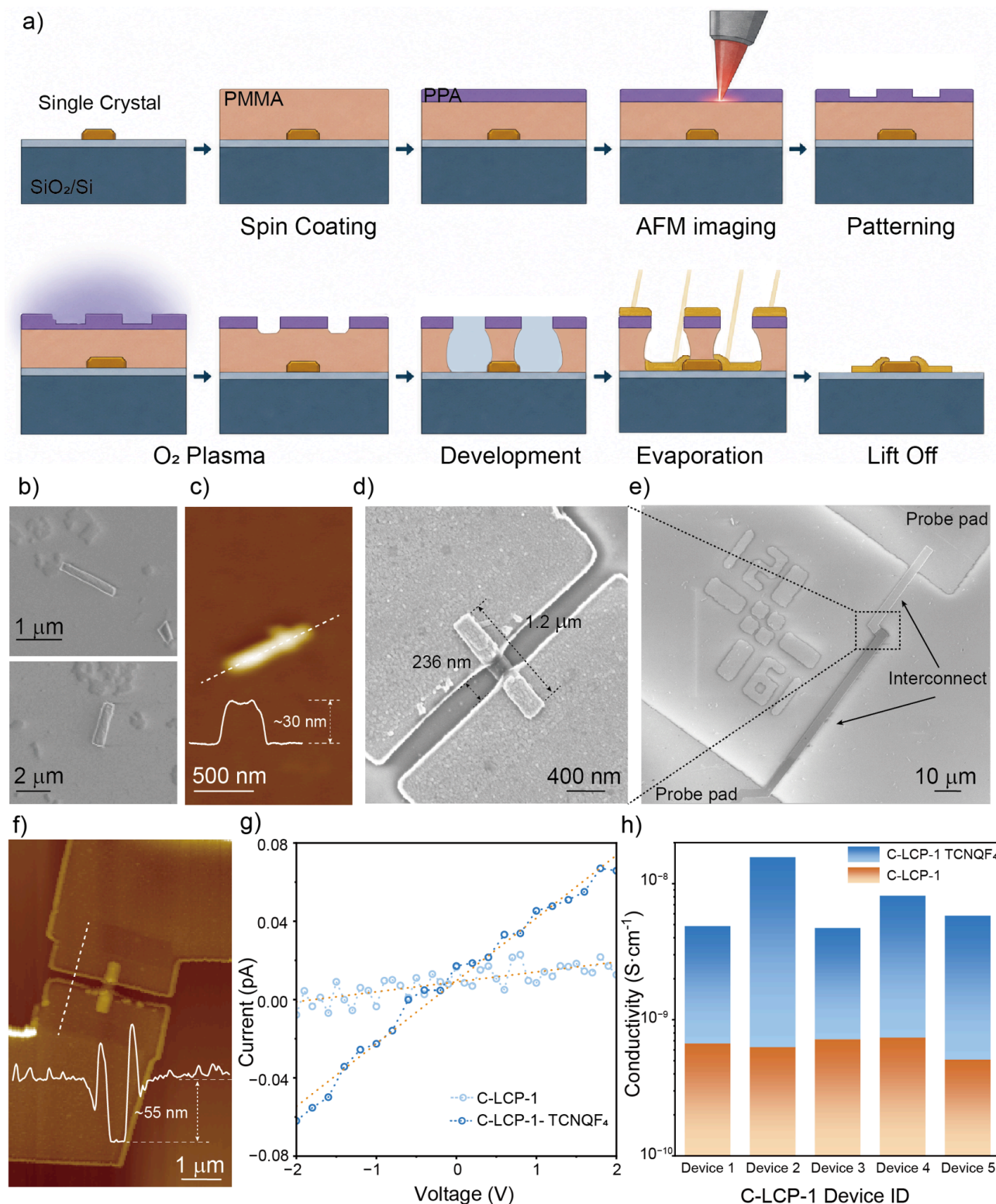


Figure 5

t-SPL fabrication and chemical modulation of single-crystal devices of C-LCP-1. a) Schematics of t-SPL-based device fabrication. b) Representative optical micrographs of randomly dispersed single crystals on SiO₂/Si substrate. c) AFM topographic image and corresponding height profile of a representative crystal. d) High-magnification SEM image of a completed device, showing a 236 nm channel across a micrometer-scale crystal. e) SEM overview of the device architecture, showing the

probe pads and interconnects. f) AFM topographic image and corresponding line profile of the completed device. g) Current–voltage characteristics of a C-LCP-1 single-crystal device before and after TCNQF₄ treatment and h) corresponding statistics from five devices.

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