Electronic supplementary information for

D- π -D molecular semiconductors for perovskite solar cells: the superior role of helical versus planar π -linker

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Experimental section

Materials. Perylo[1,12-b,c,d]thiophene^{S1} (PET) and dinaphtho[2,1-b:1',2'-d]thiophene^{S2} (T5H) were prepared according to the literature protocols. N-bromosuccinimide (NBS, 99.0%, Aladdin), tetrahydrofuran (THF, 99%, Sinopharm Chemical Reagent Co., Ltd), 4,4'-dimethoxyphenylamine (98%, Zhengzhou Alfa Chemical Co., Ltd.), tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃, 98%, Energy sodium *tert*-butoxide (NaO(t-Bu),98%. Energy Chemical), 2-Chemical). dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (Ruphos, 95%, Aldrich), toluene (99%, Sinopharm Chemical Reagent Co., Ltd), dichloromethane (99%, Sinopharm Chemical Reagent Co., Ltd), heptane (98%, Aladdin), titanium diisopropoxide bis(acetylacetonate) (TIACA, 75% in isopropanol, Sigma-Aldrich), acetylacetone (ACAC, >99.0%, TCI), acetylacetone (ACAC, 99.0%, TCI), ethanol (99.8%, Aladdin), TiO₂ paste (30NR-D, Greatcell Solar), formamidinium iodide (FAI, 99.0%, Greatcell Solar), methylammonium bromide (MABr, 99.0%, Greatcell Solar), PbI₂ (99.99%, TCI), PbBr₂ (99.99%, TCI), CsI (99.0%, TCI), lithium bis(trifluoromethane)sulfonimide (LiTFSI, 99.0%, 99.9%. Sigma-Aldrich), dimethyl sulfoxide (DMSO, N,N-Sigma-Aldrich), dimethylformamide (DMF, 99.8%, Sigma-Aldrich), 4-tert-butylpyridine (TBP, 96%, Sigma-Aldrich), spiro-OMeTAD (≥99.8%, Xi'an Polymer Light Technology Corp.), and chlorobenzene (99.8%, Acros Organics) were purchased and used without further purification.

Instrumentation. ¹H NMR and ¹³C NMR spectra were recorded with an AVANCE III 400 spectrometer or an AVANCE III 500 spectrometer. Chemical shifts were reported with respect to THF-*d*₈. High resolution mass spectra (HR-MS) were measured with a Bruker Ultraflex MALDI-TOF spectrometer. Single-crystal XRD measurements were performed on a Bruker D8 Venture diffractometer. Crystal structures were defined using the SHELXTL software. The attached single crystal .cif files provide detailed refinement parameters. Diagrams were prepared with Mercury 3.10. The crystallographic data are summarized in Table S1. Atom force microscopy (AFM) images were recorded with a Park NX-10. Steady-state photoluminescence (PL) spectra and time-resolved PL traces were measured with a Life-Spec-II fluorescence spectrometer. Ultraviolet photoelectron spectra (UPS) were measured with a ThermoFisher ESCALAB 250Xi. Electronic absorption spectra were recorded on a Cary 8454 spectrophotometer (Agilent Technologies). Impedance spectra were

recorded on an Autolab electrochemical workstation in the dark by applying a 40 mV voltage perturbation over a series of forward bias, with the frequency range from 3 MHz to 1000 Hz. The measured impedance spectra were further fitted using the Z-view software (v2.80, Scribner Associates Inc.).

Synthesis of N³, N³, N¹⁰, N¹⁰-tetrakis(4-methoxyphenyl)perylo[1,12-bcd]thiophene-3,10-diamine (PET-OMeDPA). A solution of PET (2.82 g, 10.0 mmol) in dry THF (300 mL) was cooled to 0 °C. Then a solution of NBS (3.74 g, 21.0 mmol) in dry THF (100 mL) was added dropwise. The reaction was stirred at 0 °C for 30 min, warmed to room temperature, and stirred for another 3 h. A yellow precipitate was formed with the progress of the reaction. The yellow precipitate was filtered and washed with methanol. The orange solid was collected and dried at 100 °C under vacuum. Next, the obtained solid was transferred to a 200 mL one-neck flask without further purification. Subsequently, 4,4'-dimethoxyphenylamine (5.04 g, 22.0 mmol), NaO(t-Bu) (2.30 g, 24 mmol), Pd₂(dba)₃ (458 mg, 0.5 mmol), Ruphos (467 mg, 1.0 mmol), and toluene (200 mL) were added to the flask. The reaction mixture was refluxed overnight under argon before cooled to room temperature. The mixture was filtered through a silica gel pad to get rid of the inorganic salt. The filtrate was concentrated in vacuo and purified by column chromatography on alumina to afford the title product PET-OMeDPA (5.59 g, 7.6 mmol, 76% yield) as a red solid. Mp 306–307 °C. ¹H NMR (400 MHz, THF- d_8) δ = 8.66 (d, J = 7.6 Hz, 2H), 8.06 (d, J = 8.3 Hz, 2H), 7.82 (s, 2H), 7.67 (dd, J = 8.3, 7.6 Hz, 2H), 7.06–6.96 (m, 8H), 6.86–6.73 (m, 8H), 3.73 ppm (s, 12H). ¹³C NMR (125 MHz, THF) δ = 156.3, 144.7, 143.9, 135.2, 131.9, 130.1, 128.3, 127.4, 127.1, 125.0, 124.8, 122.3, 121.9, 115.4, 55.6 ppm. HR-MS (MALDI-TOF) m/z calc. for [M]+: 736.23903, found: 736.23903.

Synthesis of N^5 , N^9 , N^9 -tetrakis(4-methoxyphenyl)dinaphtho[2,1-*b*:1',2'-*d*]thiophene-5,9diamine (T5H-OMeDPA). T5H-OMeDPA was was synthesisd from T5H as a yellow solid in 87% yeild, by use of a similar proceduce for PET-OMeDPA. Mp 296–297 °C. ¹H NMR (400 MHz, THF d_8): $\delta = 8.86$ (dd, J = 8.5, 1.2 Hz, 2H), 8.21 (dd, J = 8.4, 1.4 Hz, 2H), 7.61 (s, 2H), 7.48 (ddd, J = 8.4, 6.8, 1.4 Hz, 2H), 7.40 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H), 7.02–6.90 (m, 8H), 6.81–6.76 (m, 8H), 3.72 ppm (s, 12H). ¹³C NMR (125 MHz, THF- d_8) $\delta = 156.6$, 145.1, 143.8, 139.7, 132.1, 130.6, 129.9, 127.3, 126.7, 126.2, 125.8, 125.0, 120.3, 115.5, 55.7 ppm. HR-MS (MALDI-TOF) m/z calc. for [M]⁺: 738.25468, found: 738.25468. **Crystal growth.** Single crystals of T5H, PET-OMeDPA, and T5H-OMeDPA were obtained from nearly saturated solutions in dichloromethane/heptane mixtures at room temperature, by slow evaporation of solvent.

QTAIM analysis. The quantum theory of atoms in molecules (QTAIM) analysis was carried out for dimers in single-crystals with the MultiWFN package (version 3.3.9), based on single-point energy calculation at the M06-2X/6-31G(d,p) level of theory with Gaussian 09.^{S3,S4}

EDA analysis. Energy decomposition analysis (EDA) was carried out using AMBER force field for dimers in single-crystals with the MultiWFN package (version 3.3.9),^{S4,S5} also based on single-point energy calculation at the M06-2X/6-31G(d,p) level of theory with Gaussian 09. The total intermolecular interaction energy (E^{int}) can be decomposed into the electrostatic (E^{ele}), repulsion (E^{rep}), and dispersion (E^{disp}) energies as described by

$$E^{\rm int} = E^{\rm ele} + E^{\rm rep} + E^{\rm disp}.$$

 E^{ele} is defined by the Coulomb's law as

$$E_{\rm AB}^{\rm ele} = \frac{q_{\rm A}q_{\rm B}}{r_{\rm AB}},$$

where q represents the atomic charge and r_{AB} is the interatomic distance. E^{rep} can be described by

$$E_{\rm AB}^{\rm rep} = \varepsilon_{\rm AB} \left(\frac{R_{\rm AB}^0}{r_{\rm AB}} \right)^{12},$$

where ε_{AB} represents the depth of the van der Waals interaction potential well and R_{AB}^0 is the nonbonding contact distance in the AMBER force field. E^{disp} is defined by

$$E^{\rm disp} = -2\varepsilon_{\rm AB} \left(\frac{R_{\rm AB}^0}{r_{\rm AB}}\right)^6.$$

Single-crystal hole-mobility calculation. The calculation of theoretical hole mobility of PET single crystal was based on the structure from the Cambridge Crystallographic Data Centre (CCDC-129291). The theoretical hole mobility of T5H, PET-OMeDPA, and T5H-OMeDPA single crystal was calculated based on the structure from our crystallographic analysis.

The hole-transfer integral (v) is defined as the strength of electronic coupling between the highest occupied molecular orbitals (HOMO) of molecules in dimers of single crystals by equation

$$v = \left\langle \psi_{i}^{\text{HOMO}} \mid F \mid \psi_{f}^{\text{HOMO}} \right\rangle$$

where ψ represents the wavefunction and F is the Fock operator. The hole-transfer integral was calculated with the Gaussian 09 program package at the M06-2X/6-31G(d,p) level of theory. The hole-transfer rate constant (K_i) can be described by Marcus-Hush theory^[S6] as follows:

$$K_{\rm i} = \frac{2\pi v^2}{\rm h} \left(\frac{\pi}{\lambda k_{\rm B}T}\right)^{1/2} \exp\left(-\frac{\lambda}{4k_{\rm B}T}\right),$$

where v is the hole-transfer integral and λ is the reorganization energy of hole-transfer. h, k_B, and *T* correspond to the Planck constant, the Boltzmann constant, and the Kelvin temperature, respectively. The reorganization energy (λ) of hole-transfer is composed of internal reorganization energy and external reorganization energy. The external part can be ignored because of its little contribution in the solid state. The internal part is dependent of the change of molecular geometry during hole-transfer process. By definition,

$$\lambda \approx \lambda_{\rm in} = (E_0^* - E_0) + (E_+^* - E_+),$$

where E_0^* is the energy of neutral in ion geometry, E_0 is the energy of neutral in neutral geometry,

 E_{+} is the energy of ion in ion geometry, and E_{+}^{*} is the energy of ion in neutral geometry. The diffusion coefficient (D) is defined as

$$D=\frac{1}{2n}\sum_{i}d_{i}^{2}K_{i}p_{i},$$

where *n* represents the dimensionality of the single crystal with a value of 3. d_i and k_i are the centroid distance and the hopping rate, respectively. p_i is the relative hopping probability via path i, which can be generalized as

$$p_i = \frac{K_i}{\sum_i K_i}.$$

In the end, the charge mobility (μ) can be derived via Einstein-Smoluchowski equation

$$\mu = \frac{eD}{k_{\rm B}T},$$

where e is the elementary charge.

Band structure. Energy bands of single crystals were calculated with BAND package of the Amsterdam Modeling Suite, based on single-point energy calculation at the GGA-PW91/TZP level.

SCLC mobility measurement. An indium-doped tin-oxide (ITO) glass was patterned via laser etching for the fabrication of a hole-only device. The substrate was cleaned in ultrasonic baths of Hellmanex (2%, deionized water), deionized water, ethanol, and acetone in turn. A 30-nm-thick, PEDOT:PSS layer was spin-coated onto the substrate and annealed at 150 °C for 15 min in air. A flat thin film of PET-OMeDPA (or T5H-OMeDPA) was further spun from a 40 mM chlorobenzene solution at 5000 rpm for 30 s. The thickness of thin film was measure with KLA Tencor D-500 contact profilometer. An 80-nm-thick gold layer was finally evaporated under a <10⁻⁴ Pa vacuum. Dark Current density–voltage (*J*–*V*) curve of a hole-only device was measured with a Keithley 2400 source-measure unit in a nitrogen-filled glovebox. The hole mobility was derived by fitting *J–V* curve with equation

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3},$$

where ε_0 and ε_r are the vacuum and relative permittivities, respectively. *d* is the thickness of a hole-transporting layer.

Surface structure calculation. Surface structure calculation was performed using ADF BAND package. Geometry optimization was carried out at the GGA:PBEsol/DZ level, and single point calculation was performed at the GGA:PBEsol-D3/DZ level. The perovskite model system was made by a $2 \times 2 \times 3$ perovskite slab orientated along the 110 direction for the PbI₂-terminated surface.

Reorganization energy of hole extraction. The reorganization energy of hole extraction (λ_h) is composed of the internal reorganization energy and the external reorganization energy. The external part can be ignored because of its negligible contribution in the solid state. The internal part $(\lambda_{n,h})$ is dependent of the change of molecular geometry during the hole extraction process. The elementary

hole transfer from perovskite to a molecule is characterized by two energies: E_+ (ion in ion geometry) and E_+^* (ion in neutral geometry). By definition,

$$\lambda_{\rm h} \approx \lambda_{\rm in \, h} = E_+^* - E_+$$

Device fabrication. A laser etched fluorine doped tin oxide (FTO) glass (TEC 14, Nippon Sheet Glass Co., Ltd, white glass, 1.6 mm thickness) was rinsed in turn with detergent, deionized water, acetone, and ethanol using an ultrasonic bath. A 30 nm TiO₂ blocking layer was then deposited by spray pyrolysis employing O₂ as the carrying gas at 450 °C from a precursor solution of 0.6 mL titanium diisopropoxide bis(acetylacetonate) and 0.4 mL acetylacetonate in 9 mL anhydrous ethanol. Next, a 200-nm-thick mesoporous TiO₂ layer was coated on the substrate by spin-coating for 10 s at 4000 rpm with a ramp rate of 2000 rpm s⁻¹, using the commercial TiO₂ paste (30NR-D) diluted with anhydrous ethanol at a 1:6 weight ratio. After drying at 100 °C for 10 min, the TiO₂ film was annealed at 450 °C for 30 min under dry air flow to remove organic components. Perovskite precursor solution contains 1.30 M PbI₂, 1.19 M FAI, 0.14 M PbBr₂, and 0.14 M MABr in the DMSO/DMF (1/4, $v/v_{,}$) mixture. 1.5 M CsI stock solution in DMSO was added into the perovskite desired precursor to obtain the triple cation composition (FAPbI₃)_{0.875}(MAPbBr₃)_{0.075}(CsPbI₃)_{0.05}(PbI₂)_{0.03}. The perovskite film was deposited by a consecutive two-step spin-coating process at 1000 rpm for 10 s (ramp rate 200 rpm s⁻¹) and 6000 rpm for 30 s (ramp rate 2000 rpm s⁻¹) on the electron-transporting layer. At the time of 15 s prior to the program end, 150 µL of chlorobenzene was dripped on the spinning substrate, and the film was then annealed at 120 °C for 1 h. A hole-transporting layer was spin-coated atop the annealed perovskite films from a 40 mM solution in chlorobenzene at 4000 rpm for 20 s. The hole-transporters were doped with LiTFSI and TBP in a molar ratio of 0.5 and 3.3, respectively. The depositions of perovskite layer and hole-transporting layer were carried out in a dry air-filled glove box with a <2% relative humidity. Finally, a 120 nm-thick, gold layer was thermally evaporated under a $\leq 1 \times 10^{-4}$ Pa vacuum to complete the cell fabrication.

Current density–voltage measurement. Current density–voltage characteristic was measured by applying a series of potential biases to a perovskite solar cell and measuring the corresponding currents, with a Keithley 2400 source meter under the full computer control using Labview 14.0. A

Sirius-SS150A solar simulator (Zolix, China) was employed to give an irradiance of 100 mW cm⁻². The light intensity was tested with a calibrated monocrystalline silicon solar cell (Model HG-SS20, No. L0013, Beijing Henggong Instrument Co. Ltd., China). A metal mask with an aperture area of 0.16 cm² was covered on a testing cell during all measurements in a nitrogen-filled glovebox.

External quantum efficiency measurement. An Omni- λ 300 monochromator (Zolix, China) collocated with a 150 W xenon lamp (Zolix, China) was employed to supply monochromatic lights for external quantum efficiency measurements, at a 10 nm wavelength interval. A Keithley 2400 source meter under the full computer control with Labview 14.0 was deployed to short-circuit a solar cell and meanwhile measure the currents at a current sampling time of 1 s. A Hamamatsu S1337-1010BQ silicon diode calibrated at the National Institute of Metrology, China was used to measure the intensities of monochromatic lights.



Fig. S1 Differential scanning calorimetry thermograms of PET-OMeDPA and T5H-OMeDPA samples.



Fig. S2 (A) Molecular geometry of PET extracted from single-crystal. (B–D) Single-crystal structures of PET viewed from the crystallographic *a* axis (B), *b* axis (C), and *c* axis (D). Hydrogen atoms are omitted for clarity. (E) IH4 isohedral tiling with PET molecules projected in the *ac* plane. Each orientied molecule is put into one colored tile. PET crystallizes in monoclinic $P2_1a$ space group with four molecules in a primitive unit cell.^{S7} As Fig. S2 shows, coplanar PET molecules (Fig. S2A) stack along the crystallographic *b* axis with a tilt angle of 39.8°, forming a molecular column. In the *ac* plane are observed four types of columns in terms of orientation (Fig. S2C). One column can be converted to another by means of inversion or glide operation. As illustrated in Fig. S2E, molecules projected in the *ac* plane fit well with IH4 (one of 93 isohedral tilings) which belongs to [3⁶] topological class.^{S8}



Fig. S3 (A–G) Space-filling packing structures of dimers from the PET single-crystal. (H–N) Molecular graphs showing intermolecular interactions. The covalently bonded atoms are additionally linked via a "bond path" (marked in red), a line along which electron density is maximal. The "bond path" is used here for depiction of non-covalent interactions in a dimer. The total interaction energy (E^{int}) is calculated by energy decomposition analysis. (O–U) Isodensity surface plots of intermolecular HOMO overlaps. The isodensity value is set at 1×10⁻⁶. The red and blue isosurfaces refer to the same and opposite phase overlap, respectively. In terms of orientation and centriod distance seven types of dimers can be extracted from PET single crystal, and are further ranked in

Fig. S3 according to the total intermolecular interaction energy (E^{int}). E^{int} is calculated as the sum of electrostatic energy (E^{ele}), repulsion energy (E^{rep}), and dispersion energy (E^{disp}). As presented in Fig. S3, multiple "bond paths" depicting $\pi \cdots \pi$ and $S \cdots \pi$ interactions exist in dimer 1 (two adjacent molecules in the column) with a large E^{int} value of 656 meV. Moreover, $CH \cdots \pi$, H–H, CH–S, and S–S interactions are discovered for other dimers composed of inter-columnar molecules. However their E^{int} values are all smaller than 150 meV, likely because of the much less "bond paths" for edge-to-edge interactions. As shown in Fig. S3O, there is a sizable HOMO overlap for dimer 1 in PET single-crystal, leading to a large v of 232.7 meV, suggesting fast hole transport along the crystallographic b axis. Note from Fig. S3P–U that the HOMO overlaps in edge-to-edge oriented dimers 2–7 are not so conspicuous, leading to small v values of less than 5 meV. Our analysis has implied the one-dimensional hole transport character of PET single-crystal with a theoretical hole mobility of 8.2 cm² V⁻¹ s⁻¹. This value is close to that of 5.3 cm² V⁻¹ s⁻¹ calculated by another research team.^{S9} PET single-crystal was integrated into a field-effect transistor by Sun et al., showing an experimental hole mobility of 0.8 cm² V⁻¹ s⁻¹.^{S10}



Fig. S4 (A) Geometries of T5H enantiomers extracted from single-crystal analysis. The dihedral angle between two terminal benzene rings of T5H: 44.2° . Hydrogen atoms are omitted for clarity. (B–C) Single crystal structures of T5H viewed from the crystallographic *b* axis (B), *c* axis (C), and *a* axis (D). Sulfur atoms are marked in green for better presenting the molecular orientation in panel B. (E) IH17 isohedral tiling with T5H molecules projected in the *ab* plane.

We carried out X-ray diffraction measurement of T5H single-crystal in view of incomplete crystallographic data reported in the literature.^{S11} T5H is geared to orthorhombic space group *Pbcn* with four molecules in a primitive unit cell (Table S1). As Fig. S4A shows, T5H molecule has a C₂ symmetry axis, and the dihedral angle of two outermost benzene rings is 44.2°. A couple of enantiomers (*M* and *P*) lie in T5H single-crystal (Fig. S4B). Along the crystallographic *c* axis (Fig. S4C), enantiomers *M* and *P* stack on top of each other in an antiparallel fashion, forming a racemic column. In the *ab* plane there are two types of columns with different orientations, which can be converted to one another through glide operation. As Fig. S4E presents, the IH17 isohedral tiling which is also classified into [3⁶] topological class^{S8} can be used to nicely accommodate T5H molecules in the *ab* plane.



Fig. S5 (A–D) Space-filling packing structures of dimers selected from the T5H single-crystal. (E– H) Molecular graphs showing intermolecular interactions. (I–L) Isodensity surface plots of intermolecular HOMO overlaps. The isodensity value is set at 1×10^{-6} . As shown in Fig. S5, amongst four dimers in T5H single-crystal dimer 1 in the column possesses the largest E^{int} value of 597 meV and numerous "bond paths", which stem from $\pi\cdots\pi$, $S\cdots\pi$, and CH–S interactions. Furthermore, CH $\cdots\pi$ and H–H interactions bring together two molecules from different columns at the same orientation to yield tail-to-tail dimer 2 with an E^{int} value of 296 meV, while CH–S and H–H interactions afford head-to-tail dimer 3 with an E^{int} value of 177 meV. Dimer 4, which is formed only via H–H interaction with two molecules from columns of different orientations, has the smallest E^{int} value of 61 meV. We note that for PET and T5H single-crystals, the difference in E^{int} of

two types of dimer 1 is less than one tenth. However, the v value for dimer 1 of T5H is almost two times reduced, being 118.1 meV, which is associated with the damped HOMO overlap (Fig. S5I versus Fig. S5O). The v value of dimer 2 with two T5H molecules even from two columns is also not too small, being 29.3 meV, owing to the considerable HOMO overlap of two terminal benzene rings of T5H (Fig. S5J). However, the v values for dimer 3 and dimer 4 are less than 3 meV. The hole-transfer λ value of 174 meV for T5H (Table S5) is larger than that of 141 meV for PET, which could be understood by structural relaxation to a greater extent. We further calculated the theoretical hole mobility of T5H crystal as 1.7 cm² V^{-1} s⁻¹. The experimental filed-effect mobility of T5H single-crystal was reported to be 0.15 cm² V⁻¹ s⁻¹ by Takeya et al.^{S11}

Compound	T5H	PET-OMeDPA	T5H-OMeDPA
Empirical formula	$C_{20}H_{12}S$	$C_{48}H_{36}N_2O_4S$	$2(C_{48}H_{38}N_2O_4S){\cdot}CH_2Cl_2$
Formula weight	284.36	736.85	1562.65
Temperature	296 K	170 K	170 K
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>P</i> b c n	$P\overline{1}$	$P\overline{1}$
<i>a</i> [Å]	21.4461 (12)	9.2973(3)	10.5796(14)
<i>b</i> [Å]	8.4399 (4)	11.5371(4)	13.7266(18)
<i>c</i> [Å]	7.3436 (4)	17.8524(6)	14.3680(18)
α [°]	90	99.629(1)	85.956(5)
β[°]	90	101.049(1)	83.941(5)
γ [°]	90	97.562(1)	82.064(5)
Volume [Å ³]	1329.21 (12)	1826.25 (11)	2051.7 (5)
<i>Z</i> , [Å ³]	4	2	1
$\rho_{\rm calc}[{\rm g~cm^{-3}}]$	1.421	1.340	1.265
μ [mm ⁻¹]	0.232	0.140	0.191
F [000]	592	772.0	818.0
Crystal size [mm ³]	0.43×0.33×0.18	0.30×0.23×0.11	0.521×0.073×0.065
2Θ range for data collection [°]	1.171 to 35.11	2.265 to 26.373	2.301 to 33.270
Refl. Collected	7848	21478	35678
Independent reflections	1219	7441	15578
Data/restraints/parameters	1219/0/96	7441/0/500	15578/0/527
Data completeness	0.999	0.994	0.985
Goodness-of-fit on F ²	1.091	1.023	1.126
Final <i>R</i> indexes [$I \ge 2\sigma(I)$]	R1 = 0.0490,	R1 = 0.0453, wR2 = 0.1154	R1 = 0.1059, wR2 = 0.3102
Final <i>R</i> indexes [all data]	R1 = 0.0568,	R1 = 0.0566, wR2 = 0.1241	R1 = 0.1839, wR2 = 0.3784
Largest diff. peak/hole [e Å ⁻³]	0.433/-0.649	0.456/-0.295	2.583/-0.455
CCDC deposition number	1873375	1949110	1949111

Table S1 Crystal data and structure refinement for T5H, PET-OMeDPA, and T5H-OMeDPA

Molecule	Dimer	E^{ele} [meV]	E^{rep} [meV]	E^{disp} [meV]	E^{int} [meV]
	1	51	451	-1158	-656
	2	-6	69	-207	-144
	3	-5	53	-175	-127
PET	4	-7	34	-152	-125
	5	4	105	-209	-101
	6	-5	44	-132	-93
	7	-8	33	-97	-71
	1	3	422	-1022	-597
	2	-16	154	-433	-296
13H	3	-20	85	-243	-177
	4	10	38	-109	-61

Table S2 Intermolecular interaction energy of dimers in PET and T5H crystals^a

^{*a*} Total intermolecular interaction energy (E^{int}) , electrostatic energy (E^{ele}) , repulsion energy (E^{rep}) , and dispersion energy (E^{disp}) were calculated by EDA.



Fig. S6 The geometries of two enantiomers extracted from the crystallographic analysis of PET-OMeDPA, with the π -linker of PET being convex and concave, are marked in magenta and cyan.



Fig. S7 IH4 isohedral tiling with PET-OMeDPA molecules projected in the ac plane



Fig. S8 The geometries of enantiomers in T5H-OMeDPA single crystal: Blue, M; Red, P.



Fig. S9 Tiling IH47 associated with the structure of T5H-OMeDPA projected on *bc* plane.

Molecule	Dimer	E^{ele} [meV]	E^{rep} [meV]	E^{disp} [meV]	E^{int} [meV]
	1	-30	363	-1365	-1032
	2	-12	415	-1105	-703
	3	-115	315	-892	-692
PET-OMeDPA	4	39	330	-994	-626
	5	-37	206	-737	-568
	6	-29	182	-698	-545
T5H-OMeDPA	1	-14	556	-1613	-1071
	2	-49	361	-1018	-706
	3	-12	202	-738	-547
	4	-20	281	-744	-483
	5	-29	121	-561	-469
	6	-2	24	-190	-168

Table S3 Intermolecular interaction energy of dimers in PET-OMeDPA and T5H-OMeDPA crystals

λ	Dimer	$d_{ m i}$	V	$k_{ m i}$	μ
[eV]		[Å]	[meV]	$[s^{-1}]$	$[cm V^{-1} s^{-1}]$
	1 (red)	4.525	232.65	6.18×10 ¹⁴	
0.141	2 (pink)	8.293	2.10	5.02×10 ¹⁰	
	3 (magenta)	8.763	4.43	2.24×10 ¹¹	
	4 (blue)	8.788	2.82	9.09×10 ¹⁰	8.2
	5 (orange)	9.622	1.17	1.57×10 ¹⁰	
	6 (yellow)	10.046	2.74	8.59×10 ¹⁰	
	7 (cyan)	10.032	4.31	2.12×10 ¹¹	

Table S4 Reorganization energy (λ) , center-of-mass distance (d_i) , transfer integral (v), hole hoping rate (k_i) , and theoretical hole mobility (μ) of PET in single-crystal

Dimer 1 and dimer 2 have distinctively large k value. The presence of dimer 1 and dimer 2-forming molecules above and below a randomly selected molecule suggests the one-dimensional hole transport characteristic in PET single crystal.

λ	Dimor	$d_{ m i}$	v	$k_{ m i}$	μ	
[eV]	Dimer	[Å]	[meV]	$[s^{-1}]$	$[cm V^{-1} s^{-1}]$	
	1 (blue)	5 108	118 10	1.03×10 ¹⁴	1.7	
		5.100	110.10			
	2	6.115	29.25	6.34×10 ¹²		
0.174 (green) 0.174 3 (red) 4 (magent	(green)					
	3	8.440	1.66	2.04×10 ¹⁰ 3.42×10 ¹⁰		
	(red)					
	4	11.524	2.15			
	(magenta)					

Table S5 Reorganization energy (λ) , center-of-mass distance (d_i) , transfer integral (v), hole hoping rate (k_i) , and theoretical hole mobility (μ) of T5H in single-crystal

There are two channels with relatively large k value in the crystallographic *bc* plane, dimer 1 and dimer 2 have the largest k. dimer 3 and dimer 4 with the second largest k value also exists. The presence of dimer 1, dimer 2, dimer 3, and dimer 4-forming molecules at one set of four corners of a randomly selected molecule suggests the two-dimensional hole transport characteristic in T5H single crystal.

λ	Dimer	$d_{ m i}$	v	$k_{ m i}$	μ	
[eV]	[eV]	[Å]	[meV]	[s ⁻¹]	$[cm V^{-1} s^{-1}]$	
	1 (pink)	6316	ΔΔΔ	2.29×10^{10}		
		0.510	7.77	2.27×10		
	2	10 880	5.02	2 93×10 ¹⁰		
0 221	(white)	10.000	5.02	2.)5×10		
	3	9 297	3.22	1.21×10 ¹⁰		
	(grey)).2)1			6 1×10 ⁻³	
0.551	4	10.180	7.61	6.74×10 ¹⁰	0.17710	
	(orange)					
	5	12 029	7.79	7.05×10 ¹⁰		
	(green)	15.750				
	6	12 405	8 64	8.69×10 ¹⁰		
	(red)	12.705	0.04			

Table S6 Reorganization energy (λ) , center-of-mass distance (d_i) , transfer integral (v), hole hoping rate (k_i) , and theoretical hole mobility (μ) of PET-OMeDPA in single-crystal

λ	D.	d_{i}	v	$k_{ m i}$	μ	
[eV]	Dimer	[Å]	[meV]	$[s^{-1}]$	$[cm V^{-1} s^{-1}]$	
	1	6.743	25.75	1.17×10 ¹²		
	(grey)			1.17/10		
	2 (red)	10.58	1.64	A 75×109	3.3×10 ⁻²	
		10.36	1.04	4.75×10		
	3	9.571	3.29	1.91×10 ¹⁰		
0.204	(magenta)					
0.274	4	18.746	1 82	5 82~109		
	(dark blue)		1.02	5.82×10		
	5	11 800	2 15	1.065×1010		
	(purple)	11.077	2.45	1.00L×10**		
	6	10.613	0.14	3.45E×10 ⁷		
	(blue)	10.013	0.14			

Table S7 Reorganization energy (λ) , center-of-mass distance (d_i) , transfer integral (v), hole hoping rate (k_i) , and theoretical hole mobility (μ) of T5H-OMeDPA in Single-crystal



Fig. S10 Band structures of PET single crystal calculated at the DFT/GGA-PW91 level of theory. In the band graphic, points of high symmetry in the first Brillouin zone are as follows: $\Gamma = (0, 0, 0)$, A = (-0.5, 0.5, 0), C = (-0.5, 0, 0.5), D = (0, 0.5, 0.5), E = (-0.5, 0.5, 0.5), H = (-0.3733, 0, 0.6521), H₁ = (-0.6267, 0, 0.3497), M = (-0.3733, 0.5, 0.6521), M₁ = (-0.6267, 0.5, 0.3479), X = (-0.5, 0, 0), Y = (0, 0, 0.5), and Z = (0, 0.5, 0). Path: Γ-Y-H-C-E-M₁-A-X-H₁|M-D-Z|Y-D.



Fig. S11 Band structures of T5H single crystal calculated at the DFT/GGA-PW91 level of theory. In the band graphic, points of high symmetry in the first Brillouin zone are as follows: $\Gamma = (0, 0, 0)$, R = (0.5, 0.5, 0.5), S = (0, 0.5, 0.5), T = (0.5, 0.5, 0), U = (0.5, 0, 0.5), X = (0, 0, 0.5), Y = (0, 0.5, 0), and Z = (0.5, 0, 0). Path: Γ -X-S-Y- Γ -Z-U-R-T-Z|Y-T|U-X|S-R



Fig. S12 Band structures of (A) PET-OMeDPA and (B) T5H-OMeDPA single crystal calculated at the DFT/GGA-PW91 level of theory. (C) In the band graphic, points of high symmetry in the first Brillouin zone are as follows: $\Gamma = (0, 0, 0)$; $A_1 = (0, 0.5, -0.5)$; $A_2 = (0, 0, -0.5)$; $A_3 = (0.5, -0.5, -0.5)$; $A_4 = (0.5, 0, -0.5)$; $A_5 = (0, -0.5, 0)$; $A_6 = (-0.5, 0.5, 0)$; $A_7 = (-0.5, 0, 0)$. Path: $A_1 - \Gamma - A_2 | A_3 - \Gamma - A_4 | A_5 - \Gamma - A_6 | \Gamma - A_7$.



Fig. S13 Circular dichroism spectrum of T5H-OMeDPA thin film spin-coated from chlorobenzene.

sample	τ_1 [ns]	A_{1}	τ_2 [ns]	A_2	$\overline{ au}$ [ns]	$ au_{ m h}$	$\phi_{ m h}$
perovskite	125.0	0.02	2399	0.98	2353	/	/
perovskite/PET-OMeDPA	21.15	0.48	52.33	0.52	37.4	38	0.99
perovskite/T5H-OMeDPA	21.47	0.22	78.47	0.78	65.9	68	0.96

Table S8 Time Constants of PL Decays^a and Hole Extraction Yields Estimated from Static PLSpectra^b

^{*a*} τ_1 and τ_2 are the time constants of the fast and slow decays, A_1 and A_2 are the corresponding relative amplitudes, and $\overline{\tau}$ is the amplitude-averaged time constant which can be obtained via equation $\overline{\tau} = A_1 \tau_1 + A_2 \tau_2$. ^{*b*} Hole extraction yield (ϕ_h) can be derived by comparing the integral area of PL curves.



Fig. S14 UPS spectra of CsMAFA, PET-OMeDPA, and T5H-OMeDPA in the cutoff (A) and onset (B) energy regions. The derived HOMO energy levels of CsMAFA, PET-OMeDPA, and T5H-OMeDPA are -5.45 eV, -5.21 eV, and -5.28 eV versus vacuum, respectively.



Fig. S15 Electronic absorption spectra of CsMAFA perovskite, PET-OMeDPA and T5H-OMeDPA. The CsMAFA perovskite film is spin-coated on the mesoporous TiO₂ substrate. PET-OMeDPA and T5H-OMeDPA are spun from chlorobenzene onto glass.



Fig. S16 Optimized geometries of PET-OMeDPA (A) and T5H-OMeDPA (B) on a modelled FAPbI₃ slab. To illustrate the interaction between hole-transporter and perovskite, the distances between the interacting oxygen and lead atoms are marked.



Fig. S17 AFM height images (5 μ m × 5 μ m) of perovskite films coated with PET-OMeDPA (A) and T5H-OMeDPA (B). The reference without HTL is shown in panel C.



Fig. S18 J-V with reverse and forward scans of PSCs employing PET-OMeDPA or T5H-OMeDPA as hole-transporting layer under simulated AM1.5G solar light (100 mW cm⁻²).



Fig. S19 J-V curve measured under 100 mW cm⁻², AM1.5G illumination of a typical PSC with spiro-OMeTAD.



Fig. S20 Statistical graphs of J_{SC} (A), V_{OC} (B), FF (C), and PCE (D) of PSCs with PET-OMeDPA and T5H-OMeDPA measured at the simulated AM1.5G conditions.



Fig. S21 (A) Nyquist plots at the forward bias of 0.90 V for cells with PET-OMeDPA and T5H-OMeDPA. (B) The equivalent circuit used for the fitting of impedance spectra of PSCs.



Fig. S22 The ¹H NMR (400 MHz) spectrum of PET-OMeDPA in THF- d_8 .



Fig. S23 The ¹³C NMR (100 MHz) spectrum of PET-OMeDPA in THF- d_8 .

MALDI-TOF Mass Spectrum



Fig. S24 The high-resolution mass spectrum (MALDI-TOF) of PET-OMeDPA.



Fig. S25 The ¹H NMR (400 MHz) spectrum of T5H-OMeDPA in THF- d_8 .



Fig. S26 The ¹³C NMR (100 MHz) spectrum of T5H-OMeDPA in THF- d_8 .

MALDI-TOF Mass Spectrum



Fig. S27 The high-resolution mass spectrum (MALDI-TOF) of T5H-OMeDPA.

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