Electronic Supplementary Information

Suppressed Non-Radiative Loss and Efficient Hole Transfer at Small Highest Occupied Molecular Orbital Offset Enables 19.73% Efficiency Binary Organic Solar Cells with Small Efficiency-Cost Gap

Xiaolei Kong, Nana Yang, Xixi Zhang, Jinyuan Zhang, Zhenyu Li, Xinrui Li, Yilei Wu, Rui Sun, Jing Li, Aoxiang Li, Jie Min, Guang Yang, and Chenkai Sun**

X. Kong, N. Yang, X. Zhang, Z. Li, X. Li, A. Li, G. Yang, Prof. C. Sun
College of Chemistry, Zhengzhou University, Zhengzhou 450001, China
E-mails: xlkong@zzu.edu.cn; schenkai@zzu.edu.cn

J. Zhang
Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

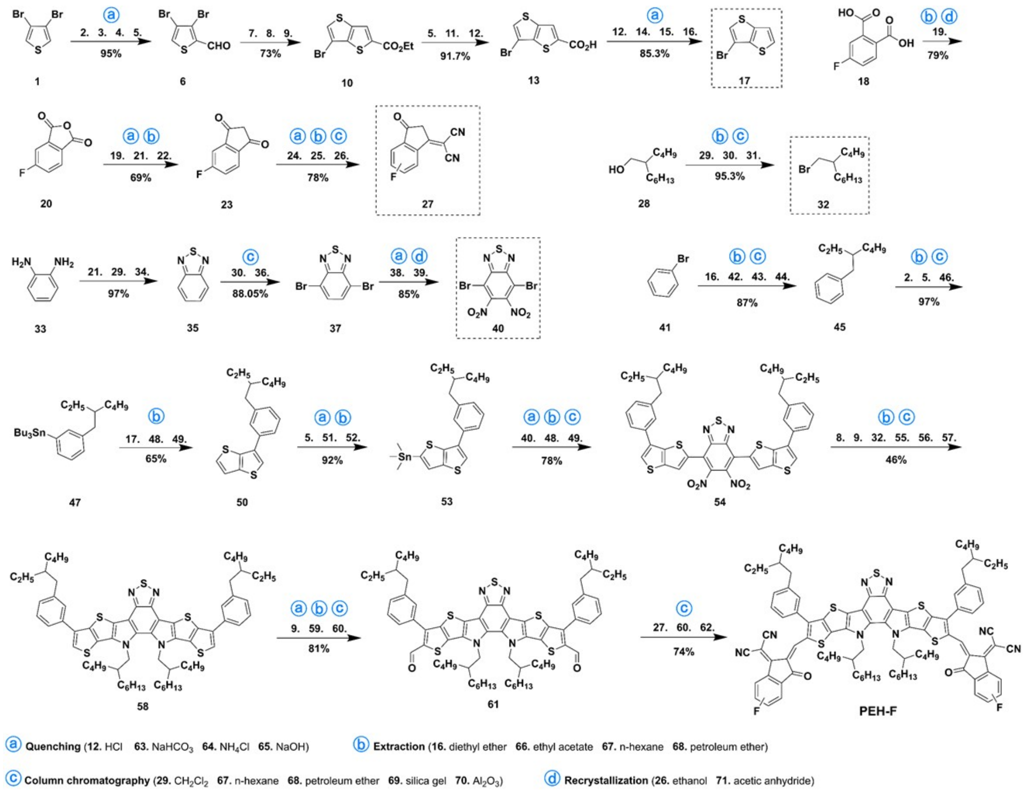
Y. Wu
Department of Chemistry, Stanford University, Stanford, California 94305-4125, United States

R. Sun, J. Min
The Institute for Advanced Studies, Wuhan University, Wuhan 430072, China

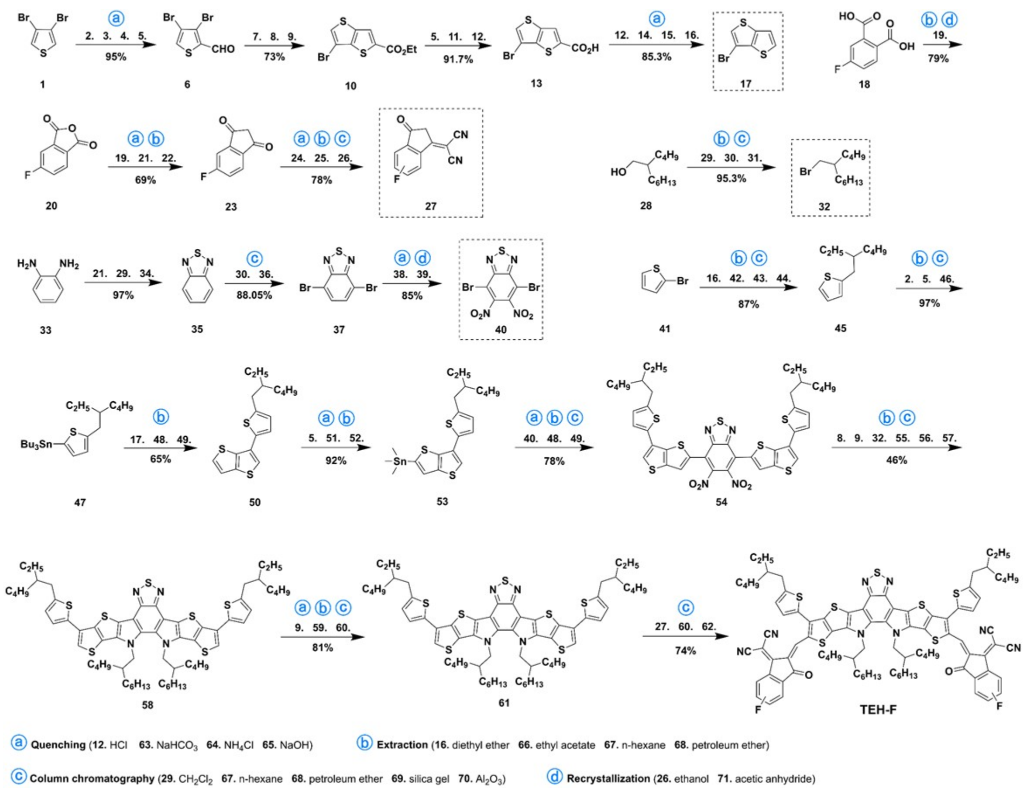
J. Li
Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Experimental Section

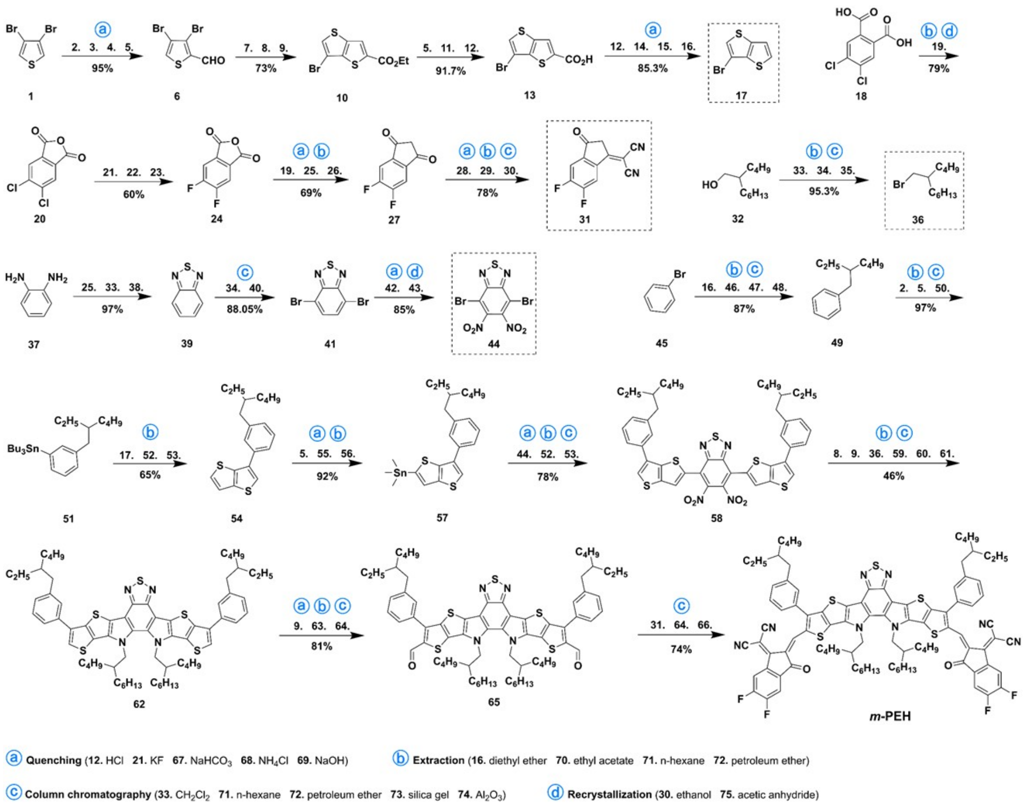
1. Synthetic Procedures



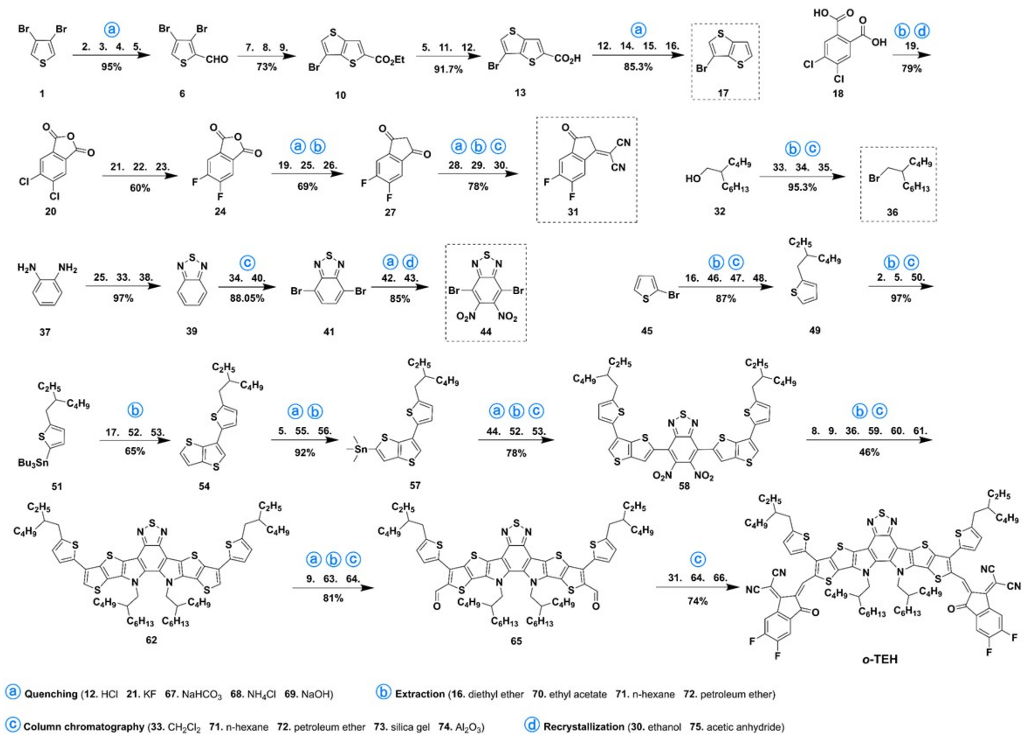
Scheme S1. Synthetic route of PEH-F.



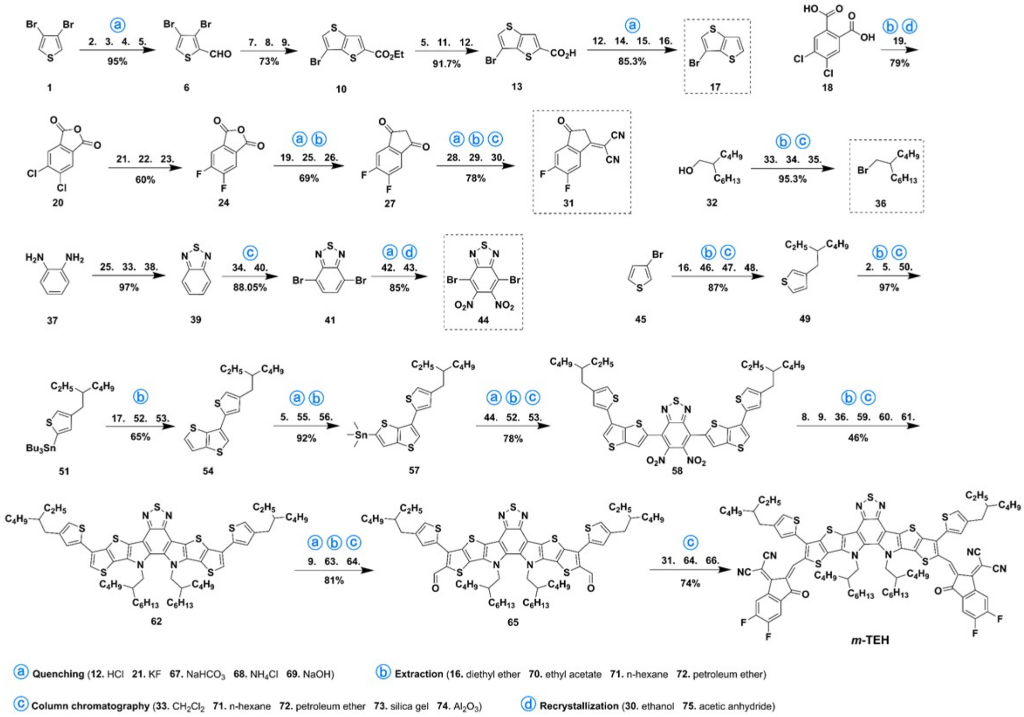
Scheme S2. Synthetic route of TEH-F.



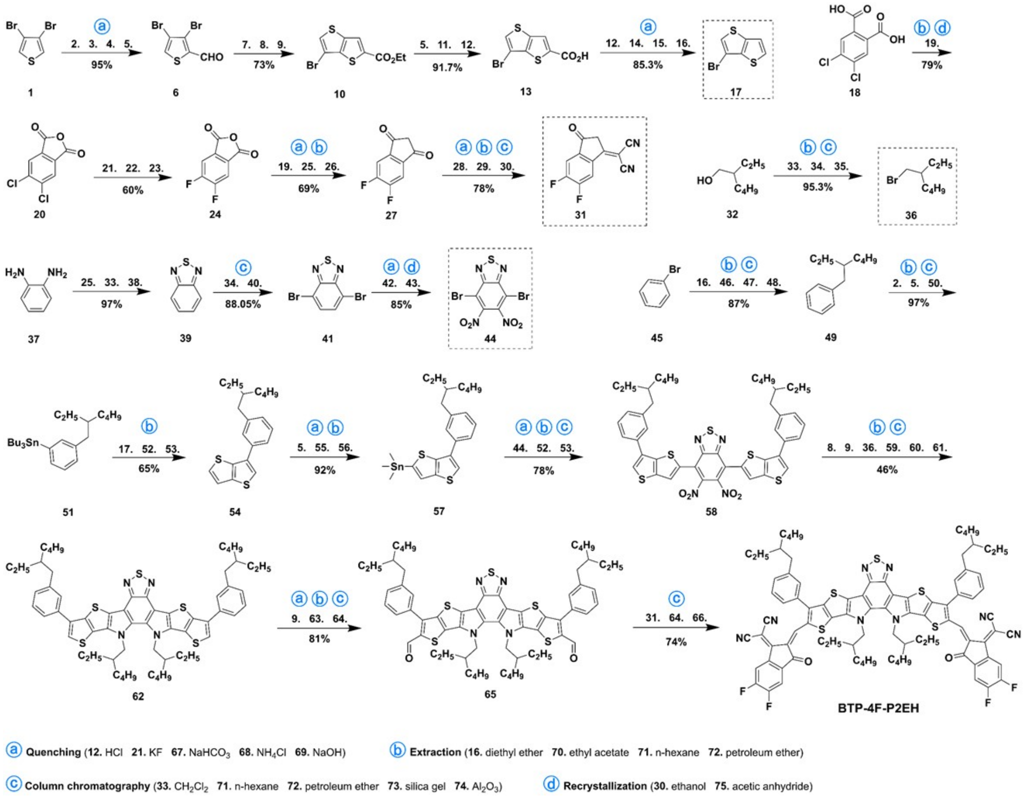
Scheme S3. Synthetic route of *m*-PEH.



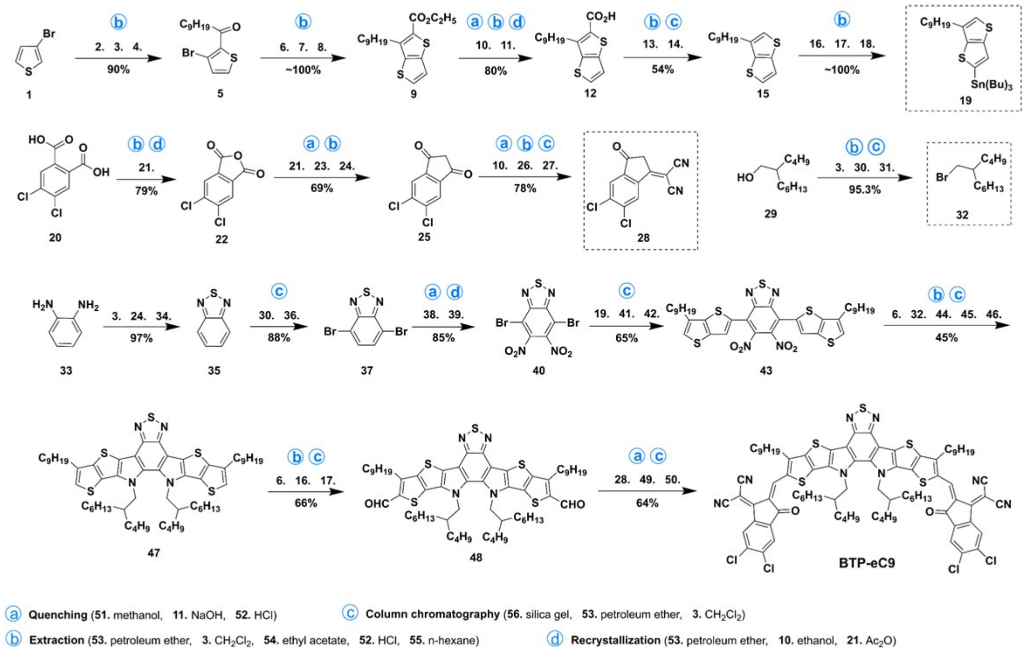
Scheme S4. Synthetic route of *o*-TEH.



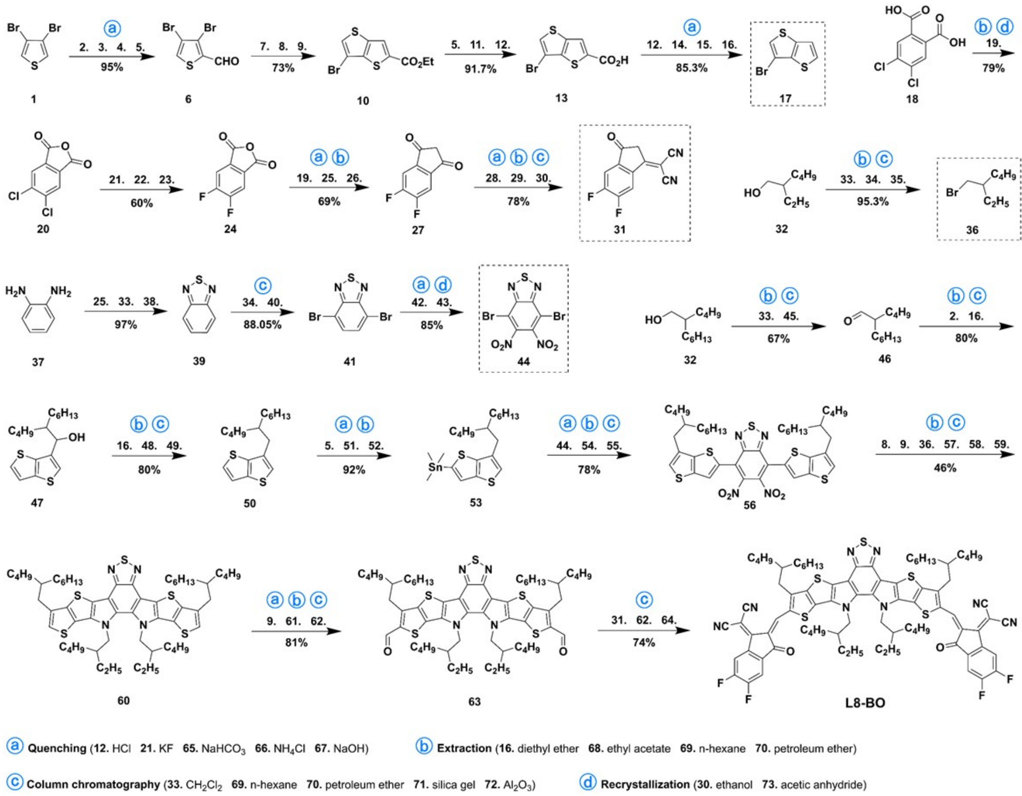
Scheme S5. Synthetic route of *m*-TEH.



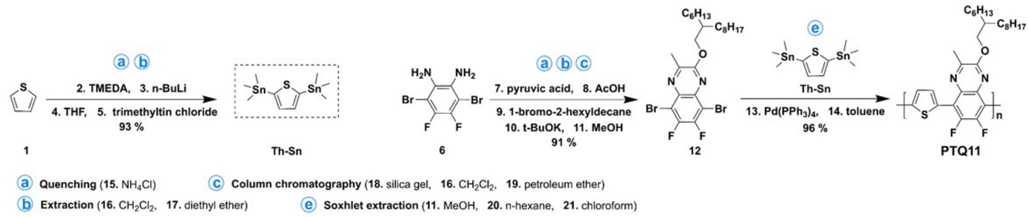
Scheme S6. Synthetic route of BTP-4F-P2EH.



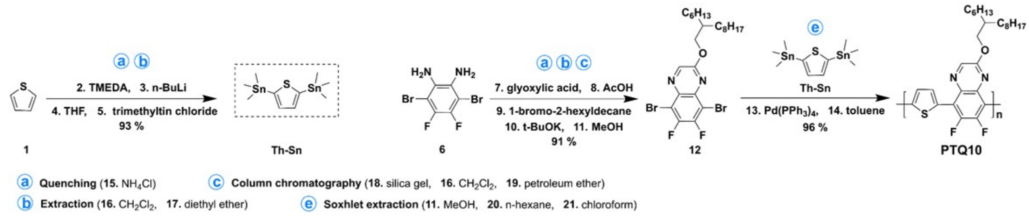
Scheme S7. Synthetic route of BTP-ec9.



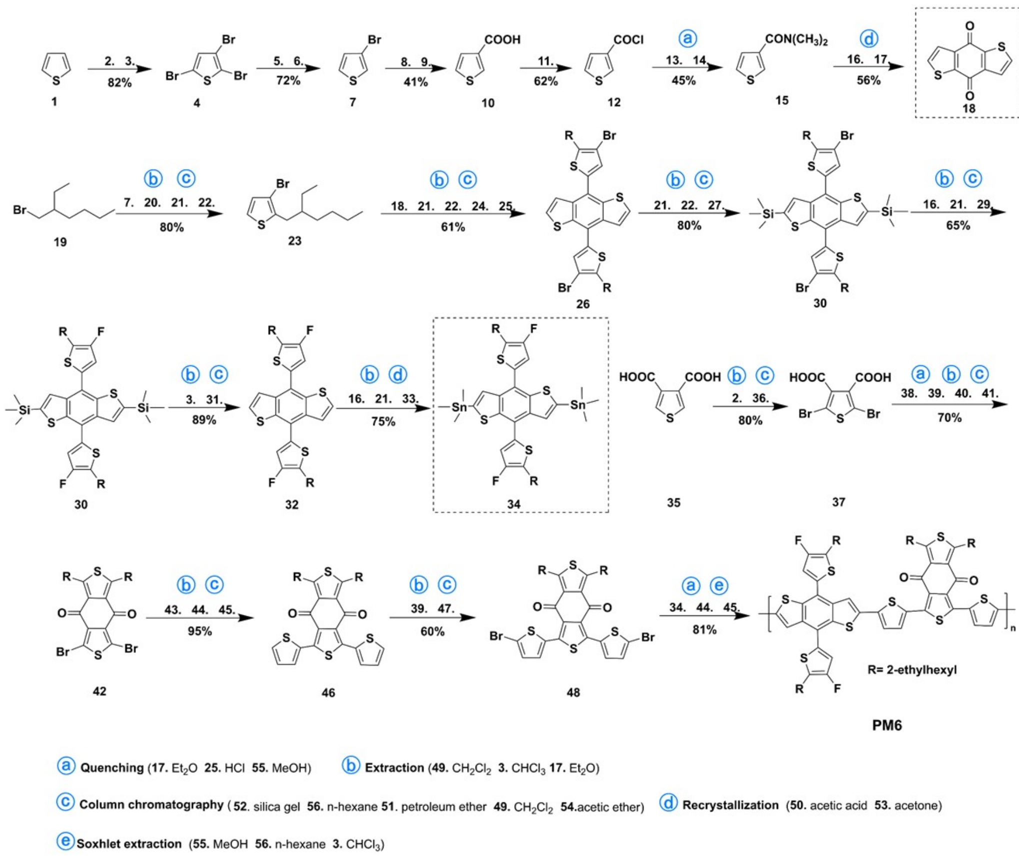
Scheme S8. Synthetic route of L8-BO.



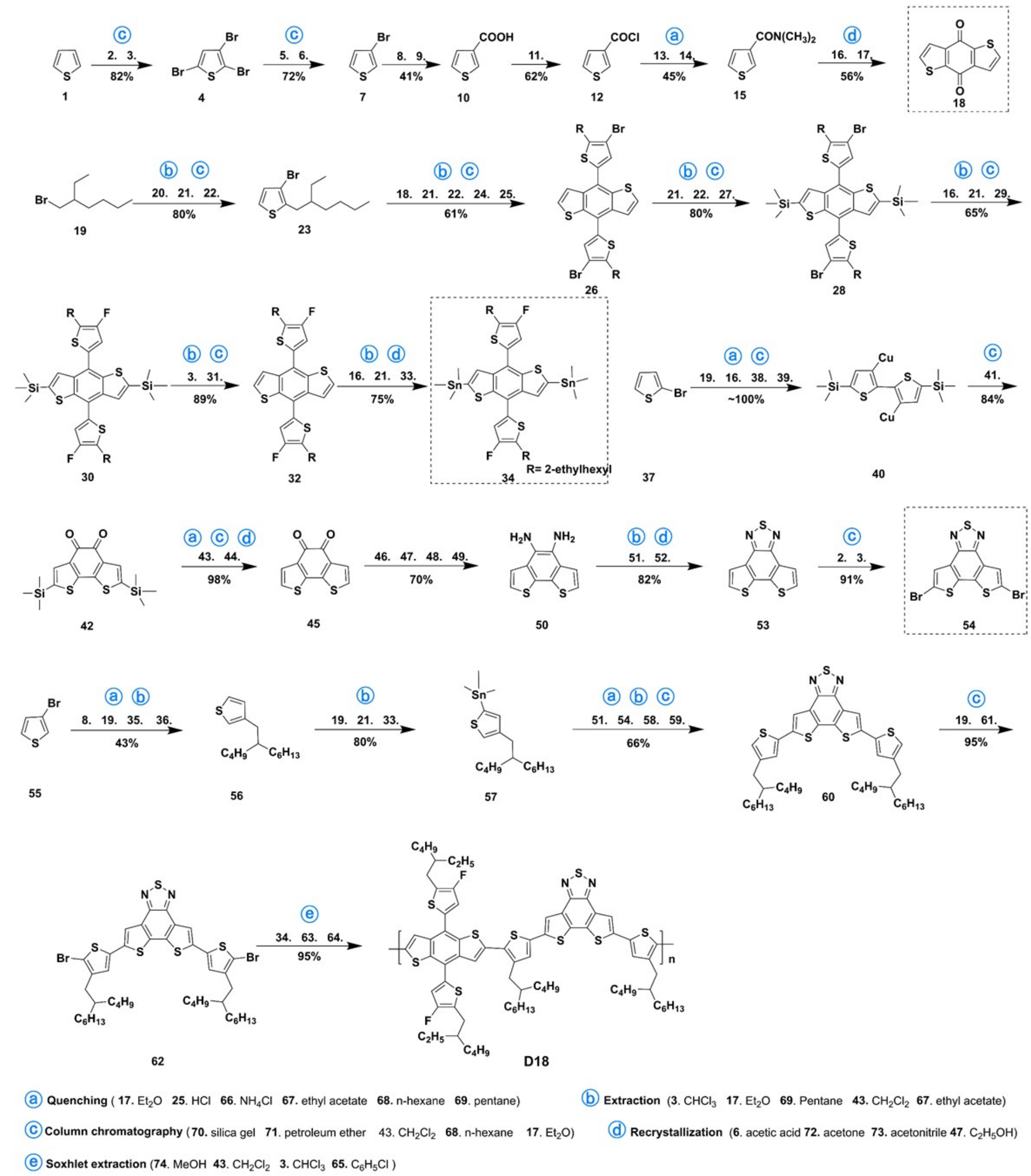
Scheme S9. Synthetic route of PTQ11.



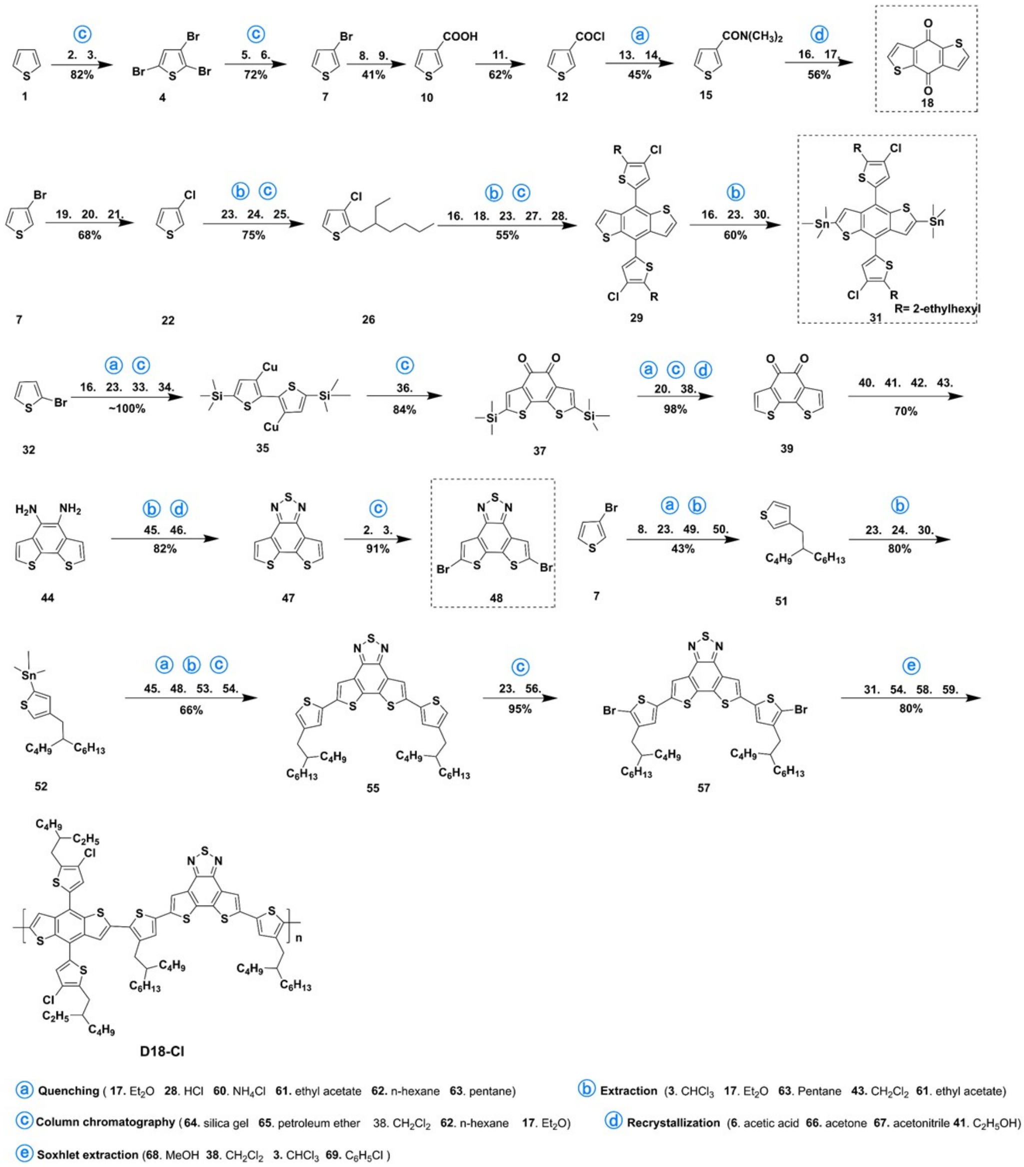
Scheme S10. Synthetic route of PTQ10.



Scheme S11. Synthetic route of PM6.



Scheme S12. Synthetic route of D18.



Scheme S13. Synthetic route of D18-Cl.

2. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H and ^{13}C NMR were measured on a Bruker AVANCE III HD 600 MHz spectrometer in deuterated chloroform. Tetramethylsilane (TMS) was used as an internal reference to record the chemical shifts.

PEH-F: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (d, J = 5.0 Hz, 1.84H), 8.66 (dd, J = 8.7, 4.2 Hz, 0.49H), 8.32 (d, J = 8.8 Hz, 1.40H), 7.95 (dd, J = 8.2, 5.1 Hz, 1.42H), 7.63 – 7.54 (m, 2.48H), 7.54 – 7.37 (m, 8.03H), 4.79 (qd, J = 16.4, 15.4, 6.6 Hz, 4.00H), 2.70 (h, J = 7.1 Hz, 3.91H), 2.19 (h, J = 6.8, 6.2 Hz, 2.04H), 1.70 (h, J = 6.2 Hz, 2.10H), 1.48 – 0.56 (m, 69.71H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.69, 167.54, 165.83, 159.79, 159.44, 151.78, 151.73, 147.43, 144.89, 143.60, 142.43, 142.36, 138.68, 138.54, 137.61, 135.96, 134.77, 134.62, 133.90, 133.56, 133.11, 132.37, 131.38, 131.24, 130.84, 129.49, 127.76, 125.70, 125.63, 121.92, 121.84, 121.55, 121.39, 114.96, 114.51, 113.66, 113.51, 112.68, 112.50, 69.72, 55.70, 41.17, 40.18, 39.25, 32.40, 31.64, 30.63, 30.48, 30.33, 29.50, 29.46, 28.97, 28.22, 27.99, 25.36, 25.19, 23.13, 22.93, 22.87, 22.53, 22.50, 14.25, 14.05, 14.03, 13.86, 13.80, 10.82.

TEH-F: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (d, J = 5.2 Hz, 1.90H), 8.67 (dd, J = 8.6, 4.2 Hz, 0.59H), 8.33 (dd, J = 8.9, 2.1 Hz, 1.31H), 7.94 (dd, J = 8.2, 5.1 Hz, 1.34H), 7.58 (dd, J = 6.5, 2.6 Hz, 0.59H), 7.42 (ddt, J = 8.1, 5.5, 2.4 Hz, 3.78H), 7.04 (d, J = 3.5 Hz, 1.93H), 4.76 (dtd, J = 19.8, 15.1, 6.7 Hz, 4.00H), 2.93 (d, J = 6.8 Hz, 3.85H), 2.16 (dt, J = 12.4, 6.6 Hz, 2.03H), 1.73 (p, J = 6.3 Hz, 2.03H), 1.54 – 0.55 (m, 66.19H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.66, 167.52, 165.81, 159.97, 159.60, 151.18, 151.16, 147.42, 144.01, 143.81, 142.46, 142.40, 138.55, 137.52, 135.98, 134.73, 134.57, 133.90, 132.98, 132.87, 132.38, 131.37, 131.29, 130.72, 127.51, 125.68, 121.92, 121.50, 121.34, 115.12, 114.69, 114.16, 114.03, 113.43, 112.65, 112.48, 69.54, 68.64, 55.71, 41.72, 39.27, 34.52, 32.41, 31.61, 31.59, 30.60, 30.48, 30.36, 29.48, 29.44, 28.95, 28.16, 27.97, 25.56, 25.27, 23.05, 22.91, 22.86, 22.51, 22.49, 14.22, 14.02, 14.01, 13.85, 13.81, 10.90.

3. Electronic Energy Levels Measurement by Cyclic Voltammetry

The cyclic voltammetry measurements were performed on the VMP3 electrochemical workstation, using a glassy carbon electrode as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode, at a potential scanning rate of 50 mV s^{-1} in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The ferrocene/ferrocene (Fc/Fc^+) pair was used as an internal reference. The E_{HOMO}/E_{LUMO} were calculated according to the equations of $E_{HOMO}/E_{LUMO} = -e\ (\varphi_{ox}/\varphi_{red} + 4.8 - \varphi_{Fc/Fc+})$ (eV), where $\varphi_{ox}/\varphi_{red}$ are the onset oxidation/reduction potentials *vs* Ag/AgCl obtained from their cyclic voltammograms, and the $\varphi_{Fc/Fc+}$ is 0.42 eV *vs* Ag/AgCl in our measurement system.

4. Femtosecond Transient Absorption Spectroscopy

Femtosecond transient absorption spectrometer was composed of a regenerative-amplified Ti: sapphire laser system (Coherent) and Helios pump-probe system (Ultrafast Systems). The regenerative-amplified Ti: sapphire laser system (Legend Elite-1K-HE, center wavelength of 800 nm, pulse duration of 25 fs, pulse energy of 4 mJ, repetition rate of 1 kHz) was seeded with a mode-locked Ti: sapphire laser system (Vitara) and pumped with a Nd: YLF laser (Evolution 30). The output 800 nm fundamental of the amplifier was split into two beam pulses. The main part of the fundamental beam went through the optical parametric amplifiers (TOPAS-C), whose output light was set as the pump light with wavelength of 810 nm and chopped by a mechanical chopper operating at frequency of 500 Hz. A small part of the fundamental beam was introduced into the TA spectrometer in order to generate the probe light. After passing through a motorized optical delay line, the fundamental beam was focused on a sapphire crystal or YAG crystal, which was used to generate the white-light continuum (WLC) probe pulses with wavelength of 430 to 820 nm or 800 to 1600 nm, respectively. The optical path difference between the pump light and the probe light, which is controlled by the motorized optical delay-line, was used to monitor the transient states at different pump-probe delay. A reference beam was split from the WLC in order to correct the pulse-to-pulse fluctuation of the WLC. The pump was spatially and temporally overlapped with the probe beam on the sample. Excitation energy of the pump pulse was set to 2 μJ cm^{-2} to avoid singlet-singlet annihilation. The film samples for TA measurements were prepared by spin coating the corresponding materials on thin quartz plates. The film samples were thermally annealed the same way as the actual device.

5. Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS images were collected with a 2D area detector in a helium chamber at beamline 11-3 of the SSRL. The sample-to-detector distance was 300 mm, and the incidence angle was 0.12°; the X-ray wavelength was 0.9758 Å, corresponding to a beam energy of 12.735 keV. The samples were solution-sheared on bare Si wafers with a thin layer of native oxide.

6. Fabrication and Characterization of OSCs

The structure of all OSCs adopts the conventional device structure, namely ITO/2PACz/active layer/PFN-Br/Ag structure. The pre-patterned ITO glass substrates (sheet resistance = 15 Ω sq^{-1}) were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried in an oven at 80 °C for 30 minutes. Then, the glass substrates were treated by UV-Ozone (Huayi Xing (Beijing) Technology Co., Ltd) for 30 min before used. 2PACz solution (ethanol) was spin-coated on the pre-cleaned ITO glass at 3000 rpm for 30 s, and then heat the ITO substrate in the air at 100 °C annealing for 10 min. The PTQ11:SMA (D:A=1:1.2, 18 mg mL^{-1} in total) was dissolved in chloroform (CF) with 1-chloronaphthalene (CN) (0.7%, v/v) additive. The blended solution was spin-coated on the PEDOT:PSS layer at 2700 rpm for 30s. It is then annealed at 90°C for 5 minutes. Then PFN-Br methanol solution with a concentration of 0.5 mg mL^{-1} was deposited on the active layer at a speed of 4000 rpm for 30 seconds to provide a PFN-Br cathode modification layer. After cooling to room temperature, the sample was transferred to the evaporation chamber. Under the pressure of 1×10^{-5} Pa, about 110 nm of Ag electrode was evaporated and deposited. The device area is 5.0 mm^2.

The current density–voltage (*J*-*V*) characteristics of OSC are measured in a nitrogen glove box equipped with a Keithley B2901BL Source Measure Unit in a glove box filled with nitrogen (oxygen and water contents are smaller than 0.1 ppm), using Oriel Sol3A Class AAA Solar Simulator (model, SS-X50) with 450W xenon lamp and air quality (AM) 1.5 filter as the light source. The light intensity is calibrated to 100 mW cm^{-2} by Newport Oriel 91150V reference cell. The external quantum efficiency (EQE) value is measured by the solar cell spectral response measurement system QE-R3-011 (Taiwan Enli Technology Co., Ltd.). Standard single-crystal silicon photovoltaic cells are used to calibrate the light intensity of each wavelength.

In the Photo-CLIVE, and TPC measures, the OSCs were fabricated with the same method as mentioned above. The data were obtained by the all-in-one characterization platform, Paios (Fluxim AG, Switzerland). In the photo-CELIV measurement, the delay time is set to 0 s, the light intensity is 100%, the light-pulse length is 100 μs, finally the sweep ramp rate rises from 20 V/ms to 100 V/ms.

7. Hole Mobility and Electron Mobility Measurements

ITO/PEDOT:PSS/active layer/MoO_3/Ag device structure is used to test hole mobility, and ITO/ZnO/active layer/PFN-Br/Ag is used to test electron mobility. The hole and electron mobilities are calculated according to the space charge limited current (SCLC) method with the equation: $J = 9\mu\varepsilon_r\varepsilon_0 V^2 /8d^3$, where J is the current density, μ is the hole or electron mobility, V is the internal voltage in the device, ε_r is the relative dielectric constant of active layer material, ε_0 is the permittivity of empty space, and d is the thickness of the active layer.

8. High-Resolution Fourier Transform Photocurrent Spectroscopy EQE spectra (FTPS-EQE)

The FTPS measurements were recorded using a Bruker Vertex 70 Fourier-transform infrared (FTIR) spectrometer, equipped with a quartz tungsten halogen lamp, a quartz beam-splitter, and an external detector option. A low noise current amplifier (Femto DLPCA-200) was used to amplify the photocurrent produced on the illumination of the photovoltaic devices with light modulated by the FTIR. The output voltage of the current amplifier was fed back into the external detector port of the FTIR. FTIR’s software collected the photocurrent spectrum.

9. Cost Feasibility of Organic Photovoltaic Materials

Molecular synthesis process, including the molecular synthetic steps, the synthetic yield of each chemical reactions, and the dosage and price of raw compounds, reagents, and solvents, *etc.*, significantly affects the synthesis cost of organic photovoltaic materials. In addition, cost of the target products is closely related to the molecular preparation scale. Generally, the larger the preparation scale, the lower the cost. Here, the synthesis cost of 1 kg product of the 13 chosen molecules is calculated based on the definite synthetic routes reported in the literatures, in combination with the dosage and price of raw compounds, intermediates, reagents, and the synthetic yield of each chemical reactions. Normally, the synthetic routes and the starting compounds for the preparation of 13 molecules are those used in the original references. However, the synthetic routes are extended to simpler starting compounds, when the starting compounds used in the original reports appeared to be relatively complex and presumably available only in small quantities from lab-chemicals suppliers. Moreover, the synthetic route with higher synthetic yield is chosen when multiple synthetic routes are available from the reported literatures, for realizing lower synthesis cost. It is worth noting that the exact synthetic yields are not available for some chemical reactions, because the flexible alkyl chains of compounds described in the literatures are different from those present on the chosen molecules. In this case, the synthetic yields of chemical reactions are assumed equal to those reported compounds with same conjugated core.

It is often inevitable to produce the by-products in organic chemical reactions, therefore it is necessary to isolate and purify the crude reaction mixtures for obtaining high purity target products. Here, we discreetly study the isolation/purification process of 13 molecules based on the reported procedures, and calculate their corresponding isolation/purification cost. To confirm an impartial comparison among the different synthetic routes, a framework is created for evaluating the isolation/purification cost of those materials. The details for each isolation/purification operations are based on the reports in the literatures and the standard organic lab techniques. The isolation/purification operations involved in the preparation of 13 molecules include: **Quenching** (quencher, such as acid, base, water, *etc.* are sometimes added to quench the crude reaction mixtures when the chemical reactions progress to a certain stage with the expected target products have been obtained. This operation is evaluated on a case-by-case basis, where molar or volumetric equivalent quenchers are assumed to be necessary based on the reported operations in the literatures.), **Extraction** (the amount of solvent required for each extraction operation is assumed to be 100 mL for extracting 1 g crude compound from the reaction mixture, and three extractions are required.),

Column chromatography (it is assumed that 200 g 200-300 mesh silica gel and 1.5 L eluent are required for purifying 1 g crude compounds, where type and polarity of the eluent is exactly the same as that reported in the literatures.), **Recrystallization** (it is assumed that 100 mL solvent is required to recrystallize 1 g crude compounds, and this operation is performed only once.), and **Soxhlet extraction** (200 mL methanol, 150 mL *n*-hexane, and 150 mL chloroform are assumed to be necessary for extracting 1 g crude polymers.).

The cost of organic photovoltaic materials consists of the synthesis cost and the isolation/purification cost. For synthesis process, the dosage of each reagent is calculated backwards based on the synthetic yield of specific chemical reactions. To realize a more reliable cost evaluation of the 13 organic photovoltaic materials, the prices of 100 g and 500 g packages of the reagents are counted with no restrictions on the single or specific suppliers, respectively. The price of 100 g package is used for cost calculation when the dosage of reagent is less than 100 g. Conversely, the price of 500 g package is used if the dosage of reagent is more than 100 g. On the other hand, the price of solvents is not limited to the dosage since their price is relatively less affected by the volume. In addition, the cost of water, anhydrous magnesium sulfate, and sea sand are ignored due to their extremely low price and dosage.

Supplementary Figures

Analysis Using Method: 20240704
Comments: 4.4MP

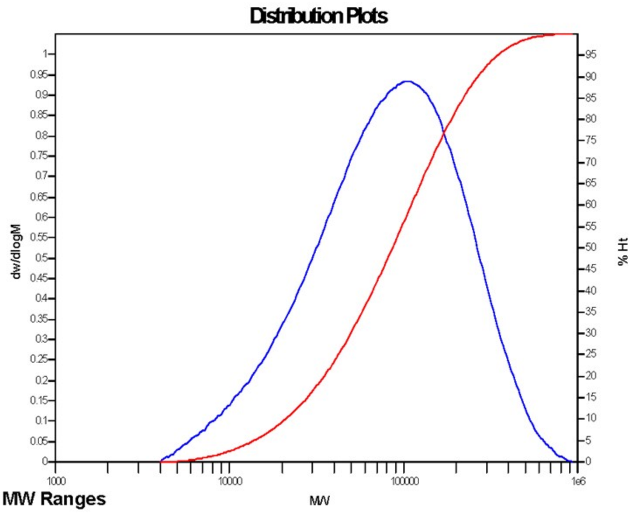
Results File: E:\Cirrus Workbooks\20231128\2024_7_7-0007.rst

Calibration Used: 2024/7/4 13:04:45
Calibration Type: Narrow Standard　　Curve Fit Used: 2
Calibration Curve: y = 13.007523 - 0.667926x^1 + 0.003272x^2

High Limit MW RT: 10.35 mins	Low Limit MW RT: 15.42 mins
High Limit MW: 2786060	Low Limit MW: 3076
K: 14.1000	FRM Name:
Alpha: 0.7000	Flow Marker RT: 0.00 mins
FRCF: 1.0000	

MW Averages

Mp: 107921	Mn: 47288	Mv: 105882	Mw: 118470
Mz: 220298	Mz+1: 326220	PD: 2.5053	



MW Ranges

Fig. S1 The GPC chart relates to the molecular weight of PTQ11.

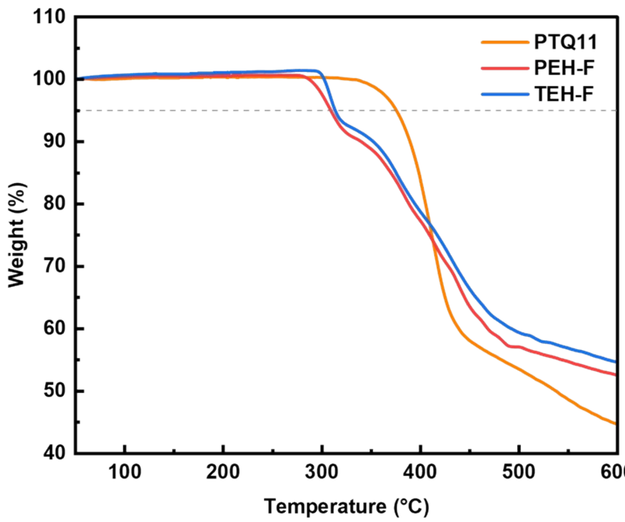


Fig. S2 The thermogravimetric analysis curves of PTQ11, PEH-F and TEH-F.

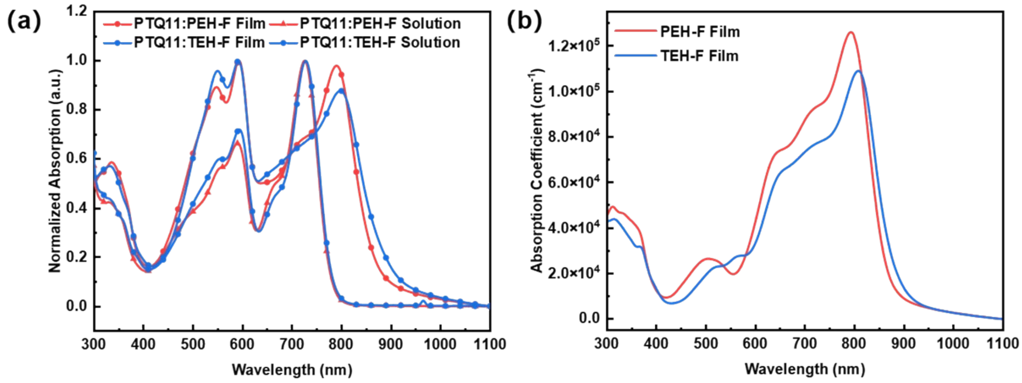


Fig. S3 (a) UV-vis absorption spectra of solutions (chloroform) and films of PTQ11:PEH-F and PTQ11:TEH-F. (b) Absorption coefficient spectra of the PEH-F and TEH-F in thin films.

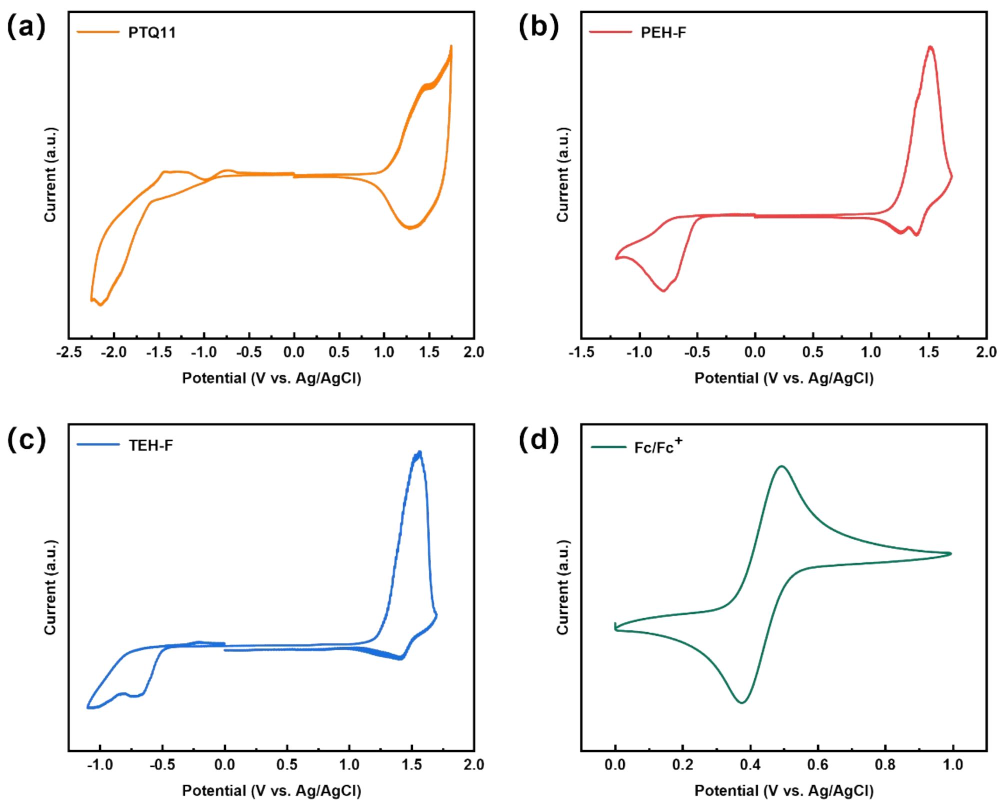


Fig. S4 Cyclic voltammograms of PTQ11, PEH-F, TEH-F, and Fc/Fc^{+}.

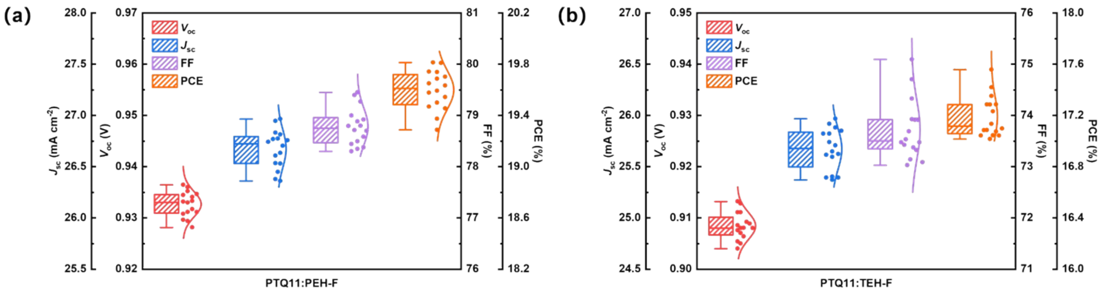


Fig. S5 Box plots and normal distribution curves for each performance parameter from sixteen individual devices based on PTQ11:PEH-F or PTQ11:TEH-F, respectively.

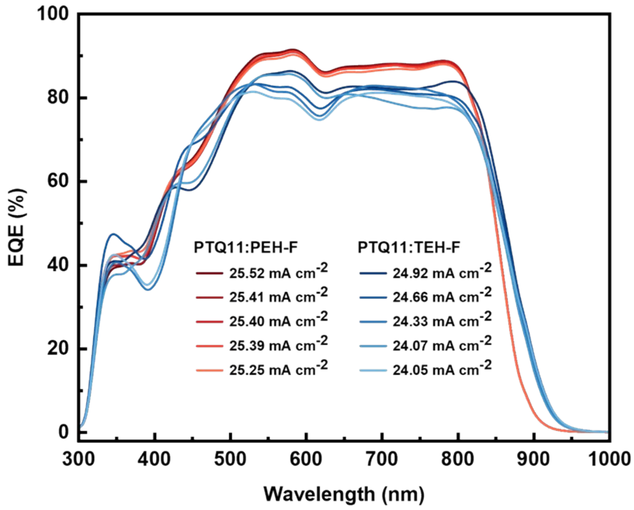


Fig. S6 EQE spectra of five individual devices based on PTQ11:PEH-F or PTQ11:TEH-F, respectively.

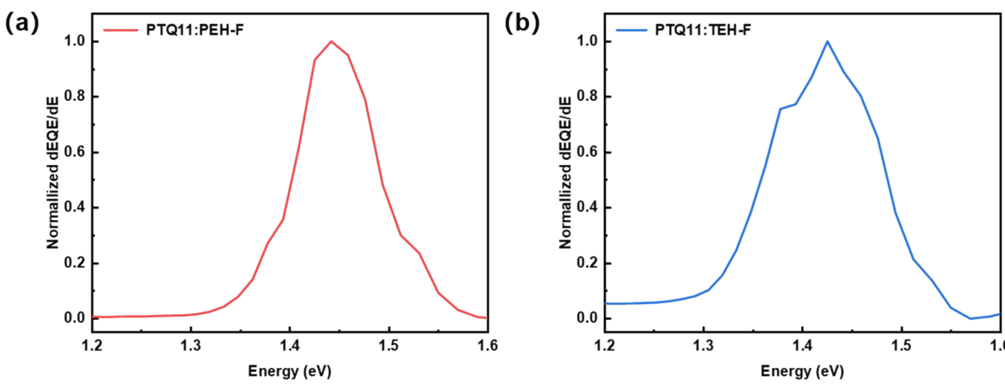


Fig. S7 The E_g values of two blends.

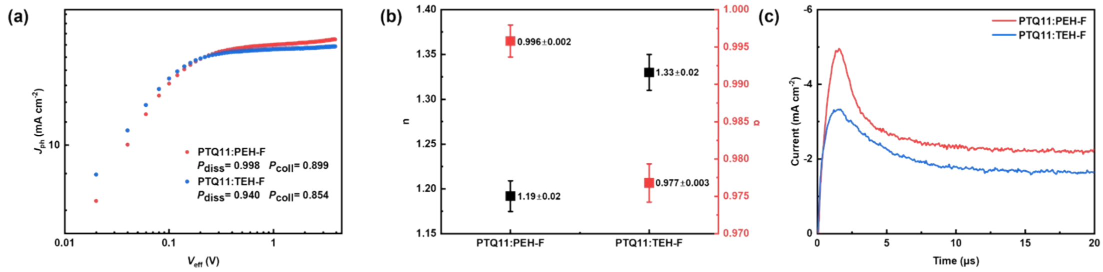


Fig. S8 (a) Plots of log J_{ph} *vs.* log V_{eff} of the optimized OSCs. (b) Error bar plots of n and α from five individual devices based on PTQ11:PEH-F or PTQ11:TEH-F, respectively. (c) Photo-CELIV curves of the devices based on PTQ11:PEH-F and PTQ11:TEH-F.

Fig. S8a illustrates the dependence of photocurrent density (J_{ph}) on the effective voltage (V_{eff}), and the J_{ph} reaches saturation (J_{sat}) at V_{eff} higher than 2 V. Then, the exciton dissociation probabilities (P_{diss}) and charge collection probabilities (P_{coll}) of the OSCs could be estimated by the values of J_{ph}/J_{sat} under the short-circuit condition and maximum power output condition, respectively. The P_{diss} and P_{coll} values of the OSCs based on PTQ11:PEH-F were measured to be 99.8 % and 89.9 %, which are markedly higher than those (94.0 % and 85.4 %) of the OSCs based on PTQ11:TEH-F.

Fig. S8c displays the transient signal of photo-CELIV. Generally speaking, the photo-CELIV could more accurately reveal the charge carrier transport information in the working devices. Under the illumination, the increment speed of the current density is determined by the conductivity of the active layer of the OSCs, and the time spent to reach the maximum extraction current density can be used to estimate the drift mobility of the photogenerated charge carriers.

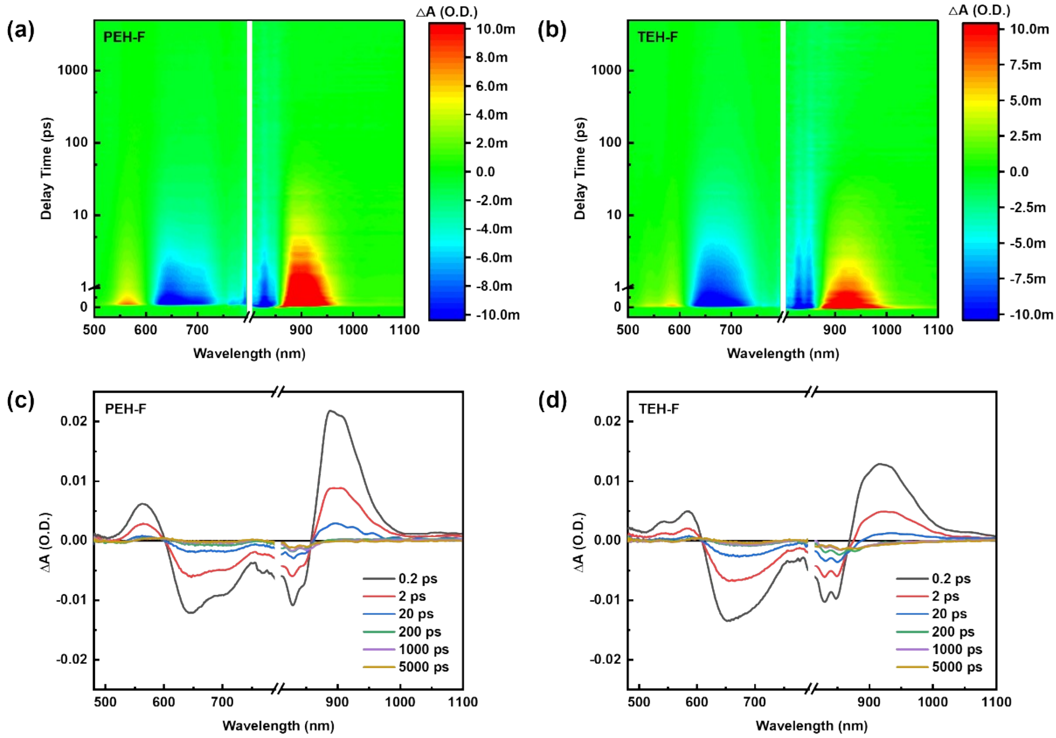


Fig. S9 2D Femtosecond transient absorption spectra of (a) PEH-F and (b) TEH-F pristine film. Transient absorption spectra profiles of (c) PEH-F and (d) TEH-F pristine film at selective delay times.

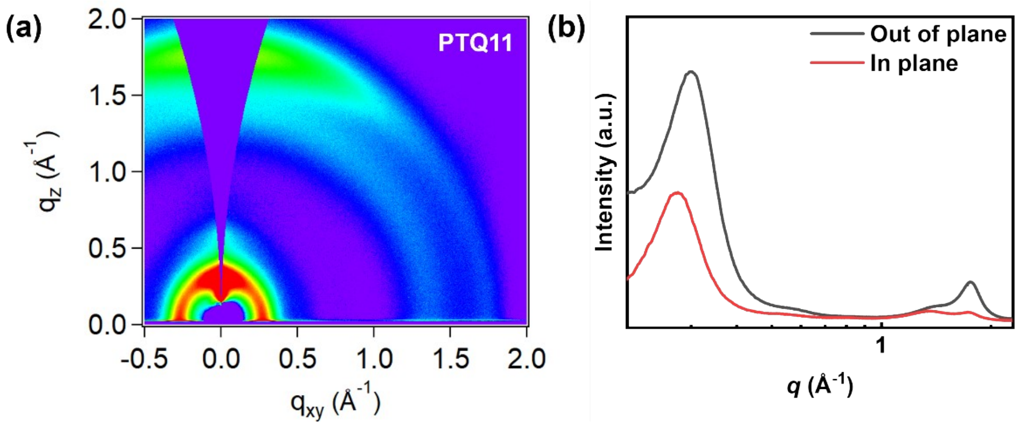


Fig. S10 2D GIWAXS patterns and 1D scattering profiles of PTQ11 pristine film.

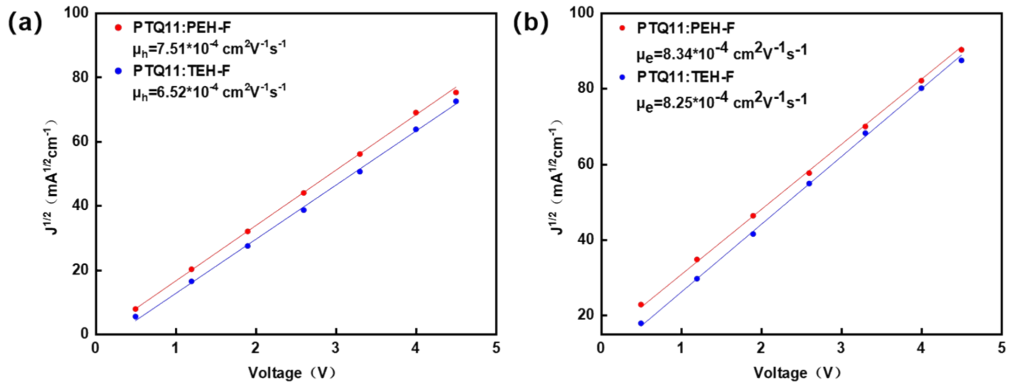


Fig. S11 $J^{1/2}$~V characteristics of the charge carrier mobility measurements of the blend films in the dark.

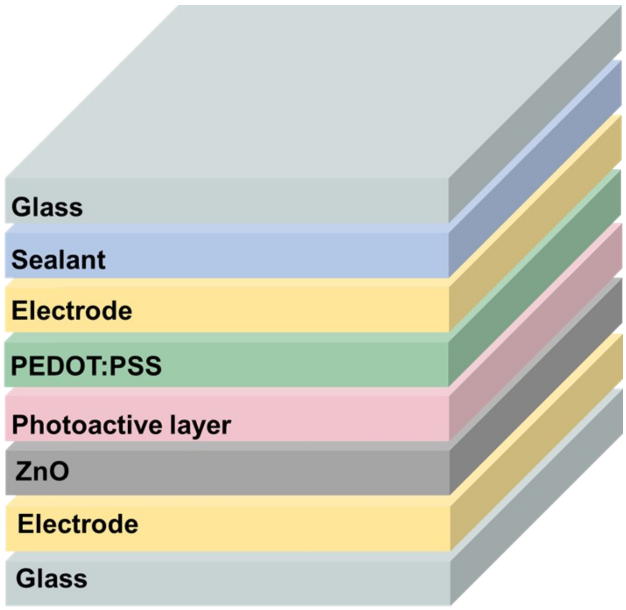


Fig. S12 The sub-device architecture for organic solar modules.

Supplementary Tables

Table S1 Survey of calculated preparation costs for PEH-F.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** 3,4-dibromothiophene	178.20/100 g; 828.00/500 g	2.16 kg	3576.96
	2. n-BuLi	163.00/500 mL	5.64 L	1838.64
	3. diisopropylamine	24.65/100 mL; 40.00/500 mL	1.28 L	102.4
	4. piperidine-1-carbaldehyde	253.30.100 g; 720.00/500 g	1.11 kg	1598.4
	5. THF	38.00/500 mL	70.44 L	5353.44
	7. $HSCH_2COOEt$	8300.00/500 mL	1.28 L	21248
	8. K_2CO_3	5.76/100 g; 28.80/500 g	5.35 kg	308.16
	9. DMF	28.80/500 mL	62.99 L	3628.22
	11. LiOH	47.50/100 g; 159.80/500 g	359.40 g	170.72
	12. HCl	20.00/500 mL	93.92 L	3756.8
	14. Cu	46.75/100 g; 91.80/500 g	215.54 g	100.76
	15. quinoline	86.70/500 mL	9.80 L	1699.32
	16. diethyl ether	40.05/500 mL	15.25 L	1221.53
	18. 4-fluorophthalic acid	866.25/100 g	9.08 kg	78655.5
	19. Ac_2O	77.94/500 mL	41.29 L	6436.29
	21. Et_3N	59.50/100 mL; 120.0/500 mL	13.32 L	3196.8
	22. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	3.47 kg	1073.62
	24. malononitrile	54.4/100 g; 209.10/500 g	1.67 kg	698.39
	25. CH_3COONa	38.25/500 g	1.55 kg	118.58
	26. ethanol	8.00/500 mL	37.89 L	606.24
	28. 2-butyloctan-1-ol	467.50/100 g; 2260.0/500 g	1.29 kg	5830.8
	29. CH_2Cl_2	20.00/500 mL	17.74 L	709.6
	30. Br_2	80.00/100 g; 150.00/500 g	13.77 L	12025.34
	31. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	33. benzene-1,2-diamine	38.70/100 g; 127.50/500 g	422.11 g	163.36
	34. $SOCl_2$	38.70/100 g; 66.30/500 g	909.26 mL	202.07
	36. HBr	37.80/500 mL	13.27 L	1003.21
	38. HNO_3	22.50/500 mL	588.32 g	16.05
	39. CF_3SO_3H	120.00/100 g; 450.00/500 g	5.88 kg	5292
	41. bromobenzene	43.00/100 g; 132.00/500 g	916.20 g	241.88
	42. 2-Ethylhexyl bromide	136.00/500 g	1.90 kg	516.8
	43. Mg	510.00/100 g; 85.00/500 g	558.25 g	94.9
	44. $Ni(dppp)Cl_2$	208.25/100 g; 1003.0/500 g	15.55 g	32.38
	46. $SnBu_3Cl$	127.50/100 g; 459.00/500 g	1.67 kg	1533.06
	48. $Pd(PPh_3)_4$	10204.20/100 g	428.38 g	43712.75
	49. Toluene	20.00/500 mL	51.39 L	2055.6
	51. LDA	215.10/500 mL	1.72 L	739.94

	52. $SnMe_3Cl$	1090/100 mL; 3870/500mL	3.45 L	26382.56
	55. $P(OEt)_3$	74.80/500 mL	11.31 L	1691.98
	56. *O*-DCB	44.00/500 mL	11.31 L	995.28
	57. KI	60.80/100 g; 229.50/500 g	362.00 g	220.1
	59. $POCl_3$	120.60/100 g; 255.00/500mL	3.72 L	1897.20
	60. $CHCl_3$	40.50/500 mL	228.02 L	18469.62
	62. Pyridine	44.00/500 mL	20.55 L	1808.40
	Subtotal cost: 261490.48 ¥/36820.83 $			
Isolation/ Purification process	**12.** HCl	20.00/500 mL	62.33 L	2493.20
	16. diethyl ether	40.05/500 mL	705.59 L	56517.76
	26. ethanol	8.00/500 mL	98.00 L	1568.00
	29. CH_2Cl_2	20.00/500 mL	4289.41 L	171576.40
	63. $NaHCO_3$	609.18/500 mL	22.55 L	27474.02
	64. NH_4Cl	24.00/100 g; 8.00/500 g	25.00 L	148.80
	65. NaOH	7.65/100 g; 38.25/500 g	588.32 g	45.01
	66. ethyl acetate	13.00/500 mL	5898.00 L	153348.00
	67. n-hexane	16.00/500 mL	6135.30 L	196329.60
	68. Petroleum ether	20.00/500 mL	9268.35 L	370734.00
	69. silica gel	13.00/100 g; 65.00/500 g	2052.27 kg	266795.10
	70. Al_2O_3	44.20/500 g	192.00 kg	16972.80
	71. acetic anhydride	77.94/500 mL	908.00 L	141539.04
	Subtotal cost: 1405541.73 ¥/197916.24 $			
Total cost: 1667032.21 ¥/234737.06 $				

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
	52. $SnMe_3Cl$	1090/100 mL; 3870/500mL	3.45 L	26382.56

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** 3,4-dibromothiophene	178.20/100 g; 828.00/500 g	2.16 kg	3576.96
	2. n-BuLi	163.00/500 mL	5.64 L	1838.64
	3. diisopropylamine	24.65/100 mL; 40.00/500 mL	1.28 L	102.4
	4. piperidine-1-carbaldehyde	253.30.100 g; 720.00/500 g	1.11 kg	1598.4
	5. THF	38.00/500 mL	70.44 L	5353.44
	7. $HSCH_2COOEt$	8300.00/500 mL	1.28 L	21248
	8. K_2CO_3	5.76/100 g; 28.80/500 g	5.35 kg	308.16
	9. DMF	28.80/500 mL	62.99 L	3628.22
	11. LiOH	47.50/100 g; 159.80/500 g	359.40 g	170.72
	12. HCl	20.00/500 mL	93.92 L	3756.8
	14. Cu	46.75/100 g; 91.80/500 g	215.54 g	100.76
	15. quinoline	86.70/500 mL	9.80 L	1699.32
	16. diethyl ether	40.05/500 mL	15.25 L	1221.53
	18. 4-fluorophthalic acid	866.25/100 g	9.08 kg	78655.5
	19. Ac_2O	77.94/500 mL	41.29 L	6436.29
	21. Et_3N	59.50/100 mL; 120.0/500 mL	13.32 L	3196.8
	22. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	3.47 kg	1073.62
	24. malononitrile	54.4/100 g; 209.10/500 g	1.67 kg	698.39
	25. CH_3COONa	38.25/500 g	1.55 kg	118.58
	26. ethanol	8.00/500 mL	37.89 L	606.24
	28. 2-butyloctan-1-ol	467.50/100 g; 2260.0/500 g	1.29 kg	5830.8
	29. CH_2Cl_2	20.00/500 mL	17.74 L	709.6
	30. Br_2	80.00/100 g; 150.00/500 g	13.77 L	12025.34
	31. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	33. benzene-1,2-diamine	38.70/100 g; 127.50/500 g	422.11 g	163.36
	34. $SOCl_2$	38.70/100 g; 66.30/500 g	909.26 mL	202.07
	36. HBr	37.80/500 mL	13.27 L	1003.21
	38. HNO_3	22.50/500 mL	588.32 g	16.05
	39. CF_3SO_3H	120.00/100 g; 450.00/500 g	5.88 kg	5292
	41. 2-bromothiophene	19.47/100 g; 69.96/500 g	916.20 g	128.19
	42. 2-Ethylhexyl bromide	136.00/500 g	1.90 kg	516.8
	43. Mg	510.00/100 g; 85.00/500 g	558.25 g	94.9
	44. $Ni(dppp)Cl_2$	208.25/100 g; 1003.0/500 g	15.55 g	32.38
	46. $SnBu_3Cl$	127.50/100 g; 459.00/500 g	1.67 kg	1533.06
	48. $Pd(PPh_3)_4$	10204.20/100 g	428.38 g	43712.75
	49. Toluene	20.00/500 mL	51.39 L	2055.6
	51. LDA	215.10/500 mL	1.72 L	739.94

Table S2 Survey of calculated preparation costs for TEH-F.

	55. $P(OEt)_3$	74.80/500 mL	11.31 L	1691.98
	56. *O*-DCB	44.00/500 mL	11.31 L	995.28
	57. KI	60.80/100 g; 229.50/500 g	362.00 g	220.1
	59. $POCl_3$	120.60/100 g; 255.00/500mL	3.72 L	1897.20
	60. $CHCl_3$	40.50/500 mL	228.02 L	18469.62
	62. Pyridine	44.00/500 mL	20.55 L	1808.40
	Subtotal cost: 261376.79 ¥/36804.82 $			
Isolation/ Purification process	**12.** HCl	20.00/500 mL	62.33 L	2493.20
	16. diethyl ether	40.05/500 mL	705.59 L	56517.76
	26. ethanol	8.00/500 mL	98.00 L	1568.00
	29. CH_2Cl_2	20.00/500 mL	4289.41 L	171576.40
	63. $NaHCO_3$	609.18/500 mL	22.55 L	27474.02
	64. NH_4Cl	24.00/100 g; 8.00/500 g	25.00 L	148.80
	65. NaOH	7.65/100 g; 38.25/500 g	588.32 g	45.01
	66. ethyl acetate	13.00/500 mL	5898.00 L	153348.00
	67. n-hexane	16.00/500 mL	6135.30 L	196329.60
	68. Petroleum ether	20.00/500 mL	9268.35 L	370734.00
	69. silica gel	13.00/100 g; 65.00/500 g	2052.27 kg	266795.10
	70. Al_2O_3	44.20/500 g	192.00 kg	16972.80
	71. acetic anhydride	77.94/500 mL	908.00 L	141539.04
	Subtotal cost: 1405541.73 ¥/197916.24 $			
Total cost: 1666918.52 ¥/234721.06 $				

Table S3 Survey of calculated preparation costs for *m*-PEH.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** 3,4-dibromothiophene	178.20/100 g; 828.00/500 g	2.16 kg	3576.96
	2. n-BuLi	163.00/500 mL	5.64 L	1838.64
	3. diisopropylamine	24.65/100 mL; 40.00/500 mL	1.28 L	102.4
	4. piperidine-1-carbaldehyde	253.30.100 g; 720.00/500 g	1.11 kg	1598.4
	5. THF	38.00/500 mL	70.44 L	5353.44
	7. $HSCH_2COOEt$	8300.00/500 mL	1.28 L	21248
	8. K_2CO_3	5.76/100 g; 28.80/500 g	5.35 kg	308.16
	9. DMF	28.80/500 mL	62.99 L	3628.22
	11. LiOH	47.50/100 g; 159.80/500 g	359.40 g	170.72
	12. HCl	20.00/500 mL	93.92 L	3756.8
	14. Cu	46.75/100 g; 91.80/500 g	215.54 g	100.76
	15. quinoline	86.70/500 mL	9.80 L	1699.32
	16. diethyl ether	40.05/500 mL	15.25 L	1221.53
	18. 4,5-dichlorophthalic acid	3102.50/100 g	9.08 kg	281707
	19. Ac_2O	77.94/500 mL	41.29 L	6436.29
	21. KF	32.30/100 g; 46.75/500 g	7.08 kg	661.98
	22. mPEG	45.90/100 g; 108.80/500 g	610.14 g	132.77
	23. Sulfolane	115.60/500 mL	24.41 L	5643.59
	25. Et_3N	59.50/100 mL; 120.0/500 mL	13.32 L	3196.8
	26. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	3.47 kg	1073.62
	28. malononitrile	54.4/100 g; 209.10/500 g	1.67 kg	698.39
	29. CH_3COONa	38.25/500 g	1.55 kg	118.58
	30. ethanol	8.00/500 mL	37.89 L	606.24
	32. 2-butyloctan-1-ol	467.50/100 g; 2260.0/500 g	1.29 kg	5830.8
	33. CH_2Cl_2	20.00/500 mL	17.74 L	709.6
	34. Br_2	80.00/100 g; 150.00/500 g	13.77 L	12025.34
	35. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	37. benzene-1,2-diamine	38.70/100 g; 127.50/500 g	422.11 g	163.36
	38. $SOCl_2$	38.70/100 g; 66.30/500 g	909.26 mL	202.07
	40. HBr	37.80/500 mL	13.27 L	1003.21
	42. HNO_3	22.50/500 mL	588.32 g	16.05
	43. CF_3SO_3H	120.00/100 g; 450.00/500 g	5.88 kg	5292
	45. bromobenzene	43.00/100 g; 132.00/500 g	916.20 g	241.88
	46. 2-Ethylhexyl bromide	136.00/500 g	1.90 kg	516.8
	47. Mg	510.00/100 g; 85.00/500 g	558.25 g	94.9
	48. $Ni(dppp)Cl_2$	208.25/100 g; 1003.0/500 g	15.55 g	32.38
	50. $SnBu_3Cl$	127.50/100 g; 459.00/500 g	1.67 kg	1533.06
	52. $Pd(PPh_3)_4$	10204.20/100 g	428.38 g	43712.75
	53. Toluene	20.00/500 mL	51.39 L	2055.6

	55. LDA	215.10/500 mL	1.72 L	739.94
	56. $SnMe_3Cl$	1090/100 mL; 3870/500mL	3.45 L	26382.56
	59. $P(OEt)_3$	74.80/500 mL	11.31 L	1691.98
	60. *O*-DCB	44.00/500 mL	11.31 L	995.28
	61. KI	60.80/100 g; 229.50/500 g	362.00 g	220.1
	63. $POCl_3$	120.60/100 g; 255.00/500mL	3.72 L	1897.20
	64. $CHCl_3$	40.50/500 mL	228.02 L	18469.62
	66. Pyridine	44.00/500 mL	20.55 L	1808.40
	Subtotal cost: 470980.32 ¥/66319.38 $			
Isolation/ Purification process	**12.** HCl	20.00/500 mL	62.33 L	2493.20
	16. diethyl ether	40.05/500 mL	705.59 L	56517.76
	21. KF	45.00/500 g	51.37 L	1581.30
	30. ethanol	8.00/500 mL	98.00 L	1568.00
	33. CH_2Cl_2	20.00/500 mL	4289.41 L	171576.40
	67. $NaHCO_3$	609.18/500 mL	22.55 L	27474.02
	68. NH_4Cl	24.00/100 g; 8.00/500 g	25.00 L	148.80
	69. NaOH	7.65/100 g; 38.25/500 g	588.32 g	45.01
	70. ethyl acetate	13.00/500 mL	5898.00 L	153348.00
	71. n-hexane	16.00/500 mL	6135.30 L	196329.60
	72. Petroleum ether	20.00/500 mL	9268.35 L	370734.00
	73. silica gel	13.00/100 g; 65.00/500 g	2052.27 kg	266795.10
	74. Al_2O_3	44.20/500 g	192.00 kg	16972.80
	75. acetic anhydride	77.94/500 mL	908.00 L	141539.04
	Subtotal cost: 1407123.03 ¥/198138.90 $			
Total cost: 1878103.35 ¥/264458.28 $				

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** 3,4-dibromothiophene	178.20/100 g; 828.00/500 g	2.16 kg	3576.96
	2. n-BuLi	163.00/500 mL	5.64 L	1838.64
	3. diisopropylamine	24.65/100 mL; 40.00/500 mL	1.28 L	102.4
	4. piperidine-1-carbaldehyde	253.30.100 g; 720.00/500 g	1.11 kg	1598.4
	5. THF	38.00/500 mL	70.44 L	5353.44
	7. $HSCH_2COOEt$	8300.00/500 mL	1.28 L	21248
	8. K_2CO_3	5.76/100 g; 28.80/500 g	5.35 kg	308.16
	9. DMF	28.80/500 mL	62.99 L	3628.22
	11. LiOH	47.50/100 g; 159.80/500 g	359.40 g	170.72
	12. HCl	20.00/500 mL	93.92 L	3756.8
	14. Cu	46.75/100 g; 91.80/500 g	215.54 g	100.76
	15. quinoline	86.70/500 mL	9.80 L	1699.32
	16. diethyl ether	40.05/500 mL	15.25 L	1221.53
	18. 4,5-dichlorophthalic acid	3102.50/100 g	9.08 kg	281707
	19. Ac_2O	77.94/500 mL	41.29 L	6436.29
	21. KF	32.30/100 g; 46.75/500 g	7.08 kg	661.98
	22. mPEG	45.90/100 g; 108.80/500 g	610.14 g	132.77
	23. Sulfolane	115.60/500 mL	24.41 L	5643.59
	25. Et_3N	59.50/100 mL; 120.0/500 mL	13.32 L	3196.8
	26. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	3.47 kg	1073.62
	28. malononitrile	54.4/100 g; 209.10/500 g	1.67 kg	698.39
	29. CH_3COONa	38.25/500 g	1.55 kg	118.58
	30. ethanol	8.00/500 mL	37.89 L	606.24
	32. 2-butyloctan-1-ol	467.50/100 g; 2260.0/500 g	1.29 kg	5830.8
	33. CH_2Cl_2	20.00/500 mL	17.74 L	709.6
	34. Br_2	80.00/100 g; 150.00/500 g	13.77 L	12025.34
	35. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	37. benzene-1,2-diamine	38.70/100 g; 127.50/500 g	422.11 g	163.36
	38. $SOCl_2$	38.70/100 g; 66.30/500 g	909.26 mL	202.07
	40. HBr	37.80/500 mL	13.27 L	1003.21
	42. HNO_3	22.50/500 mL	588.32 g	16.05
	43. CF_3SO_3H	120.00/100 g; 450.00/500 g	5.88 kg	5292
	45. 2-bromothiophene	19.47/100 g; 69.96/500 g	916.20 g	128.19
	46. 2-Ethylhexyl bromide	136.00/500 g	1.90 kg	516.8
	47. Mg	510.00/100 g; 85.00/500 g	558.25 g	94.9
	48. $Ni(dppp)Cl_2$	208.25/100 g; 1003.0/500 g	15.55 g	32.38
	50. $SnBu_3Cl$	127.50/100 g; 459.00/500 g	1.67 kg	1533.06

Table S4 Survey of calculated preparation costs for *o*-TEH.

	52. $Pd(PPh_3)_4$	10204.20/100 g	428.38 g	43712.75
	53. Toluene	20.00/500 mL	51.39 L	2055.6
	55. LDA	215.10/500 mL	1.72 L	739.94
	56. $SnMe_3Cl$	1090/100 mL; 3870/500mL	3.45 L	26382.56
	59. $P(OEt)_3$	74.80/500 mL	11.31 L	1691.98
	60. *O*-DCB	44.00/500 mL	11.31 L	995.28
	61. KI	60.80/100 g; 229.50/500 g	362.00 g	220.1
	63. $POCl_3$	120.60/100 g; 255.00/500mL	3.72 L	1897.20
	64. $CHCl_3$	40.50/500 mL	228.02 L	18469.62
	66. Pyridine	44.00/500 mL	20.55 L	1808.40
	Subtotal cost: 470866.63 ¥/66303.37 $			
Isolation/ Purification process	**12.** HCl	20.00/500 mL	62.33 L	2493.20
	16. diethyl ether	40.05/500 mL	705.59 L	56517.76
	21. KF	45.00/500 g	51.37 L	1581.30
	30. ethanol	8.00/500 mL	98.00 L	1568.00
	33. CH_2Cl_2	20.00/500 mL	4289.41 L	171576.40
	67. $NaHCO_3$	609.18/500 mL	22.55 L	27474.02
	68. NH_4Cl	24.00/100 g; 8.00/500 g	25.00 L	148.80
	69. NaOH	7.65/100 g; 38.25/500 g	588.32 g	45.01
	70. ethyl acetate	13.00/500 mL	5898.00 L	153348.00
	71. n-hexane	16.00/500 mL	6135.30 L	196329.60
	72. Petroleum ether	20.00/500 mL	9268.35 L	370734.00
	73. silica gel	13.00/100 g; 65.00/500 g	2052.27 kg	266795.10
	74. Al_2O_3	44.20/500 g	192.00 kg	16972.80
	75. acetic anhydride	77.94/500 mL	908.00 L	141539.04
	Subtotal cost: 1407123.03 ¥/198138.90 $			
Total cost: 1877989.66 ¥/264442.27 $				

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** 3,4-dibromothiophene	178.20/100 g; 828.00/500 g	2.16 kg	3576.96
	2. n-BuLi	163.00/500 mL	5.64 L	1838.64
	3. diisopropylamine	24.65/100 mL; 40.00/500 mL	1.28 L	102.4
	4. piperidine-1-carbaldehyde	253.30.100 g; 720.00/500 g	1.11 kg	1598.4
	5. THF	38.00/500 mL	70.44 L	5353.44
	7. $HSCH_2COOEt$	8300.00/500 mL	1.28 L	21248
	8. K_2CO_3	5.76/100 g; 28.80/500 g	5.35 kg	308.16
	9. DMF	28.80/500 mL	62.99 L	3628.22
	11. LiOH	47.50/100 g; 159.80/500 g	359.40 g	170.72
	12. HCl	20.00/500 mL	93.92 L	3756.8
	14. Cu	46.75/100 g; 91.80/500 g	215.54 g	100.76
	15. quinoline	86.70/500 mL	9.80 L	1699.32
	16. diethyl ether	40.05/500 mL	15.25 L	1221.53
	18. 4,5-dichlorophthalic acid	3102.50/100 g	9.08 kg	281707
	19. Ac_2O	77.94/500 mL	41.29 L	6436.29
	21. KF	32.30/100 g; 46.75/500 g	7.08 kg	661.98
	22. mPEG	45.90/100 g; 108.80/500 g	610.14 g	132.77
	23. Sulfolane	115.60/500 mL	24.41 L	5643.59
	25. Et_3N	59.50/100 mL; 120.0/500 mL	13.32 L	3196.8
	26. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	3.47 kg	1073.62
	28. malononitrile	54.4/100 g; 209.10/500 g	1.67 kg	698.39
	29. CH_3COONa	38.25/500 g	1.55 kg	118.58
	30. ethanol	8.00/500 mL	37.89 L	606.24
	32. 2-butyloctan-1-ol	467.50/100 g; 2260.0/500 g	1.29 kg	5830.8
	33. CH_2Cl_2	20.00/500 mL	17.74 L	709.6
	34. Br_2	80.00/100 g; 150.00/500 g	13.77 L	12025.34
	35. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	37. benzene-1,2-diamine	38.70/100 g; 127.50/500 g	422.11 g	163.36
	38. $SOCl_2$	38.70/100 g; 66.30/500 g	909.26 mL	202.07
	40. HBr	37.80/500 mL	13.27 L	1003.21
	42. HNO_3	22.50/500 mL	588.32 g	16.05
	43. CF_3SO_3H	120.00/100 g; 450.00/500 g	5.88 kg	5292
	45. 3-bromothiophene	113.00/100 g; 536.00/500 g	916.20 g	982.17
	46. 2-Ethylhexyl bromide	136.00/500 g	1.90 kg	516.8
	47. Mg	510.00/100 g; 85.00/500 g	558.25 g	94.9
	48. $Ni(dppp)Cl_2$	208.25/100 g; 1003.0/500 g	15.55 g	32.38
	50. $SnBu_3Cl$	127.50/100 g; 459.00/500 g	1.67 kg	1533.06

Table S5 Survey of calculated preparation costs for *m*-TEH.

	52. $Pd(PPh_3)_4$	10204.20/100 g	428.38 g	43712.75
	53. Toluene	20.00/500 mL	51.39 L	2055.6
	55. LDA	215.10/500 mL	1.72 L	739.94
	56. $SnMe_3Cl$	1090/100 mL; 3870/500mL	3.45 L	26382.56
	59. $P(OEt)_3$	74.80/500 mL	11.31 L	1691.98
	60. *O*-DCB	44.00/500 mL	11.31 L	995.28
	61. KI	60.80/100 g; 229.50/500 g	362.00 g	220.1
	63. $POCl_3$	120.60/100 g; 255.00/500mL	3.72 L	1897.20
	64. $CHCl_3$	40.50/500 mL	228.02 L	18469.62
	66. Pyridine	44.00/500 mL	20.55 L	1808.40
	Subtotal cost: 471720.61 ¥/66423.62 $			
Isolation/ Purification process	**12.** HCl	20.00/500 mL	62.33 L	2493.20
	16. diethyl ether	40.05/500 mL	705.59 L	56517.76
	21. KF	45.00/500 g	51.37 L	1581.30
	30. ethanol	8.00/500 mL	98.00 L	1568.00
	33. CH_2Cl_2	20.00/500 mL	4289.41 L	171576.40
	67. $NaHCO_3$	609.18/500 mL	22.55 L	27474.02
	68. NH_4Cl	24.00/100 g; 8.00/500 g	25.00 L	148.80
	69. NaOH	7.65/100 g; 38.25/500 g	588.32 g	45.01
	70. ethyl acetate	13.00/500 mL	5898.00 L	153348.00
	71. n-hexane	16.00/500 mL	6135.30 L	196329.60
	72. Petroleum ether	20.00/500 mL	9268.35 L	370734.00
	73. silica gel	13.00/100 g; 65.00/500 g	2052.27 kg	266795.10
	74. Al_2O_3	44.20/500 g	192.00 kg	16972.80
	75. acetic anhydride	77.94/500 mL	908.00 L	141539.04
	Subtotal cost: 1407123.03 ¥/198138.90 $			
Total cost: 1878843.64 ¥/264562.52 $				

Table S6 Survey of calculated preparation costs for BTP-4F-P2EH.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** 3,4-dibromothiophene	178.20/100 g; 828.00/500 g	2.16 kg	3576.96
	2. n-BuLi	163.00/500 mL	5.64 L	1838.64
	3. diisopropylamine	24.65/100 mL; 40.00/500 mL	1.28 L	102.4
	4. piperidine-1-carbaldehyde	253.30.100 g; 720.00/500 g	1.11 kg	1598.4
	5. THF	38.00/500 mL	70.44 L	5353.44
	7. $HSCH_2COOEt$	8300.00/500 mL	1.28 L	21248
	8. K_2CO_3	5.76/100 g; 28.80/500 g	5.35 kg	308.16
	9. DMF	28.80/500 mL	62.99 L	3628.22
	11. LiOH	47.50/100 g; 159.80/500 g	359.40 g	170.72
	12. HCl	20.00/500 mL	93.92 L	3756.8
	14. Cu	46.75/100 g; 91.80/500 g	215.54 g	100.76
	15. quinoline	86.70/500 mL	9.80 L	1699.32
	16. diethyl ether	40.05/500 mL	15.25 L	1221.53
	18. 4,5-dichlorophthalic acid	3102.50/100 g	9.08 kg	281707
	19. Ac_2O	77.94/500 mL	41.29 L	6436.29
	21. KF	32.30/100 g; 46.75/500 g	7.08 kg	661.98
	22. mPEG	45.90/100 g; 108.80/500 g	610.14 g	132.77
	23. Sulfolane	115.60/500 mL	24.41 L	5643.59
	25. Et_3N	59.50/100 mL; 120.0/500 mL	13.32 L	3196.8
	26. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	3.47 kg	1073.62
	28. malononitrile	54.4/100 g; 209.10/500 g	1.67 kg	698.39
	29. CH_3COONa	38.25/500 g	1.55 kg	118.58
	30. ethanol	8.00/500 mL	37.89 L	606.24
	32. 2-Ethyl-1-hexanol	45.00/100 g; 95.00/500 g	1.29 kg	245.10
	33. CH_2Cl_2	20.00/500 mL	17.74 L	709.6
	34. Br_2	80.00/100 g; 150.00/500 g	13.77 L	12025.34
	35. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	37. benzene-1,2-diamine	38.70/100 g; 127.50/500 g	422.11 g	163.36
	38. $SOCl_2$	38.70/100 g; 66.30/500 g	909.26 mL	202.07
	40. HBr	37.80/500 mL	13.27 L	1003.21
	42. HNO_3	22.50/500 mL	588.32 g	16.05
	43. CF_3SO_3H	120.00/100 g; 450.00/500 g	5.88 kg	5292
	45. bromobenzene	43.00/100 g; 132.00/500 g	916.20 g	241.88
	46. 2-Ethylhexyl bromide	136.00/500 g	1.90 kg	516.8
	47. Mg	510.00/100 g; 85.00/500 g	558.25 g	94.9
	48. $Ni(dppp)Cl_2$	208.25/100 g; 1003.0/500 g	15.55 g	32.38
	50. $SnBu_3Cl$	127.50/100 g; 459.00/500 g	1.67 kg	1533.06
	52. $Pd(PPh_3)_4$	10204.20/100 g	428.38 g	43712.75
	53. Toluene	20.00/500 mL	51.39 L	2055.6

	55. LDA	215.10/500 mL	1.72 L	739.94
	56. $SnMe_3Cl$	1090/100 mL; 3870/500mL	3.45 L	26382.56
	59. $P(OEt)_3$	74.80/500 mL	11.31 L	1691.98
	60. *O*-DCB	44.00/500 mL	11.31 L	995.28
	61. KI	60.80/100 g; 229.50/500 g	362.00 g	220.1
	63. $POCl_3$	120.60/100 g; 255.00/500mL	3.72 L	1897.20
	64. $CHCl_3$	40.50/500 mL	228.02 L	18469.62
	66. Pyridine	44.00/500 mL	20.55 L	1808.40
	Subtotal cost: 465394.62 ¥/65532.85 $			
Isolation/ Purification process	**12.** HCl	20.00/500 mL	62.33 L	2493.20
	16. diethyl ether	40.05/500 mL	705.59 L	56517.76
	21. KF	45.00/500 g	51.37 L	1581.30
	30. ethanol	8.00/500 mL	98.00 L	1568.00
	33. CH_2Cl_2	20.00/500 mL	4289.41 L	171576.40
	67. $NaHCO_3$	609.18/500 mL	22.55 L	27474.02
	68. NH_4Cl	24.00/100 g; 8.00/500 g	25.00 L	148.80
	69. NaOH	7.65/100 g; 38.25/500 g	588.32 g	45.01
	70. ethyl acetate	13.00/500 mL	5898.00 L	153348.00
	71. n-hexane	16.00/500 mL	6135.30 L	196329.60
	72. Petroleum ether	20.00/500 mL	9268.35 L	370734.00
	73. silica gel	13.00/100 g; 65.00/500 g	2052.27 kg	266795.10
	74. Al_2O_3	44.20/500 g	192.00 kg	16972.80
	75. acetic anhydride	77.94/500 mL	908.00 L	141539.04
	Subtotal cost: 1407123.03 ¥/198138.90 $			
Total cost: 1872517.65 ¥/263671.75 $				

Table S7 Survey of calculated preparation costs for BTP-ec9.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** 3-bromothiophene	113.00/100 g; 536.00/500 g	4.11 kg	4405.92
	2. $AlCl_3$	18.00/100 g; 35.10/500 g	3.35 kg	235.17
	3. CH_2Cl_2	20.00/500 mL	168.91 L	6756.40
	4. dodecanoyl chloride	72.16/100 g; 290.40/500 g	4.82 kg	2799.46
	6. DMF	28.80/500 mL	71.99 L	4146.62
	7. K_2CO_3	5.76/100 g; 28.80/500 g	6.26 kg	360.58
	8. ethyl thioglycolate	62.90/100 g; 285.60/500 g	2.49 L	1558.83
	10. EtOH	8.00/500 mL	97.74 L	1563.84
	11. NaOH	7.65/100 g; 38.25/500 g	1.81 kg	138.47
	13. Cu	46.75/100 g; 91.8/500 g	906.89 g	166.51
	14. quinoline	34.00/100 mL; 86.70/500 mL	45.34 L	7861.96
	16. n-BuLi	163.00/500 mL	6.37 L	2076.62
	17. THF	38.00/500 mL	122.79 L	9332.04
	18. $Sn(Bu)_3Cl$	127.50/100 g; 459.00/500 g	4.01 kg	3681.18
	20. 4,5-dichlorophthalic acid	1902.30/100 g	4.81 kg	91500.63
	21. Ac_2O	77.94/500 mL	21.67 L	3377.87
	23. Sulfolane	115.60/500 mL	16.22 L	3750.06
	24. mPEG	45.90/100 g; 108.80/500 g	405.53 g	88.24
	25. KF	32.30/100 g; 46.75/500 g	4.70 kg	439.45
	23. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	2.31 kg	714.71
	24. Et_3N	59.50/100 mL; 120.00/500 mL	4.65 L	1116.00
	26. malononitrile	54.4/100 g; 209.10/500 g	1.11 kg	464.20
	27. CH_3COONa	38.25/500 g	1.03 kg	78.80
	29. 2-butyloctan-1-ol	1157.40/500 g	1.06 kg	2460.67
	30. Br_2	80.00/100 g; 150.00/500 g	17.51 kg	5253.84
	31. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	33. benzene-1,2-diamine	127.50/500 g	0.84 kg	214.20
	34. $SOCl_2$	38.70/100 g; 66.30/500 g	2964.78 g	393.13
	36. HBr	37.8/500 mL	26.25 L	1984.50
	38. HNO_3	22.50/500 mL	1.16 kg	34.73
	39. CF_3SO_3H	120.00/100 g; 450.00/500 g	11.65 kg	10485.00
	41. $Pd(PPh_3)_2Cl_2$	14848.38/100 g	173.59 g	25775.30
	42. toulene	20.00/500 mL	28.00 L	1120.00
	44. $P(OEt)_3$	74.80/500 mL	18.18 L	2719.73
	45. *o*-DCB	50.00/500 mL	7.27 L	727.00
	46. KOH	37.40/500 g	727.35 g	54.41
	44. 2-butyloctan-1-ol	1157.40/500 g	1.06 kg	2460.67
	49. pyridine	44.00/500 mL	7.20 L	633.60
	50. $CHCl_3$	40.05/500 mL	324.05 L	25956.41
	Subtotal cost: 227353.58 ¥/32013.97 $			
	3. CH_2Cl_2	20.00/500 mL	5633.78 L	225351.20
	10. EtOH	8.00/500 mL	194.00 L	3104.00
	11. NaOH	7.65/100 g; 38.25/500 g	1.16 kg	88.74

Isolation/ Purification process	**21.** Ac_2O	77.94/500 mL	603.00 L	93995.64
	51. methanol	9.00/500 mL	324.05 L	5832.90
	52. HCl	20.00/500 mL	750.47 L	30018.80
	53. Petroleum ether	20.00/500 mL	14096.90 L	563876.00
	54. ethyl acetate	13.00/500 mL	322.00 L	8372.00
	55. n-hexane	16.00/500 mL	93.48 L	2991.36
	56. silica gel	13.00/100 g; 65.00/500 g	2822.10 kg	366873.00
	Subtotal cost: 1300503.64 ¥/183125.68$			
Total cost: 1527857.22 ¥/215139.65 $				

	54. $Pd(PPh_3)_4$	10204.20/100 g	428.38 g	43712.75

Process (Proportion)	**Reagents**	**Unit price (¥)**	**Dosage**	**Total price (¥)**
Synthesis process	**1.** 3,4-dibromothiophene	178.20/100 g; 828.00/500 g	2.16 kg	3576.96
	2. n-BuLi	163.00/500 mL	6.11 L	1991.86
	3. diisopropylamine	24.65/100 mL; 40.00/500 mL	1.28 L	102.4
	4. piperidine-1-carbaldehyde	253.30.100 g; 720.00/500 g	1.11 kg	1598.4
	5. THF	38.00/500 mL	70.44 L	5353.44
	7. $HSCH_2COOEt$	8300.00/500 mL	1.28 L	21248.00
	8. K_2CO_3	5.76/100 g; 28.80/500 g	5.35 kg	308.16
	9. DMF	28.80/500 mL	62.99 L	3628.22
	11. LiOH	47.50/100 g; 159.80/500 g	359.40 g	170.72
	12. HCl	20.00/500 mL	93.92 L	3756.8
	14. Cu	46.75/100 g; 91.80/500 g	215.54 g	100.76
	15. quinoline	86.70/500 mL	9.80 L	1699.32
	16. diethyl ether	40.05/500 mL	33.50 L	2683.35
	18. 4,5-dichlorophthalic acid	3102.50/100 g	9.08 kg	281707
	19. Ac_2O	77.94/500 mL	41.29 L	6436.29
	21. KF	32.30/100 g; 46.75/500 g	7.08 kg	661.98
	22. mPEG	45.90/100 g; 108.80/500 g	610.14 g	132.77
	23. Sulfolane	115.60/500 mL	24.41 L	5643.59
	25. Et_3N	59.50/100 mL; 120.0/500 mL	13.32 L	3196.8
	26. tert-butyl acetoacetate	47.70/100 g; 154.70/500 g	3.47 kg	1073.62
	28. malononitrile	54.4/100 g; 209.10/500 g	1.67 kg	698.39
	29. CH_3COONa	38.25/500 g	1.55 kg	118.58
	30. ethanol	8.00/500 mL	37.89 L	606.24
	32. 2-butyloctan-1-ol	467.50/100 g; 2260.0/500 g	4.39 kg	19842.80
	33. CH_2Cl_2	20.00/500 mL	110.74 L	4429.6
	34. Br_2	80.00/100 g; 150.00/500 g	13.77 L	12025.34
	35. PPh_3	38.00/100 g; 128.25/500 g	1.82 kg	466.83
	37. benzene-1,2-diamine	38.70/100 g; 127.50/500 g	422.11 g	163.36
	38. $SOCl_2$	38.70/100 g; 66.30/500 g	909.26 mL	202.07
	40. HBr	37.80/500 mL	13.27 L	1003.21
	42. HNO_3	22.50/500 mL	588.32 g	16.05
	43. CF_3SO_3H	120.00/100 g; 450.00/500 g	5.88 kg	5292.00
	45. pyridiniumchlorochromate	140.25/500 g	10.04 kg	2816.22
	48. $LiAlH_4$	81.60/100 mL; 297.5/500 mL	2.40 L	1428.00
	49. $AlCl_3$	92.00/500 g	4.00 kg	736.00
	51. LDA	215.10/500 mL	1.72 L	739.94
	52. $SnMe_3Cl$	1090/100 mL; 3870/500mL	3.45 L	26382.56

Table S8 Survey of calculated preparation costs for L8-BO.

	55. Toluene	20.00/500 mL	51.39 L	2055.6
	57. $P(OEt)_3$	74.80/500 mL	11.31 L	1691.98
	58. *O*-DCB	44.00/500 mL	11.31 L	995.28
	59. KI	60.80/100 g; 229.50/500 g	362.00 g	220.1
	61. $POCl_3$	120.60/100 g; 255.00/500mL	3.72 L	1897.20
	62. $CHCl_3$	40.50/500 mL	228.02 L	18469.62
	64. Pyridine	44.00/500 mL	20.55 L	1808.40
	Subtotal cost: 492888.56 ¥/69404.31 $			
Isolation/ Purification process	**12.** HCl	20.00/500 mL	62.33 L	2493.20
	16. diethyl ether	40.05/500 mL	721.33 L	57778.53
	21. KF	45.00/500 g	51.37 L	1581.30
	30. ethanol	8.00/500 mL	98.00 L	1568.00
	33. CH_2Cl_2	20.00/500 mL	4298.33 L	171933.20
	65. $NaHCO_3$	609.18/500 mL	22.55 L	27474.02
	66. NH_4Cl	24.00/100 g; 8.00/500 g	25.00 L	148.80
	67. NaOH	7.65/100 g; 38.25/500 g	588.32 g	45.01
	68. ethyl acetate	13.00/500 mL	5320.30 L	138327.80
	69. n-hexane	16.00/500 mL	6759.44 L	216302.08
	70. Petroleum ether	20.00/500 mL	9566.80 L	382672.00
	71. silica gel	13.00/100 g; 65.00/500 g	2156.45 kg	280338.50
	72. Al_2O_3	44.20/500 g	175.00 kg	15470.00
	73. acetic anhydride	77.94/500 mL	908.00 L	141539.04
	Subtotal cost: 1437671.48 ¥/202440.47 $			
Total cost: 1930560.04 ¥/271844.78 $				

Table S9 Survey of calculated preparation costs for PTQ11.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** thiophene	37.40/100 g; 102.00/500 g	192.71 g	39.31
	2. TMEDA	644.25/100 g; 3735.00/500 g	536.84 g	3458.59
	3. n-BuLi	163.00/500 mL	1.85 L	603.10
	4. THF	38.00/500 mL	2.31 L	175.56
	5. $(CH_3)_3SnCl$	1936.00/100 g; 3870.00/500 g	920.63 g	7125.68
	6. 3,6-dibromo-4,5-difluorobenzene-1,2-diamine	61750.00/500 g	712.72 g	88020.92
	7. pyruvic acid	33.99/100 g; 99.66/500 g	174.64 g	34.81
	8. AcOH	26.61/500 mL	23.60 L	1255.99
	9. 1-bromo-2-hexyldecane	637.50/100 g; 2534.40/500 g	704.78 g	3572.39
	10. t-BuOK	59.50/100 g; 244.80/500 g	309.96 g	151.76
	11. MeOH	9.00/500 mL	23.60 L	424.80
	13. $Pd(PPh_3)_4$	9669.60/25 g	85.96 g	33247.95
	14. toluene	20.00/500 mL	107.50 L	4300.00
	Subtotal cost: 142410.86 ¥/20053.07 $			
Isolation/ Purification process	**11.** MeOH	9.00/500 mL	242.52 L	4365.36
	15. NH_4Cl	8.16/100 g; 40.80/500 g	29.38 L	891.84
	16. CH_2Cl_2	20.00/500 mL	392.00 L	15680.00
	17. diethyl ether	40.05/500 mL	17.33 L	1388.13
	18. silica gel	13.00/100 g; 65.00/500 g	142.54 kg	18530.20
	19. Petroleum ether	20.00/500 mL	890.90 L	35636.00
	20. n-hexane	16.00/500 mL	181.89 L	5820.48
	21. $CHCl_3$	40.05/500 mL	181.89 L	14569.39
	Subtotal cost: 96881.40 ¥/13642.00 $			
Total cost: 239292.26 ¥/33695.07 $				

Table S10 Survey of calculated preparation costs for PTQ10.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** thiophene	37.40/100 g; 102.00/500 g	192.71 g	39.31
	2. TMEDA	644.25/100 g; 3735.00/500 g	536.84 g	3458.59
	3. n-BuLi	163.00/500 mL	1.85 L	603.10
	4. THF	38.00/500 mL	2.31 L	175.56
	5. $(CH_3)_3SnCl$	1936.00/100 g; 3870.00/500 g	920.63 g	7125.68
	6. 3,6-dibromo-4,5-difluorobenzene-1,2-diamine	61750.00/500 g	712.72 g	88020.92
	7. glyoxylic acid	41.65/100 g; 143.65/500 g	174.64 g	50.17
	8. AcOH	26.61/500 mL	23.60 L	1255.99
	9. 1-bromo-2-hexyldecane	637.50/100 g; 2534.40/500 g	704.78 g	3572.39
	10. t-BuOK	59.50/100 g; 244.80/500 g	309.96 g	151.76
	11. MeOH	9.00/500 mL	23.60 L	424.80
	13. $Pd(PPh_3)_4$	9669.60/25 g	85.96 g	33247.95
	14. toluene	20.00/500 mL	107.50 L	4300.00
	Subtotal cost: 142426.22 ¥/20055.23 $			
Isolation/ Purification process	**11.** MeOH	9.00/500 mL	242.52 L	4365.36
	15. NH_4Cl	8.16/100 g; 40.80/500 g	29.38 L	891.84
	16. CH_2Cl_2	20.00/500 mL	392.00 L	15680.00
	17. diethyl ether	40.05/500 mL	17.33 L	1388.13
	18. silica gel	13.00/100 g; 65.00/500 g	142.54 kg	18530.20
	19. Petroleum ether	20.00/500 mL	890.90 L	35636.00
	20. n-hexane	16.00/500 mL	181.89 L	5820.48
	21. $CHCl_3$	40.05/500 mL	181.89 L	14569.39
	Subtotal cost: 96881.40 ¥/13642.00 $			
Total cost: 239307.62 ¥/33697.23 $				

Table S11 Survey of calculated preparation costs for PM6.

Process	Regents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1**. thiophene	37.40/100 g; 102.00/500 g	10994.00 g	2242.78
	2. Br_2	80.00/100 g; 150.00/500 g	63219.20 g	18965.76
	3. $CHCl_3$	40.05/500 mL	27.19 L	2177.92
	5. Zn	49.42/100 g; 247.09/500 g	20927.40 g	10341.90
	6. acetic acid	12.00/500 mL	19.00 L	456.00
	8. Mg	510.00/100 g; 85.00/500 g	11266.00 g	1915.22
	9. C_2H_5Br	34.00/100 g; 72.25/500 g	42653.04 g	6163.36
	11. $SOCl_2$	38.70/100 g; 66.30/500 g	11710.97 g	1552.87
	13. benzene	16.00/500 mL	20.00 L	640.00
	14. dimethylamine	23.80/500 mL	25.00 L	1190.00
	16. n-BuLi	163.00/500 mL	9.92 L	3233.92
	17. Et_2O	40.05/500 mL	24.76 L	1983.28
	20. 3-bromothiophene	113.40/100 g; 536.40/500 g	3038.32 g	3259.51
	19. 1-bromo-2-ethylhexane	26.35/100 g; 113.90/500 g	5312.9 g	1210.29
	21. THF	38.00/500 mL	129.63 L	9851.88
	22. LDA	215.10/500 mL	22.38 L	9627.88
	24. $SnCl_2 \cdot 2H_2O$	70.20/100 g; 297.00/500 g	7.83 kg	4649.68
	25. HCl	20.00/500 mL	3.11 L	124.40
	27. $Si(CH_3)_3Cl$	542.36/500 g	2.02 L	2191.13
	29.N-fluorobenzenesulfonimide	88.40/100 g; 378.25/500 g	2.29 kg	1730.04
	31. trifluoroacetic acid	268.60/500 mL	7.8 5 L	4217.02
	33. $(CH_3)_3SnCl$	1936.00/100 g; 3870.00/500 g	5078.32 g	39306.20
	35. Thiophene-3,4-dicarboxylic	3034.80/100 g	565.30 g	17155.72
	36. AcOH	26.61/500 mL	5.65 L	300.69
	38. oxalyl chloride	318.75/500 mL	1.75 L	1115.63
	39. DMF	28.80/500 mL	13.55 L	780.48
	40. $AlCl_3$	18.00/100 g; 35.10/500 g	1.40 kg	98.22
	41. 2,5-bis(2-ethylhexyl)thiophene	5000.00/50 g	810.04 g	81004.00
	43. tributyl(thiophen-2-yl)stannane	634.95/100 g;3049.80/500 g	2.09 kg	12719.80
	44. $Pd(PPh_3)_4$	9669.60/25 g	77.03 g	29793.97
	45. toluene	20.00/500 mL	37.47 L	1498.80
	47. NBS	25.50/100 g; 59.50/500 g	640.00 g	76.16
	49. CH_2Cl_2	20.00/500 mL	3.50 L	140.00
	Subtotal cost: 271714.51 ¥/38260.49 $			
Isolation/ Purification process	**17.** Et_2O	40.05/500 mL	1659.05 L	132889.91
	50. acetic acid	12.00/500 mL	137.00 L	3288.00
	25. HCl	20.00/500 mL	0.26 L	10.40
	3. $CHCl_3$	40.05/500 mL	1083.21 L	86765.12
	51. petroleum ether	20.00/500 mL	12194.39 L	487775.60
	49. CH_2Cl_2	20.00/500 mL	3194.30 L	127772.00

	52. silica gel	13.00/100 g; 65.00/500 g	2544.90 kg	330837.00
	53. acetone	20.00/500 mL	86.10 L	3444.00
	54.acetic ether	13.00/500 mL	52.11 L	1354.86
	55. MeOH	9.00/500 mL	609.00 L	10962.00
	56. n-hexane	16.00/500 mL	141.75 L	4699.23
	Subtotal cost: 1189798.12 ¥/167537.09 $			
Total cost: 1461512.63 ¥/205801.80 $				

Table S12 Survey of calculated preparation costs for D18.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** thiophene	37.40/100 g; 102.00/500 g	8484.00 g	1730.74
	2. Br_2	80.00/100 g; 150.00/500 g	48806.49 g	14641.95
	3. $CHCl_3$	40.05/500 mL	129.82 L	10398.58
	5. Zn	49.42/100 g; 247.09/500 g	16149.90 g	7980.96
	6. acetic acid	12.00/500 mL	14.70 L	352.80
	8. Mg	510.00/100 g; 85.00/500 g	9010.44 g	1531.77
	9. C_2H_5Br	34.00/100 g; 72.25/500 g	32915.76 g	4756.33
	11. $SOCl_2$	38.70/100 g; 66.30/500 g	9038.50 g	1198.51
	13. benzene	16.00/500 mL	18.00 L	576.00
	14. dimethylamine	23.80/500 mL	20.00 L	952.00
	16. n-BuLi	163.00/500 mL	8.16 L	2660.16
	17. Et_2O	40.05/500 mL	19.08 L	1528.31
	20. 3-bromothiophene	113.00/100 g; 536.00/500 g	3374.16 g	3617.10
	19. THF	38.00/500 mL	206.95 L	15728.20
	21. LDA	215.10/500 mL	19.74 L	8492.15
	22. 1-bromo-2-ethylhexane	26.35/100 g; 113.90/500 g	4080.38 g	929.51
	24. $SnCl_2{\cdot}2H_2O$	70.20/100 g; 297.00/500 g	6.02 kg	3575.88
	25. HCl	20.00/500 mL	2.39 L	95.60
	27. $Si(CH_3)_3Cl$	542.36/500 g	1.55 L	1435.84
	29. N-fluorobenzenesulfonimide	88.40/100 g; 378.25/500 g	1.76 kg	1331.44
	31. trifluoroacetic acid	268.60/500 mL	6.05 L	3250.06
	33. Me_3SnCl	1936.00/100 g; 3870.00/500 g	8.97 L	88867.58
	35. 2-butyl-1-octylbromide	467.50/100 g; 2260.00/500 g	2.54 kg	11480.80
	36. $dppeNiCl_2$	205.60/100 g; 1062/500 g	48.84 g	100.42
	37. 2-bromothiophene	35.20/100 g; 122.40/500 g	467.81 g	114.52
	38. LiBr	33.15/100 g; 128.25/500 g	553.23 g	141.90
	39. CuBr	27.00/100 g; 99.45/500 g	913.78 g	181.75
	41. oxalyl chloride	318.75/500 mL	364.29 g	145.15
	43. CH_2Cl_2	20.00/500 mL	15.06 L	602.40
	44. $FeCl_3$	22.62/100 g; 20.70/500 g	1.17 kg	48.44
	46. $HONH_3Cl$	23.00/100 g; 63.75/500 g	409.89g	52.26
	47. C_2H_5OH	8.00/500 mL	26.00 L	416.00
	48. Pd/C	2664.00/100 g; 11050.00/500 g	51.98 g	1384.75
	49. $N_2H_4{\cdot}H_2O$	77.40/500 mL	3.90 L	603.72
	51. DMF	28.80/500 mL	8.54 L	491.90
	52. H_4Cl_2S	102.35/500 g	887.00 g	181.57
	58. $Pd(PPh_3)_4$	9669.60/25 g	138.40 g	53530.91
	59. toluene	20.00/500 mL	24.60 L	984.00
	61. NBS	25.50/100 g; 59.50/500 g	289.78 g	34.48
	63. $Pd_2(dba)_3$	7785.90/25 g	21.10 g	6571.30
	64. $P(o\text{-}Tol)_3$	371.20/100 g	71.04 g	263.70
	65. C_6H_5Cl	26.00/500 mL	703.38 L	36575.76

	Subtotal cost: 289537.20 ¥/40770.13 $			
Isolation Purification process	**17.** Et_2O	40.05/500 mL	2806.71 L	224817.47
	6. acetic acid	12.00/500 mL	105.71 L	2537.04
	25. HCl	20.00/500 mL	2.54 L	101.60
	66. NH_4Cl	8.16/100 g; 40.80/500 g	1162.03 L	35084.01
	67. ethyl acetate	13.00/500 mL	159.20 L	4139.20
	68. n-hexane	16.00/500 mL	5456.39 L	174604.48
	69. pentane	25.20/500 mL	45.13 L	2274.55
	3. $CHCl_3$	40.05/500 mL	330.05 L	26437.01
	43. CH_2Cl_2	20.00/500 mL	3285.78 L	131431.20
	47. C_2H_5OH	8.00/500 mL	45.25 L	724.00
	70. silica gel	13.00/100 g; 65.00/500 g	2232.13 kg	290176.90
	71. petroleum ether	20.00/500 mL	7610.95 L	304438.00
	72. acetone	20.00/500 mL	66.27 L	2650.80
	73. acetonitrile	44.93/500 mL	53.57 L	4813.80
	65. C_6H_5Cl	26.00/500 mL	109.10 L	5673.20
	74. MeOH	9.00/500 mL	145.46 L	2618.28
	Subtotal cost: 1212521.54 ¥/170736.80 $			
Total cost: 1502058.74 ¥/211506.93 $				

Table S13 Survey of calculated preparation costs for D18-Cl.

Process	Reagents	Unit price (¥)	Dosage	Total price (¥)
Synthesis process	**1.** thiophene	37.40/100 g; 102.00/500 g	8484.00 g	1730.74
	2. Br_2	80.00/100 g; 150.00/500 g	48806.49 g	14641.95
	3. $CHCl_3$	40.05/500 mL	129.82 L	10398.58
	5. Zn	49.42/100 g; 247.09/500 g	16149.90 g	7980.96
	6. acetic acid	12.00/500 mL	14.70 L	352.80
	8. Mg	510.00/100 g; 85.00/500 g	9010.44 g	1531.77
	9. C_2H_5Br	34.00/100 g; 72.25/500 g	32915.76 g	4756.33
	11. $SOCl_2$	38.70/100 g; 66.30/500 g	9038.50 g	1198.51
	13. benzene	16.00/500 mL	18.00 L	576.00
	14. dimethylamine	23.80/500 mL	20.00 L	952.00
	16. n-BuLi	163.00/500 mL	3.28 L	1069.28
	17. Et_2O	40.05/500 mL	19.08 L	1528.31
	19. NaCl	15.00/500 g	1557 g	46.71
	20. $FeCl_3$	22.62/100 g; 20.70/500 g	5.19 kg	214.87
	21. acetonitrile	42.00/500 mL	159.72 L	13416.48
	23. THF	38.00/500 mL	145.60 L	11065.60
	24. LDA	215.10/500 mL	2.16 L	929.23
	25. 1-bromo-2-ethylhexane	26.35/100 g; 113.90/500 g	4080.38 g	929.51
	27. $SnCl_2 \cdot 2H_2O$	70.20/100 g; 297.00/500 g	2.88 kg	1710.72
	28. HCl	20.00/500 mL	2.88 L	115.20
	30. Me_3SnCl	1936.00/100 g; 3870.00/500 g	8.97 L	88867.58
	32. 2-bromothiophene	35.20/100 g; 122.40/500 g	467.81 g	114.52
	33. LiBr	33.15/100 g; 128.25/500 g	553.23 g	141.90
	34. CuBr	27.00/100 g; 99.45/500 g	913.78 g	181.75
	36. oxalyl chloride	318.75/500 mL	364.29 g	145.15
	38. CH_2Cl_2	20.00/500 mL	15.06 L	602.40
	40. $HONH_3Cl$	23.00/100 g; 63.75/500 g	409.89g	52.26
	41. C_2H_5OH	8.00/500 mL	26.00 L	416.00
	42. Pd/C	2664.00/100 g; 11050.00/500 g	51.98 g	1384.75
	43. $N_2H_4 \cdot H_2O$	77.40/500 mL	3.90 L	603.72
	45. DMF	28.80/500 mL	8.54 L	491.90
	46. H_4Cl_2S	102.35/500 g	887.00 g	181.57
	49. 2-butyl-1-octylbromide	467.50/100 g; 2260.00/500 g	2.54 kg	11480.80
	50. $dppeNiCl_2$	205.60/100 g; 1062/500 g	48.84 g	100.42
	53. $Pd(PPh_3)_4$	9669.60/25 g	138.40 g	53530.91
	54. toluene	20.00/500 mL	32.60 L	1304.00
	56. NBS	25.50/100 g; 59.50/500 g	289.78 g	34.48
	58. $Pd_2(dba)_3$	7785.90/25 g	21.10 g	6571.30
	59. $P(o\text{-}Tol)_3$	371.20/100 g	71.04 g	263.70
	Subtotal cost: 241614.66 ¥/34022.09 $			
	17. Et_2O	40.05/500 mL	2132.67 L	170613.60
	6. acetic acid	12.00/500 mL	105.71 L	2537.04
	60. NH_4Cl	8.16/100 g; 40.80/500 g	1162.03 L	35084.01

Isolation/ Purification process	**61.** ethyl acetate	13.00/500 mL	132.70 L	3450.20
	62. n-hexane	16.00/500 mL	4971.33 L	159082.56
	63. pentane	25.20/500 mL	42.67 L	2150.57
	3. $CHCl_3$	40.05/500 mL	306.09 L	24510.60
	43. CH_2Cl_2	20.00/500 mL	2465.77 L	98630.80
	41. C_2H_5OH	8.00/500 mL	45.25 L	724.00
	64. silica gel	13.00/100 g; 65.00/500 g	2232.13 kg	290176.90
	65. petroleum ether	20.00/500 mL	5563.90 L	222556.00
	66. acetone	20.00/500 mL	66.27 L	2650.80
	67. acetonitrile	44.93/500 mL	53.57 L	4813.80
	68. MeOH	9.00/500 mL	145.46 L	2618.28
	69. C_6H_5Cl	26.00/500 mL	109.10 L	5673.20
	Subtotal cost: 1025272.36 ¥/144369.99 $			
Total cost: 1266887.02 ¥/178392.08 $				

Table S14 Costs of PEH-F, TEH-F and other reported small molecular acceptors.

Entry	**Materials**	**Synthesis process ($ kg^{-1})**	**Isolation/Purification process ($ kg^{-1})**	**Total cost ($ kg^{-1})**
1	PEH-F	36820.83	197916.24	234737.06
2	TEH-F	36804.82	197916.24	234721.06
3	*m*-PEH	66319.38	198138.90	264458.28
4	*o*-TEH	66303.37	198138.90	264442.27
5	*m*-TEH	66423.62	198138.90	264562.52
6	BTP-4F-P2EH	65532.85	198138.90	263671.75
6	BTP-ec9	32013.97	183125.68	215139.65
7	L8-BO	69404.31	202440.47	271844.78

Table S15 Costs of reported polymer donors.

Entry	**Materials**	**Synthesis process ($ kg^{-1})**	**Isolation/Purification process ($ kg^{-1})**	**Total cost ($ kg^{-1})**
1	PTQ11	20053.07	13642.00	33695.07
2	PTQ10	20055.23	13642.00	33697.23
3	PM6	38260.49	167537.09	205801.80
4	D18	40770.13	170736.80	211506.93
5	D18-Cl	34022.09	144369.99	178392.08

Table S16 Detailed energy losses of devices.

Active layers	E_g **(eV)**	V_{oc}^{loss} **(V)**	V_{oc}^{SQ} **(V)**	ΔE_1 **(eV)**	V_{oc}^{rad} **(V)**	ΔE_2 **(eV)**	ΔE_3 **(eV)**
PTQ11:PEH-F	1.447	0.511	1.187	0.260	1.116	0.069	0.182
PTQ11:TEH-F	1.422	0.513	1.164	0.258	1.128	0.036	0.219

Table S17 GIWAXS measurement parameters of the films.

Films	In plane			Out of plane		
	Location (Å^{-1})	*d*-spacing (Å)	CCL (Å)	Location (Å^{-1})	*d*-spacing (Å)	CCL (Å)
PTQ11	0.275	22.8	58.5	1.765	3.557	23.0
PEH-F	0.293/0.402	21.4/15.6	68.5/31.5	1.700	3.695	11.7
THE-F	0.291/0.405	21.6/15.5	72.0/35.2	1.739	3.611	14.3
PTQ11:PEH-F	0.283/0.379	22.2/16.6	63.2/32.6	1.752	3.585	18.0
PTQ11:TEH-F	0.280/0.372	22.4/16.9	67.6/35.4	1.779	3.531	19.2

Table S18 Detailed data of the hole mobility (μ_h) and electron mobility (μ_e).

Active layer	μ_h (10^{-4} cm^2 V^{-1} s^{-1})[a)]	μ_e (10^{-4} cm^2 V^{-1} s^{-1}) [a)]	μ_h/μ_e
PTQ11:PEH-F	7.51	8.34	0.90
PTQ11:TEH-F	6.52	8.25	0.79

[a)]Average values obtained from more than ten different devices.

Table S19 The details of material cost of the industrial organic solar modules with area of 1 m^2.

Materials	Unit price (¥)	Dosage	Total price (¥)
Glass	10/m^2	1 m^2/m^2	10
Ag (bottom)	10/g	1.2 g/m^2	12
PEDOT: PSS	4/mL	1.5 mL/m^2	6
ZnO	30/g	0.2 g/m^2	6
Ag (top)	15/g	1.2 g/m^2	18
Solvents	20/L	0.1 L/m^2	2
Sealant	2/g	3 g/m^2	6
Glass	10/m^2	1 m^2/m^2	10

The cost of other materials for the balance of module, such as interconnection bus bars, wiring, junction-box, back sealing substrate, etc., are assumed to be 10 ¥/m^2.

Table S20 The basic assumptions for the industrial organic solar modules.

Numbers	Assumptions
1	The dimension of organic solar module is 1.2 × 0.6 m (0.72 m^2) with the sub-device area of 1 cm^2.
2	The default production rate is 3 m^2/min, corresponding to a deposition throughout of 0.24 min/module for each production line.
3	The total plant operation time is 4000 h/year for each production line.
4	If the PCE of organic solar module is 10 % and the production capacity of manufacturer is ~200 MW/year, 4 production lines are required.
5	The footprint for each production line, including the equipment space and offices as well as other functional rooms, is estimated to be ~1.5×10^3 m^2. The floor space cost is ~200 ¥/m^2·year. Therefore, the rent of industrial parks is ~3×10^5 ¥/year for each production line.
6	For utility costs in Zhengzhou, Henan Province, China, the average electricity price for industrial customers is 0.95 ¥/kWh; the comprehensive water price for industrial customers is 5.95 ¥/m^3.
7	The labor cost in Zhengzhou, Henan Province, China, is appropriately 20 ¥/h for the manufacturing worker, and 45 ¥/h for the technical and scientific worker. The 50 manufacturing workers and 25 technical and scientific workers are required for ~200 MW/year production.
8	For printing deposition, sputtering, laser scribing, etc., the utilization rate of materials is ~80 %.
9	The density (ρ) of photoactive materials is ~1.2 g/cm^3, the photoactive layer thickness is ~150 nm.
10	The depreciation of physical properties owned by the manufacturer is linear with the lifetime of 15 years.
11	The maintenance cost for facilities is 20 % of the annual equipment depreciation.
12	The SG&A cost is 15 % of the total revenue. Considering the mature manufacturing process, the R&D cost is set to be 0. The average effective tax rate is 27 %.
13	The expected internal return for investing is 14.4 %, which is the average WACC for the China photovoltaic manufacturer.
14	Based on the above assumptions, the dosage of photoactive materials is ~225 mg/m^2, the MC cost (not including the photoactive layer cost) is ~143.80 ¥/m^2 (20.25 \$/m^2, MC2), the OH cost is ~74.21 ¥/m^2 (10.45 \$/m^2), and the WACC cost is ~35.81 ¥/m^2 (5.04 \$/m^2).

Table S21 Cost feasibility of high-performance photoactive material systems for the industrial organic solar modules.

Donors	Acceptors	D:A ratio (w/w)	Photoactive layer cost ($ m^{-2})	PCE (%)	MC + OH + WACC ($ m^{-2})	MSP ($ W_p^{-1})	Ref.
PM6	L8-BO:BTP-eC9	1:0.65:0.65	51.10	20.17	86.84	0.44	1
PM6	BTP-eC9	1:1.2	47.45	19.70	83.19	0.43	2
D18-Cl:PM6	L8-BO:BTP-eC9	0.5:0.5:0.6:0.6	49.53	19.61	85.27	0.44	3
PM6:D18	L8-BO	0.8:0.2:1.2	54.53	19.60	90.27	0.47	4
PM6+1% L8-BO	L8-BO+1% PM6	1:1.2	54.40	19.40	90.14	0.47	5
PM6	L8-BO	1:1	53.74	19.40	89.48	0.47	6
PM6	L8-BO:BTP-eC9	1:0.65:0.65	51.10	19.35	86.84	0.46	7
PTQ10	*m*-TEH:*m*-PEH	1:0.9:0.3	35.91	19.34	71.65	0.38	8
PM6	BTP-eC9	1:1.2	47.45	19.31	83.19	0.44	9
PM6	L8-BO	1:1.25	54.56	19.25	90.30	0.48	10
PM6:D18-Cl	L8-BO	0.7:0.3:1.2	53.57	19.22	89.31	0.47	11
D18	L8-BO	1:1	54.38	19.16	90.12	0.48	12
PM6	BTP-eC9	1:1	47.36	19.10	83.10	0.44	13
D18	L8-BO	1:1	54.38	19.10	90.12	0.48	14
PM6:D18-Cl	L8-BO	0.8:0.2:1.2	53.85	19.10	89.59	0.48	15
PM6:PTQ10	BTP-eC9	0.8:0.2:1.2	43.93	19.10	79.67	0.43	16
D18	L8-BO	1:1	54.38	19.05	90.12	0.48	17
PM6	L8-BO	1:1	53.74	19.02	89.48	0.48	18
PM6	L8-BO	1:1.2	54.41	19.00	90.15	0.48	19
D18	L8-BO	1:1.2	54.99	20.00	90.73	0.46	20
D18-Cl	BTP-4F-P2EH	1:1	49.73	20.80	85.47	0.42	21
PTQ11	**PEH-F**	**1:1.2**	**32.25**	**19.73**	**67.99**	**0.35**	**This work**

Table S22 Photovoltaic performance parameters of PTQ11:PEH-F-based OSCs with or without mask (2.1 mm × 1.6 mm), under illumination of AM 1.5G (100 mW cm^{-2}).

Mask	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
With	0.925	26.52	80.27	19.69
Without	0.936	26.53	79.45	19.73

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