

Supporting Information

Over 16% Efficiency Organic Solar Cell Enabled by Low-cost Pyrazine-based Polymer Donor

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Experimental Details

Materials

The acceptor material BTP-eC9 was purchased from Solarmer Materials Inc. The raw materials were purchased from J&K Scientific, Innochem Science & Technology co., LTD. and other enterprises, and directedly used without any further purification. The detailed synthetic procedures are stated as follows:

2-bromo-3-(3-butylonyl)thiophene (Compound 2)

To a solution of 3-(3-butylundecyl)thiophene (5.64 g, 21.1 mmol) in tetrahydrofuran (50 mL) in ice bath under darkness, N-bromosuccinimide (3.76 g, 21.1 mmol) was added into the reaction flask in small portions. After stirring for 30 minutes, 30 mL of water was poured into the reaction mixture to quench the reaction. And the crude product was extracted twice by using dichloromethane (50 mL) as organic solvent, then washed with water (20 mL) and dried over MgSO₄. After removing solvent under vacuum, the titled compound was gained by column chromatography on a silica gel using petroleum ether as eluant (7.14 g, yield 98%). ¹H NMR (400 MHz, CDCl₃) (ppm): δ 7.18 (d, *J* = 5.6 Hz, 1H), 6.79 (d, *J* = 5.6 Hz, 1H), 2.56 – 2.50 (m, 2H), 1.50 (td, *J* = 8.1, 6.7, 4.0 Hz, 2H), 1.27 (s, 17H), 0.89 (td, *J* = 6.6, 4.1 Hz, 6H).

(3-(3-butylonyl)thiophen-2-yl)trimethylstannane (Compound 3)

Compound 2 (5.0 g, 14.5 mmol) was dissolved in 30 mL of anhydrous tetrahydrofuran, and when the solution was cold to -78 °C, n-butyllithium (5.8 mL, 2.5 M) was injected dropwise slowly into the flask. After stirring at the temperature for 20 minutes, chlorotrimethylstannane (15.9 mL, 1M) was added to the reaction mixture, and then warmed to room temperature to stir overnight. The reaction mixture was poured into 50 mL of water and the crude product was extracted with diethyl ether as solvent, and then dried over MgSO₄.

After removing organic solvents and the crude product used directly for the next step without further purification.

2,5-bis(3-(3-butylnonyl)thiophen-2-yl)pyrazine (Compound 4)

2,5-dibromopyrazine (880 mg, 3.73 mmol), compound 3 (4.0 g, 9.32 mmol), Pd₂(dba)₃ (51.2 mg, 0.056 mmol) and P(*o*-tol) (51.1 mg, 0.17 mmol) are dissolved in 20 mL of *N,N*-Dimethylformamide, and the solution was purged with argon for 15 minutes. Then the mixture was heated at 140 °C. After 2 hours, the solution was cooled to room temperature and 50 mL of water was poured into mixture. The crude product was extracted with dichloromethane and dried over MgSO₄. After removing organic solvent by rotary evaporator, the crude product was purified by column chromatography on a silica gel with petroleum ether/dichloromethane (v/v, 4/1) as eluant. The pure compound 4 was obtained as yellowish liquid (1.14 g, yield 51%). ¹H NMR (300 MHz, CDCl₃) δ 8.82 (s, 2H), 7.39 (d, *J* = 5.1 Hz, 2H), 7.03 (d, *J* = 5.1 Hz, 2H), 3.00 – 2.86 (m, 4H), 1.63 (dt, *J* = 11.2, 6.0 Hz, 4H), 1.27 (d, *J* = 8.5 Hz, 34H), 0.87 (q, *J* = 6.6, 6.1 Hz, 12H).

2,5-bis(3-(3-butylnonyl)-5-(trimethylstannyl)thiophen-2-yl)pyrazine (Compound 5)

To a solution of compound 4 (1.0 g, 1.64 mmol) in 20 mL of anhydrous tetrahydrofuran under argon atmosphere, the lithium diisopropylamide (1.72 mL, 2 M) was added into the mixture slowly in -78 °C. This temperature was kept for 1 hour and trimethyltin chloride (3.6 mL, 1M) was added to the mixture. After stirring at room temperature for 2 hours, 50 mL of water was added to quench the reaction. Diethyl ether (50 mL) was used to extract the crude product from the reaction mixture. Evaporating organic solvent under vacuum, the crude product was purified through recrystallization from ethanol to gain the pure compound 5. (1.34 g, yield 82%) ¹H NMR (400 MHz, Acetone-d₆) δ 8.82 (s, 2H), 7.22 (s, 2H), 3.10 – 3.00 (m, 4H), 1.70 – 1.59 (m, 4H), 1.27 (q, *J* = 4.1, 3.3 Hz, 34H), 0.87 (dt, *J* = 10.2, 6.6 Hz, 12H), 0.41 (t, *J* = 28 Hz, 18H). ¹³C NMR (75 MHz, Acetone-d₆) δ 146.51, 144.22, 141.18, 140.20, 139.69, 139.02, 37.33, 34.55, 33.44, 33.21, 31.86, 28.86, 26.60, 26.56, 22.90, 22.53, 13.61, 13.55.

2,5-bis(5-bromo-3-(3-butylnonyl)thiophen-2-yl)pyrazine (Compound 6)

Compound 4 (0.70 g, 1.15 mmol) was added into 100 mL round-bottom flask and dissolved in 20 mL of anhydrous tetrahydrofuran under darkness. *N*-bromosuccinimide (0.45 g, 2.53 mmol) was fed into the flask in batches at 0 °C. After reacting for 1h, the mixture was poured into water and extracted with dichloromethane to afford the crude product. The crude product was recrystallized from ethanol to provide purified compound 6. (0.79 g, Yield 89%) ¹H NMR (300 MHz, Acetone-d₆) δ 8.83 (s, 2H), 7.21 (s, 2H), 3.09 – 2.93 (m, 4H), 1.67 (dt, *J* = 11.0, 5.9

Hz, 4H), 1.29 (d, J = 9.9 Hz, 34H), 0.87 (q, J = 6.4 Hz, 12H). ¹³C NMR (75 MHz, Chloroform-d) δ 145.70, 143.42, 140.89, 136.01, 133.79, 114.96, 37.48, 34.33, 33.47, 33.13, 31.95, 29.79, 28.85, 27.37, 26.61, 23.12, 22.72, 14.16, 14.12.

Polymerization of PPz

Compound 5 (140.2 mg, 0.15 mmol) and compound 6 (115.0 mg, 0.15 mmol) were successively dissolved into a mixed solvent of anhydrous toluene (10 mL) with Pd₂(dba)₃ (2.06 mg, 0.00225 mmol) coupling P(*o*-tol)₃ (2.05 mg, 0.00675 mmol) as catalyst. Then the reaction mixture was purged with argon for 10 min and allowed to stir at 120 °C for 12 h under argon atmosphere. After that, the reactant was cooled down to room temperature, and the polymer was precipitated into methanol, filtrated and further purified by silica gel column chromatography by using chlorobenzene as eluent. The polymer was precipitated again in methanol and dried by vacuum, with a yield of 85%. C₃₈H₆₀N₂S₂ (PPz): Calculated C: 74.94 H: 9.93 N: 4.60. Found C: 74.88 H: 9.62 N: 4.59.

Polymerization of PPz-T

The polymerization of PPz-T was same with that of PPz, with a yield of 87%.

C₃₈H₆₀N₂S₂ (PPz-T): Calculated C: 72.99 H: 9.04 N: 4.05. Found C: 72.81 H: 8.77 N: 4.01.

DFT calculation

The molecular geometries were optimized by Gaussian 09 with a functional of B3LYP and a basis set of 6-31G(d,p).^[1] To save time, the alkyls in the ester groups were replaced with methyl groups. The average ESP values of atoms are extracted by Multiwfn software.^[2]

Device Fabrication

The devices were fabricated with a conventional architecture of ITO/PEDOT: PSS/Active layer/PDINN/Ag. The ITO-coated glass substrates were washed ultrasonically in water/detergent, water, acetone, and isopropanol in sequence for 15 min. After oxygen plasma treatment for 20 min, the substrate was spin-coated with a thin layer of PEDOT: PSS (30 nm) and then dried under argon at 120 °C for 20 min. The polymer: eC9 (1:1, w/w) blends was dissolved in chloroform with a concentration of 7 mg mL⁻¹ (for polymer), with DIO (0.5% by volume) as additive. The solution was stirred for 2 hours at 40 °C and then spin-coated on the surface of PEDOT: PSS layer in nitrogen-based atmosphere glove box, and the optimal film of the active layer is ca. 100 nm. The active layer was then thermal annealed for 10 min at 100°C. 10 nm thick of PDINN was spin-coated on the top of the active layers at 3000 rpm for 30 s. Finally, 100 nm thick of Ag layer were deposited onto the active layer under high vacuum

of $\sim 3 \times 10^{-4}$ Pa. The overlapping area between the cathode and anode was 4 mm². The *J-V* curves were measured under 100 mW cm⁻² of the standard AM 1.5G spectrum.

Instruments and Measurements

Gel permeation chromatography (GPC) was performed to provide the molecular weight and the polydispersity (PDI) by using trichlorobenzene as eluent at 140 °C on a PL GPC-220 instrument. The UV-visible absorption spectroscopy measurements were conducted on a Hitachi UH4150 spectrophotometer. Thermo gravimetric analysis (TGA) measurements were carried out on TGA-2050 from TA Instruments, Inc. The cyclic voltammograms (CV) measurements were recorded on a Zahner IM6e electrochemical workstation by using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode with a scanning rate of 20 mV s⁻¹ in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution, and the potential of Ag/Ag⁺ reference electrode was internally calibrated by using ferrocene/ferroncenium (Fc/Fc⁺) as the redox couple. UV-vis absorption spectra are measured by Perkin Elmer Lambda 950 spectrophotometer. The characteristics of current density as a function of voltage were recorded on a source measurement unit, and the measurement was carried out under 1 sun (AM 1.5G) illumination based on a class A+AA+ solar simulator (Enlitech SS-X50). The light intensity (100 mW cm⁻²) was calibrated by using a certified reference solar cell (Enlitech, SRC-2020 certified by NREL). SS-X50 Solar simulator adopted a Xe short-arc lamp as the broadband light source. The SS-X50 adopts the medical-device-level power supply system, which provides the smaller electrical ripples. The external quantum efficiency (EQE) was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). Fluorescence decay dynamics were recorded by TCSPC (Becker&Hickl, SPC-150). The excitation wavelength is 500 nm with a laser power of *ca.* 20 μJ cm⁻². The laser spot diameter is 2 μm. The photo-CELIV measurements reported were performed by the all-in-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland. The tapping mode Atom Force Microscopy (AFM) measurements were performed on a Bruker Nanoscope V AF microscope. GIWAXS measurements were performed on a XEUSS SAXS/WAXS system (XENOCS, France) at the National Center for Nanoscience and Technology (NCNST, Beijing). Highly sensitive EQE (s-EQE) was measured using an integrated system (PECT-600, Enlitech). External quantum efficiency of electroluminescence (EQE_{EL}) and electroluminescence (EL) spectra were collected by applying external voltage (0-5 V) through the devices (ELCT-3010, Enlitech).

Table S1. The MOC evaluation of PPz and PPz-T.

PPz (1g)			
Compound 5			
Reagent	Quantity	Unit (source) ^{b,c} (By June 2022)	Cost (\$)
Thiophene-3-carboxaldehyde	0.87g	86.7\$/25g (J&K)	3.017
2-butyloctan-1-ol	1.54g	92.3\$/100g (aladdin)	1.421
Pyridinium chlorochromate (PCC)	1.85g	62\$/500g (J&K)	0.229
N ₂ H ₄ ·H ₂ O (ρ=1.032g/cm ³)	1.45g	26.9\$/500mL (Innochem)	0.076
NBS	1.09g	32\$/1kg (J&K)	0.035
n-BuLi (2.4M)	2.5mL	43.6\$/800 mL,2.4M (J&K)	0.136
Sn(Me) ₃ Cl	6.3ml	760\$/800 mL,1M (J&K)	5.982
2,5-dibromopyrazine	0.546g	339.2\$/100g (J&K)	1.852
Pd ₂ (dba) ₃	31.1mg	1010.2\$/25g (J&K)	1.256
P(o-tol) ₃	31.4mg	285.8\$/100g (J&K)	0.089
LDA	1.3mL	76.2\$/500 mL,2M (J&k)	0.991
Sn(Me) ₃ Cl	2.7mL	220.3\$/100 mL,1M (J&K)	5.948
Total Cost			21.032 (24.258\$/1g)
Compound 6			
Reagent	Quantity	Unit (source) ^{b,c} (By June 2022)	Cost (\$)
Thiophene-3-carboxaldehyde	0.803 g	86.7\$/25g (J&K)	2.785
2-butyloctan-1-ol	1.42 g	92.3\$/100g (aladdin)	1.31
Pyridinium chlorochromate (PCC)	1.71 g	62\$/500g (J&K)	0.212
N ₂ H ₄ ·H ₂ O	1.34 g	26.9\$/500mL (Innochem)	0.072
NBS	1.01 g	32\$/1kg (J&K)	0.032
n-BuLi (2.4M)	2.3 mL	43.6\$/800 mL,2.4M (J&K)	0.125
Sn(Me) ₃ Cl	5.8 ml	760\$/800 mL,1M (J&K)	5.51
2,5-dibromopyrazine	0.50 g	339.2\$/100g (J&K)	1.69
Pd ₂ (dba) ₃	28.7 mg	1010.2\$/25g (J&K)	1.16
P(o-tol) ₃	29.0 mg	285.8\$/100g (J&K)	0.082
NBS	0.42g	32\$/1kg (J&K)	0.0134
Total Cost			12.991 (17.651\$/1g)
Polymerization of PPz (1g)			
Reagent	Quantity	Unit (source) ^{b,c} (By June 2022)	Cost (\$)
Pd ₂ (dba) ₃	13.2 mg	1010.2\$/25g (J&K)	0.533
P(o-tol) ₃	13.1 mg	285.8\$/100g (J&K)	0.0374
Overall Cost for 1g PPz			34.59
Polymerization of PPz-T (1g)			
Reagent	Quantity	Unit (source) ^{b,c} (By June 2022)	Cost (\$)
Pd ₂ (dba) ₃	21.0 mg	1010.2\$/25g (J&K)	0.848
P(o-tol) ₃	20.9 mg	285.8\$/100g (J&K)	0.0597
compound 6	1.17 g	17.65\$/1g	20.65
2,5-bis(trimethylstannyl)thiophene	0.62 g	13.89\$/1g	8.611
Overall Cost for 1g PPz-T			30.17

Table S2. The PCEs, synthesis steps, MOCs and estimated prices of some typical polymer donors with PCEs over 16%, PPz and PPz-T in this work.

Polymer	PCE (%)	Steps ^{a)}	MOC ^{b)} (\$/1g)	Price ^{c)} (\$/1g)	Ref.
PBDB-TF	17.8	12	46.9	3380	[3]
D18	18.2	17	63.4	3850	[4]
PTQ10	16.2	3	149.2	1650	[5]
PTzBI- <i>d</i> F	17.3	21	539.8	4200	[6]
PBTATBT-4f	16.1	15	55.3	2470	[7]
PTVT-T	16.2	5	35.0	1500	[8]
PTVT-BT	16.3	5	29.6	-	[9]
PPz	1.40	5	34.59	-	This work
PPz-T	16.16	5	30.17	-	This work

^{a)}The synthesis routes of the polymers are started with the rule that the raw materials are commercially available in hectograms or kilograms (excluding the catalysts).

^{b)}MOC: material-only cost, which is the cost of the raw materials used for polymer synthesis. The cheap materials, including organic solvents, inorganic substances (acids, bases and salt), solvents for post-treatment and water, are not included.

^{c)}The prices were quoted from material suppliers and the website, and may be changed with subsequent updates.

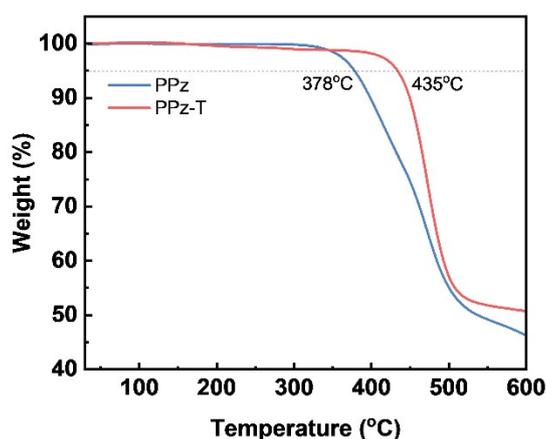


Fig. S1. TGA curves of PPz and PPz-T measured in nitrogen atmosphere.

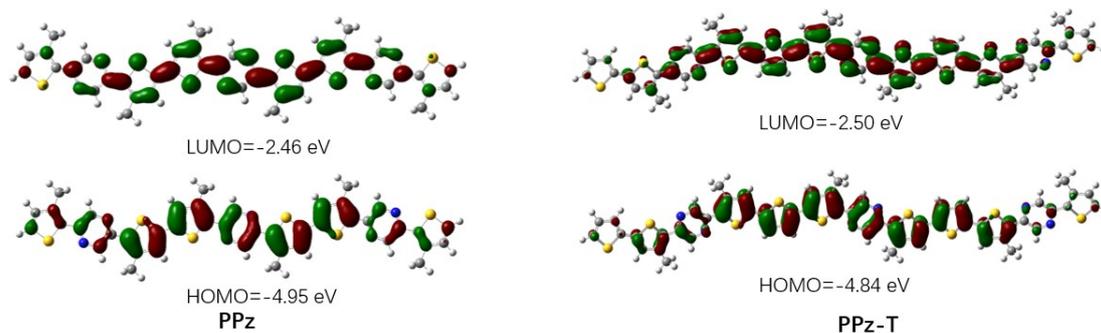


Fig. S2. Frontier molecular orbitals of PPz and PPz-T trimers.

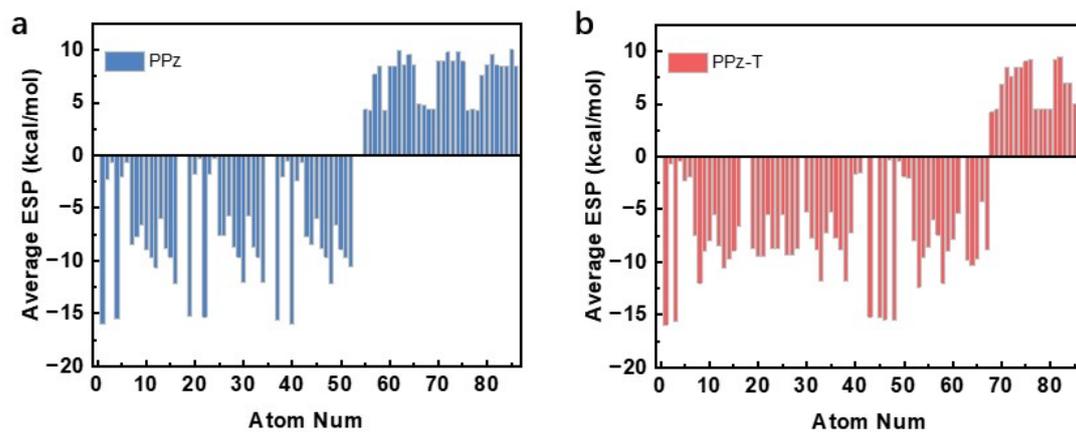


Fig. S3. Averaged ESP values of individual atoms for PPz (a) and PPz-T (b) trimers.

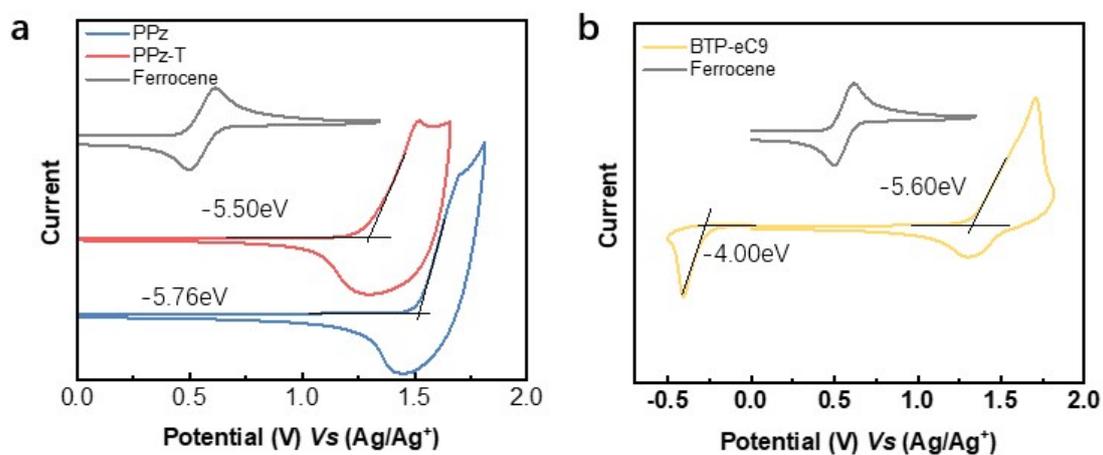


Fig. S4. Cyclic voltammetry curves of PPz, PPz-T (a) and BTP-eC9 (b) with Ferrocene as internal reference.

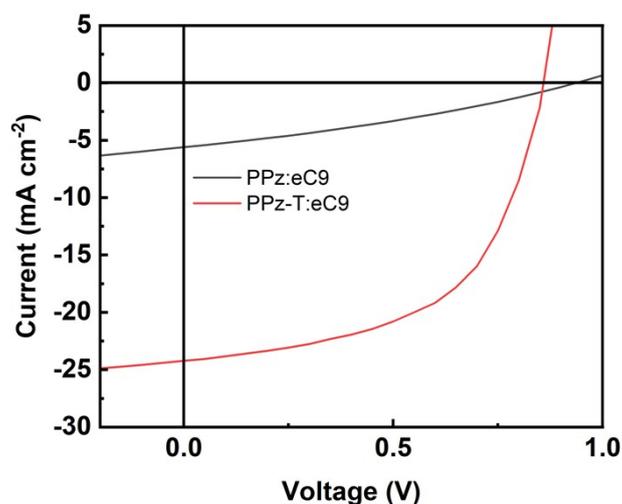


Figure S5. *J-V* curves of as-cast devices based on PPz and PPz-T.

Table S3. The photovoltaic parameters of as-cast devices based on PPz and PPz-T.

blend	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
PPz:eC9	0.94	5.60	0.32	1.66
PPz-T:eC9	0.86	24.23	0.56	11.58

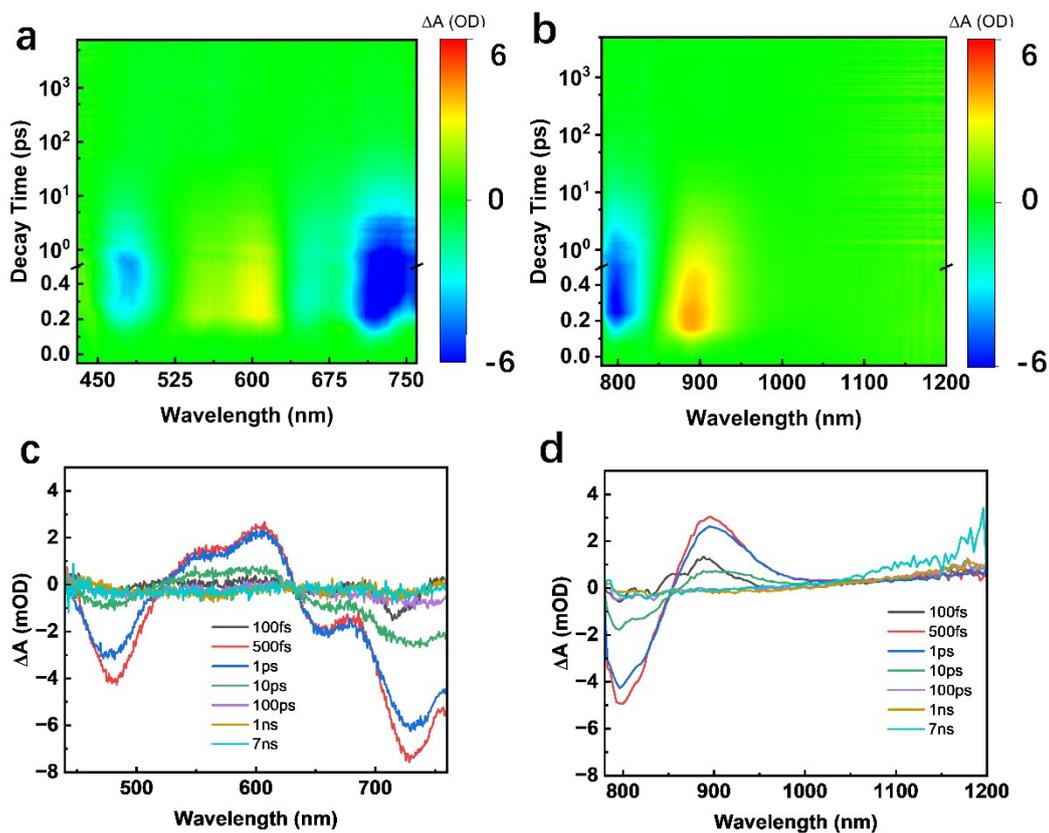


Fig. S6. a-b) Color plot of 2D TA spectra of PPz: eC9 blends under 800 nm excitation. c-d) TA spectra of PPz: eC9 blend at indicated delay times.

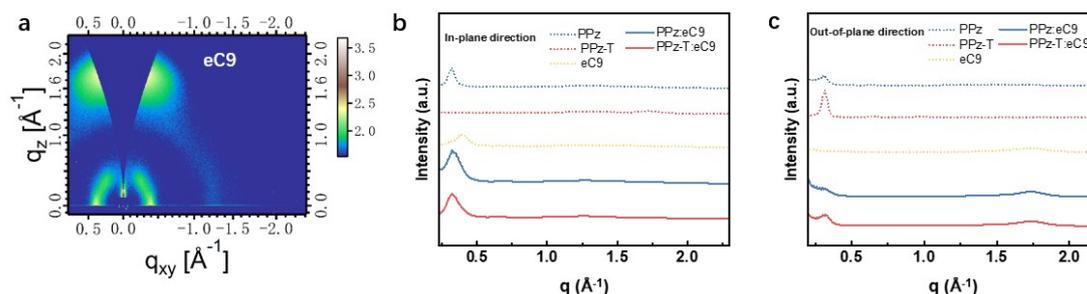


Fig. S7. a) 2D-GIWAXS patterns of eC9. b-c) 1D- GIWAXS curves along in-plane direction (b) and out-of-plane direction (c) of PPz, PPz-T, eC9, PPz: eC9 and PPz-T: eC9.

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