

*Supporting Information*

**A comprehensive optical and electrical study of unsymmetrical imine with four thiophene rings and their binary and ternary compositions with PTB7 and PC<sub>70</sub>BM towards organic photovoltaics**

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**Synthesis of (E)-N-([2,2':5',2''-terthiophen]-5-ylmethylene)-4-(thiophen-3-yl)aniline (PV-BLJ-SC9)**

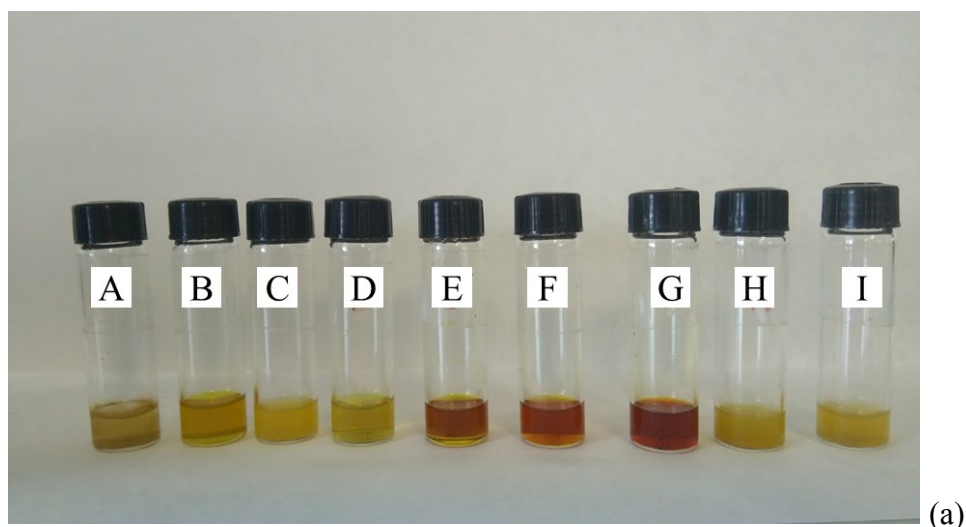
The imine PV-BLJ-SC9 was obtained using a one-step high temperature condensation reaction in melted state under reflux equipped with anhydrous CaSO<sub>4</sub> as the water trap. A single-neck flask with a magnetic stir bar was charged with 4-(thiophene-3-yl)aniline (250 mg; 1.427 mmol), 2,2':5',2''-terthiophene-5-carboxaldehyde (315.42 mg, 1.141 mmol) and *p*-toluenesulfonic acid (27.135 mg, 0.285 mmol). The reaction mixture was stirred for 48 h at 160 °C in an oil bath. The raw imine was precipitated in water, and collected by centrifugation. The

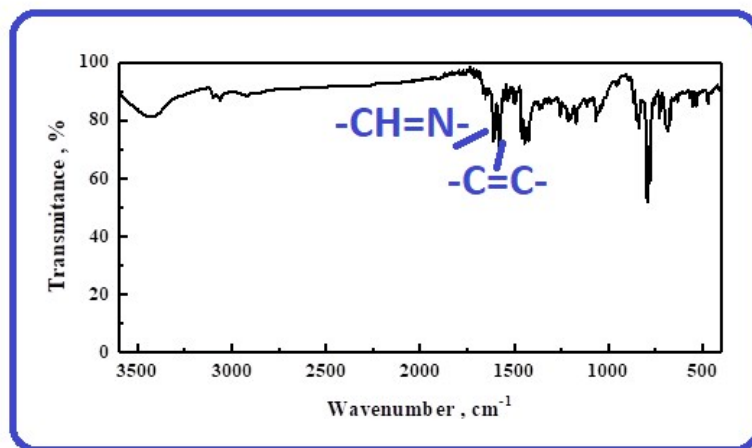
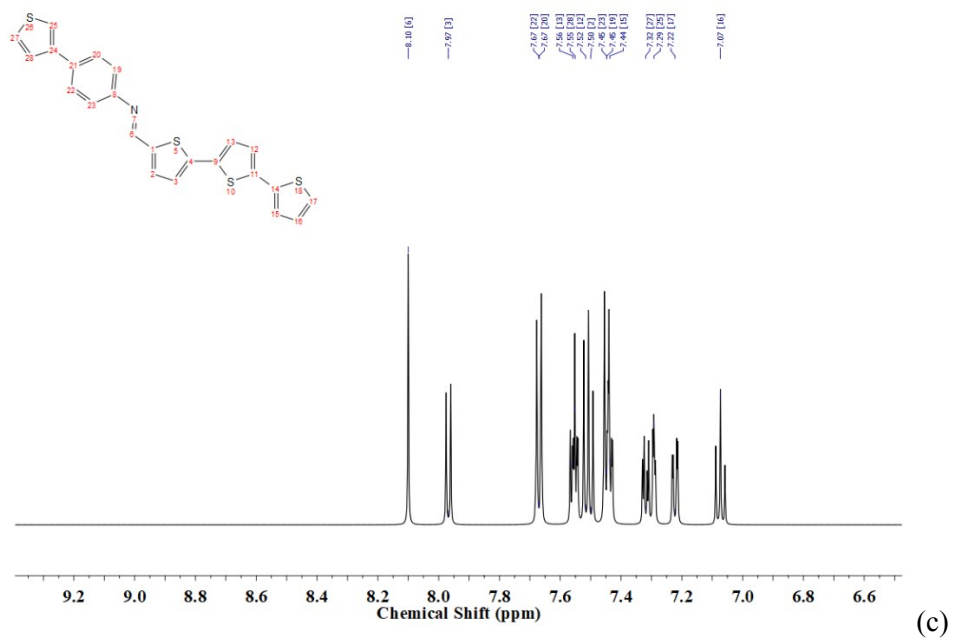
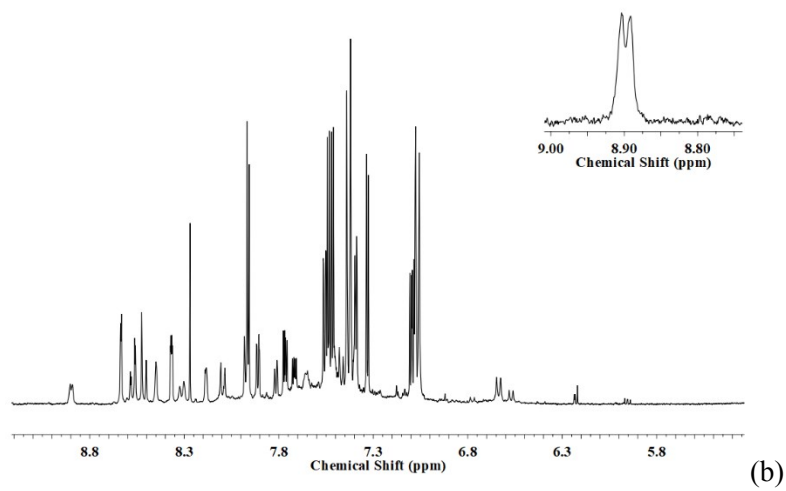
solid was washed with ethanol, acetone, and recrystallized from acetone:hexane. The final imine was dried overnight at 60 °C.

PV-BLJ-SC9: dark brown powder, Yield: 38%,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  [ppm]: 8.54 ( $^1\text{H}$ , d,  $-\text{HC}=\text{N}-$ ); 7.65-7.55 (4H, m, arom.  $-\text{Ph}-$ ); 7.4-7.0 (10 H, arom. thiophen); FTIR (KBr,  $\text{cm}^{-1}$ ): 3098  $\nu(\text{CH})_{\text{ar}}$ , 3062  $\nu(\text{CH})_{\text{ar}}$ , 1658, 1609  $\nu(\text{HC}=\text{N})$ , 1580  $\nu(\text{C}=\text{C})_{\text{ar}}$ , 1461, 1445, 1423, 1256, 1215, 1200, 1172  $\delta(\text{CH})_{\text{ar ip}}$ , 1067  $\delta(\text{CH})_{\text{ar ip}}$ , 852, 845, 837, 794, 780, 728, 699, 683, 668, 550, 534, 471. ( $\nu$  – stretching;  $\delta$  – bending; in plane (ip) modes; ar – aromatic).

Sample was characterized with  $^1\text{H}$  NMR, using deuterated chloroform ( $\text{CDCl}_3$ ) as a solvent with a Jeol ECZ-400 S spectrometer ( $^1\text{H}$  - 400 MHz) with delay time 5 s. Measurements were carried out at room temperature on 10-15% (w/v) sample solutions.

The Fourier transform mid infrared (MIR) spectra of the imine in the region of 4000-400  $\text{cm}^{-1}$  were measured at 2  $\text{cm}^{-1}$  resolution with co-addition of 32 scans on a Nicolet-Nexus spectrometer using the KBr pellet technique.



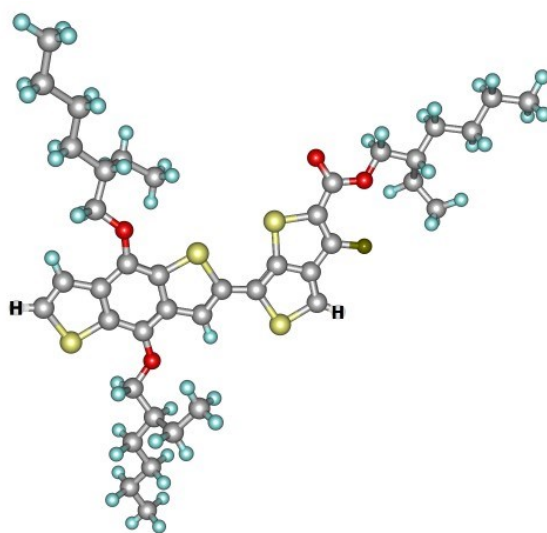


**Fig. S1.** (a) The results of solubility test after adding 1mL of solvent to 1mg of imine and after 15 minutes in sonification bath for following solvents: n-heptane (A), o-xylene (B), isopropanol (C), acetone (D), 1,2-dichlorobenzene (E), 1,2-dichloroethane (F), dichloromethane (G), ethanol (H) and methanol (I).

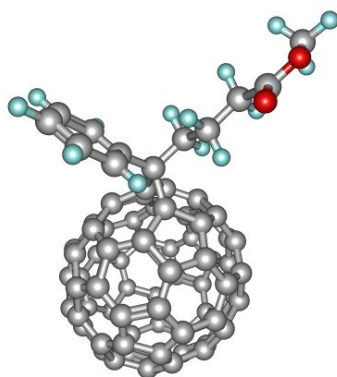
(b)  $^1\text{H}$  NMR spectrum of PV-BLJ-SC9, with an onset for the imine signal. The biggest issue in recording NMR spectra was low solubility in common solvents used in nuclear magnetic spectroscopy hence the ratio between the final product (imine) and noise is very low.

(c) Simulated  $^1\text{H}$  NMR spectrum of PV-BLJ-SC9.

(d) FT-IR in KBr pellet of PV-BLJ-SC9.

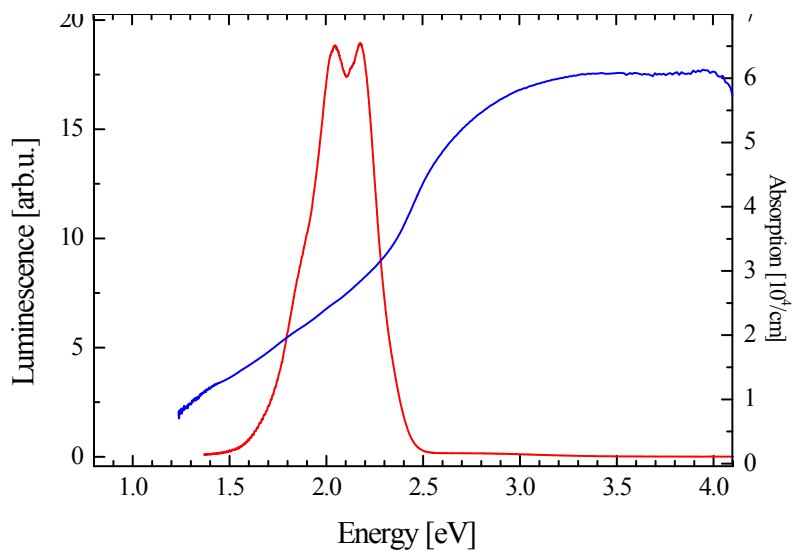


(a)

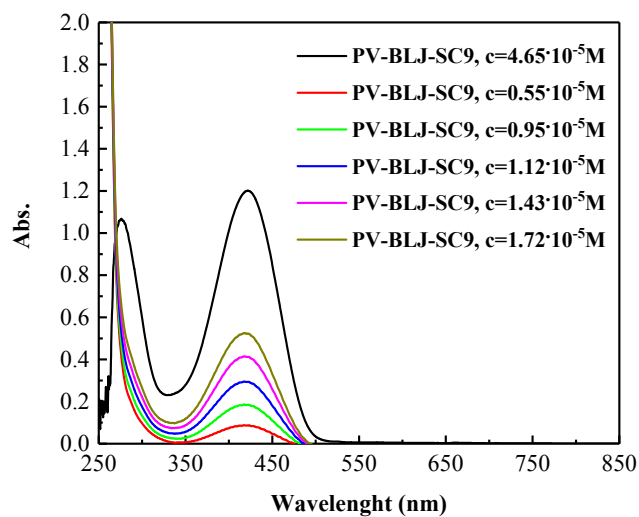


(b)

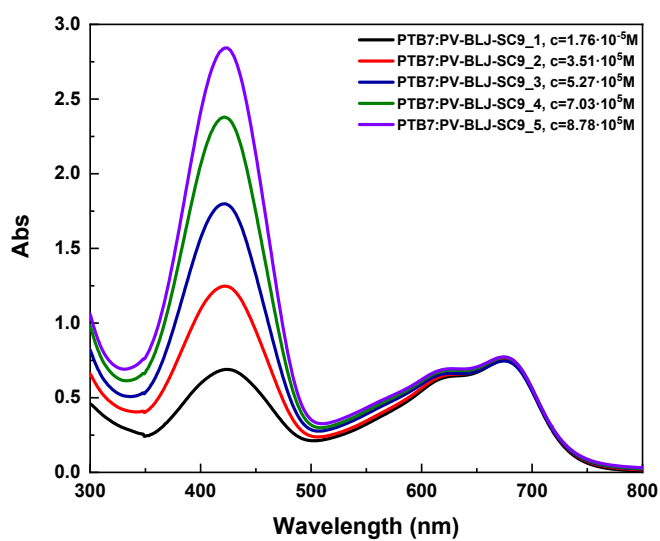
**Fig. S2.** Optimized geometry of the PTB7 monomer (a) and PC<sub>71</sub>BM (b). The marked H atoms indicate the propagation sites of the PTB7 chain.



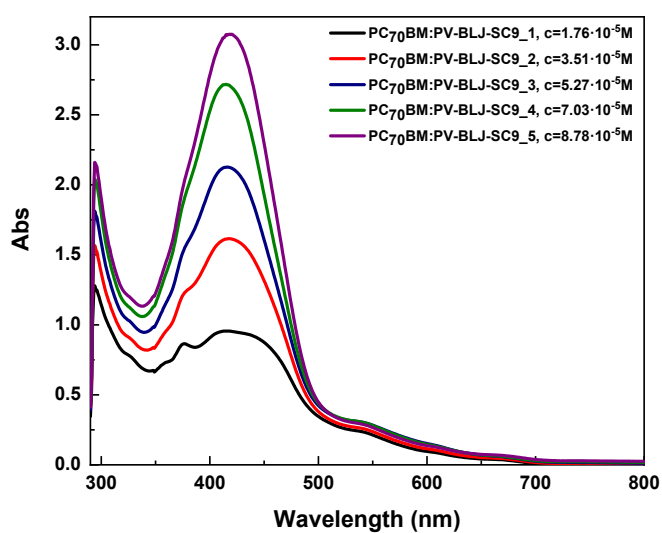
**Fig. S3.** Absorption (blue) and photoluminescence (red) spectra of PV-BLJ-SC9 imine thin film.



(a)

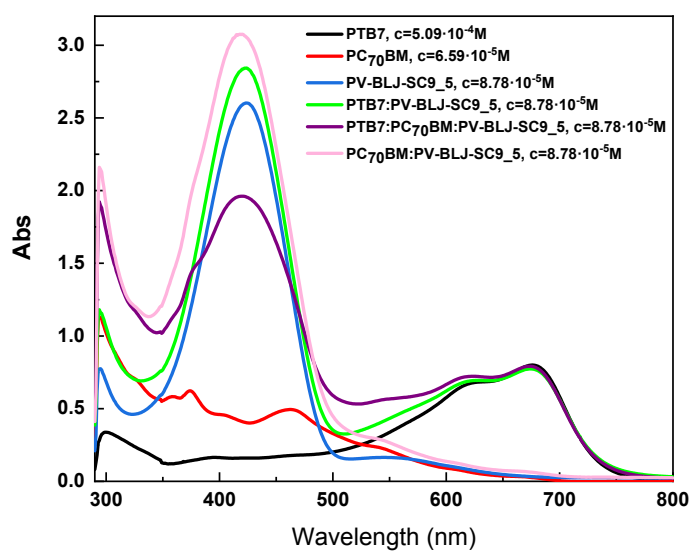


(b)

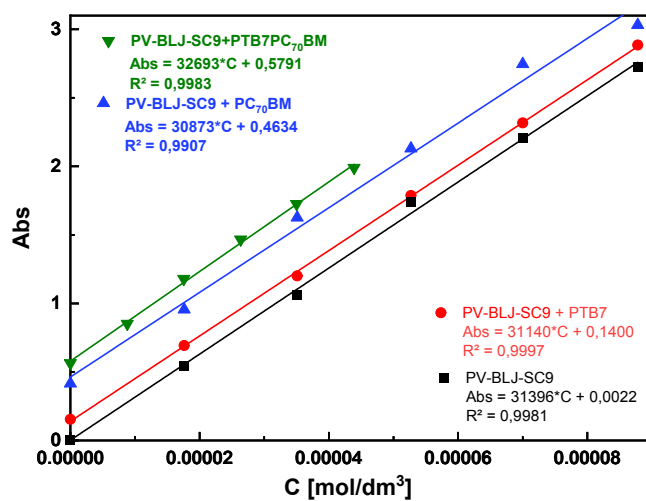


(c)

**Fig. S4.** UV-Vis absorption of imine in DMA (a), imine:PTB7 (b) and imine:PC<sub>70</sub>BM (c) in DCB solution.

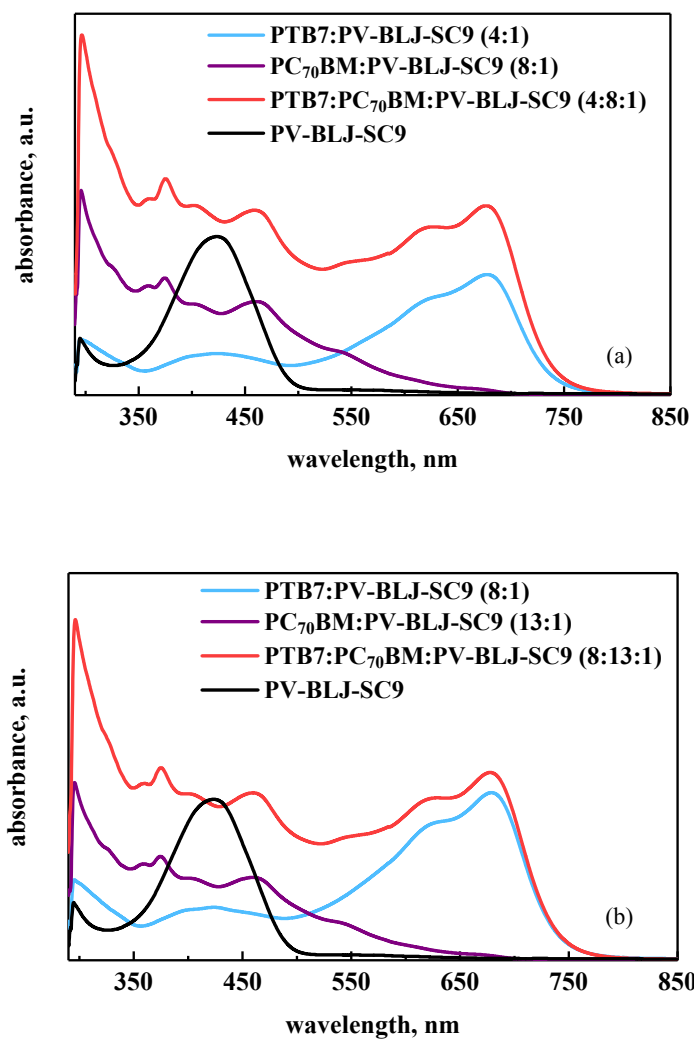


(a)



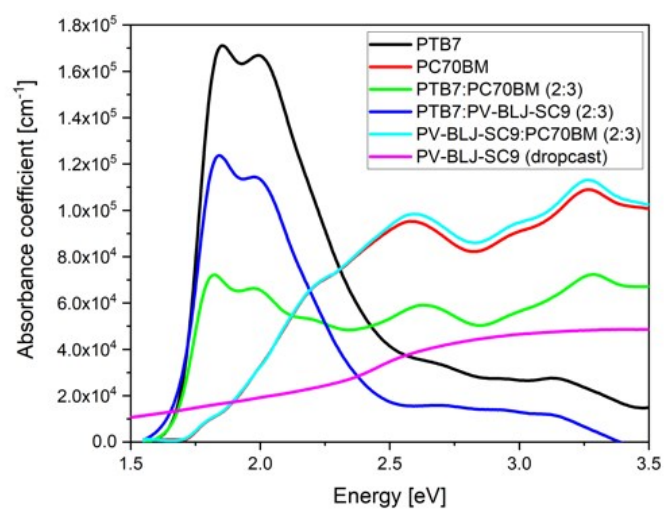
(b)

**Fig. S5.** UV–Vis spectra of imine and binary and ternary compositions in DCB with isobestic points (a) together with calibration curves (b).

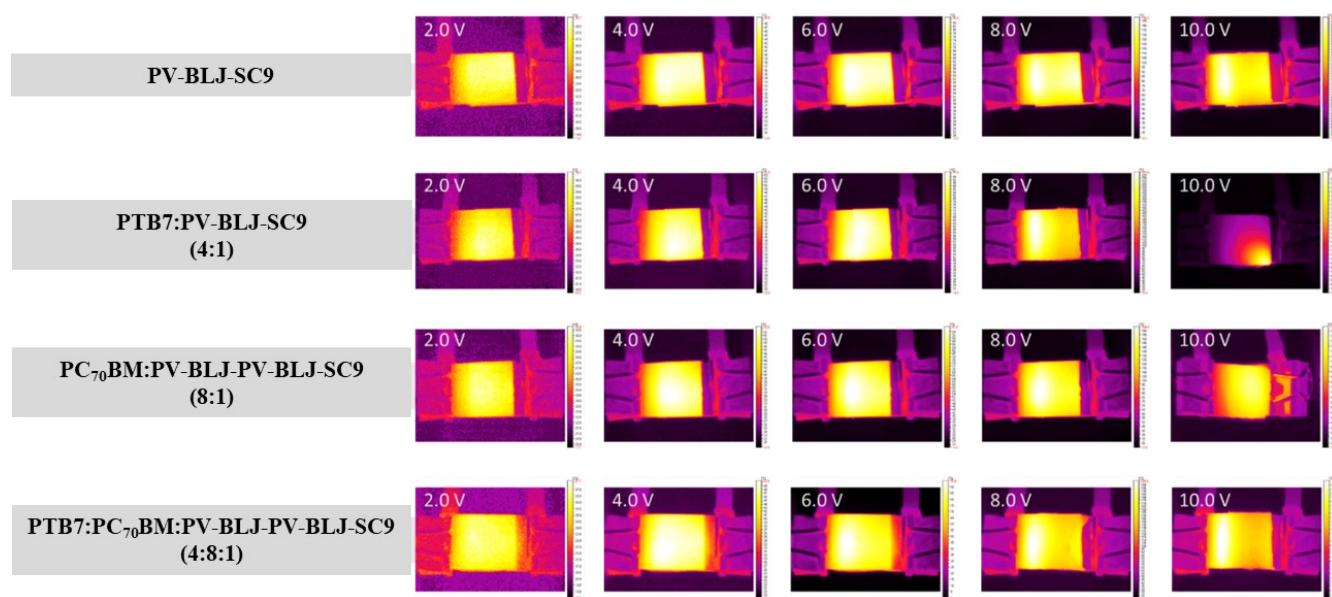


**Fig. S6.** Absorption spectra of mixtures composed of: imine, PTB7:imine, PC<sub>70</sub>BM:imine and PTB7:PC<sub>70</sub>BM:imine with two different proportions 4:8:1 (a) or 8:13:1 (b) of PTB7:PC<sub>70</sub>BM:imine.

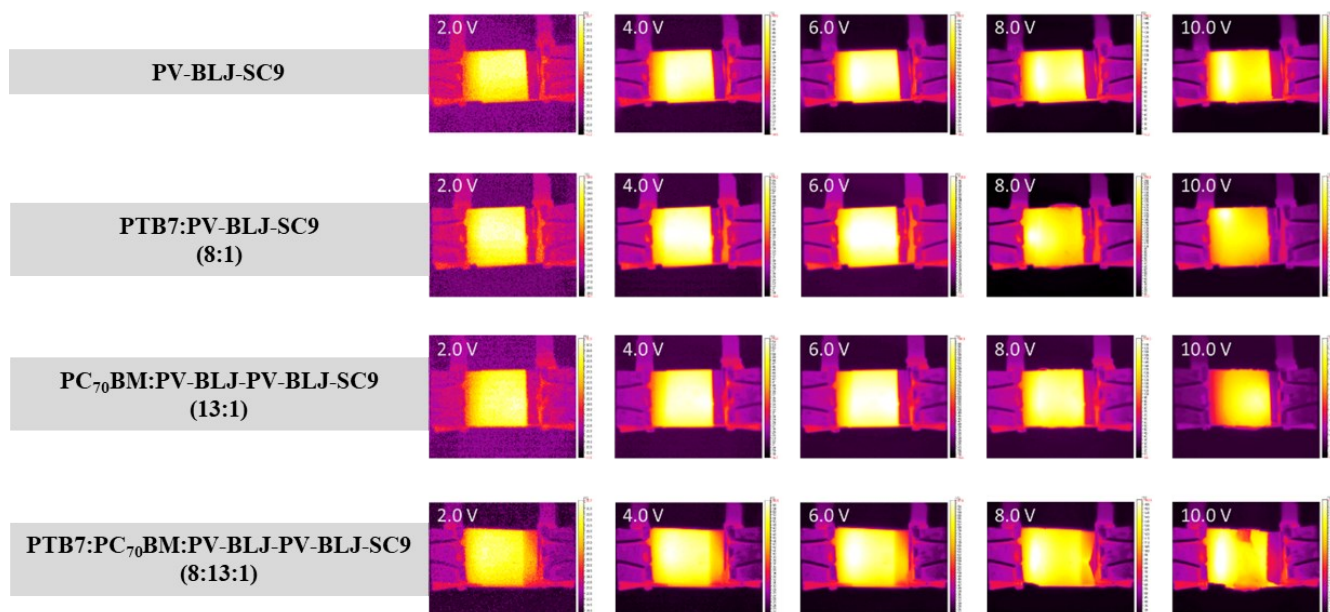




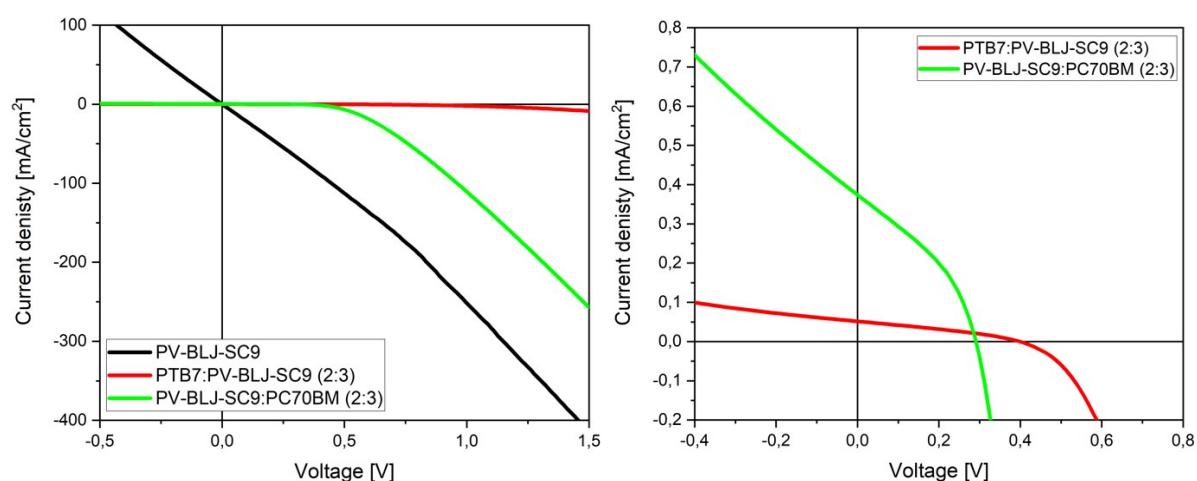
**Fig. S7.** The optical absorption spectra in solid layer of PV-BLJ-SC9, PC<sub>70</sub>BM, PTB7, and binary mixtures of PTB7:PC<sub>70</sub>BM, PTB7:PV-BLJ-SC9 and PV-BLJ-SC9:PC<sub>70</sub>BM.



**Fig. S8.** The summary of thermal experiments for device composed of imine, PTB7:imine (4:1), PC<sub>70</sub>BM:imine (8:1), PTB7:PC<sub>70</sub>BM:imine (4:8:1): thermal images for devices at 2.0 V, 4.0 V, 6.0 V, 8.0 V and 10.0V.



**Fig S9.** The summary of thermal experiments for device composed of imine, PTB7:imine (8:1), PC<sub>70</sub>BM:imine (13:1), PTB7:PC<sub>70</sub>BM:imine (8:13:1): thermal images for devices at 2.0 V, 4.0 V, 6.0 V, 8.0 V and 10.0V.

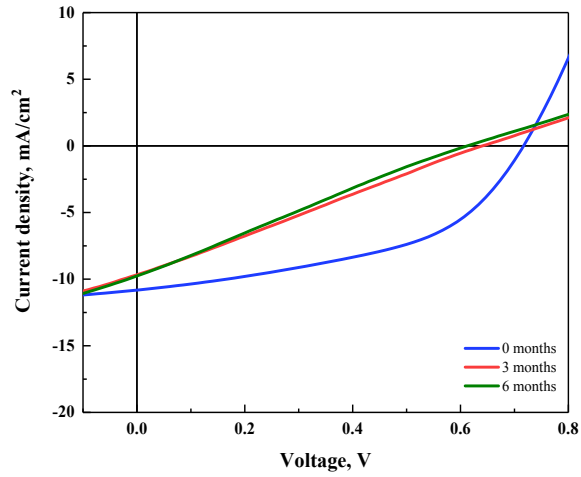


**Fig. S10.** J-V characteristics of solar cells with active layer in form of pure imine PV-BLJ-SC9 (black curve), binary mixture of PV-BLJ-SC9 imine with PTB7 donor material (red curve) ordinary mixture of PV-BLJ-SC9 imine with PC<sub>70</sub>BM acceptor material (green curve). The right graph is a magnification of the left one.

**Table S1.** Electrical parameters of organic solar cells with active layer in form of pure imine PV-BLJ-SC9 and binary mixtures of PV-BLJ-SC9 imine with PTB7 donor or PC<sub>70</sub>BM acceptor.

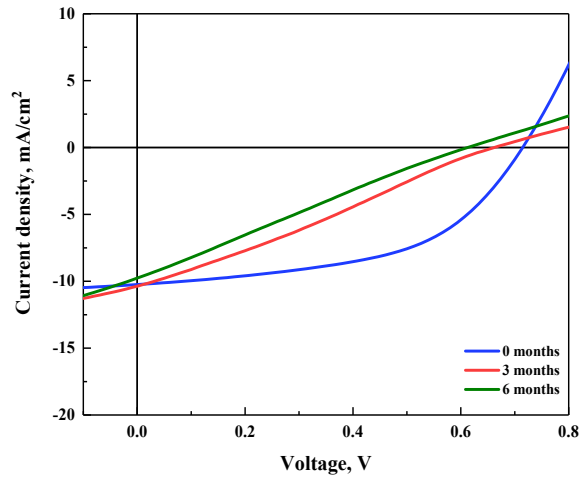
Active layer	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA/cm <sup>2</sup> ]	FF [%]	R <sub>s</sub> [ $\Omega$ *cm <sup>2</sup> ]	R <sub>sh</sub> [ $\Omega$ *cm <sup>2</sup> ]	PCE [%]
PV-BLJ-SC9	0	0	-	6.9	3.2	0
PTB7:PV-BLJ-SC9 (2:3)	0.393	0.052	32	130	12 300	0.007
PV-BLJ-SC9:PC <sub>70</sub> BM (2:3)	0.287	0.379	37	4.1	1430	0.040

Glass/ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM:PV-BLJ-SC9 (4:8:1)/In/Al



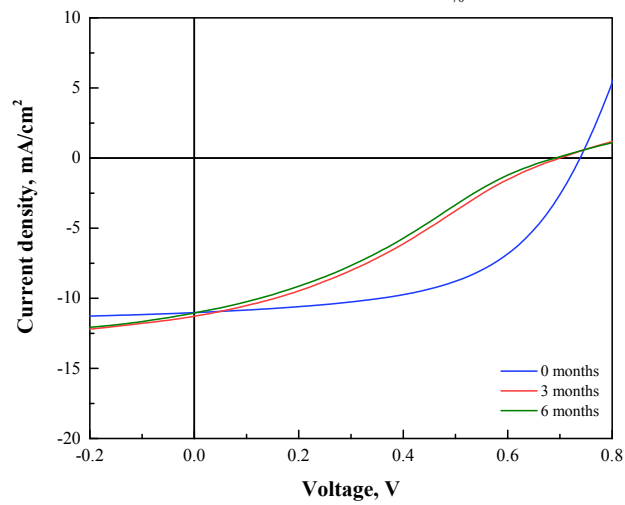
(a)

Glass/ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM:PV-BLJ-SC9 (8:1:13)/In/Al



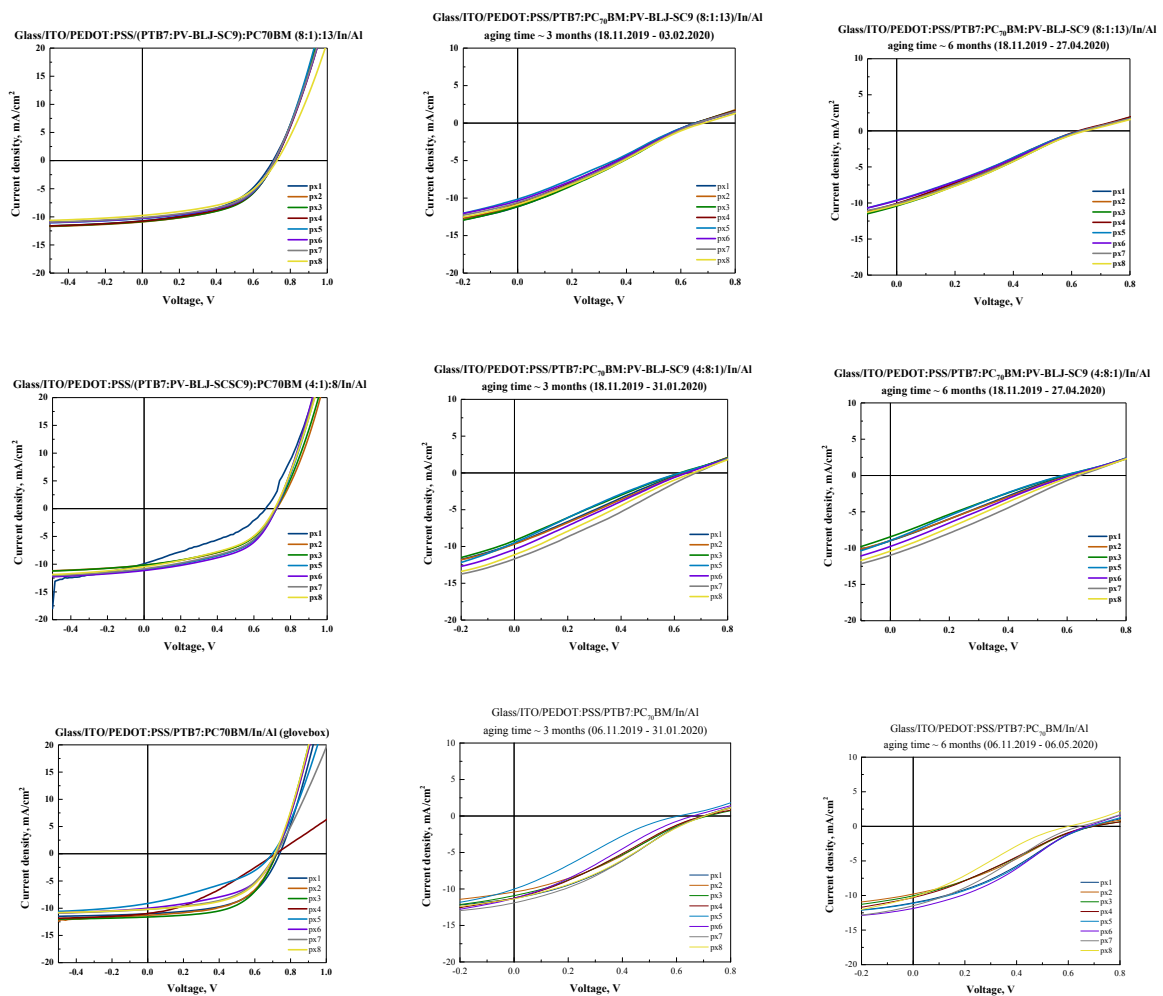
(b)

Glass/ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM/In/Al



(c)

**Fig. S11.** Current density-voltage characteristics of the devices: glass/ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM:PV-BLJ-SC9 (4:8:1)/In/Al (a) and glass/ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM:PV-BLJ-SC9 (8:13:1)/In/Al (b) and glass/ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM/In/Al (c) measured immediately after construction, after 3 months and after 6 months.



**Fig. S12.** Current density-voltage characteristics of device glass/ITO/PEDOT:PSS/active layer/In/Al measured immediately after construction, after 3 months and after 6 months.