Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary material for:

Green solvent-processed organic solar cells based on small-molecule Ir(III) complex as electron donor materials

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Materials

All solvents were purchased from Sigma Aldrich Co., Energy Chemical Co., Alfa Aesar without further purification. PY-IT was purchased from Nanjing Zhiyan Technology Co., Ltd. TBz3Ir was synthesized according to our previous study.[1]

Characterizations

Absorption spectra of solution in chloroform and thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer. The electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer, in a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) at a potential scan rate of 100 mV s^{-1}. The conventional three electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode. The samples were coated on the platinum sheet of working electrode. The reference electrode was checked versus ferrocenium-ferrocene (Fc/Fc^+) as internal standard as recommended by IUPAC (the vacuum energy level: 24.8 eV). All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements. HOMO energy levels were calculated from the equation of $E_{HOMO} = -(4.80+E_{ox})$ eV, and LUMO from $E_{LUMO} = (E_{HOMO}+E_g^{opt})$ eV. Photoluminescence spectra were carried out using Edinburgh FLS980 spectrophotometer. J–V curves of PSCs were measured on a computer-controlled Keithley 2400 Source Measure Unit. Oriel Sol3A Class Solar Simulator (model, Enlitech SS-F5-3A) with a 450 W xenon lamp and an air mass 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm^{-2} by a silicon reference cell. EQE spectra were measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology, Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The dependence of J_{SC} on light intensity was plotted to investigate the charge recombination in devices with the formula $J_{SC} \propto I^{\alpha}$, the factor α reflects the bimolecular recombination degree. And photo-generated current density (J_{ph}) was plotted as a function of the effective voltage (V_{eff}). The ratios of current density under short-circuit and saturated outputting conditions (J_{ph}/J_{sat}) were used to estimate the exciton dissociation probabilities ($P_{(E,T)}$). Blend film morphologies were characterized via Bruker Dimension ICON atomic force microscopy.

Fabrication of OSC devices

OSCs with conventional structure of ITO/PEDOT:PSS/active layer/PDINN/Ag were fabricated as follows. Indium tin oxide (ITO) glass substrates were cleaned in an ultrasonic bath with detergent, deionized water, acetone and isopropanol, respectively, and followed by treatment of UV-ozone for 30 minutes. Then, PEDOT:PSS (Baytron PVP Al 4083) was spin-coated on the ITO at 3500 rpm for 40 seconds and baked at 150°C for 15 min in air to give a film thickness around 30 nm. After that, the substrates with PEDOT:PSS thin film were transferred to a nitrogen glove box. For the active layer, When the blend films were dissolved in XY or DCB solvents, the D:A = 1:0.8

w/w with the concentration of 18 mg mL^{-1} and then stirred over 8 hours under 60^{o}C. After cooling to room temperature, 1.0 v/v% DIO was added to the solution and then spin-coated at 1000 rpm. In addition, the solution was prepared with a concentration of 16mg mL^{-1} in CF and then stirred over 1 hour at 50^{o}C. 0.5 v/v% DIO was added to the solution before spin-coated at 3000 rpm. No thermal annealing was employed during the fabricating process. In particular, the configured solution and the substrate with PEDOT:PSS were heated at the corresponding temperature for 2 minutes. Subsequently, the high-temperature blend solution was rapidly spin-coated on the PEDOT:PSS. All steps above were controlled within 10 seconds. The cathode buffer layers of PDINN were spin-coated at 3500 rpm for 60 seconds. Finally, Ag with a thickness of 100 nm was evaporated under vacuum (≈10 $^{-5}$ Pa) as the back electrode. As for the hole-only and electron-only devices for space charge limited current (SCLC) measurements, the device structure of ITO/PEDOT:PSS/active layer/Au was used to measure the hole mobility and the electron-only devices were fabricated with the configuration of ITO/ZnO/active layer/Al. And the processing details of blend films were the same with the fabricating conditions of OSCs. Hole and electron mobility was measured using the SCLC method based on Mott-Gurney equation.[2,3]

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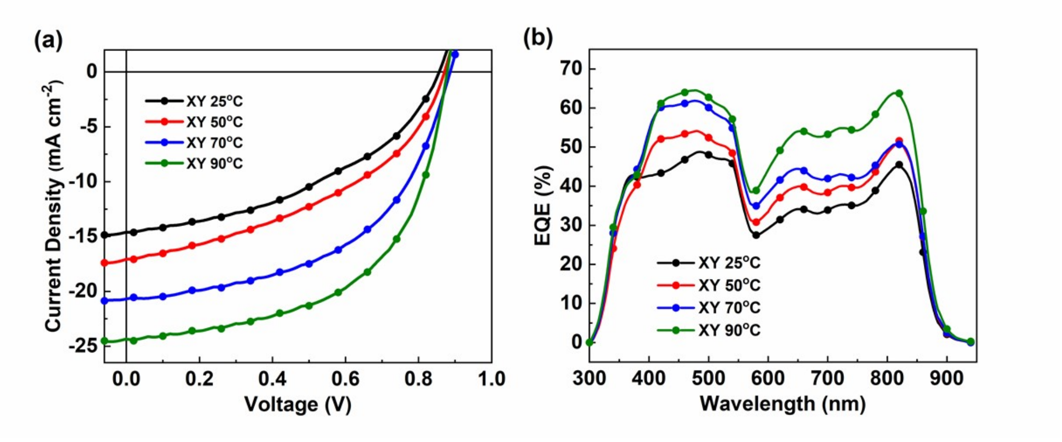

Fig. S1 *J*-*V* curves and (b) EQE curves of devices processed with XY at different spin-coating temperatures

Table S1 Optimization of D:A weight ratio for TBz3Ir: PY-IT-based active layers in CF at a total D/A concentration of 14 mg/mL with spin coating speed of 2000 rpm

D:A	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]	PCE [%]
1:1.4	0.92	12.16	0.41	4.48	4.40
1:1.2	0.92	12.61	0.41	4.71	4.61

1:1	0.92	13.19	0.45	5.42	5.28
1:0.8	0.92	12.66	0.48	5.57	5.43
1:0.7	0.91	11.92	0.48	5.26	5.12

Table S2 Optimization of solution concentration and spin-coating speed for XY dissolved TBz3Ir:PY-IT-based active layers with spin-coating temperature of 70^{o}C and D/A ratio of 1:0.8.

Concentration [mg/mL]	Speed [rpm]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]	PCE^{a} [%]
10	1000	0.87	9.39	0.44	3.60	3.39
10	2000	0.72	7.66	0.33	1.83	1.67
10	3000	0.50	5.78	0.31	0.91	0.86
12	1000	0.88	10.94	0.49	4.70	4.52
12	2000	0.65	7.51	0.31	1.50	1.23
12	3000	0.56	6.89	0.31	1.22	1.01
14	1000	0.90	13.89	0.46	5.76	5.49
14	2000	0.79	8.25	0.34	2.19	1.99
14	3000	0.54	6.51	0.33	1.15	1.10
16	1000	0.89	15.90	0.49	6.91	6.76
16	2000	0.88	11.03	0.45	4.40	4.18
16	3000	0.82	9.83	0.39	3.14	3.01
18	1000	0.90	18.48	0.50	7.96	7.79
20	1000	0.90	17.50	0.47	7.23	7.10

Table S3 Optimization of additives for XY dissolved TBz3Ir:PY-IT-based active layers at the condition of 70^{o}C, 1:0.8, 18 mg/mL and 1000 rpm.

Additive	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]	PCE^{a} [%]
without	0.89	18.48	0.50	7.96	7.79
0.6% DIO	0.89	20.01	0.50	9.05	8.89
0.8% DIO	0.89	19.87	0.52	9.33	9.12
1.0% DIO	0.89	20.42	0.53	9.68	9.57
1.2% DIO	0.89	19.98	0.49	8.75	8.55

Table S4 Optimization of spin-coating temperature of active layers based on XY dissolved TBz3Ir:PY-IT at 1:0.8, 18 mg/mL and 1000 rpm.

Temperature [^{o}C]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]	PCE^{a} [%]
25	0.86	14.61	0.42	5.25	5.13
50	0.87	17.07	0.43	6.39	6.21
60	0.88	20.38	0.43	7.74	7.54
70	0.88	20.68	0.52	9.57	9.32
80	0.89	22.88	0.52	10.56	10.45
90	0.89	24.34	0.56	12.04	11.78
100	0.89	23.39	0.53	10.92	10.78