This journal is © the Partner Organisations 2020

Supporting Information

“Constructing High Efficiency Non-Fullerene All-Small-Molecule Ternary Organic Solar Cells by Employing Structural Similar Acceptors”

by Ziyun Huang, Ruimin Zhou, Min Lv, Hao Zhang, Chen Yang, Yanan Shi, Yi Tang, Jianqi Zhang, Kun Lu and Zhixiang Wei

Materials

All solvents and common reagents were purchased from commercial resources. The detailed synthesis and purification processes of the small molecule donor ZR1-Cl as well as non-fullerene acceptors IDIC-4Cl and IDIC can be found in literatures[1-3].

Fabrication and Characterization

The photovoltaic devices were fabricated with a conventional structure of glass/ITO/PEDOT:PSS/active layer/Al architecture. The 1.5cm×1.5cm ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, DI water, ethanol and isopropyl alcohol for 20 min respectively. A hole transporting layer of PEDOT:PSS was spin-coated at 3500 r.p.m. onto the ITO surface before baking at 150 °C for 15 min. Subsequently, the weighted amount of ZR1-Cl, IDIC-4Cl and IDIC were dissolved in chloroform at a concentration of around 20mg/mL and stirred at 50°C for approximately 30 min before spin-coated upon PEDOT:PSS inside nitrogen-filled glove box. Finally, a layer of 100 nm Al layer was deposited on top of active layer via vacuum vapor deposition (cal. 1×10^{-5} Pa), serving as top electrode.

J–V curves measurements were conducted under AM 1.5 G ($100 mWcm^{-2}$) by Newport Thermal Oriel

91159A solar simulator, with Newport Oriel PN 91150 V Sibased solar cell as light intensity calibration reference. Signals of J–V measurements were recorded by a Keithley 2400 source-measure unit. EQE tests were conducted by Oriel Newport system (Model 66902) with a standard Si diode. Device structure of Al/active layer/Al and ITO/PEDOT:PSS/active layer/Au architecture were employed to measure the electron and hole mobility, respectively. The current density-voltage (*J-V*) curves in the range of 0-5 V were obtained by a Keithley 2420 Source-Measure Unit in the dark. Mobility could be calculated by fitting the results in the equation:

$$J = 9\varepsilon_0\varepsilon_r\mu(V-V_{bi})^2/8L^3$$

where J is the current density, L is the thickness of active layer, μ is the constant mobility, $\varepsilon_0\varepsilon_r$ is the dielectric permittivity of the active layer and V_{bi} is the built-in potential across the device.

The differential scanning calorimetry (DSC) was performed on TA DSC Q2000 differential scanning calorimeter with a heating/cooling rate of 10 °C/min from 0°C to 300°C for two heating/cooling circles. The data of the first circle was presented. The molecular interaction parameter (χ) was calculated from the Nishi-Wang equation:[4]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_f}\frac{V_2}{V_1}\left[\frac{In\emptyset_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right) \times (1-\emptyset_2) + \chi(1-\emptyset_2)^2\right]$$

Where subscript 1 is identified with amorphous molecule and 2 is identified with the semi-crystalline molecule, T_m is the melting temperature of the mixture, and T_m^0 is the melting temperature of pure semi-crystalline polymer, R is the ideal gas constant, ΔH_f is the heat of fusion of pure semi-crystalline polymer, V is the monomer molar volume of the polymers, ϕ is the volume fraction, and m is the degree of polymerization.[5]

Table S1. Photovoltaic parameters of binary and ternary devices with various amount of IDIC under the illumination of AM 1.5 G, 100 mW/cm^2

Active layers	Ratio	V_{OC}（V）	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
ZR1-Cl:IDIC-4Cl	1:1	0.868	18.300	68.03	10.81
ZR1-Cl:IDIC-4Cl:IDIC	1:0.9:0.1	0.882	18.600	68.71	11.13
ZR1-Cl:IDIC-4Cl:IDIC	1:0.8:0.2	0.897	18.644	69.66	11.65
ZR1-Cl:IDIC-4Cl:IDIC	1:0.7:0.3	0.911	17.281	68.32	10.81
ZR1-Cl:IDIC-4Cl:IDIC	1:0.6:0.4	0.925	18.127	64.46	10.80
ZR1-Cl:IDIC-4Cl:IDIC	1;0.5:0.5	0.935	16.702	63.04	9.84
ZR1-Cl:IDIC-4Cl:IDIC	1:0.4:0.6	0.949	14.809	57.93	8.13
ZR1-Cl:IDIC-4Cl:IDIC	1:0.2:0.8	0.988	12.280	48.94	5.94
ZR1-Cl: IDIC	1:1	1.022	13.455	47.46	6.53

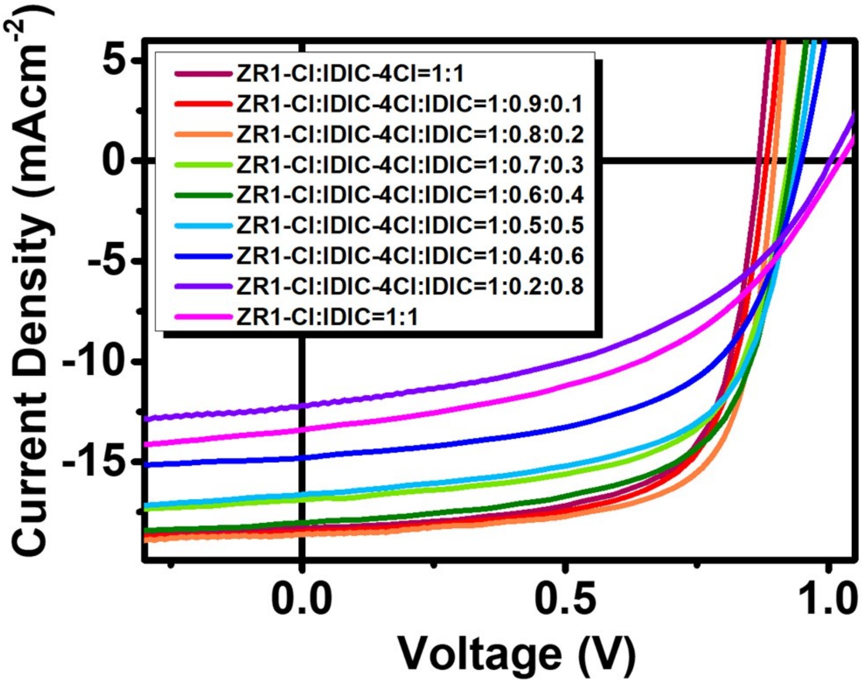

Fig. S1 J-V curves of binary and ternary devices with various amount of IDIC listed in Table S1

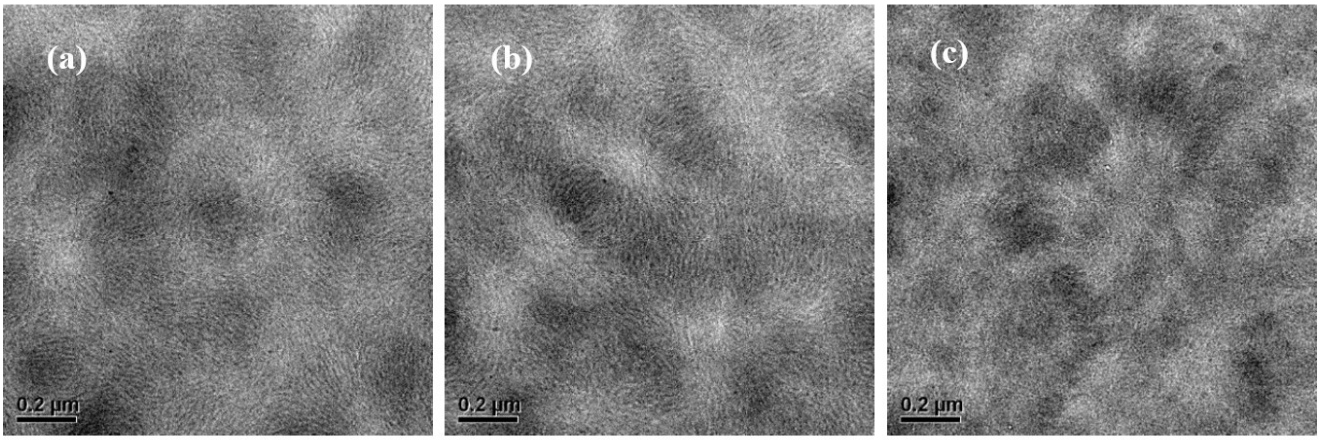

Fig. S2 TEM images of (a) ZR1-Cl: IDIC-4Cl (b) ZR1-Cl: IDIC-4Cl: IDIC and (c) ZR1-Cl: IDIC blend films. The scale bars of TEM images are 200 nm.

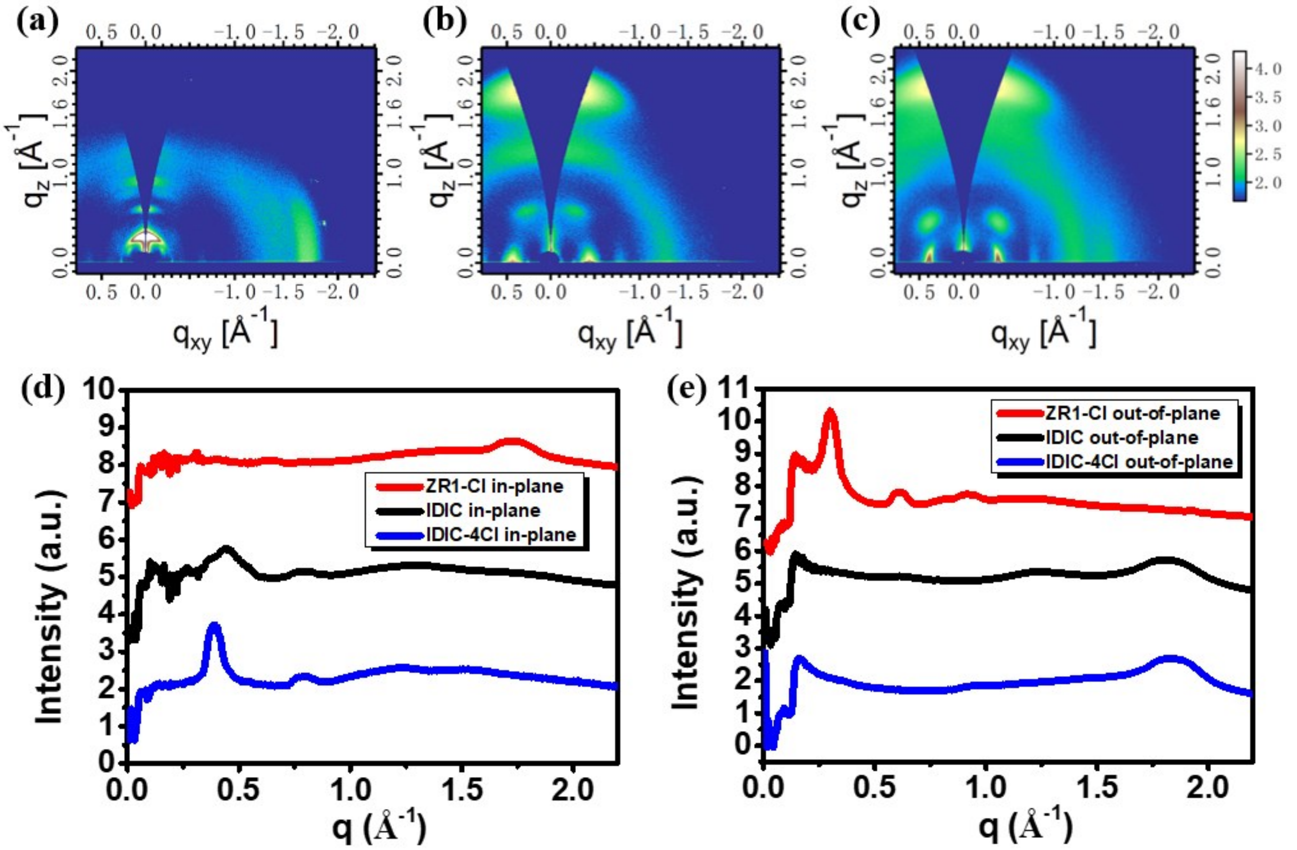

Fig. S3. GIWAXS pattern for pristine (a) ZR1-Cl (b) IDIC-4Cl and (c) IDIC films. (d) In-plane and (e) out-of-plane line cuts of the corresponding 2D-GIWAXS pattern.

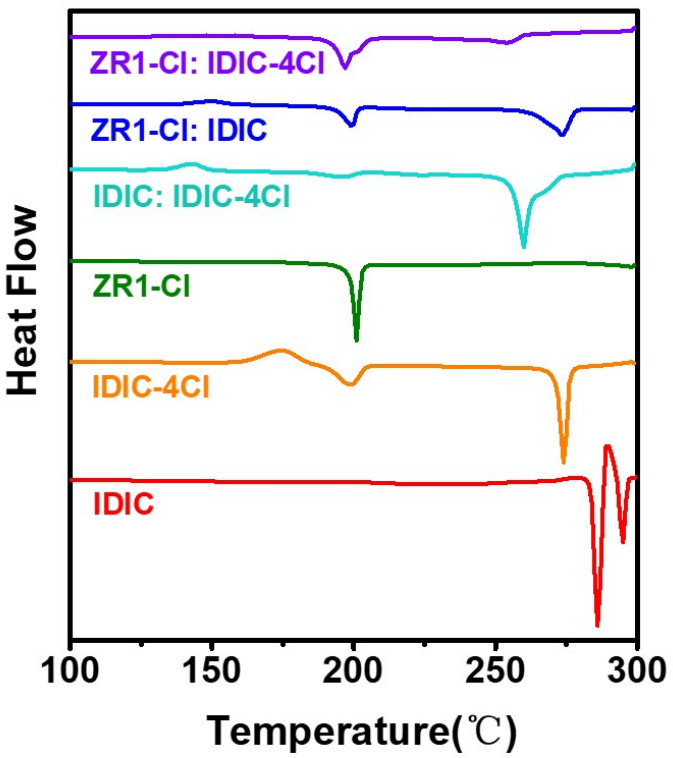

Fig. S4. DSC curves for pure small molecules and blend films.

Supplementary References

1. Y. Lin, Q. He, F. Zhao, L. Huo, J. Mai, X. Lu, C. J. Su, T. Li, J. Wang, J. Zhu, Y. Sun, C. Wang and X. Zhan, A Facile Planar Fused-Ring Electron Acceptor for As-Cast Polymer Solar Cells with 8.71% Efficiency, *J Am Chem Soc*, 2016, **138**, 2973-2976.
2. R. Zhou, Z. Jiang, C. Yang, J. Yu, J. Feng, M. A. Adil, D. Deng, W. Zou, J. Zhang, K. Lu, W. Ma, F. Gao and Z. Wei, All-small-molecule organic solar cells with over 14% efficiency by optimizing hierarchical morphologies, *Nat Commun*, 2019, **10**, 5393.
3. R. Zhou, C. Yang, W. Zou, M. Abdullah Adil, H. Li, M. Lv, Z. Huang, M. Lv, J. Zhang, K. Lu and Z. Wei, Combining chlorination and sulfuration strategies for high-performance all-small-molecule organic solar cells, *Journal of Energy Chemistry*, 2021, **52**, 228-233.
4. T. Nishi and T. Wang, Melting point depression and kinetic effects of cooling on crystallization in poly (vinylidene fluoride)-poly (methyl methacrylate) mixtures, *Macromolecules*, 1975, **8**, 909-915.
5. H. Bin, Y. Yang, Z.-G. Zhang, L. Ye, M. Ghasemi, S. Chen, Y. Zhang, C. Zhang, C. Sun and L. Xue, 9.73% Efficiency Nonfullerene All Organic Small Molecule Solar Cells with Absorption-Complementary Donor and Acceptor, *J. Am. Chem. Soc.*, 2017, **139**, 5085-5094.