ELECTRONIC SUPPLEMENTARY INFORMATION

Exploring the Significance of Packing Modes and 3D Framework Sizes Utilizing Three Chlorine-mediated Acceptors and the "Like Dissolves Like" Approach for Achieving an Efficiency Over 19%

Hanjian Lai,‡[a] Hui Chen, ‡[a] Zi-Yi Chen, ‡[a] Yongwen Lang, ‡[a, c] Yulin Zhu,[a] Shi-Tong Zhang,[d] Xue Lai,[a] Pu Tan,[a] Yuanzhu Zhang,[a] Bing Yang,[d] Gang Li,[c] and Feng He *[a, b]

[a] Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China

[b] Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, China

[c] Department of Electronic and Information Engineering, Research Institute for Smart Energy (RISE), The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

[d] State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun, 130012, PR China

‡ These authors contributed equally to this work

Corresponding authors: hef@sustech.edu.cn

1. General Methods

Fabrication and Characterization of OSCs. The fabrication and measurement methods of OSCs devices are as follows: After a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone, and isopropyl alcohol followed by ultra-sonication for 15 min each and subsequently dried in an oven at 80 °C. The ITO glass substrates were treated with UV-ozone for 15 min and then the PEDOT: PSS were spin-coated onto the ITO substrates followed by thermal treatment at 150 °C for 15 min. The total concentration of the PBDB-TF: Acceptors (1:1.1) blend solution for spin-coating was 12.6 mg mL^{-1} with chlorobenzene as the processing solvent. The additive, chloronaphthalene (CN) (volume content: 0.5%) was added into solution 30 min before the spin-coating process. The blend was stirred at room temperature in the glove box overnight. The active layer was spin-coating at 3000 rpm for 30 s to get blend film. PDINO-solution (1 mg/ml in alcohol) was then spin-coated as interface and a 100 nm Ag layer were subsequently evaporated through a 0.045 cm^2 shadow mask to define the active area of the devices. The integrated device structure is ITO/PEDOT: PSS/PBDB-TF: Acceptors/PNDIT-F3N/Ag. A solar simulator (Enlitech.Inc) with an AM 1.5G filter was used as a light source to produce an intensity of 100 mW cm^{-2} for the illumination of the photovoltaic

cells. The light intensity was calibrated by a 2 cm × 2 cm calibrated silicon solar cell with KG-5 visible color filter. A shadow mask was placed onto the devices in order to accurately define the photoactive area.

Steady-state current-voltage (*J-V*) curves were measured with a Keithley 2400 source-measurement unit under an AM 1.5 G spectrum from a solar simulator (Enlitech.Inc) calibrated by a silicon reference cell (Hamamatsu S1133 color, with KG-5 visible fifth). The relationship of *J*sc to the light intensity was measured by steady-state current-voltage measurement, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD). The external quantum efficiency (EQE) was measured by a solar cells–photodetector responsibility measurement system.

Electron-only and hole-only devices fabrication. Electron-only devices were fabricated with the device structure of ITO/ZnO/PBDB-TF: Acceptors/PNDIT-F3N/Al, while the hole-only devices were fabricated with the device structure of ITO/PEDOT: PSS/ PBDB-TF: Acceptors /MoO_3/Ag. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC, [1,2] which is described by the equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$$

where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage.

Crystal growth: diffraction quality crystals were grown by solvent diffusion method. Acceptors (5 mg) was dissolved in CH_2Br_2 or $CHCl_3$ or toluene (5 mL) in the 15 mL sample bottle, then 10 mL of ethanol or methanol or ether was added it slowly. The bottle was then sealed tightly, and left undisturbed for 10 days[3].

Crystallography: The single crystal X-ray diffraction (SCXRD) data were collected at 100K or 150K on a Bruker D8 VENTURE diffractometer using Cu Kα radiation (λ = 1.54178 Å) or Ga Kα radiation (λ = 1.34139 Å). Lorentz/polarization corrections were applied during data reduction and the structures were solved by the direct method (SHELXT). Refinements were performed by using full-matrix least squares (SHELXL-2014) on F^2 in the Olex2 program.[4] Severe disorder problems were encountered during all the refinements, and considerable amounts of constrains and restrains such as DFIX, SADI, SIMU, AFXI and DANG were used when necessary. Anisotropic thermal parameters were applied to most of the non-hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model where possible. The severe disorder of the long and bulky alkyl chains hindered us to collect diffraction data with a satisfactory resolution.

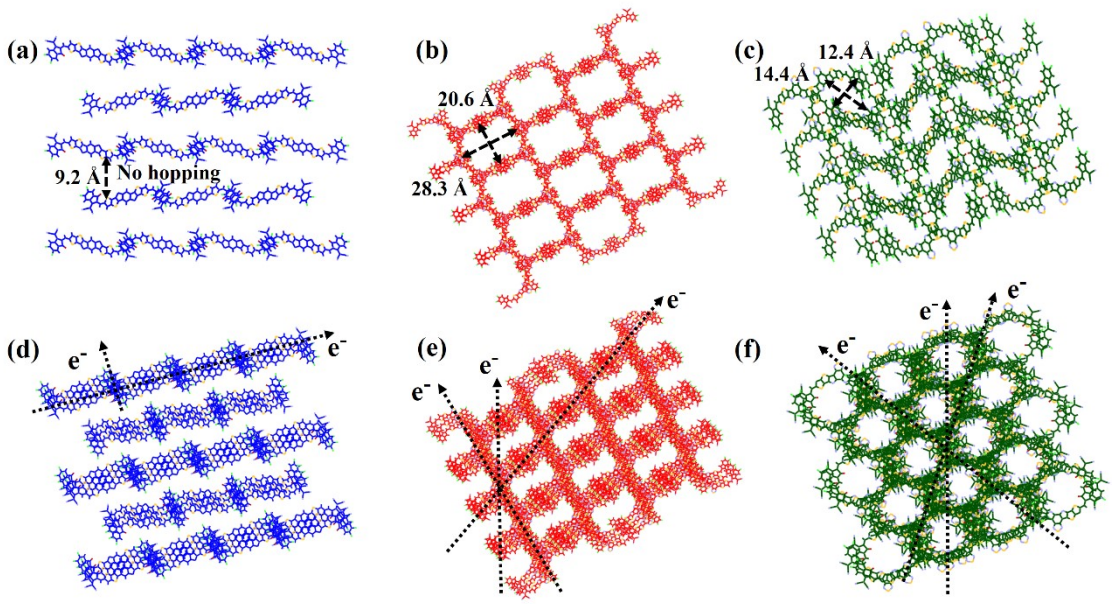

Fig. S1 The aggregation behaviors in single crystals of ITIC-4Cl (a, d), BTIC-EH-4Cl (b, e), and BTIC-C9-4Cl (c, f).

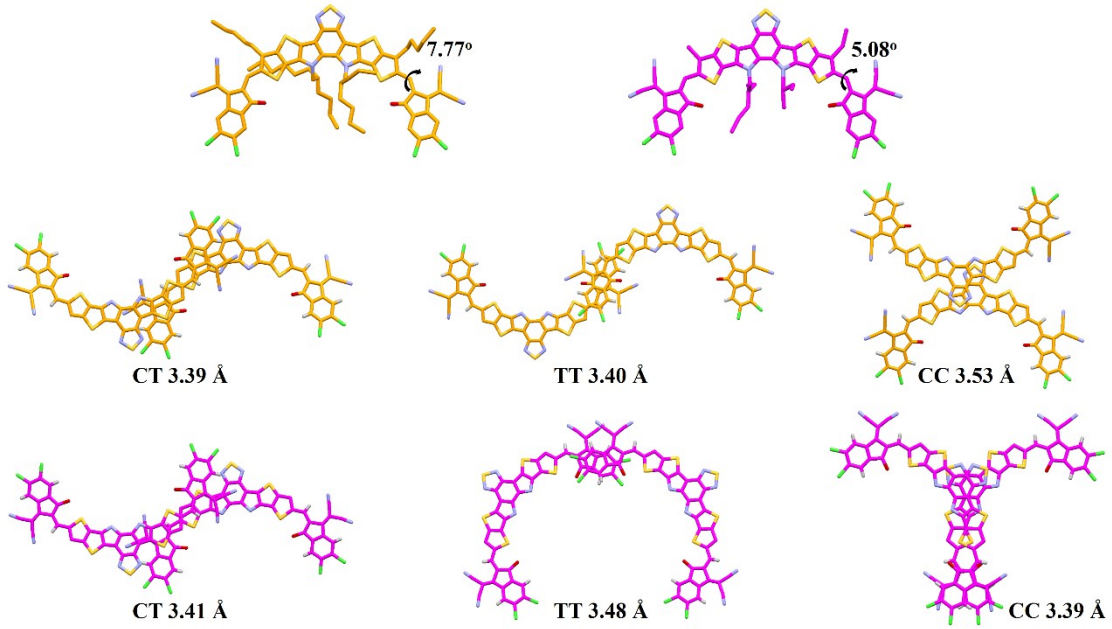

Fig. S2 The configurations and packing modes in single crystals of BTIC-C9-4Cl, the orange color (the single crystal from toluene/methanol solvent), the purple color (the

single crystal from dibromomethane/ether solvent).

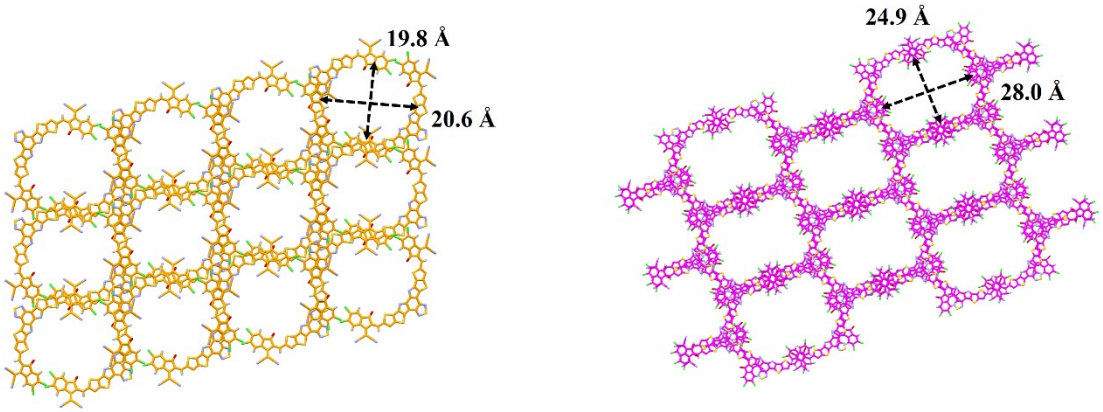

Fig. S3 The aggregation behaviors in single crystals of BTIC-C9-4Cl, the orange color (the single crystal from toluene/methanol solvent), the purple color (the single crystal from dibromomethane/ether solvent).

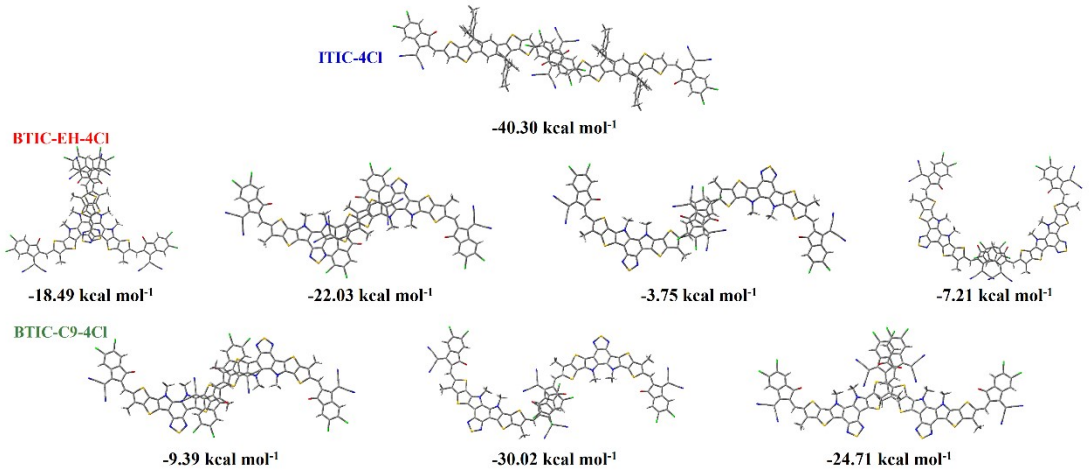

Fig. S4 The molecular binding energies by density functional theory calculation from the single crystal data of molecules.

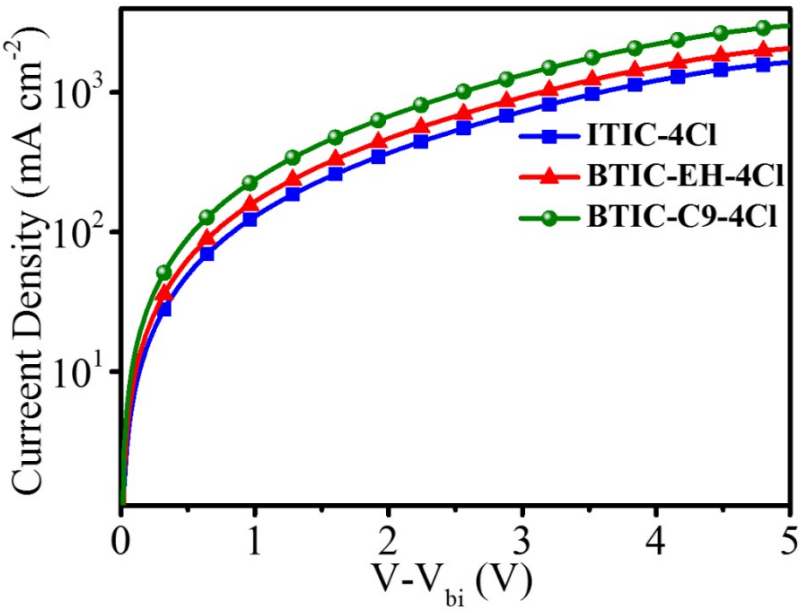

Fig. S5 The electron mobilities of three chloro-NFAs based neat films.

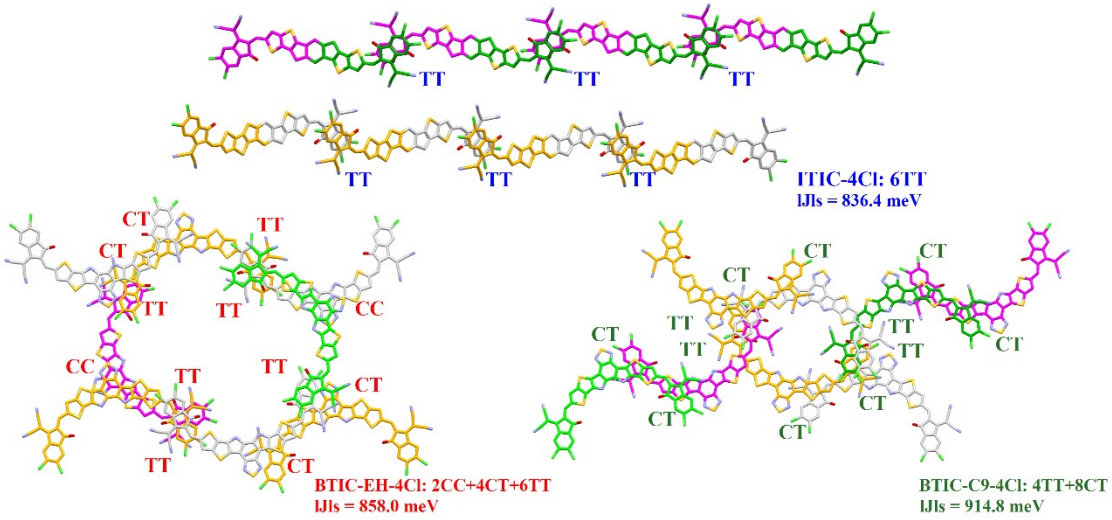

Fig. S6 The packing modes and electronic coupling analysis of three chloro-NFAs.

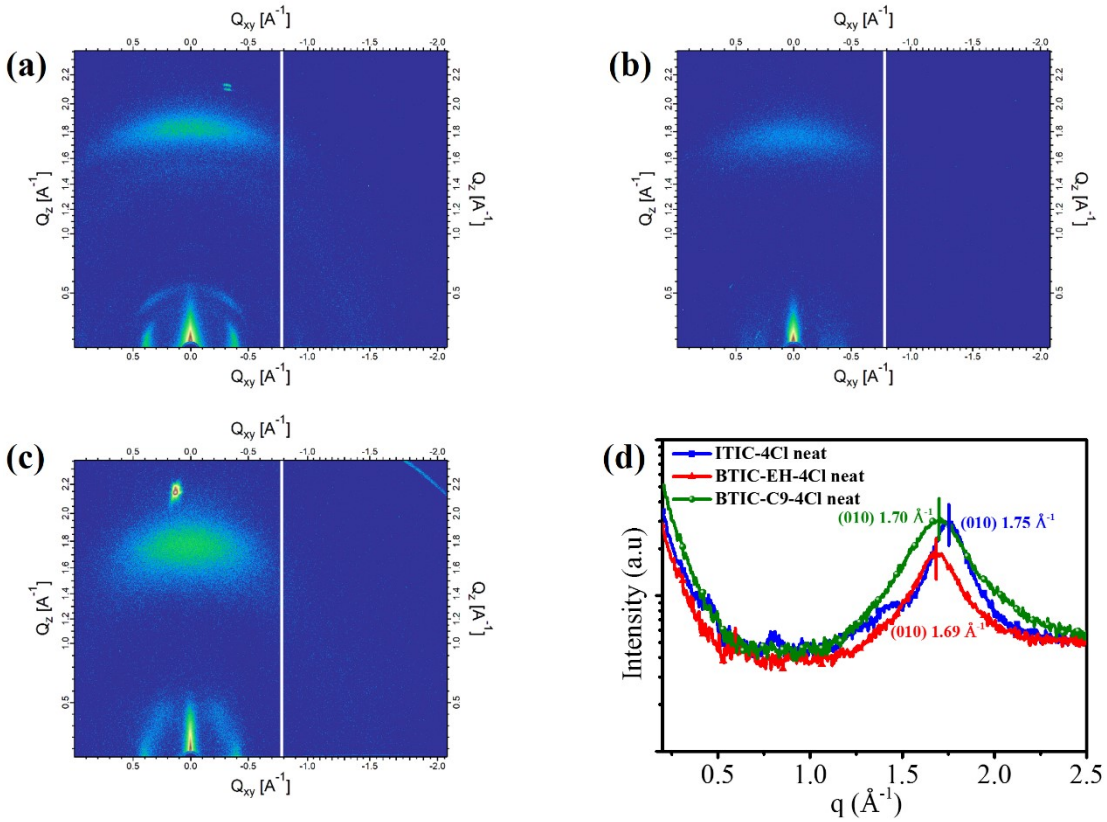

Fig. S7 The GIWAXS of neat films (a) ITIC-4Cl, (b) BTIC-EH-4Cl, (c) BTIC-C9-4Cl, and (d) out-of-plane 2D line-cut data.

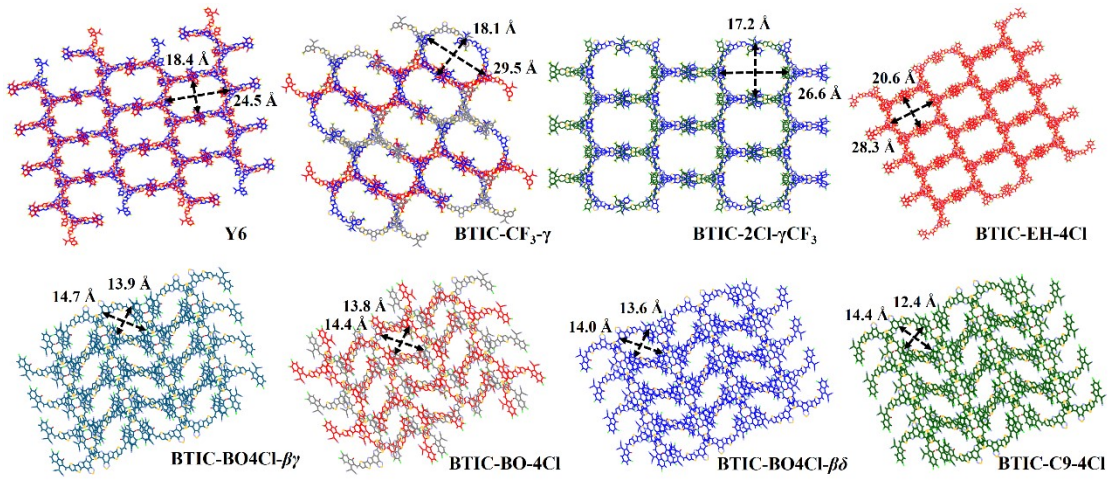

Fig. S8 The typical Y-series molecular framework sizes in single crystal.

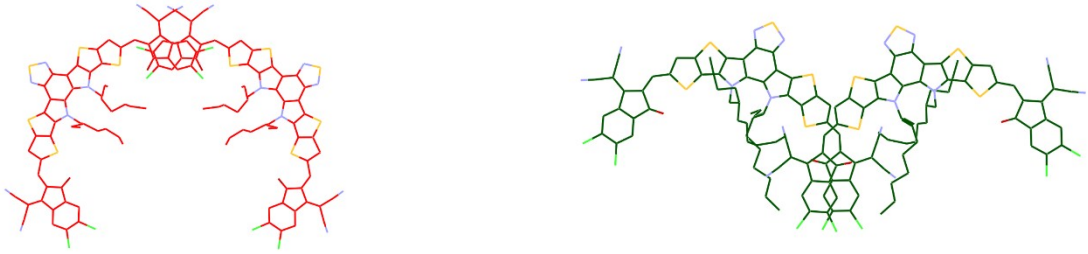

Fig. S9 The TT-2 packing modes in single crystal of BTIC-EH-4Cl and BTIC-C9-4Cl with branched chains.

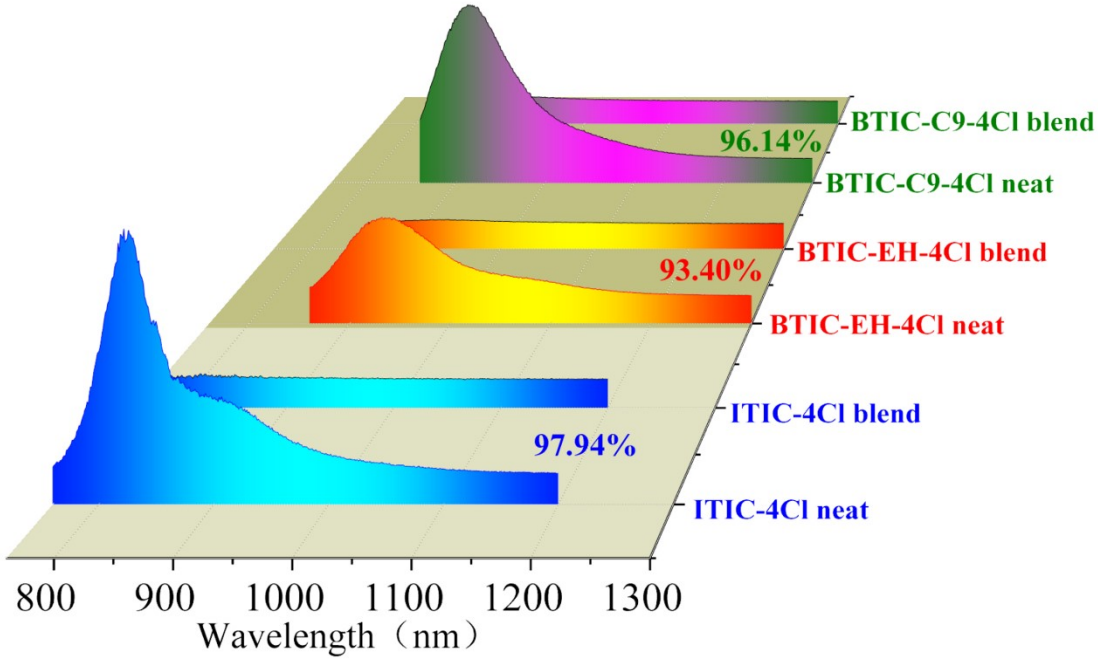

Fig. S10 The photoluminescence spectrums of three chloro-NFAs based neat and blend films.

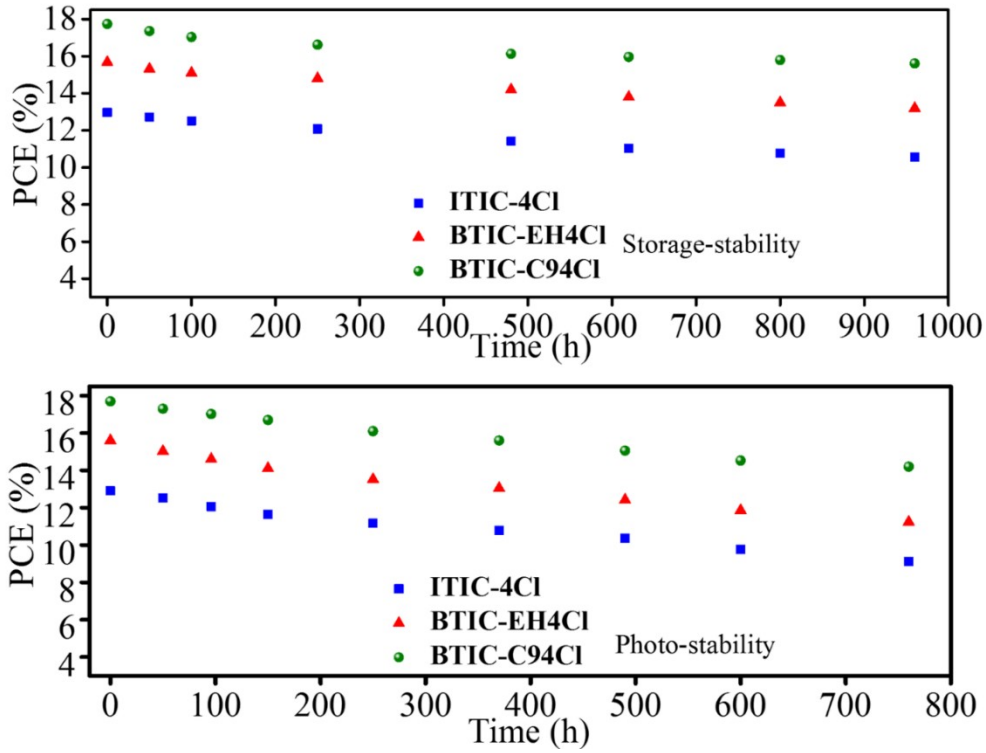

Fig. S11 The storage and photo stabilities of devices based on three chloro-NFAs.

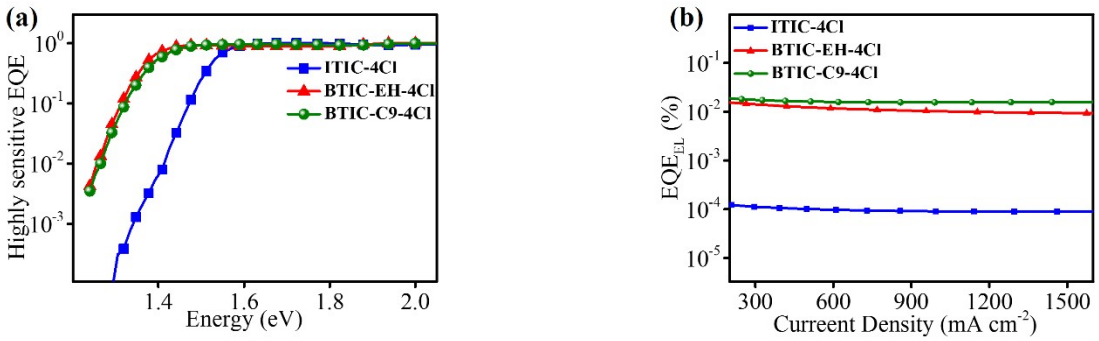

Fig. S12 The (a) fourier transform photocurrent and (b) electroluminescence spectroscopy of OSC devices.

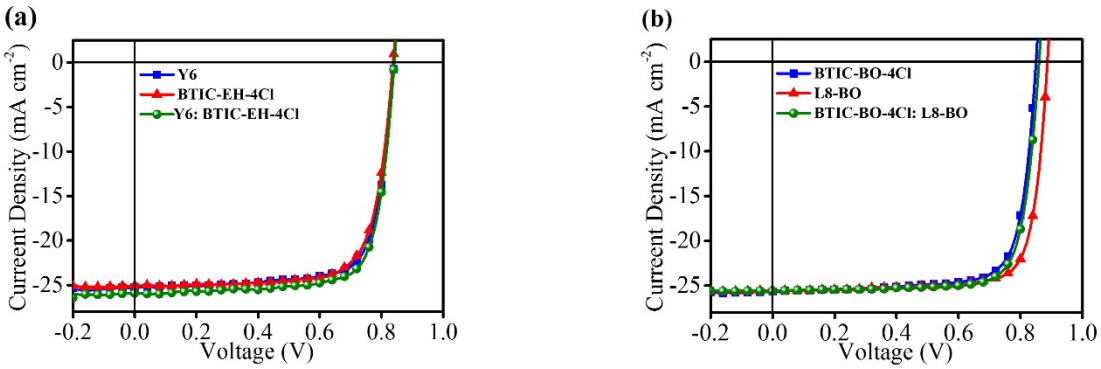

Fig. S13 The J-V curves of the binary and ternary devices based on the acceptors with the larger (a) and the smaller (b) single crystal framework size.

Tab. S1 The OSC devices performances of the binary and ternary devices based on the acceptors with the larger single crystal framework size.

Acceptors	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{max} (%)
Y6	0.84	25.26	75.60	16.04
BTIC-EH-4Cl	0.84	25.06	75.02	15.74
Y6: BTIC-EH-4Cl (1: 0.1)	0.84	25.92	76.59	16.68

Tab. S2 The OSC devices performances of the binary and ternary devices based on the acceptors with the smaller single crystal framework size.

Acceptors	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{max} (%)
BTIC-BO-4Cl	0.85	25.67	77.14	16.83
L8-BO	0.89	25.53	79.57	18.08
BTIC-BO-4Cl: L8-BO (1: 0.1)	0.86	25.62	78.76	17.35

Tab. S3 The crystal parameters of ITIC-4Cl.

Acceptor	ITIC-4Cl
CCDC	2278929
Growth solutions	toluene/ethanol
Empirical formula	$C_{94}H_{78}Cl_4N_4O_2S_4$
Formula weight	1565.724
Temperature / K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	8.7351(7)
b / Å	19.5191(17)
c / Å	26.799(2)
α/°	90
β/°	97.543(8)
γ/°	90
Volume / $Å^3$	4529.7(7)
Z	2
ρ_{calc} / mg mm^{-3}	1.302
μ / mm^{-1}	2.420
F(000)	1832
2Θ range for data collection	5.608≤2θ≤97.378
Index ranges	-8≤h≤8, -11≤k≤19, -26≤l≤25
Reflections collected	18103
Independent reflections	4759 [R_{int} = 0.1439, R_{sigma} = 0.1441]
Data/restraints/parameters	4759/395/458
Goodness-of-fit on F2	0.867
Final R indexes [I>2σ (I)]	R_1=0.1620; wR_2=0.3196
Final R indexes [all data]	R_1=0.3004; wR_2=0.4253
Largest diff. peak/hole / e $Å^{-3}$	1.056/-0.811

Tab. S4 The crystal parameters of BTIC-EH-4Cl.

Acceptor	BTIC-EH-4Cl
CCDC	2278931
Growth solutions	dibromomethane/ethanol
Empirical formula	$C_{82}H_{86}Cl_4N_8O_2S_5$
Formula weight	1517.744
Temperature / K	102 (2)
Crystal system	monoclinic
Space group	C2/c
a / Å	24.082(2)
b / Å	57.855(6)
c / Å	13.8091(11)
α/°	90
β/°	104.745(4)
γ/°	90
Volume / $Å^3$	18606(3)
Z	8
ρ_{calc} / mg mm^{-3}	0.943
μ / mm^{-1}	2.990
F(000)	5328
2Θ range for data collection	5.94≤2θ≤81.66
Index ranges	-18≤h≤13, -44≤k≤45, -10≤l≤10
Reflections collected	31112
Independent reflections	5978 [R_{int} = 0.0335, R_{sigma} = 0.0478]
Data/restraints/parameters	5978/674/714
Goodness-of-fit on F2	0.888
Final R indexes [I>2σ (I)]	R_1=0.1834; wR_2=0.4215
Final R indexes [all data]	R_1=0.2127; wR_2=0.4439
Largest diff. peak/hole / e $Å^{-3}$	1.148/-0.538

Tab. S5 The crystal parameters of BTIC-C9-4Cl (2278932).

Acceptor	BTIC-C9-4Cl
CCDC	2278932
Growth solutions	chloroform/ethanol
Empirical formula	$C_{86}H_{94}Cl_4N_8O_2S_5$
Formula weight	1573.852
Temperature / K	102 (2)
Crystal system	monoclinic
Space group	C2/c
a / Å	26.6758(17)
b / Å	22.3323(15)
c / Å	29.799(2)
α/°	90
β/°	105.664(3)
γ/°	90
Volume / Å^3	17093(2)
Z	8
ρ_{calc} / mg mm^{-3}	0.947
μ / mm^{-1}	2.685
F(000)	4960
2Θ range for data collection	5.24≤2θ≤73.10
Index ranges	-18≤h≤20, -17≤k≤17, -23≤l≤22
Reflections collected	29008
Independent reflections	4269 [R_{int} = 0.0284, R_{sigma} = 0.0330]
Data/restraints/parameters	4269/549/694
Goodness-of-fit on F2	1.060
Final R indexes [I>2σ (I)]	R_1=0.1394; wR_2=0.3733
Final R indexes [all data]	R_1=0.1593; wR_2=0.3904
Largest diff. peak/hole / e Å^{-3}	1.262/ -0.353

Tab. S6 The crystal parameters of BTIC-C9-4Cl (2290214).

Acceptor	BTIC-C9-4Cl
CCDC	2290214
Growth solutions	toluene/methanol
Empirical formula	$C_{86}H_{94}Cl_4N_8O_2S_5$
Formula weight	1573.852
Temperature / K	102 (2)
Crystal system	triclinic
Space group	P-1
a / Å	11.4138(19)
b / Å	18.519(4)
c / Å	20.916(3)
α/°	97.168(11)
β/°	104.322(9)
γ/°	107.723(8)
Volume / $Å^3$	3983.4(12)
Z	2
ρ_{calc} / mg mm^{-3}	1.203
μ / mm^{-1}	1.959
F(000)	1492
2Θ range for data collection	5.24≤2θ≤96.56
Index ranges	-12≤h≤12, -19≤k≤19, -22≤l≤21
Reflections collected	56363
Independent reflections	9102 [R_{int} = 0.0793, R_{sigma} = 0.0926]
Data/restraints/parameters	9102/76/796
Goodness-of-fit on F2	0.980
Final R indexes [I>2σ (I)]	R_1=0.1532; wR_2=0.3562
Final R indexes [all data]	R_1=0.1940; wR_2=0.3802
Largest diff. peak/hole / e $Å^{-3}$	0.901/ -0.609

Tab. S7 The crystal parameters of BTIC-C9-4Cl (2290213).

Acceptor	BTIC-C9-4Cl
CCDC	2290213
Growth solutions	dibromomethane/ether
Empirical formula	$C_{86}H_{94}Cl_4N_8O_2S_5$
Formula weight	1573.852
Temperature / K	102 (2)
Crystal system	monoclinic
Space group	C2/c
a / Å	24.068(5)
b / Å	59.021(12)
c / Å	13.648(3)
α/°	90
β/°	101.855(9)
γ/°	90
Volume / Å^3	18974(7)
Z	8
ρ_{calc} / mg mm^{-3}	0.935
μ / mm^{-1}	2.148
F(000)	5352
2Θ range for data collection	5.10≤2θ≤110.96
Index ranges	-30≤h≤27, -71≤k≤73, -16≤l≤17
Reflections collected	230978
Independent reflections	19349 [R_{int} = 0.0447, R_{sigma} = 0.0815]
Data/restraints/parameters	19349/480/758
Goodness-of-fit on F2	0.985
Final R indexes [I>2σ (I)]	R_1=0.1901; wR_2=0.4027
Final R indexes [all data]	R_1=0.2202; wR_2=0.4162
Largest diff. peak/hole / e Å^{-3}	1.473/ -0.735

Rferences

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