

New Anthracene-Fused Nonfullerene Acceptors for High-Efficiency Organic Solar Cells: Energy Level Modulations Enabling Match of Donor and Acceptor

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Two new nonfullerene small molecule acceptors (NF-SMAs) AT-NC and AT-4Cl based on heptacyclic anthracene(cyclopentadithiophene) (AT) core and different electron-withdrawing end groups are designed and synthesized. Although the two new acceptor molecules use two different end groups, naphthyl-fused indanone (NINCN) and chlorinated INCN (INCN-2Cl) demonstrate similar light absorption. AT-4Cl with chlorinated INCN as end groups are shifted significantly due to the strong electron-withdrawing ability of chlorine atoms. Thus, desirable V_{oc} and photovoltaic performance are expected to be achieved when polymer PBDB-T is used as the electron donor with AT-NC as the acceptor, and fluorinated analog PBDB-TF with down-shifted energy levels is selected to blend with AT-4Cl. Consequently, the device based on PBDB-TF:AT-4Cl yields a high power conversion efficiency of 13.27% with a slightly lower V_{oc} of 0.901 V, significantly enhanced J_{sc} of 19.52 mA cm⁻² and fill factor of 75.5% relative to the values based on PBDB-T:AT-NC. These results demonstrate that the use of a new electron-rich AT core, together with energy levels modulations by end-group optimizations enabling the match with polymer donors, is a successful strategy to construct high-performance NF-SMAs.

Organic photovoltaics (OPVs) have emerged as one of the most promising renewable energy applications for their potential advantages of light weight, low cost, mechanical flexibility, and large area fabrication.^[1,2] Most recently, nonfullerene small molecule acceptors (NF-SMAs) have attracted tremendous attentions and undergone great advances for their excellent performance with power conversion efficiencies (PCEs) over 14% for single junction cells and over 17% for tandem cells.^[3–7] Although the

performance of the nonfullerene OPVs has been improved significantly and high efficiency has been obtained, it is believed that there is still large room to significantly enhance OPVs performance.^[7,8]

To date, both the most successful small molecule donor and acceptor materials share an acceptor-donor-acceptor (A-D-A) architecture.^[9,10] The highly tunable optoelectronic properties of A-D-A structured materials have facilitated the optimizations of their absorption, molecular energy levels, and charge mobilities, and thus improved PCEs can be achieved in the corresponding OPVs.^[9,11–13] For example, by fine tuning D and A units, 3,9-bis (2-methylene-(3-(1,1-dicyanomethylene)-in-danone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d':2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) analog based devices have reached over 14% PCE, indicating there still a giant room for further constructing highly efficient NF-SMAs based OPVs.^[5,8] As such,

the simultaneous tuning of D and A units, is still on the cutting edge to further elevate photovoltaic performance.

For the A-D-A structured molecules, the central “D” unit not only functions as an electron-rich moiety to induce intramolecular charge transfer, but also plays a critical role in realizing suitable energy levels and molecular packing for charge separation and transport as well as providing an adequate solubility for solution processability. To date, most of the reported NF-SMAs with A-D-A architectures are using IDT,^[14–17] fluorene, benzo[1,2-b:4,5-b']-dithiophene,^[18,19] and thieno[3,2-b]thiophene^[20,21] as the donor cores. With extended aromatic fused-ring system based on naphthalene(cyclopentadithiophene) (NDT), we recently demonstrated a series of NF-SMAs and achieved PCE over 11%.^[22,23] Moreover, the strategy of extending donor core in NF-SMAs have been proved successfully to improve photovoltaic performance in many other systems.^[24–26] In general, extending the π -conjugation of fused-ring donor core in the NF-SMAs would improve its electron-donating capacity and intramolecular charge transfer effect for narrower bandgap, and enhance intermolecular interaction to enhance molecular packing for higher charge mobility.^[25–28] Thus, higher and improved performance might be expected for donor core units with more extended π -conjugation system.

On the other hand, precise modulation of the terminal acceptor “A” unit is another effective way to tune the molecular

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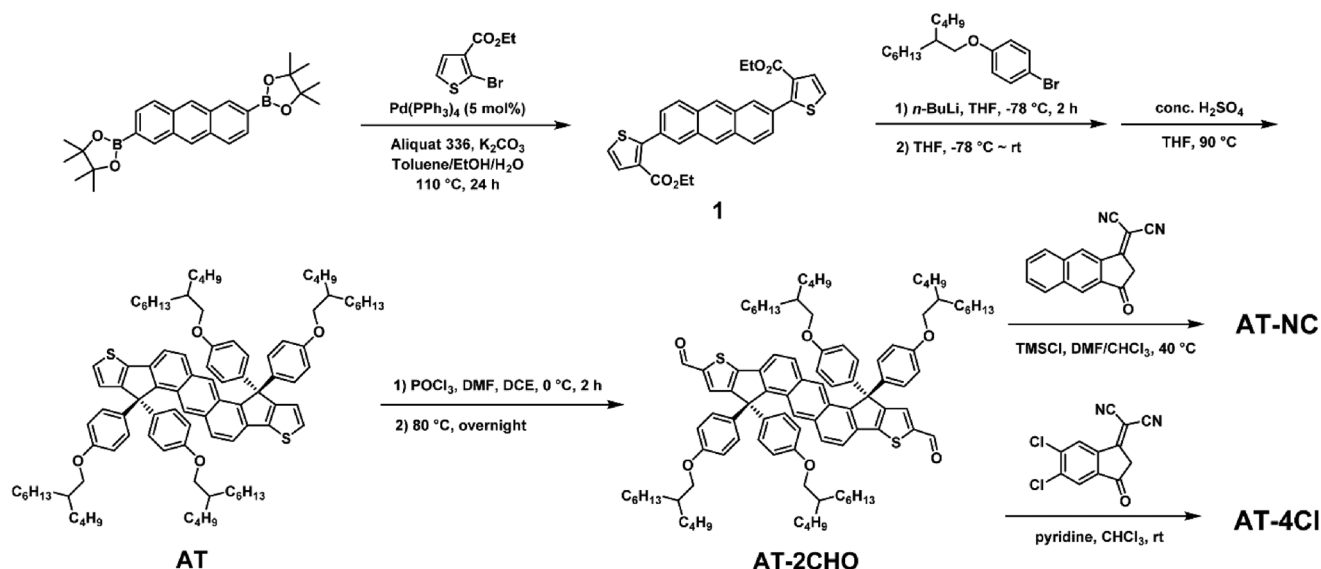
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energy level, increase intermolecular π - π interaction, and improve electron mobilities.^[29,30] Numerous optimizations on the end groups have been conducted, such as methylation or halogenation on INCN (2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile),^[5,14,31] naphthyl-fused indanone (NINCEN) (2-(3-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene)malononitrile) with extended π -conjugation area,^[30,32,33] and thiophene-fused unit CPTCN (2-(6-oxo-5,6-dihydro-4H-cyclopenta[c]thiophen-4-ylidene)malononitrile),^[34] and excellent results were obtained. Among them, the NF-SMAs with extended end unit NINCEN or chlorinated INCN showed strong aggregation tendency and high crystallinity in the solid state, and achieved much high fill factor (FF) and J_{sc} , demonstrating very promising molecular design strategy to elevate photovoltaic performance.^[3,32,35] Moreover, the alternation of end groups with different electron-withdrawing ability on NF-SMAs could result in different energy levels, thus available for better match with different donor materials.^[9,36] Recently, Hou and co-workers have demonstrated a NF-SMA (IT-4F) through utilizing halogenated end groups to enhance the intramolecular charge transfer (ICT) effect and electron delocalization as well as modulate the miscibility with the donor. Then the OPV device based on IT-4F exhibiting a much high PCE of 13.7% by using the halogenated polymer poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PBDB-TF) with matched energy levels as donor.^[14] Thus, it is of great importance to make delicate modifications and proper combination of donor core and end groups through fine molecular design.

On the basis of the above considerations, we designed and synthesized a π -extended heptacyclic anthracene(cyclopentadithiophene) (AT) as the electron-rich donor unit. Two NF-SMAs end-capped with NINCEN and chlorinated INCN (INCEN-2Cl) namely AT-NC and AT-4Cl, have been constructed and systematically characterized. Comparing with IDT and NDT, the new central donor unit AT is more electron-donating with

stronger intermolecular charge transfer effect and facilitates π -electron delocalization and yields a narrower optical bandgap. Compared with AT-NC, AT-4Cl shows similar bandgap but with down-shifted highest occupied molecular orbital (HOMO) (-5.71 vs -5.44 eV) and lowest unoccupied molecular orbital (LUMO) (-3.89 vs -3.80 eV) energy levels due to stronger electron-withdrawing ability of chlorinated INCN than that of NINCEN. Taking this into account, to match the energy levels of each acceptor and achieve high V_{oc} , two polymers PBDB-T and PBDB-TF with different energy levels were selected as donors for AT-NC and AT-4Cl, respectively. Consequently, the optimized OPV device based on PBDB-T:ATNC exhibited a PCE of 10.97% with a V_{oc} of 0.919 V. With both halogenated donor and acceptor, the PBDB-TF:AT-4Cl based device achieved a PCE of 13.27% with a V_{oc} of 0.901, much enhanced J_{sc} of 19.52 mA cm^{-2} and a high FF of 75.5%, which may be ascribed to the halogenation benefitting for stronger intramolecular interaction and more efficient charge transport.^[36]

The synthetic route toward AT-NC and AT-4Cl is shown in Scheme 1. The Suzuki coupling reaction between 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene and ethyl 2-bromo-3-thiophenecarboxylate gave compound 1 in a good yield. Compound 2 was nucleophilically attacked by excess aryl lithium reagents to get the tertiary alcohol, which could be used in the next step without purification. Then, the key intermediate AT was obtained by intramolecular Friedel-Crafts reaction mediating by concentrated H_2SO_4 in tetrahydrofuran at a temperature of 90 °C. AT-2CHO was prepared by a Vilsmeier-Haack reaction of compound AT. The NINCEN and INCEN-2Cl unit were prepared as our reported methods.^[30,31] The target molecule AT-NC and AT-4Cl were then obtained by the Knoevenagel condensation of AT-2CHO with NINCEN or INCEN-2Cl. As shown in Figure S1 in the Supporting Information, the decomposition temperature at 5% weight loss (T_d) determined from thermogravimetric analysis (TGA) curves are 366 and 353 °C for AT-NC and AT-4Cl, respectively, indicating their good thermal stability.



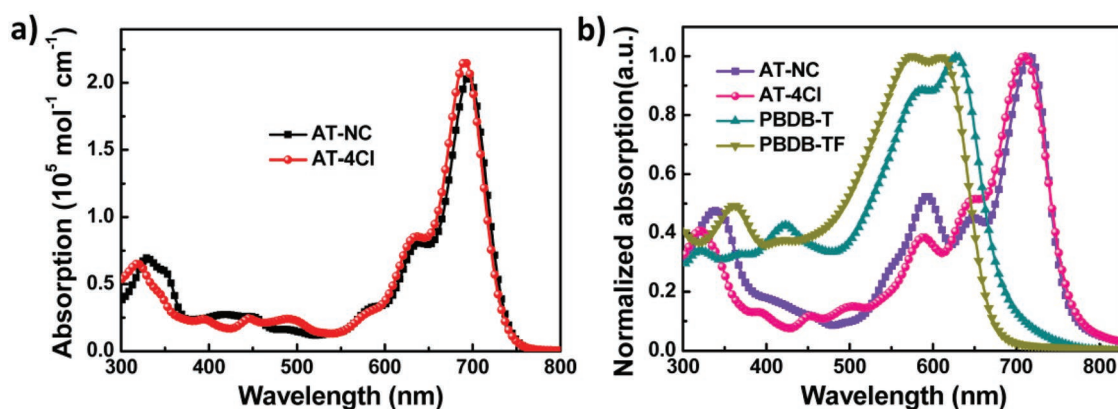


Figure 1. UV-vis absorption spectra of a) AT-NC and AT-4Cl in chloroform solution and b) AT-NC, AT-4Cl, PBDB-T, and PBDB-TF as films.

The UV-vis absorption spectra of AT-NC and AT-4Cl in chloroform solution or in thin film are shown in **Figure 1**, and the detailed parameters are summarized in **Table 1**. The two acceptors have very similar absorption profiles in solution with strong absorption in the range of 500–750 nm. With chlorinated end groups, AT-4Cl in solution displays slightly improved light harvesting properties with a larger extinction coefficient of $2.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 695 nm than that of AT-NC ($2.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 691 nm). From the solution to the solid state, the two molecules exhibit obvious red-shifts of ≈ 20 nm, indicating a relatively strong propensity to form ordered aggregates in films. The optical bandgaps (E_g^{opt}) of AT-NC and AT-4Cl estimated from absorption edges (λ_{edge}) are 1.62 and 1.60 eV, respectively. As shown in Figure 2d, PBDB-T and PBDB-TF forms complementary absorption with both acceptors, which is beneficial for enhanced light absorption.

The energy levels of AT-NC and AT-4Cl were determined by electrochemical cyclic voltammetry (CV) referenced to the energy level of Fc/Fc^+ (-4.8 eV below the vacuum level) (Figure S2, Supporting Information). According to the oxidation and reduction onsets, the HOMO and the LUMO energy levels were determined to be -5.44 and -3.80 eV for AT-NC, -5.71 and -3.89 eV for AT-4Cl. The dramatically down-shifted energy levels of AT-4Cl should be due to the electron-withdrawing effect of chlorine atoms. Thus, as shown in **Figure 2**, two polymers with different energy levels could match these two acceptors to form blends, respectively, on the considerations to avoid decreases in the V_{oc} and improve the photovoltaic performance.

Theoretical calculations were carried out using density functional theory (DFT) to understand the influence of these two end groups on the properties of A-D-A structured NF-SMAs. As shown in Figure S4 in the Supporting Information, AT-NC and AT-4Cl do not show much difference in their optimized molecular

conformations and the electron distributions of the frontier molecular orbitals. Compared with AT-NC, AT-4Cl exhibits down-shifted HOMO and LUMO energy levels. Additionally, the strength of the intramolecular interaction between the electron-rich and the electron-deficient moieties was evaluated by calculating the dipole moment of the molecules based on the half molecular models. Under the ground state, the wing of AT-4Cl shows a larger dipole moment of 8.60 D than 6.41 D of AT-NC, indicating that possible enhanced ICT effect could occur on the molecular of AT-4Cl.^[14]

To evaluate the photovoltaic properties of AT-NC and AT-4Cl, solution-processed OPVs were fabricated with an inverted device structure of indium tin oxide ($\text{ITO}/\text{ZnO}/\text{active layer}/\text{MoO}_3/\text{Ag}$). Polymer donors PBDB-T and PBDB-TF with different energy levels are used for AT-NC and AT-4Cl based devices, respectively, and it is based on the following three considerations: 1) complementary absorption band to the acceptor for higher J_{sc} , 2) suitable LUMO and HOMO levels of donor for efficient electron and hole transfer, and 3) as deeper HOMO level as possible for high V_{oc} . After systematic device optimization (Tables S1–S3, Supporting Information), chlorobenzene was used as the processing solvent with the optimized ratio of 1:0.8 for PBDB-T:AT-NC and 1:1 for PBDB-TF:AT-4Cl. Meanwhile, a tiny amount of 1,8-diiodooctane (DIO, 0.5% volume) was selected as solvent additive to tune the morphology of both active layers. As a result, the PBDB-T:AT-NC device achieved a PCE of 10.91% with a V_{oc} of 0.919 V, a J_{sc} of 17.11 mA cm^{-2} , and an FF of 69.4%. In comparison, the optimal PCE of PBDB-TF:AT-4Cl improved to 13.27% with a V_{oc} of 0.901 V and significantly improved J_{sc} of 19.52 mA cm^{-2} and FF of 75.5%. As expected, selecting PBDB-TF with down-shifted energy levels for AT-4Cl refrained from a large debasement of V_{oc} . Charge transport properties in PBDB-T:AT-NC and PBDB-TF:AT-4Cl blend were measured by the space-charge-limited current (SCLC) method

Table 1. Optical and electrochemical data of AT-NC and AT-4Cl.

Comp.	$\lambda_{\text{max}}^{\text{sol}}$ [nm]	ϵ_{max} [$\text{M}^{-1} \text{ cm}^{-1}$]	$\lambda_{\text{max}}^{\text{film}}$ [nm]	$\lambda_{\text{edge}}^{\text{film}}$ [nm]	E_g^{opt} [eV] ^{a)}	HOMO [eV] ^{b)}	LUMO [eV] ^{b)}	E_g^{cv} [eV] ^{c)}
AT-NC	695	2.0×10^5	716	765	1.62	-5.44	-3.80	1.69
AT-4Cl	691	2.2×10^5	709	774	1.60	-5.71	-3.89	1.82

^{a)}The optical bandgap estimated from the absorption onset; ^{b)} $E_{\text{HOMO}} = -(4.80 + E_{\text{ox}}^{\text{onset}})$, $E_{\text{LUMO}} = -(4.80 + E_{\text{re}}^{\text{onset}})$; ^{c)}Electrochemical bandgap obtained from $E_{\text{LUMO}} - E_{\text{HOMO}}$.

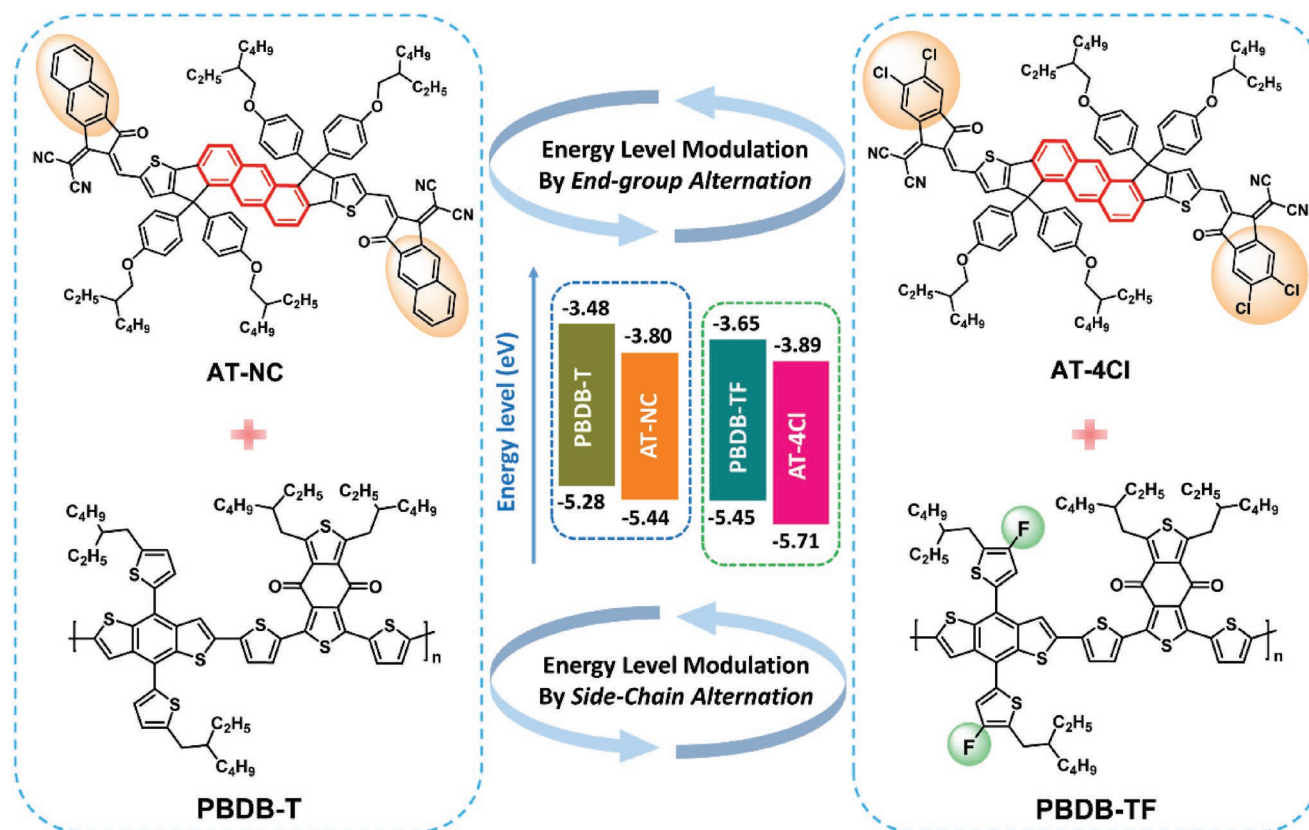


Figure 2. Chemical structures of AT-NC, AT-4Cl, PBDB-T, and PBDB-TF and the energy diagrams of donors and acceptors.

using the electron-only and hole-only devices, respectively (Figure S5, Supporting Information). The measured average electron and hole mobilities for PBDB-T:AT-NC and PBDB-TF:AT-4Cl blend films are 6.46×10^{-5} , 1.41×10^{-4} (μ_e), and 1.85×10^{-4} , 2.74×10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (μ_h) with mobility ratios (μ_h/μ_e) of 2.9 and 1.9, respectively. The relatively higher and more balanced hole and electron mobilities are beneficial for less charge recombination, which can be attributed to the halogenation on both donor and acceptor,^[36] thus contributing to the higher J_{sc} and FF values of the PBDB-TF:AT-4Cl based devices.^[37,38]

The external quantum efficiency (EQE) curves were shown in Figure 3b. The OPV devices on PBDB-T:AT-NC and PBDB-TF:AT-4Cl both show broad photocurrent response from 300 to 800 nm with the maximum values reaching 77.2% at 700 nm and 83.1% at 710 nm, respectively, indicating the efficient photon harvesting and charge collection. The PBDB-TF:AT-4Cl based OPV device shows higher and broader EQE in almost all the 300–800 nm region than the PBDB-T:AT-NC device, which results in higher J_{sc} and could be ascribed to the red-shifted and stronger absorption of AT-4Cl-based blend film (Figure S3, Supporting Information). The integrated photocurrents of PBDB-T:AT-NC and PBDB-TF:AT-4Cl from EQE spectra are 16.53 and 18.79 mA cm^{-2} , respectively, which are both in good agreement with the J_{sc} values obtained from corresponding J – V curves (Table 2).

The charge generation and recombination behavior in the PBDB-T:AT-NC and PBDB-TF:AT-4Cl based device were

then studied according to the reported methods. As shown in Figure 3d, the photocurrent (J_{ph}) versus the effective applied voltage (V_{eff}) for the corresponding devices was measured and J_{ph} for both devices reached saturation (J_{sat}). When V_{eff} exceeded 1.5 V, suggesting minimal charge recombination at high voltages.^[39,40] The overall charge dissociation probability under the short circuit conditions can be estimated from the ratio of J_{ph}/J_{sat} . Compared to J_{ph}/J_{sat} of 90% for PBDB-T:AT-NC, PBDB-TF:AT-4Cl based device demonstrated a much higher value of 97%, thus more efficient charge dissociation. Meanwhile, the higher J_{sat} indicates the enhanced exciton generation rate in PBDB-TF:AT-4Cl based device. To investigate the relationship between charge recombination and transport in the photoactive layer, the light intensity dependence of J_{sc} were measured.^[41] In Figure 3d, recombination parameters obtained by the slopes were 0.97 of PBDB-T:AT-NC and 1.00 of PBDB-TF:AT-4Cl based device, respectively, which suggest bimolecular recombination is effectively suppressed in both devices, and the negligible bimolecular recombination in PBDB-TF:AT-4Cl based device supported its high FF.^[41] Figure 3c,d showed transient photocurrent and photovoltage decay kinetics of PBDB-T:AT-NC and PBDB-TF:AT-4Cl-based devices. The charge sweep-out time at short-circuit condition were 0.68 μs of PBDB-T:AT-NC and 0.53 μs of PBDB-TF:AT-4Cl based device. The shorter charge extraction time can be attributed to the higher electron mobility in PBDB-TF:AT-4Cl-based device. The carrier lifetimes calculated from the traces of transient photovoltage (TPV) measurements (Figure 4f) were

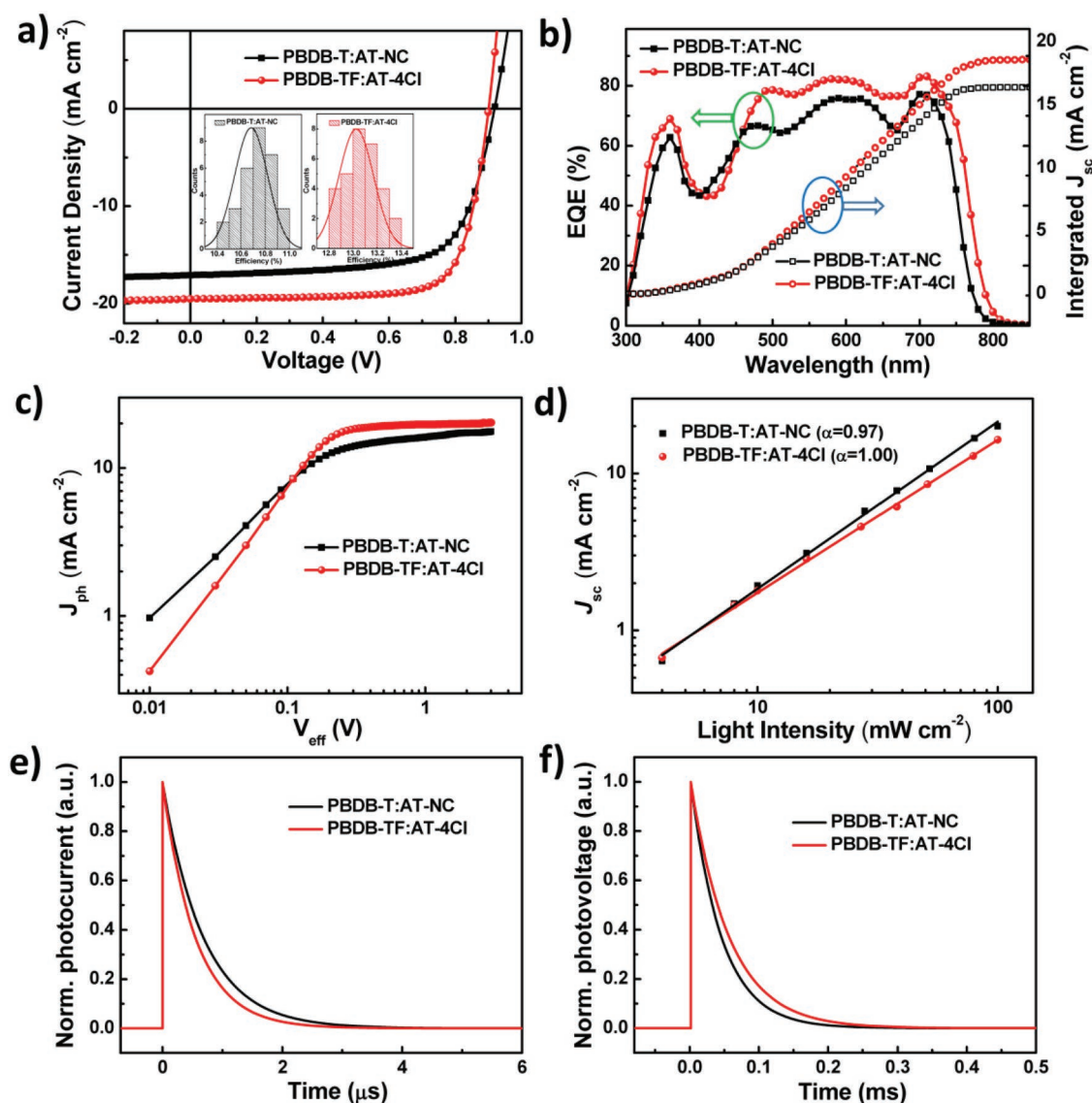


Figure 3. a) Current density–voltage (J – V) curves for the devices based on AT-NC and AT-4Cl at optimized conditions under the illumination of AM 1.5G (100 mW cm^{-2}); the inset shows the histograms of the PCE counts for 30 devices. b) EQE curves and integrated J_{sc} for the AT-NC and AT-4Cl based OPV devices. c) J_{ph} versus V_{eff} and d) light intensity (P) dependence of J_{sc} for the optimized devices. e) Transient photocurrent and f) transient photovoltage measurements of PBDB-T:AT-NC and PBDB-TF:AT-4Cl based devices.

44 and 56 μs for PBDB-T:AT-NC and PBDB-TF:AT-4Cl-based devices, respectively.^[42–44] The relatively higher lifetime of carriers at open-circuit voltage may indicate less recombination in PBDB-TF:AT-4Cl based devices. These results are consistent to the much improved the J_{sc} and FF, benefitting from the

enhanced transport with balanced mobility in PBDB-TF:AT-4Cl-based devices.

To investigate the differences between the AT-NC and AT-4Cl based active layers in the molecular packing, the AT-NC and AT-4Cl based pure and BHJ thin films were investigated by

Table 2. Optimal device parameters of PBDB-T:AT-NC and PBDB-TF:AT-4Cl based devices under the illumination of AM 1.5G (100 mW cm^{-2}) using the inverted device structure. The average values with standard deviations obtained from 30 devices are provided in the parentheses.

BHJ layer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	J_{cal} [mA cm^{-2}]	FF %	PCE %	μ_e [$\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	μ_h [$\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]
PBDB-T:AT-NC	0.919 (0.915 $\pm$ 0.004)	17.11 (16.99 $\pm$ 0.14)	16.53	69.4 (67.7 $\pm$ 0.6)	10.91 (10.68 $\pm$ 0.3)	1.34	2.60
PBDB-TF:AT-4Cl	0.901 (0.898 $\pm$ 0.003)	19.52 (19.38 $\pm$ 0.20)	18.79	75.5 (74.7 $\pm$ 0.9)	13.27 (13.10 $\pm$ 0.2)	1.85	2.93

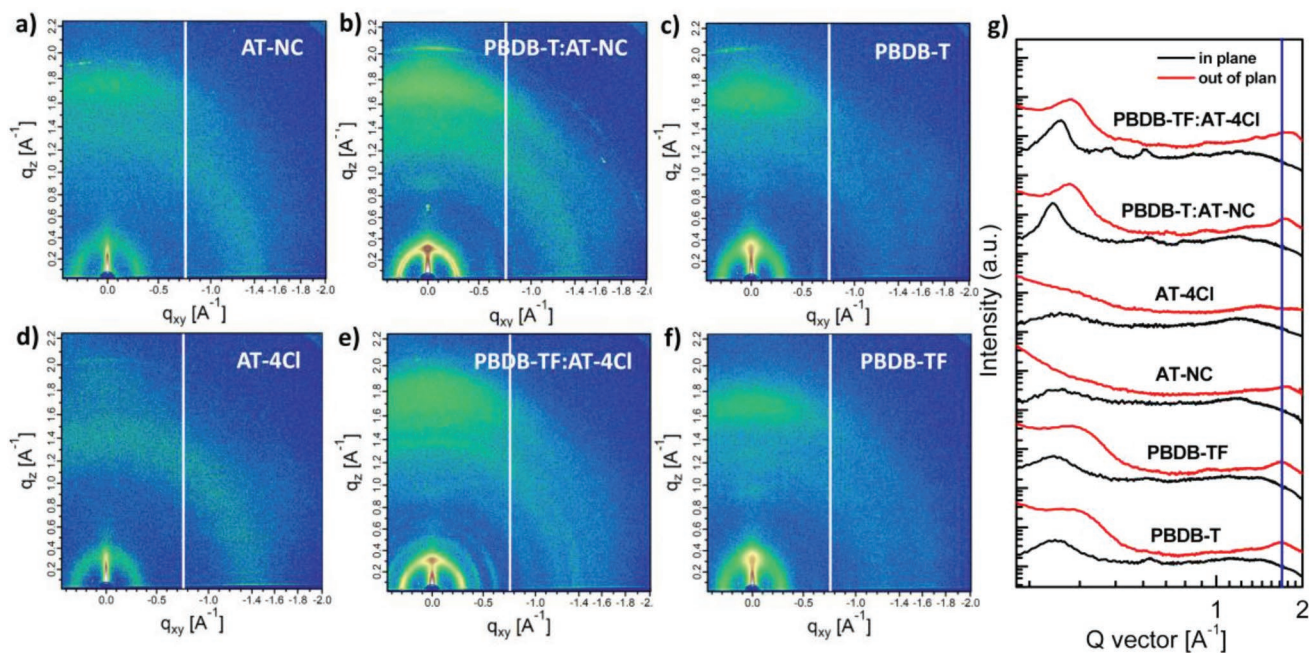


Figure 4. 2D GIWAXS patterns for a) AT-NC, c) PBDB-T, d) AT-4Cl, and f) PBDB-TF pristine film, b) PBDB-T:AT-NC blend film, and e) PBDB-TF:AT-4Cl blend film, g) out-of-plane and in-plane GIWAXS profiles for the neat and blend films.

grazing incidence wide-angle X-ray scattering (GIWAXS). As shown in Figure 4a,c, AT-NC in neat film exhibited a face-on molecular packing with an obvious (010) diffraction peak in out-of-plane direction (OOP) at $1.75 \text{ \AA}^{-1}$, corresponding to a π - π stacking distance of $3.59 \text{ \AA}$ and the crystal coherence length (CCL) was estimated to $22 \text{ \AA}$. AT-4Cl also showed more preferential face-on molecular packing with a (010) diffraction at $1.89 \text{ \AA}^{-1}$ (d spacing: $3.32 \text{ \AA}$) along the OOP direction, though the diffraction peak was relatively weak with a shorter CCL of $18 \text{ \AA}$. Both AT-NC and AT-4Cl neat film showed quite weak and broad scattering peak around $0.29 \text{ \AA}^{-1}$ with a d spacing of $22 \text{ \AA}$. On the other hand, as shown in Figure 4c,f, both PBDB-T and PBDB-TF showed obvious face-on packing with a broad (100) diffraction peak around $0.30 \text{ \AA}^{-1}$ (d spacing: $20.9 \text{ \AA}$) and a π - π stacking (010) diffraction around $1.69 \text{ \AA}^{-1}$ (d spacing: $3.71 \text{ \AA}$) in the out-of-plane direction corresponding to preferential face-on orientation. In both PBDB-T:AT-NC and PBDB-TF:AT-4Cl optimized blend films, donors and acceptors contents showed enhanced crystalline feature as seen from stronger scattering profiles caused by the addition of DIO to effectively plasticize the blended thin films, reducing glass transition thus improving the molecular packing.^[30] In particular, as shown in PBDB-TF:AT-4Cl film, enhanced diffraction features from AT-4Cl are seen in π - π stacking regions by the (010) peak broadened to higher q region than that of PBDB-T:AT-NC blend film, indicating a smaller π - π stacking in PBDB-TF:AT-4Cl film. The smaller π - π stacking distance of PBDB-TF:AT-4Cl blend film can be attributed to the enhanced intermolecular interactions of AT-4Cl molecules in blend, which is a benefit for charge transport in the OPV device.

The morphological differences between the PBDB-T:AT-NC blend film and PBDB-TF:AT-4Cl blend film were also characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in Figure 5a,d, neat

AT-NC film was featured with grain-like domains and exhibited a root-mean-square surface roughness (R_q) value of 0.69 nm and AT-4Cl showed slightly smaller surface with R_q value of 0.45 nm . In the blended films (Figure 5b,e), PBDB-TF:AT-4Cl film exhibits larger and more finely dispersed phase separation with R_q value of 1.95 nm compared with 1.59 nm of PBDB-T:AT-NC blend film. Furthermore, in Figure 5c,f of TEM images, more obvious interpenetrating network with nanoscale phase separation is observed in PBDB-TF:AT-4Cl film. The distinctive morphologies for PBDB-TF:AT-4Cl blend film are highly in favor of charge generation and transport in support of the aforementioned results.^[45]

In order to investigate the miscibility between donor and acceptor in the two blends, we measured the contact angle and calculated their surface tensions for all four pristine materials and the interfacial tensions of PBDB-T/AT-NC and PBDB-TF/AT-4Cl (Table 3; Figure S6, Supporting Information) following the literature method.^[46,47] The film of PBDB-T and PBDB-TF show similar surface tension and both are lower than the two NF-SMAs. For the two NF acceptors, the AT-4Cl film demonstrates lower surface tension than the AT-NC film. The same trend was observed for glycerol contact angles. Then the equation $\chi \propto (\sqrt{\gamma_{\text{donor}}} - \sqrt{\gamma_{\text{acceptor}}})^2$ suggested by Moons and co-workers in which χ is the Flory-Huggins interaction parameter of two blends was used to further compare the miscibility of the two blends.^[48] As a result, the χ parameter of the PBDB-TF:AT-4Cl is about 11 times higher than that of PBDB-T:AT-NC, indicating of a much lower miscibility and thus the potential for higher domain purity and device performance in the PBDB-TF:AT-4Cl device.^[49,50]

In conclusion, two new NF-SMAs AT-NC and AT-4Cl have been designed and synthesized by developing a novel AT electron-rich core and introducing two different electron-withdrawing end-groups, NINC and INCN-2Cl, respectively. AT-4Cl exhibited

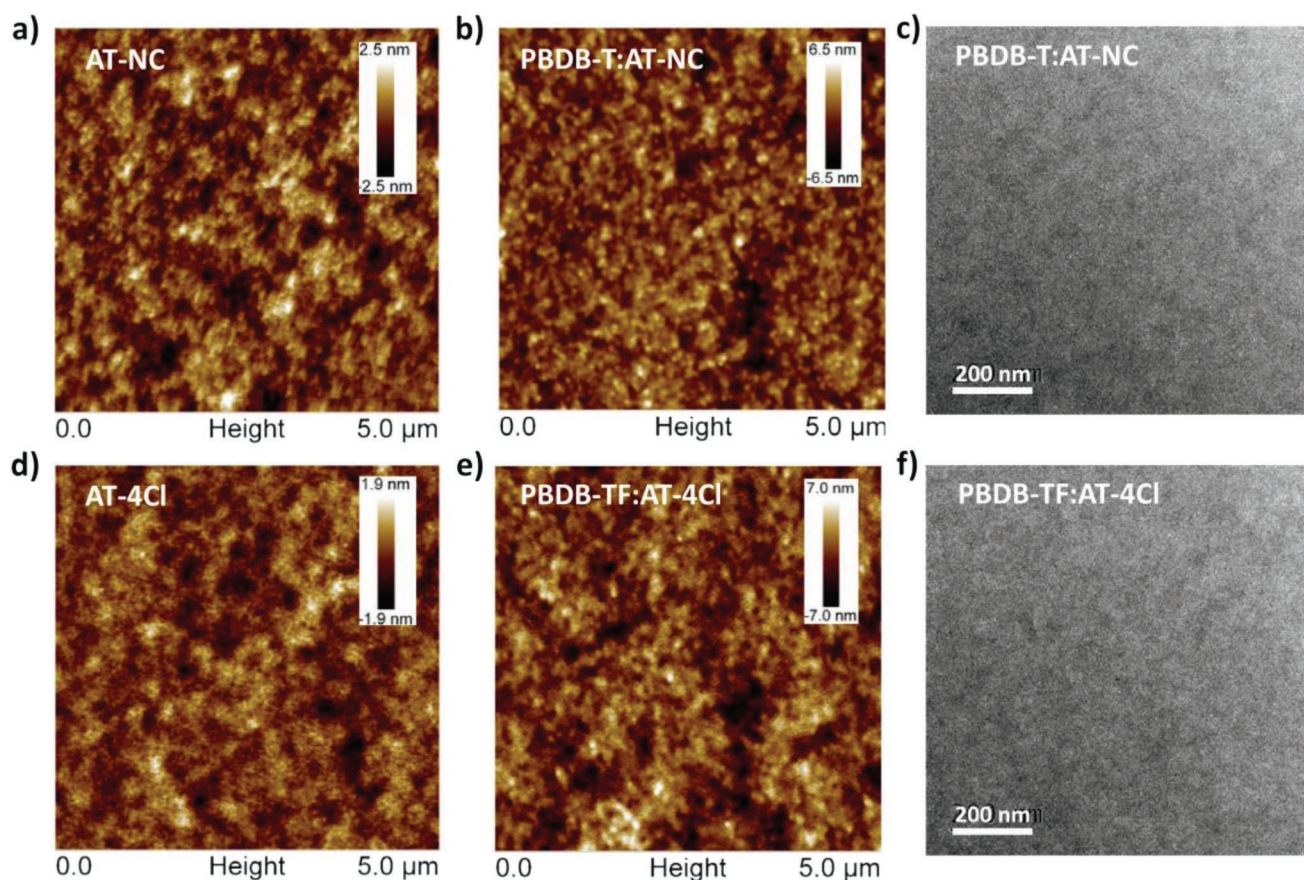


Figure 5. AFM images for a) AT-NC neat film and d) AT-4Cl neat film. AFM and TEM images for b,c) PBDB-T:AT-NC film and e,f) PBDB-TF:AT-4Cl film.

significantly down-shifted energy levels though similar absorption spectrum relative to AT-NC. Thus, two different donors PBDB-T and PBDB-TF were selected for better energy level match and higher V_{oc} . Compared with PBDB-T:AT-NC, the PBDB-TF:AT-4Cl blend film with down-shifted molecular energy levels showed an appropriate phase separation with favorable molecular packing and miscibility and extended absorption spectrum with enhanced absorption coefficient. Consequently, PBDB-T:AT-NC-based device exhibited a PCE of 10.91% with a V_{oc} of 0.919 V. The device based on PBDB-TF:AT-4Cl yielded a much improved PCE of 13.27% with a V_{oc} of 0.901 V, significantly enhanced J_{sc} of 19.52 mA cm⁻², and FF of 75.5%. These results demonstrate that the use of new electron-rich AT core, together with energy levels modulations by end-group optimizations enabling the match with polymer donors, is a promising and successful strategy to construct high-performance NF-SMAs.

Table 3. Contact angle of water and glycerol and surface tension of PBDB-T, PBDB-TF, AT-NC, and AT-4Cl.

Film	θ_{water} [°]	θ_{GL} [°]	γ [mN m ⁻¹]
PBDB-T	95.4	87.1	22.9
PBDB-TF	100.1	89.0	22.4
AT-NC	90.5	82.5	24.0
AT-4Cl	86.6	78.5	26.0

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anthracene, end-group modulation, energy level match, nonfullerene acceptors

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