

Asymmetric Alkyl Chain Engineering of Non-fullerene Acceptors for Efficient Organic Solar Cells

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Electronic supplementary information

Abstract The asymmetric molecular design strategy, with advantages in modulating the molecular dipole moment and intermolecular interactions and achieving more favorable molecular packing and orientation, has been an effective approach for designing high-performance non-fullerene acceptors (NFAs). Herein, two asymmetric NFAs, Y-CN-2F and Y-CN-2Cl, were designed and synthesized by introducing a linear alkyl chain terminated with the 4-cyanobiphenyl group, a well-known mesogenic unit, at one of the inner pyrrole positions instead of the normal 2-butyloctyl branched alkyl chain. The difference between Y-CN-2F and Y-CN-2Cl is the terminated IC-groups, which was modified with F and Cl halogens, respectively. Both NFAs displayed strong absorption in the near-infrared to visible-light range, which is complementary to that of typical medium-bandgap donor polymers. After optimization with D18 donor in organic solar cells (OSCs), Y-CN-2F and Y-CN-2Cl provided comparable power conversion efficiencies (PCEs) of 15.33% and 15.88%. While the D18:Y-CN-2F based devices displayed higher fill factors (FFs), those based on D18:Y-CN-2Cl exhibited higher current densities and open-circuit voltages. The Y-CN-2Cl film showed longer light absorption than Y-CN-2F, which is beneficial for more light harvesting. Moreover, D18:Y-CN-2Cl displayed a lower fluorescence lifetime and faster carrier transfer processes, which could be attributed to its higher mobility. For the D18:Y-CN-2F blended film, a more pronounced fiber network structure and balanced carrier mobility were observed, which contributed to the higher FFs values. This work presents new efforts to develop more asymmetric NFAs with specific functional segments for efficient organic electronics.

Keywords Asymmetric strategy; Side-chain engineering; Non-fullerene acceptors; Organic solar cells

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INTRODUCTION

Organic solar cells (OSCs) have become attractive candidates for clean energy because of their unique properties, such as light weight, low cost, intrinsic flexibility, and potential for large-scale roll-to-roll fabrication.^[1–6] In the past years, owing to the rapid development of non-fullerene acceptors (NFAs), especially the emergence of Y-series NFAs, the power conversion efficiencies (PCEs) of single-junction OSCs have been over 19%, reducing

greatly the efficiency gap between OSCs and the commercial inorganic solar cells.^[7–12] To date, NFAs have achieved a vast expansion in diversity through rational molecular design, including central core engineering, side chain engineering, and end-group engineering.^[13–18]

From the perspective of molecular structure, asymmetric molecular design strategies such as asymmetric terminal units, asymmetric backbones, and asymmetric side-chain engineering have often resulted in larger dipole moments, stronger intermolecular interactions, more favorable molecular packing, and lower non-radiative energy loss (E_{loss}).^[19–24] For instance, Min *et al.* designed an asymmetric guest acceptor with different halogen atoms on terminal group, resulting in an extended absorption spectrum and improved molecular packing, and achieved a high PCE of 19.17% in ternary OSCs.^[25] Jen *et al.* synthesized an asymmetric acceptor

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molecule, BS3TSe-4F, by introducing a selenium atom into the central core of the acceptor molecule, which reduced the bandgap to 1.280 eV. Upon blending with the polymer donor D18, the dielectric constant increased, leading to enhanced exciton dissociation and reduced radiative recombination losses, achieving a short-circuit current density (J_{SC}) of 29.40 mA·cm⁻² and a PCE of 18.48%.^[26] Huang *et al.* reported an asymmetric NFA by replacing one alkyl chain with a polyfluoroalkyl in the inner pyrrole position. This modification led to a favorable vertical morphology and a PCE exceeding 18%.^[27] Some studies have suggested that the asymmetric design of the inner alkyl chain connected to the pyrrole ring not only balances the solubility and crystallinity of NFAs but also promotes more favorable molecular orientation, enhances carrier mobility, and ultimately improves device performance.^[28,29] However, the advancement of asymmetric side-chain engineering remains relatively lagged behind. Therefore, it is important to further probe the advantages of asymmetric alkyl side-chain engineering of NFAs and explore their applications in organic electronics such as OSCs.

Herein, two asymmetric NFAs, Y-CN-2F and Y-CN-2Cl, with a typical mesogenic unit, 4-cyanobiphenyl, terminating at the end of the linear alkyl chain, were designed and synthesized. The absorption spectra of the two acceptor films exhibited strong complementarity with that of the donor polymer, and the energy levels of both acceptors were well-aligned with those of the donor polymer. Compared to Y-CN-2F, which has two fluorine atoms substituted at the terminal group, Y-CN-2Cl with two chlorine substituents at the terminal group exhibited a red-shifted absorption spectrum and a lower energy level. In addition, devices based on Y-CN-2Cl displayed higher but unbalanced carrier mobility, and the lower fluorescence lifetime indicated faster carrier transfer processes in the device. As a result, Y-CN-2Cl-based devices achieved a higher open-circuit voltage (V_{OC}) and J_{SC} , resulting in a PCE of 15.88%, while Y-CN-2F-based devices showed a slightly high-

er fill factor (FF) and a PCE of 15.33%.

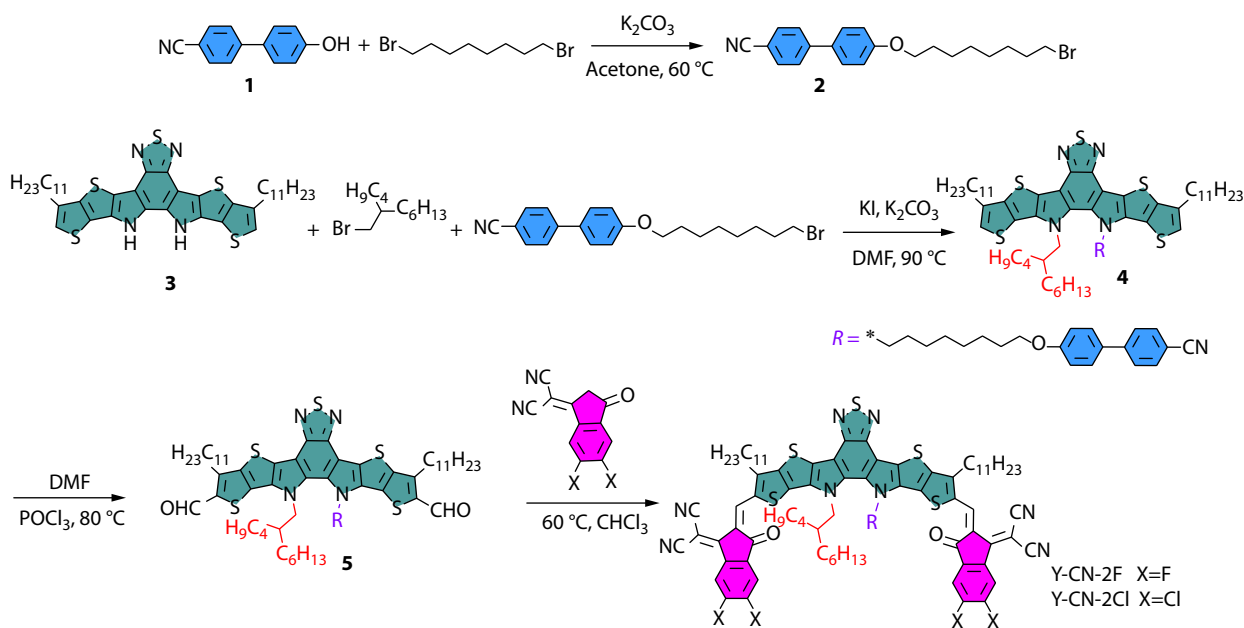
EXPERIMENTAL

The synthetic details, experimental section and complementary data are presented in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

The synthetic pathway for the small-molecule acceptors is depicted in Scheme 1, and details are provided in the ESI. Compound **2** was synthesized using Williamson ether synthesis between compound **1** and 1,8-dibromooctane. Subsequently, compound **4** with asymmetric alkyl groups was synthesized *via* nucleophilic substitution between compound **2**, 5-(bromomethyl)undecane, and compound **3** in a one-pot reaction. The Vilsmeier-Haack reactions were then performed to obtain the key dialdehyde intermediates of compound **5**. Finally, the desired small-molecule acceptors Y-CN-2F and Y-CN-2Cl were obtained *via* Knoevenagel condensation.

The molecular structures of Y-CN-2F and Y-CN-2Cl are shown in Figs. 1(a) and 1(b). The asymmetric design of the alkyl side chains was aimed at ensuring good solubility of the acceptor materials in commonly used organic solvents, and the introduction of a mesogenic unit was intended to enhance the ordered stacking of acceptor molecules, thereby improving the charge transfer efficiency.^[30] In addition, two types of halogen atoms with different electron-withdrawing capabilities, fluorine atoms and chlorine atoms, were employed at the terminal groups to modulate the intramolecular charge push-pull effect and the distribution of electrostatic potential. Both acceptors showed excellent solubility in common solvents, such as dichloromethane, chloroform, and chlorobenzene. Moreover, the thermal stabilities of both acceptors were evaluated by thermogravimetric analysis, as



Scheme 1 The synthetic route of Y-CN-2F and Y-CN-2Cl.

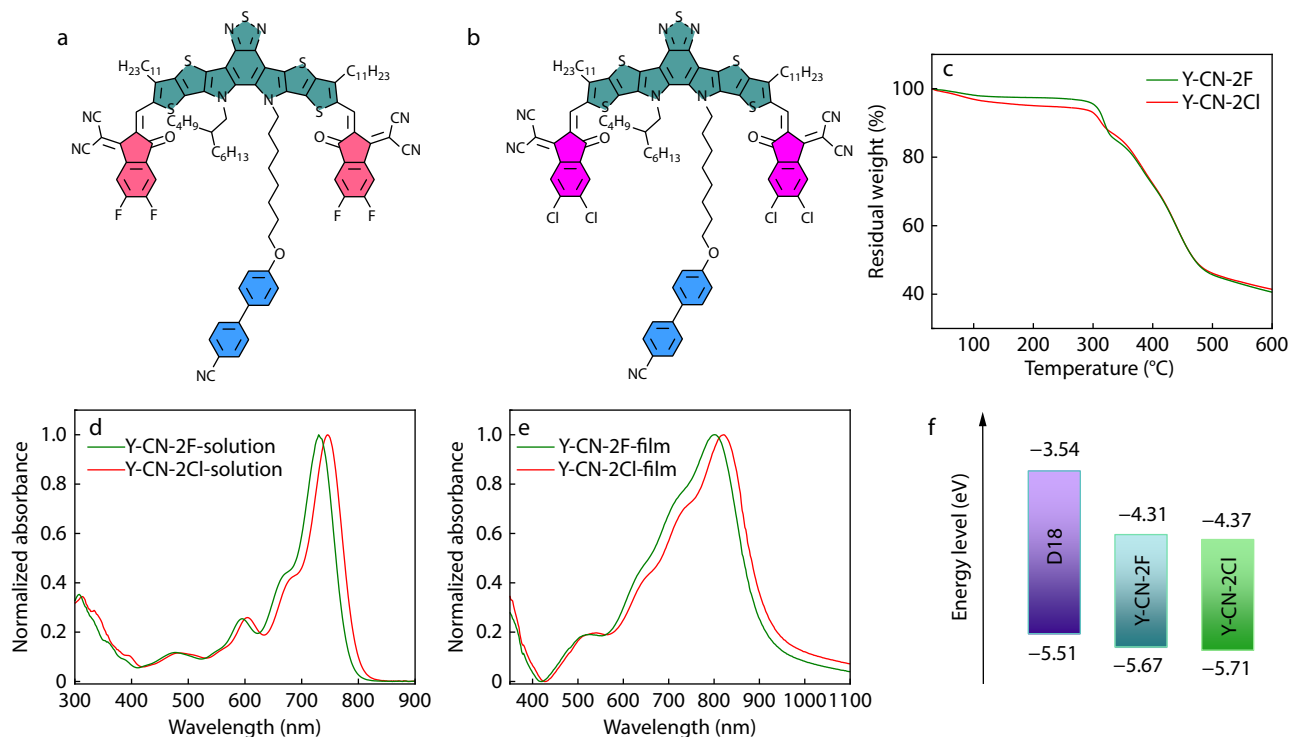


Fig. 1 Molecular structures of Y-CN-2F (a) and Y-CN-2Cl (b). (c) Thermogravimetric analysis (TGA) curves of Y-CN-2F and Y-CN-2Cl at a scan rate of 10 °C·min⁻¹. Normalized UV-Vis absorption spectra of Y-CN-2F and Y-CN-2Cl in chloroform solution (d) and in thin films (e). (f) The energy level diagrams of D18, Y-CN-2F and Y-CN-2Cl.

Table 1 Optical and electrochemical properties of two acceptors.

Acceptor	$\lambda_{\max}^a$ (nm)	λ_{onset}^a (nm)	$\lambda_{\max}^b$ (nm)	λ_{onset}^b (nm)	E_g^c (eV)	HOMO ^d (eV)	LUMO ^e (eV)
Y-CN-2F	729.8	784.4	801.2	913.4	1.36	-5.67	-4.31
Y-CN-2Cl	745.9	799.0	821.5	928.5	1.34	-5.71	-4.37

^a In chloroform solution; ^b Neat film; ^c Calculated from the empirical formula: $E_g = 1240/\lambda_{\text{onset}}$; ^d Using cyclic voltammetry (CV) method; ^e Calculated from the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$.

shown in Fig. 1(c), which revealed good thermal stability, with decomposition temperatures (weight loss of 5%) of 295 and 263 °C for Y-CN-2F and Y-CN-2Cl, respectively.

The ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectra of Y-CN-2F and Y-CN-2Cl in chloroform solutions and films are shown in Figs. 1(d) and 1(e). In solution, the two acceptors displayed similar absorption spectra in the range 350–800 nm and the maximum absorption peaks of Y-CN-2F and Y-CN-2Cl were located at 730 and 746 nm, respectively. The replacement of fluorine atoms with chlorine atoms results in significant red-shift absorption spectra, which is helpful for harvesting more photons and achieving higher J_{SC} in OSC devices. From solutions to thin films, there were significant red-shifts in the spectra of Y-CN-2F and Y-CN-2Cl due to enhanced intermolecular π - π stacking in the solid state, with maximum absorption peaks red-shift by 70–75 nm. On the other hand, the absorption edges of these films were located at 913 and 928 nm, corresponding to estimated optical bandgaps (E_g^{opt}) of 1.36 and 1.34 eV for Y-CN-2F and Y-CN-2Cl, respectively. It should be pointed out that the absorption spectra of the two acceptor films showed good complementarity with that of the donor polymer D18, with a wide ab-

sorption range from 350 nm to 900 nm.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the Y-CN-2F and Y-CN-2Cl thin films were determined by cyclic voltammetry (CV) measurements (Fig. S1 in ESI), and the details of the energy level diagrams of D18, Y-CN-2F, and Y-CN-2Cl are provided in Fig. 1(f). The HOMO levels of Y-CN-2F and Y-CN-2Cl were found to be -5.67 and -5.71 eV, respectively, whereas the LUMO levels were calculated from their HOMO level and optical bandgaps, which were -4.31 and -4.37 eV, respectively. Evidently, the energy levels of the two acceptors were well aligned with those of the donor polymer, facilitating efficient exciton dissociation and charge transport. The optical and electrochemical properties of the two polymers are summarized in Table 1.

The device structure of ITO/PEDOT:PSS/D18:acceptors/HPDIN-B02/Ag was used to explore the photovoltaic properties of Y-CN-2F and Y-CN-2Cl, where HPDIN-B02 was used as the electron transport layer. The current-voltage (J - V) curves and optimal data for the OSCs are shown in Fig. 2(a) and Table 2, and the detailed fabrication procedures and optimization processes are described in the ESI (Figs. S2 and S3

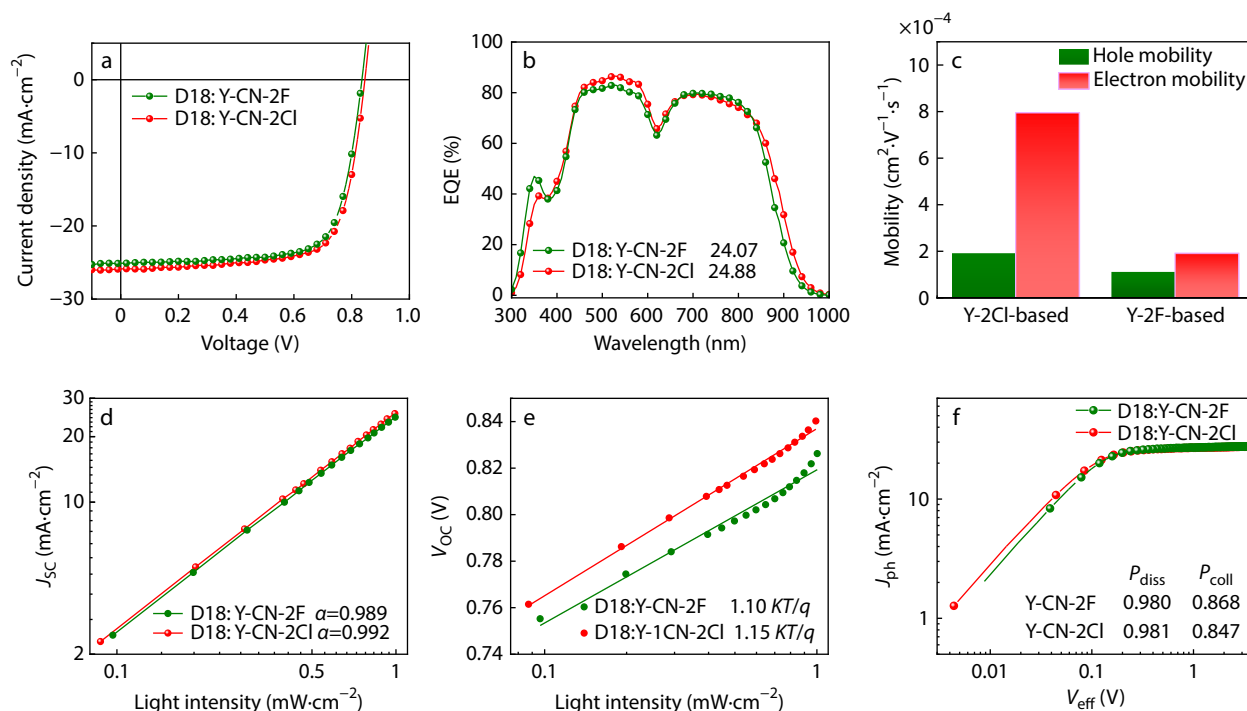


Fig. 2 (a) Current density versus voltage (J - V) curves, (b) EQE curves and (c) electron mobility and hole mobility of the OSCs based on Y-CN-2F and Y-CN-2Cl. The dependence of (d) J_{SC} and (e) V_{OC} on the light intensity. (f) J_{ph} - V_{eff} curves.

Table 2 Device performance of organic solar cells based on the active layer of D18:Y-CN-2F and D18:Y-CN-2Cl.

Active layer	V_{OC} (V)	J_{SC} ($\text{mA}\cdot\text{cm}^{-2}$)	FF (%)	PCE (%)
D18:Y-CN-2F	0.836 (0.831 $\pm$ 0.005)	25.11 (24.07) ^a (25.15 $\pm$ 0.04)	73.08 (72.70 $\pm$ 0.38)	15.33 (15.30 $\pm$ 0.03) ^b
D18:Y-CN-2Cl	0.846 (0.843 $\pm$ 0.003)	25.88 (24.88) (25.37 $\pm$ 0.21)	72.53 (72.42 $\pm$ 0.11)	15.88 (15.82 $\pm$ 0.06)

^a The integrated J_{SC} in parentheses are calculated from the EQE spectra. ^b Average PCEs in parentheses were calculated for 15 devices.

and Tables S1–S5). The devices based on Y-CN-2F provided a PCE of 15.33%, with a V_{OC} of 0.836 V, a J_{SC} of 25.11 $\text{mA}\cdot\text{cm}^{-2}$, and an FF of 73.08%. As for Y-CN-2Cl, the device achieved improvement in performance parameters, with V_{OC} increasing to 0.846 V, the J_{SC} rising to 25.88 mA, and the FF slightly decreasing to 72.53%. As a result, a PCE of approximately 16% was ultimately realized. The significant increase in J_{SC} was associated with the red-shifted absorption spectrum of Y-CN-2Cl. However, owing to its lower LUMO energy level and narrower bandgap, the higher V_{OC} is attributed to the reduced voltage loss in the Y-CN-2Cl-based device. Additionally, the external quantum efficiency (EQE) curves of both optimal devices showed a similar response range from 300 nm to 900 nm, as shown in Fig. 2(b). Notably, all the J_{SC} s from the J - V curves matched well with those integrated from the EQE curves, confirming the reliability of the device performance. Furthermore, the charge carrier mobilities were measured using the space-charge-limited current (SCLC) method in hole-only and electron-only devices (Fig. S4 in ESI),^[31] and are summarized in Fig. 2(c) and Table S6 (in ESI). The Y-CN-2Cl-based device exhibited a slightly higher hole mobility (μ_h) ($1.90\times 10^{-4} \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) and a much higher electron mobility (μ_e) ($7.60\times 10^{-4} \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) than the device based on Y-CN-2F, for which μ_h and μ_e were calculated to be 1.10×10^{-4} and $1.90\times 10^{-4} \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, respectively. It is worth noting that although the Y-CN-2Cl-based device exhibited higher mobilities, the

imbalance in the carrier mobility was also reflected in the lower FF of the device. In contrast, the Y-CN-2F-based device exhibited a more balanced carrier mobility and superior FF.

The charge recombination process of the devices based on the two acceptors was studied by measuring the dependence of J_{SC} and V_{OC} on the light intensity (P_{light}), as shown in Figs. 2(d) and 2(e). The relationship between J_{SC} and P can be described as $J_{SC} \propto P^a$. When a approaches 1, bimolecular recombination is almost negligible, leading to quick charge carrier extraction.^[32,33] The a values for the devices based on Y-CN-2F and Y-CN-2Cl were calculated to be 0.989 and 0.992, respectively, indicating the bimolecular recombination in both devices were effectively inhibited. On the other hand, the trap-assisted recombination in the devices was investigated by the relationship between V_{OC} and the light intensity (P_{light}), which follows the formula $V_{OC} \propto n(KT/q)\ln(P_{light})$, where n , q , T , and K are the ideality factor, elementary charge, temperature (K), and Boltzmann constant, respectively.^[34, 35] The slopes (kT/q) of the Y-CN-2F-based devices (1.10 kT/q) was slightly lower than that of the Y-CN-2Cl-based devices (1.15 kT/q), indicating the weaker trap-assisted recombination in the Y-CN-2F-based devices. Moreover, the charge generation and collection efficiency of the devices were calculated by measuring the photocurrent density (J_{ph}) versus the effective voltage (V_{eff})^[36] as shown in Fig. 2(f). According to the results, the value of exciton dissociation probability (P_{diss}) and charge

collection efficiency (P_{coll}) of Y-CN-2F-based devices were 97.99% and 86.82%, respectively, whereas a higher P_{diss} (98.13%) and lower P_{coll} (84.73%) were achieved in Y-CN-2CI-based devices, which is consistent with the larger energy level difference observed in Y-CN-2CI-based devices and the more balanced charge carrier mobility in Y-CN-2F-based devices.

As a powerful tool for identifying carrier lifetimes in blend

films, a time-resolved confocal imaging system comprising photoluminescence, lifetime imaging, and carrier lifetime distribution was used to investigate the hole transfer processes.^[37–39] Figs. 3(a) and 3(d) show the 2D photoluminescence (PL) excited by a 780 nm laser, revealing homogeneous PL intensities on the smooth film surface for the blend films of D18:Y-CN-2F and D18:Y-CN-2CI. The lifetime images of these films were processed by single-exponential fitting, as

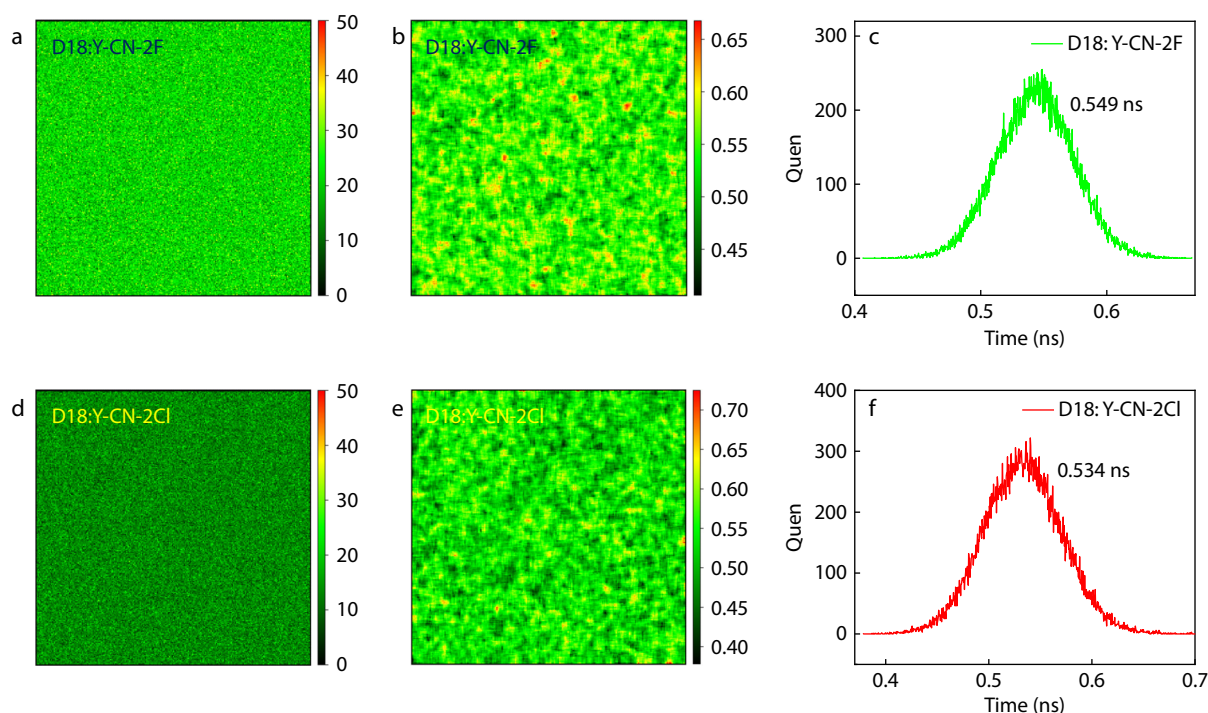


Fig. 3 The photoluminescence, lifetime imaging results and lifetime distribution of D18:Y-CN-2F (a–c) and D18:Y-CN-2CI (d–f).

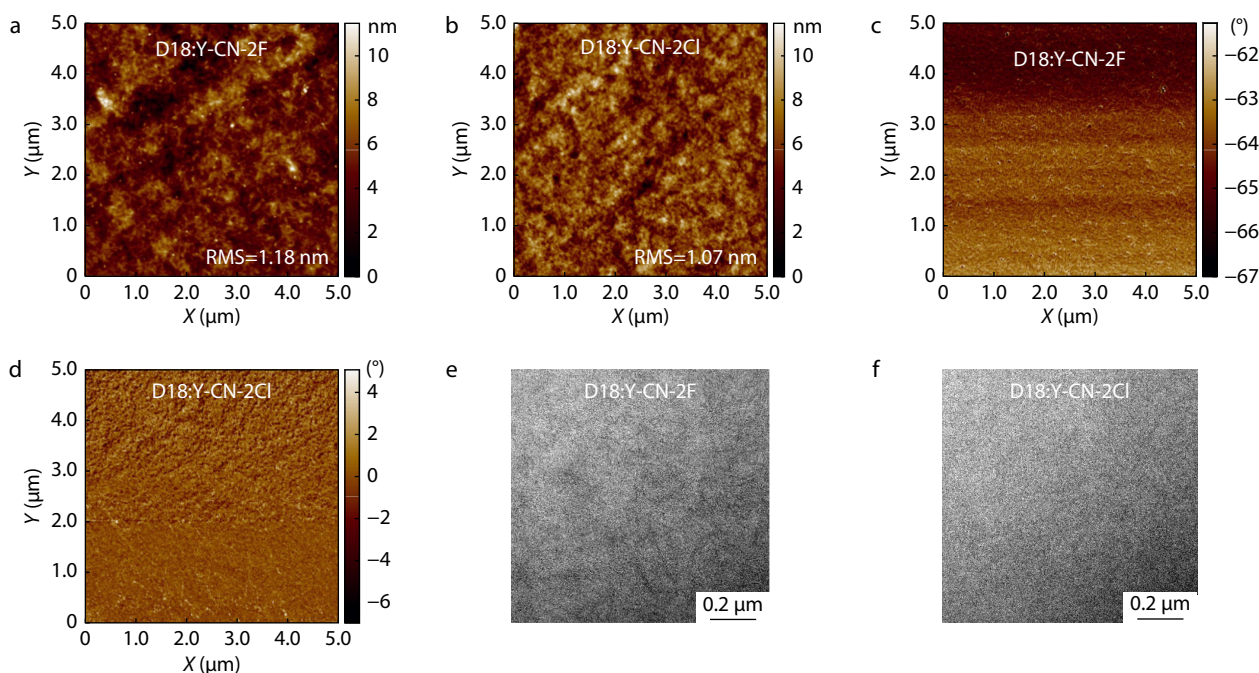


Fig. 4 AFM height images, phase images, and TEM images of blend films of D18:Y-CN-2F (a, c, e) and D18:Y-CN-2CI (b, d, f).

shown in Figs. 3(b) and 3(e), and the corresponding lifetime histograms are presented in Figs. 3(c) and 3(f). The blend film of D18:Y-CN-2Cl displayed an average lifetime of 0.534 ns, which was slightly shorter than that of D18:Y-CN-2F (0.549 ns), confirming the faster hole-transfer process in the former blend films. In addition, the electron transfer process in the blend films was explored, as shown in Fig. S5 (in ESI). According to the results, the average lifetime of blend films of D18:Y-CN-2F and D18:Y-CN-2Cl were 0.503 ns and 0.481 ns, respectively. Notably, the trend in the charge carrier lifetime for the two blend films aligns with the trend observed in their charge carrier mobility.

The film morphology evolution of blend films based on two acceptors was further explored by atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in Figs. 4(a) and 4(b), the root-mean-square (RMS) roughness were 1.18 and 1.07 nm for the blend films of D18:Y-CN-2F and D18:Y-CN-2Cl, respectively, implying a uniform and smooth surface morphology in these blend films. However, it is evident from the phase diagram (Figs. 4c and 4d) and TEM images (Figs. 4e and 4f) that more pronounced fiber-like structures are observed in the D18:Y-CN-2F blend film, which is also consistent with its higher RMS value. Notably, the fiber network structure in the active layer morphology facilitates charge transport, thereby contributing to a higher FF.

CONCLUSIONS

In summary, two asymmetric NFAs, Y-CN-2F and Y-CN-2Cl, were designed and synthesized by replacing one alkyl chain with a mesogenic unit containing an alkyl chain in the inner pyrrole position. Substitution of the terminal groups with different halogen atoms led to significant changes in the absorption spectra and energy level structures of the two acceptor molecules. Y-CN-2Cl exhibited a redshifted absorption spectrum and a lower energy level structure than Y-CN-2F. Moreover, devices based on Y-CN-2Cl displayed higher but unbalanced carrier mobility, and the lower fluorescence lifetime indicated faster carrier transfer processes in the device. On the other hand, devices based on Y-CN-2F exhibited a more balanced carrier mobility and a more pronounced fiber network structure on the active layer surface, which facilitated charge transport. As a result, Y-CN-2Cl-based devices achieved a higher V_{OC} and J_{SC} , resulting in a PCE close to 16%, whereas Y-CN-2F-based devices showed a slightly higher fill factor (FF) and a slightly lower PCE (15.33%). This study provides valuable insights into the incorporation of structural units with unique properties into Y-series acceptor molecules through asymmetric alkyl side-chain engineering.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3342-6>.

Data Availability Statement

The related data for this paper (DOI: 10.1007/s10118-025-3342-6) is available from the corresponding author upon reasonable request. The author's contact information: cwzhao114@163.com.

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