Advance Publication Cover Page



Intrinsically chemo- and thermostable electron acceptors for efficient organic solar cells

Qian-Qian Zhang, Yaokai Li, Di Wang, Zeng Chen, Yuhao Li, Shuixing Li, Haiming Zhu, Xinhui Lu, Hongzheng Chen, and Chang-Zhi Li*

Advance Publication on the web September 29, 2020 doi:10.1246/bcsj.20200231

© 2020 The Chemical Society of Japan

Advance Publication is a service for online publication of manuscripts prior to releasing fully edited, printed versions. Entire manuscripts and a portion of the graphical abstract can be released on the web as soon as the submission is accepted. Note that the Chemical Society of Japan bears no responsibility for issues resulting from the use of information taken from unedited, Advance Publication manuscripts.

Intrinsically chemo- and thermostable electron acceptors for efficient

organic solar cells

Dedicated to Professor Eiichi Nakamura on the occasion of his 70th birthday

Qian-Qian Zhang,¹ Yaokai Li,¹ Di Wang,¹ Zeng Chen,² Yuhao Li,³ Shuixing Li,¹ Haiming Zhu,² Xinhui Lu,³ Hongzheng Chen,¹ Chang-Zhi Li ^{1,*}

¹ MOE Key Laboratory of Macromolecular Synthesis and Functionalization, State Key Laboratory of Silicon Materials, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.

² Center for Chemistry of High-Performance & Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou, 310027, China.

³ Department of Physics, The Chinese University of Hong Kong, New Territories, Hong Kong 999077, P.R. China.

Email: czli@zju.edu.cn

Abstract:

The traditional excess of non-fullerene acceptors (NFAs) via Knoevenagel condensation reaction (KCR) of aldehyde and active methylene leaves the vulnerable and reversible exocyclic vinyl bonds in structures, which undermine the intrinsic chemo- and photostability of NFAs. In this work, we demonstrate the new access of acceptor-donor-acceptor (A-D-A) NFAs via Stille coupling between new electron deficient group and classic donor core in over 90% vield, wherein the robust carbon-carbon bonds, replacing the exocyclic double bonds from traditional KCR, resulting in the stable A-D-A acceptors, Q1-XF (X representing 0, 2 and 4 fluorine atoms, respectively). Among the three studied examples, Q1-4F exhibits the improved optoelectronic and electron transport properties, leading to the best photovoltaic performance with optimal charge kinetics for Q1-4F based OSCs. Overall, this strategy can direct a new way for developing the stable photovoltaic materials.

1. Introduction

With the development of non-fullerene acceptors (NFAs), organic solar cells (OSCs) have rapidly reached over 17 % power conversion efficiency (PCE) in recent years.¹⁻⁵ Though promising for the tunable optoelectronic properties of acceptor-donor-acceptor (A-D-A) NFAs,⁶⁻¹³ it is worth noting that their synthetic strategy exclusively employs the condensation of aldehyde and active methylene through Knoevenagel condensation reaction (KCR),¹⁴⁻¹⁹ leaving a vulnerable exocyclic vinyl group between the donor core and terminal acceptor group in A-D-A NFAs.²⁰⁻²⁴ These structural factors potentially undermine the intrinsic chemo- and photostability of NFAs,²⁵⁻²⁶ wherein oxygen and water can attack the vulnerable exocyclic vinyl groups between D and A units, hence accelerating the degradation of photoexcited acceptors. Meanwhile, the practice of OSCs will not be achieved without the desirable long-term photochemical stability of active components,²⁷⁻³² which are critical for determining the overall photo-to-charge conversion and stability of devices.

Besides, the condensed products from KCR exhibit the reversible reactivity under acidic or alkaline aqueous conditions, in which the vinyl group decompose back to aldehyde and methylene species.³³⁻³⁵ Researchers have also demonstrated that two exocyclic vinyl groups of neighboring molecules can yield a four-membered ring intermediate via [2+2] cvcloaddition mechanism.³⁶ The mixture of ITIC-4F and ITIC-0F can be observed in the unsymmetrical ITIC-2F:PBDB-TF blend solution after storing in glove box for 16 hours, due to the exchange and redistribution of end group via cycloaddition of the vinyl bond.³⁷ Thus, considering the long-term stabilities of OSCs, it is desirable to come up new design for NFAs by avoiding the vulnerable exocyclic vinyl groups stemming from the reversible KCRs, meanwhile remaining the advantages of A-D-A strategy in tuning optoelectronic properties of NFAs.

Herein, we have developed new access of A-D-A acceptors via Stille coupling reaction (SCR), wherein a new kind of electron deficient group, namely, indeno([2,1-b]thiophen-8-ylidene)malononitrile (A unit, IT), is applied to couple with the typical electron donating unit IDT (D unit). Therefore, O1-XF (X representing 0, 2, or 4 fluorine atoms) can be feasibly obtained in over 90% yields. The robust carbon-carbon bond linkages in the new A-D-A acceptors, replacing exocyclic double bonds from KCR, lead to the intrinsically chemo- and thermostable NFAs. The photostability and thermostability of Q1-XF films are much superior to the classic IT-4F made from KCR. Furthermore, by increasing the number of fluorine substituents at IT unit, the optoelectronic properties and electron transport of acceptors can be improved from Q1-0F, Q1-2F to Q1-4F, resulting in the best photovoltaic performance for Q1-4F:PBDT-T based OSCs. absorption Femtosecond transient (fs-TA) measurements reveal that Q1-4F exhibits the improved charge transfer and mitigated recombination in blends, hence, enhancing photovoltaic performance. Overall, this work provides a new design strategy that allows accessing stable photovoltaic materials.



Scheme 1. a) The synthetic procedures for A-D-A NFAs from traditional methods and this work; b) synthesis of Q1-XF. c) Single crystal structure and stacking model of IT-1F. d) Side-views of molecular geometry, e) isosurface of electrostatic potential, f) LUMO and g) HOMO of Q1-4F based on the DFT calculation. Reagents and conditions: (i) 3-thienyl boronic acid, Na₂CO₃ and Pd(PPh₃)₄ in THF/H₂O at 70 °C; (ii) NaOH in EtOH/H₂O, and then aqueous HCl; (iii) oxalyl chloride in DMF/CH₂Cl₂, and then with AlCl₃ in CH₂Cl₂; (iv) Br₂/CHCl₃, Na₂CO₃, 0 °C; (v) Malononitrile and CH₃COONa in EtOH at reflux; (vi) IDT-SnMe₃, Pd(PPh₃)₄ in toluene at 110 °C.

2. Results and Discussion 2.1 Synthesis and characterization

Note that the traditional method for accessing A-D-A NFAs extensively employs the KCR of aldehyde and active methylene, which yields the reactive and reversible exocyclic vinyl bonds to conjugate the terminal groups to the donor core. In this work, we develop effective and new access for A-D-A NFAs, wherein the robust carbon-carbon bonds via SCR, replacing the exocyclic double bonds, are employed to construct A-D-A NFAs, leading to the intrinsically chemo- and thermostable acceptors (Scheme 1a). The synthetic route of Q1-XF is described in Scheme 1b and the detailed information can be found in the Supporting Information (SI). Methyl benzoate derivatives 1 was employed, via Suzuki coupling with 3-thienyl boronic acid, to synthesize ester 2, then hydrolyzed to benzoic acid 3. Through the intramolecular Friedel-Crafts cyclization of compound 3, the ketone 4 is feasibly obtained. And followed by bromination of the thiophene ring, the compound 5 is synthesized and then condensed with malononitrile to yield electron deficient IT units 6 (IT0F, X₁ = X₂ = H; IT1F, X₁ = H and X₂ = F; IT2F X₁ = X₂ = F). Finally, we employed Stille coupling to obtain Q1-XF between IT and IDT with excellent yields of ~ 90%. The characterization of the chemical structure included ¹H, ¹³C and ¹⁹F nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) Mass Spectroscopy (**Figure S1**). Single crystals of IT-1F reveal the planar structure with F-substituent at meta-position (**Scheme 1c**). A π - π distance of 3.35 Å is measured for the "brick-like" stacking of IT units, which would be helpful for the intermolecular charge transportation.

Density functional theory (DFT) calculation was employed to study the molecular geometries and frontier orbitals (**Scheme 1d-g and Figure S2**). Planar molecular backbones are observed for Q1-0F, Q1-2F and Q1-4F, with the dihedral angle of 2.33°, 1.27°, and 4.39° between IT and IDT in side-view of molecular geometries, respectively. In addition, the electrostatic potential (ESP) of NFAs indicates the terminal groups with strong electronegative atoms like fluorine atoms and cyano groups have positive ESP while the conjugated thiophene surfaces have negative ESP. These results are consistent with the frontier orbital results, showing the spatial separation of HOMO and LUMO orbitals, with the down-shifted energies in the sequence of Q1-0F, Q1-2F, and Q1-4F. These results suggest that the new A-D-A acceptors with C-C bonds linkages remain planar backbones and effective conjugation among aromatic units.



Figure 1. UV-vis absorption spectra and the inserted photo images (left and right: before and after illumination) of a) Q1-4F and b) IT-4F thin films; c) The change of absorption intensity of Q1-XF and IT-4F under different aging time; d) The TGA curves of Q1-XF and IT-4F.

Q1-XF	λ_{\max}^{sol}	$\lambda_{ m max}^{ m film}$	$\lambda_{\text{onset}}^{\text{film}}$	Esol	$E_{ m g}^{ m opt}$	E homo/Lumo	$E_{ m g}$
	(nm)	(nm)	(nm)	$(\times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$	(eV) ^[a]	(eV) [b]	(eV) [b]
Q1-0F	699	727	817	5.90	1.52	-5.40/-3.78	1.62
Q1-2F	716	757	868	6.05	1.43	-5.43/-3.90	1.53
Q1-4F	716	766	888	7.42	1.40	-5.54/-3.99	1.55

Table 1. The basic photophysical and electrochemical data of Q1-XF.

^[a] Optical bandgaps are from film UV-vis absorption spectra. ^[b] Evaluated by electrochemical CV measurements.

The ultraviolet-visible (UV-vis) absorption spectra of the three acceptors in chloroform and thin film are displayed in Figure S3, and the corresponding data are summarized in Table 1. All of them possess two distinct peaks, and the small one locating at 350-550 nm may stem from the π - π * transition of the end-group. Another intense peak locating at 550-900 nm represents the intramolecular charge transfer (ICT) between the electron deficient IT and electron rich IDT units. The absorption onsets (λ_{onset}) of Q1-2F and Q1-4F are 868 nm and 878 nm, leading to narrow optical bandgaps (E_{g}^{opt}) of 1.43 eV and 1.41 eV, respectively. With the increased number of fluorine atoms, the redshift of main absorption peaks of acceptors is observed in the film samples due to the enhanced molecular aggregation. Cyclic voltammetry measurements were used to determine the energy levels of the three acceptors. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) were determined to be -3.78/-5.40 eV, -3.90/-5.43 eV, and -3.98/-5.54 eV for Q1-0F, Q1-2F, and Q1-4F, respectively. This experimental evidence indicates that the new acceptors connected with single C-C bonds possess the effective ICT between A and D units, and the fluorination of A units leads to the tunable optoelectronic properties of acceptors.

To check the stabilities of new A-D-A acceptors, a classic acceptor IT-4F with exocyclic vinyl linkage was chosen as control molecule. Photostability of neat films for Q1-XF, IT-4F and their blend films with PBDB-T polymer were tested under one sun equivalent illumination in ambient. Note that a metal halide lamp without UV filtration is employed as a light source and its light density is monitored with a silicon cell. The absorption profiles of these samples have been recorded upon the extension of illumination times. The results are depicted in Figures 1a-1c and S4-6. For neat films illuminated in ambient, the absorption profile of IT-4F decreased sharply under this harsh condition. After 10 hours, its film faded to nearly transparent, indicating the destroying of conjugation system of IT-4F. Interestingly, little change of absorption ability can be observed for Q1-XF acceptors under the same condition, indicating that Q1-XF is generally more robust than IT-4F under the same photo-aging test. Considering the major difference of molecules is at the linkage between electron deficient unit and IDT, the significant improvement of photostability for Q1-XF, can be ascribed to the merits of single C-C linkages, instead of the exocyclic C=C bonds of IT-4F. In addition, the introduction of fluorine substituents can enhance the photostability of Q1-XF. After illumination for 22 hours, the maximum absorption peak of Q1-2F and Q1-4F remained unchanged, while that of Q1-0F decreased to 70 % of its original absorption intensity. Moreover, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were applied to detect the thermal properties of Q1-XF and IT-4F. According to Figure 1d, the decomposition temperature (Td) (5% weight loss) of IT-4F is 350 °C, while for Q1-XF, the Td are generally higher than 400 °C, indicating Q1-XF exhibiting better thermal stability than IT-4F. The improvement of thermostability for Q1-XF can also be ascribed to the robust single C-C linkages, compared with the reversible exocyclic C=C bonds of ID-4F.



Figure 2. a) Schematic illustration of OSC device structure; b) Energy level diagram of Q1-XF and PBDB-T; c) J-V curves and d) EQE spectra, e) J_{sc} and (f) V_{oc} versus light intensity characteristics of the corresponding OSCs.

2.2 Photovoltaic properties

According to the optoelectronic data of Q1-XF,

we selected a wide-bandgap polymer PBDB-T to match with these acceptors, in a conventional device structure of ITO/PEDOT:PSS/active layer/PFN/Ag. The schematic device structure and energy level are shown in Figure 2a and 2b. Their photovoltaic performance and device parameters are summarized in Table 2 and Figure 2c. Q1-0F based devices exhibit relatively low PCEs of 2.75 %, with an open-circuit voltage (V_{oc}) of 0.89 V, a short-circuit current (J_{sc}) of 7.20 mA cm⁻² and a fill factor (FF) of 0.44. And devices based on Q1-2F acceptor achieve a PCE of 6.05 %, a $V_{\rm oc}$ of 0.76 V, a $J_{\rm sc}$ of 12.41 mA cm⁻² and an FF of 0.64. When increasing the number of fluorine atoms from 2 to 4, Q1-4F based devices reach the best PCE of 7.93 % among three new acceptors, wherein the slightly decreased Voc from 0.76 V to 0.72 V can be well compensated with the largely increased FF and J_{sc} values. These results indicate the relatively fine electron accepting characteristics for these robust Q1-XF molecules. In addition, the introduction of fluorine atom into these acceptors helps effectively tuning the photovoltaic parameters and stability of acceptors. The external quantum efficiency (EQE) spectra of PBDB-T:Q1-XF based OSCs are illustrated in Figure 2d. A good photoelectrical response can be observed in the brand range of 350-860 nm, which can be ascribed to the complementary absorptions of PBDB-T and Q1-XF. The calculated Jsc were 7.95, 10.75, and 14.97 mA cm-2 for Q1-0F, Q1-2F, and Q1-4F respectively, exhibiting good consistency with the experimental values from the J-V curves. The photostability of OSCs based on IT-4F and Q1-4F have been compared under continuous 1 sun equivalent illumination provided by a metal halide lamp without UV-filtration. Upon the continous illumination for 250 hours, the PCE of IT-4F based cells decreased to 30% of its original efficiency while Q1-4F based cells still maintained over 60% of its original efficiency (**SI**). Thus, Q1-XF with robust carbon-carbon bond linkage also show better device stability than that of IT-4F.

To understand the cause of varied photovoltaic performance of these acceptors, we investigated the recombination of Q1-XF based solar cells, and the function of J-V properties versus light density (Plight) is shown in Figure 2e and 2f. By fitting the curve with power-law equation $J_{\rm sc} \propto (P_{\rm light})^{\alpha}$, we found that the value of α were 0.906, 0.976, and 0.982 for PBDB-T:Q1-0F, PBDB-T:Q1-2F, and PBDB-T:Q1-4F blends correspondingly. The closer to 1 for the value of α represents the lower probability of bimolecular recombination, which demonstrates the bimolecular recombination of PBDB-T:Q1-2F and PBDB-T:Q1-4F is less than that of PBDB-T:Q1-0F. On the other hand, V_{oc} is subject to P_{light} with a slope (n) of kT/q (k is the Boltzmann constant, T is the temperature, and q is the elementary charge). As shown in Figure 2f, slopes of 1.78, 1.23, and 1.19 were obtained for the PBDB-T:Q1-0F, PBDB-T:Q1-2F, and PBDB-T:Q1-4F devices, respectively, indicating the monomolecular or trap-assisted recombination is severe in Q1-0F based devices. It could be due to the non-optimal charge generation and transportation in the Q1-0F based blend. Whereas, the slopes of 1.23 and 1.19 for PBDB-T:Q1-2F and PBDB-T:Q1-4F represent the mitigated recombination in these devices, comparing to that of PBDB-T:Q1-0F. These results suggest the fluorination of Q1-XF allow mitigating the charge recombination in the respective OSCs, hence exhibiting the improved photovoltaic performances.



Figure 3. a) 2D color plot of fs-TA spectra of PBDB-T:Q1-4F blend film. b) TA kinetics of hole transfer process

for PBDB-T:Q1-4F at indicated delay time under 725 nm excitation with a fluence below 7.25 μ J cm⁻². c) Representative TA spectra at selected delay times. Grayline: TA spectra of the neat Q1-4F film excited at 725 nm at 1 ps. d) Normalized TA kinetics of Q1-XF GSB in the blend films.

Active layer	$V_{ m oc}$	$J_{ m sc}$	FF	PCE ^[a]	$\tau_1{}^{\left[b\right]}$	$\tau_2^{\left[b\right]}$
	(V)	$(mA cm^{-2})$		(%)	(ps)	(ps)
PBDB-T:Q1-0F	0.89	7.20	0.44	$2.75~(2.55\pm 0.16)$	0.12	1.45
PBDB-T:Q1-2F	0.76	12.41	0.64	$6.05~(5.83\pm 0.12)$	0.14	4.37
PBDB-T:Q1-4F	0.73	15.63	0.69	$7.93~(7.82\pm0.10)$	0.12	6.01

Table 2. Photovoltaic parameters of OSCs under illumination of AM 1.5 G at 100 mW cm⁻²

^[a] Average PCEs with the standard deviations in parentheses from 20 devices.

^[b] τ values are from the hole transfer process of respective blends under fs-TA measurements.

2.3 Charge transportation, separation and recombination.

The charge transport properties of these blends were studied by space charge limited current method and the results are shown in Figure S7 and Table 2. Hole- and electron-only devices are fabricated with the structure of ITO/PEDOT:PSS/blend/MoO₃/Ag and ITO/ZnO/blend film/PFN-Br/Al, respectively. The hole mobilities (µh) of Q1-0F, Q1-2F, Q1-4F were 2.04×10⁻⁴, 1.41×10⁻⁴, 1.43×10⁻⁴ cm² V⁻¹ s⁻¹, while the electron mobilities (μ_e) of them were 1.36×10⁻⁵, 2.57×10⁻⁵, 3.63×10⁻⁵ cm² V⁻¹ s⁻¹. These results suggest the fluorinated Q1-XF indeed help to improve the electron transport properties of acceptors. Hence, the PBDB-T:Q1-4F showed a $\mu_{\rm h}/\mu_{\rm e}$ ratio of 3.94, which is smaller than that of PBDB-T:Q1-2F (5.49) and PBDB-T:Q1-2F (14.99). As results, due to the transportation, relatively balanced charge PBDB-T:Q1-4F blend achieved the improved FF and $J_{\rm sc}$ values, as well as PCEs, over other two blends.

Femtosecond transient absorption (fs-TA) measurement was employed to further investigate hole transfer and recombination of blend films. The results are shown in Figure 3 and Figure S8&9. Since the primary steady-state absorption peak for different acceptors and donor are well separated in spectral domain, both spectral and kinetics characteristics of hole transfer process can be extracted. A 725 nm pump pulse (below 7.5 µJ cm⁻²) was used to selectively pump acceptors without exciting donor in blends. And we, after a delay time, probe the relative transmittance change $(\Delta T/T)$ using a white light continuum. Figure 3a-b show the 2D color plot of TA spectra of PBDB-T:Q1-4F blend film and a few representative TA spectra at selected delay times, and the neat Q1-4F TA spectrum (black dashed line) for comparison. The bleach peaks at 700-800 nm appear in both neat Q1-4F film and blend film, corresponding to the combined contributions from stimulated emission (SE) and ground state bleach (GSB) of Q1-4F after photoexcitation. With the decreasing of Q1-4F bleach peak in the first 100 ps, two bleach peaks (at ~ 595 nm and ~ 645 nm), corresponding to the of PBDB-T GSB signal, emerge in the TA spectrum of PBDB-T:Q1-4F blend. As plotted in **Figure 3c**, the decay of Q1-4F matches well with the rising of PBDB-T GSB in blend film, confirming the hole transfer process from the photoexcited Q1-4F to PBDB-T. Here, the kinetics of ~608 nm was chosen to represent GSB kinetics of donor because the photoexcited QI-4F shows no signal there (**Figure 3b**). The rising kinetics of PBDB-T GSB in the blend reflect the hole transfer process, while the decay on a ps-ns time scale corresponding to the charge recombination process.³⁸

Hole transfer processes were also observed in other blends from TA spectra (Figure S8&9). The hole transfer kinetics of blend films (see Figure 3d) can be fitted by a biexponential function: i = $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, with fast and slow lifetimes of τ_1 and τ_2 and prefactors of A_1 and A_2 . As previous studies of domain size characteristics on the organic BHJ blends,^{19, 39-40} the hole transfer process consists of an ultrafast hole-transfer process at the interface, as characterized by the fast lifetime τ_1 , as well as the diffusion of excitons towards interfaces before dissociation, as characterized by the slow lifetime τ_1 .⁴¹⁻⁴² All of the fitting parameters are listed in Table S1. All the kinetics exhibit similar the fast rise account for ~ 40% with characteristic times (τ_1) for PBDB-T:Q1-0F, PBDB-T:Q1-2F, and PBDB-T:Q1-4F of 0.119, 0.141, and 0.121 ps, respectively, indicating high hole transfer rate at the polymer donor and Q1-XF acceptor interface. However, the slow rising dynamics are quite different for the three blends. The characteristic times (τ_2) are 1.446, 4.371, and 6.014 ps for PBDB-T:Q1-0F, PBDB-T:Q1-2F, and PBDB-T:Q1-4F, respectively. By comparison, the longest hole transfer time in PBDB-T:Q1-4F is probably related to the extension of the photoexcited exciton diffusion length, which is consistent with the observed fibrous aggregates in blends (discussed hereafter). More importantly, in comparison with the charge recombination rate of PBDB-T:Q1-0F, the decay dynamics in the PBDB-T:Q1-2F and PBDB-T:Q1-4F are slower, suggesting the slow hole transfer kinetics are favorable for suppressing charge recombination. These trends well agree with the improved J_{sc} and FF values in representative OSCs.



Figure 4. AFM height (a, b and c) and phase (d, e and f) images of the PBDB-T:Q1-0F film (a and d), PBDB-T:Q1-2F film (b and e), PBDB-T:Q1-4F film (c and f).

2.4 Morphology characterization.

Atom force microscopy (AFM) was conducted to examine the surface morphology of neat and blend films. The root-mean-square (RMS) surface roughness of PBDB-T:Q1-0F, PBDB-T:Q1-2F, and PBDB-T:Q1-4F were 1.16 nm, 0.916 nm, and 1.40 nm respectively. As displayed in Figure 4, relatively fine fibril-structures are observed in Q1-4F based blend films. Whereas, Q1-0F and Q1-2F based blend films exhibit large features. The characteristic results indicate that, compared with Q1-0F and Q1-2F based blend films, Q1-4F based blend film possesses more continuous carrier transport channels, resulting in better optoelectronic properties. Grazing-incidence wide-angle X-ray scattering (GIWAXS) has been performed to probe the molecular stacking and orientation of neat and blend films. The two-dimensional (2D) scattering patterns and intensity profiles in the out-of-plane (OOP) and in-plane (IP) directions are shown in Figure S10&11. All three acceptors show face-on orientation with a π - π peak in the OOP direction and lamellar peaks in the IP direction. The lamellar peak and π - π peak of Q1-4F neat film locate at q_r = 0.330 Å^{\text{-1}} (d =19.0 Å) in IP direction, and $q_z = 1.79$ Å⁻¹ (d = 3.51 Å) in OOP direction, respectively. In binary films, all the three blends exhibit lamellar peaks in IP direction and π - π stacking signal in OOP direction. Among them, the PBDB-T:Q1-4F blends display the closest π - π stacking of $q_z = 1.79$ Å⁻¹ (d = 3.51 Å) in OOP direction, with a lamellar peak at $q_r = 0.320$ Å⁻¹ (d = 19.6 Å) in IP direction, which would be benifitial for charge transport in such blend based devices.

3. Conclusion

In summary, we have demonstrated herein the new access of A-D-A non-fullerene acceptors via Stille coupling reaction in excellent yield, wherein the robust carbon-carbon bonds, replacing the exocyclic double bonds from traditional Knoevenagel condensation, are employed to conjugate electron deficient end group IT to IDT, leading to the intrinsically chemo- and thermostable acceptors. New acceptors Q1-XF (X representing 0, 2, and 4 fluorine atoms, respectively) showed better thermal stabilities upon to decomposition temperature of 400 °C, which is over 50 °C higher than that of classic A-D-A acceptor IT-4F. The photostability of Q1-XF films is also significantly improved over that of IT-4F. While IT-4F sharply decreased to transparent, little change can be found in Q1-4F films under one-sun illumination in ambient. As results, among the three studied examples, Q1-4F exhibits the improved optoelectronic and electron transport properties, leading to the best photovoltaic performance with optimal charge kinetics for Q1-4F based OSCs. Overall, we believe this design strategy can direct a new way for the development of stable photovoltaic materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was funded by the National Key Research and Development Program of China (No. 2019YFA0705900), National Natural Science Foundation of China (Nos. 21722404, 21674093, 61721005 and 21734008). C.-Z. Li thanks the support of the Zhejiang Natural Science Fund for Distinguished Young Scholars (LR17E030001).

Dedicated to Professor Eiichi Nakamura on the occasion of his 70th birthday.

References

- J. Hou, O. Inganas, R. H. Friend, F. Gao, *Nat. Mater.* 2018, 17, 119.
- C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder, X. Zhan, *Nat. Rev. Mater.* 2018, 3, 18003.
- G. Zhang, J. Zhao, P. C. Y. Chow, K. Jiang, J. Zhang, Z. Zhu, J. Zhang, F. Huang, H. Yan, *Chem. Rev.* 2018, 118, 3447.
- P. Cheng, G. Li, X. Zhan, Y. Yang, *Nat. Photo.* 2018, 12, 131.
- S. Li, C.-Z. Li, M. Shi, H. Chen, ACS Energy Lett. 2020, 5, 1554.
- X. Wan, C. Li, M. Zhang, Y. Chen, *Chem. Soc. Rev.* 2020, 49, 2828.
- Y. Lin, J. Wang, Z. G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan, *Adv. Mater.* 2015, 27, 1170.
- Z. P. Yu, Z. X. Liu, F. X. Chen, R. Qin, T. K. Lau, J. L. Yin, X. Kong, X. Lu, M. Shi, C. Z. Li, H. Chen, *Nat. Commun.* 2019, 10, 2152.
- W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, J. Am. Chem. Soc. 2017, 139, 7148.
- S. Li, L. Zhan, F. Liu, J. Ren, M. Shi, C. Z. Li, T. P. Russell, H. Chen, *Adv. Mater.* 2018, 30, 1705208.
- C. Huang, W. Fu, C. Z. Li, Z. Zhang, W. Qiu, M. Shi, P. Heremans, A. K. Jen, H. Chen, *J. Am. Chem. Soc.* 2016, 138, 2528.
- R. Qin, W. Yang, S. Li, T.-K. Lau, Z. Yu, Z. Liu, M. Shi, X. Lu, C.-Z. Li, H. Chen, *Mater. Chem. Front.* 2019, 3, 513.
- C. He, Y. Li, S. Li, Z. P. Yu, Y. Li, X. Lu, M. Shi, C. Z. Li, H. Chen, ACS Appl. Mater. Interfaces 2020, 12, 16700.
- 14. O. Inganas, Adv. Mater. 2018, 30, 1800388.
- 15. C.-C. Chueh, C.-Z. Li, A. K. Y. Jen, *Energy Environ. Sci.* 2015, 8, 1160.
- J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, Y. Zou, *Joule* 2019, 3, 1140.
- S. Li, L. Zhan, Y. Jin, G. Zhou, T. K. Lau, R. Qin, M. Shi, C. Z. Li, H. Zhu, X. Lu, F. Zhang, H. Chen, *Adv. Mater.* 2020, 32, 2001160.
- Y. Cui, H. Yao, J. Zhang, K. Xian, T. Zhang, L. Hong, Y. Wang, Y. Xu, K. Ma, C. An, C. He, Z. Wei, F. Gao, J. Hou, *Adv. Mater.* 2020, 32, 1908205.
- R. Qin, D. Wang, G. Zhou, Z.-P. Yu, S. Li, Y. Li, Z.-X. Liu, H. Zhu, M. Shi, X. Lu, C.-Z. Li, H. Chen, *J. Mater. Chem. A* 2019, 7, 27632.
- J. Guo, Y. Wu, R. Sun, W. Wang, J. Guo, Q. Wu, X. Tang, C. Sun, Z. Luo, K. Chang, Z. Zhang, J. Yuan, T. Li, W. Tang, E. Zhou, Z.

Xiao, L. Ding, Y. Zou, X. Zhan, C. Yang, Z. Li, C. J. Brabec, Y. Li, J. Min, *J. Mater. Chem. A* 2019, 7, 25088.

- 21. S. Park, H. J. Son, J. Mater. Chem. A 2019, 7, 25830.
- J. Hou, W. Ma, P. Bi, C. An, B. Gao, K. Xian, B. Lin, Y. Tang, T. Zhang, L. Hong, H. Yao, Y. Cui, *Natl. Sci. Rev.* 2020, 7, 1239.
- Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, Z. Wei, F. Gao, J. Hou, *Nat. Commun.* 2019, 10, 2515.
- S. Holliday, R. S. Ashraf, A. Wadsworth, D. Baran, S. A. Yousaf, C. B. Nielsen, C. H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C. J. Brabec, A. Salleo, J. R. Durrant, I. McCulloch, *Nat. Commun.* 2016, 7, 11585.
- H. Liu, Z. X. Liu, S. Wang, J. Huang, H. Ju, Q. Chen, J. Yu, H. Chen, C. Z. Li, *Adv. Energy Mater*. 2019, 9, 1900887.
- Y. Zhang, Y. Xu, M. J. Ford, F. Li, J. Sun, X. Ling, Y. Wang, J. Gu, J. Yuan, W. Ma, *Adv. Energy Mater.* 2018, 8, 1800029.
- 27. L. Duan, A. Uddin, Adv. Sci. 2020, 1903259.
- P. Cheng, X. Zhan, Chem. Soc. Rev. 2016, 45, 2544.
- X. Du, T. Heumueller, W. Gruber, A. Classen, T. Unruh, N. Li, C. J. Brabec, *Joule* 2019, 3, 215.
- X. Du, T. Heumueller, W. Gruber, O. Almora, A. Classen, J. Qu, F. He, T. Unruh, N. Li, C. J. Brabec, *Adv. Mater.* 2020, 1908305.
- T. Heumueller, T. M. Burke, W. R. Mateker, I. T. Sachs-Quintana, K. Vandewal, C. J. Brabec, M. D. McGehee, *Adv. Energy Mater.* 2015, 5, 1500111.
- J. Xiao, M. Ren, G. Zhang, J. Wang, D. Zhang, L. Liu, N. Li, C. J. Brabec, H.-L. Yip, Y. Cao, *Solar RRL* 2019, 3, 1900077.
- A. L. Claude F. Bernasconi, and Janie L. Zitomer, J. Am. Chem. Soc. 1985, 107, 6563.
- E. V. Dalessandro, H. P. Collin, L. G. L. Guimaraes, M. S. Valle, J. R. Pliego, Jr., *J. Phys. Chem. B.* 2017, 121, 5300.
- L. Hu, Y. Liu, L. Mao, S. Xiong, L. Sun, N. Zhao, F. Qin, Y. Jiang, Y. Zhou, *J. Mater. Chem.* A 2018, 6, 2273.
- 36. N. S. Fumio Kataoka, and Shinya Nishida, J. Am. Chem. Soc. 1980, 711.
- T. J. Aldrich, M. Matta, W. Zhu, S. M. Swick, C. L. Stern, G. C. Schatz, A. Facchetti, F. S. Melkonyan, T. J. Marks, *J. Am. Chem. Soc.* 2019, 141, 3274.
- S. Li, L. Zhan, C. Sun, H. Zhu, G. Zhou, W. Yang, M. Shi, C. Z. Li, J. Hou, Y. Li, H. Chen, J. Am. Chem. Soc. 2019, 141, 3073.
- Z.-X. Liu, T.-K. Lau, G. Zhou, S. Li, J. Ren, S. K. Das, R. Xia, G. Wu, H. Zhu, X. Lu, H.-L. Yip, H. Chen, C.-Z. Li, *Nano Energy* 2019, 63, 103807.
- D. Wang, R. Qin, G. Zhou, X. Li, R. Xia, Y. Li, L. Zhan, H. Zhu, X. Lu, H. L. Yip, H. Chen, C. Z. Li, *Adv. Mater.* 2020, 2001621.

- 41. Z. Chen, X. Chen, B. Qiu, G. Zhou, Z. Jia, W. Tao, Y. Li, Y. M. Yang, H. Zhu, *J. Phys. Chem. Lett.* 2020, 11, 3226.
- 42. Z.-P. Yu, X. Li, C. He, D. Wang, R. Qin, G. Zhou, Z.-X. Liu, T. R. Andersen, H. Zhu, H. Chen, C.-Z. Li, *Chin. Chem. Lett.* 2020, 31, 1991.