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An oxygen heterocycle-fused fluorene based non-fullerene acceptor for high efficiency organic solar cells†

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A new acceptor–donor–acceptor (A–D–A) small molecule acceptor, named FCO-2F, is designed and synthesized based on the previous acceptor F-H. By inserting an oxygen atom into the backbone of F-H and fluorination on the end group, FCO-2F shows a much red-shifted absorption compared with F-H, and also a wider absorption up to 830 nm. Using polymer PM6 as the donor, the organic solar cell (OSC) devices based on FCO-2F offer a power conversion efficiency (PCE) of 13.36%, with a much improved short circuit current (J_{sc}) of 20.90 mA cm^{-2}.

Introduction

Organic solar cells (OSCs) have continuingly received increasing attention in recent years, owing to their advantages of low cost, light weight and flexibility.[1–3] Presently, the power conversion efficiencies (PCEs) of OSCs based on non-fullerene acceptors have reached impressive values of 16–17%.[4–18] Most of the successful non-fullerene acceptors have an acceptor–donor–acceptor (A–D–A) structure,[19–27] which has some intrinsic advantages including finely tunable energy levels, absorption and charge mobilities.[28,29] Although impressively high PCEs have been achieved, the performance of OSCs still lags behind that of inorganic solar cells such as silicon or perovskite cells.[30,31] But many theoretical studies have indicated that there is still large room to further enhance the performance of OSCs,[32] and one of the reasons is the wide chemical structure versatility of organic materials.

It is intuitive to have as wide and efficient light absorption as possible for the active materials before considering other factors. Indeed, great effort has been made to broaden the absorption spectra of active materials,[33–35] aiming to improve the short circuit current (J_{sc}) of OSCs for overall high performance. One of the features for the A–D–A type of molecules is that their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are mainly decided by their corresponding central "D" and "A" units/groups.[36] This offers very convenient access to tune their HOMO/LUMO and absorption by modifying the central "D" unit and/or the end group "A" unit, either individually or together. In addition, the central "D" unit also plays an important role for forming suitable molecular packing and morphology. There are several effective methods applied to modify the donor D unit to achieve red-shifted absorption, such as extending the conjugation length,[24,25,33,37–44] changing the π bridge blocks,[45–49] and inserting oxygen into the backbone.[35,50–53] Among them, the method of inserting oxygen into the backbone could tune the HOMO energy level and give a further extended spectral response in the near-infrared region,[54] together with a fine-tuned intermolecular interaction for possible morphology optimization.[52,55] In most cases, this approach usually offers an increased J_{sc} and thus an improved PCE. In addition, great efforts have also been devoted to exploring new end groups, with the purpose of fine-tuning the "A" unit and LUMO.[56–61] Nowadays, halogen substitution on the widely used indanone end group (INCN)[62,63] has been intensively applied to adjust the LUMOs for a red-shifted absorption.[22,24,38,64,65]

In our previous work, we have designed an acceptor named FDICTF (F-H),[66] with a PCE of 10.06% when combined with the donor PBDB-T. The absorption onset of F-H is 760 nm, clearly too low for a high performance OPV material based on the theoretical works.[16,67] As discussed above, inserting oxygen into the backbone would cause a red-shifted absorption to obtain high J_{sc}. With these in mind, we design and synthesize FCO-2F with oxygen inserted in the backbone and a difluoro substituted end group (Fig. 1). Indeed, FCO-2F has a red-shifted absorption, with an absorption onset of 830 nm. Using PM6 as the donor, the OSC devices based on PM6:FCO-2F exhibit a PCE of 13.36%, with a J_{sc} of 20.90 mA cm^{-2}, much higher than F-H (PCE of 10.06% and J_{sc} of 15.81 mA cm^{-2}).[66]

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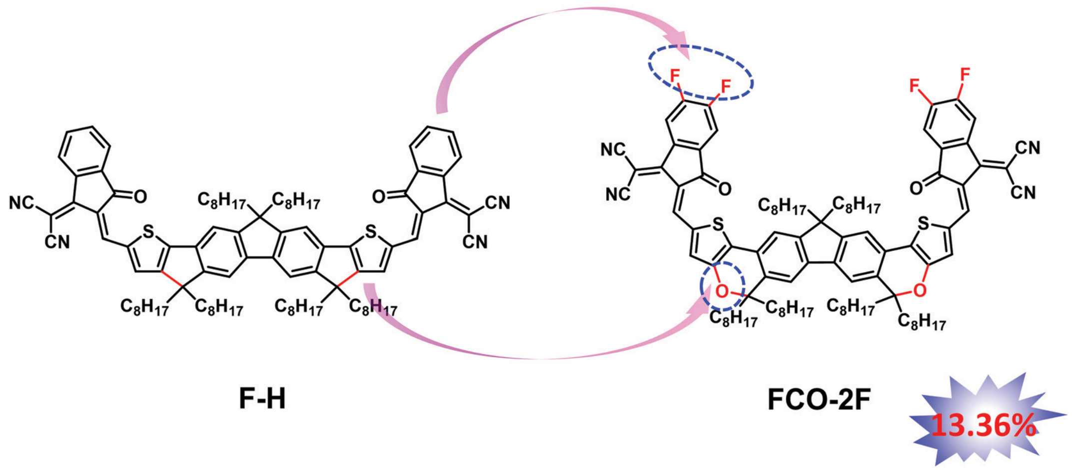


Fig. 1 Chemical structures of FCO-2F and F-H.

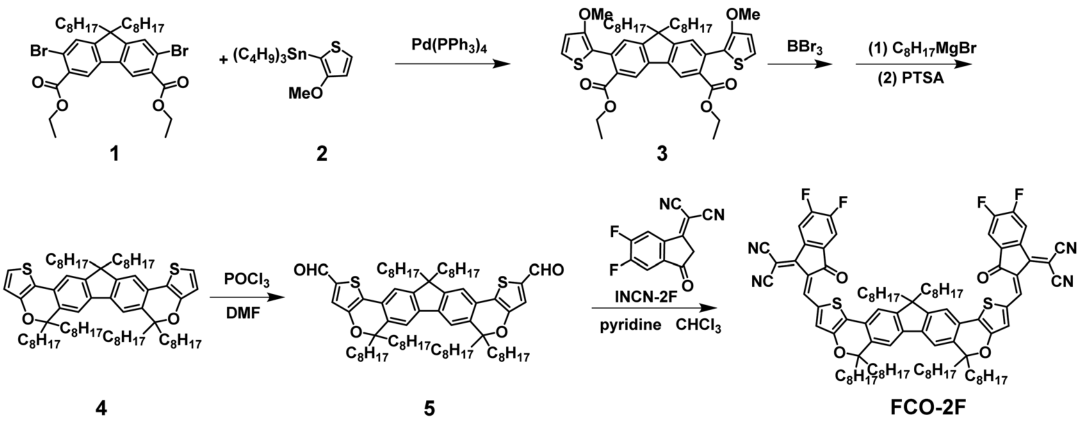
Results and discussion

The synthetic route of FCO-2F is shown in Scheme 1. The detailed procedures and characterization are summarized in the ESI.† This new molecule exhibits good solubility in common organic solvents, such as dichloromethane, chloroform and chlorobenzene. From the thermogravimetric analysis (TGA) curve in Fig. S1 (ESI†), the decomposition temperature (T_d) with 5% weight loss of FCO-2F is 307 °C, indicating its good thermal stability.

Theoretical calculation was carried out using density functional theory (DFT) at the B3LYP/6-31G* level to study its chemical geometry and molecular frontier orbitals. FCO-2F presents a nearly flat conformation similar to F-H (Fig. 2), indicating that the introduction of oxygen atoms into the backbone almost has no influence on the chemical geometry of the molecular backbone. The theoretically calculated HOMO/LUMO results of FCO-2F are −5.50/−3.48 eV. Compared with the theoretically calculated HOMO/LUMO results of F-H (−5.56/−3.30 eV),[61] the up-shifted HOMO level of FCO-2F is caused by the improvement of electron donating ability of the central core, while the down-shifted LUMO level is due to the difluoro substituted end group. These calculated results from DFT are in accordance with the experimental data discussed below.

As shown in Fig. 3a, in chloroform solution, FCO-2F has a clear red-shifted maximum absorption peak at 703 nm compared with that (665 nm) of F-H. Compared with the solution spectrum, the as-cast film of FCO-2F displays a significant red-shift of 53 nm with the maximum absorption peak at 756 nm and also a wide absorption range from 550 to 850 nm. This indicates that a more ordered aggregation is formed in the film. After thermal annealing (TA), the absorption peak of the FCO-2F film shows again an 18 nm red-shifted absorption with the absorption peak located at 774 nm. Furthermore, its absorption onset moves down to 830 nm, achieving a broader absorption spectrum than that of F-H (760 nm).

The energy levels of FCO-2F were measured by electrochemical cyclic voltammetry measurements in dichloromethane solution (Fig. S2, ESI†). The HOMO/LUMO levels for FCO-2F were estimated to be −5.37 and −3.78 eV, respectively. Compared with that (−5.43/−3.71 eV) of F-H,[66] the HOMO level of FCO-2F is up shifted and the LUMO level is down shifted, which results in a narrower bandgap as expected. These results are consistent with the calculated results discussed above.



Scheme 1 Synthetic route of FCO-2F.

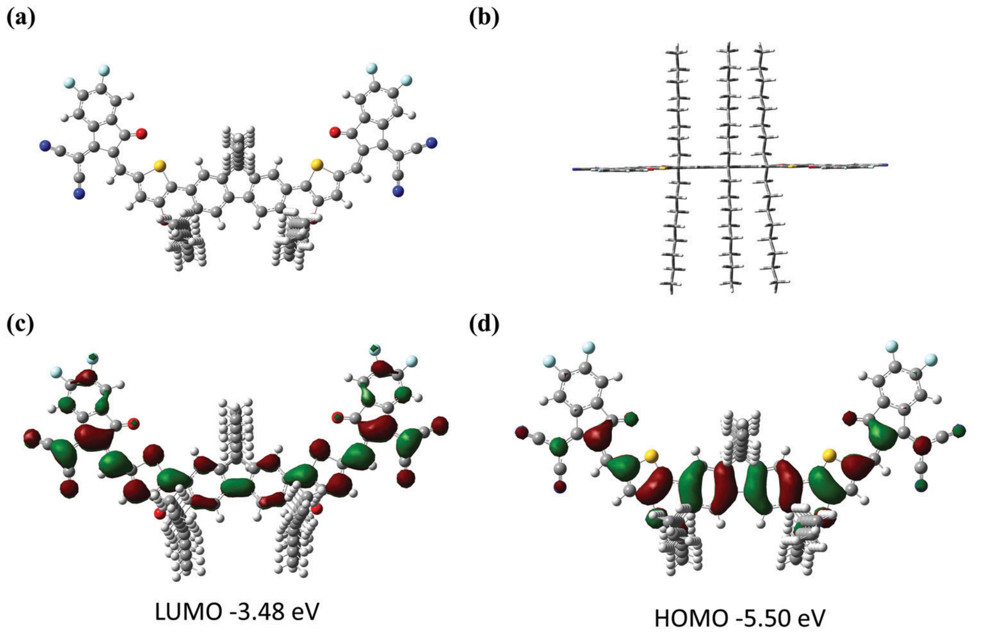


Fig. 2 The optimized geometries for FCO-2F from (a) top view and (b) side view. (c and d) Theoretical density distribution for the frontier molecular orbits of FCO-2F. All calculations were carried out using Gaussian 16.[68]

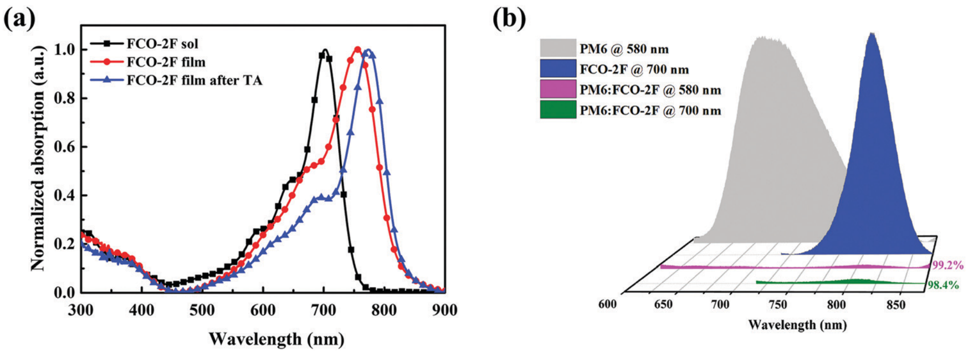


Fig. 3 (a) Normalized absorption spectra of FCO-2F in chloroform solution, its as-cast film and TA annealed film. (b) PL spectra of pure PM6, FCO-2F and the PM6:FCO-2F blend.

To evaluate the exciton dissociation efficiencies in the blend film, photoluminescence (PL) quenching tests of the pure films and blend film were measured (Fig. 3b). When excited at a wavelength of 580 nm, the PL emission peak of PM6 appears in the range of 650–850 nm. For the blend film of PM6:FCO-2F, the emission was quenched by 99.2%. When excited at a wavelength of 700 nm, the emission peak of FCO-2F was in the range of 750–850 nm. For the blend film, the emission was effectively fluorescence quenched by 98.4%. These results imply that efficient charge transfer could happen between PM6 and FCO-2F.

To assess the photovoltaic properties of FCO-2F, OSC devices were fabricated with an inverted device structure of indium tin oxide (ITO)/ZnO/PFN-Br/active layer/MoO_x/Ag. In consideration of the matched energy levels and complementary absorption with the acceptor, polymer PM6 was selected as the donor. The detailed results for device optimization are provided in the ESI† (Tables S1 and S2). The optimized photovoltaic parameters of FCO-2F together with those for F-H as a comparison are summarized in Table 1, and the corresponding J–V characteristics are shown in Fig. 4a. With the optimal weight ratio of donor and acceptor of 1 : 1, the devices based on PM6:FCO-2F with thermal annealing (TA) at 120 °C for 10 min show a PCE of 13.36%, with a high J_{sc} of 20.90 mA cm^{-2} and FF of 72.3%.

The external quantum efficiency (EQE) is measured and shown in Fig. 4b. The devices based on PM6:FCO-2F can reach a maximum EQE value of 85% and show a broader photo-to-current response range of 300–830 nm than that of F-H. The integrated current density for the FCO-2F device is 20.33 mA cm^{-2}, which is in good agreement with the J_{sc} values in the J–V measurement and a deviation of within 5%.

The charge generation and recombination behavior in the optimal PM6:FCO-2F based device were investigated. The photocurrent (J_{ph}) *versus* the effective applied voltage (V_{eff})

Table 1 Optimal device parameters of the FCO-2F based and F-H based devices under the illumination of AM 1.5G (100 mW cm^{-2})

BHJ layer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE[a] [%]
PM6:FCO-2F	0.884	20.90	72.3	13.36 (13.14)
PBDB-T:F-H[b]	0.940	15.81	66.0	10.06 (9.81)

[a] The average PCE was obtained from 10 devices, and the average results are provided in parentheses. [b] Data are obtained from ref. 66.

curve is shown in Fig. 4c. When V_{eff} reaches $\sim$2 V, the J_{ph} value reaches saturation (J_{sat}), indicating that charge recombination is minimized at higher voltage. The value of J_{ph}/J_{sat} could reflect the exciton dissociation probability in the device.[69] Under the conditions of short circuit, the J_{ph}/J_{sat} ratio for the FCO-2F based device is 96.2%, implying that the high exciton dissociation and charge collection have high efficiencies and also consistent with the high FF. The light-intensity (P) dependence of J_{sc} was also measured to further study the charge recombination properties in the device using the power-law equation $J_{sc} \propto P^{\alpha}$ (Fig. 4d). The high α value of 0.929 for the device PM6:FCO-2F indicates that the bimolecular recombination that occurred in the optimal device is very weak.

The charge mobility of the blend film was measured by the space-charge-limited current (SCLC) method (Fig. S3, ESI†). The PM6:FCO-2F photoactive layer shows a hole mobility of 3.26×10^{-4} cm^{-2} V^{-1} s^{-1} and an electron mobility of 1.37×10^{-4} cm^{-2} V^{-1} s^{-1}, both are higher than those of the F-H based device (3.37×10^{-5}/2.40×10^{-5} cm^{-2} V^{-1} s^{-1}).[70]

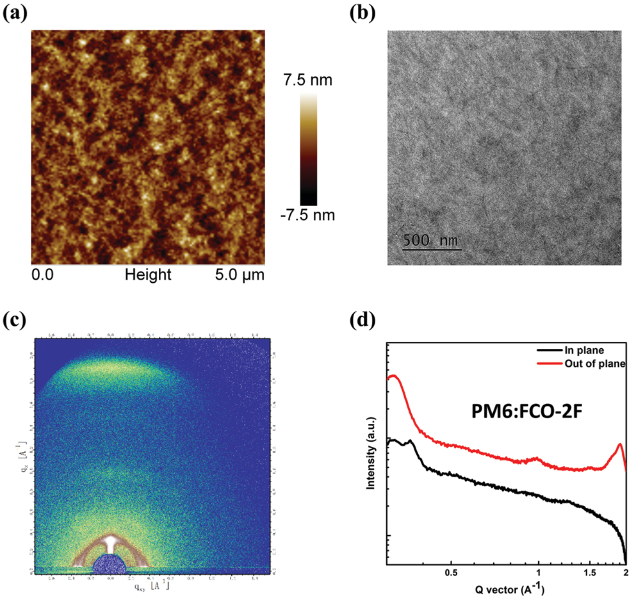


Fig. 5 (a) AFM and (b) TEM images of the PM6:FCO-2F blend film. (c) GIWAXS pattern for the PM6:FCO-2F blend. (d) In-plane and out-of-plane line cuts of the corresponding GIWAXS pattern.

The atomic force microscopy (AFM) and transmission electron microscopy (TEM) measurements were taken to study the morphologies of a PM6:FCO-2F blend film. As shown in the AFM image in Fig. 5a, the PM6:FCO-2F film shows good

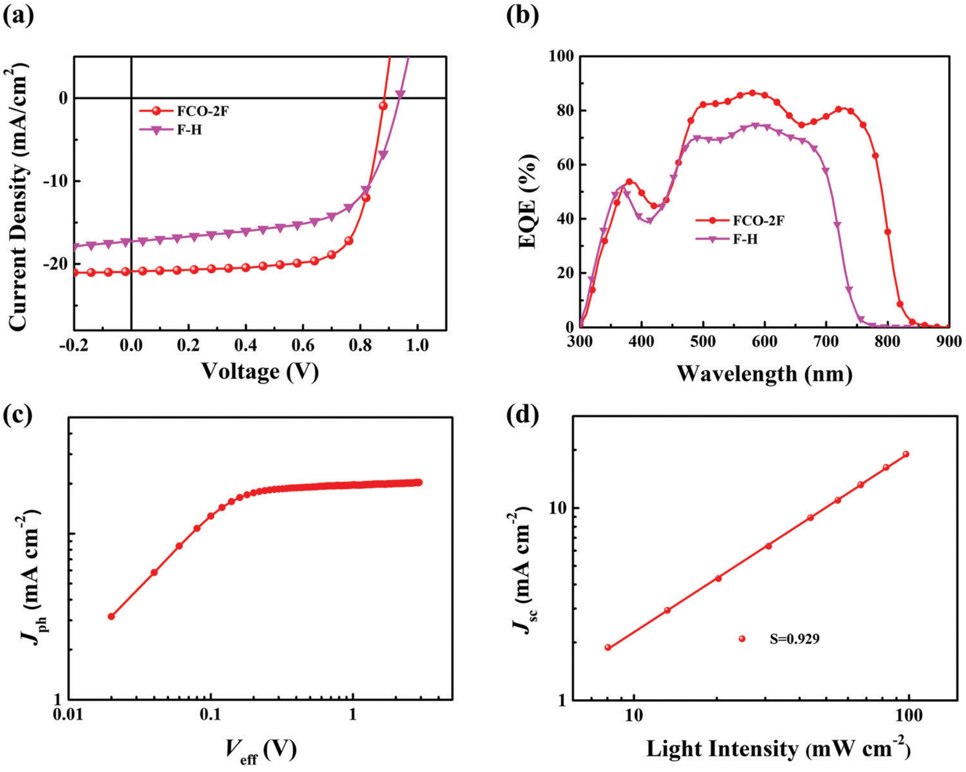


Fig. 4 (a) Optimal current density–voltage (J–V) curve of the device. (b) EQE spectra of devices at optimized conditions. (c) J_{ph} *versus* V_{eff} and (d) light intensity (P) dependence of J_{sc} for the optimized FCO-2F based devices.

miscibility of donors and acceptors with a small root-mean-square surface roughness value of 1.82 nm, which is similar to that of the F-H based film (1.69 nm shown in Fig. S4, ESI†). Furthermore, as shown in the TEM image in Fig. 5b, the PM6:FCO-2F film has obvious fiber-like interpenetrating network nanostructures, indicating an optimal morphology of the donor and acceptor mixture as that for F-H. To have a further understanding of molecular packing and morphology in the FCO-2F based active layer, the grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis was carried out. As shown in Fig. S5 in the ESI,† in the pristine film, FCO-2F shows a weak differentiation peak, while after TA, the differentiation peak becomes stronger. These indicate that there is increased ordered packing after TA. In the out-of-plane (OOP) direction, FCO-2F shows a pronounced π–π stacking diffraction peak (010) at 1.93 $Å^{-1}$ with the π–π stacking distance of 3.25 Å. In the in-plane (IP) direction, an obvious laminar packing diffraction peak (100) at 0.36 $Å^{-1}$ could be seen. These results indicate that the FCO-2F film prefers a face-on crystalline orientation. In the binary blending film of PM6:FCO-2F (Fig. 5c), a clear face-on diffraction peak is located at 1.88 $Å^{-1}$ in the OOP direction, corresponding to a π–π stacking distance of 3.33 Å. The crystal coherence length (CCL) for PM6:FCO-2F is calculated from the Scherrer equation ($\mathrm{CCL} = 2\pi k/\mathrm{fwhm}$)[71] and has the value of 44.8 Å. The shorter π–π stacking distance and the face-on molecular orientation of the PM6:FCO-2F blend film are clearly in line with its much higher electron mobility.

Conclusions

In conclusion, an A–D–A small molecule acceptor FCO-2F with inserted oxygen in the backbone of F-H and a difluoro substituted end group was designed and synthesized. FCO-2F demonstrates a much red-shifted absorption with an absorption onset of 830 nm. By blending with polymer donor PM6, the OSC devices based on PM6:FCO-2F exhibit a PCE of 13.36%, one of the highest efficiencies for oxygen heterocycle-fused non-fullerene acceptors. A much improved J_{sc} of 20.90 mA cm^{-2} is achieved due to the red-shifted absorption, which is much higher than the J_{sc} of 15.81 mA cm^{-2} for F-H based devices. Considering the absorption spectrum of this kind of oxygen heterocycle-fused acceptor is still not red-shifted enough, more efforts should be put into the absorption modification to harvest more light and further improve the performance of OSCs.

Conflicts of interest

The authors declare no conflict of interest.

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