# Concurrently Improved J<sub>sc</sub>, Fill Factor, and Stability in a Ternary Organic Solar Cell Enabled by a C-Shaped Non-fullerene Acceptor and Its Structurally Similar Third Component

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**ABSTRACT:** A ternary strategy is recognized as a promising approach that enjoys both the simplicity of fabrication conditions and potential to improve performance in organic solar cells. Herein, a C-shaped narrow band gap non-fullerene acceptor GL1 with a  $C_{2v}$  symmetry based on a new core was designed and synthesized. A power conversion efficiency (PCE) of 11.43% was achieved by employing PBDB-T:GL1 as an active layer to fabricate photovoltaic devices. To further promote photovoltaic performance, following a similar-structure prescreen principle, a middle band gap acceptor F-2Cl with the same backbone shape, side-chain distribution, and dipole moment orientation as GL1 was introduced as the guest acceptor into the active layer. Thus, benefiting from the collaboration of complementary absorption, cascade energy levels, and well-modified microstructure of the active layer, a 13.17% PCE was obtained with concurrently elevated  $J_{scr}$  fill factor, and stability for the



optimized ternary device. This work presents a successful example of prescreening the third component to simplify the workload for a high-performance ternary device.

KEYWORDS: ternary strategy, similar structure, prescreen, energy transfer, organic solar cells

# INTRODUCTION

The past few years have witnessed a continuous breakthrough of organic solar cells (OSCs), thanks to their exceptional excellence, like low cost, flexibility, and translucency.<sup>1-5</sup> Tremendous progress in this area has been made with the design of innovative materials of active layers and device engineering.<sup>6–10</sup> PCEs over 18% have been achieved with bulk heterojunction (BHJ) architecture.<sup>11–15</sup> The donor and acceptor diversity is the basis for the blossoming of OSCs. Among them, A-D-A type molecules have been proved as promising candidates due to their excellent and unique properties.<sup>16,17</sup> So far, lots of A-D-A type donors and acceptors have been designed and achieved exciting device performances.<sup>5,6,18</sup> Among them, Y6 derivatives and some other molecules like FUIC with C-shaped backbones and  $C_{2v}$ symmetric structures have shown great success and continuously boosted tremendous improvement of OSCs as acceptors.<sup>19–23</sup>

In the OSCs with the BHJ structure, the active layer is generally made up of a donor and an acceptor, namely, binary OSCs. However, there are still some challenges in such systems, i.e., (1) the absorption of most binary devices still misses a large fraction of the whole sunlight spectrum and thus end up with a limited photocurrent, (2) it is hard to precisely control the interpenetrating networks and regulate the miscibility of materials and the phase separation scale, and (3) getting suitable energy level trade-off and charge transfer channel to minimize the energy loss is a difficult task.<sup>24-28</sup> Fabricating ternary devices is an effective and facile approach to settle the above drawbacks. The corresponding ternary solar cell can deliver a clear improvement with the incorporation of the proper third component. For example, Chen et al. optimized domain sizes by using two homologous acceptors Y6 and BTP-M and achieved an enhanced external quantum efficiency and thus high PCEs.<sup>29</sup> Zhang's group systematically modulated the content of the third component MF1 in the PM6:Y6 blend and synergistically improved the efficiencies of photon harvesting, exciton dissociation, and charge transport.<sup>30</sup> Zhan's group demonstrated an outstanding ternary system

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## Scheme 1. Synthetic Route of GL1



Figure 1. Chemical structures of (a) PBDB-T, (b) GL1, and (c) F-2Cl. (d) UV-vis absorptions of PBDB-T, GL1, and F-2Cl. (e) Energy-level diagrams.

with improved phase purity, enhanced charge mobilities, and reduced monomolecular recombination with the incorporation of PC<sub>71</sub>BM as the third component.<sup>31</sup> Li's group delivered a PCE of 17.52% and got simultaneously increased  $V_{oc}$   $J_{sc}$ , and FF by introducing C8-DTC as the guest acceptor.<sup>32</sup>

For the ternary device fabrication and optimization, the majority of the work still depends on the tedious trial and error screening by means of device fabrication, with only few general rules such as absorption complementarity and energy levels matching. In this study, we report that the third component of a ternary device can be effectively preselected using a molecular structure similarity strategy, i.e., the third acceptor component with a high degree of similarity of the skeleton shape, planarity, side chain distribution, and dipole moment orientation might be the good candidate in the ternary device. First, we designed a new non-fullerene acceptor named GL1, of which the optical band gap is 1.28 eV. Different from FUIC, a similar C-shape molecule that Zhan's group<sup>23</sup> reported in 2019, GL1 holds a shorter conjugate backbone. Thus, some significant differences would be expected. First, their curvatures of the backbone would be different. Also, the relative orientation of the side chains and the terminal groups would

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Tabl	le 1	. A	bsorption	Parameters	and	Energy	Level	s of	GL1,	PBDB-T,	and	F-2C	I
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comp	$\lambda_{\max}^{CF}$ (nm)	$\lambda_{\max}^{ \text{film}} (\text{nm})$	$\lambda_{edge}^{ ext{ film }}(nm)$	HOMO (eV)	LUMO (eV)	$E_{g}^{CV}$ (eV)	$E_{\rm g}^{\rm opt}$ (eV)
GL1	817	846	965	-5.40	-3.83	1.57	1.28
PBDB-T	620	626	680	-5.33	-3.53	1.80	1.82
F-2Cl	688	732	785	-5.76	-3.91	1.85	1.58

be different. All these would impact their stacking behaviors in the solid state, including the active layer morphology and dipole moment property. When selecting PBDB-T whose band gap is relatively wide as the donor to fabricate the device, a PCE of 11.43% with a  $V_{\rm oc}$  of 0.761 V,  $J_{\rm sc}$  of 22.59 mA cm<sup>-2</sup>, and an FF of 66.5% of a PBDB-T:GL1-based device was exhibited. Then, employing the above molecular structure similarity strategy together with the cascade energy level and complementary absorption principle, F-2Cl became a promising candidate of the third component. After device optimization, the ternary device demonstrated a PCE of 13.17% with the concurrently elevated  $J_{sc}$  of 24.63 mA cm<sup>-2</sup>, FF of 70.7%, and stability compared with the binary device. These results provide a successful avenue for simplifying the prescreening of the third component for high-performance ternary devices.

# RESULTS AND DISCUSSION

**Synthesis and Characterization.** GL1 is synthesized by a series of classical reactions as shown in Scheme 1 with tributyl(thiophene[3,2-b]thiophen-2-yl)stannane 1 and 2-bromothiophene[3,2-b]thiophen-3-carboxylate 2 as starting molecules, followed by two successive Stille couplings and intramolecular Friedel–Crafts acylations (catalyzed by two different protic acids). Dialdehyde 8 is a red solid obtained by the Vilsmeier–Haack formylation reaction. The final product GL1 was obtained through the condensation reaction between compound 8 and fluorinated 2-(2,3-dihydro-3-oxo-1*H*-inden-1-ylidene)propanedinitrile (INCN-2F) as a dark green solid (Figure 1b). Detailed synthesis procedures can be found in the Supporting Information. GL1 displays good thermal stability. The mass loss at 362 °C was only 5% by thermogravimetric analysis (Figure S1).

The UV-vis absorption spectrum of GL1 is shown in Figure 1d. The absorption of it when in film covers a wide range of 600-1000 nm with an onset wavelength of 965 nm, corresponding to a narrow band gap of 1.28 eV. Its maximum absorption peak is located at 817 nm in solution, where the molar extinction coefficient is 7.67  $\times$   $10^4~M^{-1}~cm^{-1}$  (Figure S2), which redshifted to 846 nm in solid film. Compared with the dispersed state of mono-molecule in dilute solution, GL1 in solid has an obvious red shift peak and stronger shoulder peak with a broadening spectrum, which indicates that there is an effective interaction between molecules. When the electrochemical energy levels of GL1 was investigated by cyclic voltammetry (Figure S3), the HOMO and LUMO levels of the film were -5.40 and -3.83 eV, respectively, with the energy levels of Fc/Fc + as the internal standard and calculated according to the measured oxidation and reduction potential. Electrochemical and optical data are summarized in Table 1.

**Photovoltaic Device Performance.** To evaluate the potential of GL1 as a photovoltaic acceptor, we paired it with PBDB-T because their absorption ranges are complementary and their electrochemical energy levels are matched. When the OPV device adopted an inverted structure (Figure 2a), that is, ITO is the cathode, Ag is the anode, PFN-Br

modified ZnO is the cathode modification layer, and  $MoO_x$  is the anode modification layer, the device obtained a PCE of 11.43%. The corresponding parameters are as follows: the  $V_{oc}$ is 0.761 V,  $J_{sc}$  is 22.59 mA cm<sup>-2</sup>, and FF is 66.5% (Figure 2b). For more details of device fabrication, see the Supporting Information.

The ternary strategy is a prevailing method and can often cover the shortage of the binary system and bring new improvements. Our group's previous work reported an acceptor named F-2Cl<sup>33</sup> (Figure 1c), whose maximum absorption peak is at 732 nm (in the film), which just makes up for the absence of light absorption around 730 nm in the PBDB-T:GL1 system (Figure 1d). Also, the three arrange in a cascade, so the gradient arrangement has the advantage of transferring charge from the donor to the acceptor. At the same time, the performance of the PBDB-T:F-2Cl device is eye-catching, mainly reflected in the parameter FF, which reflects the morphology condition of the active layer. (Figure S4). The external quantum efficiency (EQE) response at the range from 500 to 800 nm in PBDB-T:F-2Cl-based cells that need to be improved in the PBDB-T:GL1 system is relatively high (Figure S5). Accordingly, F-2Cl is a potential third component that can effectively improve the performance of the PBDB-T:GL1 system. Theoretical calculations are carried out to further verify its suitability.

Herein, we use density functional theory (DFT) to calculate the molecular geometry, frontier molecular orbitals, and dipole moment of GL1 and F-2Cl. The information of the calculation method, basis set, and polarization function can be expressed as B3LYP/6-31G(d, p). In order to simplify the calculation, we replace all the long alkyl chains with methyl groups, which will have negligible effect on the fundamental properties we are evaluating above. As we all know, the shape of the molecules, including the planarity and curvatures of the backbone, will directly affect their aggregation and accumulation behavior in the active layer and impact the phase separation and morphology further.<sup>34–36</sup> As shown in Figure 2g, GL1 and F-2Cl both adopt a high degree of coplanar backbone in favor of efficient  $\pi - \pi$  packing and electron mobility. The conformation of GL1 and F-2Cl is C-shaped because both end groups are arranged on one side of the long axis along the backbone of the molecular skeleton, which corresponds to the symmetric properties of C<sub>2V</sub>. This is the same with the recently popular Y6 derivatives and different from the earlier S-shaped symmetric equivalents such as ITIC and 6TIC, which exhibit a  $C_{2h}$  symmetry.<sup>37</sup> There are six side chains of two kinds connected to the skeleton of both GL1 and F-2Cl, evenly on both sides of the plane; two of them are on the central  $sp^{3}$  C, and the other four are attached to the two sp<sup>3</sup> C close to the terminal group and on the other side of long axis opposite the above two. The high degree of similarity of the skeleton shape, planarity, and side chain distribution are expected to promote good compatibility of the two acceptors, which is further confirmed and supported by the contact angle measurement and morphology results discussed below.



Figure 2. (a) Structure of devices; (b) J-V curves of the devices under the illumination of AM 1.5G; (c) UV-vis-NIR absorptions of PBDB-T:GL1 blend film and ternary blend film (d) EQE spectra of the devices; (e) EQE offset ( $\Delta$ EQE) between ternary and binary devices; (f) PCE distributions counted by 10 devices. (g) Optimized geometries and dipole moment of GL1 and F-2Cl by theory calculation.

Interfacial interaction between materials in the active layer, which mainly depends on the interaction of frontier molecular orbitals (FMO), plays a key role in the process of efficient transformation of excitons and charge separation.<sup>38</sup> With these, we calculated electron-state density distributions in FMO

(Figure S6). LUMO and HOMO distributions of the two molecules are also extremely similar. HOMO and LUMO levels are calculated to be -5.16/-3.39 and -5.73/-3.53 eV for GL1 and F-2Cl, respectively, which are listed in Table S1. The dipole moments of the ground and first excited states

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## Table 2. Device Performance Parameters of Optimized Devices



Figure 3. (a)  $J_{ph}$  vs  $V_{eff}$  (b) PL spectra of PBDB-T neat film and binary and ternary blend films. (c, d)  $J_{sc}$ ,  $V_{oc}$  vs light intensity. (e) Transient photovoltage and (f) transient photocurrent measurements of the binary device and ternary device.

caused by C-shaped conformation beneficial to reinforce intermolecular interaction were calculated at the same time. For both GL1 and F-2Cl, their ground state dipole moments  $(\mu_{\alpha})$  adopt the direction that is parallel to the molecular plane and perpendicular to the molecular long axis. However, their excited state moments  $(\mu_e)$  are both parallel to the molecular plane but along the molecular long axis (Figure 2g). The calculated  $\mu_o/\mu_e$  values are 1.41/9.95 and 0.26/7.97 D for GL1 and F-2Cl, respectively (Table S1). Thus, their dipole moment change ( $\Delta \mu_{ge}$ ) values for excitation can be calculated following the formula  $\Delta \mu_{ge} = [(\mu_{gx} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ey})^2]$  $(\mu_{\rm ez})^2]^{1/2}$ , where  $\mu_{\rm gx}$ ,  $\mu_{\rm gy}$ , and  $\mu_{\rm gz}$  are the components along the x, y, and z axes of the ground state dipole moment, respectively. Similarly,  $\mu_{\rm ex},~\mu_{\rm ey}$  and  $\mu_{\rm ez}$  are the components of the coordinate axis of the excited state dipole moment. Therefore,  $\Delta \mu_{ge}$  for GL1 is 10.04 D, and for F-2Cl is 8.00 D, both values are relatively large, which means that the two molecules may produce more polarized excitons in the system and the electron-hole pair distance will be extended. Thus, the exciton binding energy should be smaller, and exciton dissociation and charge transfer should be more efficient further, which is critical for high FF and PCE values.<sup>39-43</sup> Concluded from above calculations, GL1 and F-2Cl hold the same shape of backbone, same side chains distribution, same FMO electron-state density distributions and same dipole moment orientation, which should guarantee good compatibility and effective  $\pi - \pi$  stacking when blended.

Based on the above analysis, F-2Cl was introduced to the PBDB-T:GL1-based binary system as the guest acceptor. A series of devices (Table S2-S4 and Figure S7) were prepared with a device structure as shown in Figure 2a. When the weight ratio of PBDB-T:GL1:F-2Cl was 1:0.5:0.5 and the thickness of active layer is 122 nm, an optimal PCE value of 13.17% was obtained. In line with our expectations, both elevated  $J_{sc}$  and FF of the ternary one than binary counterpart (24.63 vs 22.59 mA cm  $^{-2}$  and 70.7% vs 66.5%) were achieved. In accordance with the above analysis of absorption spectra, the ternary blend film covers a wide range from 400 to 1000 nm (Figure 2c), and the clear trough of the EQE spectrum in the binary system is filled up as circled out in Figure 2d, which can be more intuitively demonstrated from the EQE offset ( $\Delta$ EQE) between the ternary device and binary device (Figure 2e). After adding F-2Cl, the EQE response was almost overall elevated apart from a small range around 800 nm, which indicates that charge transfer between the donor and acceptor is promoted. We calculated the integral current density value  $J_{sc}^{cal}$  from the EQE curve. For binary and ternary devices, the  $J_{sc}^{cal}$  values are 22.18 and 23.53 mA cm<sup>-2</sup>, respectively. Both of them are consistent with their respective  $J_{sc}$  measured by the J-V curve with a deviation within 5%. The average PCE for the 10 device counts is shown in Table 2, and the PCE distribution with small variance is depicted in Figure 2f.

**Charge Generation, Mobility, and Recombination.** In order to obtain more information and further reveal the reasons of the ternary device for the improved  $J_{sc}$  and FF, we



Figure 4. GIWAX patterns for blend films: (a) PBDB-T:GL1:F-2Cl; (b) PBDB-T:GL1; and (c) PBDB-T:F-2Cl. (d) Line cuts of the GIWAX patterns for the blend films.

systematically carried out a series of physical dynamics characterization. The measurement of the relationship between the photocurrent  $(J_{ph})$  and the effective applied voltage  $(V_{eff})$ was first considered.  $J_{ph}$  is the difference of current density with and without light, and  $V_{\text{eff}}$  is the difference between the voltage at which  $J_{\rm ph} = 0$  and the actual applied voltage. For both binary and ternary cells, the  $J_{\rm ph}$  value has already reached its maximum  $(J_{sat})$  value at  $\sim 2$  V, ending the trend of continuous increase (Figure 3a). This is due to the fact that charge recombination is minimized at high voltages, which is also the result of the high internal electric field. The ratio of  $J_{\rm vh}$  at different points on the curve to the  $J_{\text{sat}}$  of the device (expressed as  $P(E, T)^{44}$  indicates the efficiency of charge dissociation and collection at the state corresponding to this point. Under the short-circuit condition, the P(E, T) values of the device after and before introduction of F-2Cl are 99.4 and 96.9% respectively, while under the maximum power output condition, the P(E, T) values are 85.6 and 77.5%, respectively. We can draw a conclusion that a more efficient charge extraction and collection process exist in the ternary system for a higher value in both states. On the other hand, changes in the photoluminescence (PL) intensity of PBDB-T can reflect changes in the exciton dissociation process (Figure 3b). The fluorescence quenching efficiency of the polymer in the binary blend film is 97.5%, which is lower than that in the ternary blend film (98.4%), indicating that the photoinduced charge transfer of the system is enhanced with the addition of F-2Cl.

By studying the changes of  $J_{\rm sc}$  and  $V_{\rm oc}$  under different incident light intensities (*P*), the charge recombination behavior in the device can be obtained in a more detailed manner (Figure 3c,d). In the exponential function formula  $J_{\rm sc} \propto P^{\alpha,45}$  the value of exponential  $\alpha$  is usually equivalent to the degree of bimolecular recombination, while in the formula  $V_{\rm oc} \propto \ln P^{4,5}$  the value of slope *A* represents the degree of trapassisted recombination. In the binary device,  $\alpha$  and *A* are 0.957 and 1.16 kT/q, respectively, and after the introduction of F-2Cl,  $\alpha$  and *A* are 0.963 and 1.13 kT/q, respectively. In the ternary system,  $\alpha$  is closer to 1 and *A* is closer to 1.13 kT/qthan that of the binary counterpart, which implies that both bimolecular recombination and trap-assisted recombination are inhibited (*k* is the Boltzmann constant, *T* represents the temperature, and *q* corresponds to the fundamental charge).

Transient photovoltage (TPV) and transient photocurrent (TPC) measurements were conducted to further investigate the charge recombination dynamics and extraction behaviors.<sup>46,47</sup> Photocarrier lifetime ( $\tau$ ) was extracted from the voltage decay dynamics of the device by fitting with the double exponential decay function (Figure 3e). The ternary device displayed an average  $\tau$  value of 25.23  $\mu$ s, longer than that of the binary device (14.14  $\mu$ s), suggesting a suppressed charge

recombination, in agreement with the  $J_{sc}$  values under different incident lights above. TPC was performed under the shortcircuit current condition; the charge extraction time (t) was extracted from the photocurrent decay dynamics of the device by fitting with the double exponential decay function (Figure 3f). The ternary device displayed an average t value of 0.37  $\mu$ s, shorter than that of the binary device  $(1.70 \ \mu s)$ . The four times faster charge sweep-out process of the ternary device than that of the binary device demonstrates more efficient charge transport. Meanwhile, the hole mobility and electron mobility of ternary films are  $2.78 \times 10^{-4}$  and  $3.79 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, which are higher than those of binary films (2.01  $\times 10^{-4}$  and  $1.11 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) (Figure S8 and Table S5) (see the Supporting Information for details). The enlarged mobilities and more balanced hole and electron mobility in the ternary system should explain the faster charge removal process.<sup>48</sup> Based on the above physical characterization, it can be seen that the introduction of F-2Cl into the PBDB-T:GL1 binary device can improve exciton dissociation and charge extraction, inhibit recombination, and enhance the generation and transmission of charge, which is a critical factor for the realization of the simultaneously increase of  $J_{sc}$  and FF.

**Morphology Characterizations.** For our initial consideration, prescreening a guest component with a highly similar structure, good-miscibility, and similar ground and excited states should simplify the ternary device optimization procedure. To evaluate the compatibility of GL1 and F-2Cl, AFM measurement was carried out first (Figure S9). GL1 neat film and blend film of GL1 and F-2Cl with a weight ratio of 0.5:0.5 were measured, which are both smooth with low roughness. No clear molecular over-aggregation or isolated domains were observed in the blend film, indicating the good compatibility of the two acceptors.<sup>49</sup> Meanwhile, the contact angle measurement was used to further understand the miscibility and surface tensions ( $\gamma$ ) were calculated using the Wu model<sup>50,51</sup> as below following the literature procedure,

$$\gamma_{\text{water}}(1 + \cos \theta_{\text{water}}) = \frac{4\gamma_{\text{water}}^d \gamma^d}{\gamma_{\text{water}}^d + \gamma^d} + \frac{4\gamma_{\text{water}}^p \gamma^p}{\gamma_{\text{water}}^p + \gamma^p}$$
(1)

$$\gamma_{\rm GL}(1+\cos\theta_{\rm GL}) = \frac{4\gamma_{GL}^d\gamma^d}{\gamma_{GL}^d+\gamma^d} + \frac{4\gamma_{GL}^p\gamma^p}{\gamma_{GL}^p+\gamma^p}$$
(2)

$$\gamma = \gamma^{\rm d} + \gamma^{\rm p} \tag{3}$$

where  $\gamma^{d}$  and  $\gamma^{p}$  are the dispersion and polar components of  $\gamma$ , respectively, and  $\theta$  is the droplet contact angle (water or GL) on films. As shown in Figure S10 and Table S6, there are no obvious changes of contact angle after introducing F-2Cl to the GL1 neat film, ending up with a similar  $\gamma$  value, corroborating well the compatible property between the two acceptors again.

We used grazing incident wide-angle X-ray scattering (GIWAXS) to further characterize the microstructure of the films before and after the introduction of F-2Cl to obtain more information of molecular accumulation and aggregation. First, the thin film of new molecule GL shows a diffraction peak of (100) along the direction of  $q_{zy}$  and a diffraction peak of (010) along the direction of  $q_{zy}$  which means that the molecule preferentially adopts a face-on orientation where the molecular backbone is parallel to the substrate in the thin film state. (Figure S11). GL1's (010) reflection peak is located at 1.88 Å<sup>-1</sup>, corresponding to an intermolecular  $\pi - \pi$  stacking spacing

of 3.34 Å, which is more compact than that of F-2Cl (1.84 Å<sup>-1</sup>/3.41 Å).<sup>52</sup> As for the blend films, both binary and ternary systems adopt the typical face-on orientation (Figure 4). For PBDB-T:GL1 blends, the (100) peak is located at 0.31 Å<sup>-1</sup>, which corresponds to an alkyl–alkyl spacing of 20.27 Å. Its (010) diffraction peak is at 1.75 Å<sup>-1</sup>, where a calculated  $\pi$ – $\pi$  stacking with a spacing of 3.59 Å ends up (Table 3). After the

Tal	ble	3.	Μ	lorp	hol	logical	Data	of	GIWAX
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	(010	) out of	(100) in plane			
blends	$q(A^{-1})$	d (Å)	CCL (Å)		$q(A^{-1})$	d (Å)
PBDB-T:GL1:F-2Cl	1.80	3.49	19.53		0.30	20.94
PBDB-T:GL1	1.75	3.59	16.27		0.31	20.27
PBDB-T:F-2Cl	1.83	3.43	18.35		0.30	20.94

introduction of F-2Cl, the overall molecular orientation of the thin film does not change, but the formation of a denser  $\pi - \pi$ stacking is clear and the distance was reduced to 3.49 Å, in which charge transport should be favorable. Next, we estimated the crystal coherence length in the  $q_z$  direction according to the Scherrer equation,<sup>53</sup> and an increase from 16.27 Å for binary films to 19.53 Å for ternary films was observed. The (100) diffraction of ternary blends in the direction of  $q_{xy}$  is weaker than that of binary blends with a wider peak profile. This reveals that the introduction of F-2Cl reduces the initial overly packed lamellar in the binary system. In conclusion, combining the above two directions of analysis, the crystallization of the ternary blend system changed from a "narrow and short" shape to a "wide and thick" shape. These results indicate that F-2Cl can effectively regulate the morphology of the active layer and transform that to a state effective for charge transport. Their line-cutting profiles in the OOP and IP directions are depicted in Figure 4d.

The differences in the surface morphology between the optimal binary and ternary blend films were distinguished by AFM under typing mode (Figure 5). In AFM height images, the binary blend film PBDB-T:GL1 exhibits a relatively large aggregation and also a slightly larger surface roughness with a root-mean-square (RMS) value of 3.24 nm (Figure 5a). For the PBDB-T:GL1:F-2Cl ternary blend, a much more uniform and smoother surface with an RMS of 1.81 nm was obtained (Figure 5b), possibly a result of the weaker long-range lamellar packing of the ternary device than the binary device demonstrated by the above GIWAX data. The transmission electron microscope (TEM) method was conducted here to give more information of domain distribution. In the TEM image of binary blend (Figure 5g), some conspicuous dark domains are observed in most uniformly bright area. However, with the incorporation of F-2Cl in the ternary film, such oversized aggregates were regulated to a moderate state, and a clearer nanoscale fibrillar structure and better continuous phase separation prevailed (Figure 5h). These results, in combination with GIWAX measurement, corroborate our similar-structure principle for prescreening the third component for optimized ternary systems.

**Work Mechanism in the Ternary Device.** The mechanism that governs the photovoltaic process in ternary solar cells is rather complicated, extremely different from binary devices, and generally involves four principles: charge transfer, energy transfer, and parallel-linkage or alloy structure, among which PL measurement is a powerful and convenient evidence that can clarify the type.<sup>25,54,55</sup> For the charge transfer



Figure 5. (a-c) AFM height images; (d-f) AFM phase images; (g-i) TEM images.



**Figure 6.** (a) Normalized UV-vis absorption spectrum of GL1 neat film and PL spectra of F-2Cl. (b) PL spectra of F-2Cl, GL1 neat film, and GL1:F-2Cl (0.5:0.5) blend films. (c) J-V curves of organic solar cells based on GL1, F-2Cl, and F-2Cl:GL1 blend films. (d) Energy transfer mechanism diagram working in the ternary device.

mode, which is played by two donors or two acceptors, the emission intensity of one donor (acceptor) would be quenched without increased emission intensity for the other donor (acceptor) in the blend film of the two. However, if energy transfer occurs, the emission intensity of the relatively low band gap donor (acceptor) would increase, and the emission



Figure 7. Decay curve of the thermal stability test of the devices based on PBDB-T:GL1 and PBDB-T:GL1:F-2Cl. (a) PCE; (b)  $V_{oc}$ ; (c)  $J_{sc}$ ; (d) FF.

intensity of the other would decrease at the same time. If a parallel-linkage or alloy structure exists, the emission intensity of D1:D2 (A1:A2) blend film can be gradually changed as the ratio changes, whose emission peak is located between that of the two neat films.  $^{56-58}$ 

Thus, we investigate the work mechanism in the PBDB-T:GL1:F-2Cl-based ternary device here in virtue of PL measurement. Figure 6a shows that the PL spectrum of F-2Cl is nearly totally covered by the absorption spectrum of GL1, indicating a potential nonradiative energy transfer process from F-2Cl to GL1 when in blend film, that is, Förster resonance energy transfer (FRET). To verify this, at an excitation wavelength of 720 nm, the PL spectra of GL1:F-2Cl (0.5:0.5) film together with two neat films were measured. As shown clearly in Figure 6b, in the blend film, the emission peak of F-2Cl is fully diminished, and the total intensity is almost twice than that of GL1 pure film, with the same emission peak of ~983 nm as GL. This clearly confirms the existence of another energy transfer channel from F-2Cl to GL1 in the ternary device, which obeys the energy transfer mechanism among the four mechanisms as aforementioned. Therefore, there are two sources, i.e., energy from light and FRET from F-2Cl, which promote the transition of electrons in GL1 from HOMO to LUMO to form excitons. Such a FRET process plays a critical role in elevating current in the ternary devices over binary ones. Further, we calculated the FRET efficiency between F-2Cl and GL1 using the below formula following the literature procedure,<sup>59,60</sup>

$$E = 1 - \frac{\tau_{DA}}{\tau_D}$$
(4)

where  $\tau_{DA}$  and  $\tau_{DA}$  are the lifetimes of the transient photoluminescence of the energy donor (F-2Cl) in the presence and absence of the energy acceptor (GL1), respectively. As illustrated in Figure S12, the lifetimes are 1199 ps for F-2Cl in neat film and 71 ps when blended with GL1. Thus, the FRET efficiency is 94%. Then, devices based on the neat film of F-2Cl, GL1, and F-2Cl:GL1 (1:1) were fabricated.  $J_{sc}$  values of GL1 and F-2Cl neat film-based devices are 0.602 and 0.020 mA cm<sup>-2</sup>, respectively. However, the device using GL1 and F-2Cl blend films achieved a  $J_{sc}$  of 0.141 mA cm<sup>2</sup>, which is between the values of  $J_{sc}$  of GL1 and F-2Cl neat films (Figure 6c). The results demonstrate that the charge-transfer process between GL1 and F-2Cl should be negligible, which is consistent with the PL measurement.<sup>61,62</sup> The schematic of the work mechanism energy transfer in the PBDB-T:GL1:F-2Cl-based ternary solar cell is depicted in Figure 6d.

Stability Test. The thermal stability and shelf stability of PBDB-T:GL1-based binary devices and PBDB-T:GL1:F-2Clbased ternary devices were tested. Figure 7a-d captures the photovoltaic performance as a function of time during the thermal stability test, where the unencapsulated devices were placed in a nitrogen-filled glovebox and heated at 85 °C continuously. Value retention percentages after 216 h are summarized in Table S7. The PCE of the binary devices had already decayed to 80% after 24 h, while the ternary devices still remained 80% after 216 h with a slowed down decay rate and steady trend. However, the binary counterpart had decayed to the initial 61.02% after 216 h. As shown in Figure 7, the binary and ternary device performance decays mainly come from the  $V_{\rm oc}$  and FF losses, which might be attributed to the morphology changes in the mixed region of the donor and acceptor, involving density of state broadening at donor and acceptor interfaces and the formation of local isolated NFA aggregates.<sup>63-65</sup> In the ternary devices, molecular ordering increased and accordingly, better stability of  $V_{oc}$  and FF were achieved. In contrast,  $J_{sc}$  maintained a small fluctuation up or down near the starting level during the test process in both binary and ternary devices, which should be ascribed to the good compatibilities of active layer materials. The shelf stability test was carried out in a nitrogen-filled glovebox

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under a dark condition without encapsulation. After a 1032 h test, both gave a good shelf stability. However, the binary devices lost 4% of its initial PCE, in contrast to the hardly changed PCE (merely 0.46% decay) for the ternary device (Figure S13, Table S8). The simultaneously enhanced thermal stability and shelf stability of ternary devices demonstrates that the addition of F-2Cl can effectively achieve the desired stable state, probably a result of the more stable morphology of the active layer. Together with above analysis, we can conclude that by introducing F-2Cl and optimizing the ternary film, an overlap of efficient morphology (beneficial to high PCE) and stable morphology (beneficial to high stability) can be realized.<sup>66</sup>

# CONCLUSIONS

In conclusion, we have designed and synthesized a new acceptor molecule GL1 with a C-shaped conformation, which has wide and strong absorption in the range from 600 to 1000 nm. The PCE of the device based on PBDB-T:GL1 is 11.43%. By prescreening the third component with a molecular structure similarity strategy combined with the principle of energy level matching and absorption complementarity, F-2Cl was the potential one to construct the binary device. Compared with the binary counterpart, due to the enhancement of exciton dissociation and charge transport process, reduction of recombination, and improvement of morphology, the PCE of the ternary device increased to 13.17% with simultaneously increased Jsc and FF. Synergistically improved PCE and stability are attributed to a desired morphology regulated by F-2Cl, which achieved an overlap between efficient morphology and stable morphology. This work can present a successful example and guideline to effectively prescreen the third component for the fabrication and optimization of a high-efficiency ternary device.

# EXPERIMENTAL SECTION

**Materials.** All reactions and manipulations were carried out under an argon atmosphere using the standard Schlenk techniques. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone before use, and 1,2-dichloroethane was dried with calcium hydride. All starting materials were purchased from commercial suppliers and used without further purification unless indicated otherwise. Donor polymer PBDB-T was purchased from Solarmer.

Device Fabrication and Measurements. The OSC devices were fabricated using an inverted structure of ITO/ZnO/PFN-Br/ active layers/MoOx/Ag. The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by a nitrogen blow. Subsequently, a 30 nm-thick layer of ZnO was deposited by spincoating a ZnO precursor solution on the top of the ITO glass substrates at 3000 rpm for 40 s. After being baked at 200 °C in air for 1 h, the ZnO-coated substrates were transferred into a nitrogen-filled glove box. In order to fine-tune the interfacial properties, a thin film of PFN-Br was spin-coated on ZnO. Subsequently, the active layers were spin-coated onto the PFN-Br layer from the chlorobenzene solution with a donor concentration of 10 mg/mL. For the PBDB-T:GL1based device (D:A = 1:1), a CN (1% volume) additive was added; for the PBDB-T:GL1:F-2Cl (D:A = 1:0.5:0.5)- and PBDB-T:F-2Cl-based devices (D:A = 1:1), a DIO additive (0.3% volume) was added.  $MoO_x$ (~2 nm) and Ag (~150 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca.  $10^{-4}$  Pa). The effective area for the devices is 4 mm<sup>2</sup>.

# ASSOCIATED CONTENT

# **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c13035.

Thermogravimetric graph; cyclic voltammetry measurements; <sup>1</sup>H and <sup>13</sup>C NMR spectra; Fourier transform mass spectrometry; and contact angle (PDF)

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#### Notes

The authors declare no competing financial interest.

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