High-Performance Ternary Organic Solar Cells Enabled by Synergizing Fullerene and Non-fullerene Acceptors

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Abstract With the development of the non-fullerene acceptors (NFAs), the use of ternary organic photovoltaic devices based on a fullerene acceptor and a NFA is now widespread, and the merits of both acceptor types can be fully utilized. However, the effective approach of enhancing device performance is adjusting the charge dynamics and the thin-film morphology of the active layer via introducing the second acceptor, which would significantly impact the open-circuit voltage, the short-circuit current, and the fill factor, thus strongly affecting device efficiency. The functions of the second acceptor in a ternary organic solar cell with a fullerene acceptor and a NFA are summarized here. These include a broader absorption spectrum; formation of a cascade energy level or energy transfer; modified thin-film morphology including phase separation, effects on crystallinity, size, and purity of domain; and vertical distribution along with improved charge dynamics like exciton dissociation and charge transport, collection, and recombination. Then, we discuss the hierarchical morphology in ternary solar cells, which may benefit device performance, and the outlook of the ternary device.

Key words ternary organic solar cells, fullerene acceptors, non-fullerene acceptors, power conversion efficiency

Introduction

As we all know, energy shortage has become a global issue. To address this matter, it is essential to fully utilize solar energy using photovoltaic technology. Organic photovoltaics (OPVs) have attracted considerable attention by right of their unprecedented features including low cost,

lightweight, flexibility, solution processability, and large-scalability over the existing rigid and fragile inorganic solar cells.¹ Over the past decades, many approaches have been used to promote the photovoltaic parameters of devices and to elevate power conversion efficiency (PCE), such as designing new materials,^{2–6} the introduction of additives,⁷ as well as the majorization of device structure^{8–10} and the electrode buffer layer.^{11,12}

The PCE of OPVs is usually determined by the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF): $PCE = J_{sc} \times V_{oc} \times FF / P_{in}$, where P_{in} is the incident light power (100 mW cm^{-2} under illumination of AM 1.5G), J_{sc} strongly depends on the number of absorbed photons as well as the probability of exciton dissociation and charge collection, and V_{oc} relies on the energy difference between the LUMO of the acceptor and the HOMO of the donor. FF is mainly related to the competition between exciton dissociation and recombination in the active layer. The photovoltaic parameters are related to the thin-film morphology, such as phase separation, crystallinity, size or purity of domain, as well as the charge dynamics, which will be considered in the following. The morphology of the active layer is mainly determined by corresponding photovoltaic materials and can be optimized by various post-processing methods. And the morphology plays a critical role in device performance and stability. The ideal morphology usually presents the following features: (1) a proper phase separation with a suitable domain size, which can balance the competition between exciton dissociation and charge transport. Due to the limited exciton diffusion length (10–20 nm), the photoinduced excitons would not be dissociated effectively except for excitons generated near the donor/acceptor (D/A) interface. A large domain with a limited D/A interface causes insufficient exciton dissociation and an undesired low short-circuit current. A small domain is beneficial for exciton dissociation, but is disadvantageous for charge transport.¹³ (2) The bi-

Biosketches

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continuous interpenetrating networks that afford adequate transport channels for transporting holes and electrons to electrodes.¹⁴ (3) The phase purity that is closely related to the crystallinity of the electron donor and acceptor materials. The high phase purity favors the formation of good connectivity between the donor, acceptor and the anode, cathode, respectively, and thus facilitates charge collection; while the low phase purity may cause poor connectivity, which does not obstruct the charge transport but hinder charge transfer, leading to severe charge recombination.^{15,16} To achieve the ideal thin-film morphology, solvent additives are widely used in device fabrication; however, it shows disadvantages, such as being environmentally unfriendly and unstable. A ternary strategy of directly mixing three materials with complementary spectra in a ternary device also has an ability of morphology control. The additional component can fully utilize the solar spectrum and favor form cascade energy alignment or energy transfer. To sum up, the role of the third component in the development of ternary OPVs may be multiple, and it is inevitable that the ternary OPVs should be combined with post-processing and other strategies for optimal device performance.^{17–23} The ternary system involves the two-donor and the two-acceptor system. The two-acceptor system includes the options of fullerene–fullerene, fullerene–non-fullerene, and non-fullerene–non-fullerene. A fullerene acceptor (FA) exhibits excellent charge transport properties but suffers weak absorption. A non-FA (NFA)

possesses an adjustable energy level as well as enhanced absorption compared with the FA, but sometimes shows poor thin-film morphology and low electron mobility. The matter of how to balance the various factors that affect the photovoltaic parameters to achieve a maximum PCE value via ternary OPVs will be discussed in this review.

Fullerene derivative acceptors have attracted much attention by right of its irreplaceable advantages for a long time²⁴: (1) the existence of low-lying (0.2–0.4 eV) excited states in fullerene anions is responsible for the efficient charge separation at the D/A interface; (2) the high electron mobility; (3) a favorable nanoscale morphology; (4) an outstanding electron transport, the unique three-dimensional (3D) structure would afford more electron channels than the two or one dimensions. In previous works, the research studies of OPVs were mainly concentrated on the design and synthesis of low-bandgap donor materials with broad absorption and suitable energy levels to match FAs. However, FAs show disadvantages such as limited absorption windows, insufficient long-term device stability, and relatively high cost, which may hinder further improvement of device performance and thus the progress of the commercialization of OPVs. Therefore, the emergence of NFAs as desired substitutes for the FAs is reasonable and inevitable.²⁵ In contrast to the FAs, NFAs show unique advantages: (1) NFAs exhibit a broader absorption and a higher absorption coefficient than FAs. A broad or complementary absorption can be obtained by regulating the

Table 1 Photovoltaic parameters of ternary OPV containing non-fullerene as the host acceptor (A₁) and fullerene as the guest acceptor (A₂) as well as non-fullerene-based binary OPV

Binary blend	Photovoltaic parameters (binary)				Photovoltaic parameters (ternary)					
	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF (%)	PCE (%)	A ₂	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF (%)	PCE (%)	Ref.
PM6: BTCT-2Cl	24.4	0.877	70.4	15.1	PC ₇₁ BM	25.1	0.881	72.6	16.1	20
P2F-EHp: Y6	25.27	0.78	71.1	14.16	PC ₆₁ BM	26.38	0.82	74.8	16.18	35
BTR-Cl: Y6	23.79	0.8334	69.63	13.81	PC ₇₁ BM	23.75	0.8378	77.11	15.34	38
PCE10: 3TT-OCIC	26.49	0.68	69	12.43	PC ₇₁ BM	27.58	0.69	69	13.13	41
PM6: Y18	25.71	0.84	76.5	16.52	PC ₇₁ BM	26.3	0.84	77.4	17.11	42
PBDB-T: INPIC-Si	19.80	0.901	66.09	11.79	PC ₇₁ BM	20.98	0.892	70.84	13.26	43
PPBDTBT: ITIC	13.00	0.925	63	7.72	PC ₇₁ BM	16.66	0.894	68	10.41	44
PTFBDT-BZS: ITIC	12.54	0.983	56	6.97	PC ₇₁ BM	15.63	0.932	63	9.25	45
PBDB-T: IDT-2O	15.70	0.86	71.60	9.65	PC ₇₁ BM	16.80	0.87	72.11	10.67	46
PBDB-T: IDT-EDOT	18.42	0.87	62.3	9.93	PC ₇₁ BM	20.84	0.88	66.7	12.07	48
DR3TSBDT: Y6	21.67	0.879	55.21	10.53	PC ₇₁ BM	22.19	0.858	67.27	12.84	49
PTQ10: Y6	24.64	0.851	71.67	15.03	PC ₇₁ BM	25.32	0.850	74.69	16.07	50
PBDB-T: IOTC	15.04	0.95	55.52	7.94	PC ₇₁ BM	16.35	0.93	64.90	9.85	51
PBDB-T: ITIC	15.06	0.902	69	9.38	PC ₇₁ BM	15.98	0.892	71.7	10.22	52
PBDTTT-E-T: IEICO	17.31	0.83	58	8.33	Bis-PC ₇₀ BM	18.92	0.83	65	10.21	53
PBT1-C: ITIC-2Cl	18.03	0.86	70.3	11.10	ICBA	19.30	0.89	75.9	13.40	54
P3TCO-1: ITIC	16.96	0.943	62.82	10.11	PC ₇₁ BM	18.05	0.939	66.67	11.41	55
PBDTTPD-HT: ITIC	14.86	0.97	69	9.95	PC ₇₁ BM	17.38	0.95	74	12.09	56
PBT1-C: IT-2F	17.28	0.879	72.7	11.04	PC ₇₁ BM	18.19	0.892	75.1	12.19	57
PM6: Y6	24.89	0.845	74.37	15.75	PC ₇₁ BM	25.70	0.85	76.35	16.67	58
PTB7-Th: F8IC	25.12	0.640	67.6	10.90	PC ₇₁ BM	25.61	0.670	71.5	12.30	59
PBDB-T: BDTC-4Cl	18.56	0.864	59.5	9.54	PC ₇₁ BM	21.19	0.856	67.2	12.19	60
PTBTz-2: ITIC	19.8	0.89	59.05	10.43	PC ₇₁ BM	20.75	0.89	60.94	11.26	61
PTBTz-2: IT-M	17.61	0.954	61.84	10.39	PC ₇₁ BM	18.70	0.928	70.78	12.28	62
PM6: BTP-4Cl	25.49	0.868	72.21	15.98	ICBA	26.13	0.876	73.23	16.76	63
POBDFBT: ITIC	16.59	0.82	46.5	6.16	PC ₇₁ BM	17.65	0.72	61.8	7.91	64
PBDTNS-BDD: ITIC	14.86	0.94	66.47	9.28	PC ₇₁ BM	17.77	0.93	67.81	11.21	65
PTB7: 3TT-FIC	25.89	0.662	71.2	12.21	PC ₇₁ BM	27.73	0.669	73.0	13.54	66
PTB7-Th: IFIC-i-4F	22.90	0.65	63	10.03	PC ₇₁ BM	24.03	0.67	68	11.49	67
SBDT-BDD: IDIC	15.15	0.97	62.5	9.20	PC ₇₁ BM	16.21	0.97	69.3	10.90	68
PBDB-T: IT-M	16.7	0.937	69.0	10.80	Bis-PC ₇₀ BM	17.39	0.952	73.7	12.20	69
PBDB-T: ITIC	15.9	0.92	65.6	9.60	PC ₇₁ BM	17.7	0.91	68.3	11.00	72
PTB7-Th: IEICO-4F	21.3	0.73	60	9.44	PC ₇₁ BM	22.64	0.74	63	10.55	73
P(Cl-Cl) (BDD = 0.2): IT-4F	20.0	0.878	69.1	12.10	PC ₇₁ BM	21.2	0.878	70.7	13.20	74
PM6: Y6	24.5	0.848	74.6	15.50	PC ₇₁ BM	25.1	0.861	77.2	16.7	75
PBDB-T: IPIC-4Cl	22.2	0.813	74.0	13.40	PC ₇₁ BM	23.3	0.822	74.6	14.30	76
PDBT-F: IDIC	17.65	0.87	71.50	11.02	PC ₇₁ BM	18.69	0.89	70.88	11.86	77
DR3: ICC6	15.2	0.87	64	8.80	PC ₇₁ BM	16.3	0.87	72	10.80	78
PTB7-Th: CO ₈ DFIC	23.84	0.69	63.8	10.48	PC ₇₁ BM	28.20	0.70	71	14.08	79
PM6: N3	25.81	0.837	73.9	15.98	PC ₇₁ BM	25.71	0.85	76.6	16.74	80
PBDB-T: ITIC	15.44	0.903	67.7	9.76	PC ₇₁ BM	17.84	0.882	69.8	11.22	81
PM6: ITC6-4F	20.12	0.90	74.11	13.42	PC ₆₁ BM	20.78	0.93	78.18	15.11	82
SM1: MPU4	14.91	0.90	64	8.96	PC ₇₁ BM	16.32	0.92	67	10.05	83

Table 1 (Continued)

	Photovoltaic parameters (binary)					Photovoltaic parameters (ternary)					
Binary blend	J_{sc} (mA cm ⁻²)	V_{OC} (V)	FF (%)	PCE (%)	A ₂	J_{sc} (mA cm ⁻²)	V_{OC} (V)	FF (%)	PCE (%)	Ref.	
POTz: IDIC	16.32	0.82	63.71	8.52	PC ₇₀ BM	17.47	0.82	65.14	9.33	84	
PBDB-T: IDTC-4Cl	19.19	0.822	60.2	9.50	PC ₇₁ BM	19.14	0.829	65.6	10.41	85	
J52: IEICO-4F	22.27	0.675	61.3	9.21	PC ₇₁ BM	22.70	0.698	67.4	10.68	87	
PTB7-Th: IEICO-4F	20.62	0.74	58.55	9.32	PC ₇₁ BM	23.63	0.74	58.00	10.63	88	
PBDB-T: ITIC	16.00	0.89	65	9.03	PC ₇₁ BM	17.45	0.89	68	10.43	89	
DR3: ICC6	15.2	0.87	64	8.70	PC ₇₁ BM	16.3	0.87	72	10.80	91	
PBDB-T: DTFT9-FIC	19.01	0.86	58.61	9.58	PC ₇₁ BM	20.59	0.88	65.27	11.82	94	
PM6: FCTT-FIC	19.49	0.90	69.73	12.23	PC ₇₁ BM	19.86	0.92	73.20	13.37	95	
PM6: Y6-C2	25.11	0.860	73.6	15.89	PC ₇₁ BM	25.73	0.859	77.2	17.06	96	
PBDB-TF: Y6	24.8	0.834	74.1	15.30	PC ₆₁ BM	25.4	0.845	77.0	16.50	97	
PBDB-T-2Cl: BTP-4F	26.2	0.854	70.1	15.70	PC ₆₁ BM	26.4	0.842	73.3	16.3	98	
PBDB-T: BDCPDT-IC	16.56	0.86	65.52	9.33	PC ₇₁ BM	16.84	0.84	68.79	9.73	100	
PBDB-T: IEICO-4F	20.45	0.74	65.2	9.87	NC ₇₀ BA	20.49	0.81	65.8	10.92	101	
CS01: MPU3	13.04	1.07	0.56	7.81	PC ₇₁ BM	16.27	0.97	63	9.94	102	
PTB7Th: CO ₈ DFIC	22.96	0.704	66.80	10.80	PC ₆₁ BM	27.01	0.718	73.34	14.22	105	
PMTT56: IT-2F	18.67	0.945	71.4	12.60	PC ₇₁ BM	19.75	0.932	71.4	13.20	104	
PBDB-TF: HC-PCIC	17.54	0.88	72.69	11.48	PC ₇₁ BM	19.29	0.89	70.18	12.36	106	
PM6: IT-4F	20.14	0.857	71.42	12.33	ICBA	20.64	0.871	73.30	13.70	107	
PBDTTT-OFT: IEICO-4F	24.7	0.71	68	11.90	PC ₇₁ BM	26.1	0.72	69	13.00	108	
PFBDT-8tTPD: Y6	24.99	0.84	72	15.05	PC ₇₁ BM	25.96	0.85	74	16.43	110	
PM6: N3	25.4	0.835	73.5	15.6	PC ₇₁ BM	26.0	0.840	76.6	16.7	145	

bandgap of NFAs.^{26,27} The D/A approach, first reported by Havinga's group,^{28,29} is widely used in shrinking the bandgap of NFAs with absorption extending to near-infrared, where D is the electron-donating unit and has strong ties with the HOMO energy level, and A is the electron-withdrawing unit and is bound up with the LUMO energy level. Moreover, this approach can independently mediate the HOMO or LUMO energy levels. It might be an easy method for modulating the optoelectronic properties. Much research studies have been conducted to shrink the bandgap of the NFAs for a larger overlap with the solar spectrum, such as strengthening the electron-donating capability of the donor (D) unit to lift the HOMO energy level,^{30–32} or weakening the electron-withdrawing ability of the acceptor (A) unit to lower the LUMO energy level.³³ (2) The tunable energy level of non-fullerenes that can be achieved by sensible adjusting of the molecular structure to better match the donor material, thus to improve V_{oc} . (3) NFAs show a relatively low voltage loss. (4) NFAs have a relatively low cost and are easy to purify, whereas NFA-based binary OPVs usually suffer poor thin-film morphology and charge dynamics. Therefore, the promising ternary strategy (containing three photovoltaic materials in a device) of using fullerenes and non-fullerenes as acceptors

can be a simple way of overcoming the shortcomings of FA- or NFA-based binary OPVs and preserving their advantages for optimal device performance.³⁴ Besides, ternary OPVs also show their potential in large-scale devices for commercialization.³⁵

A previous work includes a systematic and detailed summary of the ternary OPV from different aspects.³⁶ As for the change of key photovoltaic parameters, V_{oc} , J_{sc} and FF as well as the function of the second acceptor in ternary OPVs based on FA and NFA will be emphasized in this report. Herein, we collected the photovoltaic parameters of ternary devices and corresponding binary devices (Tables 1 and 2), and the chemical structures of donors and acceptors are listed in Figures 1 and 2.

Incorporation of Fullerene Derivatives into NFA-Based Binary Systems

Improving Blend Morphology

As non-fullerene small molecules with a planar structure usually pack in one preferred orientation, which may be beneficial for charge transport, sometimes this may cause

Table 2 Photovoltaic parameters of ternary OPV containing fullerene as the host acceptor (A₁) and non-fullerene as the guest acceptor (A₂) as well as fullerene-based binary OPV

Photovoltaic parameters (binary)					Photovoltaic parameters (ternary)					
Binary blend	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	A ₂	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
PfBT-DPP: PC ₇₀ BM	12.5	0.74	74	6.8	MeIC	16.1	0.76	73	9.0	34
DRTB-T: PC ₇₁ BM	9.67	0.99	65.3	6.23	IDIC	15.47	0.99	67.7	10.48	40
PBDTBDD: PC ₆₀ BM	10.99	0.87	69.19	6.63	ITIC	17.76	0.91	63.47	10.36	90
PBTTFB: PC ₇₀ BM	10.79	0.99	74	7.98	ITIC	13.73	1.01	71	9.73	92
PTB7-Th: PC ₇₁ BM	16.21	0.778	60.1	7.58	CPDT-(TIC) ₂	19.00	0.803	61.6	9.48	114
PBTBT-OTT: PC ₇₁ BM	14.43	0.92	59.1	7.83	ITIC	16.61	0.92	56.4	8.61	115
PBTA-BO: PC ₆₁ BM	8.93	0.873	73.02	5.70	IFBR	13.45	0.926	65.07	8.11	116
PPDT2FBT: PC ₇₁ BM	14.75	0.79	79	8.16	IDT2BR	15.50	0.82	71	9.02	117
PBDTBDD: PC ₇₁ BM	14.19	0.84	66.18	7.86	IEICO	17.98	0.85	68.85	10.51	119
PDOT: PC ₇₁ BM	13.92	0.94	72.9	9.54	ITIC	17.49	0.96	66.8	11.21	120
PTB7-Th: PC ₇₁ BM	17.39	0.80	65	9.16	IEICO-4F	23.68	0.77	61	11.24	121
P1: PC ₇₁ BM	12.60	0.90	70.64	8.07	ITIC	17.71	0.90	63.67	10.11	122
PBT-OTT: PC ₇₁ BM	13.3	0.83	58.5	6.74	ITIC	14.8	0.87	63	8.18	123
PM6: PC ₇₁ BM	12.59	0.92	63	7.38	N2200-F	13.01	0.91	69	8.11	125
PBTA-BO: PC ₇₁ BM	9.31	0.903	55.65	4.73	IffBR	14.52	0.908	67.47	9.06	126
PTB7-Th: PC ₇₁ BM	16.73	0.796	63.81	8.50	IT-M	17.82	0.820	67.54	9.87	127
PBDB-T: PC ₇₁ BM	14.66	0.81	61.65	7.25	ITIC	17.76	0.85	60.92	9.34	128
BTR: PC ₇₁ BM	13.80	0.90	72.86	9.03	NITI	19.50	0.94	73.83	13.64	129
PTB7-Th: PC ₇₁ BM	16.47	0.77	71.2	9.51	TPE-4PDI	17.44	0.78	73.9	10.40	130
PTB7-Th: PC ₇₁ BM	16.3	0.80	67.2	9.10	IDIC	18.7	0.79	69.6	10.70	132
PBDB-T: PC ₇₁ BM	11.40	0.89	67.8	6.98	DTCFOIC	18.46	0.87	63.3	10.13	133
PDBT-T1: PC ₇₀ BM	13.24	0.915	76.2	9.29	ITIC-Th	15.94	0.934	70.5	10.48	134
PTB7-Th: PC ₇₁ BM	18.43	0.79	64.56	9.69	DIBC	20.68	0.77	73.37	12.17	135
PTB7-Th: PC ₇₁ BM	17.2	0.78	70	9.80	TPB	19.4	0.78	68	10.60	136
PTB7: PC ₇₁ BM	16.7	0.716	50.63	6.20	IDFBR	17.38	0.731	55.56	7.10	137

serious aggregation and thus recombination.³⁷ The incorporation of a FA into a binary organic solar cell (OSC) based on NFA may help to form a favorable morphology in ternary OSCs and thus improve device performance.³⁸ Therefore, numerous works have attempted to ameliorate the binary morphology via the ternary tactics, and the introduction of fullerene derivatives as the second acceptor was found to have the following effects. (1) A fine phase separation with a suitable domain size and an adequate D/A interface is formed to balance the trade-off between exciton dissociation and charge transport. (2) The crystallinity of the NFA-based blend can be adjusted; the high material crystallinity presents excellent charge mobility and pure domains, and then facilitates the formation of a bi-continuous interpenetrating network structure for efficient charge transport. (3) An ideal vertical phase distribution can be formed, which can improve the charge generation, transport, and collection. In summary, the FA can act as a morphology

regulator to modify the thin-film morphology in NFA-based binary OSCs.

Phase separation: The domain size has great influence on charge generation and transport. The components with good miscibility may form fine phase separation with small donor and acceptor domains, which can offer sufficient D/A interface for exciton diffusion and dissociation; however, due to the discontinuous network and the limited carrier lifetime, the free charge carriers (holes and electrons) cannot be transported to the electrodes, leading to the undesired J_{sc} and FF. On the other hand, in the blend with large phase separation, effective charge transport can be expected but the insufficient D/A interface and the exciton diffusion length will lead to poor exciton dissociation. Thus, to guarantee promising charge generation and transport, the domain size should be well-controlled. NFAs with a planar core tend to form large aggregates, leading to a large phase and thus creating a poor FF in NFA-based binary cells.

Figure 1 Chemical structures of donor materials.

Figure 2 Chemical structures of NFAs and fullerene acceptors.

To settle this matter, Liu et al. introduced the second NFA, leading to a homogeneous mixed phase for superior efficiency.³⁹ Zhang et al. reported an IDIC-based solar cell limited by lamellar domains with inerratic crystallite from the aggregation of IDIC.⁴⁰ After mixing an amount of PC₇₁BM, the lamellar domains disappeared and a new befitting phase separation formed. In other word, the incorporation of FA can disperse the mass aggregation of NFAs and then form a suitable domain size in ternary OSCs to balance charge carrier generation and transport.^{41–43}

Based on the ternary strategy involving a FA and an NFA, Lu et al. used 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as acceptors and combined with PPBDTBT (poly{4,8-bis(4-(2-ethylhexylthio) phen-1-yl)benzo[1,2-b:4,5-b']dithiophen-2,6-yl}-alt-{5,5'-(5-(2-decylte-tradecyloxy)-6-fluorobenzo[c][1,2,5]thiadiazole-4,7-diyl) di(thiophen-2-yl)}) or PFTBDT-BZS (polymer containing FBDT [4-alkyl-3,5-difluorophenyl group was introduced as the lateral side chain to the benzodithiophene (BDT) unit] as the donor unit, benzothiadiazole as the acceptor unit, and thiophene as the spacer) as a donor to fabricate ternary OPVs with the overall D:A ratio of 1:2, respectively. Both PPBDTBT: ITIC⁴⁴ and PFTBDT-BZS: ITIC⁴⁵ binary OPVs exhibit limited J_{sc} of 13.00 and 12.54 mA cm⁻², as well as the unsatisfied FFs of 63% and 56%, respectively, which can be attributed to the large phase separation due to the mass aggregation of ITIC, restricting the development of J_{sc} and FF. Thus, PC₇₁BM was added as the third component to disturb the molecular packing of ITIC and reduce its aggregation. As a consequence, a smaller domain size and a larger D/A interface area can be observed in the PPBDTBT: ITIC: PC₇₁BM ternary blend (with 40 wt% PC₇₁BM). By contrast, an inhomogeneous morphology with

a large domain indicating severe aggregation of ITIC in the PPBDTBT: ITIC binary blend was revealed by transmission electron microscopy (TEM) images (Figure 3) and grazing-incidence wide-angle X-ray scattering (GIWAXS) diagrams (Figure 4). Therefore, it can be concluded that the

Figure 4 a) GIWAXS 2D scattering patterns and b) line profiles of PPBDTBT: ITIC: PC₇₁BM films with different acceptor ratios. Reprinted with permission from Ref. 44. Copyright 2016 Wiley-VCH.

aggregation of ITIC might be suppressed by PC₇₁BM. When up to 40 wt% PC₇₁BM was added, the fine phase separation ensured the presence of abundant D/A interface areas to boost exciton dissociation. With the increasing content of PC₇₁BM, nanofibers of the donor material can be observed, which may contribute to FF improvement by elevated hole transport. Moreover, the ternary blend with the more ordered molecular packing of ITIC and PC₇₁BM present enhanced electron mobility, revealed by the results of GIWAXS. With increasing PC₇₁BM content, J_{sc} first increases and then decreases, which might be related to the low absorption coefficient of PC₇₁BM. When the ratio of ITIC to PC₇₁BM was increased up to 1.2:0.8, the PPBDTBT: ITIC: PC₇₁BM ternary OPV exhibited a PCE of 10.41%, higher than 7.72% in the PPBDTBT: ITIC binary OPVs or in ternary OPVs with other ratios of ITIC: PC₇₁BM, such as PFTBDT-BZS: ITIC: PC₇₁BM ternary OPV with the ratio of 1:0.8:1.2.

Zhang et al.⁴⁶ synthesized a fused pentacyclic NFA IDT-20 (4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene) with strong crystallinity. The ternary OPV consisting of PBDB-T: IDT-20: PC₇₁BM (1:0.8:0.2) (PBDB-T, poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo(1,2-b:4,5-b')dithiophene))-alt-(5,5'-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo(1', 2'-c:4',5'-c')dithiophene-4,8-dione))]) achieved a PCE of 10.67% with a V_{oc} of 0.87 V, a J_{sc} of 16.80 mA cm⁻², and a FF of 72.1%, in contrast to the PBDB-T: IDT-20 (1:1) binary OPV with the PCE of 9.65%, a V_{oc} of 0.86 V, a J_{sc} of 15.70 mA cm⁻², and a FF of 71.6%. Here, the incorporation of FA restrained the

Figure 3 TEM images of PPBDTBT: ITIC: PC₇₁BM blend films with different acceptor ratios. Reprinted with permission from Ref. 44. Copyright 2016 Wiley-VCH.

aggregation of NFA without sacrificing the intense π - π stacking in the nanophase. The large domains of IDT-2O were seen in the PBDB-T: IDT-2O binary film, but they disappeared after 20 wt% of PC₇₁BM was doped. By contrast, a smoother surface was observed in the optimal ternary blend, revealed by the reduced root-mean-square roughness of 1.70 nm in the PBDB-T: IDT-2O: PC₇₁BM ternary blend from 5.47 nm in the PBDB-T: IDT-2O binary blend. This indicates that PC₇₁BM might suppress the aggregation of IDT-2O leading to enlarged D/A interface areas and improved exciton separation. The amorphous active layer experiences a smaller voltage loss with evident aggregation compared with the active layer.⁴⁷ When bulky side chains are introduced to the planar backbone, the aggregation of NFAs would be hampered; however, the π - π stacking distance between NFA molecules is enlarged, which is unfavorable to electron transport. Besides, because of the excellent electron mobility of the FA and its derivative, such ternary cells, based on a FA and an NFA, display a higher and more balanced hole-electron mobility (μ_h/μ_e), which can facilitate charge transport, as well as reduce trap-assisted recombination, which further promotes J_{sc} . Moreover, Zhang et al.⁴⁸ reported that the PBDB-T: IDT-EDOT: PC₇₁BM ternary OPV (IDT-EDOT, a NFA based on 4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (IDT) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile were used as the central donor core and terminal group with 3,4-ethylenedioxythiophene as π -bridging unit) achieved 21% improvement in PCE compared with the corresponding PBDB-T: IDT-EDOT binary OPV.

To further improve the device efficiency of OPVs, Xu et al.⁴⁹ fabricated an all-small-molecule DR3TSBDT: Y6: PC₇₁BM (1.25:0.6:0.4) ternary OPV (DR3TSBDT, 4-thiazolidinone, 5,5'-[4,8-bis[(2-ethylhexyl)thio]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]bis[(3,3"-dioctyl[2,2':5',2"-terthiophene]-5",5-diyl)methyl-dyne]]bis[3-ethyl-2-thioxo; Y6, (2,2'-(2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4, 5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile))bis (5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile) and obtained over 21% PCE improvement as compared with the corresponding binary OPV based on NFA. First, a smaller phase separation is formed after doping with 40 wt% PC₇₁BM as revealed by the results of TEM. To explore the change in phase separation after doping with a proper amount of FA, Xu et al. employed SasView with the Debye-Anderson-Brumberger model and a fractal model to fit one-dimensional GISAXS profiles and found that the fractal dimension decreased from 3.03 in the binary blend based on Y6 to 2.91 in the ternary blend, suggesting that a looser acceptor packing was formed with

an enlarged D/A interface with an improved exciton dissociation. Besides, the good connection between Y6 and PC₇₁BM may benefit to form bi-continuous electron transport channels for the more efficient electron transport. Moreover, the DR3TSBDT molecules in the ternary blend were rearranged and formed a 3D texture structure, which is beneficial for charge transport. As a consequence, the considerably elevated FF (from 55.21% to 67.27%) and the slightly ameliorated J_{sc} (from 21.67 to 22.19 mA cm⁻²) contribute significantly to the increase in device performance (from 10.53% to 12.84%).

Qiu et al.⁵⁰ also adopted Y6 as the host acceptor, PC₇₁BM as the second acceptor, with poly[(thiophene)-*alt*-(6,7-difluoro-2-(2-hexyldecyloxy)quinoxaline)] (PTQ10) as the host donor, and reached a PCE value of 16.07%. The improvement is mainly ascribed to the formation of a favorable face-on orientation packing and the appropriate phase separation, which is responsible for the elevated charge transport and inhibited recombination. Kang et al.⁵¹ also used PC₇₁BM as the second acceptor to dope into the PBDB-T: IOTC binary blend (IOTC, a NFA based on indenothiophene core unit with the side chains of linear 4-*n*-octylphenyl and 2-(6-oxo-5,6-dihydro-4H-cyclopenta[c] thiophen-4-ylidene)malononitrile (TC) ending group) and achieved improved device performance by decreasing the aggregation of NFA in the binary blend.

In general, a number of research groups have demonstrated that fullerene derivatives can be used as a "morphology regulator" to modify the morphology of NFA-based binary films.^{43,52-55} The addition of FA may properly regulate the phase separation to form a suitable domain. It helps balancing the competition between charge transport and recombination to gain a well-balanced hole/electron mobility and a weak charge recombination, which strongly promotes the values of J_{sc} and FF. In addition, the incorporation of FA, likewise, enlarges the D/A₁ interface areas and offers an additional D/A₂ interface or an A₁/A₂ interface for efficient exciton dissociation, in which A₁ and A₂ are the host acceptor and the guest acceptor, and thus improves the device performance.

Crystallinity: The blend crystallinity that affects charge transport can be associated with domain purity. Generally, high crystallinity helps to form bi-continuous interpenetrating networks for efficient charge transport, but might roughen the film surface and may cause insufficient connectivity between the active layer and electrodes. However, low crystallinity might be unfavorable to charge transport. Hence, it is crucial for a well-performed OPV to acquire the desired crystallinity in the active layer; the use of FA as the second acceptor is a promising strategy for fine-tuning the crystallinity of the active layer in NFA-based binary OPVs.

Hadmojo et al.⁵⁶ investigated how the incorporation of [6,6]-phenyl-C₇₀-butyric acid methyl ester (PC₇₀BM) into

the PBDTTPD-HT: ITIC binary OPV (PBDTTPD-HT, a D-A polymer containing benzo[1,2-b:4,5-b'] dithiophene and thieno[3,4-c]pyrrole-4,6-dione groups) affects the crystallinity of the binary blend. The PCE of 12.09% in the ternary OPV, compared with 9.95% in the binary-blend OPV, is attributed to the amendatory morphology of the ternary blend. Due to the weak absorption of PC₇₁BM, the absorption intensity of the ternary OPV was more insufficient than the PBDTTPD-HT: ITIC binary OPV, which corresponds with the higher external quantum efficiency (EQE) value. As can be observed from GIWAXS images (Figure 5), the pristine ITIC film shows a strong orderly

Figure 5 GIWAXS 2D scattering patterns of a) pristine PBDTTPD-HT films, b) pristine ITIC films, c) PBDTTPD-HT: ITIC (1:1.5) binary blend films, d) PBDTTPD-HT: ITIC: PC₇₁BM (1:0.9:0.6) ternary blend films, and e) PBDTTPD-HT: PC₇₁BM (1:1.5) binary blend films. f) Out-of-plane line cut of corresponding 2D GIWAXS patterns. Reprinted with permission from Ref. 56. Copyright 2019 Wiley-VCH.

lamellar packing, which, however, nearly disappeared in the binary blend PBDTTPD-HT: ITIC with a weak π - π stacking diffraction. The characteristic ITIC lamellar ordering reappeared in the ternary blend PBDTTPD-HT: ITIC: PC₇₁BM, which suggests that ITIC was rearranged after doping with PC₇₁BM due to the poorer miscibility between ITIC and PC₇₁BM than between ITIC and PBDTTPD-HT. In addition, PC₇₁BM has a fine and uniform distribution in the ternary blend, which enlarges the interface between the donor and acceptor domains for efficient exciton dissociation. The continuous frameworks of PC₇₁BM and ITIC is beneficial for charge transport. As a result, charge mobility improved without increasing the trap-assistant recombination, leading to boosted charge generation and extraction simultaneously. A higher J_{sc} of 17.38 mA cm⁻² and a FF value of 74% were obtained in the ternary blend OPV, in contrast to a J_{sc} of 14.86 mA cm⁻² and a FF of 69% in the ITIC-based binary OPV.

Fu et al.⁵⁷ used the PBT1-C: IT-2F: PC₇₁BM (1:1:0.2) ternary system [PBT1-C, a copolymer with BDT, thiophene, and BDT-4,8-dione (BDTDO) as donor unit, π spacer and

acceptor unit; IT-2F, 3,9-bis(1-oxo-2-methylene-3-(1,1-dicyanomethylene)fluoroindanone)-5,5, 11,11-tetrakis(4-*n*-hexylphenyl)dithieno[2,3d:2',3'd']-s-indaceno[1,2b:5,6b']dithiophene]] to explore the change in film morphology with the FA as the second acceptor. With 20 wt% of PC₇₁BM, the π - π stacking diffraction peak belonging to IT-2F decreased in comparison with the PBT1-C: IT-2F binary blend, which means that IT-2F displays lower crystallinity. Atomic force microscopy (AFM) images showed that the thin film based on PBT1-C: IT-2F exhibits many small grains caused by the aggregation of IT-2F, but these disappeared after the introduction of PC₇₁BM, which means that PC₇₁BM can disturb the crystalline aggregates of IT-2F, which agrees well with the abovementioned results. Moreover, PC₇₁BM had a fine distribution in the ternary blend and formed an obvious fibrous structure for better charge transport and formed its own domains, causing the reduced recombination, consistent with the increased FF. The incorporation of FAs usually acts as a trap-assisted center for charge recombination, which is, however, suppressed in this ternary system due to the suppressed aggregation of IT-2F. Besides, both charge mobility and the probability of charge generation were enhanced in the PBT1-C: IT-2F: PC₇₁BM (1:1:0.2) ternary OPV, and the ternary OPV achieved an outstanding PCE value of 12.2%, higher than that (11.0%) of the IT-2F-based binary OPV.

The ternary tactics of using FA as an additional component play a key role in the improvement of high performance of OPV devices. Yan et al.⁵⁸ successfully achieved a record high PCE of 16.67% using the PM6: Y6: PC₇₁BM ternary OPV (PM6 or PBDB-TF, poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene))-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-c:4,5-c'] dithiophene-4,8-dione))] at the ratio of 1:1.0:0.2. In contrast to the corresponding binary OPV based on PM6: Y6 (1:1.2), the ternary system showed improved J_{sc} (24.89 vs. 25.70 mA cm⁻²) and an improved FF (74.37% vs. 76.35%), accounting for the PCE enhancement from 15.75% to 16.67%. By contrast, the introduction of PC₇₁BM makes up for the weak absorption of the binary blend PM6: Y6 OPVs in short wavelength. On the other hand, the morphology of thin film is modified after the proper content of PC₇₁BM is doped. More D/A interface pathways in ternary blends were formed to accelerate charge extraction, which is shown by the high charge collection probability ($P(E,T)$) of 0.970 as compared with 0.955 in the Y6-based binary blend. From GIWAXS images (Figure 6), it was found that as doping with the isotropic PC₇₁BM, the "face-on" preferred orientation is withheld in the ternary blend for favorable intermolecular charge transport, and a similar phenomenon was also observed by Dai et al.,⁵⁹ resulting in a high and balanced hole/electron mobility as well as a suppressed charge recombination. Moreover, the coherent length related to π - π stacking in the

Figure 6 GIWAXS 2D scattering patterns of PM6:Y6:PC₇₁BM films with different ratios a) 1:1.2:0; b) 1:1:0.2; and c) 1:0:1.2. d) Out-of-plane (solid line) line and in-plane (dotted line) line cut of corresponding 2D GIWAXS patterns; and AFM images (2 $\mu\text{m} \times 2 \mu\text{m}$) of films with blend ratio of e) 1:1.2:0 and f) 1:1:0.2. Reprinted with permission from Ref. 58. Copyright 2019 Wiley-VCH.

out-of-plane direction increased from 1.628 to 1.954 nm with the presence of PC₇₁BM, corresponding to the higher crystallinity of the ternary blend for better charge generation and transport. In other reports, the higher crystallinity with the lengthened coherent lengths or the decreased π - π stacking distance would be beneficial to the formation of a bi-continuous interpenetrating network, as well as to further improve charge transport and collection and reduce recombination.^{60,61} Yan et al. also verified that there is an energy transfer between Y6 and PC₇₁BM when the third component is over 30%. Once the content of the third component exceeds 30%, the effect of a parallel mechanism should also be considered. This phenomenon suggests that the working mechanism of ternary OPVs would change with the diversification of the blending ratio.

Fullerene derivatives were used as the third component to modify thin-film morphology towards a more suitable blend crystallinity, leading to a fibrous or continuous interpenetrating network to provide more charge transport channels for efficient charge transport.^{62–66} It might be possible to modify NFA-based binary OPVs with insufficient charge mobility caused by poor morphology.⁶⁷ Thus, more balanced charge mobility with increased electron mobility is formed. All of this can provide a reasonable explanation for improved PCEs with higher J_{sc} values in the ternary devices compared to NFA-based binary devices. These findings showed that FAs could modulate the crystallinity of the active layer involved with NFAs to facilitate charge transport, extraction, and restrain charge recombination, which is beneficial for improving the device performance.

Vertical distribution: There is a report that has found that in conventional OSCs, most excitons are generated at the bottom of the conventional OSCs, and thus the electron needs to transport a long distance toward the cathode,⁶⁸ which indicates that the electron transport property strongly affects the device performance. The introduction

of a FA into a donor: an NFA blend can help the formation of an ideal vertical distribution^{69–71}; donor and acceptor may enrich in the active layer close to the anode and cathode, respectively, which would shorten the distance of charge transport and enhance charge collection, further improving J_{sc} and FF.

Bi et al. used a spin-coated PBDB-T:ITIC:PC₇₁BM (30 wt%) ternary OPV to study the effect of the second acceptor, FA, on the vertical phase distribution of both donor and acceptor.⁷² The film-depth-dependent light absorption spectrum results for the ternary blend and the corresponding binary blends are shown in Figure 7a–c. The peaks at 580 and 620 nm are from PBDB-T, and the peak centered at

Figure 7 Film-depth-dependent light absorption spectra of PBDB-T:ITIC:PC₇₁BM films with different PC₇₁BM contents: a) 0%; b) 30%; and c) 100%. (d–f) PBDB-T, ITIC, and PC₇₁BM content profiles at different film depths by fitting the evolution of spectroscopy as shown in (a–c). (In composition profiles, locations at 0 and 100 nm are active layer–MoO₃ (anode) and active layer–ZnO (cathode) interfaces.) Reprinted with permission from Ref. 72. Copyright 2018 Elsevier.

700 nm is arising from ITIC; the spectra of the three different materials varied with the film depth. It is obvious that the ternary blend displayed ideal vertical phase separation (Figure 7d–f), which is mainly rich in PBDB-T and ITIC in the active layer close to the anode and cathode respectively, which is beneficial for accelerating charge collection as well as reducing recombination. In addition, the increased hole and electron mobility owes to the outstanding charge transport property of PC₇₁BM and the desired coherence length of PBDB-T, as well as ITIC. The smaller aggregation of the polymer with an enlarged D/A interface area for efficient exciton dissociation after mixing with PC₇₁BM can be observed from the time-resolved fluorescence images. The ternary cell with 30 wt% PC₇₁BM reached 11.0% PCE, taking advantage of enhanced J_{sc} and FF in contrast to 9.6% PCE of the binary cell based on NFA.

In a research study of the invented ternary device based on PTB7-Th: IEICO-4F: PC₇₁BM (PTB7-Th, poly[[2,6'-4,8-di(5-ethylhexyl-thienyl)benzo[1,2-b;3,3-b]dithiophene][3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]-thiophenediyl]]]; IEICO-4F, 2,2'-((2Z, 2'Z)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno [1,2-b:5,6-b']di-thiophene-2,7-diyl) bis(4-((2-ethylhexyl)-oxy) thiophene-5,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile), Lee et al. found that the vertical distribution might be related to the surface energy of different materials.⁷³ In view of the relatively high surface energy of PC₇₁BM and the high surface energy of ZnO, the former tends to aggregate in the surface of the latter during film formation, which helps to effectively inhibit charge recombination, boost charge collection, and block hole leakage. However, PTB7-Th was enriched near the BHJ/air interface because of the low surface energy, and thus the desired vertical distribution was formed. Because of the similar surface energy between PC₇₁BM and IEICO-4F, the latter was also enriched at the ZnO surface, and IEICO-4F molecules could interact closely with PC₇₁BM molecules, which may enhance device performance. As a result, the ternary OPV exhibits improved PCE (from 9.44% to 10.55%) with the higher value of J_{sc} (from 21.30 to 22.64 mA cm⁻²) and showed superior stability (maintaining 80% of PCE under continuous illumination for 500 h). This indicates that the ternary strategy can improve device performance and stability simultaneously, and thus achieve the commercialization of OPVs.

Park et al.⁷⁴ introduced PC₇₁BM as the guest acceptor into the P(Cl-Cl) (BDD = 0.2): IT-4F binary blend to fabricate an inverted ternary device (P(Cl-Cl) (BDD = 0.2), a polymer consisting of a chlorinated 2D benzo(1,2-b:4,5-b') dithiophene (Cl-2DBDT) donor unit, a 3-chlorothiophene (Cl-Th) acceptor unit, and a 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo(1,2-c:4, 5-c')dithiophene-4,8-dione (BDD) acceptor unit with the ratio of Cl-2DBDT: Cl-Th: BDD = 1:0.8:0.2; IT-4F, (3,9-bis(1-oxo-2-methylene-3-(1,1-dicyanomethylene)-5,6-difluoroindanone)-5,5, 11,11-tetrakis(4-*n*-hexylphenyl)dithieno[2,3d:2',3'd']-s-indaceno [1,2b:5,6b']dithiophene)), and surprisingly noted that the formation of favorable vertical phase separation can decrease the interface resistance and recombination. Park et al. used the cross-sectional field-emission scanning electron microscopy and energy-dispersive X-ray spectroscopy to analyze the vertical distribution of three different materials in the film via various atomic signals of F_{1s}, S_{2p}, O_{1s}, and C_{1s}, in which the S_{2p} signal represents P(Cl-Cl) (BDD = 0.2), the F_{1s} signal stands for IT-4F, and the O_{1s} and C_{1s} signals represent PC₇₁BM. After loading 10 wt% PC₇₁BM, the F_{1s} signals showed that P(Cl-Cl) (BDD = 0.2) mainly appeared in the upper portion of the active layer, while the S_{2p} signals representing IT-4F as well as the O_{1s} and C_{1s} signals representing PC₇₁BM gathered in the nether portion

of the active layer, in accordance with the well-dispersed vertical phase distribution. Subsequently, a uniform morphology and fine phase separation could be observed in the AFM images of the ternary blend. The effective contact between the active layer and electrode reduced the value of interface resistance, from 105.01 Ω in the binary device to 74.83 Ω in the ternary device; furthermore, the value of EQE in the region of 550–800 nm is over 80%, indicating the enhanced charge transport and extraction in ternary device, and it would be reasonable to infer that the ternary strategy can reduce interface resistance and boost charge carrier transport and collection via forming a vertical phase separation. As a consequence, J_{sc} of the ternary OPV increased from 20.00 mA cm⁻² in the binary OPV based on IT-4F to 21.2 mA cm⁻².

To conclude, the incorporation of FA is favorable to the formation of an ideal vertical phase separation, which may be related to the surface energy of the different materials, leading to an improvement in performance with increased charge carrier transport, collection, and suppressed recombination.

Mending Charge Dynamics

The charge dynamics play a significant role in device performance and it restricts further performance improvement of NFA-based binary OPVs. The incorporation of FA into binary OPVs based on NFA can improve the electron mobility due to the outperformed electron mobility of FAs, further optimizing μ_h/μ_e and reducing recombination, consistent with a high FF.^{75–86} Besides that, the exciton dissociation is also enhanced, to boost the photoinduced current via the enlarged D/A interface. The wide application of the ternary strategy in many different binary systems based on NFA can support that the use of FA as the third component can improve device efficiency. This indicates that the ternary strategy is promising.

Shi et al.'s⁸⁷ research attested that the charge mobility dynamics strongly affect cell efficiency. The binary solar cell based on the J52: IEICO-4F binary solar cell (J52, poly[4,8-bis[5-(2-ethylhexyl)thiophen-2-yl] benzo[1,2-b:4,5-b'] dithiophene-5,5'-diyl-*alt*-4,7-bis(thien-2-yl)5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole]) shows hole and electron mobilities of 1.42×10^{-3} and 9.36×10^{-5} cm² V⁻¹ s⁻¹, respectively. The enormously unbalanced μ_h/μ_e ratio causes a low FF, thus confining device efficiency. After adding 40 wt% PC₇₁BM to the binary solar cell, the electron mobility was improved up to 9.35×10^{-4} cm² V⁻¹ s⁻¹, 1 order of magnitude higher than that of the binary cell. The μ_h/μ_e ratio decreases from 15 to 1.5 for an improved FF. Furthermore, the suppression of recombination, together with elevated charge extraction and transport, converged to achieve PCEs of 10.68% as compared with 9.21% for binary OPV based on J52: IEICO-4F.

To investigate the issue of insufficient charge separation in NFA-based binary OPVs, Wang et al.⁸⁸ fabricated a binary OPV, using PTB7-Th as a host donor and IEICO-4F as a host acceptor, and further used PC₇₁BM as a guest acceptor. In the PTB7-Th: IEICO-4F binary blend, PTB7-Th did mix well with IEICO-4F because of the excellent miscibility between them, which, however, leads to severe charge carrier recombination, corresponding to the short lifetimes of the free charge carriers. In ternary OPVs, PC₇₁BM may reduce the charge-transfer states and thus facilitate the interfacial charge transfer. As a result, J_{sc} increased to 23.63 mA cm⁻² in the ternary device from 20.62 mA cm⁻² in the binary device based on IEICO-4F.

To better explore the effects of exciton dissociation and charge transport on the photovoltaic performance, Li et al.⁸⁹ used pump-probe photoconductivity spectroscopy measurements combined with transient photoluminescence (PL) spectroscopy. The transient PL measurement can monitor the charge transfer by using a selected wavelength to excite one component and to probe its PL emission intensity. After blending with the other component (cannot be excited in this wavelength), the shorter PL intensity lifetime indicates that effective charge transfer occurs^{67,90} but the longer PL intensity lifetime may mean the existence of energy transfer.⁵⁸ In addition to transient PL measurement, the transient absorption (TA) spectroscopy can also investigate charge transfer and combination dynamics by monitoring ground-state bleaching and photo-induced polarons.^{72,91-93} As for the PBDB-T: ITIC binary OPV, it is found that the excitons generated in ITIC would separate at the PBDB-T/ITIC interface, then the electrons and holes would transfer to the cathode and the PBDB-T, respectively. The accumulation of the injected holes plus the holes generated in PBDB-T would inhibit the exciton generation in PBDB-T. Fortunately, the addition of PC₇₁BM can enlarge the D/A interface area. Although the exciton dissociation at the ITIC/PC₇₁BM interface can be ignored, that in PBDB-T/PC₇₁BM is efficient. Besides that, the PC₇₁BM would be able to accept electrons from PBDB-T, and the electron transfer to the cathode is faster than that in ITIC; thus, the ternary device exhibits a larger hole mobility (1.94×10^{-4} vs. 1.01×10^{-4} cm² V⁻¹ s⁻¹) and a lower hole-trapping state than the PBDB-T: ITIC binary device (3.25×10^{16} vs. 4.15×10^{16} cm⁻³) with reduced hole accumulation, which is favorable for charge separation and transport, consistent with the improved J_{sc} in ternary OPV. As a result, the ternary OPV achieved higher PCEs (10.43% vs. 9.03% in PBDB-T: ITIC binary OPV) depending on the increased probability of exciton dissociation and charge mobility.

Cheng et al.⁹⁴ synthesized an extremely planar NFA, incorporating two carbon bridges to fasten the central DTF core with two outer thiophene rings, forming a new ladder-type nonacyclic dithieno[3,2-b:6,7-b']fluorene(dicyclopentathiophene) (denoted as DTFT9), which combined with a

polymer donor, PBDB-T, resulting in an efficiency of 9.58%. And DTFT9 was further condensed with two FIC acceptor units (FIC, 1,1-dicyanomethylene-5,6-difluoro-3-indanone) to yield a carbon-bridged DTFT9-FIC. The PBDB-T: DTFT9-FIC binary OPV exhibits a “face-on” orientation, while the ternary OPV PBDB-T: DTFT9-FIC: PC₇₁BM shows “face-on” and “edge-on” orientations, which may favor charge transport in the vertical and parallel directions. In other words, the charge mobility of PBDB-T: DTFT9-FIC: PC₇₁BM OPV is superior to that of the PBDB-T: DTFT9-FIC binary OPV, and the former is more balanced, which is redound to elevate the value of FF. Furthermore, the PBDB-T: DTFT9-FIC: PC₇₁BM ternary OPV shows a smoother surface with smaller roughness than the binary OPV based on PBDB-T: DTFT9-FIC, which indicates a better miscibility in the ternary blend, enhancing the interface contact and boosting charge transport. The ternary OPV achieved an efficiency of 11.82% with increased J_{sc} and FF values. The same group used PC₇₁BM as the second acceptor to combine with the PM6: FCTT-FIC binary blend (FCTT-FIC, two outer thienothiophenes-terminal fluorenedicyclopentathiopheno[3,2-b]thiophene condensed with two FIC acceptor units and a carbon bridge), and achieved a PCE of 13.37% in the ternary OPV, in contrast to a PCE of 12.23% in the binary OPV of PM6: FCTT-FIC.⁹⁵ The improvement in device performance is mainly ascribed to the increased FF, which stems from the increased mobility. The electron mobility increased from 2.50×10^{-5} cm² V⁻¹ s⁻¹ in the binary device based on PM6: FCTT-FIC to 3.03×10^{-5} cm² V⁻¹ s⁻¹ in the ternary device, and the hole mobility raised from 4.71×10^{-6} cm² V⁻¹ s⁻¹ in the binary device based on PM6: FCTT-FIC to 2.32×10^{-5} cm² V⁻¹ s⁻¹ in the ternary device, leading to the higher and more balanced charge transport and thus a higher PCE with enhanced FF and J_{sc} values.

Luo et al. designed and synthesized a series of small-molecule NFA acceptors based on Y6, Y6-C2 ((2,2'-((2Z,2-Z)-((12,13-bis(3-ethylheptyl)-3,9-diundecyl-12,13-dihydro[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanelylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile), by altering the branching position of the side alkyl chains.⁹⁶ The PM6: Y6-C2 binary cell achieved a high performance of 15.89%. To further increase device performance, they incorporated an amount of PC₇₁BM into the PM6: Y6-C2 binary cell and achieved a higher PCE of 17.06%, which is mainly ascribed to the higher mobility and the more balanced μ_h/μ_e ratio. It is worth noting that the improved charge transport features could reduce recombination to some degree, accounting for the slightly increased J_{sc} and the strongly improved FF, from 73.6% to 77.2%.

Hou et al. mixed an appropriate amount of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) into the PBDB-TF: Y6 binary OPV and achieved a high PCE of 16.5%.⁹⁷ Because the

LUMO energy level is higher for PC₆₁BM than for Y6, the V_{oc} values slightly improved in the ternary cell. The electron mobility improves with the increasing PC₆₁BM contents, whereas the hole mobility is insensitive to the loading of PC₆₁BM (Figure 8). When the ratio of Y6:PC₆₁BM increased up to 1:0.2, the charge carrier mobility of the PBDB-TF: Y6:

Figure 8 a) The hole and electron mobilities and b) the charge carrier lifetimes and CELIV mobilities of the ternary blends with different PC₇₁BM content (wt%) in A₁:A₂. Reprinted with permission from Ref. 97. Copyright 2019 Wiley-VCH.

PC₆₁BM (1:1.2:0.2) ternary blend was $7.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, an increase of nearly a factor of 2 over the PBDB-TF: Y6 blend ($3.8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). With further increase in PC₆₁BM content, the charge carrier mobility decreases slightly, which can be correlated with the variation in blend morphology. The PBDB-TF: Y6: PC₆₁BM (1:1.2:0.2) ternary OPV displays the highest charge carrier mobilities and the longest charge carrier lifetimes among PBDB-TF: Y6: PC₆₁BM ternary OPVs with other ratios (from 1:1.4:0 to 1:0:1.4), which restrains charge recombination and accounts for increased FF and J_{sc} . Hou et al. also combined PC₆₁BM with PBDB-T-2Cl: BTP-4F (PBDB-T-2Cl, a polymer based on PBDB-T with chlorinated thiophene side groups; BTP-4F, also known as Y6), and gained a higher and more balanced charge mobility, leading to a PCE of 16.3%.⁹⁸ The PBDB-T-2Cl: BTP-4F: PC₆₁BM ternary OPV with a 300 nm active layer reached a PCE of 14.3%, which is important for roll-to-roll production.

The abovementioned discussion indicates that introducing FA as the second acceptor into NFA-based binary OPVs may achieve the more balanced and higher charge mobility, further leading to higher PCEs with improved J_{sc} and FF values.

Other Effects

Apart from modifying morphology and improving charge dynamics, the incorporation of FA into binary OPVs based on NFA can increase PCE by virtue of other effects such as energy transfer, cascade energy level alignment,^{99–102} and others.^{103,104}

Energy transfer: Fullerene derivatives as the third component with absorption in the short wavelength region usually serve as an energy donor to form energy transfer to the NFAs. Steady and transient PL measurements are an efficient method of verifying the existence of energy transfer. If the PL emission intensity of a low-bandgap acceptor (energy acceptor) increased and the PL emission intensity of a large-bandgap acceptor (energy donor) decreased after intermixing two acceptors, it means that an energy transfer occurred between them. Karuthedath et al.⁹¹ incorporated PC₇₁BM into the binary OPV based on DR3: ICC6 (DR3, oligothiophenes containing a backbone structure of a BDT unit as the central block and ethylrhodanine as the end group) to improve overall device performance by the ultrafast energy transfer between PC₇₁BM and ICC6. PC₇₁BM absorbs additional energy from high-energy photons, then quickly transfers it to ICC6, and subsequently ICC6 transfers holes to DR3. Furthermore, due to the inherent good electron transport property of PC₇₁BM, the ternary OPV with PC₇₁BM exhibits an increased EQE in the whole absorption range and increased charge extraction as well as reduced recombination.¹⁰⁵ As a result, the ternary OPV provides improved J_{sc} (from 15.2 to 16.3 mA cm^{-2}) and FF values (from 64% to 72%), which contributes to an increased PCE of 10.8% compared with 8.7% in the DR3: ICC6 binary OPV.

Cascade energy alignment: The addition of a FA into a binary system based on an NFA may help to form cascade energy alignment. Zhan et al.¹⁰⁶ introduced PC₇₁BM as the second acceptor into PBDB-TF: HC-PCIC binary systems (HC-PCIC, 2,2'-((2Z,2'Z)-(((2,5-difluoro-1,4-phenylene)bis(4,4-bis(2-ethylhexy-1)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methan-ylidene))bis(5,6-dichloro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile) and achieved a higher PCE (12.36%) with a J_{sc} of 19.29 mA cm^{-2} compared with a PCE of 11.48% with a J_{sc} of 17.54 mA cm^{-2} in HC-PCIC-based binary systems. The addition of PC₇₁BM formed a cascade energy level alignment, leading to enhanced charge transfer between the donor and the acceptor, as proved by the increased quantum efficiencies in the range of 600–800 nm. In addition, the enhanced charge transfer would make a positive difference in charge separation, revealed by the PL spectrum. The pure PBDB-TF displayed a PL spectrum in the range of 625–850 nm. After doping with HC-PCIC, most of the fluorescence emission is quenched, but some of it still remains in the range of 750–850 nm. In the ternary blend PBDB-TF: HC-PCIC: PC₇₁BM, the PL spectrum of pure PBDB-TF is quenched almost completely, suggesting that charge separation might increase to some extent due to the faster charge transport.

Non-radiative energy loss: Xing et al.¹⁰⁷ achieved a PCE value of 13.70% in 1.05 cm^2 devices by simultaneously synergizing blade coating and adopting a ternary approach.

A blade-coated binary device suffers a relatively high E_{loss} of 0.766 eV; E_{loss} in a ternary solar cell is 0.752 eV with blade coating, corresponding to a V_{oc} of 0.857 eV in the blade-coated binary device and 0.871 in the ternary device. On the one hand, the incorporation of FA elevated V_{oc} , from 0.857 eV in the binary device to 0.871 eV in the ternary device, due to the decreased non-radiative recombination loss (from 0.402 eV to 0.367 eV). On the other hand, the molecular stacking was rearrangement and the crystallinity was strengthened in the ternary blend, in contrast to the corresponding binary blend, which would ameliorate charge recombination and be good for J_{sc} and FF to some extent.

Flexibility: There are two key parameters, device performance and mechanical properties, for flexible OSCs. As for NFA-based binary OSCs, it is common that the superior charge transport property is achieved by enhancing the crystallinity of the NFA, which is detrimental to device flexibility. Huang et al.¹⁰⁸ found that the incorporation of proper PC₇₁BM into the PBDTTT-OFT: IEICO-4F binary blend (PBDTTT-OFT, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene -2,6-diyl-alt-(4-octyl-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2-6-diyl]) may improve device performance and flexibility, simultaneously. The crystallinity of IEICO-4F decreased after doping with a proper amount of PC₇₁BM without the formation of a rigid pure domain of PC₇₁BM, which can improve the device flexibility. In addition, the high charge transport property in the ternary device is derived predominantly from the charge transport property of PC₇₁BM. In contrast to the binary device, the exciton dissociation and charge extraction and collection are also enhanced in a ternary device. The potential of FA that can be used in semitransparent OSCs was also studied, indicating that the strategy of using ternary devices involving a FA and an NFA is very promising.¹⁰⁹

In conclusion, the role of the FA in a ternary blend could involve a synergy of ameliorative morphology, charge dynamics, and other effects, by which optimal device efficiency can be achieved. Moreover, the introduction of a FA into a binary device based on NFA may help to simultaneously improve the performance and stability of a device, and thus improve the feasibility of commercialization.^{110–113}

Incorporation of NFAs into Fullerene-Based Binary Systems

Enhancing Optical Absorption

A key bottleneck problem for binary OSCs based on fullerene derivatives is the deficient utilization of the solar spectrum because fullerene derivatives show limited and weak absorption in the short-wavelength region, leading to

unsatisfactory J_{sc} . Due to the highly adjustable optical bandgaps, NFAs usually can significantly enhance the optical absorption of OPVs based on FA, providing an effective way to improve device performance.^{114–118}

Tan et al.⁹⁰ adopted the advisable approach to construct the absorption spectrum-complementary PBDTBDD: PC₆₀BM: ITIC ternary device (PBDTBDD, a new copolymer based on 4,8-bis(5-(2-ethylhexyl-2-yl)benzo[1,2-b;4,5-b']dithiophene (BDT) and 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo-[1,2-c:4,5-c'] dithiophene-4,8-dione (BDD)). The PBDTBDD: PC₆₀BM: ITIC (with 40 wt% ITIC) ternary system achieved a higher PCE (10.36% vs. 6.63%) and J_{sc} (17.76 vs. 10.99 mA cm⁻²) than the PBDTBDD: PC₆₀BM binary OPV. The improved J_{sc} was attributed to the additional absorption from ITIC. When the ratio of PC₆₀BM: ITIC was up to 0.6:0.4, the ternary blend presented maximum photo-harvesting for the generation of photoinduced carriers. Moreover, the ternary blend displayed proper phase separation, a smooth and uniform surface that is nearly the same as the binary blend based on FA, but the domain size and roughness changed slightly, indicating that the incorporation of ITIC had a little effect on the blend morphology. By contrast, the incorporation of ITIC provides more charge transmission channels for charge transport to suppress recombination. Tan et al.¹¹⁹ also employed cathode engineering in ternary devices to improve device efficiency. The ternary OPV PBDTBDD: PC₇₁BM: IEICO with zirconium acetylacetonate (ZrAcac) was used as the cathode buffer layer and achieved a PCE of 10.51%. The binary blend based on PBDTBDD: PC₇₁BM displayed an absorption spectrum in the range of 300–700 nm, and the absorption spectrum range was extended to 900 nm with the addition of IEICO. In addition, they improved the cathode interfacial layer (CIL): substitution of Mg with ZrAcac reduced the series resistance and increased the photocurrent. Improvement of the contact between the active layer and CIL could be implemented by optimizing the ratio of PC₇₁BM: IEICO, which is beneficial for decreasing contact resistance as well as increasing electron collection. As a result, J_{sc} increased from 14.19 mA cm⁻² in the binary OPV based on a FA to 17.98 mA cm⁻² in the ternary OPV.

The ternary strategy was also implied for thick-film devices. Zhang et al.¹²⁰ designed and manufactured a thick-film ternary device (230 nm) with a PCE of 11.21% by incorporating the ITIC acceptor into the PDOT: PC₇₁BM binary system (PDOT, a copolymer based on 4,8-bis(4,5-dioctylthiophen-2-yl) benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-N-(2-hexyldecyl)-5, 5'-bis(thiophen-yl)-2,2'-bithiophene-3,3'-dicarboximide). The PDOT: the PC₇₁BM binary device presented a low J_{sc} of 13.92 mA cm⁻² because of the intrinsic narrow absorption of 300–700 nm, but the excellent FF of 72.9% owes to the efficient charge transport property. By contrast, the PDOT: ITIC binary device was constrained by the charge transport property of ITIC, compared with the efficient

charge transport property of PC₇₁BM. To balance the optical absorption and charge transport, Zhang et al. used PC₇₁BM and ITIC as acceptors in a ternary solar cell, in which PC₇₁BM and ITIC can simultaneously display their advantageous properties of outstanding electron mobility and strong optical absorption. The blend absorption was extended to 800 nm with the incorporation of ITIC (Figure 9). Although the EQE spectrum of the ternary blend slightly decreased in the range

ment in ternary device performance was mainly ascribed to the high J_{sc} (from 17.39 to 23.68 mA cm⁻²), and is consistent with the enhanced EQE values in the range of 800–1000 nm, which could generate more photoinduced charge carriers by additional IEICO-4F.

Kim et al.⁹² fabricated the PBTTFB: PC₇₀BM binary OPV (PBTTFB, a copolymer based on *N*-alkylthieno[3,4-*c*]pyrrole-4,6-dione (TPD) as the acceptor and BDT as the donor) with an ideal morphology, consistent with a high FF of 73%, but it suffered insufficient absorption. They employed ITIC to improve the absorption of the PBTTFB: PC₇₀BM binary OPV. Surprisingly, 10 wt% of ITIC could maximize the EQE value of the PBTTFB: ITIC: PC₇₀BM (1:0.15:1.35) ternary blend and inherited the ideal morphology from the FA-based binary blend, leading to the higher J_{sc} of 13.73 mA cm⁻² as compared with 10.79 mA cm⁻² of the PBTTFB: PC₇₀BM binary OPV. As the ΔE_{HOMO} = 0.05 eV of PBTTFB and ITIC is negligible, the holes can be efficiently transferred from ITIC to PBTTFB, revealed by femtosecond TA spectroscopy, which indicates that the hole transfer is not completely decided by the difference in the HOMO energy level between the acceptor and the donor, but is significantly affected by the blend morphology. In the ternary device, the presence of PC₇₀BM can suppress the large aggregation of ITIC and form a modified thin-film morphology, which can boost the transfer of holes and charge transport from ITIC to PBTTFB, and can inhibit bimolecular recombination. All of the above provide strong evidence that the direct incorporation of NFAs into FA-based binary solar cells can enhance absorption, then generate more photoinduced carriers, further improving J_{sc} and thus photovoltaic performance. This indicates that the ternary strategy is a promising candidate method for the utmost utilization of the solar spectrum.

Figure 9 a) *J*-*V* curves of PDOT: PC₇₁BM binary OPVs and PDOT: PC₇₁BM: ITIC ternary OPVs with 0%, 0.5%, and 1.0% DIO; and b) their corresponding EQE spectra. Reprinted with permission from Ref. 120. Copyright 2016 Wiley-VCH.

of 300–700 nm compared with that of the ITIC-based binary solar cell due to the reduced PC₇₁BM content, a considerable improvement in the range of 700–800 nm can be observed, which is ascribed to the direct absorption of ITIC. Consequently, optimized thick-film ternary solar cells (over 200 nm) exhibited an increase in J_{sc} of 26% (from 13.92 to 17.49 mA cm⁻²), resulting in an increase in PCE from 9.54% to 11.21%.

Bi et al.¹²¹ used an ultralow band-gap small-molecular IEICO-4F as a guest acceptor, added into a PTB7-Th: PC₇₁BM binary system and achieved a PCE of 11.24%. The improve-

Forming a Cascade Energy Level

In contrast to fullerene derivatives, NFAs exhibit an adjustable chemical structure with controllable energy levels, which may help form cascade energy level alignment in ternary blends to accelerate exciton dissociation and charge transfer, and further improve J_{sc} and FF. In this case, the NFAs are supposed to present suitable energy levels, and the HOMO and LUMO energy levels of the donor, NFA, and FA should align in a decreasing sequence. Besides, the NFAs should lay the interface between the host donor and the host acceptor and serve as an intermediate, called “bridge.” The “bridge” can accelerate the charge transfer between the host donor and acceptor, and then make contributions to J_{sc} and FF, and thus to device efficiency. The value of V_{oc} in OSCs is mainly determined by the energy difference between the HOMO energy level of the donor and the LUMO energy level of the acceptor, and in theory the incorporation of the second

acceptor as the “bridge” in the cascade model will have little effect on V_{oc} . Therefore, it offers an opportunity to simultaneously improve J_{sc} and V_{oc} via introducing NFAs with suitable energy levels as the second acceptor. In other words, the formation of a cascade energy level in ternary solar cells can provide an efficient approach to improve J_{sc} , V_{oc} , and FF simultaneously. The charge transfer in the cascade model can be detected by steady and transient PL measurements. If the charge transfer occurs between the two acceptors, the PL emission intensity of one acceptor would be quenched, and no obvious improvement in the PL emission intensity of other acceptor would be detected.

As mentioned before, the location of the third component in the ternary blend also plays a key role in the cascade energy alignment. Kranthiraja et al.¹²² studied a ternary cell consisting of an optimized P1: PC₇₁BM: ITIC (1:1:0.1) blend (P1, poly[4,8-bis(2-(4-(2-ethylhexyloxy)3-fluorophenyl)-5-thienyl)benzo[1,2-b:4,5-b']dithiophene-*alt*-1,3-bis(4-octylthien-2-yl)-5-(2-ethylhexyl)thieno[3,4-c]pyrrole-4,6-dione)], and according to the wetting coefficient value (0.086) in the ternary blend, ITIC was located at the interface between the P1 and the PC₇₁BM. Based on the surface energies of PC₇₁BM: ITIC (1:1), P1: ITIC (1:1), and P1: PC₇₁BM (1:1:0), represented by $\gamma_{PCBM-ITIC}$, $\gamma_{P1-ITIC}$, and $\gamma_{P1-PCBM}$, respectively, the wetting coefficient of ITIC (ω_{ITIC}) in the ternary blend can be calculated via Young's equation: ($\omega_{ITIC} = \frac{\gamma_{PCBM-ITIC} - \gamma_{P1-ITIC}}{\gamma_{P1-PCBM}}$). The value of ω_{ITIC} (0.086) is between -1 and 1; thus, the location of ITIC may be at the P1/PC₇₁BM interface, and it also can be revealed by TEM – energy dispersive X-ray analysis elemental mapping of the binary and ternary blends. Besides, P1, ITIC, and PC₇₁BM display a decreasing LUMO energy level of -3.62, -3.89, and -4.00 eV, respectively, as well as a deepened HOMO energy level of -5.44, -5.49, and -5.68 eV, respectively. Such a cascade energy alignment would facilitate the charge separation and transfer, and the introduction of ITIC could enhance absorption, leading to an improvement in J_{sc} (from 12.60 to 17.71 mA cm⁻²).

Hwang et al.¹²³ reported that incorporation of ITIC into the PBT-OTT: PC₇₁BM binary system [PBT-OTT, a polymer based on PBT with a 3-octylthiophene (OT) π -bridge (PBT-OT), and PBT with a 3-octylthieno[3,2-b]thiophene (OTT) π -bridge, (PBT, a copolymer based on 4,8-bis(5-ethylhexylselenophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (EHSeBDT) and 5-(2-butyloctyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (BOTPD))] might form a cascade energy level, and this can be revealed by the PL spectra. The emission signal of PBT-OTT was quenched without an increased PL signal of ITIC in the PBT-OTT: ITIC blend film, and the PL signal of ITIC decreased without an increased PL signal of PC₇₁BM in the ITIC: PC₇₁BM blend film, which suggests that efficient charge transfers occur in the ternary system. It was also found that the introduction of ITIC can facilitate charge

transport and reduce charge recombination, and achieved a higher and more balanced charge mobility. Besides, there is an obvious difference in film morphology between the binary and ternary systems. The density of surface traps decreased and crystallinity increased after adding a proper amount of ITIC; the modified film morphology also made contributions to charge carrier transport, which benefits J_{sc} and FF. As a result, the ternary device shows an enhancement in J_{sc} (from 13.3 to 14.8 mA cm⁻²), FF (from 58.5% to 63.0%), and PCE (from 6.74% to 8.78%).

Other reports would also confirm that the formation of cascade energy levels in ternary blends may accelerate the charge transfer and transport by choosing NFA with a suitable energy level, in comparison with the corresponding FA-based binary blend.^{124–127} This approach can improve the efficiency of binary OPVs based on FA by the increased J_{sc} . Despite this, the improvement in PCE would not rely only on the formation of the cascade energy level. The enhanced optical absorption or modified thin-film morphology also plays a key role.

Other Effects

As discussed earlier, the incorporation of a FA into NFA-based binary OPVs can modify the active layer morphology. It is worth noting that the incorporation of NFA into FA-based binary OPVs can also increase the device efficiency via improved morphology.^{128–131} Moreover, the addition of an NFA may form a hydrogen bond with a FA, modify the connection between the donor and the acceptor by virtue of its tunable molecular structure, and also change the dielectric constant and reduce the Coulomb capture radius to mend charge dynamics, to further improve the device performance.

Morphology: Cheng et al.¹³² reported a more controlled structure in a ternary device by the sequential solution process, which is beneficial for forming the ideal vertical distribution and thus the device performance. Orthogonal solvents were used for fabricating a ternary device by spin coating for the ideal vertical distribution in the ternary active layer. At first, Cheng et al. used the PTB7-Th: PC₇₁BM (1:2) binary device and the PTB7-Th: PC₇₁BM: IDIC (1:2:0.45) ternary device (IDIC, a planar fused-ring electron acceptor based on indacenodithiophene with four *n*-hexyl side chains) inverted device by simple spin coating, in which the donor and acceptor are simultaneously spin coated, both are limited by non-uniform vertical distribution of the materials. The mass aggregation of the donor closer to the bottom surface would impair the charge collection of the cathode. In addition, the third component would form an isolated phase in the simple ternary (S-ternary) blend OPV based on PTB7-Th: PC₇₁BM: IDIC (1:2:0.45), and this acted as a recombination center to impede charge transport. Thus, the S-ternary suffered poor

mobility consistent with poor FF. To solve this issue, a more controlled structure ternary (C-ternary) was reported, in which the guest acceptor and the host D/A binary blend are sequentially spin coated by orthogonal solvents. The C-ternary blend showed an ideal distribution of the donor in the vertical direction for the more efficient charge transport and collection, as well as weaker recombination. As a result, the C-ternary blend OPV with the highest PCE exhibits improved efficiency among the binary and S-ternary blend OPVs, with increased J_{sc} (from 16.3 to 18.7 mA cm⁻²), FF (from 67.2% to 69.6%), and PCE (from 9.10% to 10.70%) compared with the PTB7-Th: PC₇₁BM binary OPV. Moreover, introducing an NFA into a donor: FA may solve the issue of poor morphology in a binary blend with a FA, like forming a proper phase separation, suppressing mass aggregation, as well as adjusting the crystallinity and enlarging the D/A interface of the blend, to further benefit the charge dynamic.^{40,125,126,133,134}

Hydrogen bond: The formation of hydrogen bonds in a ternary device can also contribute to device performance. Du et al.¹³⁵ selected 3-(diethylamino)-7-imino-7H-benzo [4,5]imidazo [1,2-a]chromeno[3,2-c]pyridine-6-carbonitrile (DIBC) as the second acceptor to improve the efficiency of the PTB7-Th: PC₇₁BM binary OPV. The N-H bond in DIBC possessing an exposed H-atom may form a hydrogen bond with the carbonyl group of PC₇₁BM in a ternary device, which was verified by Fourier-transform infrared spectra and two-dimensional NMR. PC₇₁BM presented a higher electrostatic potential due to the presence of an intermolecular hydrogen bond, and it enlarged the potential difference in the ternary blend for efficient exciton dissociation. In addition, the fullerene-based OPV was limited by the relatively low FF because of the mass aggregation of PC₇₁BM, but the introduction of 15 wt% of DIBC can reduce the phase separation into a suitable domain as well as construct the bi-continuous interpenetrating network, which may be related to the intermolecular hydrogen bond interaction. Du et al. also synthesized 3-(diethylamino)-7-oxo-7H-(1)benzopyrano (3', 2':3,4) pyrido (1,2-a) benzimidazole-6-carbonitrile (DOBC), which had a similar chemical structure and absorption to DIBC, but would not form an intermolecular interaction with PC₇₁BM, leading to a decrease in PCE with poor morphology and charge dynamics compared with the PTB7-Th: PC₇₁BM binary OPV. The PTB7-Th: PC₇₁BM: DIBC ternary device showed an improvement of 26% in PCE (from 9.69% in the binary OPV to 12.17% in the ternary device) with increased J_{sc} and FF (from 18.43 to 20.68 mA cm⁻² and from 64.54% to 73.37%, respectively).

Interfacial connection: Given the adjustable molecular configuration of NFAs, Sharapov et al. used a unique small-molecule TPB, bearing four α -perylene diimides (PDI)s, in which the four PDIs form a cross-like molecular conformation while still being partially conjugated with the BDT-Th

core to fabricate a well-performing ternary device.¹³⁶ According to Young's equation, the value of ω_{TPB} , the wetting coefficient of TPB in the PTB7-Th: PC₇₁BM blend, is 0.47, within the range between -1 and 1, which indicates that TPB may largely be at the interface of PTB7-Th: PC₇₁BM. Thus, TPB can act as an electronic relay bridge between the polymer and PC₇₁BM domains for better connectivity between the two phases, leading to an increased charge generation. An efficient electron transfer occurs between TPB and PC₇₁BM, which may be ascribed to TPB with a cross-like molecular structure, which can offer more contact sites between TPB and PC₇₁BM, and to the LUMO energy levels that are nearly equal for PC₇₁BM. Hence, the strongly enhanced electron mobility could improve the value of J_{sc} in the ternary system compared with the binary system. In light of GIWAXS images, the fullerene-based binary blend exhibits amorphous characteristics, whereas incorporation of TPB would strengthen the crystallinity of PTB7-Th: PC₇₁BM blend for better charge transport and extraction. Therefore, J_{sc} increased from 17.2 mA cm⁻² in the PTB7-Th: PC₇₁BM binary device to 19.4 mA cm⁻² in the PTB7-Th: PC₇₁BM: TPB (1:1.5:0.1) ternary device. To summarize, Sharapov et al. manufactured a ternary OPV device with a higher PCE of 10.6% compared with 9.8% in a fullerene-based binary OPV.

Dielectric constant and Coulomb capture radius:

Duan et al. demonstrated that the introduction of an NFA, poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-1]]-[3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene-diyl (IDFBR) into a binary blend of PTB7: PC₇₁BM (PTB7: poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-1]]-[3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]) can efficiently improve device performance by adjusting the dielectric constant and reducing the Coulomb capture radius¹³⁷; the former is related to the exciton binding energy and charge carrier recombination, and the latter is associated with charge generation. Duan et al. fabricated a series of ternary OPVs (PTB7: PC₇₁BM: IDFBR) with varying amounts of IDFBR (0, 5, 10, 15, and 100 wt%), and the device PTB7: PC₇₁BM: IDFBR (with 5 wt% IDFBR) showed the highest PCE. The absorption curve of the ternary blend with 5 wt% IDFBR improved in the range of 450–800 nm compared with the binary blend, but was lower than that of the ternary blend with 10 and 15 wt% IDFBR. Nevertheless, the ternary blend with 5 wt% IDFBR displayed maximum EQE values, which may be attributed to increased dielectric constant and decreased Coulomb capture radius, leading to enhanced charge separation and transport, as well as reduced charge recombination, consistent with the increase in J_{sc} (from 16.70 to 17.38 mA cm⁻²) and FF (from 50.63% to 55.56%). Furthermore, the LUMO/HOMO energy level of IDFBR was in between those of PTB7 and PC₇₁BM, which was responsible for the improved charge transport,

and thus the value of V_{oc} (from 0.716 to 0.731 V). In summary, the strategy of using a ternary compound can elevate V_{oc} , J_{sc} , and FF with an improvement of 12% in PCE compared with the corresponding binary device.

Charge dynamics: The addition of NFA into a FA-based binary device may also amend its charge dynamics. A report found via theoretical calculations showed that combining IT-M with the PTB7-Th: PC₇₁BM binary blend may facilitate charge transport.¹³⁸ In other words, the incorporation of NFAs into binary devices based on FA is a promising strategic method to realize high-performance OPVs.

Balanced Charge Separation and Transport Enabled by Ideal Hierarchical Morphology

The film morphology of an active layer has a significant effect on the performance of OPVs. Most reports on ternary OSCs fail to explain how the changes in morphology affect the charge dynamics to further improve device performance, which is similar to conventional analysis of binary OSCs and is unable to make full use of the merits of a strategy of using a ternary compound in OPV devices. For instance, although there is morphological amelioration in crystallinity in a binary system, transverse and vertical phase separation can be achieved via the “ternary strategy”; it can also be realized by device optimization in binary OSCs. Hence, in this section, ternary systems for morphology control according to the hierarchical structure are discussed in detail.

In general, charge generation needs small phase length, while efficient charge transport needs a continuous fibrous network framework. Both of them are hardly achieved in the active layer with uniformity domain, simultaneously. Nevertheless, the hierarchical morphology with multiple phase length can balance the charge generation and transport for an optimal device performance. The formation of a hierarchical morphology consisting of multiple phases with a complex multilength scale in the ternary system may be an instructive strategy to figure out the relationship between morphology and performance of OSCs, in which the small phase separation is responsible for exciton diffusion and charge separation and the large phase separation can boost charge carrier transport and collection and thus device performance.

Our group first utilized FA (PC₇₁BM) and NFA (NITI) and a small molecular donor (BTR, BDT terthiophene rhodamine; NITI, 2,2'-(2,2,2'-((6,6'-(5,5,10,10-tetrakis(2-ethylhexyl)-5,10-dihydroindeno[2,1-a]indene-2,7-diyl)bis(2-octylthieno[3,4-b]thiophene-6,4-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile) in a ternary system, leading to high-performance OPV with a hierarchical morphology.¹²⁹ The

high-efficiency ternary OPV can greatly balance the charge carrier generation and transport and fully utilize the merits of the ternary strategy. The hierarchical morphology consists of the PC₇₁BM framework fitted by a refined phase separation of BTR: NITI, and more specifically, the NITI lies between PC₇₁BM and BTR with a preferred face-on orientation towards the PC₇₁BM (Figure 10). On the one hand, the fine BTR: NITI phase

Figure 10 a) The BTR (orange rods): PC₇₁BM (green circles): NITI (navy rods) ternary blend film with ideal hierarchical morphology. Reprinted with permission from Ref. 129. Copyright 2018 Springer Nature.

separation can offer sufficient D/A interface for efficient exciton dissociation. On the other hand, the presence of PC₇₁BM can boost charge transport and extraction, which is revealed by the results of the dependence of photocurrent density on the effective voltage among the ternary and two binary OPVs. Besides, the NITI can receive electron from the BTR and then fast transfer it to the PC₇₁BM for the demand of a passivating energetic disorder. In consequence, the trap-assisted recombination reduced in the ternary blend with the incorporation of NITI. From the investigation of electroluminescence spectroscopy, our group found that the existence of NITI would interdict the contact between PC₇₁BM and BTR to reduce non-radiative energy loss. Thus, such a ternary OSC with ideal hierarchical morphology can maximize the values of V_{oc} , J_{sc} and FF, and achieve a high PCE of 13.63% in the BTR: NITI: PC₇₁BM ternary device. Our group also expanded this research to other small-donor (DR3TSBDT/DR3TBDTT)/FA (PC₇₁BM)/NFA (ITIC/NITI-EH) ternary systems and realized the possible formation progress of a hierarchical morphology. The precondition of a hierarchical morphology is the formation of refined donor: NFA phase separation and large-scale mixing between PC₇₁BM and other components. The large PC₇₁BM framework formed via phase separation, firstly. The crystallinity of the donor domain enhanced during the solvent vapour annealing. Then the NFA squeezed out from the donor domain and congregated in the interface of the PC₇₁BM framework and formed small-size phase separation. The high-performance device can be attributed to the formation of a hierarchical morphology, and it was also demonstrated by Wei's group.¹³⁹ The combination of fullerene and NFAs has shown great potential in achieving record OPV performance.^{17,19,42,96,118,140,141}

Conclusions and Outlook

The above-mentioned discussion was meant to clarify that the ternary device synergizing a FA and an NFA can overcome the limitations of conventional OPVs based on a single D–A pair, as well as benefit from its advantages. The incorporation of FA into the binary blend based on NFA can promote the device efficiency by rearranging and suppressing the molecular stacking and mass aggregation of the host D/A, adjusting the crystallinity and vertical distribution of the active layer in the ternary device, forming bi-continuous interpenetrating network or forming energy transfer. As for binary OPVs based on FA, the addition of a NFA mainly acts as a light absorber or forms cascade energy level alignment. Surprisingly, it can also be a morphology modifier to improve device efficiency. Moreover, the ternary strategy may improve the long-term stability of the device by maintaining the morphology of the active layer. Through numerous research studies, it is firmly believed that the ternary strategy based on NFA and FA is a promising way to obtain high-performance OSCs, because it can efficiently combine the advantages of both NFA and FAs along with overcoming the respective shortcomings of each type. Recently, Liu et al. synergized Y6 and PC₇₁BM as acceptors combined with the PM6 and PM7 (poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-4-chlorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene))-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-c:4,5-c']dithiophene-4,8-dione))] donor pair, and achieved a device with a high PCE of over 18% with ameliorative charge kinetics and reduced non-radiation loss via a double cascading charge transport, which can demonstrate that the multicomponent strategy can effectively improve device performance.¹⁴¹ The ternary solar cell has reached a high performance of 18.3% via the synergy effect of n-doping and the ternary strategy.¹⁹ In addition, this ternary strategy can also efficiently improve device stability.¹³ And much research has been conducted to achieve the higher performance OSCs via the use of a ternary component (ternary strategy)^{141–147} and even a quaternary component (quaternary strategy).¹⁴⁸ However, the specific working mechanism of ternary OPVs is debatable owing to the complexity of ternary OPVs that use three different components in a single device. Thus, the working mechanism of ternary OPVs need to be further explored.

Despite the many recent successful examples and inspiring advances in ternary OPVs reported above, some fundamental issues still need to be addressed. (1) New materials with high absorption coefficients and excellent charge transport properties are supposed to be designed and synthesized to maximize the use of solar energy. (2) The selection of the third component in ternary OSCs should be deliberate to maximize all the aforementioned possible advantages of the ternary strategy. (3) The technologies of device fabrication that favor the stability and performance

of devices need to be improved, such as the design of the buffer layer, which also is a basic premise of large-scale production for commercial application. (4) Methods that reveal the relationship between structure and performance of the ternary device should be explored to get a better understanding of the working mechanism of ternary OPVs. In summary, the ternary strategy provides a promising way to improve device efficiency and stability simultaneously, and there is still much room for it to be improved.

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