



香港城市大學
City University of Hong Kong

專業 創新 胸懷全球
Professional · Creative
For The World

CityU Scholars

Suppressed recombination loss in organic photovoltaics adopting a planar–mixed heterojunction architecture

Jiang, Kui; Zhang, Jie; Zhong, Cheng; Lin, Francis R.; Qi, Feng; Li, Qian; Peng, Zhengxing; Kaminsky, Werner; Jang, Sei-Hum; Yu, Jianwei; Deng, Xiang; Hu, Huawei; Shen, Dong; Gao, Feng; Ade, Harald; Xiao, Min; Zhang, Chunfeng; Jen, Alex K.-Y.

Published in:
Nature Energy

Published: 01/11/2022

Document Version:

Post-print, also known as Accepted Author Manuscript, Peer-reviewed or Author Final version

Publication record in CityU Scholars:

[Go to record](#)

Published version (DOI):

[10.1038/s41560-022-01138-y](https://doi.org/10.1038/s41560-022-01138-y)

Publication details:

Jiang, K., Zhang, J., Zhong, C., Lin, F. R., Qi, F., Li, Q., Peng, Z., Kaminsky, W., Jang, S.-H., Yu, J., Deng, X., Hu, H., Shen, D., Gao, F., Ade, H., Xiao, M., Zhang, C., & Jen, A. K.-Y. (2022). Suppressed recombination loss in organic photovoltaics adopting a planar–mixed heterojunction architecture. *Nature Energy*, 7(11), 1076-1086. <https://doi.org/10.1038/s41560-022-01138-y>

Citing this paper

Please note that where the full-text provided on CityU Scholars is the Post-print version (also known as Accepted Author Manuscript, Peer-reviewed or Author Final version), it may differ from the Final Published version. When citing, ensure that you check and use the publisher's definitive version for pagination and other details.

General rights

Copyright for the publications made accessible via the CityU Scholars portal is retained by the author(s) and/or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights. Users may not further distribute the material or use it for any profit-making activity or commercial gain.

Publisher permission

Permission for previously published items are in accordance with publisher's copyright policies sourced from the SHERPA RoMEO database. Links to full text versions (either Published or Post-print) are only available if corresponding publishers allow open access.

Take down policy

Contact lbscholars@cityu.edu.hk if you believe that this document breaches copyright and provide us with details. We will remove access to the work immediately and investigate your claim.

This version of the article has been accepted for publication, after peer review (when applicable) and is subject to Springer Nature's [AM terms of use](#), but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: <http://dx.doi.org/10.1038/s41560-022-01138-y>.

Suppressed Recombination Loss in Organic Photovoltaics Adopting a Planar-mixed Heterojunction Architecture

Kui Jiang^{1,4,11,13}, Jie Zhang^{2,13}, Cheng Zhong^{3,13}, Francis R. Lin^{1,4,11*}, Feng Qi^{4,11}, Qian Li⁵, Zhengxing Peng⁶, Werner Kaminsky⁷, Sei-Hum Jang⁸, Jianwei Yu⁹, Xiang Deng^{1,11}, Huawei Hu¹⁰, Dong Shen⁴, Feng Gao⁹, Harald Ade⁶, Min Xiao⁵, Chunfeng Zhang^{5,12*}, and Alex K.-Y. Jen^{1,4,8,11*}

¹Department of Materials Science and Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong.

²Center for Photonics Information and Energy Materials, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen, Guangdong 518055, P.R. China.

³Department of Chemistry, Wuhan University, Wuhan, Hubei 430072, P.R. China.

⁴Department of Chemistry, City University of Hong Kong, Kowloon 999077, Hong Kong.

⁵National Laboratory of Solid State Microstructures, School of Physics, and Collaborative Innovation Center for Advanced Microstructures, Nanjing University, Nanjing, Jiangsu 210093, P.R. China.

⁶Department of Physics and Organic and Carbon Electronics Laboratories (ORaCEL), North Carolina State University, Raleigh, North Carolina 27695, United States.

⁷Department of Chemistry, University of Washington, Seattle, Washington 98195-1700, United States.

⁸Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195-2120, United States.

⁹Department of Physics Chemistry and Biology (IFM), Linköping University, Linköping SE-58183, Sweden.

¹⁰College of Materials Science and Engineering, Donghua University, Shanghai 201620, P.R. China.

¹¹Hong Kong Institute for Clean Energy (HKICE), City University of Hong Kong, Kowloon 999077, Hong Kong.

¹²Institute of Materials Engineering, Nanjing University, Nantong, Jiangsu 226019, P.R. China.

¹³These authors contributed equally: Kui Jiang, Jie Zhang, Cheng Zhong.

*E-mail: franclin@cityu.edu.hk; cfzhang@nju.edu.cn; alexjen@cityu.edu.hk.

31 **Abstract:** Present high-performance organic photovoltaics (OPVs) mostly adopt a bulk-
32 heterojunction (BHJ) architecture, in which exciton dissociation is facilitated by charge-
33 transfer (CT) states formed at numerous donor-acceptor (D-A) heterojunctions. However, the
34 spin-character of CT states originated from recombination of photocarriers allows relaxation
35 to the lowest-energy triplet exciton (T_1) at these heterojunctions, causing photocurrent loss.
36 Here, we find that this loss pathway can be alleviated in sequentially processed planar-mixed
37 heterojunction (PMHJ) devices, employing donor and acceptor with intrinsically weaker
38 exciton binding strengths. The reduced D-A intermixing in PMHJ alleviates non-geminate
39 recombination at D-A contacts, limiting the chance of relaxation thus suppressing T_1 formation
40 without sacrificing exciton dissociation efficiency. This resulted in devices with high power
41 conversion efficiencies of $>19\%$. We elucidate the working mechanisms for PMHJ discussing
42 the implications for material design, device engineering, and photophysics, thus providing
43 comprehensive understanding for future improvements in OPVs to reach their full promise.
44

45 Organic photovoltaic (OPV) is a promising technology for clean energy due to its vast
46 molecular tunability of photoactive materials.¹⁻³ The proof-of-concept OPV absorber
47 demonstrated in the 1980s adopted a sequentially vacuum-deposited bilayer architecture,⁴
48 which showed very low efficiency reflecting the limited material properties and processing
49 techniques. Until 1995, bulk-heterojunction (BHJ) architecture consisting a highly intermixed
50 donor:acceptor (D:A) network was found to greatly improve cell performance by facilitating
51 exciton dissociation in OPV absorbers.⁵ The nanoscale phase-separated domains and energy
52 offsets at numerous D-A heterojunctions help overcome the short diffusion lengths^{1, 6, 7} and
53 large exciton binding energy^{1, 8, 9} in organics. Based on this concept, very vibrant research has
54 led to the development of very efficient pseudo-2D non-fullerene acceptors (NFAs) represented
55 by BTP-4F (Y6).² They possess strong near-infrared (NIR) photoresponse in conjunction with
56 low interfacial energetic disorder due to enhanced intermolecular π - π interaction and unique
57 solid-state packing patterns.^{10, 11} Power conversion efficiencies (PCEs) of greater than 18%
58 have been reported,¹² representing the state-of-the-art of the field.

59
60 However, it is a major challenge in the field to continuously improve the OPV performance to
61 reach their theoretically achievable values. In a BHJ, the charge-transfer (CT) states with both
62 singlet/triplet (¹CT/³CT) spin characters can be formed at numerous D-A heterojunctions
63 through non-geminate recombination of free charges¹³ dissociated from photoexcited local
64 excitons (LE) with mediation of ¹CT (Figure 1a). The relaxation of CT states dominates the
65 energy loss in OPV, undermining the short-circuit current density (J_{SC}).¹⁴ To prevent such
66 cascade relaxation process, strategies have been applied to minimize the spin-mediated
67 relaxation between ³CT and the lowest-energy triplet exciton (T_1), including promoting
68 wavefunction delocalization,¹³ and molecularly engineering of T_1 energy level¹⁵⁻¹⁷ in both
69 fullerene/non-fullerene OPVs. Nevertheless, the role of these densely populated interfacial CT
70 states in BHJ is an intermediate between excitons and free carriers. The ¹CT formed prior to
71 charge-separated (CS) state facilitates exciton dissociation and thus free carrier formation
72 ($LE \rightarrow ^1CT \rightarrow CS$), but the ¹CT/³CT originated from non-geminate recombination tend to relax
73 to ground state if insufficient repopulation to CS state occurs, inevitably causing photocurrent
74 loss.

75
76 Intriguingly, spontaneous formation of intermolecular delocalized singlet excitons (DSE) in
77 neat pseudo-2D NFAs under condensed phase was observed upon photoexcitation,¹⁸ which

78 was also identified to be capable of mediating the pathway of free carrier formation in the OPV
79 blend (LE→DSE→CS). Such a pathway is indicative of the weaker dependency of ¹CT for
80 exciton dissociation in these materials, which creates hope to mitigate the CT-mediated loss
81 pathways. Along this direction, we have discovered that sequentially deposited donor/acceptor
82 (D/A) planar-mixed heterojunction (PMHJ) OPVs employing materials with intrinsically
83 weaker exciton binding strengths are capable of hindering CT-mediated loss pathways. The
84 less D-A contacts in PMHJ suppress the formation of recombined CT states and result in
85 reduced T₁ concentration, as spectroscopically evidenced in this study. Single-junction OPVs
86 with high PCEs surpassing 19% were subsequently achieved based on our findings.

87

88 **PMHJ as an effective strategy to realize efficient OPVs**

89 Sequentially processed OPVs have shown potential to compete with or even outperform one-
90 step processed BHJ cells in recent studies,^{7, 19-21} however, the reason behind these observations
91 is yet unclear. Unlike the conventional BHJ processed from a pre-mixed D:A solution, our
92 PMHJ is processed in a two-step manner by spin-casting the chloroform solution of NFA on
93 top of the thin-film of donor polymer PDTBT2T-FTBDT (D18). D18 exhibits strong
94 temperature-dependent aggregation properties and limited solubility and is pre-deposited from
95 its solution in hot chlorobenzene²² (Supplementary Figure 4). Without further post-treatments
96 and additives, a rather de-mixed blend with reduced D-A heterojunctions and non-uniform out-
97 of-plane material distribution can be achieved (Figure 1e). The obtained high PCEs of 18.22%
98 (D18/T9TBO-F) and 18.30% (D18/T9SBN-F) (Figures 1b-d) indicate extremely efficient
99 photo-to-current conversion with minimized photovoltage-photocurrent trade-offs in binary
100 PMHJ cells (Figure 2a & Supplementary Table 2). The open-circuit voltage (V_{OC}) and non-
101 radiative V_{OC} loss (Supplementary Figures 19-20 & Supplementary Table 12) are comparable
102 to those of high-performance devices reported.²³⁻²⁵ This method also shows satisfactory
103 reproducibility (Supplementary Figure 6) which is critical for OPV practical applications,
104 especially while D18 is very difficult to process in BHJ form due to its hard-to-control strong
105 aggregation.²² For comparison, BHJ cells with identical material systems were also fabricated
106 and showed lower PCEs of 17.21% (D18:T9TBO-F) and 17.07% (D18:T9SBN-F)
107 (Supplementary Figure 5 & Supplementary Table 2), due to their lower fill factors (FFs) from
108 less balanced charge carrier mobilities in BHJ blends (Supplementary Figure 10 &
109 Supplementary Table 4),²⁶ and more importantly, their inferior J_{SCs} .

110

111 The scope of this study was further broadened by conducting a comprehensive mapping of
112 material systems covering 14 NFAs in the D18/NFA PMHJ device form to prove the general
113 applicability of this approach, including Y6, T9TBO-F, T9SBN-F, and additionally 11 NIR-
114 absorbing NFAs^{11, 27, 28} (Supplementary Figures 1-3), which showed high PCEs ranging from
115 17.53 to 18.30% (Supplementary Figure 5 & Supplementary Table 3). The ternary strategy was
116 applied to successfully improve the V_{OC} of PMHJ cells (Supplementary Table 3). By adding a
117 medium bandgap NFA Y6-O²⁹ in the NFA precursor solution then spin-cast over pre-deposited
118 D18 thin-film, it gave a ternary PMHJ to achieve high PCEs of over 19% in the single-junction
119 devices of D18/T9TBO-F:Y6-O (Figure 2a) and extensively NIR-absorbing D18/S9SBO-
120 F:Y6-O (Supplementary Figure 5 & Supplementary Tables 3). Devices from D18/T9TBO-
121 F:Y6-O and D18/S9SBO-F:Y6-O PMHJ were certified by different authorities respectively,
122 one of which was acknowledged by the National Renewable Energy Laboratory in September,
123 2020 (Supplementary Figures 7-9).

124

125 **Reducing exciton binding strength benefits PMHJ cells**

126 To reveal the underlying mechanisms behind the high efficiency of PMHJ cells, comprehensive
127 characterizations were performed on neat films of D18 and two NFAs, T9TBO-F and T9SBN-
128 F, as well as their BHJ and PMHJ blends, to provide better understanding of their photophysical
129 and morphological properties. The dynamics of excitons and photocarriers in materials were
130 probed by transient absorption (TA) spectrometry. Within ~ 10 ps time scale, the Frenkel-type
131 LE states (1180 nm in neat D18; 915 and 930 nm in neat T9TBO-F and T9SBN-F, respectively,
132 and their corresponding blends) emerge, of which the decay followed by uprising excited-state
133 absorption (ESA) bands (940 nm in neat D18; 1550 and 1600 nm in neat T9TBO-F and
134 T9SBN-F, respectively, and their corresponding blends) indicating fast conversion (< 1 ps) of
135 LE into an intermediate state (Figures 3a-c & Supplementary Figures 30-32). These ESA bands
136 may correspond to an intermolecular DSE state (Supplementary Figures 33 & 42), where
137 closely packed molecules help reduce exciton binding energy and facilitate the formation of
138 excited species with CT characters.^{10, 18}

139

140 The packing of materials was then simulated by molecular dynamics (MD) calculations to
141 investigate the intermolecular interactions of the materials in condensed phase, coupling with
142 density functional theory calculations to provide information from both structural and energetic
143 aspects. The calculations revealed that the formation of DSE state with lower energy versus
144 LE (Figure 1a, Supplementary Figures 21-22 & Supplementary Tables 13-19) is facilitated by

145 intimate packing of strongly interacting molecular moieties, dithienobenzothiadiazole in D18
146 and indanone in NFAs (Figures 3d-f), respectively. The close packing of materials was also
147 confirmed by X-ray crystallography of NFA single-crystals which consistently show intense *J*-
148 aggregation-like packing patterns (Supplementary Figures 12-14 & Supplementary Tables 5-
149 8), and the grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns of neat films
150 and PMHJ blends (Supplementary Figures S15-S17, Supplementary Tables 9-10 &
151 Supplementary Notes III & IV). Besides facilitating the formation of DSE state with CT
152 characters to aid exciton dissociation, intimate molecular packing of the materials may also
153 promote exciton diffusion in D18³⁰ and NFAs. We have further confirmed the long exciton
154 diffusion length in T9TBO-F (34 nm) from fluence-dependent TA dynamics measurements
155 (Supplementary Figure 46), which correlates well with the square root of calculated Marcus
156 rate ($3.29 \times 10^6 \text{ s}^{-1/2}$) reported in the literature.³¹

157

158 In the PMHJ blends of D18/T9TBO-F and D18/T9SBN-F, the ESA bands representing the fast
159 LE→DSE conversion within 0.1 ps were observed in NFA domains (Figures 4a & 4e,
160 Supplementary Figures 39A-D & 40A-D). Later, within the time scale of 1-100 ps, polaron
161 formation is indicated by the ESA band of CS states (765 and 790 nm in the corresponding
162 blends of T9TBO-F and T9SBN-F, respectively) as confirmed by the photo-induced absorption
163 measurements (Supplementary Figure 42), followed by the decay of DSE signal, indicating the
164 hole-transfer processes in the blends follow the pathway of LE→DSE→CS that is consistent
165 with the previously findings in the blends consisting of Y6.¹⁸ The rigid molecular backbone
166 and intimate packing of materials facilitate the formation of DSE state which synergistically
167 decreases the dependency of exciton dissociation on CT states, ensuring efficient exciton
168 transport in the PMHJ blends with lower degree of D-A intermixing.^{6,31} Therefore, the criteria
169 to realize efficient PMHJ cells can be fulfilled when both donor and acceptor materials
170 employed have intrinsically weaker exciton binding strengths. This helps reduce the need for
171 large amounts of D-A heterojunctions in BHJ to facilitate exciton dissociation and allow
172 efficient generation of free carriers in PMHJ cells.

173

174 **PMHJ outperforms BHJ by suppressing recombination loss**

175 For a good absorber in OPVs, the efficiency of carrier generation should be maximized while
176 that of carrier recombination ought to be minimized. While exciton dissociation in the PMHJ
177 architecture has been proven to be efficient, we further discovered that PMHJ can also help

178 suppress recombination loss. In the PMHJ blends of D18/T9TBO-F and D18/T9SBN-F, an
179 emerging ESA band at ~1440 nm was observed within the time scale of 100-1000 ps, which is
180 consistent with the spectral feature of T_1 in NFAs (Supplementary Figures 34-37) as identified
181 by triplet sensitization, indicating T_1 formation in the blends. In terms of time scale, T_1 in PMHJ
182 blends forms closely behind the population of CS states, indicating a relaxation pathway
183 originated from non-geminate charge recombination mediated by interfacial 3CT . Changing the
184 excitation fluence in TA experiments further showed that the relative signal intensity and the
185 generation dynamics of T_1 are fluence-dependent, consolidating that T_1 originates from non-
186 geminate recombination in the blends (Supplementary Figure 38).

187

188 Interestingly, the ESA band representing T_1 formation was also observed in neat T9SBN-F
189 film, accompanying with the decay of DSE state within the time scale of 1-500 ps (Figure 3c
190 & Supplementary Figure 32). This could be due to efficient intersystem crossing between
191 optically excited singlet excitons and T_1 due to heavy-atom effect brought by introducing
192 selenium atom.^{15, 32} However, this does not affect the capability of sequentially processed
193 D18/T9SBN-F PMHJ to suppress T_1 formation compared to its BHJ counterpart (Figures 4e-
194 f). On the other hand, although the pathways of exciton dissociation are still dominated by DSE
195 state, the ESA bands of ground-state bleaching (GSB) and CS states emerge much less
196 pronouncedly in the BHJ blends of D18:T9TBO-F and D18:T9SBN-F (Figures 4b & 4f,
197 Supplementary Figures 39E-H & 40E-H). Moreover, the T_1 ESA band appears significantly
198 over time (10-500 ps), indicating the densely formed T_1 is relaxed from recombined 3CT ,
199 leading to irreversible photocarrier loss. These results suggest that the PMHJ architecture is
200 capable of suppressing T_1 formation (Figures 4c-d & 4g-h), which is a unique example of
201 demonstrating efficient T_1 suppression in non-fullerene OPVs through the carefully engineered
202 active layer architecture using identical material systems. Similar trend of T_1 suppression could
203 also be observed in the ternary PMHJ blends of D18/T9TBO-F:Y6-O and D18/T9SBN-F:Y6-
204 O (Supplementary Figures 43-45).

205

206 Considering different $CS \rightarrow T_1$ relaxation pathways (Figure 1a), the reduced signal intensity of
207 T_1 in PMHJ may stem from (1) fewer polarons formed, which is contradictory to the higher J_{SC}
208 observed from PMHJ devices (Supplementary Table 2); (2) low transfer efficiency of
209 $CS \rightarrow ^1CT/^3CT$ or $^3CT \rightarrow T_1$, which is more material-related thermodynamic properties and
210 should be excluded since the material compositions used in this study are identical in the BHJ

211 and PMHJ blends; and most likely (3) the reduced D-A heterojunctions suppress the formation
212 of recombined $^1\text{CT}/^3\text{CT}$, therefore, hinders the back transfer pathways. To validate the
213 hypothesis, the structural and morphological differences between BHJ and PMHJ blends were
214 investigated by GIWAXS and resonant soft X-ray scattering (RSoXS) (Supplementary Figures
215 16-18 & Supplementary Tables 9-11). Both types of blends show similar GIWAXS profiles,
216 including stacking distance, coherence length and molecular orientation. It should be noted that
217 the best-performing D18/T9SBN-F exhibits the highest relative degree of ordering for (100),
218 (010) and (002) peaks, as well as the highest face-on/edge-on ratio. The backbone peak (002)
219 of D18 in PMHJ also exhibits higher relative degree of ordering than that in BHJ, implying the
220 distribution of more donor-rich phase in PMHJ (Supplementary Note IV). Importantly, RSoXS
221 shows higher scattering intensity and thus higher in-plane composition variations in PMHJ,
222 which can only arise due to some interpenetrations between the two layers. Moreover,
223 following basic scattering theory and prior arguments,^{33, 34} higher scattering intensity is
224 corresponding to smaller numbers of D-A contacts from distributed A molecules in the mixed
225 amorphous domains and the more discrete interfaces to D or A aggregates. Accordingly, a
226 lower degree of molecular mixing as implied from the larger and purer domains is found in
227 PMHJ than in BHJ (Supplementary Note V). Differences in composition gradients between
228 BHJ and PMHJ were further confirmed with time-of-flight secondary ion mass spectrometry
229 (ToF-SIMS) on D18/T9SBN-F, indicating some selenium enrichment towards the top of PMHJ
230 layer (Figure 1e). Consequently, the non-geminately recombined $^1\text{CT}/^3\text{CT}$ states at D-A
231 heterojunctions competing with charge extraction are depopulated, leading to less $^3\text{CT} \rightarrow \text{T}_1$
232 relaxation and improved J_{SC} in PMHJ cells. This can be further supported by the higher
233 normalized CS state intensity in the PMHJ samples than the BHJ ones, while normalizing the
234 amplitude of CS state to that of LE in each of the corresponding samples (Supplementary
235 Figure 47).

236

237 Discussion

238 In addition to hindering the pathway mediating irreversible loss of photocarriers, it has been
239 reported that suppressing T_1 formation could reduce non-radiative recombination to benefit
240 V_{OC} in certain material systems where energetic inversion of ^1CT and ^3CT is possible due to
241 the LE-CT hybridization.³⁵ However, similar effect is not observed in the well-studied PM6:Y6
242 in which energetic inversion of ^1CT and ^3CT is absent.³⁵ Whereas in our PMHJ and BHJ cells,
243 not only the V_{OC} s, but also the non-radiative V_{OC} losses are comparable (Figures 2c-e,
244 Supplementary Figures 19-20 & Supplementary Table 12). Therefore, the photovoltage and T_1

245 formation might not be directly correlated in our material systems containing Y6 derivatives.
246 This finding provides an effective way to enhance J_{sc} without sacrificing V_{oc} in our PMHJ
247 cells, while the non-radiative V_{oc} losses of ~ 0.24 eV in both D18/T9TBO-F and D18/T9SBN-
248 F cells are comparable to those derived from high-efficiency narrow-bandgap organic
249 absorbers.²³⁻²⁵

250

251 In summary, we report a strategy to alleviate non-geminate recombination by depopulating the
252 recombined CT states in sequentially deposited PMHJ OPVs with intrinsically reduced D-A
253 heterojunctions, of which the suppressed T_1 formation can be observed as a signature. The
254 efficient exciton dissociation in our PMHJ cells is ensured by employing photoactive materials
255 with lower exciton binding strengths. High PCEs surpassing 19% were subsequently achieved
256 in OPVs with a PMHJ active layer based on the composites of polymer donor D18 and pseudo-
257 2D Y6 NFA derivatives. The correlation between photocarrier generation efficiency and
258 formation of recombined $^1CT/{}^3CT$ that affects J_{sc} in OPV is identified, consequently showing
259 that a spin-mediated relaxation pathway causing irreversible energy loss is suppressed. The
260 working mechanism lying in PMHJ has also been elucidated to provide a better understanding
261 for improving OPV performance. Future efforts toward improving the stability of these PMHJ
262 cells and uncovering the fundamental mechanisms of V_{oc} loss in these high-performance
263 devices will further minimize the photovoltage-photocurrent trade-off, leading to PCEs greater
264 than 20% to reach the theoretical limit of OPVs.

265

266 **Methods**

267 **Materials.** The synthesis of the unreported NFA structures is illustrated in Supplementary Scheme S1,
268 with the detailed regarding procedure and structural characterizations included in the Supplementary
269 Information. Polymer donor D18 was synthesized according to literature.¹² The full names of T9TBO-
270 F: (2,10-bis(2-methylene-(3-(1,1-dicyanomethylene)-5,6-difluoroindanone))-12,13-bis(2-butyloctyl)-
271 3,9-dinonyl-dithieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*e*:2',3'-*g*][2,1,3]benzothiadiazole;
272 T9SBN-F: (2,10-bis(2-methylene-(3-(1,1-dicyanomethylene)-5,6-difluoroindanone))-12,13-bis(3-
273 butylnonyl)-3,9-dinonyl-diselenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*e*:2',3'-
274 *g*][2,1,3]benzothiadiazole. The full names of the rest of the synthesized NFAs are included in the
275 Supplementary Information.

276
277 **Material synthesis.** Unless stated otherwise, all chemicals and reagents were used as received from
278 commercial sources (Sigma-Aldrich, Acros, Matrix Scientific, Combi-Blocks, J&K Scientific, Energy)
279 without further purification. Solvents for chemical synthesis were purified by distillation under nitrogen
280 or by a solvent purification system (Innovative Technology, WellTech). All chemical reactions were
281 carried out under an argon or nitrogen atmosphere. The ¹H and ¹³C nuclear magnetic resonance spectra
282 were recorded on a Bruker AV500, Bruker 400 MHz AVANCE III or a Bruker 600 MHz ASCEND
283 AVANCE III HD spectrometer in CDCl₃ or *d*₆-DMSO. Mass spectrometry was performed on a Bruker
284 APEX III 47e Fourier Transform mass spectrometer, or a Q Exactive Focus Hybrid Quadrupole
285 Orbitrap Mass Spectrometer (QE Orbitrap MS, Thermo Fisher Scientific). The chemical structures and
286 detailed synthetic procedure of the synthesized NFAs are included in the Supplementary Information.

287
288 **Optical characteristics.** UV-vis-NIR absorption spectra were recorded on a Shimadzu 1700 UV-vis
289 spectrometer. The samples were spin-cast on quartz substrates and the thicknesses of films were
290 measured by a Bruker Dektak XT stylus profilometer.

291
292 **Energy level measurements.** Ultraviolet photoelectron spectrometry (UPS) was performed to study the
293 valence states of the materials with a He-discharge lamp providing He-I photos of 21.22 eV and a VG
294 ESCALAB 220i-XL surface analyzer. The absolute energy resolution of the analyzer was set as 0.018
295 eV for the UPS measurement so that the spectral resolution was 0.09 eV as estimated from the Fermi
296 edge of Au. During UPS measurement, a bias of -5.0 eV was applied to observe the lowest inelastic
297 electrons kinetic energy cut-off. The bandgap (E_g) of the material was calculated from the optical
298 absorption onset (λ_{onset}) of thin-film samples using the following equation: E_g (eV) = 1240 / λ_{onset} .

299
300 **OPV cells.** The OPV cells were fabricated with a conventional device architecture of glass/indium tin
301 oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)/active
302 layers/poly[(9,9-bis(3'-(*N,N*-dimethyl)-*N*-ethylammonium)propyl)-2,7-fluorene)-*alt*-5,5'-bis(2,2'-
303 thiophene)-2,6-naphthalene-1,4,5,8-tetracarboxylic-*N,N'*-bis(2-ethylhexyl)imide] (PNDIT-F3N)/Ag.
304 The ITO glass substrates (~15 Ω/sq) were cleaned with detergent (DECON 90), and then sequentially
305 washed with deionized water, acetone and isopropanol in a sonication bath, each for 30 min. The cleaned
306 ITO substrates were then dried in an oven overnight at 100 °C. Plasma treatment of 30 min was applied
307 to ITO substrates prior to cell fabrication, after which PEDOT:PSS (Heraeus CLEVIOS™ P VPAI 4083)
308 solution was spin-cast onto the ITO substrates at (5000 r.p.m., 25 s), and then annealed at 120 °C for 15
309 min in ambient air.

310
311 **Sequential deposition of PMHJ (D/A) cells.** The preparation of solutions and processing of thin films
312 were carried out in a nitrogen-filled glove box with controlled environment ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 3$ ppm,
313 temperature = 25±2 °C). Polymer donor (D18) solutions were prepared in chlorobenzene at a
314 concentration of 6 mg/mL. Neat NIR-absorbing NFA solutions or their mixtures with Y6-O (10-20 wt%,
315 Supplementary Table S3) were prepared in chloroform at a concentration of 10 mg/mL. To completely
316 dissolve the materials, the D18 solution was stirred at 90 °C for at least 2 h and the NFA solution was
317 stirred at 40 °C for 1 h. The D18 solutions were maintained at 90 °C during the whole fabrication
318 procedure to avoid crush-out of polymer, while the NFA solutions were cooled to room temperature
319 before use. The D18 layer was first dynamically spin-cast from its warm solution onto a pre-heated

320 substrate (90 °C) at 3000 r.p.m. (1500 r.p.m. acceleration ramp) for 35 s to achieve a typical thickness
321 of ~60 nm. Then an NFA layer was dynamically spin-cast from its solution on top of D18 layer at 2000-
322 2200 r.p.m. (1200 r.p.m. acceleration ramp) for 35 s to achieve an overall film thickness of ~110 nm,
323 following with a thin layer of PNDIT-F3N (0.5-1 mg/mL in methanol at room temperature) dynamically
324 spin-coated on top of the PMHJ active layer at 1500 r.p.m. for 30 s (1200 r.p.m. acceleration ramp).
325 Finally, a layer of Ag (~110 nm) was thermally evaporated at 5×10^{-5} Pa through a shadow mask at a
326 rate between 2.5-5 Å s⁻¹.

327

328 **One-step deposition of BHJ (D:A) active layer.** The mixture of D18 and NFA (1:1.6 w/w) was
329 dissolved in chloroform at a total concentration of 10 mg/mL and stirred at 50 °C overnight, then cooled
330 to room temperature before use. The BHJ layer was processed by dynamically spin-coating onto a
331 substrate at room temperature from its solution at 2000-3000 r.p.m. for 40 s (1500 r.p.m. acceleration
332 ramp), followed by chloroform solvent vapor annealing for 3 min in a petri dish (size: 60 mm × 15 mm)
333 with 30 µL of chloroform.

334

335 **J-V and EQE measurements.** The thicknesses of films were measured by a Bruker Dektak XT stylus
336 profilometer. The efficiencies of the cells were measured by a Keithley 2400 Source Meter under AM
337 1.5G (100 mW cm⁻²) irradiation using an EnliTech SS-F5 solar simulator. The light intensity was
338 calibrated using a silicon solar cell (with a KG-2 filter) from the National Renewable Energy Laboratory.
339 The cell area is defined by a metal mask with an aperture area of 4 mm² to ensure the accuracy of the
340 current density obtained from the J-V measurements. EQE spectra were collected using an Enlitech QE-
341 S EQE system equipped with a standard Si diode.

342

343 **Single-crystal growth – ternary solvent diffusion.** A solution prepared with ~1 mg NFA in 0.3 mL
344 CHCl₃ was transferred into an NMR tube. On top of the CHCl₃ solution was carefully layered around
345 0.2 mL of CH₂Cl₂, followed by careful layering of acetone, using a glass pipet. The NMR tube was then
346 sealed with parafilm and left standing undisturbed for 1-2 weeks until the color of the solution faded
347 away. The detailed information regarding the X-ray diffraction of single-crystals are included in the
348 Supplementary Information.

349

350 **Grazing-incidence wide angle X-ray scattering (GIWAXS) measurements.** GIWAXS measurements
351 were performed at beamline 7.3.3³⁶ at the Advanced Light Source. Samples were prepared on Si
352 substrates using optimized conditions for OPV fabrication. The incident angle of the 10 keV X-ray
353 beam was set at 0.13° to maximize the scattering intensity from the samples. The scattered X-rays were
354 detected using a Dectris Pilatus 1-M photon-counting detector. All measurements were conducted under
355 a helium atmosphere to reduce air scattering. In-plane and out-of-plane sector averages were calculated
356 using the Nika software package. The coherence length was calculated using the Scherrer equation: CL
357 = $2\pi K/\Delta q$, where Δq is the full-width at half-maximum of the peak and K is a shape factor (1 was used
358 in this work).

359

360 **Resonant soft X-ray scattering (RSoXS) measurements.** RSoXS transmission measurements were
361 performed at beamline 11.0.1.2³⁷ at the Advanced Light Source. Samples for RSoXS measurement were
362 prepared on PSS-coated Si substrates using optimized conditions for OPV fabrication, and then
363 transferred by floating in deionized water to a 1.5 mm × 1.5 mm, 100 nm thick Si₃N₄ membrane
364 supported by a 5 mm × 5 mm, 200 µm thick Si frame (Norcada Inc.). Two-dimensional scattering
365 patterns were collected on an in-vacuum CCD camera. The in-plane composition variation (related to
366 the relative domain purity) over the length scales probed can be extracted by integrating scattering
367 profiles to yield the integrated scattering intensity (ISI). The purer the average domains are, the higher
368 the ISI. Owing to a lack of absolute flux normalization, the absolute composition cannot be obtained
369 only by RSoXS.

370

371 **Time-of-flight secondary ion mass spectrometry (ToF-SIMS).** ToF-SIMS measurement was performed
372 using a TOF-SIMS V instrument (ION-TOF GmbH, Cameca IMS 4F), where a 3 keV Cs⁺ ion beam
373 was used for erosion and a 25 keV Bi³⁺ pulsed primary ion beam was used for the analysis. The area of
374 analysis was 50×50 µm² while the sputtering area was 300×300 µm². The measurement was performed

375 on the D18/T9SBN-F PMHJ blend and D18:T9SBN-F BHJ blend, in which the distribution of T9SBN-
376 F was tracked using Se^{2-} ion as the characteristic species.

377

378 **Molecular dynamics (MD) calculation: MD force field parameter optimization.** The MD simulation
379 was performed on different types of D18-NFA blends to mimic different degree of D-A mixing,
380 including blends in bilayer (BL) and BHJ forms. The BL blend was used as a simplified model of PMHJ,
381 which possesses less D-A interfaces and higher domain purity. The BL film was first constructed by a
382 layer of D18, followed by constructing another layer of NFA molecules on top. The BHJ film was
383 constructed by randomly dispersing D18 and NFA molecules in a confined space.

384

385 The MD simulation was performed in Gromacs 2021 package³⁸. The GAFF2 force field was used as
386 initial parameters. The equilibrium bond lengths and angles were updated based on optimized
387 geometries. The atomic partial charges were calculated at the PBE0/def2SVP level of theory, and fitted
388 using the restrained electrostatic potential (RESP) method by Multiwfn. The dihedral potentials that
389 dictate the planarity of the conjugated molecules were fitted to the PBE0-D3BJ/def2SVP potential
390 energy surfaces. For MD simulation of D18:T9SBN-F, the Lennard-Jones parameters of element Se in
391 T9SBN-F were calculated by methods described in J. Cole's paper³⁹. The force constants of bonds and
392 angles containing Se were calculated by modified Seminario method⁴⁰. The obtained ϵ and σ for Se is
393 1.26 kJ/mol and 0.364 nm, respectively.

394

395 **MD calculation: MD System construction and simulation.** For all systems, 900 NFA molecules and
396 150 segments of D18 hexamers were used for the simulation, to give a 1:1 molar ratio between D18
397 repeating units and NFAs.

398

399 The bilayer (BL) blends were constructed using the following procedure. First, the D18 hexamers were
400 randomly placed into a rectangle box with edge lengths of $15 \times 15 \times 150$ nm using packmol software
401 ⁴¹. Two VDW walls were placed at $z=0$ nm and $z=z_{\text{max}}$ for the following simulations. The isothermal-
402 isobaric ensemble (NPT) run was performed for 20 ns with 5 annealing cycles between 500 K and 300
403 K. During the annealing, semi-isotropic Berendsen barostat with pressure and compressibility of xy was
404 set to zero to compress the system in z direction. A vacuum slab of 20 nm was built on top of the
405 compressed D18 film, followed by a minimization and a Canonical ensemble (NVT) run at 300 K to
406 relax the surface. The NFA molecules were then added loosely on top of the slab with $z_{\text{max}}=150$ nm.
407 Another annealing NPT run was performed with similar condition to compress the NFA layer. The
408 system was then equilibrated at 300 K NPT for 10 ns. Finally, the production NPT run was performed
409 at 300 K for 10 ns to obtain the trajectories.

410

411 The BHJ blends were constructed using the following procedure. First, the molecules were randomly
412 placed into a cubic box with an edge length of 40 nm using packmol software⁴¹. Then, the NPT run was
413 performed for 20 ns with 5 annealing cycles between 500 K and 300 K to compress the structures. The
414 system was further equilibrated at 300 K for a 10 ns NPT run. Lastly, the production NPT run was
415 performed at 300 K for 10 ns to obtain the trajectories.

416

417 All of the MD simulations were employed with velocity-Verlet integrator at 2.0 fs time step with LINCS
418 algorithm to constrain bonds with hydrogen. The temperature was controlled with V-rescale
419 thermostat⁴². The pressure was controlled using Berendsen barostat. Three independent simulations
420 were performed for each system. And the analysis was performed on the frames extracted from the 10
421 ns production run with 200 ps interval.

422

423 **MD calculation: Neighbor atom analysis.** The D18 donor is divided into D_A (electron-accepting
424 moiety), D_D (electron-donating moiety), D_π (π -bridge) fragments, and the NFA is divided into A_A
425 (electron-accepting moiety), A_D (electron-donating moiety) fragments as shown in Fig. S3. Heavy
426 atoms within a distance of 3.6 Å to each other, and hydrogen atoms within a distance of 3 Å to heavy
427 atoms, are defined as "neighbor atoms" for all fragments. The count of neighbor atoms was then
428 summed over all the 150 frames from three trajectories followed by classification according to
429 correlating fragments. The analysis was performed using MDAnalysis package⁴³.

430

431 **Density functional theory (DFT) calculation.** For isolated D18 dimer, T9TBO-F and T9SBN-F, all the
432 alkyl chains were replaced with ethyl groups. The ground-state (S_0) geometries were optimized at
433 PBE0/def2-SVP level with Grimme's D3 dispersion correction with BJ dampening⁴⁴. The excited-state
434 (LE) geometries of D18 monomer, T9TBO-F and T9SBN-F are optimized at TD-PBE0-D3BJ/def2-
435 SVP level followed by ω -tuned TD-LC-wHPBE/def2-SVP⁴⁵ calculations to obtain electronic structure
436 of LE state. Electron-hole analysis was performed using Multiwfn v.3.8⁴⁶ to obtain electron-hole overlap
437 and visualize exciton delocalization. SMD solvation model⁴⁷ was used for all the calculations using
438 diphenylether ($\epsilon=3.73$) as a solvent to imitate the dielectric environment in solids. For the formation of
439 DSE, the molecular pairs of D18 monomer and NFAs were constructed by extracting close contact pairs
440 from MD simulations of blend films. The electronic structure of S_1 state of these molecular pairs were
441 obtained following the same procedures as that of isolated molecules. All the DFT calculations were
442 carried out using Gaussian 16 program⁴⁸.

443

444 **Transient absorption (TA) measurements.** The fs-TA measurements were conducted using a Yb:KGW
445 laser (Pharos, Light Conversion). The wavelength of fundamental output was at ~ 1030 nm. We used a
446 home-built noncollinear optical parametric amplifier to generate the pump pulses at 800 nm, 900 nm,
447 and 610 nm, respectively. The probe beam was supercontinuum by focusing a small fraction of the
448 fundamental 1030 beam to a 5 mm sapphire plate for visible detection or a 6 mm Yttrium Aluminum
449 Garnet (YAG) plate for infrared detection. A short pass filter (10SWF-1000-B, Newport) or a long pass
450 filter (FELH1100, Thorlabs) was employed in the supercontinuum to exclude the fundamental beam for
451 visible detection (550-950 nm) or infrared detection (1100-1600 nm), respectively. The pump and
452 visible probe pulses were compressed by chirp mirrors and wedge pairs to maintain a time resolution
453 better than 40 fs. The supercontinuum light was split into two beams for balanced detection. The probe
454 and reference beams were then routed to either a double line Si camera (S14417, Hamamatsu) for visible
455 detection or a double line InGaAs camera (G11608, Hamamatsu) for infrared detection. The cameras
456 were mounted on a monochromator (Acton 2358, Princeton Instrument). Pulse-to-pulse spectral
457 analysis was conducted at 50 kHz for visible detection and 16 kHz for infrared detection using a
458 homemade field-programmable gate array (FPGA) control board. The signal-to-noise ratio ($\Delta T/T$) was
459 better than 1×10^{-5} after averaging 25k pump-on and pump-off shots for each data point. In the ns-TA
460 measurements, the pump laser was replaced by a pulsed laser diode emitted at 670 nm (LDH-P-C-670M,
461 Picoquant). The time delay between the two lasers was synchronized and enabled by a digital delay
462 generator (DG645, Stanford Research System). The pump fluence was set at $2 \mu\text{J}/\text{cm}^2$ unless otherwise
463 specified. The samples were kept in a nitrogen atmosphere during the measurement to prevent photo-
464 degradation.

465

466 **Photo-induced absorption (PIA) measurements.** The PIA measurements were also conducted using
467 the Yb:KGW laser (Pharos, Light Conversion). In the PIA measurements, the pump light was replaced
468 with a cw laser (MW-ZIR-808 Co., Ltd.) at 800 nm modulated at 2.5 kHz by a chopper. The pump
469 fluence was set at $60 \text{ mW}/\text{cm}^2$ at the same level of pump density of AM 1.5G in the visible range. The
470 probe light was set 180 μs after the pump light to obtain the PIA signals. For the probe range of 950–
471 1100 nm, the probe light was generated by focusing the output beam at 1500 nm from a homemade
472 OPA onto a 5-mm sapphire plate.

473

474 **Triplet sensitization of NFAs.** For the solution samples, we mixed the NFA with an appropriate amount
475 of platinum octaethylporphyrin (PtOEP, Sigma-Aldrich) triplet sensitizer (total concentration=0.5
476 mg/mL, PtOEP:NFA=3:1 w/w) in a quartz cuvette to ensure sufficient energy transfer from PtOEP to
477 NFA molecules in the rather diluted environment. The sample was pumped at 355 nm (third harmonic
478 generation of 1064 nm, piccolo 50, INNOLAS Germany). The time delay between the pump and probe
479 lasers was synchronized and enabled by a digital delay generator (DG645, Stanford Research System).
480 The film samples were prepared by coating a solution containing NFA and PtOEP (total
481 concentration=10 mg/mL, PtOEP:NFA=1:3 w/w) onto the substrates. The TA measurements were
482 conducted employing a Ti:sapphire regenerative amplifier (Libra, Coherent Inc.) at ~ 800 nm with a
483 repetition rate of 1 kHz and pulse duration of 90 fs. An optical parametric amplifier (OperA Solo,
484 Coherent Inc.) pumped by the regenerative amplifier was used to generate the pump beam at 385 nm.

485 The probe beam of supercontinuum in the infrared wavelength range were generated by focusing a
486 small portion of the femtosecond laser beam onto a 1-cm thick sapphire plate. A long pass filter
487 (FGL850, Thorlabs) was employed in the supercontinuum to exclude the fundamental beam for infrared
488 detection (900-1600 nm). The supercontinuum light was split into two beams for balanced detection.
489 The probe and reference beams were then routed to a homemade double line InGaAs camera (G11608,
490 Hamamatsu) for infrared detection. The camera was mounted on a monochromator (Acton 2358,
491 Princeton Instrument). The signal-to-noise ratio reaches 1×10^{-4} after averaging 1k couples of pump-on
492 and pump-off spectra. The pump fluence was set at about $2 \mu\text{J}/\text{cm}^2$. The samples were kept in a nitrogen
493 atmosphere during the measurement.
494

495 **Data availability**

496 The authors declare all data supporting the findings of this study are available within the manuscript
497 and the Supplementary Information. The .cif files corresponding to single-crystal structures reported in
498 this work are available from CCDC (T9TBO-F: 2081901; T9SBN-F: 2084244 & 2081902). The source
499 data of Supplementary Table 2 and Supplementary Figures 6C-D are provided as Supplementary Data
500 Files.
501
502

503 **Acknowledgments:** The work has been supported by the sponsorship of the Lee Shau-Kei Chair
504 Professor (Materials Science) (A.K.Y.J.); the City University of Hong Kong under the APRC Grant
505 9380086 (A.K.Y.J.); the Innovation and Technology Commission of Hong Kong under the TCFS Grant
506 GHP/018/20SZ (A.K.Y.J.), and MRP Grant MRP/040/21X (A.K.Y.J.); the Environment and Ecology
507 Bureau of Hong Kong under the Green Tech Fund 202020164 (A.K.Y.J.); the US Office of Naval
508 Research under the grant numbers N00014-20-1-2191 (A.K.Y.J.), N000141712204 (Z.P. and H.A.),
509 and N000142012155 (Z.P. and H.A.); the Research Grants Council of Hong Kong under General
510 Research Fund 11307621 (A.K.Y.J.), the Collaborative Research Fund C6023-19GF (A.K.Y.J.), and
511 the Hong Kong Postdoctoral Fellowship Scheme (F.R.L.); the Guangdong Major Project of Basic and
512 Applied Basic Research under the grant number 2019B030302007 (A.K.Y.J.); the Guangdong-Hong
513 Kong-Macao Joint Laboratory of Optoelectronic and Magnetic Functional Materials under the grant
514 number 2019B121205002 (A.K.Y.J.); the National Key R&D Program of China under the grant
515 numbers 2017YFA0303703 (C. Zhang), and 2018YFA0209100 (C. Zhang); the Fundamental Research
516 Funds for the Central Universities under the grant number 0204-14380177 (C. Zhang); the National
517 Natural Science Foundation of China under the grant numbers 22225305 (C. Zhang), 21922302 (C.
518 Zhang), 21873047 (C. Zhang), 52002393 (J.Z.), and 51873160 (C. Zhong). The authors also gratefully
519 acknowledge Dr. H. Zhang and Prof. Z. Cai from the Hong Kong Baptist University for the
520 experimental assistances on MALDI-ToF measurements, and Prof. S. B. Jo from the Sungkyunkwan
521 University for his help on analyzing TA data.

522

523 **Author contributions:** K.J., F.R.L., J.Z., C. Zhang and A.K.Y.J. conceived the project. K.J., F.R.L.
524 and J.Z. designed the experiments. K.J. fabricated and characterized the cells. F.R.L. and F.Q.
525 synthesized the materials and grew the single-crystals. J.Z., Q.L., M.X. and C. Zhang conducted TA
526 experiments and corresponding analysis. C. Zhong conducted the MD, DFT and Marcus rate
527 calculations. W.K. solved the single-crystal structures. S.H.J. and F.R.L. analyzed the molecular
528 interactions in single-crystals. Z.P. and H.A. carried out the GIWAXS and RSoXS experiments and
529 corresponding analysis. J.Z., J.Y. and F.G. carried out the photovoltage loss measurements and
530 corresponding analysis. X.D. provided help on optical measurements. H.H. carried out the ToF-SIMS
531 measurement. D.S. carried out the UPS measurement. F.R.L., K.J., J.Z., C. Zhang and A.K.Y.J. wrote
532 the manuscript with input from all authors. A.K.Y.J. and C. Zhang supervised the study.

533

534 **Competing interests:** The authors declare no competing interests.

535

536 **Additional information:** Supplementary information is available in the online version of the paper.
537 Correspondence and requests for materials should be addressed to A.K.Y.J., C. Zhang, and F.R.L.

538

539

540 **Figure Legends/Captions**

541 **Figure 1. The Jablonski diagram and the active materials used for OPV fabrication. (a)**

542 Illustration of excited state dynamics in OPV: (1) photoexcitation of singlet excitons: $S_0 \rightarrow LE$;
543 (2, 4) transfer pathways of photoexcited singlet excitons: (2) $LE \rightarrow {}^1CT$, or (4) $LE \rightarrow DSE$; (3,
544 5) dissociation of loosely bound singlet excitons into free charges: (3) ${}^1CT \rightarrow CS$, or (5)
545 $DSE \rightarrow CS$; (6, 7) CT states formation through non-geminate recombination: $CS \rightarrow {}^1CT/{}^3CT$,
546 possibly with ${}^1CT/{}^3CT \rightarrow CS$ repopulation and spin-allowed ${}^1CT \rightarrow S_0$ relaxation; (8) ${}^3CT \rightarrow T_1$
547 relaxation, where further $T_1 \rightarrow S_0$ relaxation can happen via triplet-charge annihilation, leading
548 to permanent loss of photocarriers. **(b)** Molecular structures of D18 and two major NFAs used
549 in this study. **(c)** Thin-film optical absorption of D18, NFAs, and D18/NFA PMHJ blends. **(d)**
550 Energy level diagram of materials. **(e)** ToF-SIMS Se^{2-} ion yield of D18/T9SBN-F PMHJ and
551 D18:T9SBN-F BHJ blends plotted over sputtering time. The inset shows the schematic
552 illustration of PMHJ and BHJ blends.

553

554 **Figure 2. Photovoltaic cells characterizations. (a) $J-V$ characteristics of the best-performing**

555 PMHJ cells of binary D18/NFA (dashed lines) and ternary D18/NFA:Y6-O (solid lines). **(b)**
556 External quantum efficiency (EQE) spectra (solid lines) and integrated current densities
557 (dashed lines) of the optimized cells. **(c-d)** Semi-logarithmic plots of the normalized Fourier
558 transform photocurrent spectroscopy-EQE (FTPS-EQE, gray line) and electroluminescence
559 (red line) profiles of **(c)** D18/T9TBO-F, and **(d)** D18/T9SBN-F cells plotted as a function of
560 energy. The low-energy tailing of FTPS-EQE is theoretically proportional to the ratio of
561 electroluminescence flux (ϕ_{EL}) and blackbody radiation spectrum (ϕ_{BB} , at the temperature of
562 300 K), as indicated by the dark blue dash line^{49, 50}.

563

564 **Figure 3. TA results and MD-simulated DSE dimers of neat materials. (a-c) TA profiles**

565 for **(a)** D18, **(b)** T9TBO-F, and **(c)** T9SBN-F. The GSB/LE/DSE bands: 590/1180/940 nm
566 (D18); 825/915/1550 nm (T9TBO-F); 840/930/1600 nm (T9SBN-F). The intense ESA band at
567 ~ 1440 nm in T9SBN-F film matches the spectral feature of T_1 in NFAs identified by triplet
568 sensitization, possibly indicating efficient singlet-triplet intersystem crossing due to heavy-
569 atom effect (selenium). **(d-f)** Representative packing patterns facilitating DSE formation in **(d)**
570 D18, **(e)** T9TBO-F, and **(f)** T9SBN-F. Distribution of delocalized electron/hole are in
571 orange/blue, respectively.

572

573 **Figure 4. TA results of different blends.** (a, b, e, f) TA profiles of (a) D18/T9TBO-F PMHJ,
574 and (b) D18:T9TBO-F BHJ, (e) D18/T9SBN-F PMHJ, and (f) D18:T9SBN-F BHJ. The GSB
575 band of D18: 590 nm. The CS bands of blends: 765 nm (D18/T9TBO-F, D18:T9TBO-F); 790
576 nm (D18/T9SBN-F, D18:T9SBN-F). The T_1 signals of blends: ~ 1440 nm. (c, g) The TA
577 dynamics of ESA signals probed at 1440 nm of (c) D18/T9TBO-F and D18:T9TBO-F, and (g)
578 D18/T9SBN-F and D18:T9SBN-F. The slope dot lines were added for helping guide the eyes.
579 (d, h) TA spectra probed at 1000 ps time delay of (d) D18/T9TBO-F and D18:T9TBO-F, and
580 (h) D18/T9SBN-F and D18:T9SBN-F. The arrow shows the trend of T_1 suppression in the
581 PMHJ blend in comparison to the BHJ blend. All traces in (c, d, g, h) were respectively
582 normalized to the minimum of corresponding CS bands in each sample.

583 **References**

- 584 1. Yan, C. *et al.* Non-fullerene acceptors for organic solar cells. *Nat. Rev. Mater.* **3**, 18003
585 (2018).
- 586 2. Yuan, J. *et al.* Single-Junction Organic Solar Cell with over 15% Efficiency Using
587 Fused-Ring Acceptor with Electron-Deficient Core. *Joule* **3**, 1140-1151 (2019).
- 588 3. Lin, Y. *et al.* An Electron Acceptor Challenging Fullerenes for Efficient Polymer Solar
589 Cells. *Adv. Mater.* **27**, 1170-1174 (2015).
- 590 4. Tang, C. W. Two-layer organic photovoltaic cell. *Appl. Phys. Lett.* **48**, 183-185 (1986).
- 591 5. Yu, G., Gao, J., Hummelen, J. C., Wudl, F., Heeger, A. J. Polymer Photovoltaic Cells:
592 Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions.
593 *Science* **270**, 1789 (1995).
- 594 6. Cha, H. *et al.* Exciton and Charge Carrier Dynamics in Highly Crystalline PTQ10:IDIC
595 Organic Solar Cells. *Adv. Energy Mater.* **10**, 2001149 (2020).
- 596 7. Jiang, K. *et al.* Pseudo-bilayer architecture enables high-performance organic solar
597 cells with enhanced exciton diffusion length. *Nat. Commun.* **12**, 468 (2021).
- 598 8. Hou, J., Inganäs, O., Friend, R. H., Gao, F. Organic solar cells based on non-fullerene
599 acceptors. *Nat. Mater.* **17**, 119-128 (2018).
- 600 9. Zhu, L., Yi, Y., Wei, Z. Exciton Binding Energies of Nonfullerene Small Molecule
601 Acceptors: Implication for Exciton Dissociation Driving Forces in Organic Solar Cells.
602 *J. Phys. Chem. C.* **122**, 22309-22316 (2018).
- 603 10. Zhang, G. *et al.* Delocalization of exciton and electron wavefunction in non-fullerene
604 acceptor molecules enables efficient organic solar cells. *Nat. Commun.* **11**, 3943 (2020).
- 605 11. Lin, F., Jiang, K., Kaminsky, W., Zhu, Z., Jen, A. K. Y. A Non-fullerene Acceptor with
606 Enhanced Intermolecular π -Core Interaction for High-Performance Organic Solar
607 Cells. *J. Am. Chem. Soc.* **142**, 15246-15251 (2020).
- 608 12. Liu, Q. *et al.* 18% Efficiency organic solar cells. *Sci. Bull.* **65**, 272-275 (2020).
- 609 13. Rao, A. *et al.* The role of spin in the kinetic control of recombination in organic
610 photovoltaics. *Nature* **500**, 435-439 (2013).
- 611 14. Schlenker, C. W. *et al.* Polymer Triplet Energy Levels Need Not Limit Photocurrent
612 Collection in Organic Solar Cells. *J. Am. Chem. Soc.* **134**, 19661-19668 (2012).
- 613 15. Qin, L. *et al.* Triplet Acceptors with a D-A Structure and Twisted Conformation for
614 Efficient Organic Solar Cells. *Angew. Chem. Int. Ed.* **59**, 15043-15049 (2020).
- 615 16. Wang, R. *et al.* Nonradiative Triplet Loss Suppressed in Organic Photovoltaic Blends
616 with Fluoridated Nonfullerene Acceptors. *J. Am. Chem. Soc.* **143**, 4359-4366 (2021).
- 617 17. Chen, Z. *et al.* Triplet exciton formation for non-radiative voltage loss in high-
618 efficiency nonfullerene organic solar cells. *Joule* **5**, 1832-1844 (2021).

- 619 18. Wang, R., Zhang, C., Li, Q., Zhang, Z., Wang, X., Xiao, M. Charge Separation from
620 an Intra-Moiety Intermediate State in the High-Performance PM6:Y6 Organic
621 Photovoltaic Blend. *J. Am. Chem. Soc.* **142**, 12751-12759 (2020).
- 622 19. Sun, R. *et al.* A Layer-by-Layer Architecture for Printable Organic Solar Cells
623 Overcoming the Scaling Lag of Module Efficiency. *Joule* **4**, 407-419 (2020).
- 624 20. Weng, K. *et al.* Optimized active layer morphology toward efficient and polymer batch
625 insensitive organic solar cells. *Nat. Commun.* **11**, 2855 (2020).
- 626 21. Ye, L. *et al.* Sequential Deposition of Organic Films with Eco-Compatible Solvents
627 Improves Performance and Enables Over 12%-Efficiency Nonfullerene Solar Cells.
628 *Adv. Mater.* **31**, 1808153 (2019).
- 629 22. Wang, Z. *et al.* Thermodynamic Properties and Molecular Packing Explain
630 Performance and Processing Procedures of Three D18:NFA Organic Solar Cells. *Adv.*
631 *Mater.* **32**, 2005386 (2020).
- 632 23. Zhang, Z., Li, Y., Cai, G., Zhang, Y., Lu, X., Lin, Y. Selenium Heterocyclic Electron
633 Acceptor with Small Urbach Energy for As-Cast High-Performance Organic Solar
634 Cells. *J. Am. Chem. Soc.* **142**, 18741-18745 (2020).
- 635 24. Liu, S. *et al.* High-efficiency organic solar cells with low non-radiative recombination
636 loss and low energetic disorder. *Nat. Photonics.* **14**, 300-305 (2020).
- 637 25. Qian, D. *et al.* Design rules for minimizing voltage losses in high-efficiency organic
638 solar cells. *Nat. Mater.* **17**, 703-709 (2018).
- 639 26. Armin, A. *et al.* A History and Perspective of Non-Fullerene Electron Acceptors for
640 Organic Solar Cells. *Adv. Energy Mater.* **11**, 2003570 (2021).
- 641 27. Jiang, K. *et al.* Alkyl Chain Tuning of Small Molecule Acceptors for Efficient Organic
642 Solar Cells. *Joule* **3**, 3020-3033 (2019).
- 643 28. Cui, Y. *et al.* Single-Junction Organic Photovoltaic Cells with Approaching 18%
644 Efficiency. *Adv. Mater.* **32**, 1908205 (2020).
- 645 29. Chen, Y. *et al.* Alkoxy substitution on IDT-Series and Y-Series non-fullerene acceptors
646 yielding highly efficient organic solar cells. *J. Mater. Chem. A.* **9**, 7481-7490 (2021).
- 647 30. Chen, H. *et al.* 17.6%-Efficient Quasiplanar Heterojunction Organic Solar Cells from a
648 Chlorinated 3D Network Acceptor. *Adv. Mater.* **33**, 2102778 (2021).
- 649 31. Firdaus, Y. *et al.* Long-range exciton diffusion in molecular non-fullerene acceptors.
650 *Nat. Commun.* **11**, 5220 (2020).
- 651 32. Yang, L. *et al.* Triplet Tellurophene-Based Acceptors for Organic Solar Cells. *Angew.*
652 *Chem. Int. Ed.* **57**, 1096-1102 (2018).
- 653 33. Karki, A. *et al.* Unifying Charge Generation, Recombination, and Extraction in Low-
654 Offset Non-Fullerene Acceptor Organic Solar Cells. *Adv. Energy Mater.* **10**, 2001203
655 (2020).

- 656 34. Ye, L. *et al.* Quantitative relations between interaction parameter, miscibility and
657 function in organic solar cells. *Nat. Mater.* **17**, 253-260 (2018).
- 658 35. Gillett, A. J. *et al.* The role of charge recombination to triplet excitons in organic solar
659 cells. *Nature* **597**, 666-671 (2021).
- 660 36. Hexemer, A. *et al.* A SAXS/WAXS/GISAXS Beamline with Multilayer
661 Monochromator. *J.Phys. Conf. Ser.* **247**, 012007 (2010).
- 662 37. Gann, E. *et al.* Soft x-ray scattering facility at the Advanced Light Source with real-
663 time data processing and analysis. *Rev. Sci. Instrum.* **83**, 045110 (2012).
- 664 38. Abraham, M. J. *et al.* GROMACS: High performance molecular simulations through
665 multi-level parallelism from laptops to supercomputers. *SoftwareX* **1-2**, 19-25 (2015).
- 666 39. Cole, D. J., Vilseck, J. Z., Tirado-Rives, J., Payne, M. C., Jorgensen, W. L.
667 Biomolecular Force Field Parameterization via Atoms-in-Molecule Electron Density
668 Partitioning. *J. Chem. Theory Comput.* **12**, 2312-2323 (2016).
- 669 40. Allen, A. E. A., Payne, M. C., Cole, D. J. Harmonic Force Constants for Molecular
670 Mechanics Force Fields via Hessian Matrix Projection. *J. Chem. Theory Comput.* **14**,
671 274-281 (2018).
- 672 41. Martínez, L., Andrade, R., Birgin, E. G., Martínez, J. M. PACKMOL: A package for
673 building initial configurations for molecular dynamics simulations. *J. Comput. Chem*
674 **30**, 2157-2164 (2009).
- 675 42. Bussi, G., Donadio, D., Parrinello, M. Canonical sampling through velocity rescaling.
676 *J. Chem. Phys.* **126**, 014101 (2007).
- 677 43. Michaud-Agrawal, N., Denning, E. J., Woolf, T. B., Beckstein, O. MDAAnalysis: A
678 toolkit for the analysis of molecular dynamics simulations. *J. Comput. Chem* **32**, 2319-
679 2327 (2011).
- 680 44. Grimme, S., Ehrlich, S., Goerigk, L. Effect of the damping function in dispersion
681 corrected density functional theory. *J. Comput. Chem* **32**, 1456-1465 (2011).
- 682 45. Henderson, T. M., Izmaylov, A. F., Scalmani, G., Scuseria, G. E. Can short-range
683 hybrids describe long-range-dependent properties? *J. Chem. Phys.* **131**, 044108 (2009).
- 684 46. Lu, T., Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem*
685 **33**, 580-592 (2012).
- 686 47. Marenich, A. V., Cramer, C. J., Truhlar, D. G. Universal Solvation Model Based on
687 Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk
688 Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **113**, 6378-6396
689 (2009).
- 690 48. Frisch, M. J. *et al.* Gaussian 16 Rev. C.01 (2016).
- 691 49. Rau, U. Reciprocity relation between photovoltaic quantum efficiency and
692 electroluminescent emission of solar cells. *Phys. Rev. B.* **76**, 085303 (2007).

- 693 50. Ziffer, M. E. *et al.* Long-Lived, Non-Geminate, Radiative Recombination of
694 Photogenerated Charges in a Polymer/Small-Molecule Acceptor Photovoltaic Blend. *J.*
695 *Am. Chem. Soc.* **140**, 9996-10008 (2018).
696