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Journal:	<i>ACS Applied Materials & Interfaces</i>
Manuscript ID	am-2018-128328.R2
Manuscript Type:	Article
Date Submitted by the Author:	01-Nov-2018
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Organic Single-Crystalline p-n Heterojunctions for High-Performance Ambipolar Field-Effect Transistors and Broadband Photodetectors

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KEYWORDS: Single-crystalline heterojunction; ambipolar charge transport; broadband; organic photodetector; organic field-effect transistors.

ABSTRACT: Organic semiconducting single crystals are ideal building blocks for organic field-effect transistors (OFETs) and organic photodetectors (OPDs) because they can potentially exhibit the best charge transport and photoelectric properties in organic materials. Nevertheless, it is usual for single-crystal OFETs to be built from one kind of organic material in which the dominant transport is either electron or hole; such OFETs showing unipolar charge transport. Furthermore, single-crystal OPDs present high performance only in restricted regions because of the limited absorption of one-component single crystals. In an ideal situation, devices which comprise both

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4 electron and hole transporting single crystals with complementary absorptions, like
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6 single-crystalline p-n heterojunctions (SCHJs), can permit broadband photo-response
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8 and ambipolar charge transport. In this paper, a solution-processing crystallization
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10 strategy to prepare an SCHJ composed of C₆₀ and 6,13-
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12 bis(triisopropylsilylethynyl)pentacene (TIPS-PEN) was shown. These SCHJs
13
14 demonstrated ambipolar charge transport characteristics in OFETs with a balanced
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16 performance of 2.9 cm² V⁻¹ s⁻¹ for electron mobility and 2.7 cm² V⁻¹ s⁻¹ for hole
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18 mobility. This demonstration is the first of single-crystal OFETs in which both electron
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20 and hole mobilities were over 2.5 cm² V⁻¹ s⁻¹. OPDs fabricated upon as-prepared
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22 SCHJs exhibited highly-sensitive photo-conductive properties ranging from ultraviolet
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24 to visible and further to near-infrared regions as a result of complementary absorption
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26 between C₆₀ and TIPS-PEN; thereby attaining the photo-responsivities amongst the
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28 highest-reported values within the organic photodetectors. This work would provide
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30 valuable references for developing novel SCHJ systems to achieve significant progress
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32 in high-performance ambipolar OFETs and broadband OPDs.
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45 **Introduction**

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48 Recently, continuous research attention has been drawn to organic field-effect
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50 transistors (OFETs) for lightweight and deformable electronic applications like
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52 photodetectors,¹ sensors,² displays,³ and circuits.⁴ Included in these, organic
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54 photodetectors (OPDs), which translate optical signals into electrical signals, occupy
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56 an essential position in optical interconnection techniques, light-wave communications,
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4 and high-resolution imaging.⁵⁻¹⁰ Since single crystals are free of molecular disorder and
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6 grain boundary, they are considered to be a favorable charge transport medium for OPD
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8 and OFET devices.¹¹⁻¹⁴ High-performance single-crystal electronics are generally
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10 constructed from one kind of organic semiconducting crystals in which either electron
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12 or hole transport is dominant. Devices which comprise both p-type and n-type single
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14 crystals like single-crystalline p-n heterojunctions can instinctively allow more
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16 functions such as broadband photo-response and ambipolar charge transport.¹⁵
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22 Two-dimensional materials such as graphene have been appearing as promising
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24 contenders within p-n heterojunction for photoelectronic and electronic
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26 applications.^{16,17} Organic semiconductors are dissimilar to 2D nanosheets which
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28 comprise an atomic layer, in that they can form quasi-2D single crystals in which
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30 molecules are bonded weakly by van der Waals interaction rather than by covalent
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32 bonds.¹⁸ Therefore, they have the potential for solution processing at room temperature
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34 as well as for chemical modification.¹⁸ Nevertheless, literature has shown only a small
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36 number of pioneering studies on SCHJs as a result of difficulty in obtaining such a
37
38 highly-ordered nanostructure of this kind. Physical vapor transport (PVT) method and
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40 one-pot mixed-solution crystallization method have been demonstrated to successfully
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42 prepare organic SCHJ p-n systems.^{15,19} However, there are drawbacks with the PVT
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44 technique in that it needs complex equipment and is energy consuming, whereas the
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46 one-pot mixed-solution crystallization technique needs one crystal to grow quickly and
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48 the other to grow particularly slowly, so as to avert mutual disturbance of these two
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50 crystals in order to obtain overlapping bilayer single crystals instead of a combination
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4 of two solids.¹⁵ It was reported that this one-pot crystallization technique successfully
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6 prepared only two specific p-n pairs (DPP-PR/C₆₀ and C8BTBT/C₆₀) up to the present
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8 time as a result of this stringent requirement. Due to such limits, the device performance
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10 in such system remains moderate. As summarized in **Table 1**, for reported single
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12 crystal-based ambipolar OFETs, the hole and electron mobility are usually low and
13
14 unbalanced; Single-crystal based OFETs with both hole and electron mobility
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16 exceeding 1 cm² V⁻¹ s⁻¹ is rarely seen in the literature.^{12,15,20–26} Single-crystal OPDs
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18 have been demonstrated to exhibit higher photo-responsivity than polycrystalline thin
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20 film devices, as shown in **Table 2**. However, due to the limited absorption of one-
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22 component single crystals, these single-crystal OPDs present high performance only in
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24 limited regions. Therefore, to achieve significant advancements in both high-
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26 performance ambipolar OFETs and broadband OPDs, developing facile crystallization
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28 method to prepare novel SCHJ p-n nanostructures is urgently necessary.
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38 In this paper, a facile two-step aligned crystallization strategy is reported; this is
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40 for the purpose of acquiring single-crystalline p-n heterojunctions which comprise two
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42 “benchmark” organic semiconductors, being C₆₀ (n-type) and 6,13-
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44 bis(triisopropylsilylethynyl)pentacene (TIPS-PEN, p-type) and also to study its
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46 application in ambipolar OFETs and broadband photodetectors. The SCHJs presented
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48 herein show a balanced ambipolar charge transport with an average performance of
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50 (2.44 ± 0.222) cm² V⁻¹ s⁻¹ for electron mobility (μ_e) and (2.17 ± 0.309) cm² V⁻¹ s⁻¹ for
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52 hole mobility (μ_h) which demonstrate the first of single crystal OFETs with both
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54 electron and hole mobilities greater than 2 cm² V⁻¹ s⁻¹. Photodetectors based upon as-
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4 prepared SCHJs offer a highly-sensitive photo-response with fast photo-switching and
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6 repeatable characteristics in broadband UV-Vis-NIR regions due to the complementary
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8 absorption between C₆₀ and TIPS-PEN; furthermore, the photo-responsivities achieved
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10 here are among the highest values in the reported organic photodetectors. The presented
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12 work here is a valuable reference for the development of novel single-crystalline
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14 heterojunction nanostructures and the exploration of the fundamental studies on organic
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16 electronics at new organic/organic interfaces and enables significant advancements in
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18 high-performance ambipolar OFETs and broadband OPDs.
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25 **Result and Discussion**

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27 TIPS-PEN and C₆₀ are among the most extensively-utilized p-type and n-type
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29 semiconductors respectively with both μ_h (TIPS-PEN) and μ_e (C₆₀) greater than 5 cm²
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31 V⁻¹ s⁻¹ in single-crystal OFETs.^{27,28} Furthermore, they demonstrate superior
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33 performance in several photoelectronic devices like hybrid perovskite solar cells,²⁹
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35 OPVs,³⁰⁻³² and OLEDs.³³ Therefore, C₆₀ and TIPS-PEN, on this work, were utilized to
36
37 grow single-crystalline p-n heterojunctions. **Figure S1** (Supporting Information)
38
39 depicts the molecular structures of C₆₀ and TIPS-PEN, whereas **Figure 1a** illustrates
40
41 the fabrication of SCHJs *via* a two-step aligned crystallization technique. Two-step
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43 crystallization method using orthogonal solvents have been reported to successfully
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45 prepare high-quality SCHJs for optoelectronics and FET-based memory devices and
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47 the devices based on the SCHJs prepared by this two-step crystallization method exhibit
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49 superior performance due to the high-quality interface formed by this method.^{20,34} In
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51 addition, this method is also called interfacial solution-processed crystallization
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4 method, where a second layer of single crystals forms on the interface with the first
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6 single crystal layer, leading to bilayered single-crystalline structures.²⁰ Therefore, this
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8 two-step crystallization method can offer high-quality interface. For aligned crystal
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10 growth, a preferential drying direction is imposed upon the drop casted solution in order
11
12 to control the direction of the crystal growth which is attained by placing the substrate
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14 in a Petri dish at an angle of 5° to the horizontal line on a hot plate at a temperature of
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16 (25±1) °C. Following this procedure, the lid was replaced immediately in order to trap
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18 the solvent vapor, thereby creating a vapor-saturated condition within the Petri dish.
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20 Firstly, this technique was applied to grow C₆₀ ribbons by drop-casting a C₆₀ solution
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22 in an *o*-dichlorobenzene (ODCB) solvent; subsequently we rotated the substrates by
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24 90°, and following this, we drop-casted TIPS-PEN solution using the same technique
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26 as aforementioned. In this way, TIPS-PEN single crystals formed over the top of the
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28 first due to slow solvent evaporation; this results in bilayer structures as depicted in
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30 **Figure S2** (Supporting Information). Avoidance of damaging the first layer in the
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32 crystallization process of second layer is a principal challenge in the second stage, the
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34 key to this being obviously the choice of solvent for the second layer.³⁵ Thus, 4-methyl-
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36 2-pentanone, which can effectively dissolve TIPS-PEN but cannot dissolve C₆₀, is
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38 chosen as the solvent to grow TIPS-PEN single crystals without dissolving the first
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40 layer. In order to remove the remaining solvents, the substrate was treated by vacuum
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42 annealing following the TIPS-PEN crystal growth. Consequently, as shown in **Figure**
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44 **S3** (Supporting Information), a bilayer structure having both ribbons of a few microns
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46 wide was acquired.
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4 As shown in **Figure 1c and d**, the crystals were studied by energy dispersive
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6 spectrum (EDS) on a scanning electron microscope (SEM) to identify the chemical
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8 composition of the overlapping bilayer in **Figure 1b**. It was distinctly demonstrated by
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10 element mapping of Si (TIPS-PEN) and C (both TIPS-PEN and C₆₀) that the TIPS-PEN
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12 ribbon was over the top of the C₆₀ ribbon to form a single-crystalline heterojunction.
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14 Atomic force microscopy (AFM) height profile was employed in order to study the
15
16 thickness of the overlapping SCHJ as illustrated in **Figure 1e** and it was shown that the
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18 thickness of one SCHJ was 160 nm including 71 nm of C₆₀ layer and 89 nm of TIPS-
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20 PEN layer. As illustrated in **Figure 1f and g**, crystallography studies of the bilayers
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22 was performed *via* select area electron diffraction (SAED) on transmission electron
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24 microscopy (TEM). Two groups of diffraction spots (blue and yellow circles) in **Figure**
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26 **1g** were shown by the SAED of the bilayers, indicating two different single crystals.
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28 This is similar to the SAED patterns reported for C₆₀/DPP-RP and CuPc/F₁₆CuPc
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30 single-crystalline heterojunctions, where two sets of diffraction spots were also
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32 observed.^{15,19} It should be noted that the growth of TIPS-PEN crystal on top of C₆₀
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34 crystal is not the epitaxial growth; the lattice mismatch of both crystals is unable to
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36 provide significant condition for epitaxial growth.¹⁹ We indexed the SAED pattern of
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38 TIPS-PEN with a triclinic crystal system, and the cell dimensions of TIPS-PEN ribbon
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40 crystal are $a = 7.58 \text{ \AA}$, $b = 7.72 \text{ \AA}$ and $c = 16.81 \text{ \AA}$, which is in accordance well with
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42 the reported literature.³⁶ A face center cubic (FCC) crystal structure having a lattice
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44 constant of $a = 1.414 \text{ nm}$ was indexed by the SAED pattern for the C₆₀ ribbon crystals,
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46 according with this value of pristine C₆₀ crystals (1.415 nm).³⁷ It is shown by the
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4 evidence of the AFM, EDS OM, SAED, SEM and TEM that the SCHJ of C₆₀ and TIPS-
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6 PEN ribbon crystals were indeed obtained.
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9 Our p-n heterojunctions' single-crystalline nature demonstrates their high quality
10 and possible utilization in high-performance ambipolar OFETs; therefore, we
11 artificially designed an asymmetric device structure having a top-contact and bottom-
12 gate configuration in order to study their ambipolar charge transport properties. The
13 schematic diagram and the corresponding SEM image of the as-fabricated OFETs are
14 respectively depicted in **Figure 2a and b**. Three different circuit models will be induced
15 while applying different source and drain pairs because of the asymmetric device
16 structure. When S1/D1 or S2/D2 is utilized as a source and drain pair, the performance
17 of the device will be dominated by the charge transport through single-component
18 ribbon crystals (C₆₀ or TIPS-PEN ribbon), but when S1/D2 or S2/D1 is used as the
19 source and drain electrodes, the charge transport performance is determined by single-
20 crystalline heterojunction. Firstly, to study the charge transport through single-
21 crystalline heterojunction, we selected S1/D2 as the electrode pair. **Figure 2c and d**
22 depicts the typical transfer characteristics of devices, showing V-shaped curves in
23 which both arms correspond to hole transport and electron transport, indicating the
24 ambipolar charge transport characteristics in SCHJs. The excellent gate modulation was
25 confirmed by the output characteristics (**Figure S4 and S5**, Supporting Information).
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27 **Figure S6 and S7** illustrates the histograms of electron and hole mobility acquired from
28 50 devices based on as-prepared SCHJs. Based on these, an average μ_h of (2.17 ± 0.309)
29 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and an average μ_e of $(2.44 \pm 0.222) \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ were obtained on as-
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4 fabricated SCHJ OFETs. Secondly, we selected S1/D1 as the electrode pair to examine
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6 the charge transport properties of individual TIPS-PEN ribbon crystal. In this condition,
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8 only p-channel devices exhibited effective field-effect mobility. 50 devices were
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10 studied and an average μ_h of $(2.83 \pm 0.402) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were achieved as shown in
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12 **Figure S8**. Thirdly, we selected S2/D2 as the electrode pair to study the charge
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14 transport characteristics of individual C_{60} ribbon crystal. On the contrary, effective
15
16 field-effect mobility can only be extracted from n-channel devices and we achieved an
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18 average μ_e of $(2.74 \pm 0.266) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**Figure S9**). We found that compared to the
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20 hole and electron mobility of the individual ribbon crystal, the mobility values of the
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22 single-crystalline p-n heterojunctions are comparable but slightly lower. This phenome
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24 was also observed by Bao *et al.*²⁴ In addition to the different channel coverage, this
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26 disparity may be due to the slight incorporation of one molecule inside the crystal of
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28 the other and therefore potential crystal lattice disruption.²⁴
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38 When S1/D2 was selected as the electrode pair, the conductive channel contains
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40 C_{60} , the SCHJ, and TIPS-PEN. The schematic band diagram of the charge transport
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42 process is shown in **Figure S10**. When bias voltage is applied, band bending happens
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44 at the interface between C_{60} and TIP-PEN. As shown in **Figure S10b**, when $(V_{\text{GS}} - V_{\text{T}})$
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46 = 0, the energy difference between the LUMO of C_{60} and HOMO of TIPS-PEN is
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48 defined as V_{b1} , and the energy difference between the HOMO of TIPS-PEN and the
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50 HOMO of C_{60} is defined as V_{b2} . As shown in **Figure S10c**, when $(V_{\text{GS}} - V_{\text{T}}) > 0$ (n-
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52 channel operation mode), V_{b1} decreases by continuously increasing V_{GS} , and the
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54 probability that the electrons at the TIPS-PEN HOMO hopping to C_{60} LUMO increases,
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4 leading to increases of electron concentration in C_{60} and hole concentration in TIPS-
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6 PEN accordingly. In this case, IDS of this n-channel operation mode will increase.
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8 While for the p-channel operation mode where $(V_{GS} - V_T) < 0$ (**Figure S10d**), V_{b2}
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10 decreases when the value of V_{GS} is increasing. In this case, there is a large amount of
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12 hole accumulation at the valence band of TIPS-PEN. Due to the decreasing V_{b2} , the
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14 holes at the valence band of TIPS-PEN recombine, at the interface, with the electrons
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16 in C_{60} HOMO, forming the recombination current. This recombination current
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18 increases when V_{GS} is more negative, leading to the field effect.
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25 For ambipolar FETs, balanced electron and hole mobility are desirable, because
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27 this is important for a broad range of electronic devices such as complementary circuits
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29 and light-emitting field-effect transistors.³⁸ The maximum performance we achieved in
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31 SCHJ based OFETs is a balanced hole and electron mobility of $2.71 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and
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33 $2.89 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. To better demonstrate the improvement of present
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35 SCHJs for ambipolar OFETs, we make a comparison of some recently reported SCHJs
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37 applied in OFETs. The donor-acceptor system and the corresponding parameters of the
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39 OFETs based on these SCHJs are tabulated in **Table 1**. It clearly shows that most of
40
41 the SCHJs present relatively low ambipolar charge transport mobilities with both hole
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43 and electron mobility below $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. But there are two exceptions: $\text{CdCl}_3/\text{C}_{60}$
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45 SCHJ presents an electron mobility as high as $1.28 \pm 0.41 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in OFETs but its
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47 hole mobility is not given;²⁰ While DPTTA/ F_2TCNQ gives OFETs a relatively higher
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49 hole mobility of $1.57 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ but its electron mobility is about 4 times lower (0.47
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51 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).²¹ The TIPS-PEN/ C_{60} SCHJ in the present work, which gives ambipolar
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4 OFETs balanced charge transport properties with average hole mobility of $2.17 \text{ cm}^2 \text{ V}^{-1}$
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6 s^{-1} and average electron mobility of $2.44 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, is the first demonstration for SCHJ-
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8 based OFETs with both hole and electron mobility above $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, making it a
9
10 potential candidate for high-performance ambipolar OFETs.
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14 TIPS-PEN/ C_{60} SCHJ is endowed with high-mobility ambipolar charge transport
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16 property, providing considerable potential in high-performance photoelectronic devices
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18 like organic photodetectors. The absorption spectra of TIPS-PEN/ C_{60} single-crystalline
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20 heterojunctions, pristine TIPS-PEN single crystal, and C_{60} single crystal are depicted in
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22 **Figure 3d**, whereas the TIPS-PEN single crystals' spectrum present a dominant band
23
24 centered at 653 nm with absorption being extended to the NIR region, and also two
25
26 fractionally weaker shoulder bands having peaks at 547 and 598 nm outside the C_{60}
27
28 single crystals' spectral coverage. The TIPS-PEN/ C_{60} SCHJ exhibits broadband
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30 absorption in the region of 350-750 nm as a result of this complementary absorption
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32 enabling it to be a possible candidate for broadband photodetection.
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41 As depicted in **Figure 3a and b**, a discrete heterojunction was employed to
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43 construct a photodetection device which used the asymmetrical (ITO/Al) electrodes in
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45 order to reduce the energy barrier between the semiconducting crystals and the
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47 electrodes, thereby effectively easing the charge injection.³⁹ The reason for this, as
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49 depicted in **Figure 3c**, is that the Al's work function being a good match with the
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51 LUMO energy of the n-type C_{60} while the ITO work function being a good match with
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53 the HOMO energy level of the p-type material TIPS-PEN.
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4 The diode characteristic and rectifying properties are typical characteristics of p-n
5 heterojunctions.⁴⁰ In a typical p-n heterojunction, rectification results from the
6 potential barrier formed at the interface between two types of semiconductor materials,
7 p- and n-types.⁴⁰ In the forward bias, the current increased with increase in the applied
8 bias due to decrease in the potential barrier while in the reverse bias only a small amount
9 of current can flow as the barrier height is increased with the applied bias.⁴⁰ **Figure 3e**
10 illustrates the comparison of the current-voltage (*I-V*) curves of as-fabricated
11 photodetectors under dark and upon illumination by 1.5 mW cm⁻² laser with different
12 wavelengths at room temperature. The TIPS-PEN/C₆₀ SCHJ device, as expected,
13 presents typical diode characteristics and demonstrates good rectifying property,
14 indicating that high-quality heterojunctions are formed between TIPS-PEN and C₆₀
15 ribbons.
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35 Meanwhile, photodetectors based on a pure TIPS-PEN or pure C₆₀ single crystal
36 were also studied under the identical condition for comparison. **Figure 3e** shows how
37 a weak dark current (5.7 nA at 30 V bias) was given by this SCHJ photodetector, but
38 when illuminated by the laser of different wavelengths, there was a considerable
39 increase in the photo currents. In order to evaluate the photodetectors' performances
40 quantitatively, their spectral responsivity (*R*) was calculated according to Equation (1):
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$$R = \frac{I_{light} - I_{dark}}{PS} \quad (1)$$

50 where *I*_{light} is the current when illuminated by the laser, *I*_{dark} is the current under
51 dark condition, *P* is the incident power density, and *S* is the effective illuminated area.
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4 With regard to the SCHJ photodetector, R was calculated as 165.5 A W^{-1} at 350
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6 nm, 149.6 A W^{-1} at 650 nm and 22.5 A W^{-1} at 720 nm when applying a bias voltage of
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9 30 V (**Figure 3f**), thereby showing the broadband photo-response attributes of SCHJ
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11 OPDs. Contrastingly, the R for the pure C_{60} single crystal photodetector was calculated
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13 as being significantly less at 96.7 A W^{-1} at 350 nm, 16.6 A W^{-1} at 650 nm and 8.9 A
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15 W^{-1} at 720 nm. Likewise, photodetectors based upon the TIPS-PEN single crystal
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17 indicate weaker photo-response attributes than do SCHJ devices, having an R of 79.9
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19 A W^{-1} and 114.5 A W^{-1} respectively, attained at 350 nm and 650 nm; furthermore,
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21 negligible photo-response was detected in the NIR area. It was revealed by all of these
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23 results that the single-crystalline heterojunction formed between C_{60} and TIPS-PEN
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25 single crystals led to a considerable enhancement in the response in the ultraviolet
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27 region and also provided the extension of response to the visible and near-infrared
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29 regions.
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38 Literatures reveals that with regard to the heterojunction photodetectors, when
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40 applying a bias voltage, the heterojunction interface is able to improve the excitons'
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42 dissociation (photogenerated in both TIPS-PEN and C_{60} single crystals) into more
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44 separated free charge carriers, thereby resulting in the photocurrent improvement of the
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46 SCHJ photodetector.^{41–43} The deeper-lying LUMO level of C_{60} is able to transfer the
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48 photogenerated electrons from TIPS-PEN to C_{60} , thereby, leading to spatial separations
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50 of holes and electrons. Resultantly, the carrier recombination was suppressed and the
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52 holes' lifetime was extended in TIPS-PEN single crystals, leading to greater
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54 enhancement in the photodetector performance.
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4 **Figure 4a** depicts the SCHJ device's spectral responsivity as function of the bias
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6 voltage, which is also shown in a contour (**Figure 4b**). It is distinctly observable that
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8 the device responsivity is considerably improved by increasing bias voltage, resulting
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10 in the sensitive identification of NIR and fully-visible light at bias voltages greater than
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12 10V. Furthermore, **Figure 3f** shows that the spectral responsivity displays clear
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14 absorption peaks coincident with the peaks observed in the SCHJs' absorption
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16 spectrum. **Figure 4c** depicts time-resolved current response in different illumination
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18 conditions with and without illumination at an applied bias of 30V. The "on" and "off"
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20 states maintain the same current level for several cycles under illumination of identical
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22 wavelength, thereby showing these photodetectors' excellent stability and reversibility.
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24 Additionally, it is demonstrated by the analysis of an enlarged photo-response process
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26 involving one rise and one reset that the SCHJ devices have fast photo-switching
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28 attributes with both rising and reset response times under one second (**Figure 4d**).
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38 The performance of representative organic photodetectors is summarized in **Table**
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40 **2** which indicates that high responsivities are normally obtained in single crystal
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42 devices; for example, C8-BTBT single crystal device (124 A W^{-1} under 365 nm UV
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44 illumination) and C_{60} single crystal device (90.4 A W^{-1} under 360 nm UV
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46 illumination);^{44,45} nevertheless, as the result of the limited absorption regions of these
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48 single crystals, the photodetectors on which they are based demonstrate only high
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50 performance in restricted regions. The current TIPS-PEN/ C_{60} photodetectors exhibit
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52 higher responsivities than the majority of these devices;⁴⁴⁻⁵⁸ furthermore, they
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4 demonstrate highly-sensitive photo-response from NIR to Vis to UV regions, showing
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6 their excellence for broadband UV-Vis-NIR photodetection
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9 **Conclusion**

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11 In summary, a simple solution-processed crystallization strategy was developed
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13 to prepare a novel organic SCHJ system comprising TIPS-PEN and C₆₀. TIPS-PEN/C₆₀
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15 single-crystalline heterojunctions present balanced high-performance ambipolar charge
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17 transport property in OFETs and highly-sensitive broadband UV-Vis-NIR responsivity
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19 in OPDs. The device performances of presented SCHJ were among the highest for
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21 single crystal based ambipolar OFETs and OPDs, respectively. The presented work
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23 here is a valuable reference for the development of novel single-crystalline
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25 heterojunction nanostructures and the exploration of the fundamental studies on organic
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27 electronics at new organic/organic interfaces and enables significant advancements in
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29 high-performance ambipolar OFETs and broadband OPDs.
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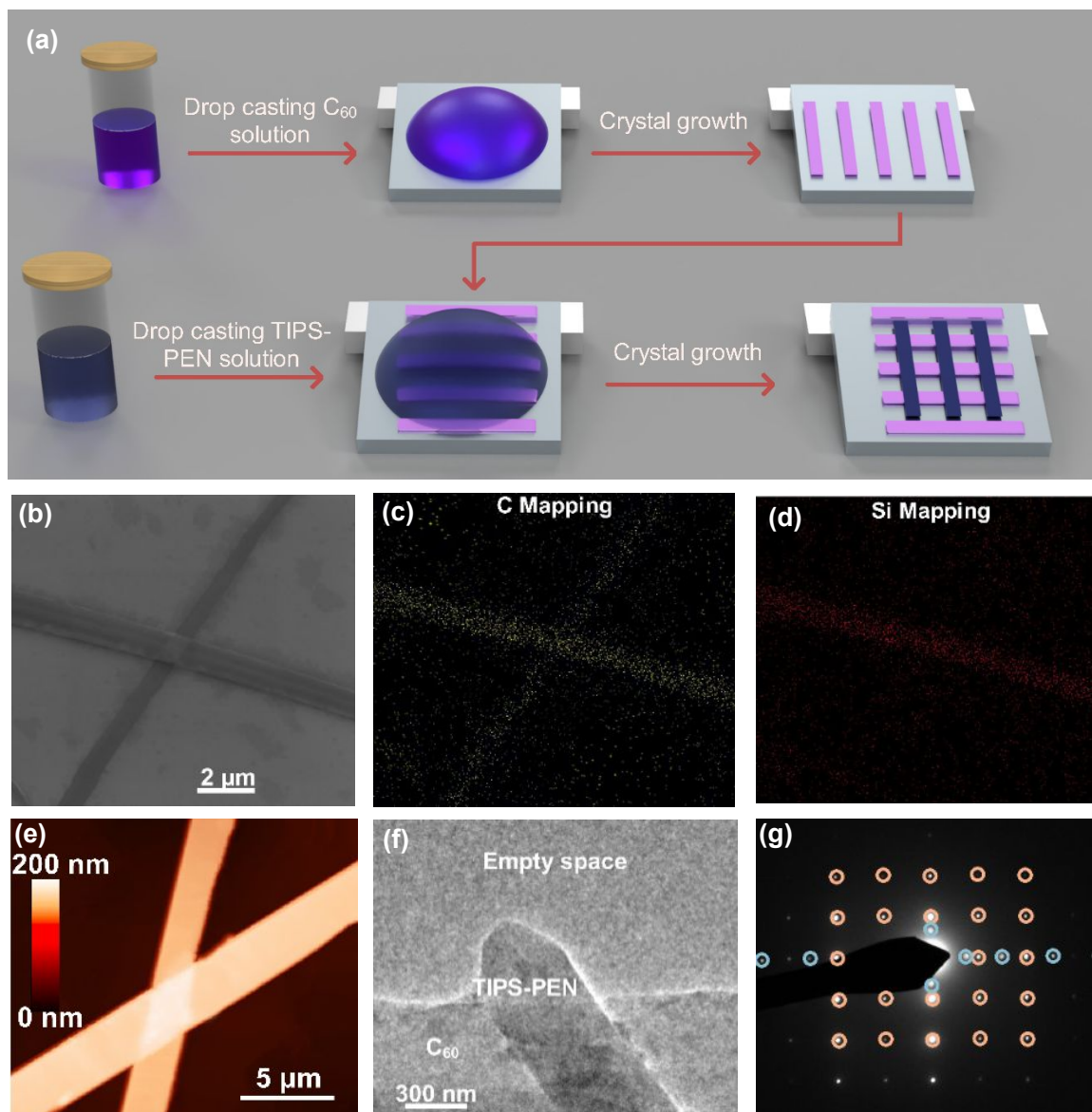


Figure 1 (a) Schematic diagram of preparation of TIPS-PEN/C₆₀ single-crystalline heterojunctions; (b) SEM image, associate element mappings of (c) C and (d) Si using EDS and (e) AFM image of one single-crystalline p-n heterojunction; (f) TEM image and (g) associate electron diffraction pattern of one SCHJ.

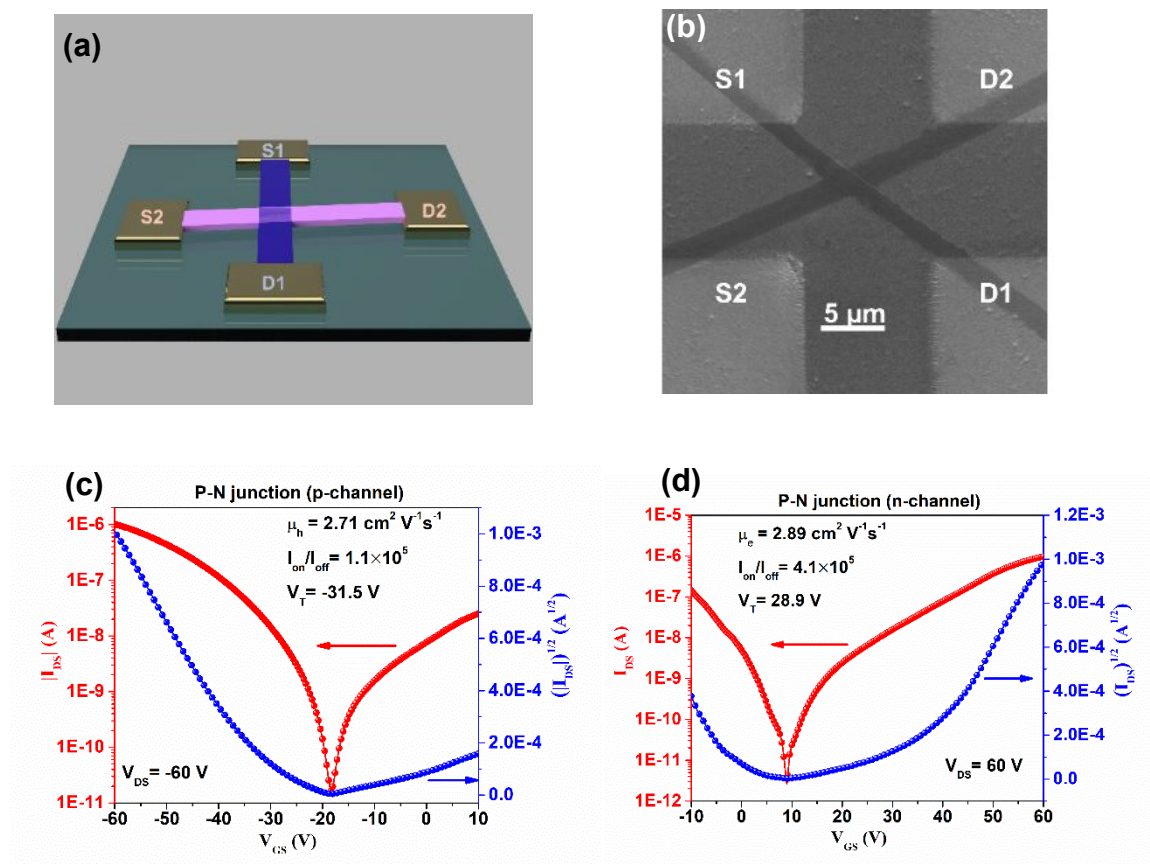


Figure 2 (a) Schematic diagram and (b) SEM image of as-fabricated OFET device based on TIPS-PEN/C₆₀ SCHJ. Typical transfer curves of s as-fabricated OFET device in (c) p-channel operation mode and (d) n-channel operation mode, respectively.

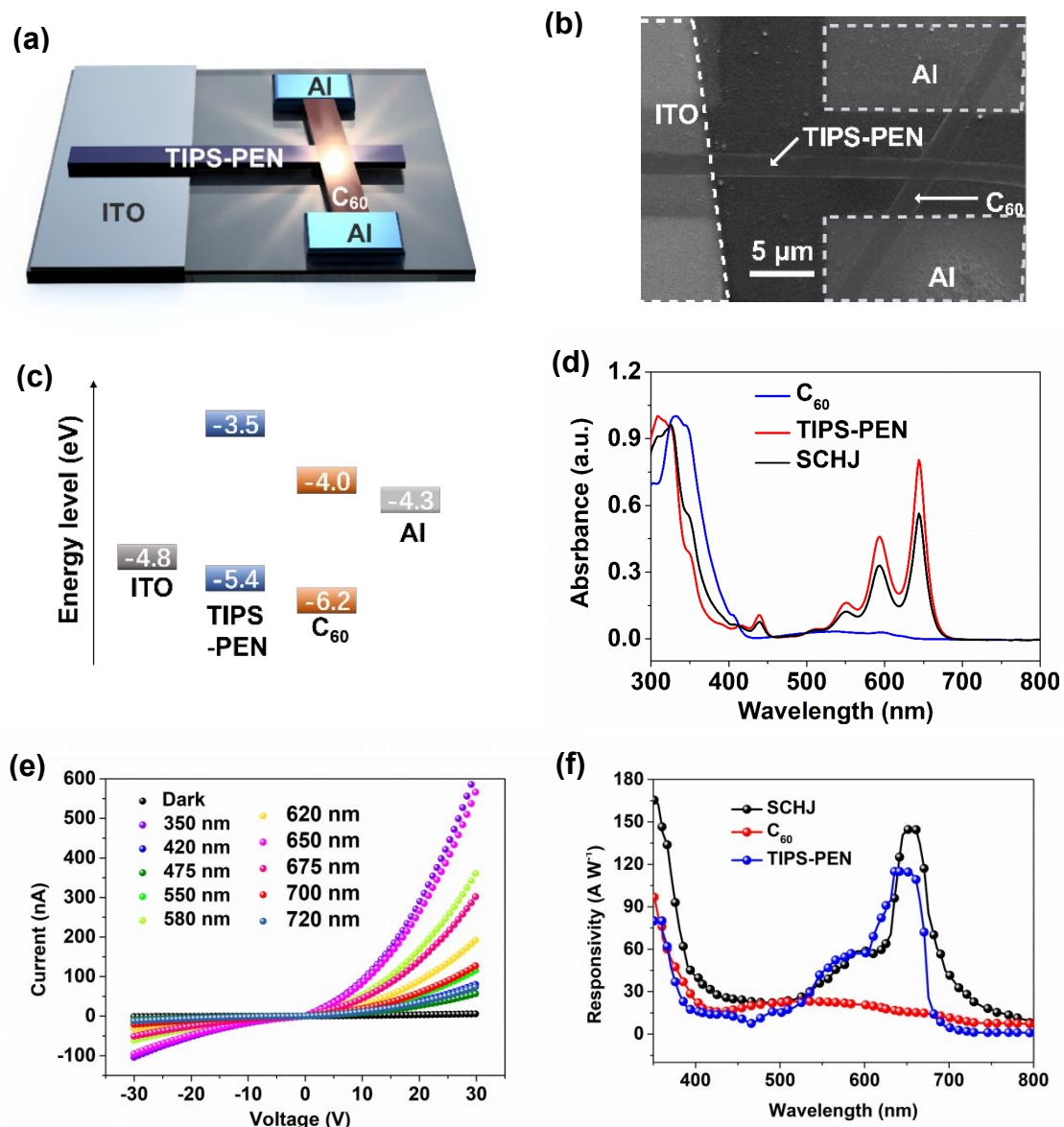


Figure 3 (a) Schematic configuration and (b) SEM image of a single p-n heterojunction device; (c) Energy level alignment of the device structures; (d) Absorption spectra of C_{60} single crystals, TIPS-PEN single crystals and C_{60} /TIPS-PEN single-crystalline heterojunctions; (e) Current-voltage (I - V) characteristic of a single TIPS-PEN/ C_{60} single-crystalline heterojunction device in dark and under laser illuminations; (f) Spectral responsivity of C_{60} , TIPS-PEN and SCHJ devices.

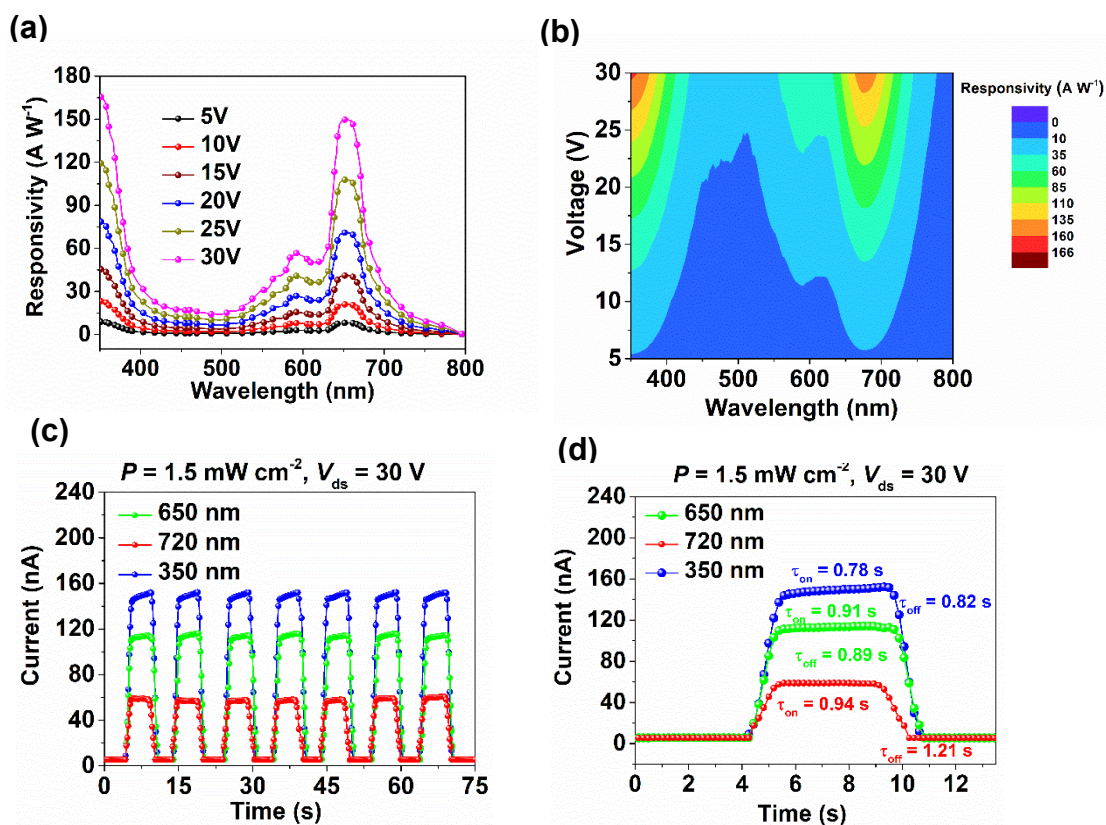


Figure 4 (a) Spectral responsivity of the SCHJ devices measured as a function of applied bias voltage; (b) Responsivity of the SCHJ device shown in 2D contour plot; (c) time-resolved photo-response and (d) an analysis of one response and reset process of SCHJ device under different laser illuminations.

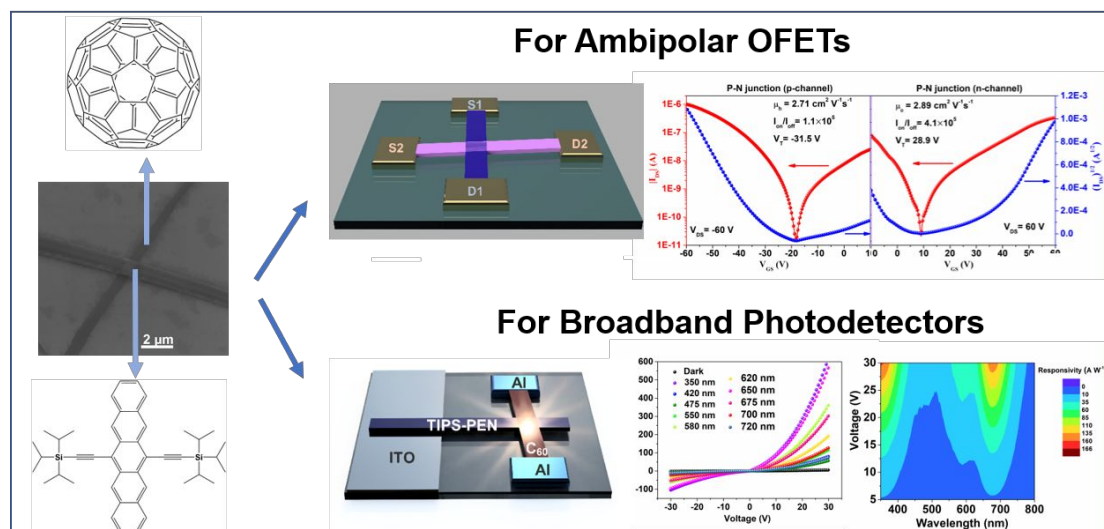
Table 1 Comparison of the device performance for the TIPS-PEN/C₆₀ SCHJ and other characteristic organic SCHJs.

Donor	Acceptor	μ_h [cm ⁻² V ⁻¹ s ⁻¹]	μ_e [cm ⁻² V ⁻¹ s ⁻¹]	P_{in} [mW cm ⁻²]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	PCE [%]	Ref.
CdCl ₃	C ₆₀	NA	1.28 ± 0.41	NA	NA	NA	NA	NA	20
DPTTA	TCNQ	0.03	0.04	NA	NA	NA	NA	NA	59
DPTTA	F ₂ TCNQ	1.57	0.47	NA	NA	NA	NA	NA	21
DPTTA	DTTCNQ	0.77	0.24	NA	NA	NA	NA	NA	60
CuPc	F ₁₆ CuPc	0.05	0.07	100	0.054	0.35	0.36	0.007	19
CuPc	H ₂ TPyP	NA	NA	5.51	0.029	0.64	0.23	0.08	23
C8-BTBT	C ₆₀	0.16	0.17	NA	NA	NA	NA	NA	24
DPP-PR	C ₆₀	0.0061	0.59	100	1.56	0.56	0.38	0.33	15
DPTTA	C ₆₀	0.3	0.01	10	0.3	0.48	0.18	0.27	25,26
DPTTA	C ₇₀	0.07	0.06	10	0.002	0.17	0.15	0.0005	
TPB	C ₆₀	0.066	0.087	100	1.152	0.53	0.39	0.24	12
TIPS-PEN	C ₆₀	2.71	2.89	100	4.37	0.52	0.59	1.34	Present work

Table 2 Comparison of the device performance for the TIPS-PEN/C₆₀ SCHJ photodetectors and other characteristic OPDs.

Photodetector	Light source [nm]	P_{in} [mW cm ⁻²]	$ V_{ds} $ [V]	R [A W ⁻¹]	Ref.
Pentacene	365	1.55	50	50	46
CuPc	365	1.55	50	2	46
Spiro-4p-CPDT	370	NA	20	25	47
Spiro-DPSP	370	0.127	10	1	48
C ₆₀	360	4.38	10	90.4	44
6T	365	1.5	50	2.4	49
BPTT	380	1.55	50	82	50
C8-BTBT	365	1.0	30	124	45
	365	0.2	30	117	
F8T2	405	3	10	0.0004	51
Graphene	532	NA	0.02	8.61	52
Pentacene	650	5	50	0.45	46
Pentacene/C ₆₀ PHJ	580	NA	10	0.122	53
P3HT/PC ₆₁ BM BHJ	468	40	1	0.1	54
MEH-PPV/PC ₆₁ BM BHJ	488	0.001	4	0.14	55
F8T2/PC ₆₁ BM BHJ	460	9	10	0.67	56
PDDTT/PC ₆₁ BM BHJ	800	0.22	0.5	0.1	57
PTT/PC ₆₁ BM BHJ	800	NA	5	0.267	58
TIPS-PEN/C ₆₀ SCHJ	350	1.5	30	165.5	Present work
TIPS-PEN/C ₆₀ SCHJ	650	1.5	30	149.6	Present work
TIPS-PEN/C ₆₀ SCHJ	720	1.5	30	22.5	Present work

TOC



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4 ASSOCIATED CONTENT
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7 **Supporting Information.**
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11 Experimental Section; Molecular structures of TIPS-PEN and C₆₀; OM image and SEM
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13 image of bulk single-crystalline p-n heterojunctions. Output characteristics of SCHJ
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15 OFETs in p-channel operation mode; Output characteristics of SCHJ OFETs in n-
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17 channel operation mode; Histograms of hole and electron mobilities acquired from 50
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19 SCHJ OFETs.
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37 **Notes**
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39 The authors declare no competing financial interest.
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45 ACKNOWLEDGMENT
46

47 X. Zhao, T. Liu, X. Hou and Z. Liu thank the China Scholarship Council for funding.
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