Supplementary information

Novel cost-effective acceptor:P3HT based organic solar cells exhibiting

highest ever reported industrial readiness factor

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Materials and methods

Unless stated otherwise, solvents and chemicals were obtained commercially and were used directly without further purification. ZnO was synthesized according to literature¹. IDT42 (4,9-dihydro-4,4,9,9-tetraoctyl-s-indaceno[1,2-b:5,6-b']-dithiophene-dicarbaldehyde, namely the A1-dialdehyde core) was purchased from Derthon Optoelectronic Materials Science Technology Co. LTD (Shenzhen, China). 6-(5-formylthiophen-2-yl)-4,4-dioctyl-4H-indeno[1,2-b]thiophene-2-carbaldehyde, 5,5,10,10-tetraoctyl-5,10-dihydrothieno[2',3':3,4]cyclopenta[1,2-g]thieno[3,2-c]isochromene-2,8-

dicarbaldehyde, and 5,5'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis(thiophene-2-carbaldehyde) was synthesized according to literature.²

1H NMR spectra were obtained on a Bruker Avance III 600 MHz nuclear magnetic resonance (NMR) spectroscope. Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) was carried out on Reflex(TM)III from Bruker. UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu4NPF6) CH₂Cl₂ solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc+) redox couple (4.8 eV below the vacuum level). The equation of ELUMO/HOMO = - $e(E_{red}/_{ox}+4.36)$ (eV) was used to calculate the LUMO and HOMO levels (the redox potential of Fc/Fc+ is found to be 0.44 V).

Synthesis

A1, (5E,5'E)-5,5'-((4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)

Four drops of piperidine were added to a solution of 4,9-dihydro-4,4,9,9-tetraoctyl-s-indaceno[1,2b:5,6-b']-dithiophene-dicarbaldehyde (IDT42, as the A1-dialdehyde core) (0.50 g, 0.65 mmol) and 3ethylrhodanine (1.05 g, 6.5 mmol) in chloroform (30 mL). The resulting solution was heated to reflux and stirred for 24 h. The mixture was poured into ice cold water and extracted with dichloromethane. The collected organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/chloroform V/V = 1:3) and recrystallized from hexane and chloroform two times to give the product as a dark purple powder (0.491 g, 72 % yield).

1H NMR (CDCl₃, 600 MHz), (ppm): 7.96 (s, 2H), 7.42 (s, 2H), 7.30 (s, 2H), 4.24 (q, 4H), 2.05 (m, 4H), 1.93 (m, 4H), 1.33 (m, 6H), 1.26-1.08 (m, 48H), 0.83 (m, 12H).

MS (MALDI-TOF): 1056.560. Calculated: 1056.486 (M+).

A2, (Z)-3-ethyl-5-((5-(2-((E)-(3-ethyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl)-4,4-dioctyl-4H-indeno[1,2-b]thiophen-6-yl)thiophen-2-yl)methylene)-2-thioxothiazolidin-4-one

The experimental procedure for the synthesis of Acceptor 2 is identical to the procedure described in section 7.1.3. For this synthesis 6-(5-formylthiophen-2-yl)-4,4-dioctyl-4H-indeno[1,2-b]thiophene-2-carbaldehyde (the A2-dialdehyde core (0.265 g, 0.50 mmol) and 3-ethylrhodanine (0.80 g, 5.0 mmol) was mixed in chloroform (20 mL). The amount of piperidine was unchanged. After column chromatography (hexane/chloroform V/V = 1:3) the compound was recrystallized only one time to give the product as a deep red powder (0.203 g, 50 % yield).

1H NMR (CDCl₃, 600 MHz), δ (ppm): 7.95 (s, 1H), 7.91 (s, 1H), 7.69 (m, 1H), 7.60-7.55 (m/s+d, 2H), 7.50 (d, 1H), 7.45 (d, 1H), 7.31 (s/m, 1H), 4.24 (q, 4H), 2.06 (m, 2H), 1.96 (m, 2H), 1.38-1.31 (m, 6H), 1.28-0.80 (m, 30H)

MS (MALDI-TOF): 820.293. Calculated: 820.235 (M+)

A3, (5Z,5'Z)-5,5'-((5,5,10,10-tetraoctyl-5,10-dihydrothieno[2',3':3,4]cyclopenta[1,2-g]thieno[3,2-c]isochromene-2,8-diyl)bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)

The experimental procedure for the synthesis of Acceptor 3 is identical to the procedure described in section 7.1.3. For this synthesis 5,5,10,10-tetraoctyl-5,10-dihydrothieno[2',3':3,4]cyclopenta[1,2-g]thieno[3,2-c]isochromene-2,8-dicarbaldehyde (the A3-dialdehyde core (0.153 g, 0.28 mmol) and 3-ethylrhodanine (0.450 g, 2.8 mmol) was mixed in chloroform (20 mL). The amount of piperidine was unchanged. The crude product was purified with column chromatography several times (hexane/chloroform V/V = 1:3) and recrystallized from hexane and chloroform two times to give the product as a deep red powder (0.088 g, 38 % yield).

1H NMR (CDCl₃, 600 MHz), δ (ppm): 7.89 (s, 1H), 7.77 (s/d, 1H), 7.59 (m, 1H), 7.34 (d, 1H), 7.43 (m, 2H), 6.99 (s, 1H), 4.23 (m, 4H), 2.03 (m, 2H), 1.96 (m, 2H), 1.43 (m, 2-3H), 1.36-1.12 (m, 26H)

MS (MALDI-TOF): 836.1. Calculated: 836.230 (M+)

A4, (5Z,5'E)-5,5'-((5,5'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis(thiophene-5,2-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)

The experimental procedure for the synthesis of Acceptor 4 is identical to the procedure described in section 7.1.3. For this synthesis 5,5'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis(thiophene-2-carbaldehyde) (the A4-dialdehyde core (0.4 g, 0.72 mmol) and 3-ethylrhodanine (1.16 g, 7.2 mmol) was mixed in chloroform (20 mL). The amount of piperidine was unchanged. After column chromatography (hexane/chloroform V/V = 1:2) the compound was recrystallized only one time to give the product as a deep red powder (0.364 g, yield 60 %).

1H NMR (CDCl₃, 600 MHz), δ (ppm): 7.94 (s, 2H), 7.67 (d, 2H), 7.45 (d, 2H), 7.36 (s, 2H), 4.23 (q, 4H), 4.12 (d, 4H), 1.98 (m, 2H), 1.78-1.71 (m, 2H) 1.71-1.66 (m, 2H), 1.66-1.61 (m, 4H), 1.40 (m, 8H), 1.33 (t, 6H), 1.04 (t, 6H), 0.94 (t, 6H).

MS (MALDI-TOF): 840.11. Calculated: 840.225 (M+)

Small area device Fabrication and Characterization

Organic solar cells were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO) with the structure of ITO/Al4083/P3HT:A1-A4/ZnO/Ag. Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone and isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 15 min. A thin layer of Al4083 PEDOT:PSS was spin coated onto pre-cleaned ITO-coated glass substrates at 3500 rpm for 60 s and then annealed at 170 °C for 20 min. Then the substrates were transferred to a glovebox, the active layer was spin coated from 16 mg/mL (P3HT:A1-A4) chloroform solution at 3500 rpm for 30 s followed by a layer of ZnO (10 nm). Then a pre-annealing at 120-140 °C for 4-10 min was performed. Finally, the Ag (100 nm) electrode were deposited by thermal evaporation to complete the device with an active area of 3.8 mm².

The *J-V* measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mV/cm². The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (RE-R, Enlitech).

Large area device fabrication

Large area organic solar cells were fabrication by primarily printing and coating techniques with a structure of Ag/PEDOT:PSS/P3HT:A1/ZnO/AI, initially conductive grid of Ag fingers where flexographically printed onto a PET substrate, followed by a slot-die coated layer of PH1000 (Heraeus) PEDOT:PSS with a thickness of 200 nm as described previously³. P3HT and A1 were dissolved in a 90:10 mixture of chlorobenzene and chloroform & an eventual additive, the solid concentration was 12.6 mg mL⁻¹ with a P3HT:A1 ratio of 1:0.8 to ensure a sufficient wet thickness during ink deposition. The active layer was deposited by slot-die coating with a substrate temperature of 60 °C unless stated otherwise with a web-speed of 1 m min⁻¹. ZnO was slot-die coated with a web-speed of 1 m min⁻¹ with a substrate temperature of 70 and 80° C for acetone and ethanol based ZnO inks, respectively. The ink formulations had a concentration of 15 mg mL⁻¹ and was printed with a wet thickness of 6 µm. Finally, the top electrode was deposited by thermal evaporation in a vacuum deposition chamber (background pressure $\approx 5 \times 10-4$ Pa) to deposit 100 nm thick aluminum cathode through a shadow mask.

J-V curves were measured of device with an area 0.80 cm² as described above.

Charge carrier mobility

The charge carrier mobilities of the Donor:Acceptor films were measured using the space charge limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/Donor:Acceptor/MoO₃/Ag, electron-only devices were fabricated in a structure of ITO/ZnO/Donor:Acceptor/PFN-Br/AI. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \quad (1)$$

Here, $\mathcal{E}_r \approx 3$ is the average dielectric constant of the blend film, \mathcal{E}_0 is the permittivity of the free space, μ is the carrier mobility, $L \approx 50-70$ nm is the thickness of the film, and V is the applied voltage.

Blended film light absorbance spectra



Figure S1: Normalized absorbance spectra of P3HT:acceptor blended film is a 1:1 ratio.





Figure S2: Cyclic voltammograms for A1-A4 in acetonitrile with 0.1 M Bu_4NPF_6 at 100 mV s-1. A calomel electrode was used as reference electrode and measurements were calibrated against ferrocene.

Device optimization

A1



Figure S3: Photovoltaic characteristics for the small area P3HT:A1 device optimized for annealing temperature and time, donor:acceptor ratio, and film thickness.



Figure S4: Photovoltaic characteristics for the small area P3HT:A2 device optimized for annealing temperature and time, donor: acceptor ratio, and film thickness.



Figure S5: Photovoltaic characteristics for the small area P3HT:A3 device optimized for annealing temperature and time, donor: acceptor ratio, and film thickness.



Figure S6: Photovoltaic characteristics for the small area P3HT:A4 device optimized for annealing temperature and time, donor:acceptor ratio, and film thickness.

Table S1: Device efficiency as a function of annealing time at 140° C

	PCE (%)	Voc (V)	Jsc (mA cm ⁻²)	FF (%)
5 min 140° C	0.67	0.66	2.89	35.21
10 min 140° C	0.62	0.62	2.90	34.33
30 min 140° C	0.27	0.63	1.51	27.80

i-FOM calculations and corrections to literature

There appear to be some discrepancies in literature regarding the calculations of the *i*-FOM value. The formula for calculating *i*-FOM is as presented in the main text of this paper and as seen below in equation 1:

$$i - FOM = \frac{PCE \times Stability}{SC \ index \ (M)} (1)$$

Where PCE is the device efficiency, stability is the percentage of PCE retained after 200 h, and SC index (M) is the combined synthetic complexity of the active layer materials including considerations such as donor:acceptor ratio. And it is within this third part that the discrepancies are present. The original paper presenting the synthetic complexity calculations was published by Po *et al.*⁴ using the following equation 2:

$$SC = 35 \frac{NSS}{NSS_{max}} + 25 \frac{Log(RY)}{Log(RY_{max})} + 15 \frac{NUO}{NUO_{max}} + 15 \frac{NCC}{NCC_{max}} + 10 \frac{NHC}{NHC_{max}} (2)$$

Where NSS is the number of synthetic steps ($NSS_{Max} = 22$), RY is the reciprocal overall synthetic yield ($RY_{Max} = 86.9$), NUO is the number of unit operations for purification ($NUO_{Max} = 39$), NCC is the number of column chromatographic purifications (counted in both NUO and NCC to weight column chromatographic purifications higher than other purification techniques) ($NCC_{Max} = 13$) and NHC is the number of hazardous chemicals used during the synthesis ($NHC_{Max} = 44$).

The initial i-FOM paper by Li et al.⁵ presents a slightly modified formula presented in equation 3:

$$SC = 35 \frac{NSS}{NSS_{max}} + 25 \frac{RY}{RY_{max}} + 15 \frac{NUO}{NUO_{max}} + 15 \frac{NCC}{NCC_{max}} + 10 \frac{NHC}{NHC_{max}} (3)$$

Which they of course are entitled to do if they have determined that this formula is better suited for their purpose. The authors have, however, directly transferred the SC values and calculations for P3HT and PCE10 from Po *et al.*⁴ (entry 61 and 1 in the Po *et al.* paper, respectively), thereby presenting data calculated with both equation 2 and 3 as SC data. Moreover, the authors of Li *et al.*⁵ have recently published another paper including *i*-FOM values (Du *et al.*⁶), herein they have utilized equation 2 to calculate the SC value of their presented materials. These discrepancies have let us to believe that the utilization of Equation 3 in Li *et al.*⁵ was an oversight and we have therefore recalculated the presented *SC* values presented therein with equation 2 as seen in Table S2.

Material	NSS/NSS _{Max}	RY/RY _{Max}	RY	NUO/NUO _{Max}	NCC/NCC _{Max}	NHC/NHC _{Max}	SC
Literature values calculated with equation 3							
PCBM	0.227	0.266	23.2	0.154	0.154	0.136	20.6
PCE11	0.364	0.07	6.08	0.333	0.231	0.5	27.9
O-IDTBR	0.5	0.267	23.1	0.615	0.461	0.364	43.9
Corrected values calculated with equation 2							
PCBM	0.227	0.703	23.2	0.154	0.154	0.136	31.5
PCE11	0.364	0.404	6.08	0.333	0.231	0.5	36.3
O-IDTBR	0.5	0.704	23.1	0.615	0.461	0.364	54.9

Table S2: Recalculation of synthetic complexity values presented in Li et al. with Equation 2 instead of Equation 3.

These changes in synthetic complexity translate to the following changes in *i*-FOM values Table S3

Material	SC _{Donor}	SC _{Acceptor}	Ratio	SC index	PCE	Stability	i-FOM	i-FOM
combination				(M)	(%)	(200 h)	published	corrected
P3HT:PCBM	7.7	31.5	1:1	19.6	2.8	0.92	0.183	0.131
PCE10:PCBM	64.3	31.5	1:2	42.4	8.87	0.91	0.229	0.190
PCE11:PCBM	36.3	31.5	1:1.2	33.7	9.2	0.67	0.258	0.183
P3HT:O-IDTBR	7.7	54.9	1:1	31.3	6.05	0.98	0.230	0.189
PCE10:O-	64.3	54.9	1:1.5	58.7	12.0	0.95	0.219	0.194
IDTBR								
PCE11:O-	36.3	54.9	1:1.4	47.2	9.5	1	0.255	0.201
IDTBR								

Table S3: The corrected i-FOM values with the SC values calculated using Equation 2.



Figure S6. 1H-NMR of acceptor A1, molecule A) (5E,5'E)-5,5'-((4,4,9,9-tetraoctyl-4,9-dihydro-sindaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(methanylylidene))bis(3ethyl-2-thioxothiazolidin-4-one), B) A2, (Z)-3-ethyl-5-((5-(2-((E)-(3-ethyl-4-oxo-2-thioxothiazolidin-5ylidene)methyl)-4,4-dioctyl-4Hindeno[1,2-b]thiophen-6yl)thiophen-2-yl)methylene)-2thioxothiazolidin-4-one, C) A3, (5Z,5'Z)-5,5'-((5,5,10,10-tetraoctyl-5,10dihydrothieno[2',3':3,4]cyclopenta[1 ,2-g]thieno[3,2-c]isochromene-2,8diyl)bis(methanylylidene))bis(3ethyl-2-thioxothiazolidin-4-one), D) A4, (5E,5'E)-5,5'-((4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6b']dithiophene-2,7diyl)bis(methanylylidene))bis(3ethyl-2-thioxothiazolidin-4-one)

Molecular weight (MALDI-TOF MS)



Figure S7. MS (MALDI-TOF) of A) A1, (5E,5'E)-5,5'-((4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one); B) A2, (Z)-3-ethyl-5-((5-(2-((E)-(3-ethyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl)-4,4-dioctyl-4H-indeno[1,2-b]thiophen-6-yl)thiophen-2-yl)methylene)-2-thioxothiazolidin-4-one; C) A3, (5Z,5'Z)-5,5'-((5,5,10,10-tetraoctyl-5,10-dihydrothieno[2',3':3,4]cyclopenta[1,2-g]thieno[3,2-c]isochromene-2,8-diyl)bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one); and D) A4, (5Z,5'E)-5,5'-((5,5'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis(thiophene-5,2-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one); thioxothiazolidin-4-one)

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