SUPPLEMENTARY INFORMATION

Low-Gap Zinc Porphyrin as an Efficient Dopant for Photomultiplication Type Photodetectors

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Material Characterization

The nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova 400 MHz spectrometer (¹H, 400 MHz; ¹³C, 100 MHz) and a Bruker Avance 600 MHz spectrometer (¹H, 600 MHz) (The solvents were chloroform-d and pyridine-d5, and tetramethylsilane (TMS) was the internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were recorded on a Bruker Daltonics Autoflex MALDI-TOF mass spectrometer, using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile as the matrix.

Synthesis

All reagents and starting material 4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene were purchased from commercial sources and used without further purification. The synthesis for compound ZnP-TIPS₄ has been previously reported.¹ Por4IC was synthesized by modifying procedures reported in the literature.^{1,2}All moisture and oxygen-sensitive reactions were carried out using Schlenk techniques in oven-dried glassware.



Scheme S1 Synthesis of Por4IC.



Compound 1. To a round bottom flask equipped with a condenser containing dimethylformamide (2g, 27.32mmol), phosphorus oxychloride (3.49g, 22.75mmol) was added dropwise and the mixture was stirred at room temperature for 1h. After 1h a solution of 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (10g, 24.83mmol) in chloroform (40mL) was added slowly into the flask and the mixture was heated to 60°C. After 4h the reaction was quenched with a saturated sodium acetate aqueous solution. The resulting mixture was extracted with CH₂Cl₂ and the extract was washed with brine and water and dried with MgSO₄. After removing the solvent under reduced pressure, the residue was purified by column chromatography (Dichloromethane: Heptane 2:3) to yield compound 1 as a pale-yellow oil (11.63g, 92% yield). ¹H NMR (400 MHz, Chloroform-d) δ 9.81 (s, 1H), 7.54 (t, *J* = 3.6 Hz, 1H, due to racemic 2-ethylhexyl groups), 7.34 (d, 1H), 6.97 (dt, *J* = 4.9, 2.5 Hz, 1H, due to racemic 2-ethylhexyl groups), 1.96 – 1.83 (m, 4H), , 0.98 – 0.82 (m, 18H), 0.75 – 0.69 (m, 6H), 0.61 – 0.48 (m, 8H). ¹³C NMR (101 MHz, Chloroform-d) δ 182.50, 161.97, 157.71, 147.95, 142.83, 135.91, 130.80, 129.10, 122.55, 53.74, 43.10, 35.15, 35.13, 34.25, 34.03, 31.87, 29.01, 28.50, 27.36, 27.21, 22.70, 22.68, 14.11, 14.03, 14.01, 10.58.



Fig. S1 HH-COSY (Chloroform-d) spectrum of compound 1.



To a round bottom flask containing compound 1 (11.44g, 26.5 mmol) 250ml of degassed THF was added. The mixture was cooled to 0 °C and then N-bromosuccinimide (5.2g, 29.2 mmol) dissolved in THF (40mL) was added in dark. The mixture was allowed to warm to room temperature and stirred for 6h. At that point aqueous sodium thiosulfate solution was added to the mixture, extracted with CH_2Cl_2 and the combined organic phase was dried over MgSO4. The crude compound was purified by column chromatography (Dichloromethane: Heptane 7:3) to yield a pale-yellow oil (11.8g, 87.2%).¹H NMR (400 MHz, Chloroform-*d*) δ 9.83 (s, 1H), 7.55 (t, *J* = 3.8 Hz, 1H, due to racemic 2-ethylhexyl groups), 7.02 (t, *J* = 3.7 Hz,

1H, due to racemic 2-ethylhexyl groups), 2.06 – 1.79 (m, 4H), 1.08 – 0.82 (m, 16H), 0.76 (dtd, J = 13.8, 6.9, 1.1 Hz, 6H), 0.65 - 0.56 (m, 8H). ¹³C NMR (101 MHz, Chloroform-d) δ 182.55, 147.02, 160.73, 156.75, 143.21, 136.24, 130.48, 125.53, 115.77, 54.57, 42.99, 35.20, 35.18, 34.16, 34.14, 34.05, 34.04, 28.49, 28.45, 27.41, 27.25, 22.70, 14.03, 10.62, 10.61 , 10.56 ·.



Fig. S2 HH-COSY (Chloroform-d) spectrum of compound 2.



Compound 3. ZnP-TIPS₄ (0.351g, 0.31mmol) was dissolved in dry THF (50mL) under inert atmosphere and 5.2 mL of TBAF solution (1.0 M in THF) were added slowly in room

temperature. The reaction mixture was left to react for 30min after which a mixture of cold ethanol (50mL) and water (50mL) was added to the flask. THF was evaporated and the compound precipitated. The product was filtered under N_2 atmosphere, extensively washed with ethanol and water and then collected and used directly for the next step without any further purification.

Por4CPDT . Compound 3 was drying under a vacuum for 30min and then compound 2 (0.923g, 1.9mmol), CuI(0.036mg, 0.19mmol), TEA(2mL) and THF(30 mL) were added in the flask. The mixture was bubbled with argon for 10min and Pd(PPh₃)₄(0.074mg, 0.063mmol) was finally added. The mixture was stirred overnight at 50°C. Then the reaction mixture was filtered through a pad of silica and was purified with column chromatography over silica gel (toluene:pyridine = 99:1) to yield Por4CPDT, (282mg, 40.92%).¹H NMR (400 MHz, Pyridine-d5) δ 10.32 (t, J = 7.0 Hz, 4H), 9.67 (tp, J = 29.0, 9.0, 8.5 Hz, 8H), 8.28 (d, J = 4.8 Hz, 4H), 2.36 (s, 16H), 1.58 – 0.63 (m, 157H). MALDI-TOF: calcd for C₁₃₂H₁₅₆N₄O₄S₈Zn [M+], 2181.92; found: 2181.934



Fig. S3 MALDI-TOF *m/z* spectrum of Por4CPDT



Por4IC. In a two-neck flask, Por4CPDT (0.15g, 0.068mmol) and 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (0.21g, 1.1mmol), chloroform (50mL) and pyridine (1mL) were added and the mixture was heated to 65°C under nitrogen. After stirring at 65°C for 7h, the solvents were removed under reduced pressure and the compound was purified by size exclusion chromatography (toluene:pyridine = 99:1). After solvent evaporation the compound was redissolved in 10mL of a chloroform : pyridine (99:1), precipitated in ethanol(100mL)and filtered to give a dark blue solid (0.185g, 93.25% yield). ¹H NMR (600 MHz, Pyridine-d5) δ 9.46 (s, 8H), 8.98 (s, 4H), 8.46 – 8.25 (m, 12H), 8.08 (s, 4H), 7.85 (d, *J* = 29.4 Hz, 8H), 2.62 (s, 16H), 2.05 – 1.41 (m, 72H), 1.39 – 0.73 (m, 48H). MALDI-TOF: calcd for C180H172N12O4S8Zn [M+], 2887.07; found: 2886.914



Fig. S4 MALDI-TOF *m/z* spectrum of Por4IC.

Density Functional Theory Calculation

Density functional theory (DFT) calculations were carried out using the Gaussian 16 program (revision B.01).³ The graphical visualization was done with the Visual Molecular Dynamics 1.9.3 (VMD) software,⁴ while the density of states (DOS) and orbital overlap integrals were processed using the Multiwfn 3.7 program.⁵ A model compound of Por4IC was used, where the alkyl chains were truncated to methyl groups to save computational time. Both *cis* and *trans* isomers were calculated initially in gas phase using the B3LYP functional,^{6,7} LANL2DZ basis set for Zn atom with the LANL2 pseudopotential for core electrons,⁸ and the 6-31G(d,p) basis set for lighter atoms (here, we refer to the *cis/trans* conformation of the CPDT and IC groups about the single bond).⁹ The conformation with lowest ground-state energy was adopted for reoptimization of the geometry using the long-range corrected CAM-B3LYP¹⁰ functional and Grimme's D3 dispersion correction with BJ damping function.¹¹ This functional was previously found to represent the experimental electronic transitions of other Zn-porphyrins.¹ Further optimization of the geometry was carried out in toluene (dielectric constant, $\varepsilon = 2.3741$) using the polarizable continuum model (PCM).¹² The vertical excitations were assessed *via* single-point time-dependent density functional theory (TD-DFT) calculations in toluene.

For the P3HT:Por4IC complex, 11-repeat unit P3HT structure was used as model compound where the side chains were truncated to methyl groups. Geometry optimization of the complex in gas phase was facilitated by using the same CAM-B3LYP method described above; keeping Por4IC at the optimized geometry of the isolated molecule and allowing P3HT freely relax to the energy minimum.¹³ Parallel and antiparallel configurations relative to the porphyrin core were used as initial guesses (see Fig. S6), both converging to identical parallel configurations. Single-point TD-DFT calculations were employed to assess the excitation energies and oscillator strengths based on the Tamm–Dancoff approximation.^{14,15} Natural transition orbital (NTO) analysis for the two overlapping lowest-energy transitions is illustrated in Fig. S7.¹⁶ The stronger charge-transfer character of the left side transition in Fig. S7 suggests an effective depletion of the electron density at P3HT and gain at Por4IC, while the right side transition in Fig. S7 displays more localized excitation character, both transitions featuring significant oscillator strengths.



Fig. S5 Superimposed geometry-optimized structures of Por4IC (top left), as calculated in gas phase (green structure) and using PCM with toluene as solvent (red structure). Optically accessible frontier orbitals describing the electronic ground state of Por4IC in toluene.

Table S1 TD-DFT-calculated energies (eV), wavelengths (nm) and oscillator strengths (*f*) of the electronic transitions of Por4IC. The percentage stands for the contribution of such orbitals. Only the main transitions ($f \ge 0.05$) and orbital contributions ($\ge 10\%$) are listed.

Transition	eV	nm	f
66% HOMO → LUMO	1.78	697	2.119
$66\% \text{ HOMO} \rightarrow \text{LUMO+1}$	1.78	697	2.120
24% HOMO–1 \rightarrow LUMO	2.37	522	3.393
10% HOMO-4 \rightarrow LUMO			
24% HOMO-1 \rightarrow LUMO+1	2.37	522	3.389
$10\% \text{ HOMO}-4 \rightarrow \text{LUMO}+1$			
19% HOMO–1 \rightarrow LUMO	2.86	434	0.202
18% HOMO-1 \rightarrow LUMO+1			
14% HOMO \rightarrow LUMO+4			
11% HOMO-1 \rightarrow LUMO+5			
19% HOMO-1 \rightarrow LUMO+1	2.86	434	0.203
$18\% \text{ HOMO}-1 \rightarrow \text{LUMO}$			
14% HOMO \rightarrow LUMO+5			
11% HOMO-1 \rightarrow LUMO+4			
$24\% \text{ HOMO} \rightarrow \text{LUMO+4}$	3.10	400	0.199
20% HOMO-4 \rightarrow LUMO			
$17\% \text{ HOMO} \rightarrow \text{LUMO+5}$			
$16\% \text{ HOMO} \rightarrow \text{LUMO+1}$			
$24\% \text{ HOMO} \rightarrow \text{LUMO+5}$	3.10	400	0.199
20% HOMO-4 \rightarrow LUMO+1			
$17\% \text{ HOMO} \rightarrow \text{LUMO+4}$			
16% HOMO \rightarrow LUMO			
$23\% \text{ HOMO} \rightarrow \text{LUMO+8}$	3.34	371	0.052
$23\% \text{ HOMO} \rightarrow \text{LUMO+9}$	3.34	3.71	0.052
22% HOMO-4 \rightarrow LUMO	3.44	360	0.066
14% HOMO-4 \rightarrow LUMO+4			
22% HOMO-4 \rightarrow LUMO+1	3.44	360	0.066
14% HOMO-4 \rightarrow LUMO+5			
25% HOMO-2 \rightarrow LUMO+2	3.95	314	0.111
$25\% \text{ HOMO-}3 \rightarrow \text{LUMO+}2$	3.95	314	0.111



Fig. S6 Parallel and antiparallel configurations of P3HT (orange structure) and Por4IC (blue structure) used as initial guesses in the geometry-optimization of the P3HT:Por4IC complex.



Fig. S7 TD-DFT-calculated excitation energies (oscillator strengths in the parentheses) and illustration of the natural transition orbitals, distance between the centroids of the hole and electron distributions (*D*) and hole-electron wave function overlap ($O_{h,e}$) for the two lowest-energy excited states of the P3HT:Por4IC complex (h = hole, e = electron). The top structure is P3HT and the bottom structure is Por4IC. The percentage stands for contribution of such orbitals to the transition. Value $O_{h,e} = 1$ corresponds to complete orbital overlap and $O_{h,e} = 0$ signifies no orbital overlap.

Photophysical Properties

The absorbance spectra were measured using a Perkin Elmer LAMBDA 1050+ UV/Vis/NIR spectrophotometer in a $10 \times 10 \text{ mm}^2$ quartz cuvette. Emission spectra were collected on an Edinburgh FLS-920 fluorospectrophotometer equipped with a R928P photomultiplier tube and a Hamamatsu R5509 photomultiplier tube with response range from 300 to 1700 nm. The measurements were performed in toluene + 1% pyridine solution.



Fig. S8 a) Emission (solution) spectra of Por4IC b) Absorption coefficient of Por4IC as an average of three different concentrations.

Cyclic Voltametry

The cyclic voltammetry measurement was carried out under a N₂ atmosphere with a CH-Instruments 650A Electrochemical Workstation. The working and counter electrodes were a Pt wire, while the reference was an Ag wire. The electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in anhydrous acetonitrile, which was bubbled with N2 prior to each measurement to avoid the presence of any oxygen residue. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal standard. The E_{ox} and E_{red} were defined as the intersection of the baseline and the tangent of the current at the halfpeak height. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were calculated from the E_{ox} and E_{red}, respectively, by setting the Fc/Fc⁺ oxidation potential versus the normal hydrogen electrode (NHE) to 0.63 V and the NHE to -4.5 V in the Fermi vacuum scale, which gives the following formulas: HOMO = $-(E_{ox} + 5.13)$ eV and LUMO = $-(E_{red} + 5.13)$ eV.



Fig. S9 CV traces of Por4IC recorded at a scan rage of 100 mV/s.

Device Fabrication and characterization

The indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 15 Ω per square were successively cleaned by detergent, deionized water, and ethanol in ultrasonic cleaning. Then the ITO substrates were blow-dried with high-purity nitrogen gas. The cleaned ITO substrates were treated by oxygen plasma for 90 s to increase the work function of the ITO and further clean the substrates. The aqueous solution of poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP AI.4083, purchased from H.C. Starck Co., Ltd.) was spin-coated onto the cleaned ITO substrates at a spin speed of 5000 rounds per minute (rpm) for 30 s. The PEDOT:PSS/ITO substrates were annealed at 150 °C for 15 min in the atmosphere. Then the processed PEDOT:PSS/ITO substrates were transferred to a high-purity nitrogen-filled glove-box. The polymer poly(3hexylthiophene) (P3HT) (purchased from Solarmer Materials Inc.) and Por4IC were dissolved in chlorobenzene (CB) to prepare 40 mg/mL and 10 mg/mL solutions, respectively. The incorporation weight ratio of P3HT:Por4IC was 100:1. The mixed solution was spin-coated onto the PEDOT:PSS/ITO substrates at 800 rpm for 30 s to prepare the active layers. The 100 nm aluminum (Al) layers was formed on the active layers by thermal evaporation in a high vacuum (10⁻⁴ pa) chamber, acting as the electrode of the PM type OPDs. The active area of the PM type OPDs is about 3.8 mm² defined as the vertical overlap of the Al and ITO electrodes.

The current density versus voltage (*J-V*) curves of the PM type OPDs were measured by Keithley 2400 source meter in dark and under white light illumination with the intensity of 2 mW cm⁻². The incident light used in experiments was provided by a 150 W xenon lamp coupled with the optical fiber. The monochromatic light was provided by the 150 W xenon lamp coupled with a monochromator. The wavelength of incident light was scanned from 300 to 750 nm. All measurements were carried out in the high-purity nitrogen-filled glove-box.

EQE is calculated as

$$R = \frac{J_L - J_D}{I_{in}} \tag{1}$$

$$EQE = \frac{Rh\nu}{e} \tag{2}$$

where R is the responsivity, J_L is the light current density, J_D is the dark current density, I_{in} is the intensity of incident light, e is absolute value of electron charge and hv is the energy of incident photon, respectively

(3)

D* was estimated according to the following equation:



 $D^* = \frac{R}{\left(2eJ_D\right)^{1/2}}$

Fig. S10 *J-V* curves of the ITO/PEDOT:PSS/P3HT/Al device measured in dark and under 2 mW cm⁻² white light illumination conditions.

The LDR of the PM type OPDs was calculated under monochromatic light of 650 nm generated by diode laser. The incident light intensity was manipulated by utilizing different neutral density filters. The LDR can be estimate according to the Equation (4):

$$LDR = 20log \frac{I_{upper}}{I_{lower}} \tag{4}$$

where I_{upper} and I_{lower} are the maximum and minimum detectable light intensity in linear range, respectively.



Fig. S11 LDR of the PM type OPDs measured at -15 V bias under 650 nm light illumination, the solid red line is the linear fitting.

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