Electronic Supplementary Information (ESI) for:

Enhancing Optoelectronic Performance of Organic Phototransistors through Surface Doping of Tetra-bromo Perylene Diimide Single Crystals

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Supplementary Contents

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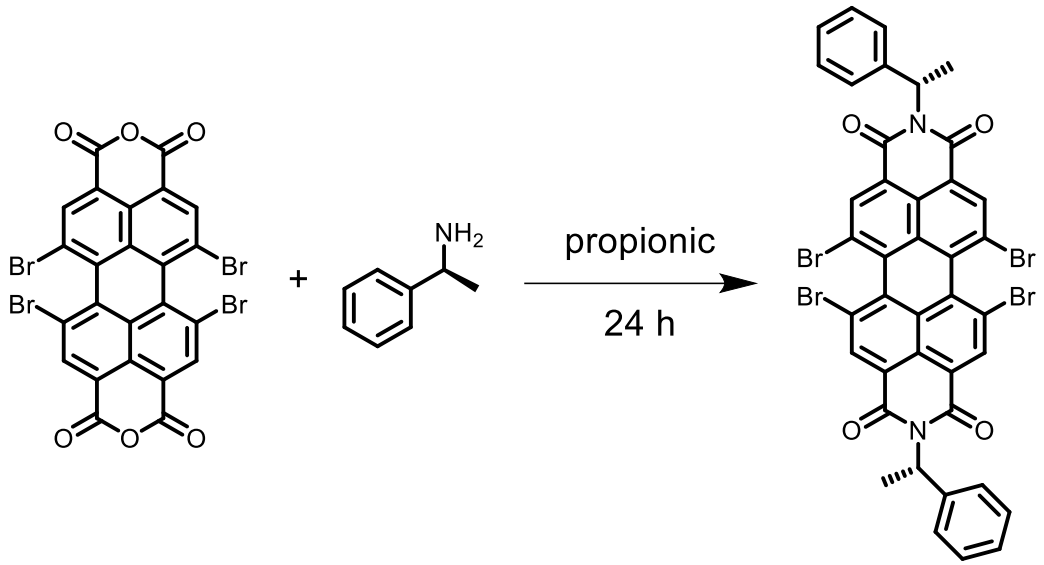
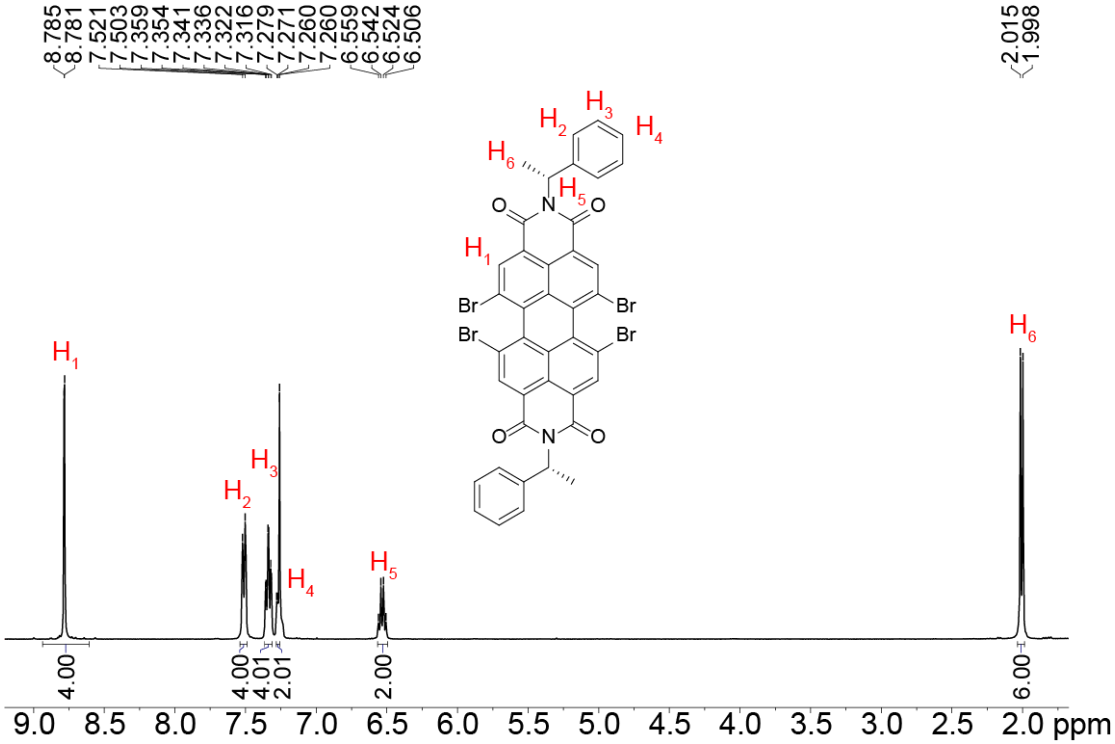
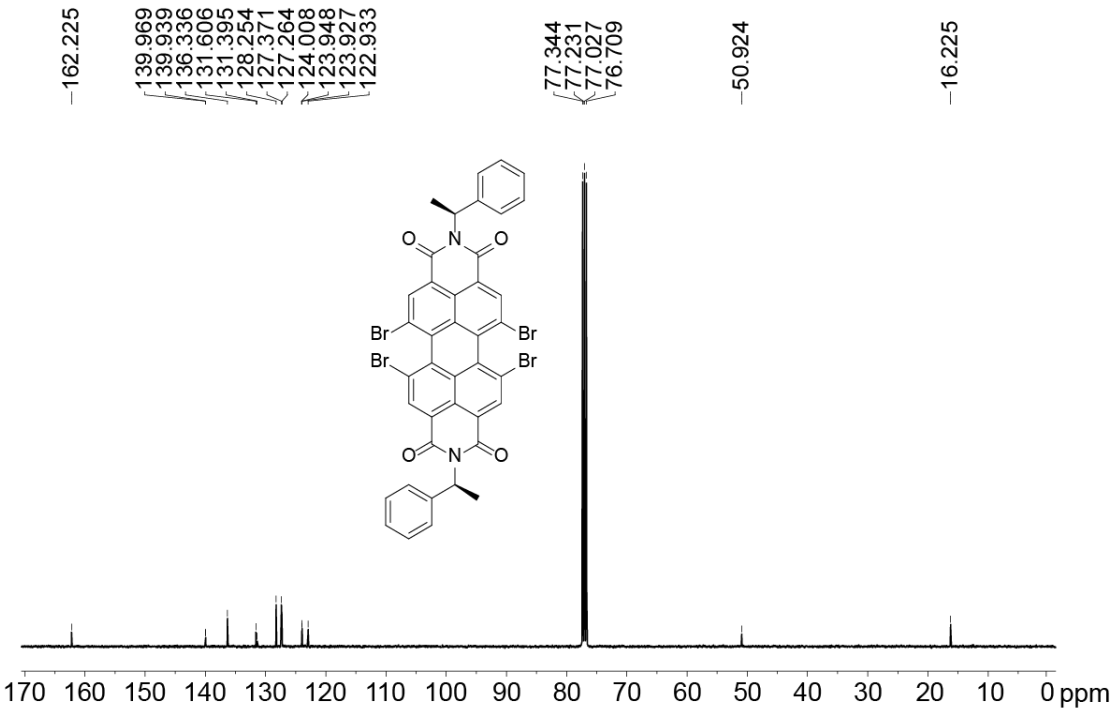


(*S*)-4Br-CPDI-Ph: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.78 (s, 2 H), 8.78 (s, 2 H), 7.51 (d, J = 7.6 Hz, 4 H), 7.32-7.36 (m, 4 H), 7.23-7.28 (m, 2 H), 6.53 (q, J = 7.2 Hz, 2 H), 2.01 (d, J = 7.2 Hz, 6 H) ppm. ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.2, 140.0, 139.9, 136.3, 131.6, 131.4, 128.3, 127.4, 127.3, 124.0, 123.9, 123.9, 122.9, 50.9, 16.2 ppm. **HRMS** (ESI) *m/z*: $[M+K]^+$ Calcd for $C_{40}H_{22}Br_4N_2O_4^+$ 948.7950; Found: 948.7956.




162.225
139.969
139.939
136.336
131.606
131.395
128.254
127.371
127.264
124.008
123.948
123.927
122.933
77.344
77.231
77.027
76.709
50.924
16.225
O
N
O
Br
Br
Br
Br
O
N
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Estimation of Optoelectrical Properties

To investigate the external quantum efficiency (EQE) (η) of OPTs was calculated which can be defined as the ratio of number of photogenerated carriers that practically enhances the drain current to the number of photons incident onto the OPT channel area, using the following equation:

$$\eta = \frac{(I_{light} - I_{dark})hc}{eP_{int}A\lambda_{peak}}$$

where h is the plank constant, c the speed of light, e the fundamental unit of charge, A the area of the transistor channel, and λ_{peak} the peak wavelength of the incident light, respectively. Detectivity usually describes the smallest detectable signal, which allows comparisons of photodetector devices with different configurations and areas. D^* was evaluated within this study using the following Equations:

$$D^* = \frac{\sqrt{A}}{NEP}$$

$$NEP = \frac{\sqrt{\overline{I_n^2}}}{R}$$

In these equations, A is the photodetector active area, NEP the noise equivalent power, and $\overline{I_n^2}$ the measured noise current. If the major limit to detectivity is shot noise from the drain current under dark conditions, D^* can be simplified as:

$$D^* = \frac{R}{\sqrt{(2e \cdot I_{dark}/A)}}$$

X-ray Crystallography

X-ray Crystallographic Data for 4Br-PDI-Ph Single Crystal

$C_{54}H_{38}Br_4N_2O_4$ (M =1098.50 g/mol): monoclinic, space group $C2$ (no. 5), a = 20.414(4) Å, b = 7.438(2) Å, c = 15.499(3) Å, α = 90.00(3)°, β = 106.15(3)°, γ = 90.00(3)°, V = 2260.49(3) Å^3, Z = 2, T = 100(2) K, μ(synchrotron) = 3.611 mm^{-1}, $Dcalc$ = 1.614 g/cm^3, 17942 reflections measured (8.212° ≤ 2θ ≤ 59.342°), 6306 unique which were used in all calculations. The final R_1 was 0.0381 (I > 2σ(I)) and wR_2 was 0.0874 (all data). Flack parameter: 0.005(8); the enantiomer has been assigned by reference to an unchanging chiral centre in the synthetic procedure. CCDC: 2416410

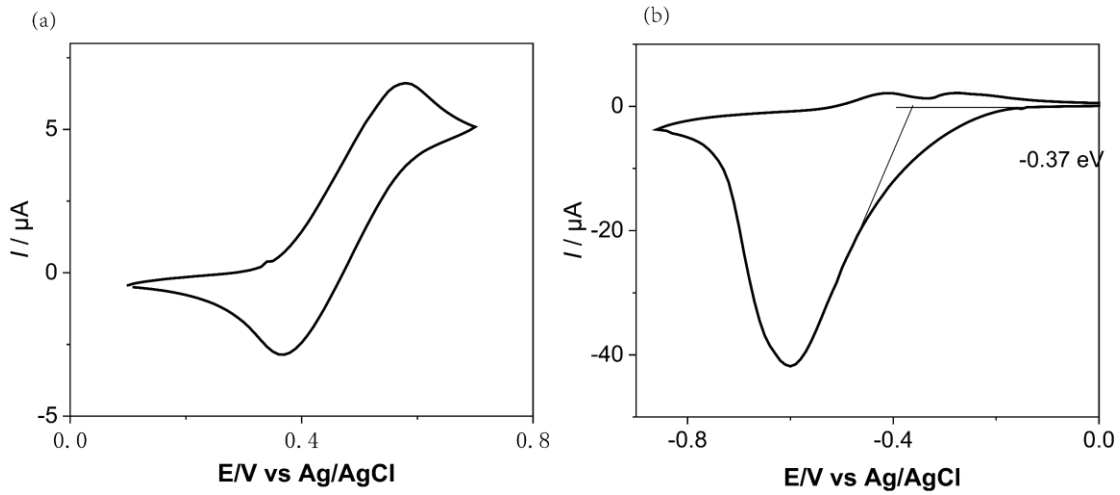


Figure S1. Cyclic voltammetry results of (a) ferrocene reference and (b) (*S*)-4Br-PDI-Ph in chloroform solution (10^{-4} M) with tetrabutylammonium hexafluorophosphate (0.1 M).

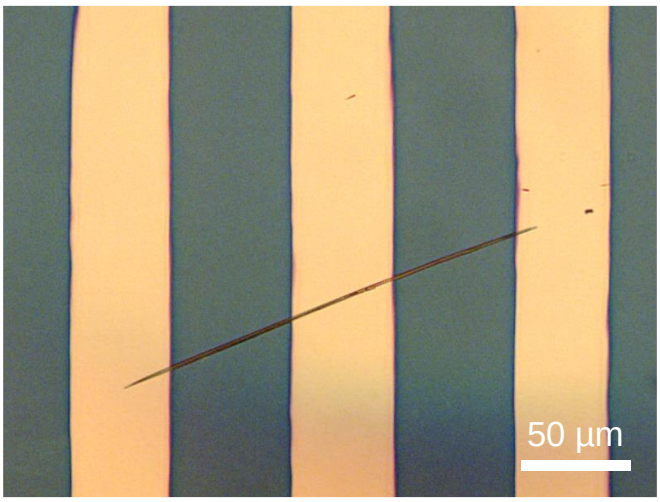


Figure S2. Optical microscope images of (*S*)-4Br-PDI-Ph single crystal based OPTs with bottom gate top contact configuration.

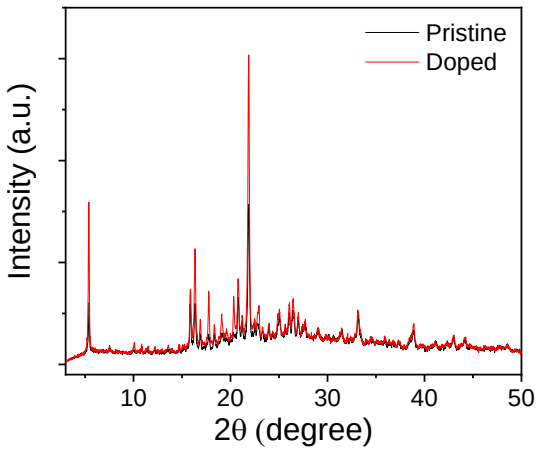


Figure S3. Powder X-ray diffraction results of pristine and doped (*S*)-4Br-CPDI-Ph single crystals.

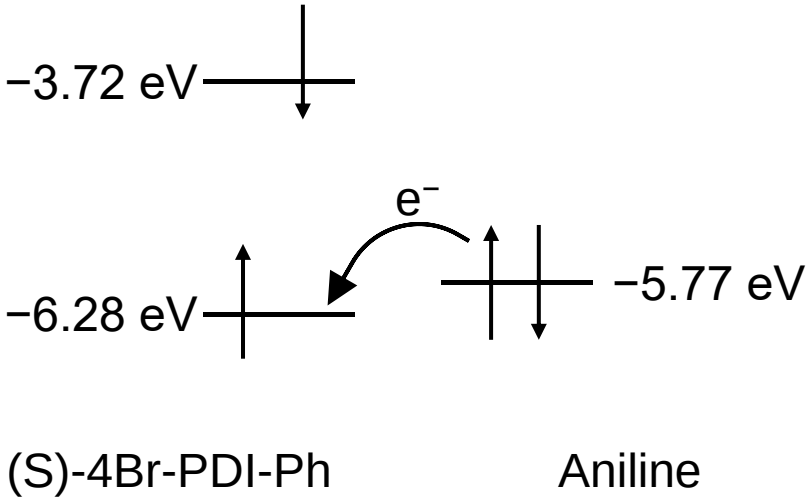


Figure S4. Energy diagrams for electron transfer from aniline vapor to (*S*)-4Br-PDI-Ph single crystals.

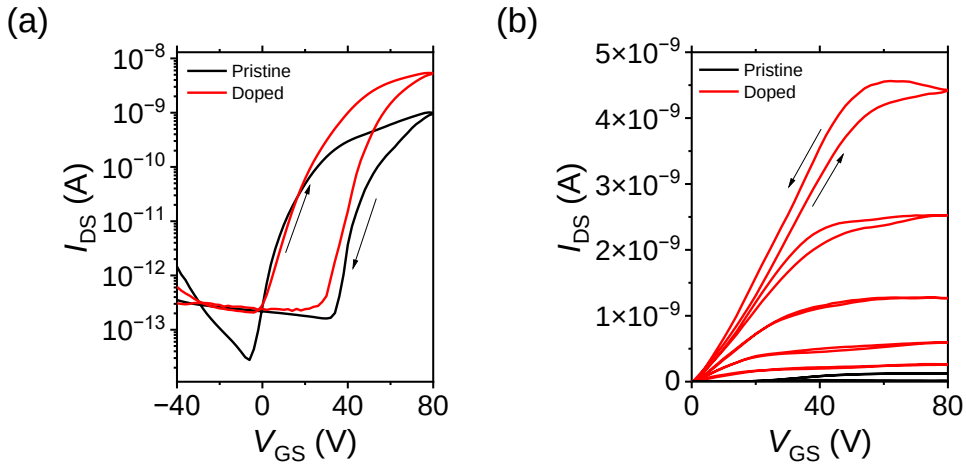


Figure S5. (a) Transfer and (b) output current hysteresis curves of pristine and doped (*S*)-4Br-PDI-Ph single crystal-based OPTs.

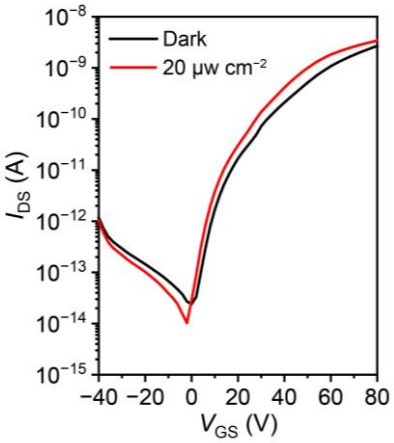


Figure S6. Transfer characteristics of pristine (*S*)-4Br-PDI-Ph single crystal based OPT under monochromatic light irradiation (λ = 532 nm).

Table S1. Energy levels of (*S*)-4Br-PDI-Ph estimated from CV measurements and DFT calculations.

Material	Frontier Orbital	Energy level (eV)	
		CV measurements	DFT calculations
4Br-PDI-Ph	LUMO	−3.96	−3.72
	HOMO	−6.16	−6.28

Table S2. Summary of on/off ratio, threshold voltages, average electron mobilities, and the number of deep interface trap states under dark condition.

Material	Doping	I_{on}/I_{off}	V_T (V)	μ (cm^2 V^{-1} s^{-1})	N_{trap} [×10^{11} cm^{-2}]
(*S*)-4Br-PDI-Ph	Pristine	> 10^3	12.5	2.95×10^{-3}	4.8
	Doped	> 10^3	8.4	1.19×10^{-2}	1.9

Table S3. Several literatures comparing the performance improvement after doping.

Materials	Doping time	μ	EQE	D^*	Reference
(*S*)-4Br-PDI-Ph	5 min	4 times	2.3 times	2 times	This work
(*R*)-CPDI-2CN-Ph	30 min	3 times	9 times	2 times	*Chin. Chem. Lett.*, 2024, **35**, 109777.
(*R*/*S*)-ClCPDI-C6	1 h	3 times	3 times	8 times	*Chem. Mater.* 2022, **34**, 8675–8683