**Electronic Supplementary Information** 

## n-Channel Organic Phototransistors with n-type Conjugated Polymer Based on Indacenodithiophene and Naphthalenediimide Units

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**Table S1.** Summary of major reports on organic phototransistors with n-type semiconducting materials. The photoresponsivity (**R**) and related sensitivity are taken from the literatures.

Authors	Materials	Device Structure and Performances	Year	Ref.
H. Yu, et al. (UNIST, Korea)	BPE-PTCDI	[ Device Structure ] n-Doped Si/SiO <sub>2</sub> /BPE-PTCDI/Au ( <i>No Flexible Devices</i> ) [ Performances ] $\lambda = 532 \text{ nm}, P_{IN} = 113000 \mu\text{W/cm}^2$ $R = 1.4 \times 10^4 \text{ A/W}$ (too higher than theoretical limit) $S_N$ (net sensitivity) = 4.96 × 10 <sup>3</sup>	2013	SR-1
S. Nam, et al. (KNU, Korea)	P3HT:PBDTTPD (80:20) $\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$	[ Device Structure ] Glass/Ag/P3HT:PBDTTPD/PMMA/PVA/AI ( <i>No Flexible Devices</i> ) [ Performances ] $\lambda = 675 \text{ nm}, P_{IN} = 21 \mu W/cm^2$ R = 14.2 A/W (higher than theoretical limit)	2016	SR-2
F. Li, et al. (CSU, China)	BODIPY-BF2 $ \begin{array}{c}                                     $	[ Device Structure ] n-Doped Si/SiO <sub>2</sub> /BODIPY-BF2/Au ( <i>No Flexible Devices</i> ) [ Performances ] $\lambda = 850 \text{ nm}, P_{IN} = 500 \mu\text{W/cm}^2$ R = 1.14 × 10 <sup>4</sup> A/W (too higher than theoretical limit) S <sub>N</sub> (net sensitivity) = 1.04 × 10 <sup>4</sup>	2017	SR-3
S. Nam, et al. (KNU, Korea)	PTB7:P(NDI2OD-T2) $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_5$ $C_2H_$	[ Device Structure ] Glass/Ag/PTB7:P(NDI2OD-T2)/PMMA /PVA/AI ( <i>No Flexible Devices</i> ) [ Performances ] $\lambda = 675 \text{ nm}, P_{IN} = 21 \mu W/cm^2$ R = 14.2 A/W (higher than theoretical limit) $S_N$ (net sensitivity) = ~10 <sup>3</sup>	2017	SR-4

	$\begin{array}{c} C_{10}H_{21} \\ C_{8}H_{17} \\ O \\ \downarrow \\ \downarrow \\ O \\ \downarrow \\ O \\ \downarrow \\ C_{10}H_{21} \\ C_{10}H_{21} \\ P(NDI2OD-T2) \end{array}$			
M. Liu, et al. (NNU, China)	PTCDI-C13 C <sub>13</sub> H <sub>27</sub> -N O O O O O O O O O O O O O O O O O O O	[ Device Structure ] PVA/Au/PMMA/BPE-PTCDI/Au ( <i>Flexible Devices</i> ) [ Performances ] $\lambda = 489 \text{ nm}, P_{IN} = 100 \mu W/cm^2$ R = 30.73 A/W (higher than theoretical limit) $S_N$ (net sensitivity) > 1 × 10 <sup>4</sup>	2018	SR-5
K. Yeliu, et al. (FU, China)	$\begin{array}{c} \textbf{P(ND12OD-T2)} \\ & \overbrace{\substack{C_{8}H_{17} \\ O \\ \downarrow \\ \downarrow \\ O \\ \downarrow \\ O \\ I \\ C_{10}H_{21}}}^{C_{10}H_{21}} \\ \end{array}$	[ Device Structure ] n-Doped Si/SiO2/P(NDI2OD-T2):PMMA(25:1)/Au (No Flexible Devices) [ Performances ] $\lambda = 400 \text{ nm}, P_{IN} = 200 \mu\text{W/cm}^2$ R = 34.8 A/W (higher than theoretical limit) S <sub>N</sub> (net sensitivity) =4.78 × 10 <sup>4</sup>	2019	SR-6
This work	$\begin{array}{c} \textbf{PIDTT-NDI} \\ \hline \\ (c_{a}H_{9} + c_{a}H_{9} + c_{a}H_{17} + c$	[ Device Structure ] Glass/ITO/PMMA/PIDTT-NDI/Ag ( <i>Flexible Devices</i> ) [ Performances ] $\lambda = 434 \text{ nm}, P_{IN} = 96.3 \mu W/cm^2$ $R = 14.9 \times 10^{-3} A/W$ $S_A$ (apparent sensitivity) = 2.5 $S_N$ (net sensitivity) = 1.5 $\lambda = 754 \text{ nm}, P_{IN} = 101 \mu W/cm_2$ $R = 8.42 \times 10^{-3} A/W$ $S_A$ (apparent sensitivity) = 1.88 $S_N$ (net sensitivity) = 0.88	2020	

## < References for Table S1 >

SR-1. H. Yu, Z. Bao, J. H. Oh, Adv. Funct. Mater., 2013, 23, 629.

- SR-2. S. Nam, H. Kim, D. D. C. Bradley, Y. Kim, Org. Electron., 2016, 39, 199.
- SR-3. F. Li, Y. Chen, C. Ma, U. Buttner, K. Leo, T. Wu, Adv. Electron. Mater., 2017, 3, 1600430.
- SR-4. S. Nam, J. Seo, H. Han, H. Kim, D. D. C. Bradley and Y. Kim, ACS Appl. Mater. Interfaces, 2017, 9, 14983.
- **SR-5.** M. Liu, H. Wang, Q. Tang, X. Zhao, Y. Tong and Y. Liu, *Sci. Rep.*, 2018, 8, 16612.
- SR-6. K. Yeliu, J. Zhong, X. Wang, Y. Yan, Q. Chen, Y. Ye, H. Chen, T. Guo, Org. Electron., 2019, 67, 200.



## PIDTT-NDI

**Figure S1.** Illustration for the electron injection from the source electrode (Ag) to the LUMO energy level ( $E_{LUMO}$ ) of the PIDTT-NDI polymer due to the small energy barrier (0.39 eV). Note that the hole injection is relatively unexpected because of the large energy barrier (1.09 eV) between the source electrode and the HOMO energy level ( $E_{HOMO}$ ) of the PIDTT-NDI polymer.



**Figure S2.**  $I_D^{0.5} \sim V_G$  plots (from the transfer curves) for the OFETs with the PIDTT-NDI channel layers according to the PIDTT-NDI thickness. The V<sub>TH</sub> position is marked with arrows, while the electron mobility of devices was calculated from the linear slopes above V<sub>TH</sub>.



**Figure S3.** V<sub>TH</sub> as a function of the PIDTT-NDI thickness for the OPTRs with the PIDTT-NDI sensing channel layers.



**Figure S4.** Comparison between gate current (I<sub>G</sub>, dashed lines) and drain current (I<sub>D</sub>, solid lines) in the output (top) and transfer (bottom) curves for the OPTRs with the PIDTT-NDI sensing channel layers upon illumination with blue light (434 nm,  $P_{IN}$  = 96.3  $\mu$ W/cm2, blue lines) and NIR light (754 nm,  $P_{IN}$  = 101  $\mu$ W/cm2, red lines). The black lines denote the gate and drain current in the dark.



**Figure S5.** Height-mode (left) and phase-mode (right) AFM images (2  $\mu$ m x 2  $\mu$ m) for the ITO/PMMA layer (450 nm, a) and the ITO/PMMA/PIDTT-NDI layers (b-f) according to the PIDTT-NDI thickness (t): (a) PMMA, (b) t = 50 nm, (c) t = 60 nm, (d) t = 70 nm, (e) t = 80 nm, (f) t = 100 nm.



**Figure S6.** <sup>1</sup>H-NMR (500 MHz) spectra for the PIDTT-NDI polymer (solvent:  $CDCl_3$ ). The chemical shift on the marked atoms (1~5 and a~c) in the molecular structure (top) is given in the experimental section.



**Figure S7.** <sup>13</sup>C-NMR (500 MHz) spectra for the PIDTT-NDI polymer (solvent:  $CDCl_3$ ). The chemical shift on the marked atoms (1~11 and a~d) in the molecular structure (top) is given in the experimental section.