## [Supporting Information to accompany] Highly Sensitive Phototransistor with Crystalline Microribbons from New π-Extended Pyrene Derivative via Solution-Phase Self-assembly

by

Youn Sun Kim,<sup>a</sup> Suk Young Bae,<sup>a</sup> Kyung Hwan Kim,<sup>a</sup> Tae Wan Lee,<sup>a</sup> Jung A Hur,<sup>a</sup> Mai Ha Hoang,<sup>a</sup> Min Ju Cho,<sup>a</sup> Sung-Jin Kim,<sup>b</sup> Youngmee Kim,<sup>b</sup> Minsik Kim,<sup>a</sup> Kwangyeol Lee,<sup>a</sup> Suk Joong Lee,<sup>\*a</sup> Dong Hoon Choi<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-gu, Seoul, 136-701 Korea <sup>b</sup>Department of Chemistry and NanoScience, Ewha Womans University, Seoul 120-750, Korea (E-mail: <u>dhchoi8803@korea.ac.kr</u> and slee1@korea.ac.kr)

## **Experimental Section**

## 1. Materials and Instruments

All chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations carried out under  $N_2$  with the use of standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvent used in inert-atmosphere reactions were dried and degassed using standard procedures. Flash column chromatography was carried out with 230-400 mesh silica gel from Aldrich using wet-packing method. All deuterated solvent were purchased from Cambridge Isotope Laboratories, Inc.

<sup>1</sup>H NMR spectra were recorded on a Varian AS400 (399.937 MHz for <sup>1</sup>H and 100.573 MHz for <sup>13</sup>C) spectrometer. <sup>1</sup>H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and <sup>13</sup>C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Elemental analyses were performed by the Center for Organic Reactions using an EA1112 (Thermo Electron Corp.) elemental analyzer. Absorption and emission spectra were obtained using an HP 8453 spectrophotometer (photodiode array type) and Hitachi F-7000 fluorescence spectrophotometer. All scanning electron microscopy (SEM) images were obtained using a Jeol JSM-7500F (Basic Science Research Institute, Sungshin Women's University). All transmission electron microscopy (TEM) images, electron diffraction and contrast images of the crystals were obtained at 200 keV with LaB6 filament, using a Tecnai G2 F20 S-Twin and recorded with a 2K x 2K pixel resolution Veleta TEM camera (Olympus) on Cu TEM grids. Powder X-ray diffraction measurements were recorded with a Rigaku D/MAX Ultima III using nickel-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418$ Å) over a range of  $2^{\circ} < \theta < 40^{\circ}$  and X'celerator detector operating at 40 kV and 30 mA. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821<sup>e</sup> instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 (temperature rate 10°C/min under N<sub>2</sub>). The Xray diffraction data for two compounds were collected on a Bruker SMART APEX diffractometer equipped with a monochromater in the Mo Ka ( $\lambda = 0.71073$  Å) incident beam. Each crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12. All hydrogen atoms except disordered hexyl groups were placed in the calculated positions.

(1)

(2) PY-4(THB)

Scheme 1S. Synthesis of 1,3,6,8-tetrakis((4-hexylphenyl)ethynyl)pyrene (2).

## 2. Synthesis

Synthesis of 1,3,6,8-tetrabromopyrene (1): 1,3,6,8-tetrabromopyrene was synthesized in 95% yield by a reaction of pyrene with bromine in nitrobenzene according to a literature procedure.<sup>1</sup>

**1,3,6,8-Tetrakis**((**4-hexylphenyl)ethynyl)pyrene** (**2, PY-4(THB**)) - An oven dried, mag.-stirred, 100 mL round bottom flask (RBF) was charged with a solution of (1) (1.50 g, 2.9 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.101 g, 0.14 mmol), and copper iodide (0.027 g, 0.14 mmol) in a mixture of freshly distilled THF (30 mL), triethylamine (20 mL) and diisopropylamine (5 mL). 1-Ethynyl-4-hexylbenzene (2.15g, 11.6 mmol) was then added and the mixture heated at 80 °C for 16 h. After completing the reaction, the solution was poured into methanol to collect the precipitates. Purification was performed by silica-gel column chromatography (eluent: hexane/chloroform (3:1, v/v)). The crude product was purified by recrystallization from mixture of acetone/toluene to give the desired product (**2**) as yellowish orange crystals. Yield 1.63g, 60 %.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.56 (s, 4H), 8.30 (s, 2H), 7.63 (d, J = 8.2 Hz, 8H), 7.23 (d, J = 8.2 Hz, 8H), 2.66 (t, 8H), 1.70-1.62 (m, 8H), 1.40-1.31(m, 24H), 0.91 (t, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 143.75, 133.37, 131.71, 131.41, 128.58, 126.52, 123.74, 120.46, 118.84, 96.19, 87.31, 36.03, 31.75, 31.30, 29.02, 22.65, 14.14. Elemental analysis; Anal. Calcd. for C<sub>72</sub>H<sub>74</sub> : C, 92.06 ; H, 7.94 found : C, 92.19 ; H, 7.99.

## **3.** Sample preparation

Film preparation for Absorption and PL spectroscopy: In order to study absorption behavior, the thin film was fabricated on quartz substrates as follows. The solution (1 wt%) of molecules in chloroform was filtered through an acrodisc syringe filter (Millipore 0.2  $\mu$ m) and subsequently spin-cast on the quartz glass. A film was dried overnight at 80 °C for 12 h under vacuum.

**Crystal Growth and Microribbon Preparation.** Single crystals were grown in air by careful layering a 1-mM chloroform solution of **PY-4(THB)** over MeOH inside a glass tube (5-8 mm in diameter). The tube was then capped and allowed to reach equilibrium under darkness. Single crystals appear at the interface of the two solvents over a period of 2-7 days.

## 4. Device Fabrication.

To characterize the FET performance, a bottom-gate top-contact device geometry was employed. Spin-coated films (thickness:  $\sim 40 - 50$  nm) were prepared on the heavily n-doped SiO<sub>2</sub>/Si substrate with chloroform as a solvent. Surface modification was carried out with OTS to produce a hydrophobic dielectric surface. Slow diffusion method was employed with methanol or acetone to grow high quality microribbons on the surface of OTS-treated

SiO<sub>2</sub> insulator. The source and drain electrodes were then thermally evaporated (120 nm). All field effect mobilities were extracted in the saturation regime. The device performance was evaluated in air using 4200-SCS semiconductor characterization system in ambient conditions. For the light source, a Xenon lamp (Thermo Oriel) equipped with an optical fiber and high-speed monochromator (Oriel Cornerstone<sup>TM</sup> 130 1/8 m Monochromator) was employed. The light illumination power was measured by a Newport 2385-C Si photodetector with a calibration module. To obtain the PL absolute quantum yield (PLQY) of **PY-4(THB)**, absolute PL quantum yield measurement system, C9920-02 DynaSpect Series, (Hamamatsu Photonics, Japan) was employed.

## **5. Thermal Properties**



**Fig. 1S**. a: TGA thermograms of **PY-4(THB**), b: DSC traces during the heating (solid line) and cooling (dotted line) cycles.

Thermal decomposition temperature was monitored in TGA thermogram, which was found to be around 380 °C. DSC measurement was performed at a heating (cooling) scan rate of 10 (-10) °C/min under nitrogen, with the highest temperature limited to a value below the decomposition temperature. The **PY-4(THB)** molecule exhibited distinct crystallineisotropic transition temperature and cold crystallization temperature of 162°C and 142 °C. Due to the rigidity and planarity of pyrene core unit and high density of tightly packed molecules, a relatively high melting and a crystallization temperature were measured.



## 6. Results of DFT calculation

Fig. 2S. HOMO/LUMO levels of PY-4(THB) used to calculate the theoretical molecular

orbitals.

To estimate the position and molecular energies of frontier orbitals for **PY-4(THB)**, Density Functional Theory (DFT) calculations were performed using the Spartan '06 program at the B3LYP/6-31G\* level. The hexyl peripheral groups were sustained in calculation to observe the effect of substituents on the optimized geometries and theoretical energy levels. As shown in Figure 2S, the largest coefficients in the HOMO orbitals are located on the 2-D axis  $\pi$ -system centered at a pyrene unit. The coefficients in the LUMO orbital are mainly located on the pyrene unit along 1,3,6,8-substituted positions.

## 7. Single-crystal X-ray Crystallography.

X-ray data for **PY-4(THB)** were collected on a Bruker SMART APEXII diffractometer equipped with graphite monochromated MoKa radiation ( $\lambda = 0.71073$  Å). Preliminary orientation matrix and cell parameters were determined from three sets of  $\omega/\phi$ scans at different starting angles. Data frames were obtained at scan intervals of  $0.5^{\circ}$  with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS (Sheldrick, G. M. SADABS, A program for area detector absorption corrections, University of Gottingen, Germany, 1994). The structures were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL (Sheldrick, G. M. SHELXTL, version 5, Bruker AXS: Madison, Wisconsin, 1995.) program. All hydrogen atoms were calculated at idealized positions and refined with the riding models.

The space group is P-1. Although PLATON analysis suggested the presence of a higher symmetry with a possible space group P21/c, we were unable to obtain a suitable structural solution with this space group based on the collected data. *Crystal data for PY-*4(THB): C<sub>72</sub>H<sub>53</sub>, MW = 918.14, Triclinic (*P*-1), a = 8.9660(18) Å, b = 15.540(3) Å, c = 40.712(8) Å,  $\alpha = 90.01(3)^{\circ}$ ,  $\beta = 90.28(3)^{\circ}$ ,  $\gamma = 90.04(3)^{\circ}$ , V = 5672(2)Å3, Z = 4, (Mo -K $\alpha$ ) = 0.061 mm<sup>-1</sup>, 31412 reflections measured, 21548 unique (R<sub>int</sub> = 0.2075) which were used in all calculations, final R = 0.1151 (Rw = 0.2078) with reflections having intensities greater than  $2\sigma$ , GOF (F<sup>2</sup>) = 0.841. CCDC reference number CCDC 809193 for **PY-4(THB)**.

	PY-4(THB)
Empirical formula	C <sub>72</sub> H <sub>53</sub>
Formula weight	918.14
Temperature (K)	170(2)
Wavelength (Å)	0.71073
Space group	P-1
a(Å)	8.9660(18)
b(Å)	15.540(3)
c(Å)	40.712(8)
α(°)	90.01(3)
β(°)	90.28(3)
γ(°)	90.04(3)
Volume(Å <sup>3</sup> )	5672(2)
Z	4
Density (calc.) (Mg/m <sup>3</sup> )	1.075
Absorption coeff. (mm <sup>-1</sup> )	0.061
Crystal size (mm <sup>3</sup> )	0.20 x 0.20 x 0.02
Reflections collected	31412
Independent reflections [R(int)]	21548 [R(int) = 0.2075]
Data/restraints/parameters	21548 / 74 / 1290
Goodness-of-fit on F <sup>2</sup>	0.841
Final R indices [I>2 $\sigma$ (I)]	$R_1 = 0.1151, wR_2 = 0.2078$
R indices (all data)	$R_1 = 0.4805, wR_2 = 0.3586$
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.240 and -0.261

 Table S1. Crystal data and structure refinement for PY-4(THB).



Fig. 3S. Single crystal structure of PY-4(THB) showing four independent molecular orientations in a unit cell.



Fig. 4S. Structure of the first one in four molecules and its J-type layered packing.



Fig. 5S. Structure of the second one in four molecules and its J-type layered packing.



Fig. 6S. Structure of the third one in four molecules and its J-type layered packing.



Fig. 7S. Structure of the fourth one in four molecules and its J-type layered packing.



**Fig. 8S.** Packing diagram of four independent **PY-4(THB)**s (left) showing channels in the middle of four **PY-4(THB)**s (right).

## 8. FET device characterization



**Fig. 9S.** Transfer curve of microribbon based-FET device and the gate leakage current through an insulator.

The gate leakage currents ( $I_{GS}$ ) of microribbon based-FET device through OTS-SiO<sub>2</sub> dielectric layer are measured with a Keithley 4200-SCS semiconductor characterization system. The gate leakage current ( $I_{GS}$ ) was in the range of 10<sup>-1</sup> nA – 1.0 nA under operation voltages. This value is reasonably low enough to operate the transistor device properly. The value of leakage current is not so significantly high to affect the large variation of the carrier mobility in the devices. It was supported by some references we cited. <sup>2-5</sup>



**Fig. 10S.** (a) Pictorial representation of microrribon-based FET device and (b) Transfer curves of PY-4(THB) TFT device and gate leakage current.

In Fig. 11S, we observed the hysteresis behavior of  $I_{DS}$  in one of the microribbon-based FET under a forward and a reverse bias. According to the data we obtained, no significant hysteresis behavior was observed at ambient conditions.



Fig. 11S. Hysterisis behavior of I<sub>DS</sub> in microribbon based-FET device at ambient conditions.



9. UV-Vis absorption and Photoluminescence (PL) Spectra of PY-4(THB)

**Fig. 12S**. UV-Vis absorption spectra and PL spectra of **PY-4(THB)**. Solution (black), film (blue), and microribbons (red) of absorption (solid) and PL (dashed) spectra.

In order to study the interaction between the molecules, the absorption spectra of the samples in chloroform (conc.  $1 \times 10^{-6}$  mol/L), thin film, and crystalline microribbon were obtained. (see **Fig. 12S**) We found very interesting chromic behavior comparing the spectra of three samples. We observed a bathochromic shift ( $\Delta\lambda$  (film) = 35 nm; ( $\Delta\lambda$  (microribbon) = 38 nm,) and formation of greatly resolved vibronic peaks in the absorption spectra upon film and crystal formation, which indicated the existence of strong intermolecular interactions.

Corresponding PL spectra were illustrated in Figure 12S. As was expected, the emission spectra of solid film and single-crystalline microribbon were shifted to a longer

wavelength significantly. The Stoke shifts in the spectra of thin film and microribbon are 12 and 13 nm, respectively, which are smaller than that in solution (~20 nm). The significant red-shift of  $\lambda_{max}^{abs}$  and smaller Stokes shifts support the formation of J-aggregation in solid states.



#### **10.** Organic Phototransistor (OPT) devices made of microribbons of PY-4(THB)

Fig. 13S. I<sub>DS</sub> characteristics of microribbon based-FET device at ambient conditions

In Fig 13S, three  $I_{DS}$  curves were illustrated as a function of gate voltage. The curves of two dark current were compared before and after light irradiation. The figure told that after turning off the light (light intensity I=2.0  $\mu$ W/cm<sup>2</sup>), the transfer curves showed that the threshold voltage was shifted by 10V. ( $\Delta V_{th} \sim 10$  V).

We also did the experiments for investigating the rising and decaying behaviors of  $I_{DS}$  in the microribbon-devices during OPT operation. As can be seen in the following Fig. 14S, the rising curves and decaying curves were fitted to the double exponential functions obtaining two rate constants ( $k_1$  and  $k_2$ ).

$$-I_{DS}(t) = (-I_o) + a (1 - exp(-k_1 t)) + b (1 - exp(-k_2 t)) : \text{Rising curve}, k_1 \text{ fast rate constant}$$
$$-I_{DS}(t) = (-I_o) + a \exp(-k_1 t) + b \exp(-k_2 t) : \text{Decaying curve}, k_1 \text{ fast rate constant}$$

In each condition, we can get fast and slow components of the rate. For instance, the fast rising rate is 1.42 s<sup>-1</sup> ( $\tau$ = 1/k<sub>1</sub>= 0.70 sec) and the fast decaying rate is 0.819 s<sup>-1</sup> ( $\tau$ = 1/k<sub>1</sub>=1.22 sec). (V<sub>G</sub> = 0 V, V<sub>DS</sub>= -50 V)



Fig. 14S. Rising and relaxation curves of photoinduced current (I<sub>DS</sub>) under light conditions.

 $(I=2.0 \ \mu W/cm^2).$ 

It is noted that, compared with commercial photosensors, the measured  $I_{on/off}$  switching time of the OPTs was still large. It is necessary to perform further studies in order to reduce the large  $I_{on/off}$  switching time.



Fig. 15S.  $I_{on/off}$  switching behaviors of microribbon-based FET with applying both light (I=1.5  $\mu$ W/cm<sup>2</sup>) and a gate bias.

Fig.15S shows the  $I_{on/off}$  switching performance when applying both light (I=1.5  $\mu$ W/cm<sup>2</sup>) and a gate bias. In order to observe  $I_{on/off}$  switching behavior, the gate biases of  $V_G$ = -20 V and +20V were applied for achieving the current on and off states, respectively, under a constant drain voltage ( $V_{DS}$ =-60 V). Under repeated light illumination, the on-current ( $I_{on}$ ) showed slight increasing behavior with the number of cycle; however it approached to certain level asymptotically. It might be due to the slow relaxation of discharge of photocharges.

## 11. Organic phototransistors made of thin films of PY-4(THB)

Compared to the microribbon-based OPTs, the device with thin film ( $\lambda_{ex} = 506$  nm, I = 12  $\mu$ W/cm<sup>2</sup>, V<sub>DS</sub>= -80 V, L= 80  $\mu$ m) exhibited lower photosensitivity of around ~ 420 -430 WA<sup>-1</sup> and switching ratio of ~ 1.4 × 10<sup>6</sup>, (I<sub>dark</sub>= 4.35 × 10<sup>-12</sup> A, I<sub>light</sub>=6.02 × 10<sup>-6</sup> A, V<sub>G</sub> = -3V) under I = 12  $\mu$ W cm<sup>-2</sup> which might be attributed to lowering the quantum yield arising from self-quenching behavior of photoluminescence. In addition, resulting from time resolved fluorescence experiments, the fluorescence life-time of the film was determined to be 0.12-0.16 ns ( $\lambda$ = 518, 548, 594 nm ) which is much smaller than those of microribbon ( $\tau$ = 0.44 - 0.57 ns at 522, 550, 594 nm).



Fig. 16S. (a) Transfer curves of OPTs in the dark (black) and under monochromatic light irradiation (red) with 12  $\mu$ W cm<sup>-2</sup>; (b) Photoresponsivity (R) and photoswitching ratio (P) vs V<sub>G</sub> for the TFT.

# 12. Time correlated single-photon counting (TCSPC) measurement: Life-time measurement

Fluorescence lifetime measurements were performed by exciting solution, thin film, and microribbon samples with 50 ps pulses at 375 nm obtained by picosecond pulsed diode laser system. (FluoroTime 200, PicoQuant GmbH, Germany) Fluorescence lifetimes for a series of films and microribbins were measured (Figure 17S). Film lifetimes were found to be 0.12 - 0.16 ns ( $\lambda$ = 518, 548, 594 nm). In the single-crystalline state, it was measured to be  $\tau = 0.44 - 0.57$  ns at 522, 550, and 594 nm.

Compared to the life-time of the solution ( $\tau = 4.24$  ns at 490 nm; 3.58 ns at 521 nm), the solid samples showed much faster decaying behavior of fluorescence.



**Fig. 17S**. Fluorescence decay profiles of PY-4(THB) monitored at each emission band. A: Solution (c=1 x  $10^{-6}$  mol/L), B: Film and microribbons (MR).

## References

- 1. G. Venkataramana and S. Sankararaman, Eur. J. Org. Chem. 2005, 19, 4162.
  - M. Halik, H. Klauk, U. Zschleschang, G. Schmid, C. Dehm, M. Schütz, S. Malsch, F. Effenberger, M. Brunnbauer and F. Stellacci, *Nature*. 2004, 431, 963
  - H. S. Lee, K. M. Park, J. D. Kim, T. H. Han, K. H. Ryu, H. S. Lim, D. R. Lee, Y. J. Kwark, and J. H. Cho, J. Mater. Chem. 2011, 21, 6968
  - H. Klauk, M. Halik, U. Zschieschang, G. Schmid, and W. Radlik, J. Appl. Phys. 2002, 92, 5259
  - S. Y. Lee, B. W. Koo, J. H. Shin, E. K. Lee, and H. J. Park, *Appl. Phys. Lett.* 2006, 88, 162109