Supporting Information for:

Revisiting Zethrene: Synthesis, Reactivity and Semiconductor Property

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1. Synthesis and Reactions

General: The reagents and starting materials employed were commercially available and used without any further purification if not specified elsewhere. Anhydrous and oxygen-free THF was purified by an Advanced Technology Pure-Solv PS-MD-4 system. ¹H-NMR (400 MHz) or ¹³C-NMR (100 MHz) spectra were recorded on a Brucker ADVANCE III spectrometer. Mass spectra were recorded on a Therno Finnigan MAT 95 XL spectrometer. X-ray crystallography data were collected on a Bruker AXS Kappa ApexII Duo Diffractometer. Melting points were measured using a Nikon Polarizing Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage or using differential scanning calorimetry (PERKIN ELMER DSC 6) as indicated.

1,8-Dibromonaphthlene (2): prepared from 1,8-diaminonaphthalene following a reported procedure. ¹



1,8-Bis(triphenylposphoniomethyl)naphthalene dibromide (3): prepared from 1,8-naphthalenedicarboxylic anhydride in three steps following reported procedures.²



8-bromo-1-naphthaldehyde (**4**): 4.7 mL (7.5 mmol) of n-butyl lithium solution (1.6 M in hexane) was added into a solution of 1.43 g (5 mmol) of 1,8-dibromonaphthlene in 15 mL of anhydrous and oxygen free THF at -78 °C under an atmosphere of N₂. The resulting reaction mixture was stirred at -78 °C for 20 minutes, treated with 0.7 mL of anhydrous DMF, and then kept stirred at -78 °C for another 15 minutes. The cooling bath was then removed, and the reaction mixture was slowly warmed to room temperature with stirring for 15 minutes and finally quenched with water. After concentration under a reduced pressure, the residue was extracted with dichloromethane for several times. The organic extracts were washed with water and brine, dried with anhydrous Na₂SO₄ and concentrated under a reduced pressure. Purification by column chromatography on silica gel with CH₂Cl₂/n-hexane 2/3 (v/v) as eluent yielded 1.02g (87%) of 8-bromo-1-naphthaldehyde as white powder. m.p. 84.0 °C (measured with DSC under a stream of N₂). ¹H-NMR (400 MHz CDCl₃) δ (ppm): 11.44 (s, 1H), 8.02 (d, 8.0Hz, 1H), 7.92 (m, 3H), 7.57 (t, 7.6Hz, 1H), 7.40 (t, 7.6Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) : 192.9, 136.4, 136.0, 133.9, 133.5, 130.8, 130.0, 129.1, 127.2, 126.2, 118.6. HRMS (ESI⁺): calcd. for C₁₁H₇⁷⁹BrO ([M+H]⁺): 234.9759, found: 234.9757

Vyskočil, Š.; Meca, L.; Tišlerová, I.; Císařová, I.; Polášek, M.; Harutyunyan, S. R.; Belokon, Y. N.; Stead, R. M. J.; Farrugia, L.; Lockhart, S. C.; Mitchell, W. L.; Kočovský, P. *Chem. Eur. J.* 2002, 8, 4633

^{2.} Yeo, H. M.; Ryu, B. J.; Nam, K. C. Org. Lett. 2008, 10, 2931.



(E)-1-bromo-8-(2-(8-vinylnaphthalen-1-yl)vinyl)naphthalene (5): 560mg (5 mmol) of t-butoxide added suspension of potassium was to a 1.68 of g 1,8-bis(triphenylposphoniomethyl)naphthalene dibromide (2mmol) in 12ml THF under an atmosphere of N₂. The resulting reaction mixture was stirred at room temperature for 1 hour. A solution of 470 mg (2 mmol) of 8-bromo-1-naphthaldehyde in 7 ml of THF was added dropwise via an addition funnel into this mixture during 1.5 hours. After stirring at room temperature for another 0.5 hours, to this reaction mixture was added 300 mg (10 mmol) of paraformaldehyde. The resulting mixture was stirred for 2 hours at room temperature, quenched with water, and extracted with CH₂Cl₂ for several times. The organic extracts were combined, dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. Purification of the crude product with column chromatography on silica gel with CH₂Cl₂/n-hexane 1/20 (v/v) as eluent vielded 474 mg (1.22 mmol, 61%) of (E)-1-bromo-8-(2-(8-vinylnaphthalen-1-yl)vinyl)naphthalene as a yellow solid. m.p.: decomposed at 250 °C (for yellow crystals grown from ethyl acetate as measured with DSC under a stream of N₂). ¹H-NMR (400MHz CDCl₃) δ (ppm) : 8.05 (d, 15.6Hz, 1H), 7.89~7.70 (m, 8H), 7.56~7.43 (m, 5H), 7.30 (t, 8Hz 1H), 5.60 (dd, J₁=17.2Hz, J₂=17.6Hz, 1H), 5.31 (dd, J₁=11.2Hz, J₂=10.8Hz, 1H). ¹³C-NMR (100MHz CDCl₃) δ (ppm) : 141.3, 138.0, 137.7, 137.6, 136.3, 134.8, 133.3, 131.8, 131.2, 131.2, 130.4, 130.3, 129.2, 129.0, 128.9, 128.6, 127.3, 127.1, 126.4, 126.2, 125.9, 125.8, 120.2, 114.3. HRMS (EI^+): calcd. $\text{C}_{24}\text{H}_{17}^{-81}\text{Br}$ for ([M]⁺): 386.0493, found: 386.0489.



Zethrene: 232 mg of (E)-1-bromo-8-(2-(8-vinylnaphthalen-1-yl)vinyl)naphthalene, 162 mg (0.72mmol) of palladium acetate and 636 mg (3 mmol) of K₃PO₄ were mixed and dissolved in 6 ml of anhydrous DMF under an atmospheres of N₂. The resulting reaction mixture was stirred at 25~30°C under the atmospheres of N₂ in dark for 16 hours, then poured into water and extracted with diethyl ether for several times. The ether exacts were combined, dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification of the crude product with column chromatography on silica gel with CH₂Cl₂/n-hexane 1/20 (v/v) as eluent yielded 120 mg of zethrene in a yield of 67% as black powders. m.p.: 253~254 °C with partial decomposition (for black crystals grown from CHCl₃ as measured in air); 271.2 °C (measured with DSC under an stream of N₂). ¹H-NMR (400 MHz CDCl₃) δ (ppm) : 8.18 (d, 7.6Hz, 1H), 7.69 (d, 8Hz, 1H), 7.66 (s, 1H), 7.53(m, 2H), 7.35 (t, 8Hz, 1H), 7.30 (d, 6.8Hz, 1H). ¹³C-NMR (CDCl₃) δ (ppm): 134.1, 133.1, 132.5, 132.1, 128.3, 127.7, 127.2, 127.1, 127.0, 125.0, 122.0, 120.7. HRMS (EI⁺): calcd. for C₂₄H₁₄ ([M⁺]): 302.1096, found: 302.1052.

Heck Reactions between 1,8-divinylnaphthalene³ and 1,8-diiodonaphthalene⁴

For the Heck reaction between 1,8-divinylnaphthalene and 1,8-diiodonaphthalene with a catalytic amount of $Pd(OAc)_2$, the following reaction conditions were tested:

(1) 0.05 eq. $Pd(OAc)_2$, 2 eq. $Bu_4N^+Br^-$, 8 eq. K_2CO_3 , in DMF; (2) 0.05 eq. $Pd(OAc)_2$, 0.1 eq. PPh_3 , 2 eq. $Bu_4N^+Br^-$, 8 eq. K_2CO_3 , in DMF; (3) 0.025 eq. $Pd(OAc)_2$, 0.05 eq. PPh_3 , 1.2 eq. Et_3N , in toluene.

These reactions yielded 1-(8-vinylnaphthalen-1-yl)acenaphthylene (6) as well as 1-iodonaphthalene. A representative procedure for the first condition is shown below.

45 mg (0.25 mmol) of 1,8-divinylnaphthalene, 95 mg (0.25mmol) of 1,8-diiodenaphthalene, 3 mg (0.0125 mmol) palladium acetate, 161 mg of (0.5 mmol) tetrabutylammonium bromide and 276 mg (2 mmol) of K_2CO_3 were mixed and dissolved in 3 ml of anhydrous DMF, which was degassed by bubbling N₂ through for 30 minutes. The reaction mixture was heated at 100 °C with stirring under an atmosphere of N₂ for 18 hours, cooled to room temperature, and then poured into 50 ml of water. The resulting suspension was filtered, and the brown solids were collected. Purification of the crude product with column chromatography on silica gel with n-hexane as eluent yielded 7 mg (9%) of 1-(8-vinylnaphthalen-1-yl)acenaphthylene as a red solid.



1-(8-vinylnaphthalen-1-yl)acenaphthylene (6): m.p. $104 \sim 105^{\circ}$ C. ¹H-NMR (400 MHz CDCl₃) δ (ppm): 8.23 (d, 7.6Hz, 1H), 7.86 (d, 7.2Hz, 1H), 7.80 (d, 19.6Hz, 1H), 7.78~7.40 (m, 4H), 7.25 (m, 1H), 7.01 (m, 2H), 6.70 (d, 6.8Hz, 1H), 6.65 (d, 7.2Hz, 1H), 6.19 (s, 1H), 6.06 (d, 12.4Hz, 1H), 5.53 (d, 12.4Hz, 1H). ¹³C-NMR (100Mz, CDCl₃) δ (ppm): 142.2, 140.4, 139.3, 139.2, 139.1, 138.7, 138.5, 138.2, 134.3, 131.5, 131.3, 129.3, 128.9, 128.8, 128.7, 128.5, 128.3, 127.1, 127.0, 126.5, 126.4, 126.3, 126.1, 125.2. HRMS (ESI⁺): calcd. for C₂₄H₁₆ ([M]⁺): 304.1252, found: 304.1254.

Reaction of 1,8-divinylnaphthalene and 1,8-diiodonaphthalene with 1.4 eq. of Pd(OAc)₂

90 mg (0.5 mmol) of 1,8-divinylnaphthalene, 190 mg (0.5 mmol) 1,8-diiodonaphthalene, 150 mg (0.7 mmol) palladium acetate and 850 mg (4 mmol) K_3PO_4 were mixed and dissolved in 6 ml of anhydrous DMF under an atmosphere of N_2 . The reaction mixture was heated at 100 °C with stirring under the atmosphere of N_2 for 18 hours, cooled to room temperature, and then poured into 150 ml of water. The resulting suspension was filtered, and the red solids were collected. Purification of the crude product with chromatography on silica gel with n-hexane/dichloromethane 20/1 (v/v) as eluent yielded 15 mg of zethrene in a yield of 10%.

^{3.} Prepared from 1,8-Bis(triphenylposphoniomethyl)naphthalene dibromide following reported procedures. See: Mitchell, R. H.; Ghose, B. N.; Williams, M. E. *Can. J. Chem.* **1977**, *55*, 210.

^{4.} Weimar, M.; Dürner, G. ; Bats J. W.; Göbel, M. W. J. Org. Chem., 2010, 75, 2718.

N-alkyl-naphtho[8,1,2-bcd]perylene-13,14-dicarboxylic imides (8a/b)

30 mg (0.1 mmol) of zethrene and 0.3 mmol of N-alkylmaleimide were dissolved in 5 mL of anhydrous toluene under an atmosphere of N₂. The resulting solution was refluxed for 24 hours. A small portion (~0.2 ml) of this solution was concentrated under reduced pressure and then monitored with ¹H NMR spectroscopy. To the solution of reaction mixture was added 70 mg (3 mmol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. After refluxing for another 24 hours, the red mixture was cooled to room temperature, filtered, and washed with CH₂Cl₂. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel with dichloromethane/n-hexane 2/3 (v/v) as eluent. N-alkyl-13,14 -naphtho[8,1,2-bcd]perylene dicarboxylic imide was collected as a red solid.



N-hexyl-naphtho[8,1,2-bcd]perylene-13,14-dicarboxylic imide (8a) : yield: 69%. m.p.: 219~220°C. ¹H-NMR (400 MHz CD₂Cl₂, 2mg/ml) δ (ppm) :9.18(d, 9.2Hz, 1H), 8.92(d, 7.2Hz, 1H), 8.66(s, 1H), 8.35(d, 7.2Hz, 1H), 8.19(d, 7.6Hz, 1H), 8.14(d, 8.8Hz, 2H), 8.02(t, 7.6Hz, 1H), 7.87(t, 7.6Hz, 2H), 7.62(m, 2H), 3.80(t,7.2Hz, 2H), 1.79(m,2H), 1.46~1.36(m, 6H), 0.92(t, 6.8Hz, 3H). ¹³C NMR was not recorded due to its low solubility. HRMS (EI⁺): calcd. for C₃₄H₂₅NO₂ ([M⁺]): 479.1885, found: 479.1891



N-dodecyl-naphtho[8,1,2-bcd]perylene-13,14-dicarboxylic imide (8b): yield: 58%, m.p. 136~137 °C. ¹H-NMR (400 MHz CDCl₃, 1mg/ml) δ (ppm) : 9.22 (d, 8.8Hz, 1H), 8.95 (d, 7.6Hz, 1H), 8.70 (s, 1H), 8.35 (d, 7.6Hz, 1H), 8.16 (d, 7.6Hz, 1H), 8.14 (m, 2H), 8.02 (t, 7.6Hz, 1H), 7.87 (t, 8.8Hz, 2H), 7.61 (m, 2H), 3.83 (t, 7.6Hz, 2H), 1.78 (m, 2H), 1.40 (m, 4H), 1.27 (m, 15H), 0.86 (t, 6.8Hz, 3H). ¹³C-NMR (100Mz, CDCl₃) δ (ppm): 168.4, 168.2, 133.1, 130.7, 130.4, 130.2, 130.1, 129.9, 129.7, 129.6, 128.8, 128.3, 128.2, 128.0, 127.2, 126.5, 126.3, 126.0, 125.9, 125.8, 125.6, 123.6, 123.3, 122.5, 122.4, 120.8, 38.3, 32.1, 29.8, 29.8, 29.5, 29.0, 27.3, 22.8, 14.3. HRMS (EI⁺): calcd. for C₄₀H₃₇NO₂ ([M]⁺): 563.2824, found: 563.2823

N,N'-Diakyl-benzo[pqr]naphtho[8,1,2-bcd]perylene-6,7,13,14-tetracarboxylic 6,7:13,14 -diimide

0.1 mmol of N-alkyl-naphtho[8,1,2-bcd]perylene-13,14-dicarboxylic imide (**8a** or **8b**) and 0.2 mmol of N-alkylmaleimide were dissolved in 5 mL of diphenyl ether under an atmosphere of N₂. The resulting solution was refluxed for 48 hours, cooled to room temperature and then poured into 200 mL methanol. The resulting suspension was filtered and washed with

methanol yielding N,N'-dialkyl-benzo[pqr]naphtho[8,1,2-bcd]perylene-6,7,13,14 -tetracarboxylic 6,7:13,14-diimide as red solids.



N,N'-Dihexyl-benzo[pqr]naphtho[8,1,2-bcd]perylene-6,7,13,14-tetracarboxylic

6,7:13,14-diimide (**9a**): yield: 95%, m.p.: 280~281°C, ¹H-NMR (400 MHz CDCl₃) δ (ppm) :9.54(d,7.6Hz, 2H), 9.31(d, 8.8Hz, 2H), 8.30(d, 8.0Hz, 2H), 8.27(d, 9.2Hz, 2H), 8.11(t, 7.6Hz, 2H), 3.90(t, 7.6Hz, 4H), 1.87(m 4H), 1.41(m, 12H), 0.93(t, 6.8Hz, 6H). ¹³C NMR was not recorded due to its low solubility. HRMS (FAB⁺): calcd. for C₄₄H₃₇N₂O₄ ([M+H]⁺): 657.2753, found: 657.2737.



N,N'-Didodecyl-benzo[pqr]naphtho[8,1,2-bcd]perylene-6,7,13,14-tetracarboxylic

6,7:13,14-diimide (**9b**): yield 84%, m.p. $320 \sim 321^{\circ}$ C. ¹H-NMR (400 MHz CDCl₃) δ (ppm) : 8.96 (d, 7.6Hz, 2H), 8.78 (d, 8.8Hz, 2H), 7.91 (d, 7.6Hz, 2H), 7.83 (d, 8.8Hz, 2H), 7.73 (t, 7.6Hz, 2H), 3.74 (t, 7.6Hz, 4H), 1.83 (m, 4H), 1.48 (m, 8H), 1.30 (m, 28H), 0.89 (t, 6.6Hz, 6H). ¹³C-NMR (100Mz, CDCl₃) δ (ppm): 168.2, 130.6, 130.1, 129.7, 128.6, 126.3, 126.2, 125.3, 124.9, 124.0, 123.9, 122.5, 122.0(3), 121.9(8), 38.5, 32.1, 29.8(9), 29.8(6), 29.6, 29.1, 27.4, 22.9, 14.3. HRMS (FAB⁺): calcd. for C₅₆H₆₁N₂O₄ ([M+H]⁺): 825.4631, found: 825.4639.

2. Absorption and Fluorescence Spectra

UV-Vis absorption and fluorescence spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer and a Hitachi F-4500 spectrofluorometer respectively.



Figure S-1 UV-vis absorption and fluorescence spectra of zethrene recorded from a solution in CHCl₃ (2×10^{-5} M).



Figure S-2 UV-vis absorption spectra of 9a as recorded from a 2×10^{-5} M solution in CH₂Cl₂.

3. Cyclic Voltammetry

The cyclic voltammetry was performed in a solution of anhydrous DMF (or CH_2Cl_2) with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte, at a scan rate of 50mV/s. A platinum bead was used as a working electrode, a platinum wire was used as an auxiliary electrode, and a silver wire was used as a psedo-reference. Ferrocene/ferrocenium was used as an internal standard, and potentials were recorded versus $FeCp_2^{-1}/FeCp_2^{0}$.



Figure S-3 Cyclic voltammogram of zethrene recorded from a solution in DMF



Figure S-4 Cyclic voltammogram of 9a recorded from a solution in CH₂Cl₂



Figure S-5 Cyclic voltammogram of 9b recorded from a solution in CH₂Cl₂

4. Fabrication and characterization of vacuum deposited thin films and transistors

(1) Deposition of thin films and fabrication of transistors

Thin films of zethrene and **9a** were deposited onto silicon wafers using an Edwards Auto 306 vacuum coater with a Turbomolecular pump with a deposition rate of ca. 1 Å/s to desired thickness. The silicon wafers had highly n-doped silicon as gate electrode and had a 300 nm-thick SiO₂ as dielectrics, which were modified with octadecyltrimethoxysilane (OTMS) before deposition by following the reported procedures.⁵ During vacuum deposition, the pressure of chamber was kept at 2.0×10^{-6} torr or lower, the distance between source and substrate was 18.5cm, and the substrates were kept at room temperature or 60 °C. Top contact drain and source gold electrodes were vacuum-deposited through a shadow mask onto the films in the same vacuum chamber, and the resulting semiconducting channels were $50\mu m(L) \times 1mm(W)$, $100\mu m(L) \times 1mm(W)$, $150\mu m(L) \times 1mm(W)$, $50\mu m(L) \times 2mm(W)$ and $100\mu m(L) \times 2mm(W)$.

(2) Characterization of Thin Film Transistors

X-ray diffraction (XRD): XRD patterns were recorded on a SmartLab X-Ray Refractometer from the thin films of zethrene, which were about 40 nm thick and vaccum-deposited on OTMS-treated SiO₂ surface at a substrate temperature of 60 °C.

^{5.} Ito, Y.; Virkar, A. A.; Mannsfeld, S.;Oh, J. H.; Toney, M.; Locklin, A.; Bao, Z. J. Am. *Chem. Soc.* **2009**, *131*, 9396–9404.



Figure S-6 X-ray diffraction from a 40 nm-thick film of zethrene.

Atomic Force Microscopy (AFM): The AFM images were collected with a Nanoscope IIIa Multimode Microscope (Digital Instruments) using tapping mode and in air under ambient conditions The topographic images were collected from multiple samples, and for each sample, different regions were scanned to ensure reproducibility.



Figure S-7 AFM image for a 40 nm-thick film of Zethrene, which was deposited on octadecyltrimethoxysilane-modified SiO₂ at a substrate temperature of 60 $^{\circ}$ C.

(3) Electrical Characterization of Thin Film Transistors

The current-voltage measurement was carried out on a probe station with a Keithley 4200 Semiconductor Characterization System at room temperature. Devices made from zethrene were tested in ambient air, while devices made from **9a** were tested under vacuum. The measured electron mobility of **9a** is up to 2×10^{-4} cm²V⁻¹s⁻¹ and 6×10^{-5} cm²/V·s in average.



Figure S-8 Transfer curves of the best performing thin film transistor made from **11** deposited on OTMS-treated SiO₂ at a substrate temperature of 60 °C with channel $100\mu m(L) \times 1mm(W)$, showing electron mobility of $2 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$ (tested in vacuum).





¹³C NMR spectrum of (E)-1-bromo-8-(2-(8-vinylnaphthalen-1-yl)vinyl)naphthalene (CDCl₃)





(CDCl₃)



¹H NMR spectrum of N,N'-didodecyl-benzo[pqr]naphtho[8,1,2-bcd]perylene -6,7,13,14-tetracarboxylic 6,7:13,14-diimide (CDCl₃)





