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. $^1$H-NMR (400 MHz) or $^{13}$C-NMR (100 MHz) spectra were recorded on a Brucker ADVANCE III spectrometer. Mass spectra were recorded on a Thermo 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-Dibromonaphthalene (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-dibromonaphthalene in 15 mL of anhydrous and oxygen free THF at -78°C under an atmosphere of N$_2$. 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 Na$_2$SO$_4$ and concentrated under a reduced pressure. Purification by column chromatography on silica gel with CH$_2$Cl$_2$/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 N$_2$). $^1$H-NMR (400 MHz CDCl$_3$ $\delta$ (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) $^{13}$C-NMR (100 MHz, CDCl$_3$ $\delta$ (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 C$_{11}$H$_7^{79}$BrO [(M+H)$^+$]: 234.9759, found: 234.9757

(E)-1-bromo-8-(2-(8-vinylnapthalen-1-yl)vinyl)naphthalene (5): 560mg (5 mmol) of potassium t-butoxide was added to a suspension of 1.68 g of 1,8-bis(triphenylposphiomethyl)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 hour. 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 yielded 474 mg (1.22 mmol, 61%) of (E)-1-bromo-8-(2-(8-vinylnapthalen-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, 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. C24H17Br for ([M]+): 386.0493, found: 386.0489.

Zethrene: 232 mg of (E)-1-bromo-8-(2-(8-vinylnapthalen-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-divinylnaphthalene and 1,8-diiodonaphthalene

For the Heck reaction between 1,8-divinylphthalene 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$_4$N$^+$Br$^-$, 8 eq. K$_2$CO$_3$, in DMF;
2. 0.05 eq. Pd(OAc)$_2$, 0.1 eq. PPh$_3$, 2 eq. Bu$_4$N$^+$Br$^-$, 8 eq. K$_2$CO$_3$, in DMF;
3. 0.025 eq. Pd(OAc)$_2$, 0.05 eq. PPh$_3$, 1.2 eq. Et$_3$N, in toluene.

These reactions yielded 1-(8-vinylphthalalen-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-divinylphthalene, 95 mg (0.25 mmol) of 1,8-diiodonaphthalene, 3 mg (0.0125 mmol) palladium acetate, 161 mg of (0.5 mmol) tetrabutylammonium bromide and 276 mg (2 mmol) of K$_2$CO$_3$ were mixed and dissolved in 3 ml of anhydrous DMF, which was degassed by bubbling N$_2$ through for 30 minutes. The reaction mixture was heated at 100 °C with stirring under an atmosphere of N$_2$ 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-vinylphthalalen-1-yl)acenaphthylene as a red solid.

1-(8-vinylphthalalen-1-yl)acenaphthylene (6): m.p. 104~105°C. $^1$H-NMR (400 MHz CDCl$_3$) 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). $^{13}$C-NMR (100Mz, CDCl$_3$) 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 C$_{23}$H$_{16}$ ([M$^+$]): 304.1252, found: 304.1254.

Reaction of 1,8-divinylphthalene and 1,8-diiodonaphthalene with 1.4 eq. of Pd(OAc)$_2$

90 mg (0.5 mmol) of 1,8-divinylphthalene, 190 mg (0.5 mmol) 1,8-diiodonaphthalene, 150 mg (0.7 mmol) palladium acetate and 850 mg (4 mmol) K$_3$PO$_4$ 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%.

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, 7.2H, 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 C₃₄H₂₉NO₂ ([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), 1.87 (s, 9H), 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, $^1$H-NMR (400 MHz CDCl$_3$) $\delta$ (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). $^{13}$C NMR was not recorded due to its low solubility. HRMS (FAB$^+$): calcd. for C$_{44}$H$_{37}$N$_2$O$_4$ ([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. 320~321°C. $^1$H-NMR (400 MHz CDCl$_3$) $\delta$ (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). $^{13}$C-NMR (100Mz, CDCl$_3$) $\delta$ (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 C$_{56}$H$_{61}$N$_2$O$_4$ ([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.

![UV-vis absorption and fluorescence spectra of zethrene recorded from a solution in CHCl₃ (2×10⁻⁵ M).](image)

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

![UV-vis absorption spectra of 9a as recorded from a 2×10⁻⁵ M solution in CH₂Cl₂.](image)

**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 CH₂Cl₂) with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) 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 pseudo-reference. Ferrocene/ferrocenium was used as an internal standard, and potentials were recorded versus FeCp₂⁺/FeCp₂₀.

![Figure S-3](image1.png)

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

![Figure S-4](image2.png)

**Figure S-4** Cyclic voltammogram of 9a 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 SiO$_2$ as dielectrics, which were modified with octadecyltrimethoxysilane (OTMS) before deposition by following the reported procedures. 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 50μm(L)×1mm(W), 100μm(L)×1mm(W), 150μm(L)×1mm(W), 50μm(L)×2mm(W) and 100μm(L)×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 vacuum-deposited on OTMS-treated SiO$_2$ surface at a substrate temperature of 60 °C.

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 SiO\(_2\) at a substrate temperature of 60 °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 $2 \times 10^{-4}$ cm$^2$/V·s and $6 \times 10^{-5}$ cm$^2$/V·s in average.

![Graph](image.png)

**Figure S-8** Transfer curves of the best performing thin film transistor made from 11 deposited on OTMS-treated SiO$_2$ at a substrate temperature of 60 °C with channel 100μm(L)×1mm(W), showing electron mobility of $2 \times 10^{-4}$ cm$^2$/V·s (tested in vacuum).
5. NMR Spectra

$^1$H NMR spectrum of 8-bromo-1-naphthaldehyde (CDCl$_3$)

$^{13}$C NMR spectrum of 8-bromo-1-naphthaldehyde (CDCl$_3$)
$^1$H NMR spectrum of (E)-1-bromo-8-(2-(8-vinylnaphthalen-1-yl)vinyl)naphthalene (CDCl$_3$)

$^{13}$C NMR spectrum of (E)-1-bromo-8-(2-(8-vinylnaphthalen-1-yl)vinyl)naphthalene (CDCl$_3$)
**1H NMR spectrum of zethrene (CDCl₃)**

**13C NMR spectrum of zethrene (CDCl₃)**
$^1$H NMR spectrum of N-dodecyl-naphtho[8,1,2-bcd]perylene-13,14-dicarboxylic imide (1mg/mL in CDCl$_3$)

$^1$C NMR spectrum of N-dodecyl-naphtho[8,1,2-bcd]perylene-13,14-dicarboxylic imide (CDCl$_3$)
1H NMR spectrum of N-hexyl-naphtho[8,1,2-bcd]perylene-13,14-dicarboxylic imide (2mg/mL in CD$_2$Cl$_2$)

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 (CDCl$_3$)
$^{13}$C NMR spectrum of N,N'-didodecyl-benzo[pqr]naphtho[8,1,2-bcd]perylen-6,7,13,14-tetracarboxylic 6,7:13,14-diimide (CDCl$_3$)

$^1$H NMR spectrum of N,N'-dihexyl-benzo[pqr]naphtho[8,1,2-bcd]perylen-6,7,13,14-tetracarboxylic 6,7:13,14-diimide (CDCl$_3$)
$^1$H NMR spectrum of 1-(8-vinylnaphthalen-1-yl)acenaphthylene (CDCl$_3$)

$^{13}$C NMR spectrum of 1-(8-vinylnaphthalen-1-yl)acenaphthylene (CDCl$_3$)