Supporting Information for:

Ambipolar Organic Semiconductors From Electron-Accepting Cyclopenta-Fused Anthracene

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1. Synthesis

**General:** The reagents and starting materials employed were commercially available and used without any further purification or made following reported methods. Anhydrous and oxygen-free THF was purified by an Advanced Technology Pure-Solv PS-MD-4 system. $^1$H-NMR or $^{13}$C-NMR spectra were recorded on a Brucker ADVANCE III 400MHz spectrometer. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL spectrometer.

**Representative synthetic procedure:** To a stirred suspension of 258 mg (1.0 mmol) of 1,6-dihydro-cyclopenta[hi]aceanthrylene-2,7-dione (2) in anhydrous 20 ml of THF was injected Grignard reagent (4.0 mmol) at 0 °C under a N$_2$ atmosphere. The resulting solution was refluxed for 24 h and quenched with saturated NH$_4$Cl aqueous solution and then extracted with ether for three times. The organic layers were combined and dried over anhydrous sodium sulfate, and concentrated under a reduced pressure. The resulting gel-like solid was purified by filtration through a thin silica gel pad with CH$_2$Cl$_2$/hexane 1/1 (v/v) then EtOAc/CH$_2$Cl$_2$ 1/4 (v/v) as eluents. The latter filtrate containing diol was collected and concentrated under a reduced pressure yielding the corresponding diol as a yellow solid, which was used directly in the next step without separation.

The diol obtained in last step was dissolved in 20 ml of CH$_2$Cl$_2$. To the resulting solution was added 0.5 mL of trifluoroacetic acid until the yellow solution turned black. After refluxing for 1 hour, the reaction mixture was poured into 100 ml of water and extracted with dichloromethane twice. The combined organic layers were washed with 1M NaOH aqueous solution, dried with anhydrous sodium sulfate and filtered through a thin pad of silica gel with dichloromethane as eluent. The green filtrate was concentrated under a reduced pressure and purified by column chromatography on silica gel with hexane/CH$_2$Cl$_2$ 4/1 (v/v) as eluent.

**Trimethylsilylethynyl magnesium chloride** was prepared by adding 0.63 ml (4.4 mmol) of trimethylsilylacetylene into a solution of 2 ml (2M, 4 mmol) of isopropyl magnesium chloride in 10 ml of anhydrous and oxygen-free THF at 0 °C under a N$_2$ atmosphere. The resulting solution was stirred at room temperature for 30 minutes before use.

**2,7-bis((trimethylsilyl)ethynyl)cyclopenta[hi]aceanthrylene (1a)**

Yield: 91 mg (20%) for the step of 3a, 26 mg (31%) for the step of 1a, drak-green crystals.

Melting point: > 250 °C (decomposed). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.16 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 7.71 (m, 4H), 0.34 (s, 18H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 140.5, 138.0, 131.3, 129.5, 128.0, 126.3, 125.6, 124.5, 123.2, 102.8, 100.7, 0.25. HRMS (EI$^+$): cacl.d. for ([M]+): 418.1568, found: 418.1571.

2,7-dimethylcyclopenta[hi]aceanthrylene (1b)
Yield: 66 mg (25%) for the step of 3b, 13 mg (21%) for the step of 1b, drak-green crystals. Melting point: 205~206 °C (decomposed). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.10 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 6.4 Hz, 2H), 7.62 (dd, J = 8.4 Hz, J = 6.8 Hz, 2H), 7.16 (d, J = 0.8 Hz, 2H), 2.52 (d, J = 1.2 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 142.3, 138.9, 136.8, 128.3, 128.2(5), 125.7, 123.7, 123.6, 123.3, 13.4. HRMS (EI$^+$): cacld. for ([M]+): 254.1090, found: 254.1083.

Attempt to synthesize cyclopenta[hi]aceanthrylene:

1,2,6,7-tetrahydrocyclopenta[hi]aceanthrylene-2,7-diol (4)
258 mg (1.0 mmol) of 1,6-dihydro-cyclopenta[hi]aceanthrylene-2,7-dione (2) $^1$ and 226 mg (6.0 mmol) of sodium borohydride were suspended in 20 mL of THF. The reaction mixture was stirred at room temperature for 24 h and then quenched with saturated NH$_4$Cl aqueous solution and extracted with diethyl ether twice. Organic layers were combined and dried over anhydrous sodium sulfate and concentrated under a reduced pressure. Purification via column chromatography on silica gel with ethyl acetate/CH$_2$Cl$_2$ 1/4 (v/v) as eluent yielded 84 mg (32%) of 1,2,6,7-tetrahydrocyclopenta[hi]aceanthrylene-2,7-diol (4) as light yellow crystals. Melting point: 208~210 °C. $^1$H NMR (400 MHz, Acetone-d$_6$) δ (ppm): 7.85 (d, J = 8.4 Hz, 2H), 7.58 (dd, J$_1$ = 8.0 Hz, J$_2$ = 6.8 Hz, 2H), 7.50 (d, J = 6.4 Hz, 2H), 5.86 (d, J = 5.2 Hz, 2H), 4.09 (dd, J$_1$ = 8.8 Hz, J$_2$ = 6.8 Hz, 2H),3.51 (d, J = 9.2 Hz, 2H). $^{13}$C NMR was not recorded due to its low solubility and poor stability. HRMS (ESI$^+$): cacld. for ([M-H$_2$O+H]+): 245.0961, found: 245.0964.

Treating diol 4 with p-toluenesulfonic acid in refluxing benzene, or trifluoroacetic acid in refluxing dichloromethane or neutral alumina in refluxing benzene failed to yield cyclopenta[hi]aceanthrylene.
2. Cyclic Voltammetry

The cyclic voltammetry was performed in a solution of anhydrous CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) as supporting electrolyte, at a scan rate of 50mV s$^{-1}$. 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$_2^+$/FeCp$_2^0$.

![Figure S-1. Cyclic voltammogram of 1a](image)

![Figure S-2. Cyclic voltammogram of 1b](image)
3. Crystal structures of 1a-c

Table S-1. Summary of crystallographic data of 1a-c

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<th>1a</th>
<th>1b</th>
<th>1c</th>
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4. Fabrication and Characterization of Vacuum-Deposited Thin Films and Transistors

(1) Deposition of thin films and fabrication of transistors

Thin films of 1a-d were deposited on silicon wafers, which had 300 nm-thick SiO$_2$ on highly n-doped Si, using an Edwards Auto 306 vacuum coating system at a pressure of $1.0 \times 10^{-6}$ torr or lower with a deposition rate of ca. 0.1 nm/s to a thickness of 60 nm as measured with a quartz crystal microbalance. The SiO$_2$ surface was modified with octadecyltrimethoxysilane (OTMS) before deposition by following the reported procedures. During vacuum deposition the distance between source and substrate was 18.5 cm. The substrates were kept at room temperature without extra heating or cooling during deposition. 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). The resulting transistors had highly n-doped silicon as gate electrode, and 300 nm-thick SiO$_2$ as dielectrics.

(2) Characterization of Thin Film Transistors

Atomic Force Microscopy (AFM): Thin films deposited at room temperatures on OTMS treated SiO$_2$/Si were used for AFM studies. The topographic images were obtained using a Nanoscope IIIa Multimode Microscope from Digital Instruments. All AFM images were collected 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.

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**Figure S-5.** AFM images of 60 nm-thick film of 1a

**Figure S-6.** AFM images of 60 nm-thick film of 1b
**Figure S-7.** AFM images of 60 nm-thick film of 1c

**Figure S-8.** AFM images of 60 nm-thick film of 1d
X-ray diffraction (XRD): XRD data were recorded on a SmartLab X-Ray Refractometer from the thin films, which were about 60 nm thick and deposited on OTMS-treated SiO$_2$ surface at a substrate temperature of room temperature.

![Figure S-9. X-ray diffraction from 60 nm thin films of 1a](image)

![Figure S-10. X-ray diffraction from 60 nm thin films of 1b](image)
**Figure S-11.** X-ray diffraction from 60 nm thin films of 1c

**Figure S-12.** X-ray diffraction from 60 nm thin films of 1d
(3) Electrical Characterization of Thin Film Transistors

The current-voltage measurement was carried out on a JANIS ST-500-20-4TX probe station with a Keithley 4200 Semiconductor Characterization System at room temperature.

![Figure S-13](image)

**Figure S-13.** (a) Transfer I-V curves (b) output I-V curves of p-type performance for a typical transistor of 1d with channel width of 1 mm and channel length of 50 μm tested in air; (c) Summary of p-type field-effect mobility measured from thin film transistor of 1d (film deposited on OTMS treated SiO₂ at a substrate temperature of room temperature and tested in air); (d) Transfer I-V curves of n-type performance for a typical transistor of 1d with channel width of 1 mm and channel length of 150 μm tested under vacuum.
5. NMR Spectra

\(^{1}H\) NMR of 2,7-bis((trimethylsilyl)ethynyl)cyclopenta[hi]aceanthrylene in CDCl$_{3}$

\(^{13}C\) NMR of 2,7-bis((trimethylsilyl)ethynyl)cyclopenta[hi]aceanthrylene in CDCl$_{3}$
$^1$H NMR of 2,7-dimethylcyclopenta[h]aceanthrylene in CDCl$_3$

$^{13}$C NMR of 2,7-dimethylcyclopenta[h]aceanthrylene in CDCl$_3$
$^1$H NMR of 1,2,6,7-tetrahydrocyclopenta[hi]aceanthrylene-2,7-diol in Acetone-$d_6$