

Supporting Information for:

**Ambipolar Organic Semiconductors From Electron-Accepting
Cyclopenta-Fused Anthracene**

Hai Xia,¹ Danqing Liu,¹ Xiaomin Xu,¹ Qian Miao*^{1,2}

¹ *Department of Chemistry, the Chinese University of Hong Kong, Shatin, New Territories,
Hong Kong, China*

² *Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants
Committee), Hong Kong, China*

Table of Contents

1. Synthesis
2. Cyclic voltammetry
3. Summary of crystal structures
4. Fabrication and Characterization of Vacuum-Deposited Thin Films and Transistors
5. NMR spectra

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. $^1\text{H-NMR}$ or $^{13}\text{C-NMR}$ spectra were recorded on a Bruker ADVANCE III 400MHz 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. UV-vis absorption spectra were recorded on a Varian CARY 1E UV-vis spectrophotometer. Melting points were measured using a Nikon Polarizing Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage.

Representative synthetic procedure: To a stirred suspension of 258 mg (1.0 mmol) of 1,6-dihydro-cyclopenta[*hi*]aceanthrylene-2,7-dione (**2**)¹ 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_4Cl 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_2Cl_2 /hexane 1/1 (v/v) then EtOAc/ CH_2Cl_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_2Cl_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_2Cl_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**)

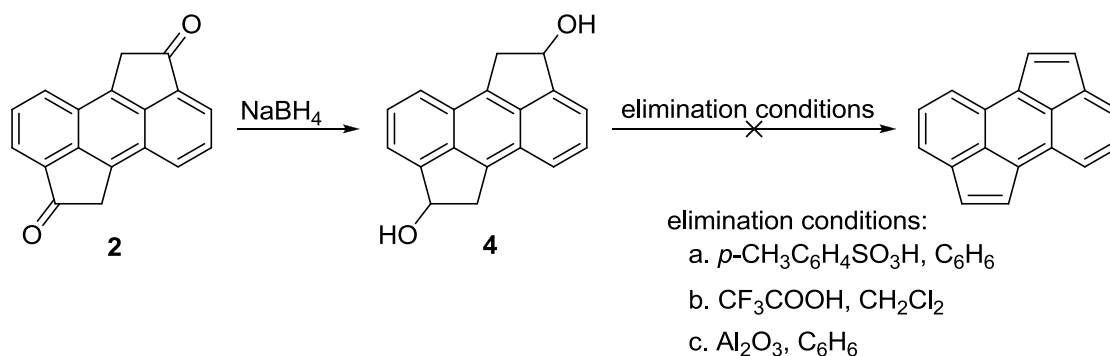
Yield: 91 mg (20%) for the step of **3a**, 26 mg (31%) for the step of **1a**, drak-green crystals. Melting point: > 250 °C (decomposed). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 8.16 (d, $J = 8.8$ Hz, 2H), 7.92 (d, $J = 7.8$ Hz, 2H), 7.71 (m, 4H), 0.34 (s, 18H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 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. for ($[\text{M}]^+$):418.1568, found: 418.1571.

1. A. R. Mohebbi, C. Munoz,; F. Wudl, *Org. Lett.*, 2011, **13**, 2560–2563

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). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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⁺): cacl. 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 NH₄Cl 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/CH₂Cl₂ 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. ¹H NMR (400 MHz, Acetone-d₆) δ (ppm): 7.85 (d, J = 8.4 Hz, 2H), 7.58 (dd, J₁ = 8.0 Hz, J₂ = 6.8 Hz, 2H), 7.50 (d, J = 6.4 Hz, 2H), 5.86 (d, J = 5.2 Hz, 2H), 4.09 (dd, J₁ = 8.8 Hz, J₂ = 6.8 Hz, 2H), 3.51 (d, J = 9.2 Hz, 2H). ¹³C NMR was not recorded due to its low solubility and poor stability. HRMS (ESI⁺): cacl. for ([M-H₂O+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_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_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 pseudo-reference. Ferrocene/ferrocenium was used as an internal standard, and potentials were recorded versus $\text{FeCp}_2^+/\text{FeCp}_2^0$.

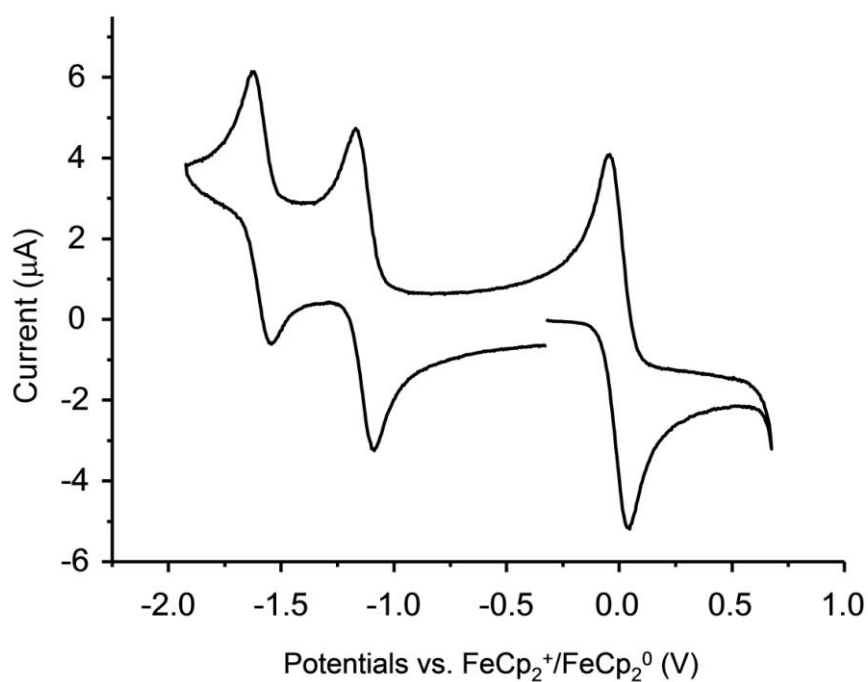


Figure S-1. Cyclic voltammogram of **1a**

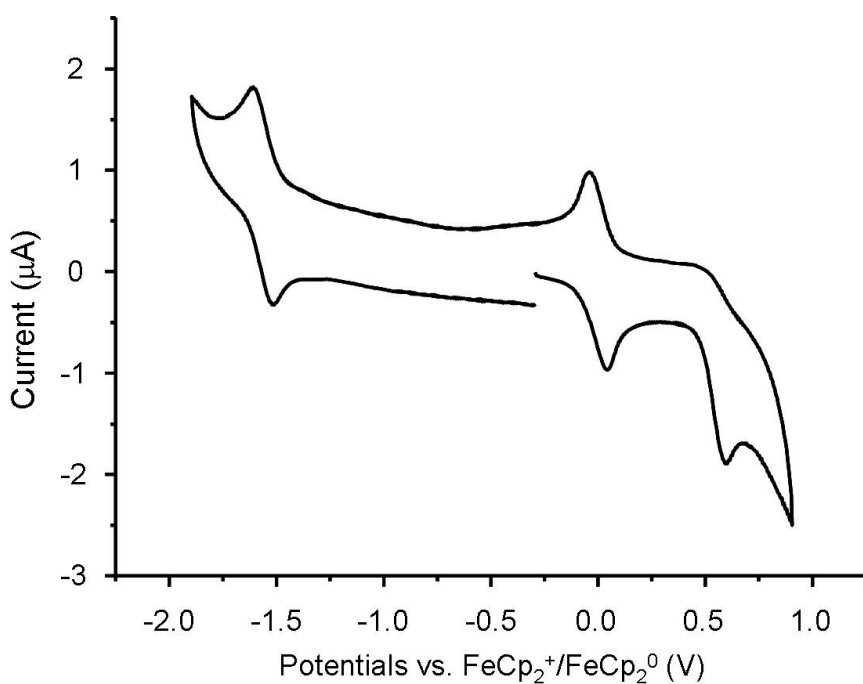


Figure S-2. Cyclic voltammogram of **1b**

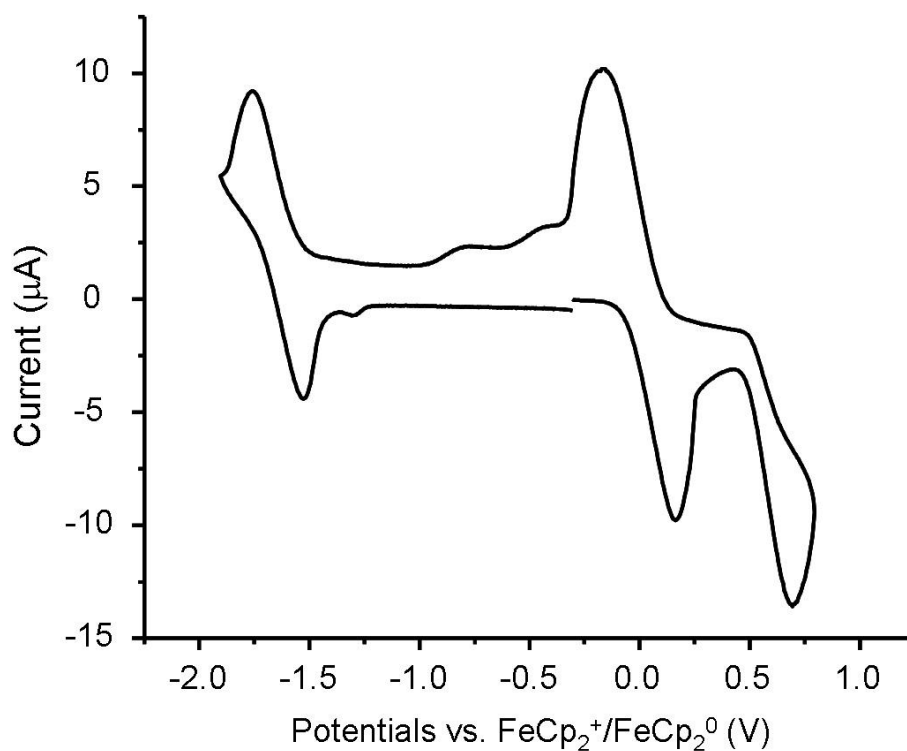


Figure S-3. Cyclic voltammogram of **1c**

3. Crystal structures of **1a-c**

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

	1a	1b	1c
Space Group	P-1	P2(1)/c	P-1
Unit Cell Lengths (Å)	a = 6.1885(10) b = 6.8198(12) c = 16.531(3)	a = 10.2176(15) b = 10.4839(15) c = 12.2150(17)	a = 4.8931(7) b = 10.3024(15) c = 11.9639(18)
Unit Cell Angles (°)	α = 82.438(3) β = 87.220(3) γ = 83.216(3)	α = 90 β = 92.507(3) γ = 90	α = 85.254(3) β = 80.129(3) γ = 86.958(3)
Cell Volume (Å ³)	617.37(18)	1307.2(3)	591.68(15)
Z	1	4	1
Number of reflections	5967 collected, 2130 unique	9471 collected, 2374 unique	8626 collected, 2144 unique
Final R (all data)	0.0773	0.1124	0.1239
wR (all data)	0.1875	0.1835	0.1768

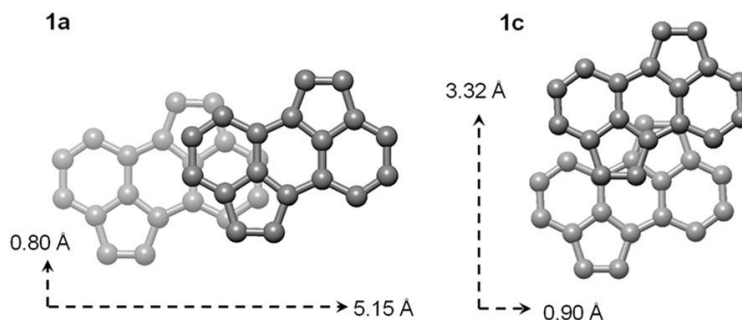


Figure S-4. Relative shifts of π -stacked cyclopent[hi]acanthrylene backbones along the long molecular axis and short molecular axis for **1a** and **1c**. (Hydrogen atoms are removed for clarity.)

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 SiO₂ on highly n-doped Si, using an Edwards Auto 306 vacuum coating system at a pressure of 1.0×10^{-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 SiO₂ surface was modified with octadecyltrimethoxysilane (OTMS) before deposition by following the reported procedures.² 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 50 μ m(L) \times 1mm(W), 100 μ m(L) \times 1mm(W), 150 μ m(L) \times 1mm(W), 50 μ m(L) \times 2mm(W) and 100 μ m(L) \times 2mm(W). The resulting transistors had highly n-doped silicon as gate electrode, and 300 nm-thick SiO₂ as dielectrics.

(2) Characterization of Thin Film Transistors

Atomic Force Microscopy (AFM): Thin films deposited at room temperatures on OTMS treated SiO₂/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.

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

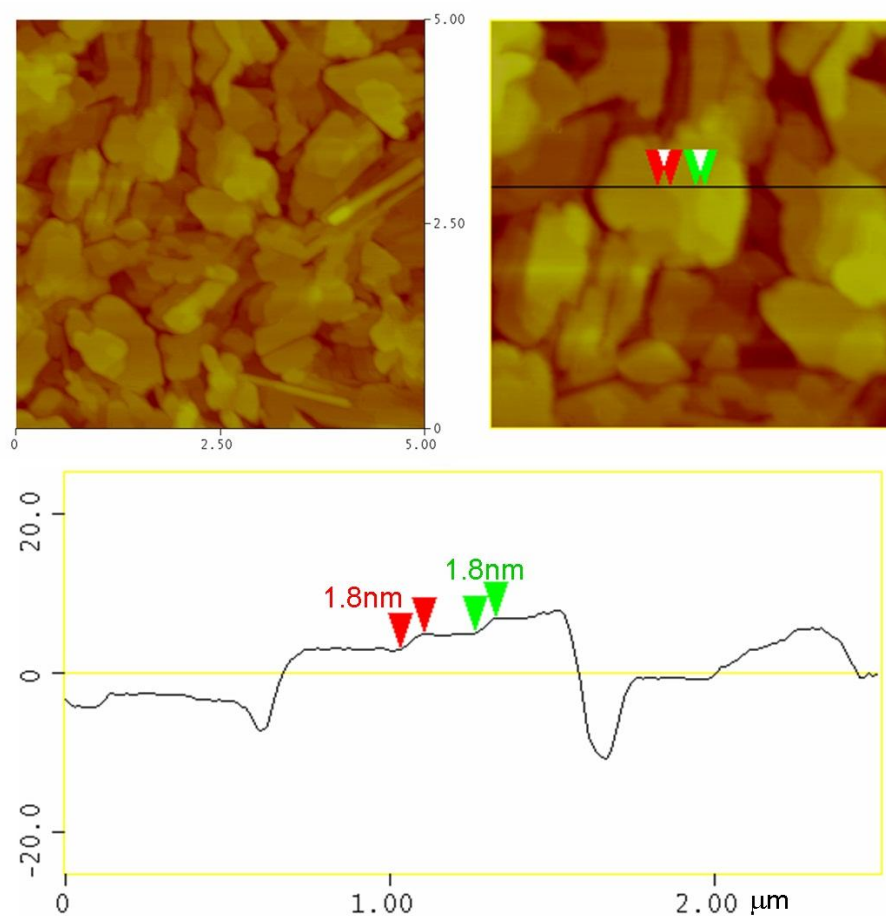


Figure S-5. AFM images of 60 nm-thick film of **1a**

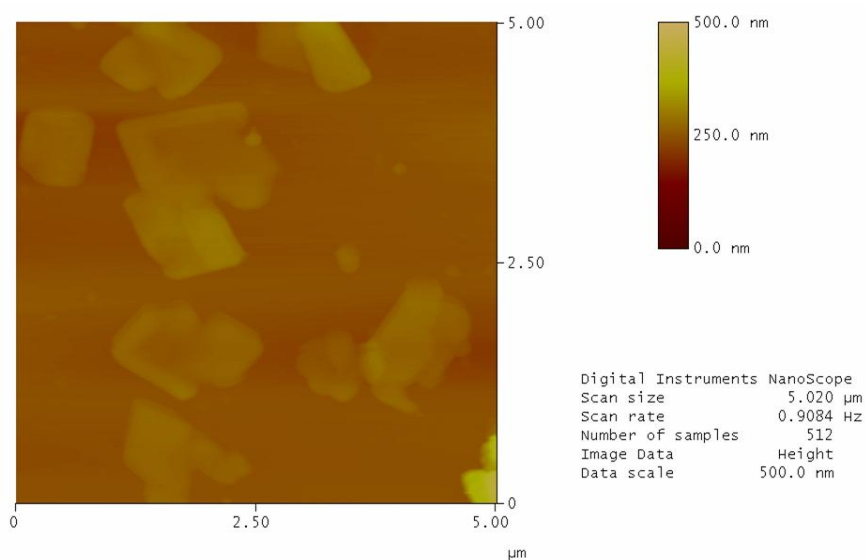


Figure S-6. AFM images of 60 nm-thick film of **1b**

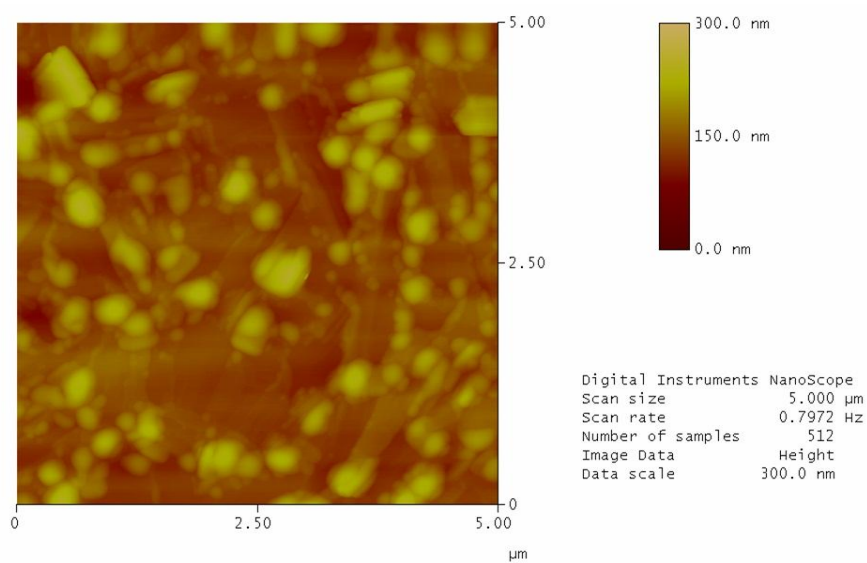


Figure S-7. AFM images of 60 nm-thick film of **1c**

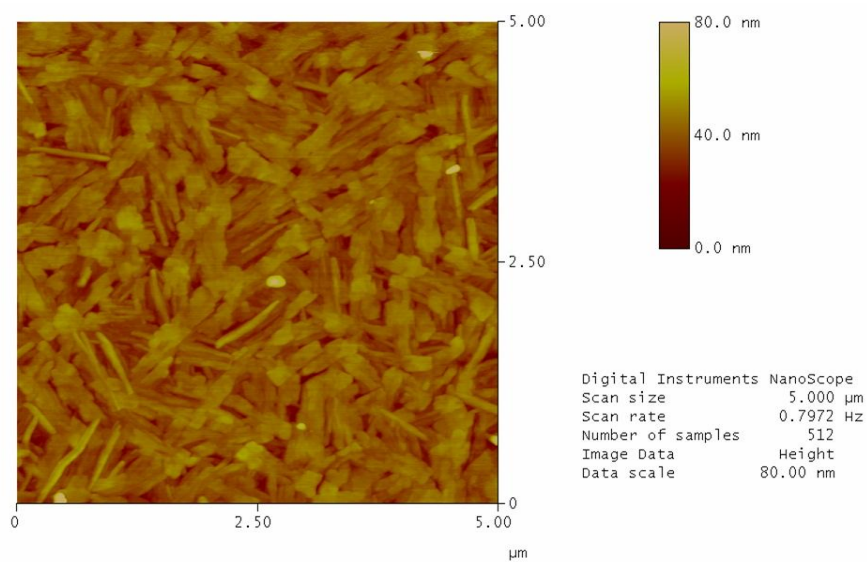


Figure S-8. AFM images of 60 nm-thick film of **1d**

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 SiO₂ surface at a substrate temperature of room temperature.

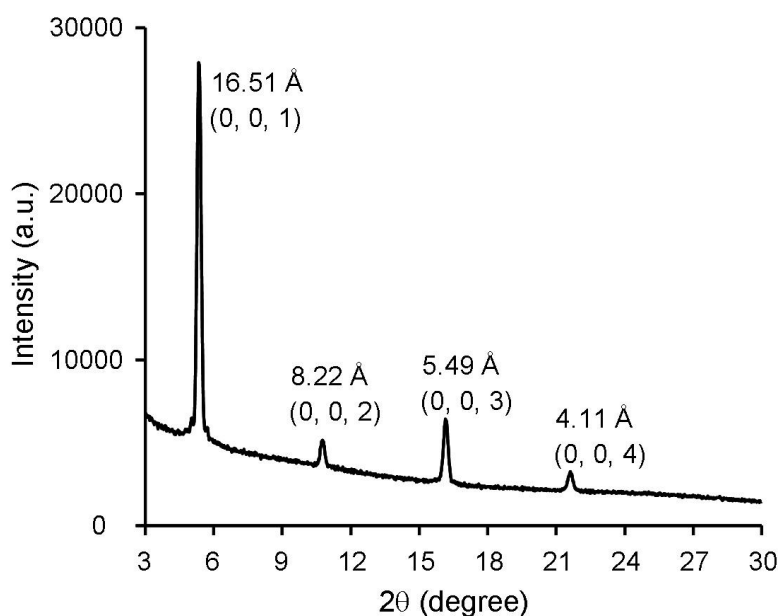


Figure S-9. X-ray diffraction from 60 nm thin films of **1a**

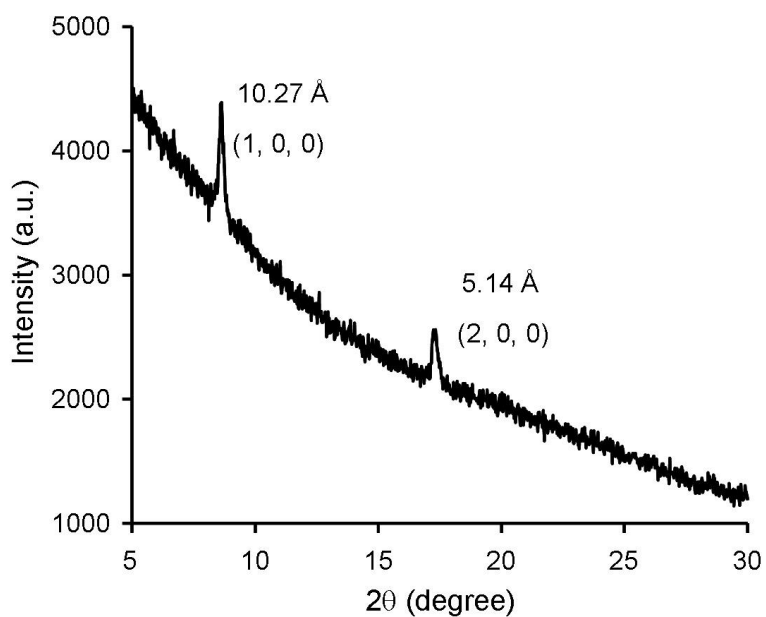


Figure S-10. X-ray diffraction from 60 nm thin films of **1b**

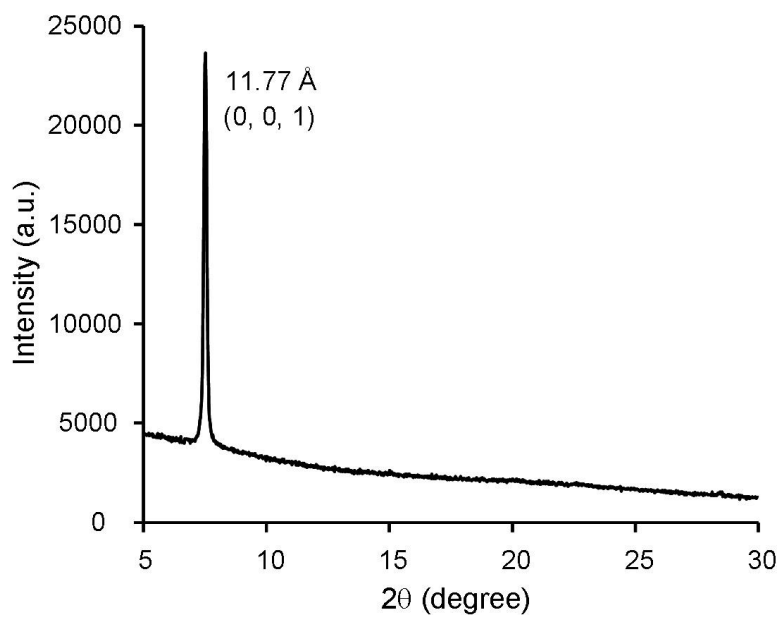


Figure S-11. X-ray diffraction from 60 nm thin films of **1c**

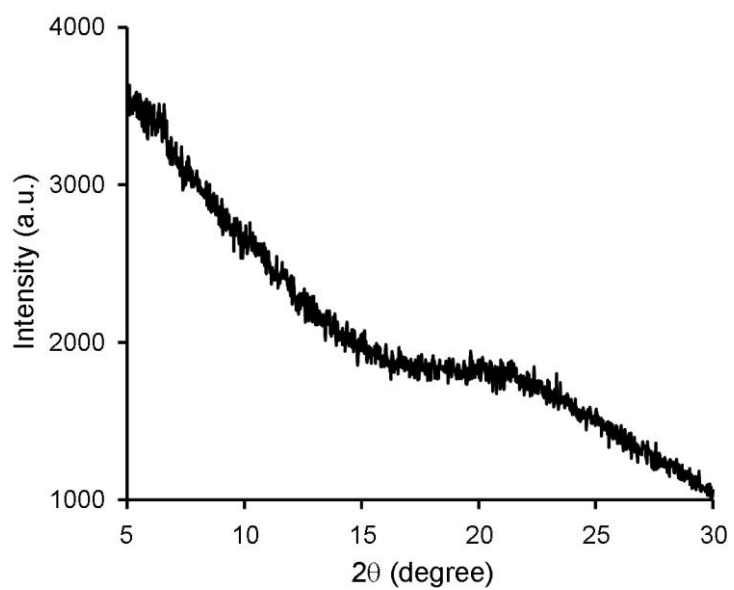


Figure S-12. X-ray diffraction from 60 nm thin films of **1d**

(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.

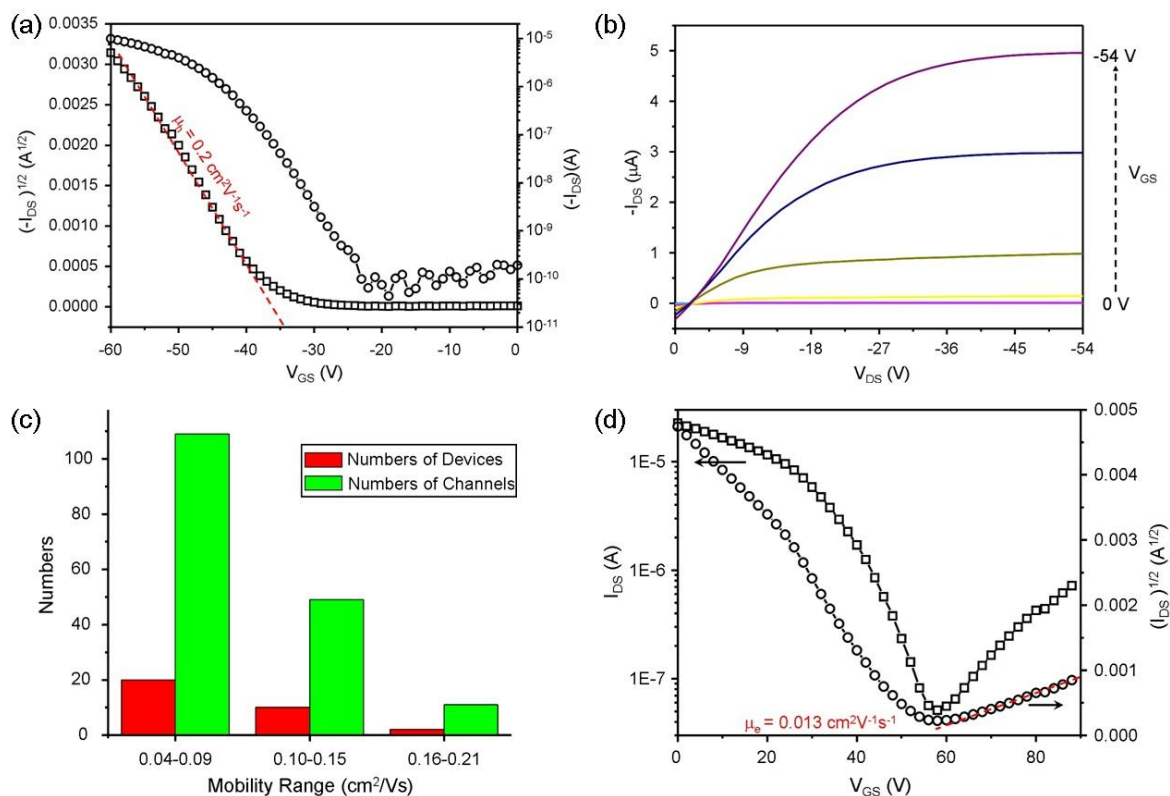
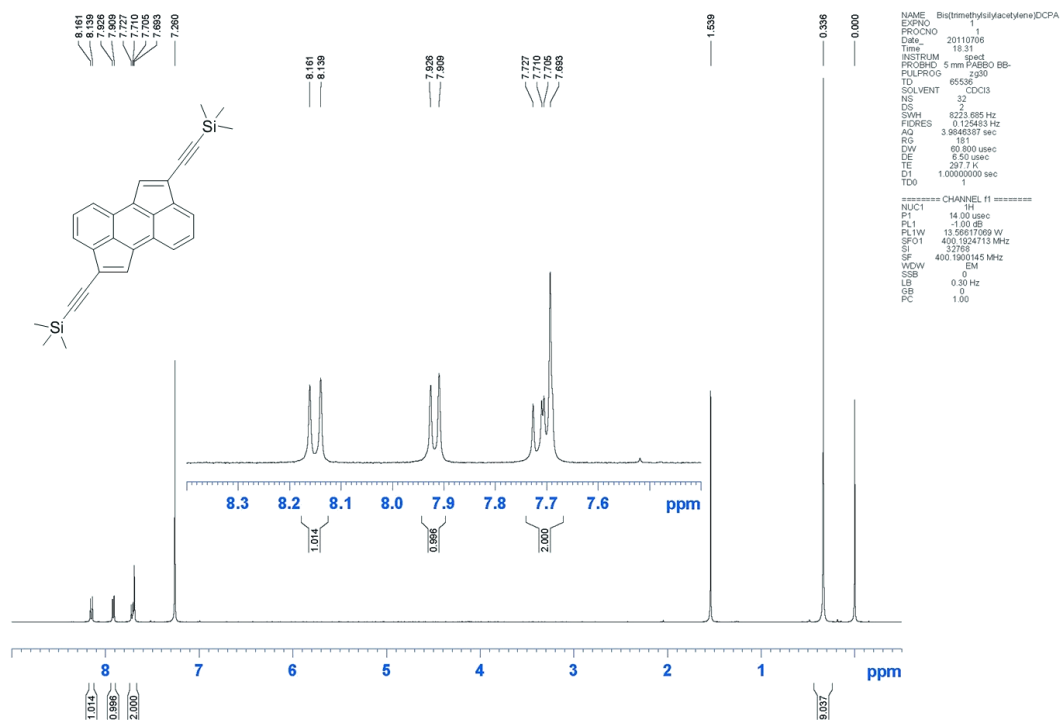
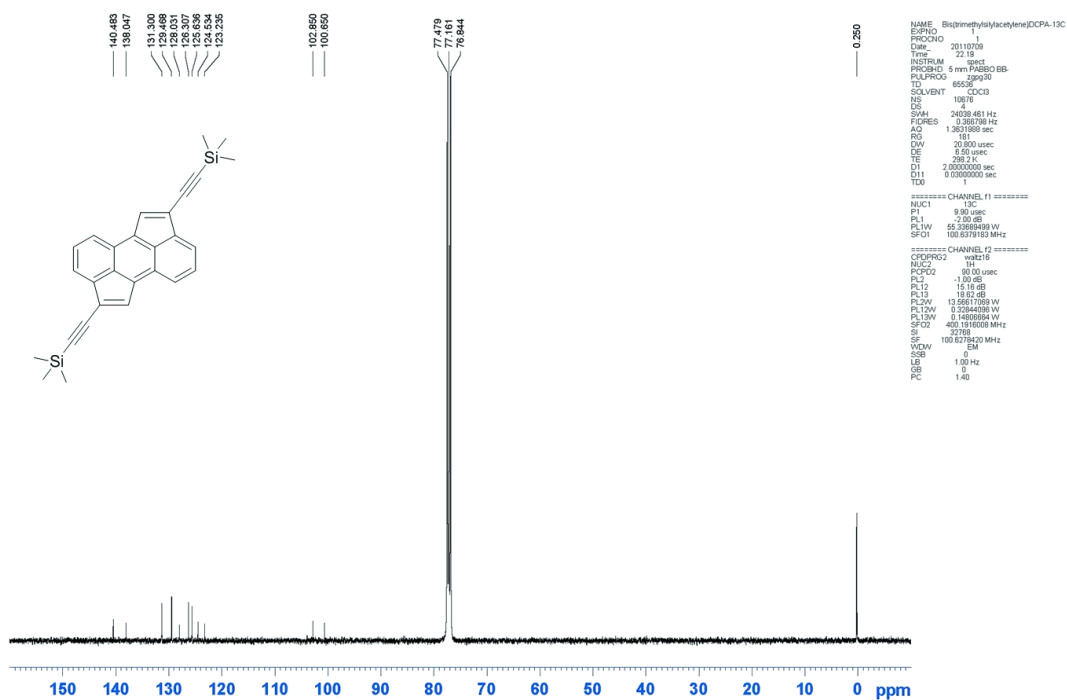


Figure S-13. (a) Transfer I-V curves (b) output I-V curves of p-type performance for a typical transistor of **1d** with channel width of 1 mm and channel length of 50 μm tested in air; (c) Summary of p-type field-effect mobility measured from thin film transistor of **1d** (film deposited on OTMS treated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

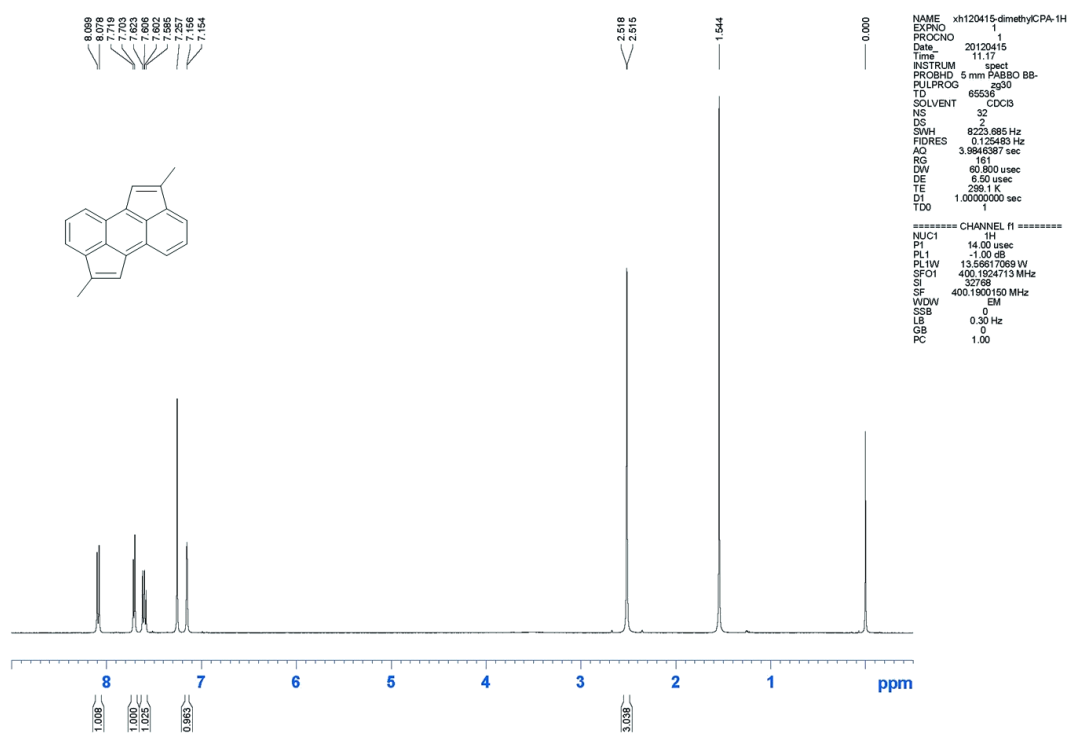
5. NMR Spectra



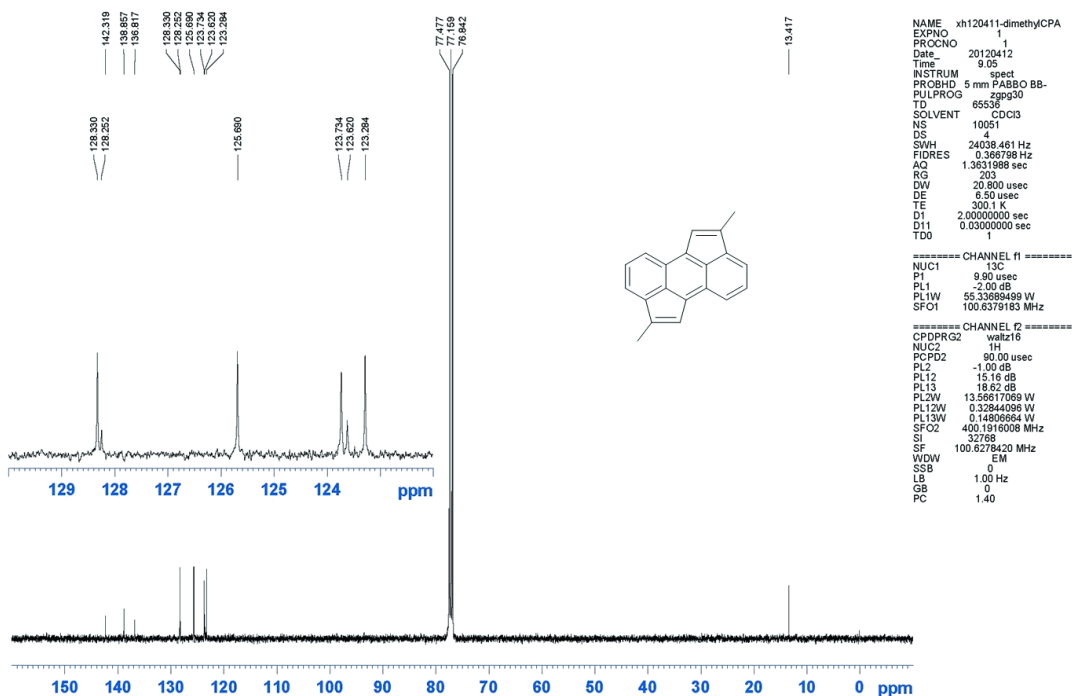
¹H NMR of 2,7-bis((trimethylsilyl)ethynyl)cyclopenta[hi]acanthrylene in CDCl₃



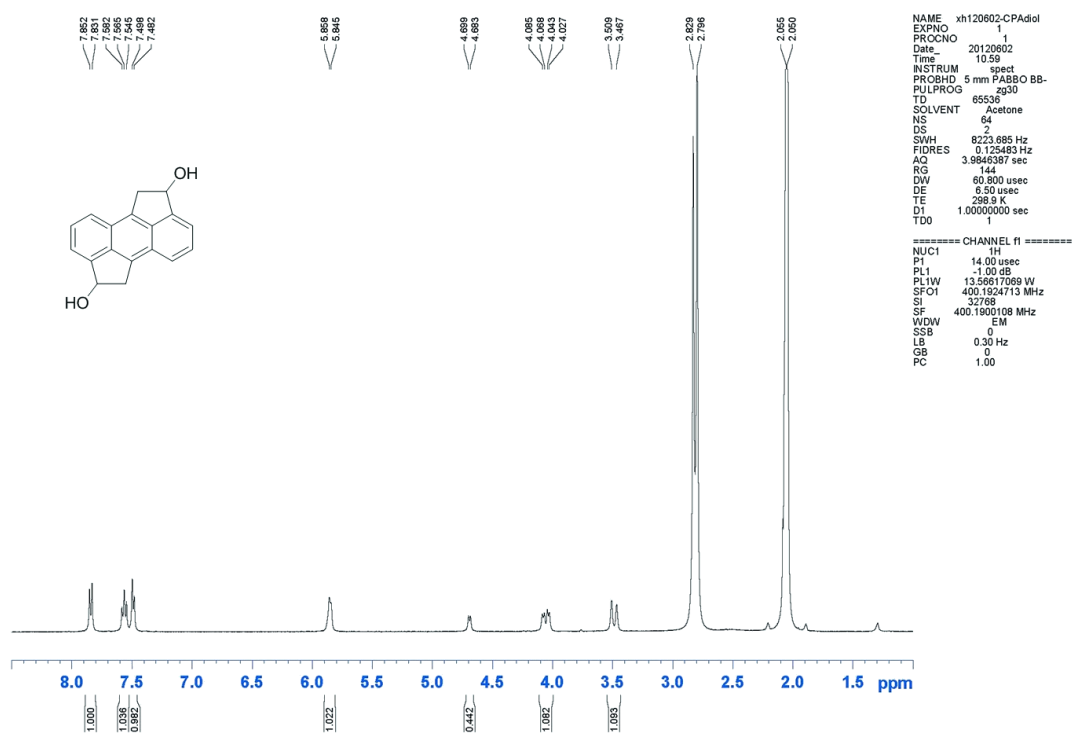
¹³C NMR of 2,7-bis((trimethylsilyl)ethynyl)cyclopenta[hi]acanthrylene in CDCl₃



¹H NMR of 2,7-dimethylcyclopenta[hi]aceanthrylene in CDCl₃



¹³C NMR of 2,7-dimethylcyclopenta[hi]aceanthrylene in CDCl₃



¹H NMR of 1,2,6,7-tetrahydrocyclopenta[hi]aceanthrylene-2,7-diol in Acetone-d₆