

Supporting Information for:

A Meaningful Analogue of Pentacene: Charge Transport, Polymorphs and Electronic Structures of Dihydrodiazapentacene

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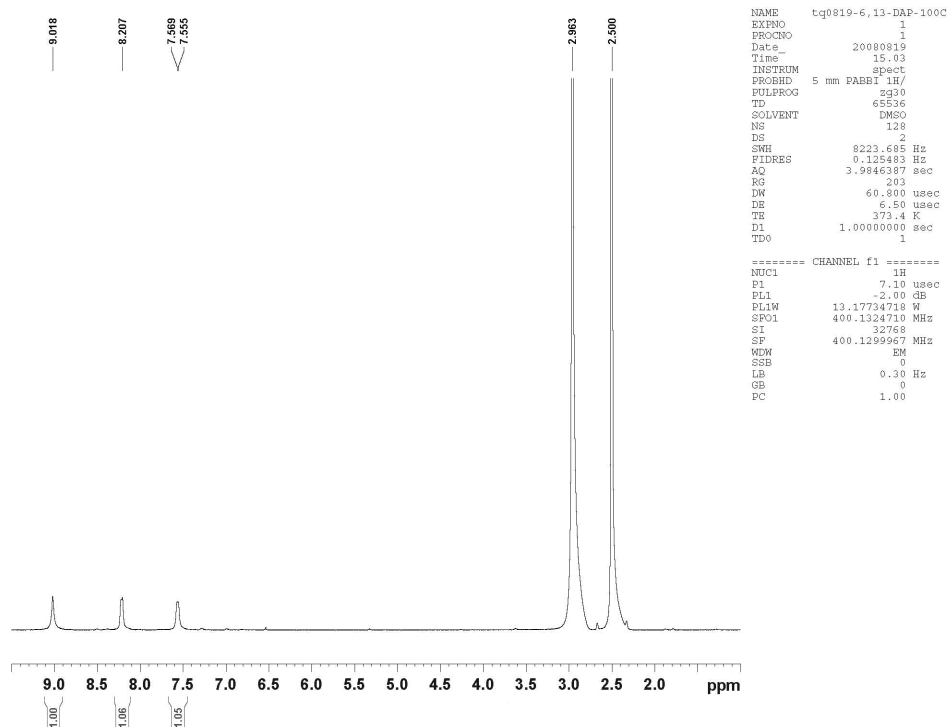
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Characterization of DHDAP and DAP

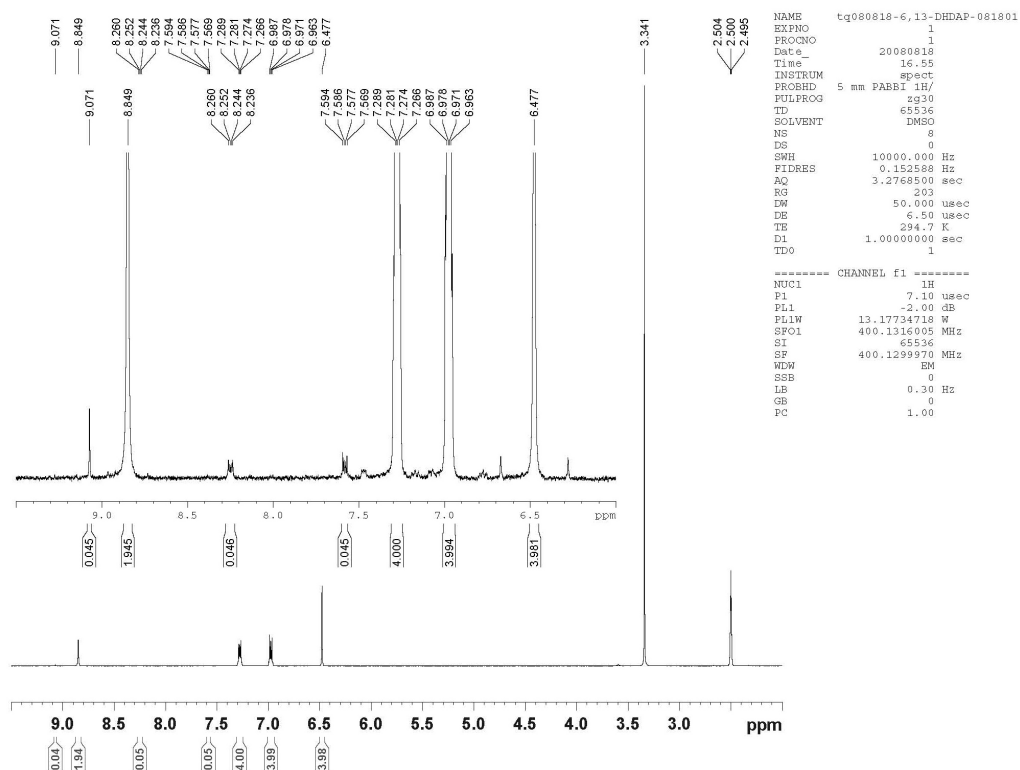
¹H-NMR spectra were recorded on a Bruker DPX 300MHz or Bruker AVANCE III 400MHz spectrometer. Mass spectra were recorded on Thermo Finnigan MAT 95 XL spectrometer.

6,13-diazapentacene (DAP): ¹H-NMR (DMSO-d₆, 100°C) δ(ppm): 9.02(s, 4H), 8.21(m, 4H), 7.56 (m, 4H). HRMS (EI): cald. for C₂₀H₁₂N₂: 280.1000, found 280.0995.

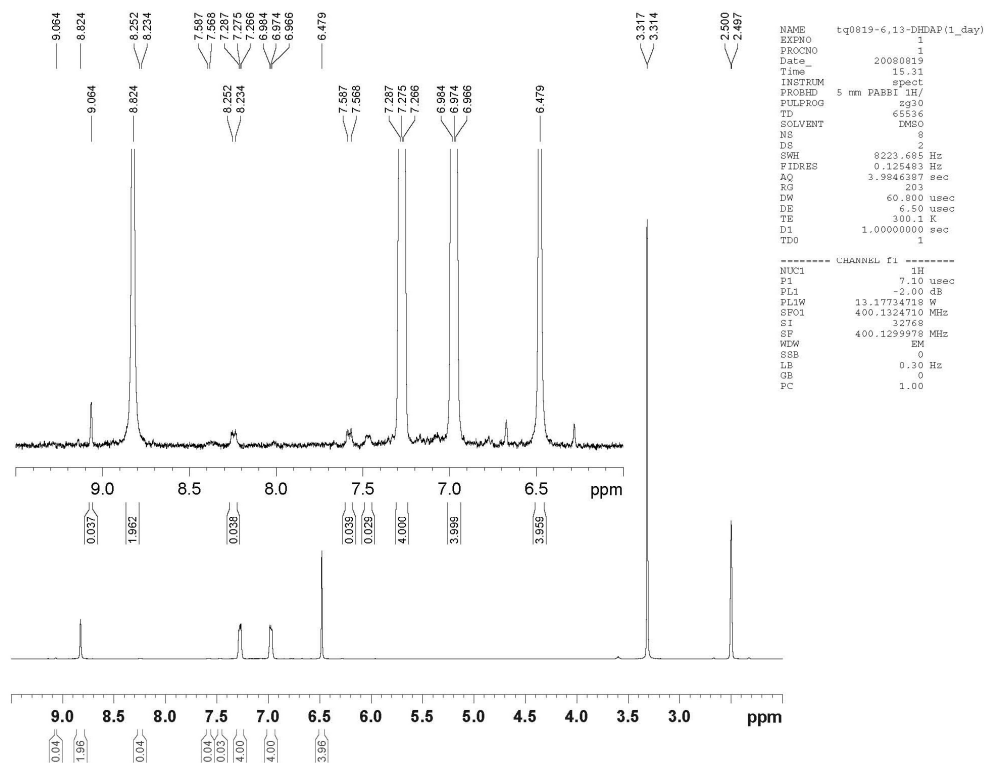


¹H-NMR of DAP (DMSO-d₆, 100°C)

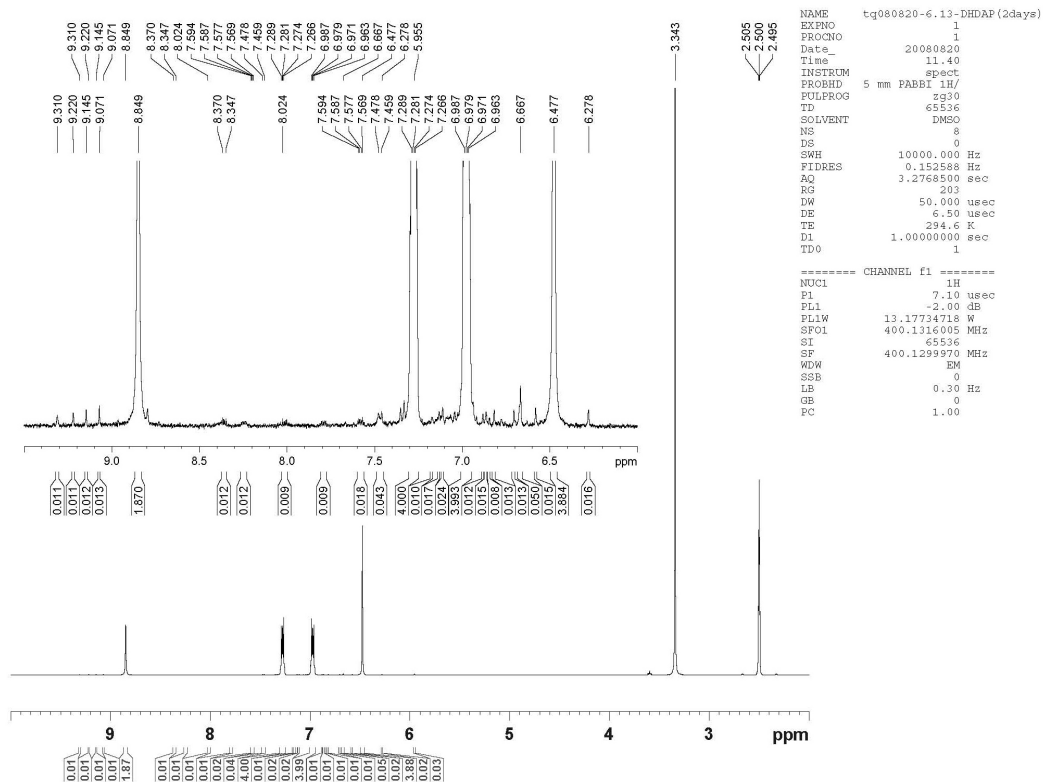
Environmental stability of DHDAP in DMSO-d₆ monitored by ¹H NMR:



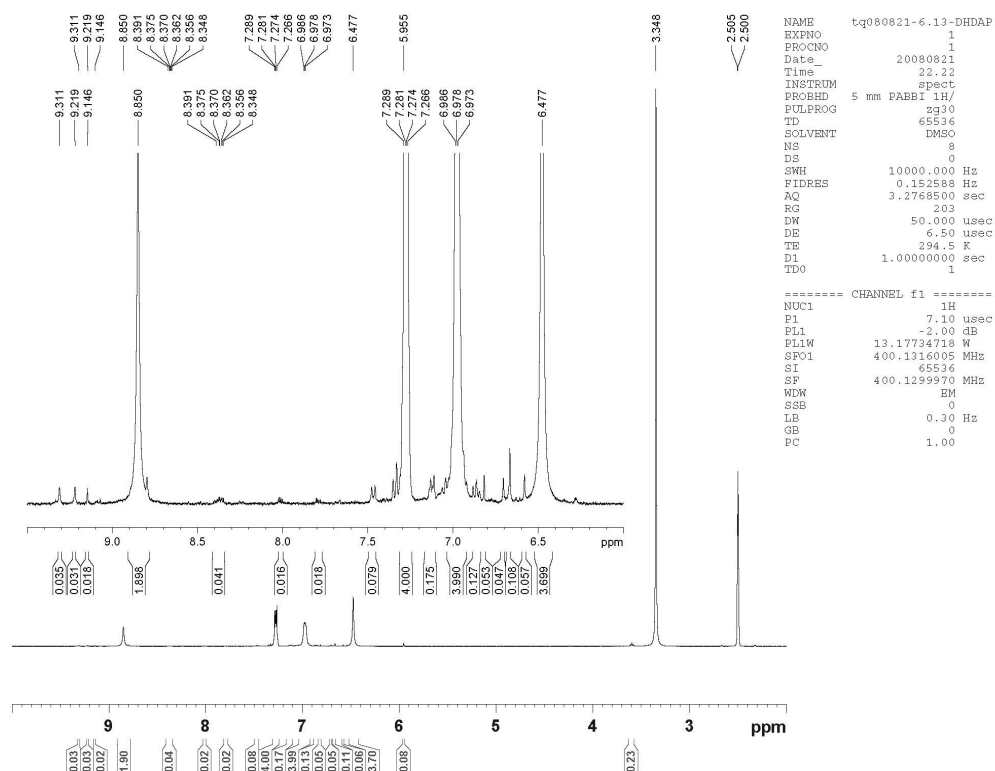
¹H-NMR of a freshly prepared solution of DHDAP in DMSO-d₆



¹H-NMR of a solution of DHDAP in DMSO-d₆ exposed to air and ambient light for 1 day



¹H-NMR of a solution of DHDAP in DMSO-d₆ exposed to air and ambient light for 2 days



¹H-NMR of a solution of DHDAP in DMSO-d₆ exposed to air and ambient light for 3 days

SiO₂ surface modification with OTS

An oxidized silicon wafer (Si is highly n-doped with resistivity smaller than 0.005 $\Omega\cdot\text{cm}$ and the thermally grown SiO₂ is 300nm thick) was used as substrates for organic thin film transistors. The following surface treatments of the SiO₂ were performed on the dielectric surface before vacuum sublimation of the semiconductor film: a 10 min sonication in acetone, followed by a 70:30 H₂SO₄/H₂O₂ (piranha) etch for 1 hour at 100°C, then a 1:1:5 NH₃:H₂O/H₂O₂/deionized H₂O wash for 20 min at 70°C, and finally a soak in a 2.5mM solution of octadecyltrichlorosilane (OTS) in toluene at 28°C for 1 hour. The dielectric surface was characterized using contact angle measurements, which were <5° after cleaning and >105° after OTS monolayer formation. The contact angle of the OTS monolayer confirms a tight-packed hydrophobic surface.

Transistor fabrication, capacitance measurement, and transistor measurements

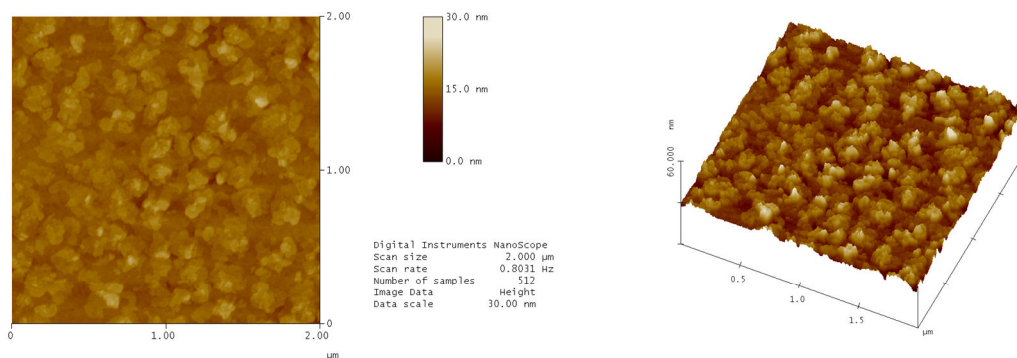
The thin films composed of DHDAP and pentacene were vacuum-deposited by an Edwards Auto 306 vacuum coater with the Turbomolecular pump at a pressure of 2.0×10^{-6} Torr or lower, with a deposition rate of ca. 1Å/s to the desired thickness. During vacuum deposition the distance between source and substrate was 18 cm. Different substrate temperatures for deposition were achieved using a radiant heater and measured with a thermocouple. Top-contact drain and source gold electrodes were vacuum-deposited through a shadow mask onto the films of DHDAP in the same vacuum chamber, and the resulting semiconducting channels were 50 μm (L) \times 1mm(W), 100 μm (L) \times 1mm(W), 50 μm (L) \times 2mm(W) and 100 μm (L) \times 2mm(W). In these transistors highly n-doped silicon functioned as gate electrode and SiO₂ of 300nm thick (untreated or treated with octadecyl trichlorosilane) functioned as dielectrics.

The current-voltage measurement for thin-film transistors was carried out on a probe station using a HP 4145B semiconductor parameter analyzer. During the measurement, the samples were kept at room temperature in the ambient atmosphere.

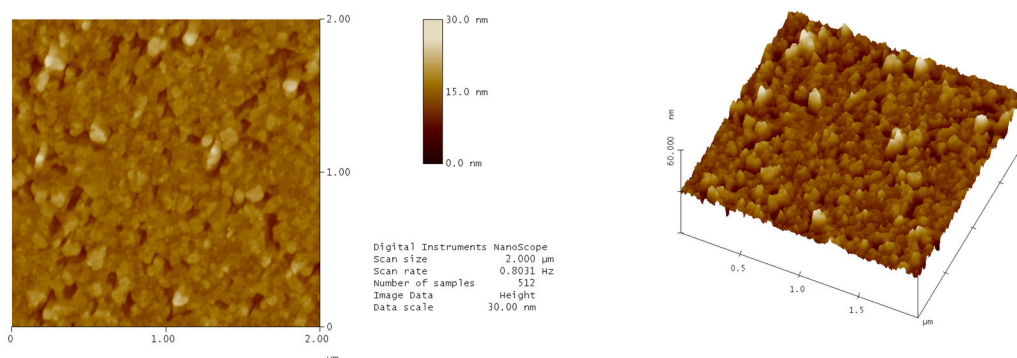
Characterization of thin films

UV-visible spectra were taken on a Virian Cary 1E UV-Visible Spectrophotometer. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance Diffractometer with high-intensity Cu K α 1 irradiation ($\lambda=1.5406\text{\AA}$). X-ray crystallography was taken on a Bruker KAPPA APEX2 with Mo irradiation ($\lambda=1.71073\text{\AA}$).

Thin films of DHDAP (ca. 40 nm and 8 nm thick) on OTS treated and bare 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 the reproducibility.



8 nm thick film of DHDAP deposited on bare SiO₂ at 25°C

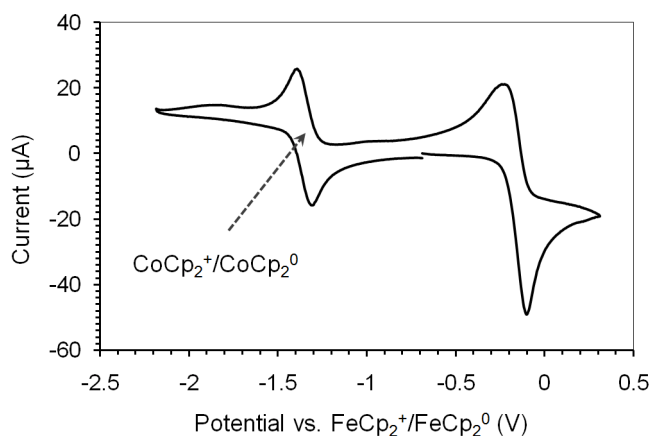


8 nm thick film of DHDAP deposited on OTS-treated SiO₂ at 25°C

AFM images of thin films of DHDAP (ca. 8nm thick) vacuum deposited on bare SiO₂ and OTS-treated SiO₂ substrates that were held at 25 °C.

Cyclic Voltammetry

The cyclic voltammetry was performed in a saturated solution in anhydrous DMF with 0.1M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte, at a scan rate of 50mv s⁻¹. A platinum bead is used as a working electrode, with a platinum disc as an auxiliary electrode and a silver rod is used as a pseudo-reference. Bis(cyclopentadienyl)cobalt(III) hexafluorophosphate (CoCp₂⁺/CoCp₂⁰ is -1.35V vs. FeCp₂⁺/FeCp₂⁰) was used as the internal standard because the oxidation potential of DHDAP is very close to FeCp₂⁺/FeCp₂⁰ (FeCp₂: ferrocene). Potentials were referenced to FeCp₂⁺/FeCp₂⁰.



Electrochemical potentials (vs. $\text{FeCp}_2^+/\text{FeCp}_2^0$) and estimated HOMO energy for DHDAP.

E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	HOMO (eV)
-0.237	-0.104	-0.171	-4.63

E_{pc} : cathodic peak potential; E_{ac} : anodic peak potential; $E_{1/2}$: half-wave potential