## ELECTRONIC SUPPLEMENTARY INFORMATION

## Hydrogen-bonded azaphenacene: a strategy for the organization of $\pi$ -conjugated materials.

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## EXPERIMENTAL SECTION

*General methods.* Reagents used as starting materials were purchased from commercial sources and were used without further purification. Solvents were dried following the usual protocols. Unless stated otherwise, all reactions were carried out under nitrogen atmosphere. Column chromatography was run with silica gel 60 A CC 70-200  $\mu$ m as stationary phase using HPLC grade solvents. The final purification of the materials was performed by gradient sublimation under high vacuum conditions (<10<sup>-6</sup> mbar).

Melting points were measured in a Reichert instrument and are not corrected.

*OFETs fabrication and Characterization:* P-doped n++ silicon wafers covered with 300 nm thermally grown SiO<sub>2</sub> (Siltronix) were cleaned by immersing in acetone and isopropanol in an ultrasonic bath for 20 min respectively. Subsequently, a coating layer of atactic polystyrene (PS,  $M_W$ =3350) was deposited from toluene solution (1% wt) by spin-coating (3000 rpm, 1000 rpm s<sup>-1</sup>, 30 s). The resulting layer had a thickness of 30 ± 2 nm as measured by scratching the surface and measuring the step by profilometry (Veeco DekTak 150). The PS layer was imaged by AFM and found to be smooth with RMS surface roughness of 0.05 nm over an area of 500×500 nm (Figure S9).

Thin films of compound **2** were evaporated in vacuum  $(1 \times 10^{-7} \text{ mbar})$  onto the PS-coated substrates at a rate of 0.1 Å s<sup>-1</sup> and 0.3 Å s<sup>-1</sup>, respectively, with final thicknesses of 50 nm.

The OFET structures were finished by evaporating  $MoO_3$  followed by Au through a shadow mask at a rate of 0.1 Å s<sup>-1</sup> and 0.2 Å s<sup>-1</sup> respectively, with thicknesses of 9 nm and 25 nm respectively as measured by profilometry. The OFET channels were 3 mm wide and 80-240  $\mu$ m long. The channel lengths were confirmed by profilometry. The

current-voltage characteristics were measured with a Keithley 2636A semiconductor parameter analyzer at room temperature under ambient atmosphere.

The Field-Effect mobility was extracted in the saturation regime by Equation 1:

$$\mu = \left(\frac{d\sqrt{I_{SD}}}{dV_{SG}}\right)^2 \frac{2L}{WC_i} \tag{1}$$

Where  $\mu$  is the field-effect mobility in the saturation regime,  $I_{SD}$  is the source-drain current,  $V_{SG}$  is the source-gate voltage, *L* is the channel length, *W* is the channel width, and  $C_i$  is the gate capacitance per unit area. The polystyrene layer acts as an additional insulator in series with the SiO<sub>2</sub>, and thus the total series capacitance  $C_i$  was calculated by Equation 2:

$$C_i = \frac{C_1 C_2}{C_1 + C_2} \tag{2}$$

Where  $C_1$  and  $C_2$  are the capacitances per unit area of the SiO<sub>2</sub> and PS layers,

$$C = \frac{A\varepsilon_0\varepsilon_r}{d} \tag{3}$$

where *A* is the area,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  is the relative permittivity of the insulator, and *d* is the thickness of the insulator. For a 300 nm layer of SiO<sub>2</sub> ( $\varepsilon_r$ =3.9) in series with a 30 nm layer of PS ( $\varepsilon_r$ =2.4), the total capacitance is  $C_i$ =9.9 nF cm<sup>-2</sup>. It is noted that if the polystyrene layer is not considered as an additional insulator in series with the SiO<sub>2</sub>, the capacitance per unit area would be 11.5 nF cm<sup>-2</sup> and the mobility would be underestimated by a factor of 1.16.



**Figure S1.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of compound **1**.



**Figure S2.** Evolution of the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra during the purification by sublimation.



Figure S3. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of compound 2.



Figure S4. TGA (a) and DSC (b) of compound 2.



**Figure S5.** TD-DFT simulation of the absorption spectra of compound **2**. Molecular orbitals with major contribution to the corresponding electronic transitions.



**Figure S6.** Final Rietveld refinement plot for compound **2**, showing the experimental (red circles), calculated (black line) and difference profiles (blue line); green marks indicate reflection positions.

Compound	2			
Formula	$C_{16}H_{10}N_4$			
Formula weight	258.28			
(g/mol)				
Crystal system	Triclinic			
Space group	<i>P</i> -1			
<i>a</i> (Å)	4.1021(13)			
<i>b</i> (Å)	8.259(3)			
<i>c</i> (Å)	9.176(2)			
α (°)	98.51(2)			
β (°)	89.43(4)			
γ (°)	105.65(3)			
$V(Å^3)$	295.93(15)			
Z	1			
Radiation type	Synchrotron			
Diffusitomator	SpLine (BM25A) at			
Dimactometer	the ESRF, Grenoble			
Data collection mode	Transmission			
Wavelength (Å)	0.953892			
$R_{p}$ (%)	4.83			
$R_{wp}$ (%)	6.60			
$R_{exp}$ (%)	5.59			
$R_B(\%)$	4.12			
Goodness-of-fit	1.18			

 Table S1. Crystallographic data and Rietveld refinement summary for compound 2.



**Figure S7.** Sequential expansion of the crystal packing: (a) Molecule of 7-azaindolo[2,3-*h*] $\alpha$ -carboline, 2; (b) Hydrogen bond-directed self-assembly of 2; (c)  $\pi$ -stacking of hydrogen-bonded substructures; (d) Front view of packing depicted in (c); (e) Expansion of the crystal packing with adjacent stacks.



**Figure S8.** Hirshfeld surfaces and 2D-fingerprints of 7-azaindolo[2,3-*h*] $\alpha$ -carboline, **2** (from left to right) H…N interactions, H…C interactions and C…C interactions.

## **Computational details**

(λ= 226 meV)

Optimized neutral form			Optimized cationic form				
С	0.24020	1.70750	5.05860	С	0.24170	1.70550	5.04730
Ν	0.90130	0.54540	4.98710	Ν	0.90440	0.54060	5.00660
С	1.19340	-0.00150	6.15920	С	1.17730	0.02780	6.18670
С	0.87420	0.52420	7.44260	С	0.85680	0.55650	7.45460
С	0.18650	1.73430	7.47320	С	0.16930	1.76570	7.47110
С	-0.13300	2.33130	6.25490	С	-0.13820	2.34100	6.23660
Ν	1.86710	-1.19060	6.32280	Ν	1.86190	-1.18140	6.37020
С	2.00270	-1.46920	7.67860	С	1.99500	-1.45260	7.68870
С	1.38950	-0.41020	8.41860	С	1.37490	-0.38240	8.43900
С	1.38260	-0.43360	9.81530	С	1.37540	-0.42100	9.81430
Н	-0.00660	2.16850	4.10680	Η	0.00380	2.15070	4.08790
Н	-0.66690	3.27290	6.22160	Η	-0.67180	3.28130	6.18740
Н	-0.09390	2.20210	8.41070	Η	-0.12090	2.25070	8.39540
Н	2.19770	-1.75470	5.55770	Н	2.19460	-1.74720	5.59920
С	3.75240	-4.69650	13.05080	С	3.75240	-4.69360	13.06210
Ν	3.09150	-3.53430	13.12230	Ν	3.08980	-3.52870	13.10280
С	2.80050	-2.98670	11.95030	С	2.81700	-3.01590	11.92270
С	3.12070	-3.51190	10.66680	С	3.13750	-3.54450	10.65480
С	3.80810	-4.72210	10.63610	С	3.82500	-4.75380	10.63830
С	4.12650	-5.31980	11.85440	С	4.13240	-5.32910	11.87280
Ν	2.12720	-1.79740	11.78660	Ν	2.13250	-1.80660	11.73920
С	1.99230	-1.51840	10.43080	С	1.99940	-1.53540	10.42070
С	2.60640	-2.57680	9.69080	С	2.61950	-2.60560	9.67040
С	2.61340	-2.55340	8.29420	С	2.61900	-2.56700	8.29510
Н	3.99830	-5.15810	14.00250	Η	3.99030	-5.13880	14.02150
Н	4.66020	-6.26150	11.88770	Η	4.66600	-6.26940	11.92200
Н	4.08940	-5.18930	9.69870	Η	4.11520	-5.23870	9.71400
Н	1.79580	-1.23380	12.55180	Н	1.79950	-1.24090	12.51010
Н	0.92130	0.36060	10.39080	Н	0.92250	0.35930	10.41400
Н	3.07250	-3.34890	7.71860	Н	3.07180	-3.34730	7.69550



Figure S9. AFM image of the polystyrene layer.



**Figure S10.** (Black) Transfer characteristic of the bottom gate top contact OFET (Si/SiO<sub>2</sub>/Polystyrene/Compound 2/MoO<sub>3</sub>/Au<sub>source & drain</sub>):  $\mu = 1.3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ,  $I_{\text{on/off}} = 10^2$  and  $V_{ON} = -24$  V; (Grey) Leakage current plot.