# Supporting Information

1.S. MIS device: Flat band voltage definition

In a MIS structure the flat band voltage $V_{FB}$, in the absence of fixed charge in the insulator or at the insulator/silicon interface, is generally expressed by[1S]:

$$V_{FB} = (\phi_m - \phi_s)/q \qquad (1)$$

where $\phi_m$ is the metal work function (going from $\phi_m$ = 5.1 eV, clean gold and 4.7 eV for contaminated gold 4.7 eV), $\phi_s$ is the semiconductor work function and q the *elementary charge* $q=1.6\ 10^{-19}$ C.[2S] Specifically, for a pSi, the work function $\phi_s$ is expressed by

$$\phi_s = \chi + E_g-(E_{FS} - E_V) = \chi + E_g/2+ kT\cdot\ln(N_a/n_i) \qquad (2)$$

with $E_g$ the silicon energy gap, $\chi$ the silicon electron affinity (4.01 eV), k the Boltzmann constant, T the absolute temperature, $N_a$ the p-type silicon dopant density (in our case $5x10^{15}$ $cm^{-3}$) and $n_i \sim 10^{10}$ $cm^{-3}$ the silicon intrinsic carrier density. It is noteworthy to observe that the resulting values of the flat band voltage for a pSi is generally negative. (see **Figure 1S**). When a dipole is present at a MIS interface the flat band voltage expression modifies as:

$$V_{FB} = (\phi_m - (\phi_s + \Delta\phi))/q \qquad (3)$$

where $\Delta\phi = qN (\mu_n/ \varepsilon_r \varepsilon_o)$ with, N the molecular layer surface coverage, $\mu_n$ the component of the dipole moment normal to the surface, $\varepsilon_r$ the molecular layer relative dielectric constant and $\varepsilon_o = 8.85x10^{-14}$ $Fcm^{-2}$ the vacuum dielectric permittivity. The dipole moment is conventionally defined as positive (negative) when pointing towards (outward) the Si surface.[3S] In the case of pSi, a positive dipole moment ($\mu_n$ >0) will add a contribution $\Delta\phi$ >0. Since $V_{FB} =(\phi_m - (\phi_s+\Delta\phi))/q$ this will correspond to an increase of the flat band voltage towards more negative values i.e. to a flat band voltage shift $\Delta V_{FB} = (- \Delta\phi/q)<0$ . As a consequence, the dipole effect is evidenced by a left shift of the capacitance vs voltage characteristics. Conversely, a negative dipole moment adds a contribution $\Delta\phi$ <0 which in turn decreases the flat band voltage value (i.e. $\Delta V_{FB} = (-\Delta\phi/q)>0$ ) with a corresponding right shift observed in the C-V curves

2.S. MIS device functioning regimes

The working conditions of a MIS device depend on the applied continuous voltage, $V_G$; basically, three typical bias voltage regions are considered (see Figure 1S): referring to a device on p-type semiconductor, the first region corresponds to $V_G$ lower (i.e. more negative) than the flat band voltage $V_{FB}$, the second is between $V_{FB}$ and a threshold voltage $V_T$ (termed as inversion threshold) and the third when $V_G$ is larger than $V_T$.

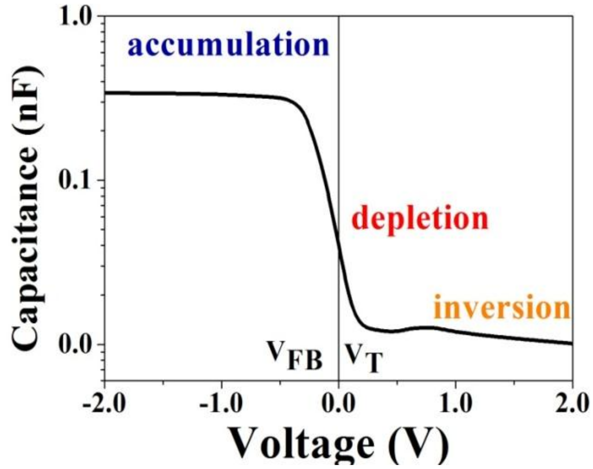



**Figure 1S.** Typical high frequency capacitance vs voltage response of a MIS structure on a p-type semiconductor and corresponding working conditions. Flat band and threshold voltages are indicated too.

The MIS device works, in the first case, under the so called *accumulation* condition, in the second, under *depletion* and in the third, under *inversion regime*.[1S] The corresponding value of the capacitance is defined using the same assumption of the working regime, therefore considering the MIS as the series of two capacitors, the depletion width capacitance ($C_d$) of the semiconductor and the insulator capacitance ($C_I$). Moreover, this MIS capacitance depends also on the frequency. In accumulation, there is no depletion layer, therefore the bias acts only on the insulating layer:

$$C_{HF} = C_{LF} = C_I \text{ for } V_G < V_{FB} \qquad (4)$$

It should be noticed that the condition $C_{HF} = C_{LF}$ holds if there is not frequency dispersion in the insulator dielectric constant. In depletion condition voltage drops across both the depletion layer and the insulator. Therefore:

$$C_{LF} = C_{HF} = \frac{1}{\frac{1}{C_I} + \frac{x_d}{\varepsilon_s}} \quad \text{for } V_{FB} < V_G < V_T \qquad (5)$$

where $x_d$ is the depletion layer width given by:

$$x_d = \sqrt{\frac{2\varepsilon_s V_s}{q N_a}} \qquad (6)$$

where $\varepsilon_s = 11.9$ is the silicon relative dielectric constant and $V_s$ is the potential drop across the depletion layer. In order to find the MIS capacitance corresponding to the applied voltage, $V_G$, it is necessary to know the relation between $V_s$ and $V_G$ given by:

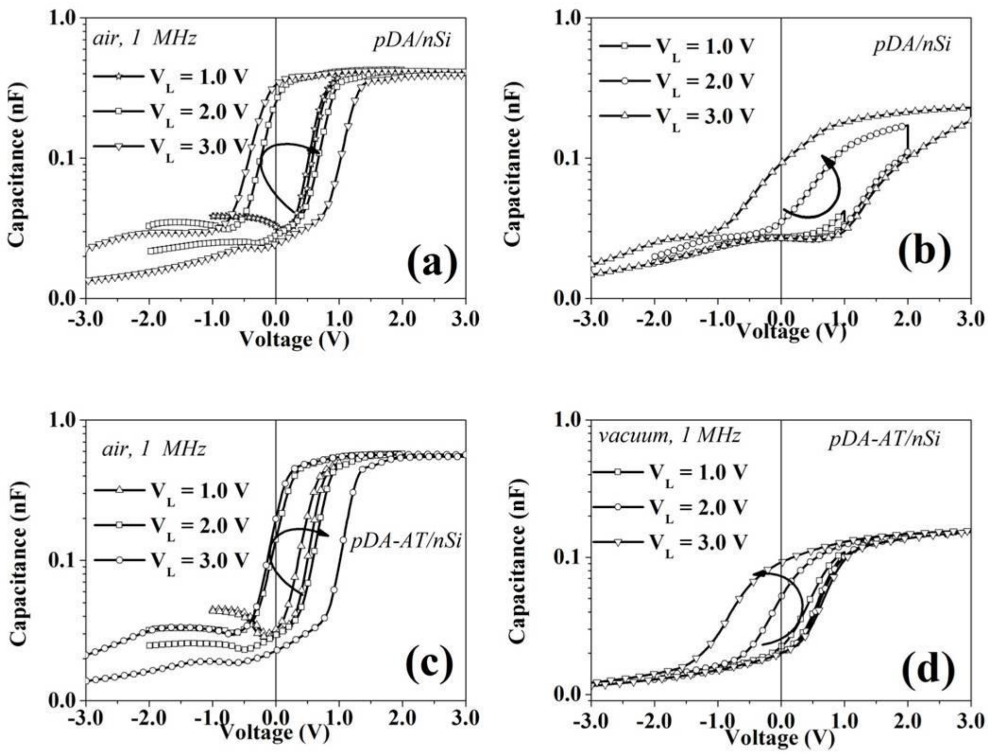
$$V_G = V_{FB} + Vs + \frac{\sqrt{2 \cdot \varepsilon_{s} \cdot \varepsilon_0 \cdot q \cdot N_a \cdot Vs}}{C_I} \qquad 0 \le V_s \le 2\phi_F, \quad (7)$$

with $\phi_F = \frac{kT}{q} \ln \frac{N_a}{n_i}$ the Fermi level displacement respect to semiconductor mid gap.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C


When the potential $V_s$ is equal to $2\phi_F$, $V_G = V_T$ the inversion regime starts, i.e. the Si surface becomes to have a n-type behavior rather than a p-type one. Such a behavior is enhanced as the flat band voltage is increased. In the inversion regime the capacitance of the depletion layer does not depend anymore on the applied bias, since the depletion width reaches its maximum extension. Therefore, at high frequency the MIS capacitance is the series of the insulator and of the depletion width capacitance at its minimum value $\frac{\varepsilon_s}{x_{d,T}}$ where $x_{d,T} = \sqrt{\frac{2\varepsilon_s(2\phi_F)}{qN_a}}$. At low frequency, the capacitance moves toward the insulator capacitance when the amount of the inversion layer charge overcomes the doping concentration of pSi.

**Figure 2S**. Comparative studies on pDA, pDA-AT structure on nSi by C-V hysteresis loops collected on under different environment conditions (air-vacuum) at a frequency of the AC signal fixed at 1 MHz.




3.S C-V results on comparative studies on nSi substrates.
In **Figure 2S** the results on the eumelanin based MIS structures on nSi have been shown. The voltage loop amplitudes have been varied from a minimum of $V_L$ = 1.0 V up to a maximum of $V_L$ = 3.0 V depending on the achievement of the flat band conditions and the closing of the hysteresis loop . In air the reversal of the hysteresis loops directions respect to those collected on structure on pSi has been observed, therefore confirming also in this case the ambipolar behavior of water traps. In vacuum, a pronounced behavior ascribed to the presence of a net mobile ion concentration has been evidenced. The observed reversal respect to pSi again confirms the presence of an ambipolar ion-drif mechanisms, similar to those observed in synthetic melanin [see ref.2, main text]

4.S. Preparation of pDA-AT copolymers.
A freshly prepared solution of dopamine (DA) hydrochloride in 1% $NH_3$ (50 mL) was rapidly mixed with a solution of 3-amino-L-tyrosine (AT) in 1% $NH_3$ (50 mL) at room temperature and was left under vigorous stirring. The solutions of the two monomers were prepared in order to keep constant the overall substrate concentration (10 mM) but vary the DA:AT ratio in the range 100% pDa- 100% AT. After 24 hours, the reaction mixture was diluted in water and the absorption spectrum was recorded. ATR spectra of pDA, pDA-AT and pDA-PD versus ammonium chloride

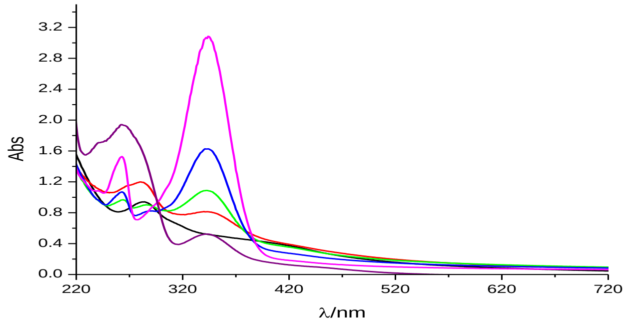



**Figure 3S** . UV-visible absorption spectra of pDA–AT copolymers in water at 1: 70 dilution . Samples were obtained as described above. pDA-PD 60:40 (—, magenta); 75:25 (—, blue); 85:15 (—, green), 95:5 (—, orange), pDa 100 (—, black); pAT 100 (—, violet).

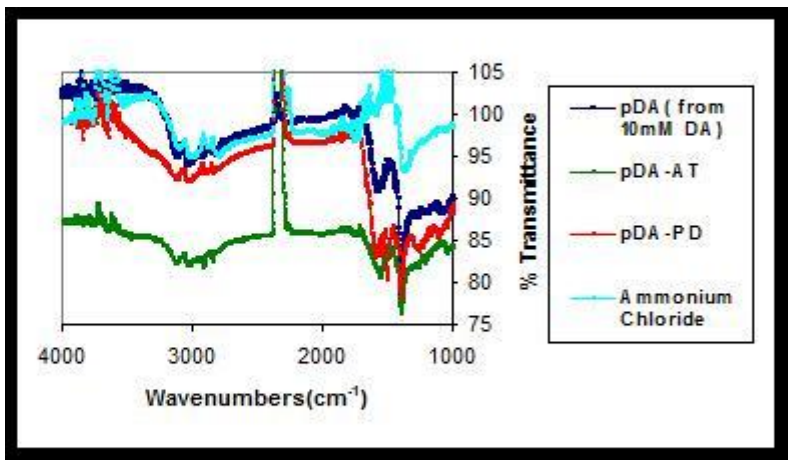



**Figure 4S.** ATR spectra of pDA, pDA-AT and pDA-PD versus ammonium chloride

### References

[1S] E.H. Nicollian, J.R. Brews, *MOS (Metal Oxide Semiconductor) Physics and Technology*, Wiley, New York **1981**.
[2S] A. Wan, J. Hwang, F. Amy, A. Kahn, *Organ. Electron.* **2005**, *6*, 47-54.
[3S] J.S. Park, B.R. Lee, J.M. Lee, J.-S. Kim, S.O. Kim, M.H. Song, *Appl. Phys. Lett.* **2010**, *96*, 243306.