SUPPORTING INFORMATION PARAGRAPH

CALCULATION OF THE ENERGY SHIFT The dipole moment between two sites 1 and 2 depends on the distance *d* between the sites and their charges:

$$D(t) = \frac{q_2(t) - q_1(t)}{2} d \tag{i}$$

where $q_1(t)$ and $q_2(t)$ are the charges at time *t* on site 1 and 2, respectively, and *d* the distance between site 1 and 2.

Therefore, the average dipole moment for an electron switching between site 1 and 2 is:

$$D = \langle D(t) \rangle = e\frac{d}{2}(P_1 - P_2) \tag{ii}$$

where *e* is the electron charge, P_1 and P_2 the probability that the electron is on site 1 or 2, respectively.

The Hamiltonian Ĥ for the transfer of an electron from site 1 to site 2 with the energy difference $\Delta e = 2E$ can be written by:

$$\hat{H} = \begin{pmatrix} E & \beta \\ \beta & -E \end{pmatrix} \tag{iii}$$

where β is the transfer integral between site 1 and 2.

The Eigen vectors are:

$$\begin{cases} |+\rangle = \sqrt{\frac{1}{2} - \frac{E}{\sqrt{E^2 + \beta^2}}}|1\rangle + \sqrt{\frac{1}{2} + \frac{E}{\sqrt{E^2 + \beta^2}}}|2\rangle = a|1\rangle + b|2\rangle \\ |-\rangle = \sqrt{\frac{1}{2} + \frac{E}{\sqrt{E^2 + \beta^2}}}|1\rangle - \sqrt{\frac{1}{2} - \frac{E}{\sqrt{E^2 + \beta^2}}}|2\rangle = b|1\rangle - a|2\rangle \end{cases} \tag{iv}$$

The average dipole moment results from equation *ii* and *iv*.

$$D = e\frac{d}{2}(P_1 - P_2) = e\frac{d}{2}(aa^* - bb^*) = \frac{e \cdot d \cdot E}{\sqrt{E^2 + \beta^2}} \tag{v}$$

where a^* and b^* are the conjugated values of a and b.

For the charge transfer through a SAM molecule at dielectric-pentacene interface, site 1 is the energy level of the defect on the dielectric surface and site 2 the *HOMO* level of pentacene. As distance between defect and pentacene molecule, the length of the SAM molecule is taken. Then the energy difference ΔE_{SAM} in the SAM molecule due to the dipole moment is calculated by using equation *v*:

$$\Delta E_{SAM} = 2E = \frac{-2D\beta}{|e|L \cdot \sqrt{1-\left(\frac{-D}{|e|L}\right)^2}} \qquad \text{(vi)}$$

where D is the dipole moment in the SAM molecule, L the length of the SAM molecule and e the electron charge.