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Supporting information

Probing Charge Transfer Dynamics in a Single Iron Tetraphenylporphyrin Dyad Adsorbed on an Insulating Surface

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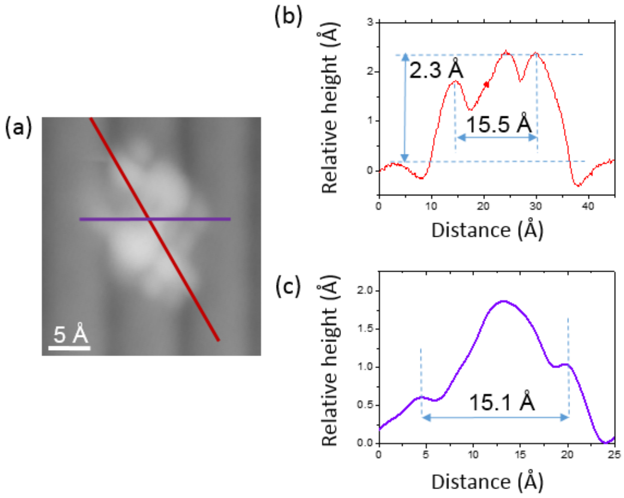

Figure S1: (a) STM topography (V_s = -2.2 V, 5 pA) of a Fe-TPP molecule in a CR conformation. (b) and (d) apparent height profiles of the Fe-TPP molecule along two different lines reported in (a) in red and purple.

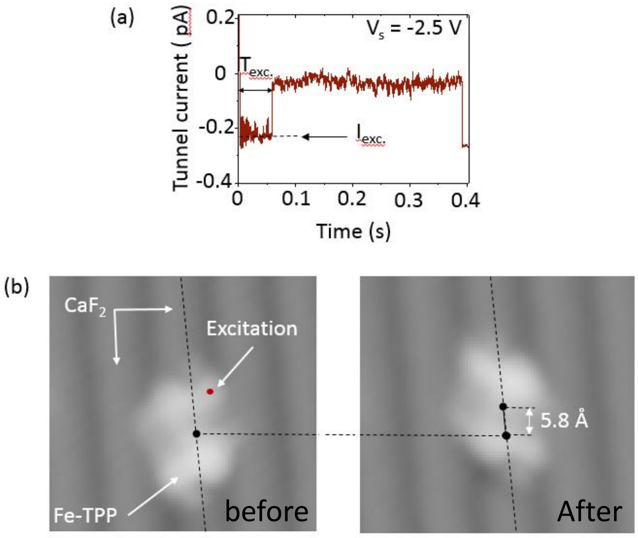

Figure S2: (a) Example of tunnel current trace recorded during the excitation procedure to move one single Fe-TPP molecule (b) and (c) STM topographies (V_s = -2.2 V, 5 pA, same area) before (left) and after the excitation (red dot) of a single Fe-TPP molecule. The movement of the molecule is detailed by reporting the vertical motion distance of ~ 5.8 Å.

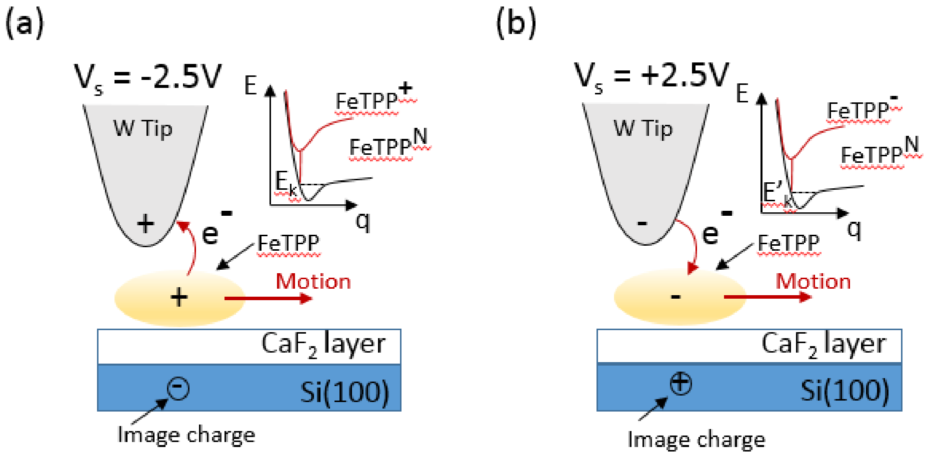

Figure S3: (a) and (b) sketches describing the processes responsible of the single molecule motion for negative (a) or positive biases (b).

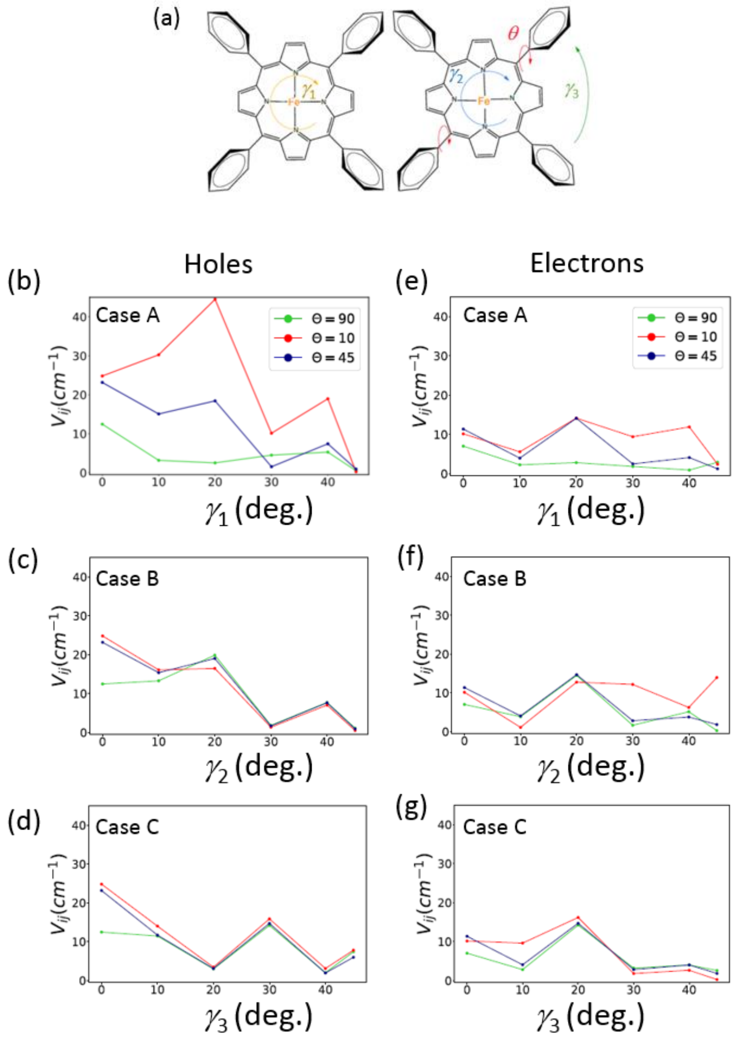

Figure S4: (a) sketch of two Fe-TPP molecules and the corresponding defined angles. (b) to (g) Variations of the electronic coupling parameter V_{ij} for the three detailed cases (see note) as a function of the angles γ_1, γ_2 and γ_3 for a set of three values of $\theta = 10$, 45 and 90 °. The V_{ij} values for holes (b)-(d) takes into account the HOMO orbitals of the fragments of the dyad while the V_{ij} values for electrons (e)-(g) concerns the LUMO+1 and LUMO+2. The LUMO orbital being strongly located at the iron atom they are disregarded for these simulations.

Figure S4 note: In the first case (case A), the rotation (γ_1) is applied on the left (donor) monomer with respect to its center. The second case (case B) explore the variations of V_{ij} as a function of a rotation around γ_2 of the right (acceptor) monomer with respect to its center. Finally, the case C corresponds to the rotation of the acceptor monomer with respect to the center of the supramolecular system (*i.e.* the origin located at the donor monomer). In all the three cases, the angles γ_{1-3} varies from 0° to 45°. In addition, three conformations of the acceptor Fe-TPP were additionally considered. Each of them is related to the rotation of two opposite benzene substituents the porphyrin ring (the θ angles are: 10°, 45° and 90°). These rotations are chosen for the simulations to resemble as closely as possible the experimental setup.

We see that the highest coupling for hole transfer can be found at values of γ between 0 and 20° in any of the three conformations of the angle θ. For conformations with γ at 30° and 45°, the

HOMO or LUMO+1, 2 overlap are reduced. Therefore, the coupling decreases dramatically and a lower transfer rate is expected for those configurations. Interestingly for γ values of 40 and 20°, the coupling is not negligible and charge transfer becomes a possibility mediated by the phenyl ligands especially when $\gamma = 40$ °. As the acceptor porphyrin is rotated with respect to γ, and the phenyl ring rotated, higher overlap between the fragment orbitals is achieved. Specifically, when γ is 0 and 10 ° the two rings are aligned and their separation is optimal, which peaks the hole transfer coupling.

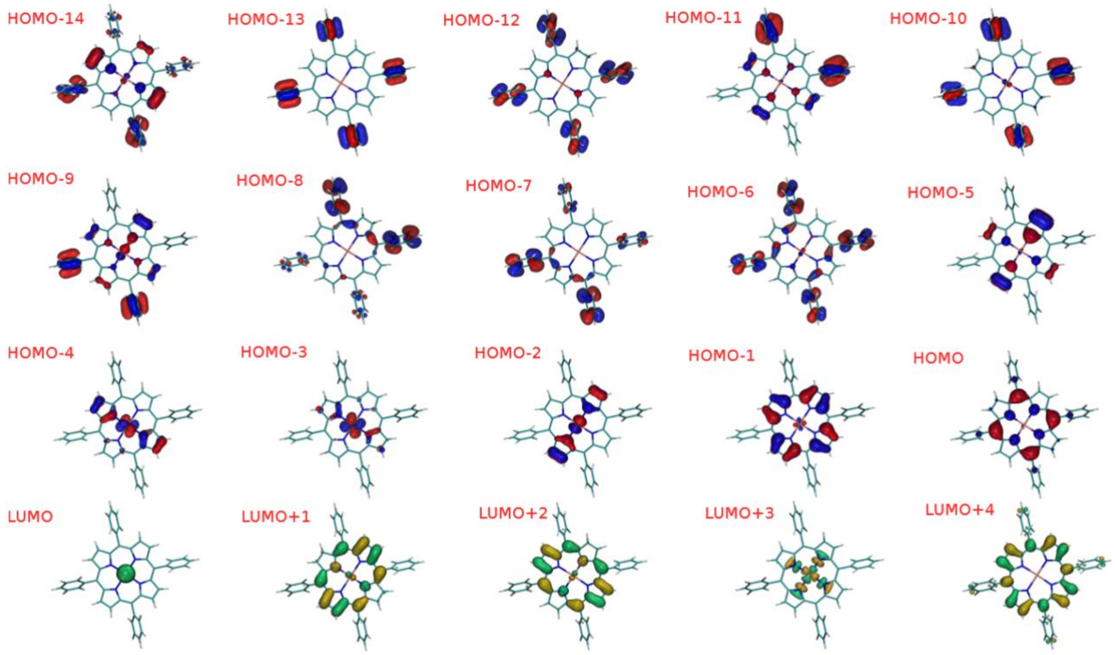

Figure S5: Plots of the calculated orbitals of a Fe-TPP in gas phase (no rotations of the aryl groups) for the fourteen first HOMO and the four first LUMOs orbitals.

Note S5: The measured yield $Y_{CL\rightarrow CRd}$ for the CL → CR_{down} movement of a single FeTPP molecule is provided in Fig. 2b and is optimized for the excitation points 2 and 3. This yield worth in average $Y_{CL\rightarrow CRd} = 2.9 \times 10^{-7}$. This quantity can be compared to the yield measured to move the acceptor when the donor is excited which can be considered as a succession of two sequential processes: the probability to induce the CT between fragments followed by the probability to trigger a molecular motion of the acceptor molecule (i.e. $Y_{CT+move}$). Therefore, the ratio $Y_{CT+move} / Y_{CL\rightarrow CRd}$ can be considered as similar to the ratio of each particular subsequent process life time (i.e. $Y_{CT+move} / Y_{CL\rightarrow CRd} \sim 0.3$ to 0.7). Hence, if we consider that the life time for a physisorbed FeTPP molecule to move from the CL → CR_{down} configuration is ~ 1 to 10 ps[1], then the life time of the CT process can be estimated ~ 0.3 to 7 ps. These values are coherent with our theoretical estimation.

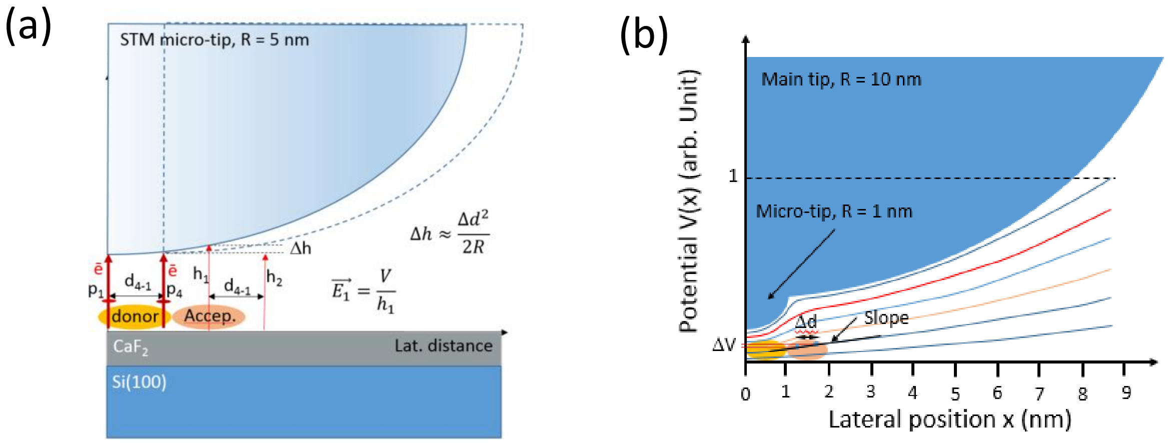

Figure S6: Estimation of the variation of the electrostatic field at the acceptor molecule when the STM tip excites the donor at four various locations. (a) Estimation of the variation of filed **E** = V/h at two different positions p_1 and p_4 separated by *Δd* for a STM tip radius R = 50 nm and a micro-tip radius R=5 nm. (b) Estimation of the variation of the potential V(x) calculated by solving the Poisson equation with a STM tip radius R = 10 nm and a micro-tip radius R = 1 nm while the STM-tip shifts of a distance *Δd*.

Figure S6 note: The variation of the electrostatic field over the molecular dyad can be estimated in a worst case via two methods:

(a) For an STM tip having a radius of curvature ~ 50 nm and a micro tip of ~5 nm (Figure S6a), the absolute variation of the electrostatic field is related to the variation of height Δh between the two positions at point 5 and point 8 (i.e. the two most distant excitation points). Considering a weak gradient at this location, the filed can be considered as linear in the STM junction and the ratio of the two vectors $\mathbf{E_1}/\mathbf{E_2}$ is :

$$\frac{\vec{E_1}}{\vec{E_2}} = \frac{V}{h_1} \Big/ \frac{V}{h_2} = \frac{h_2}{h_1} = \frac{(h_1 - \Delta h)}{h_1} = 1 - \frac{\Delta h}{h_1}$$

While $\Delta h = h_2 - h_1$ is :

$$\Delta h \approx \frac{\Delta d^2}{2R}$$

For a tip – surface distance h_1 = 1.5 nm, R = 5 nm, Δd = $d_{1\text{-}4}$ = 0.9 nm and a bias V = 2.5 V, $\mathbf{E_1}/\mathbf{E_2}$ = 0.947. Hence, the variation of electrostatic filed at the acceptor when the tip moves from point 1 to point 4 is ~ 5 % (Figure 1a below). While the sole presence of the electrostatic field is not ruling alone the dynamics of the acceptor molecule motion, this small variation of electrostatic field within one molecule of the dyad cannot explain our finding while the highest variation of CT yield (30 %) is observed between the two nearest points p_1 and p_4 for which $d_{4\text{-}3}$ = 0.5 nm leading to $\mathbf{E_1}/\mathbf{E_2}$ = 0.983 (i.e. variation less than 2 %).

(b) Another method that confirm this trend consist in computing the variation of the potential in the STM junction by using the SEMITIP code written by R. Feenstra[2]. The result of this calculation that takes into account the electronic properties of the surface (degenerated dopant concentration) presented in Figure 1b with an even worse case (R_{tip} = 10 nm and $R_{micro\ tip}$ = 1 nm) show that the variation of the potential V(x) between the two considered points separated by Δd ~ 0.9 nm is very weakly changing, leading to an identical slopes (**E** = **- Grad** (V)). Hence $\mathbf{E_1} \sim \mathbf{E_2}$.

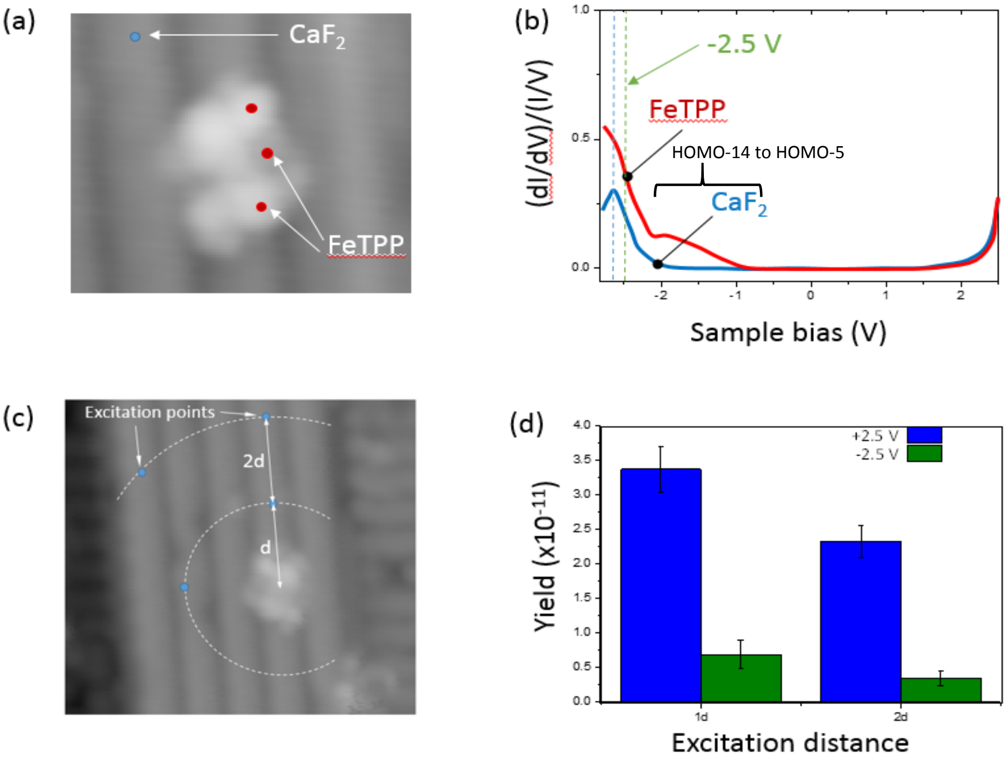

Figure S7: (a) (38.5 x 38.5 $Å^2$) STM topography (V_s = -2.2 V, 5 pA) of a single Fe-TPP molecule in the CL conformation. The blue and red dots indicate where the dI/dV curves have been acquired. (b) Averaged normalized (dI/dV)/(I/V) curves acquired on the CaF_2 insulating layer (blue) and on the molecule (red). The excitation bias is reported (green dot line) as well as a low lying energy surface state in the valance band of the surface (blue doted line). (c) (77 x 77 $Å^2$) STM topography (V_s = -2.2 V, 11 pA) of a ribbon of insulating stripes of CaF_2 surrounded by silicon. The Fe-TPP molecule that is adsorbed on it can be moved when the STM tip located at various points on the circles (white dashed) excites the surface at a distance d or 2d from the center of the molecule. (d) Evolution of the quantum yield to move a single Fe-TPP molecule as describe in (c) for the 2 distances d and 2d.

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[1] National Research Council. 2003. Beyond the Molecular Frontier: Challenges for Chemistry and Chemical Engineering. Washington, DC: The National Academies Press. https://doi.org/10.17226/10633.

[2] This code can be found at http://www.andrew.cmu.edu/user/feenstra/semitip_v3/