Nanoconfined self-assembly on a grafted graphitic surface under electrochemical control

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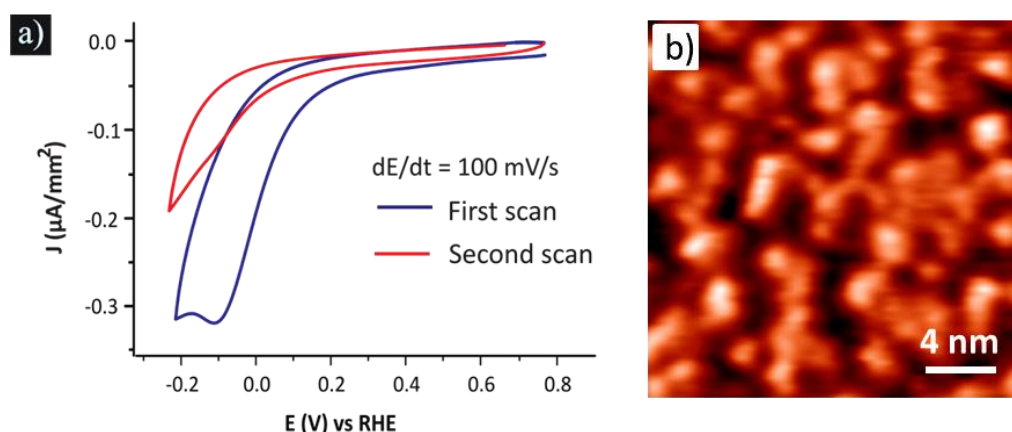
Figure S1: a) First two voltammetric cycles of HOPG in 2 mM 3,5-TBD + 50 mM HCl. The first scan (blue trace) shows an irreversible reduction peak at E = -96 mV vs RHE. This peak is assigned to the reduction of the 3,5-TBD cations forming the corresponding radicals that immediately graft to the graphitic surface.[1] The second cycle (red trace) however, displays a featureless curve in the same potential regime. The disappearance of the well-defined reduction peak in the subsequent cycle is the result of the formation of a non-conductive grafted film at the interface that inhibits the electron transfer from the electrode surface to the 3,5-TBD cations; b) High resolution EC-STM images of HOPG surface covalently grafted by 3,5-TBD, substrate potential E = +147 mV vs RHE, U_b = -179 mV, I_t = 0.2 nA.
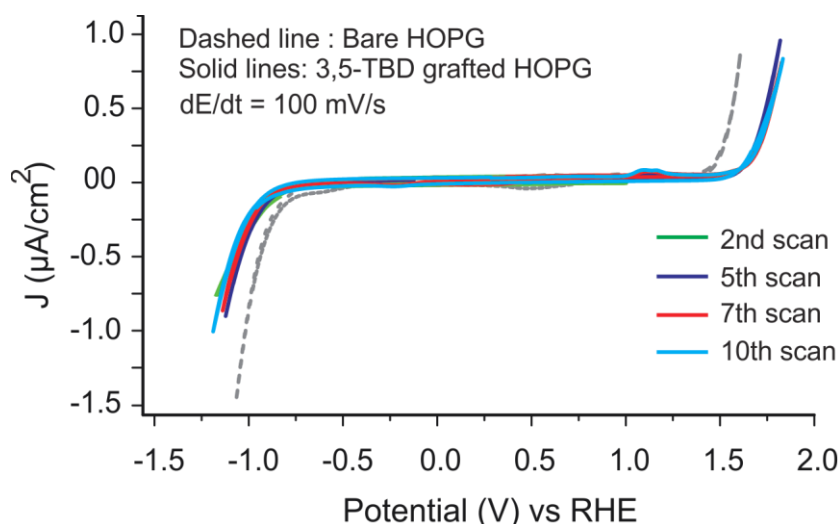

Figure S2: Multiple CV cycling on 3,5-TBD grafted HOPG showing the consistency of the onset of both OER and HER.
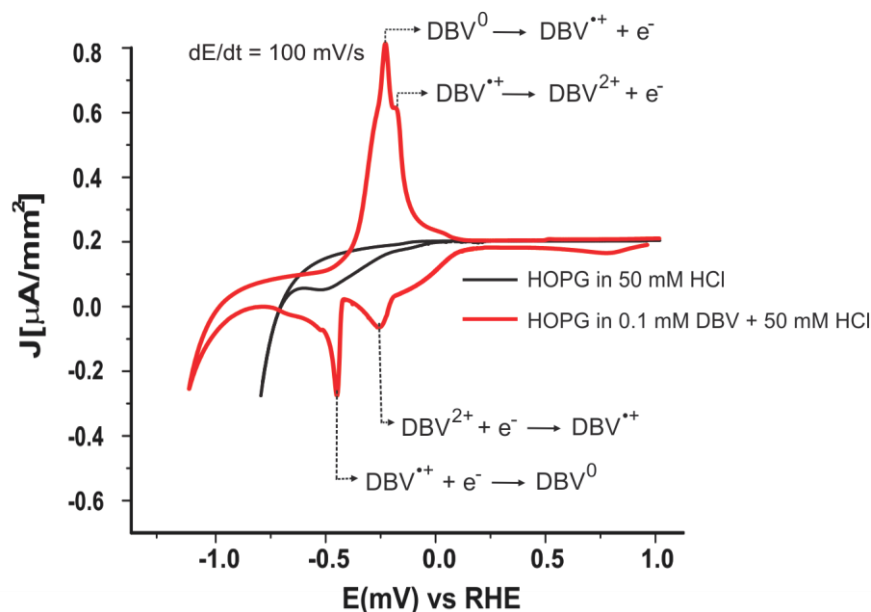
Figure S3: CVs of HOPG electrode in contact with 50 mM HCl (black curve) and 0.1 mM DBV + 50 mM HCl (red curve). The presence of DBV molecules leads to the appearance of two reduction peaks at E_1 = -280 mV and E_2 = -450 mV vs RHE that are assigned to the stepwise reduction from dicationic DBV^{2+} to the corresponding radical monocationic $DBV^{\bullet+}$ and uncharged DBV^0 species, respectively.
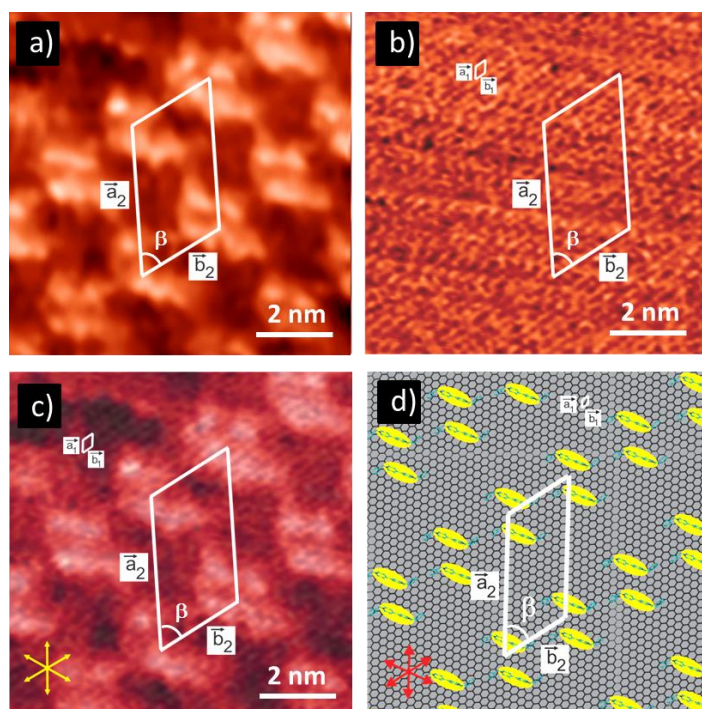

Figure S4: Structural correlation between the $DBV^{\bullet+}$ layer in the dimer phase and the underlying HOPG lattice; a) ECSTM image of the molecule covered HOPG: E = -340 mV, U_b = +200 mV, I_t = 0.1 nA; b) HOPG lattice underneath after the removal of the molecule: E = -340 mV vs RHE, U_b = +10 mV, I_t = 2.0 nA; c) superposition of panels a and b; d) tentative model of the dimer phase forming on hexagonal HOPG surface including the unit cell is proposed with the lattice constants of $|\vec{a_2}| = 2.6 \pm 0.4\ nm$ and $|\vec{b_2}| = 1.6 \pm 0.4\ nm$, respectively, enclosing an angle of $\beta = 60 \pm 4^0$.
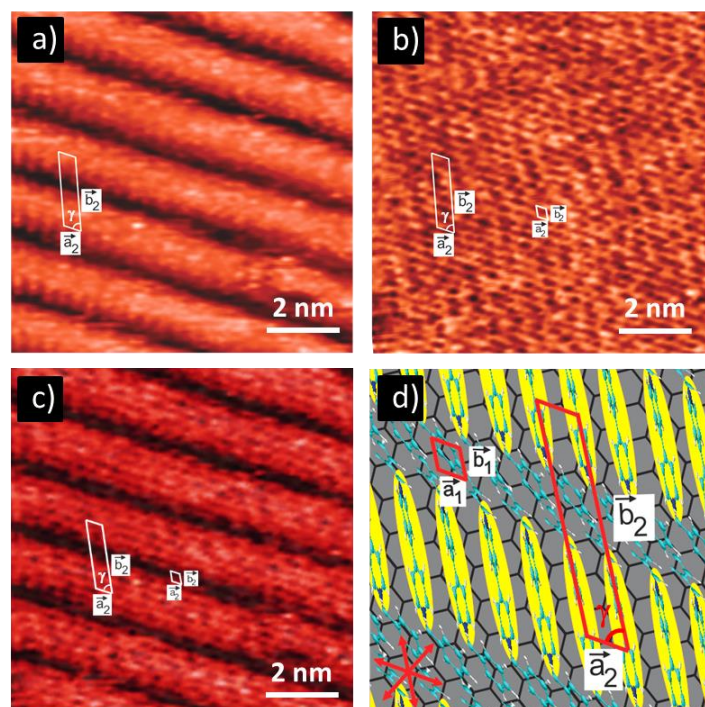
Figure S5: Structural correlation between the DBV^0 layer in the stacking phase and the underlying HOPG lattice, a) EC-STM image of the molecule covered HOPG: E = -510 mV vs RHE, U_b = +350 mV, I_t = 0.2 nA; b) EC-STM image of the HOPG lattice underneath after the removal of the molecule: E = -510 mV vs RHE, U_b = +20 mV, I_t = 1.8 nA; c) superposition of panels a and b; d) tentative model of the stacking phase forming on hexagonal HOPG surface. The unit cell of the DBV^0 adlayer is proposed with the lattice constants of $|\vec{a_2}| = 0.6 \pm 0.4\ nm$ and $|\vec{b_2}| = 2.5 \pm 0.4\ nm$, respectively, enclosing an angle of $\gamma = 59 \pm 4^0$
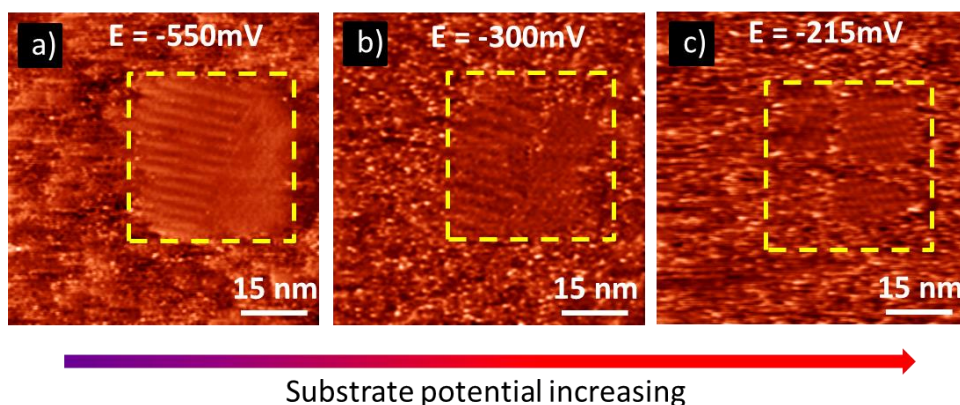

Substrate potential increasing

Figure S6: Dynamics of phase transition from the stacking phase to the dimer phase within nanocorrals: U_b = +120mV, I_t = 0.2 nA
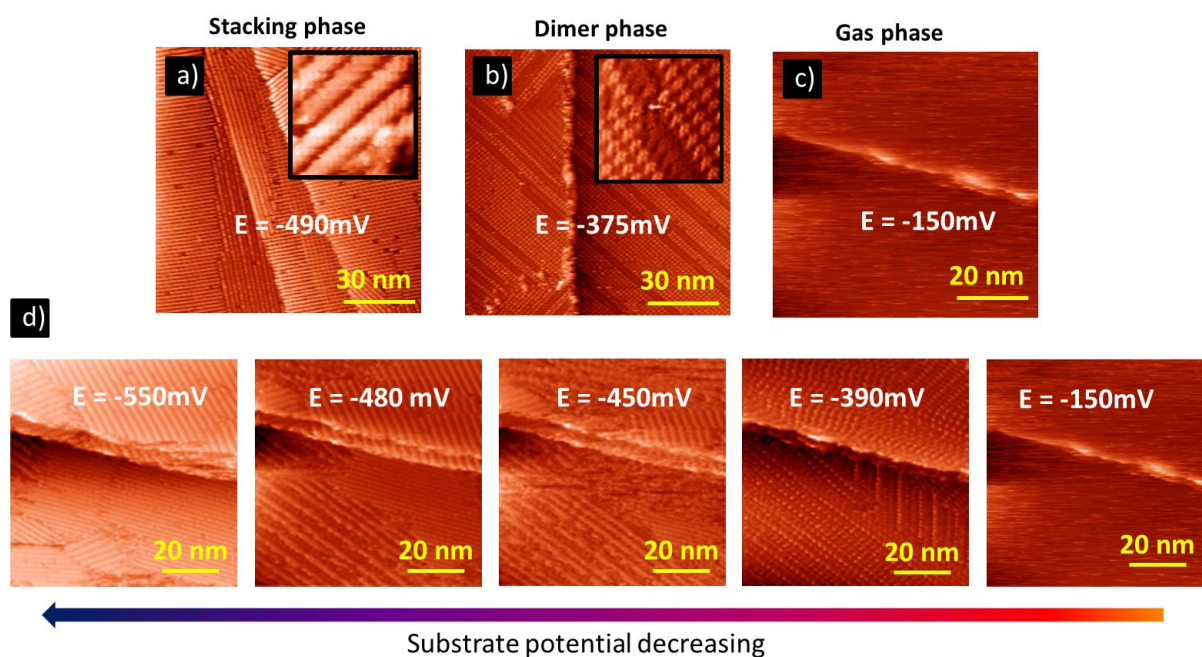
Figure S7: EC-STM images of (a) stacking phase, (b) dimer phase and (c) gas phase forming on bare HOPG at different electrode potentials indicated in the figures: U_b = +150 mV, I_t = 0.1 nA; c) dynamics of phase transition; the gas phase - the dimer phase - the stacking phase: U_b = +175mV, I_t = 0.1 nA.

References

1.   J. Greenwood, T. H. Phan, Y. Fujita, Z. Li, O. Ivasenko, W. Vanderlinden, H. Van Gorp, W. Frederickx, G. Lu, K. Tahara, Y. Tobe, H. Uji-i, S. F. L. Mertens and S. De Feyter, *ACS Nano*, 2015, **9**, 5520-5535.