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Supporting Information

Driving Organic Nanocrystals Dissolution Through Electrochemistry

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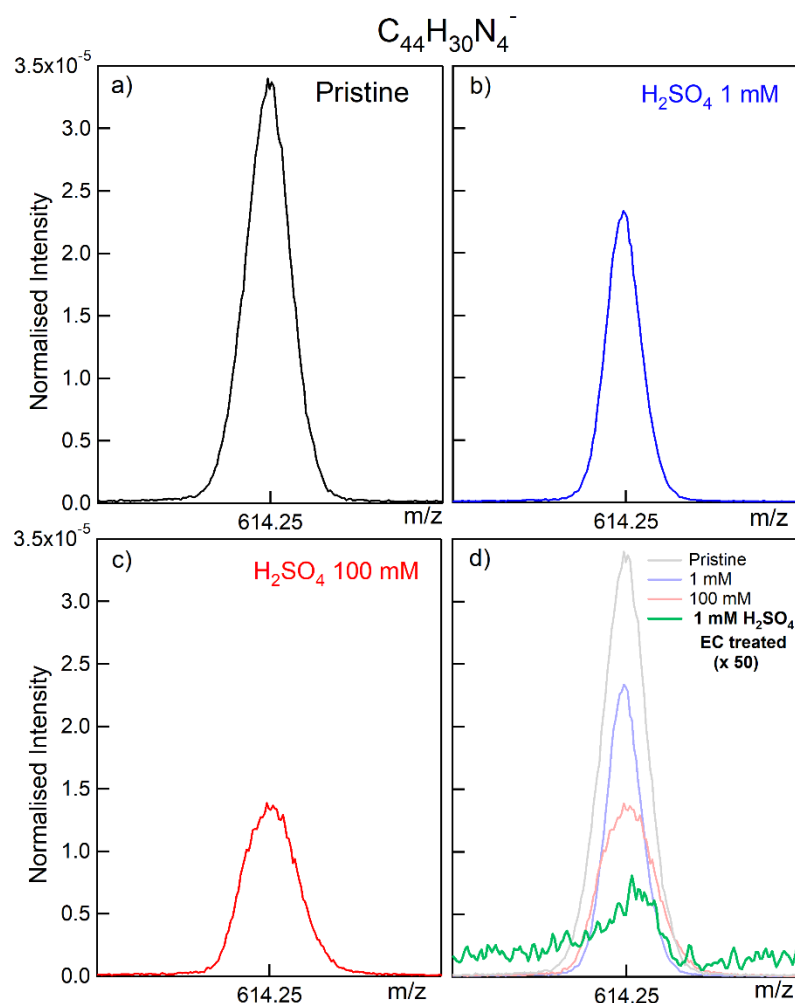


Figure S1. Normalized ToF-SIMS peaks intensity of $C_{44}H_{30}N_4^-$ ($m/z = 614.25$) ion from pristine H_2 TPP/HOPG electrode (panel *a*), H_2 TPP/HOPG electrode immersed in 1 mM and 100 mM H_2SO_4 electrolyte (panels *b* and *c*, respectively), and from H_2 TPP/HOPG electrode after ten subsequent CVs in 1 mM H_2SO_4 electrolyte (green line in panel *d*) compared with the peaks of pristine and immersed samples.

ToF-SIMS experiments were conducted on the as grown H_2 TPP film on HOPG substrate, H_2 TPP/HOPG electrode immersed in 1 mM and 100 mM H_2SO_4 solutions, and H_2 TPP/HOPG electrode after tens of subsequent CVs in 1 mM H_2SO_4 electrolyte. Secondary ions from the H_2 TPP fragmentation process were collected for the four samples. We monitored the intensity evolution of two representative ion peaks of the porphyrin macrocycle ($C_{44}H_{30}N_4^-$ at 614.25 m/z and $C_9H_5N_2^-$ at m/z 141.05), in order to further illustrate the changes in the surface chemistry of the samples. The plots in **Figure S1(a-c)** show the normalized signal intensity of the H_2 TPP molecular ion peak

($C_{44}H_{30}N_4^-$) of the as grown sample, the electrode immersed in the 1 mM H_2SO_4 solution, where etch pits have been observed, and the sample characterized by bulges (immersed in 100 mM H_2SO_4 solution), respectively^[1]. The signal intensity drops together with the increase of the acid concentration, as previously observed^[1]. The decrease of the $C_{44}H_{30}N_4^-$ signal intensity could suggest the degradation of the H_2TPP macrocycle. The $C_{44}H_{30}N_4^-$ peak of the electrochemically treated sample is reported in Figure S1*d* (green line). In this latter case, the $C_{44}H_{30}N_4^-$ normalized intensity is very low. Compared to the pristine and immersed samples, the secondary ion from the whole porphyrin molecule seems to be almost absent. This result could suggest that the EC treatment in 1 mM H_2SO_4 solution has a much more destructive effect on the $H_2TPP/HOPG$ sample surface than simple immersion in the acid solution with the same concentration (1 mM) and also with the higher one (100 mM).

In **Figure S2**, the normalized intensity of the $C_9H_{30}N_4^-$ ion peaks, probably coming from the fragmentation of two pyrrole units of the tetrapyrrolic macrocycle, are shown. The changes in $C_9H_{30}N_4^-$ ion peak intensity among the pristine, immersed, and EC treated samples follow substantially the same behavior of the H_2TPP molecular ion peak. Starting from the pristine sample, the gradual decrease in intensity, increasing the acid concentration, is still appreciable in Figure S2(*a-c*). In Figure S2*d*, the $C_9H_{30}N_4^-$ ion low intensity confirms the more aggressive action of the EC routine on the $H_2TPP/HOPG$ sample surface, compared to that of the simple immersion.

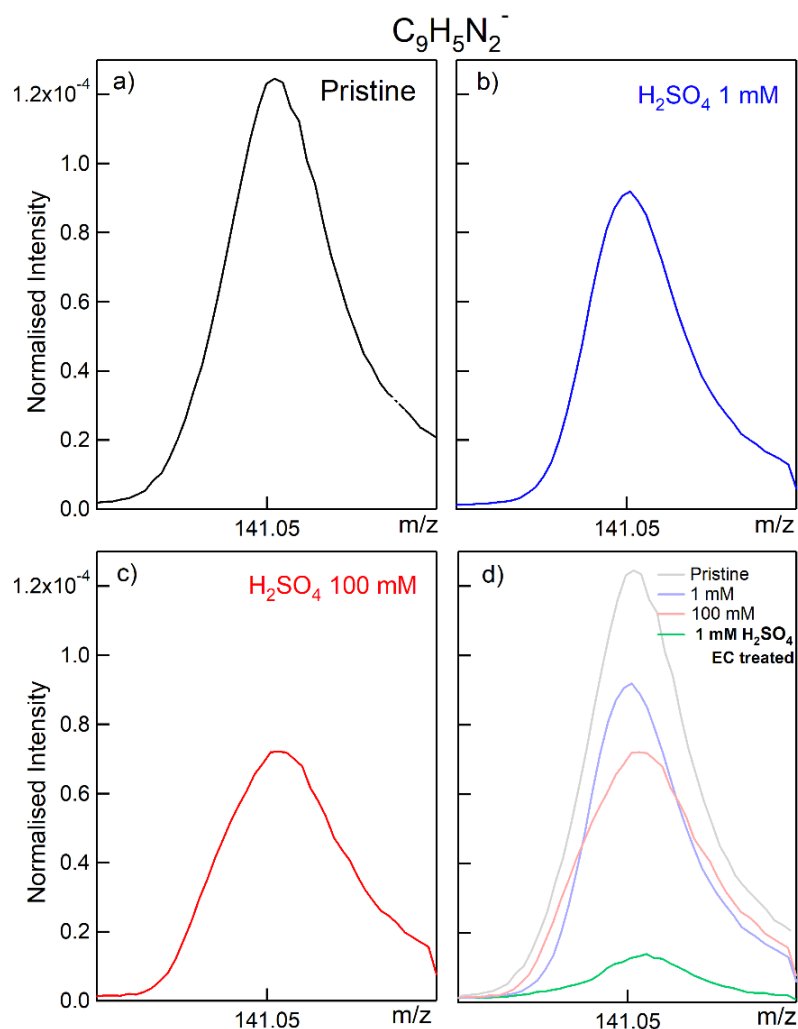


Figure S2. Normalized ToF-SIMS peak intensity of $C_9H_5N_2^-$ ($m/z = 141.05$) ion from pristine H_2 TPP/HOPG sample (panel *a*), H_2 TPP/HOPG sample immersed in 1 mM and 100 mM H_2SO_4 electrolyte (panels *b* and *c*, respectively), and from H_2 TPP/HOPG sample after ten subsequent CVs in 1 mM H_2SO_4 electrolyte (green line in panel *d*) compared with the peaks of pristine and immersed samples.

References

C. Filoni, L. Duò, F. Ciccacci, A. Li Bassi, A. Bossi, M. Campione, G. Capitani, I. Denti, M. Tommasini, C. Castiglioni, S. De Rosa, L. Tortora, G. Bussetti, *Chem. NanoMat.*, **2020**, 6, 567.