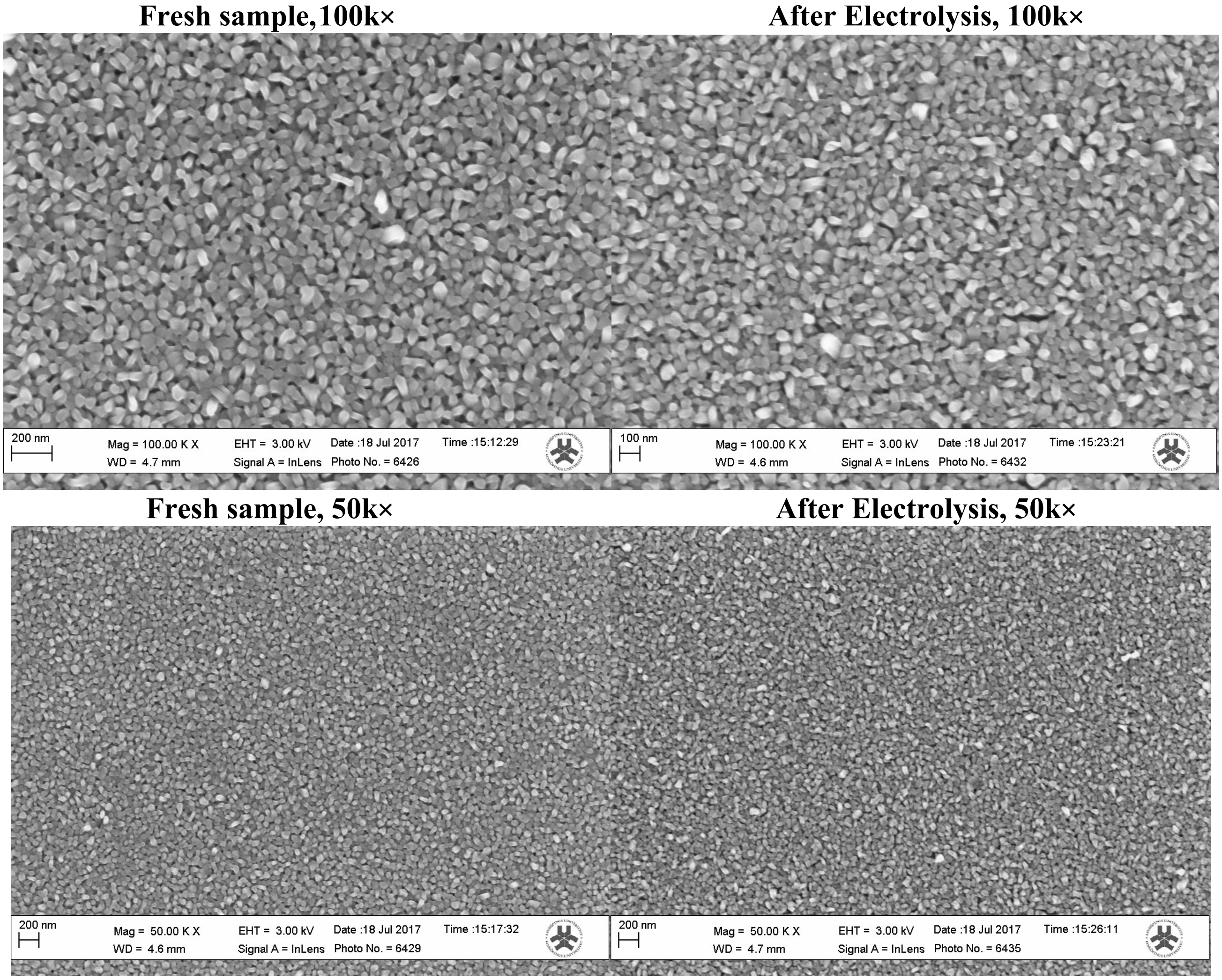
ESI for:

Organic semiconductor Perylenetetracarboxylic diimide (PTCDI) electrodes for electrocatalytic reduction of oxygen to hydrogen peroxide



Fresh sample,100k×

After Electrolysis, 100k×

Fresh sample, 50k×

After Electrolysis, 50k×

Fig. S1. SEM images of PTCDI layers (100 nm thickness) on gold electrodes. Gold with a thickness of 50 nm was evaporated, using a 2-nm sticking layer of chromium, onto cleaned Si wafers with 1 µm of thermal oxide. Here the same electrode is measured before and after running in the oxygen-to-peroxide galvanostatic electrolysis experiment with a current density of 0.5 mA/cm^2 for 100 hours. No obvious morphological changes were visible, evidencing stability of the PTCDI layers.

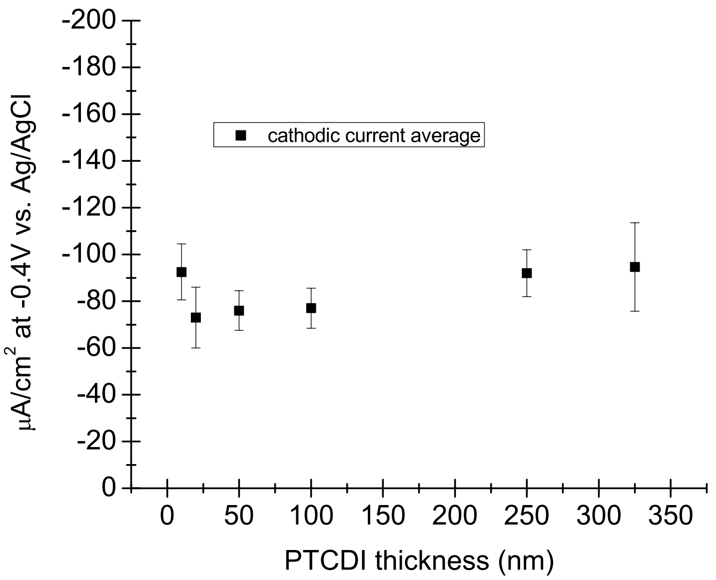


Fig. S2. Average cathodic current density at -400 mV versus Ag/AgCl during CV of PTCDI in pH 1 electrolyte (H_2SO_4) under ambient conditions, for samples of varying PTCDI thickness. Error bars represent one standard deviation.

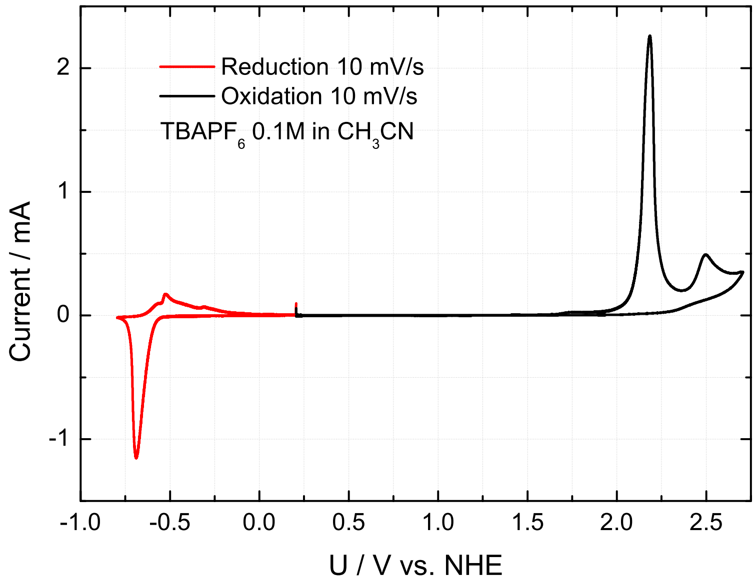


Fig. S3.CV of PTCDI/Au in 0.1M $TBAPF_6/CH_3CN$, 10 mV/s scan rate.

In order to estimate the HOMO and LUMO energy levels (in other words, valence and conduction band edges, respectively) of PTCDI we performed cyclic voltammetry measurements on Au/PTCDI in oxygen and water-free conditions using 0.1M tetrabutylammonium tetrafluorophosphate in CH_3CN in an N_2-filled glove box. Scan rate 10 mV/s. Reduction and oxidation scans were recorded separately on fresh samples.

Frontier molecular orbital energy level estimations were calculated according to formula given by Baran *et al., Chem. Mater. 2010, 22, pp.2978-2987*, are HOMO: -6.72 eV and LUMO: -3.9 eV respectively, and the electrochemical band gap E_g from CV is 2.82 eV.

$$\mathbf{E_{HOMO} = -(E_{onset,\ ox\ vs.\ NHE} + 4.75)(eV);\quad E_{onset,\ ox\ vs.\ NHE} = 1.97\ V\ ;\quad E_{HOMO} = -6.72\ eV}$$

$$\mathbf{E_{LUMO} = -(E_{onset,\ red\ vs.\ NHE} + 4.75)(eV);\quad E_{onset,\ red\ vs.\ NHE} = -0.6\ V\ ;\quad E_{LUMO} = -\ 3.9\ eV}$$

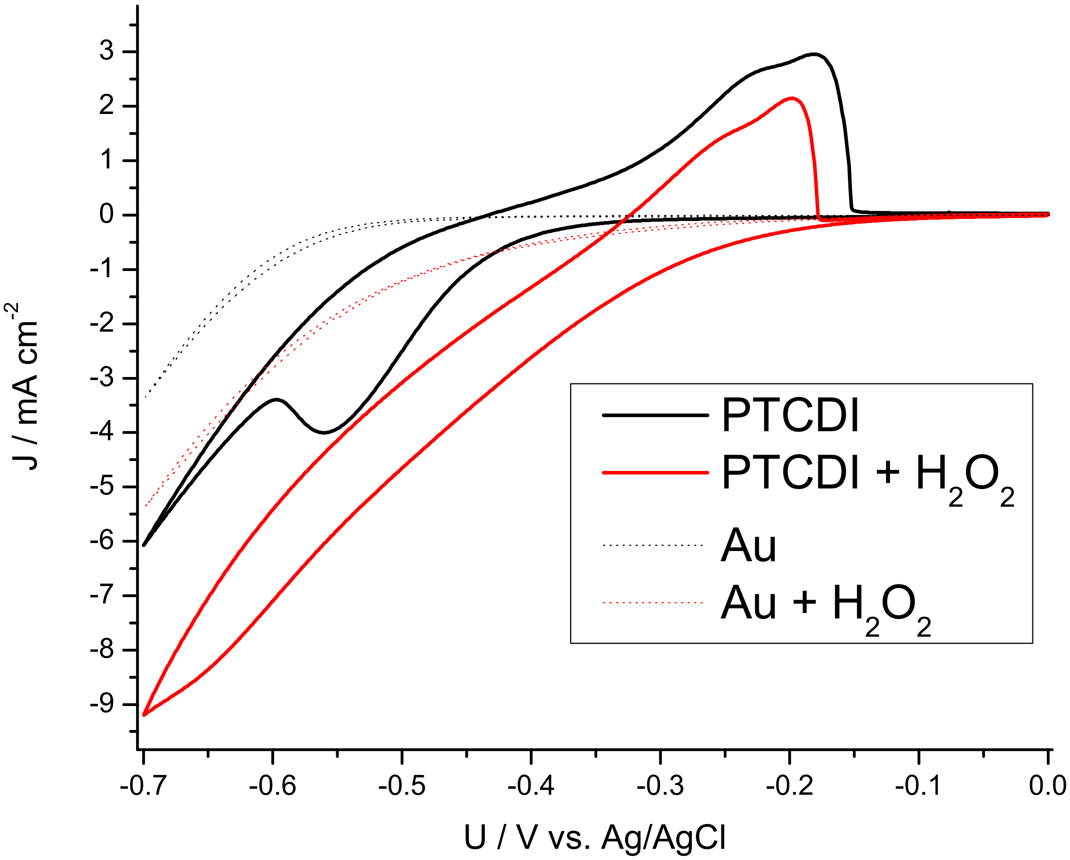


Fig. S4. CV of PTCDI/Au in thoroughly deoxygenated (under argon) in pH 1 electrolyte and with the addition of 0.1M H_2O_2. For reference, the measurements are compared with a bare gold electrode. The cathodic reaction on PTCDI at potentials more negative than roughly -0.4V is the hydrogen evolution reaction (black scan). This scan was cycled 10 times without any observed changes or degradation. With the addition of H_2O_2, a substantial cathodic current is observed, with a lower onset potential (red scan). Corresponding measurements on bare Au are shown in dotted lines, as a reference/control. Clearly, the further reduction of H_2O_2 remains an issue with PTCDI and limits obtaining higher equilibrium H_2O_2 concentrations in the galvanostatic electrolysis experiments.

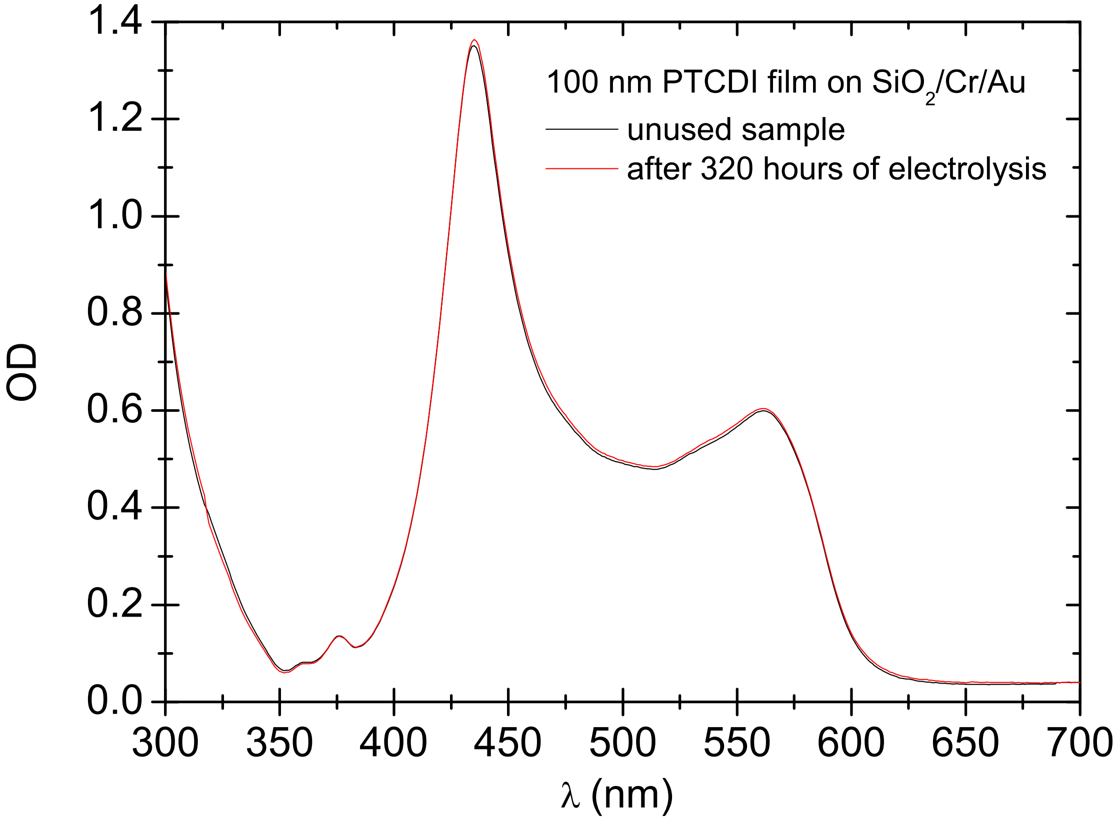


Fig. S5. UV-Vis reflectance measurement of a 100 nm PTCDI film on SiO$_2$/Cr/Au before and after 320 hours of electrolysis. The lack of changes in the absorbance spectra evidences stability of the PTCDI layer.