SUPPLEMENTARY INFORMATION
Organic photoelectrochemical cells with quantitative photocarrier conversion

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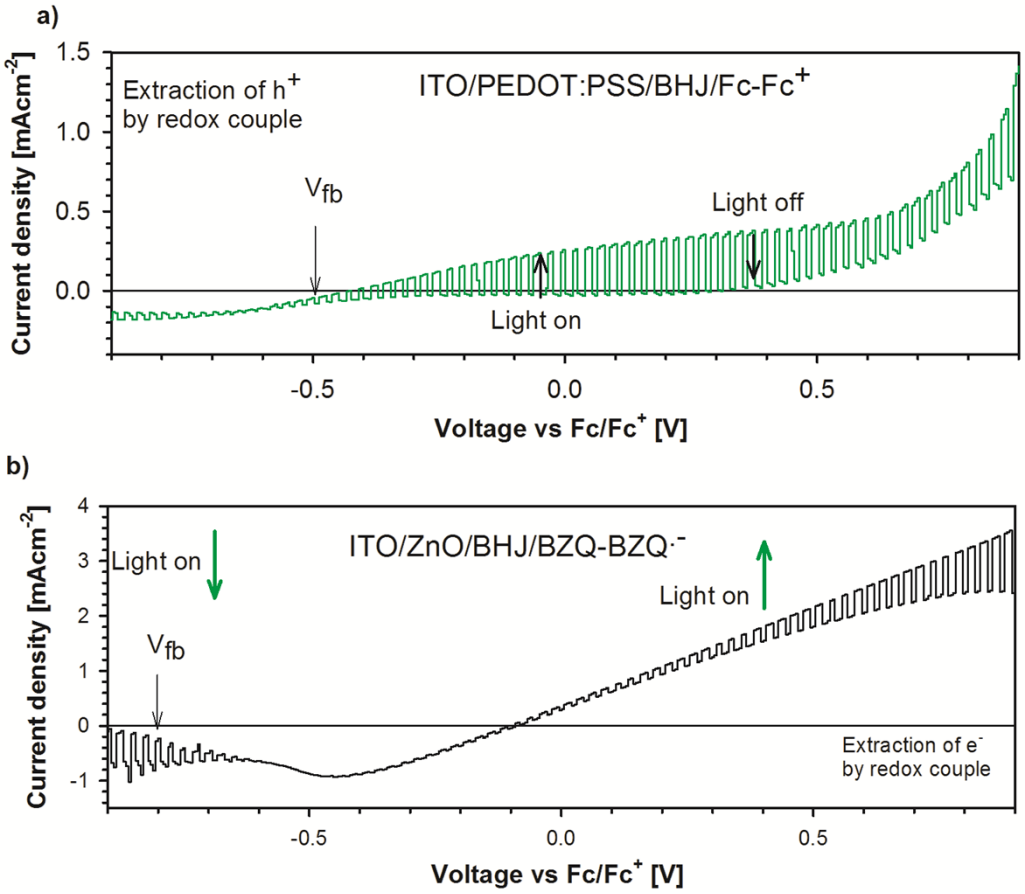
S1.- Additional ITO/IFL/BHJ/redox couple configurations

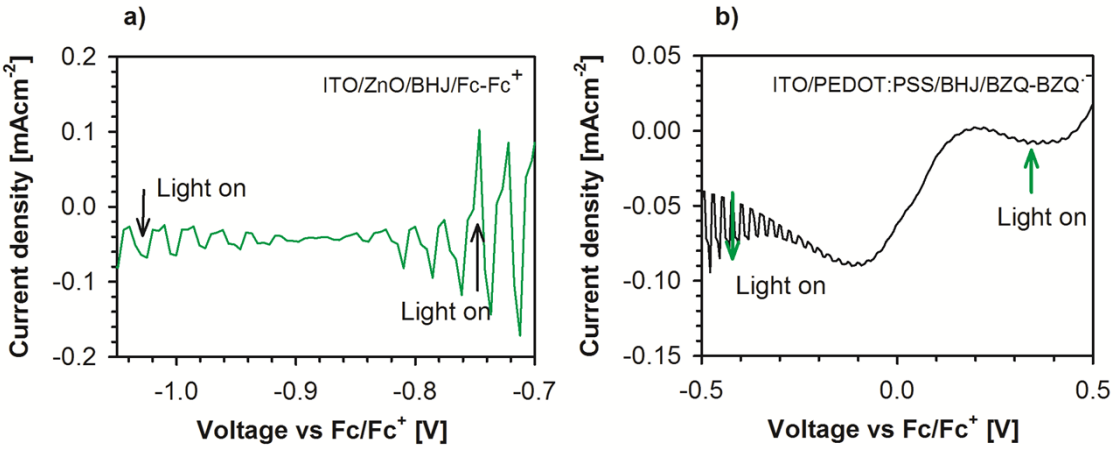


Supplementary Figure S1: Shuttered J-V curves in acetonitrile (0.1M tetrabutyl hexafluorophosphate) recorded at 5 mVs^{-1} for ITO/ZnO/BHJ/BZQ-$BZQ^{\cdot-}$ (a) and ITO/ZnO/BHJ/Fc-Fc^{+} (b).

Supplementary Figure S1 shows the *j-V* plots under chopped illumination for complementary ITO/IFL/BHJ/redox couple configurations to those reported in Figure 3. In this case, both the IFL and the redox couple are selective to the same carriers; holes in the case of PEDOT:PSS and BZQ-$BZQ^{\cdot-}$ (a) and electrons for ZnO and Fc/Fc^{+} (b). For these systems, the inversion of the photocurrent is clearly observed with a significant dark current indicating poor rectification and lower amount of photogenerated charge extracted to the electrolyte solution. This behavior can be explained by the inadequate alignment of the energy levels, hindering the extraction of the photogenerated charge

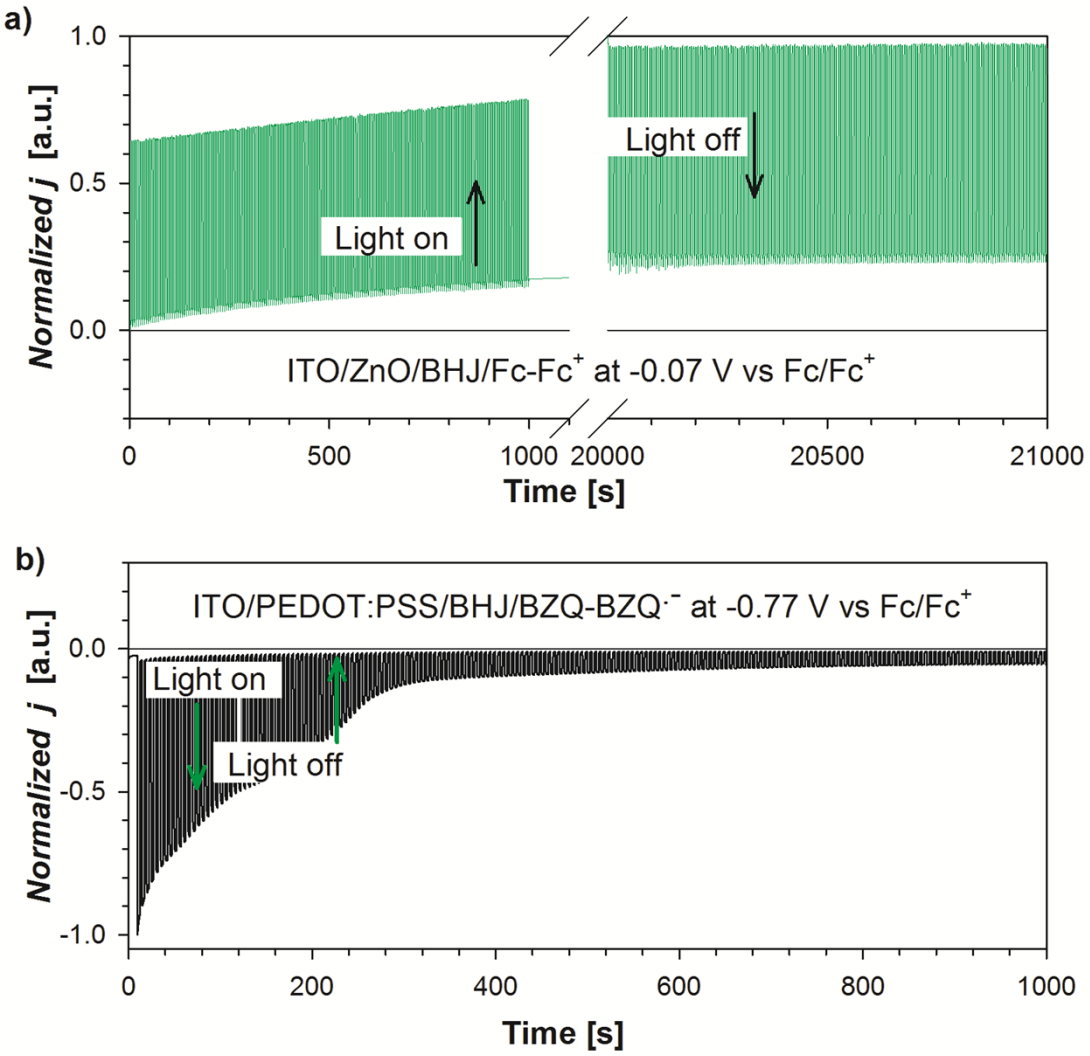
(electrons in the system ITO/PEDOT:PSS/Fc-Fc^{+} and holes in the system ITO/ZnO/BHJ/BZQ-$BZQ^{\cdot-}$).

S2.- Inversion of the photocurrent



Supplementary Figure S2: Zoom of the Shuttered J-V curves showed in Figure 3 in acetonitrile (0.1M tetrabutyl hexafluorophosphate) recorded at 5 mV s^{-1} for ITO/PEDOT:PSS/BHJ/Fc-Fc^{+} (a) and ITO/ZnO/BHJ/BZQ-$BZQ^{\cdot-}$ (b). The inversion of the photocurrent is clearly observed.

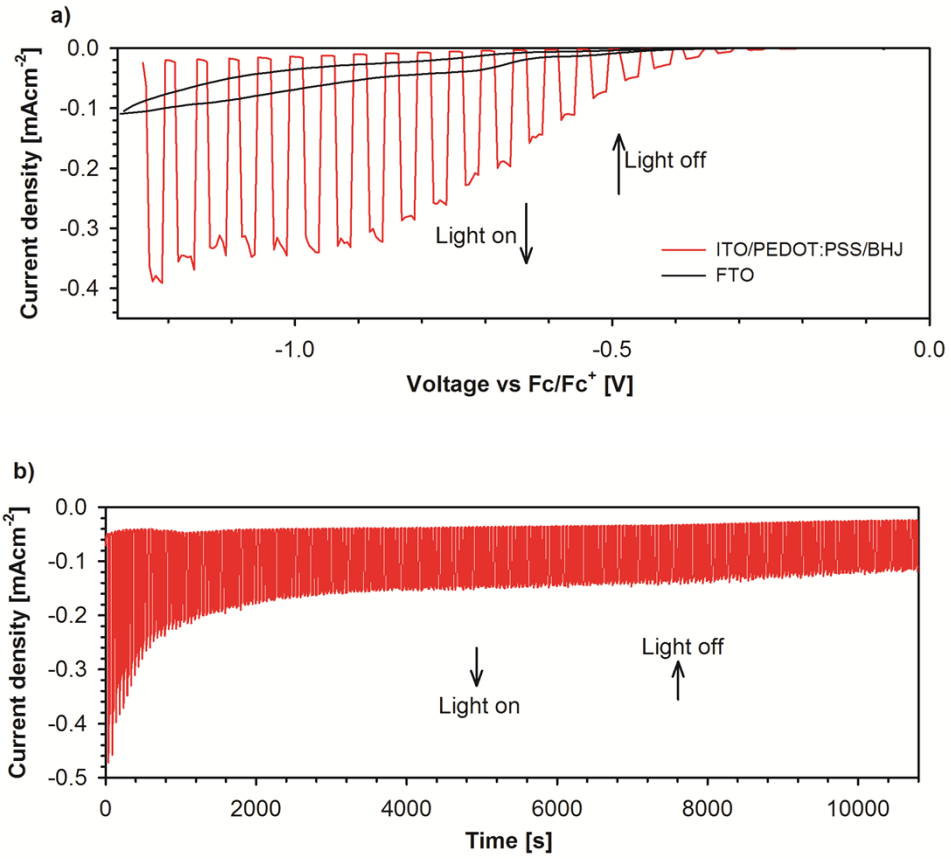
S3.- Stability tests



Supplementary Figure S3: Shuttered chronoamperometric curves measured in acetonitrile (0.1M tetrabutyl hexafluorophosphate) for ITO/ZnO/BHJ/Fc-Fc^+ (a) and ITO/ZnO/BHJ/BZQ-$BZQ^{\cdot-}$ (b) at applied voltages of -0.07V and -0.77 V vs Fc/Fc^+, respectively.

S4.- Labeling experiments

The production of H_2 in the system ITO/PEDOT:PSS/BHJ/cobaloxime was confirmed by the characterization of the outlet gas of a sealed PEC cell by gas chromatography. Ar was used as carrier gas in this experiment. In these measurements, the electrode was placed in the middle of the cell and illuminated through the active organic film. For this reason, the electrolyte solution was 5 mM in cobaloxime, since higher concentrations led to the decrease of the photocurrent due to the turbidity of the solution. Figure S4a shows the photoelectrochemical behaviour of the cobaloxime catalyst in the presence of a proton donor (HCl, 5mM) when FTO and ITO/PEDOT:PSS/BHJ were used as working electrode. When a reference FTO electrode is used, the irreversible peak of Co(III) to Co(II) at -0.66 V vs Fc^+/Fc can be clearly observed. However, this peak is not observed when the OPEC system is employed. Additionally, catalytic activity of the cobaloxime system is doubled for the OPEC system compared to the reference FTO when the electrode is illuminated. The system was polarized at different V_{bias} (from -0.7 to -1.6 V vs Fc^+/Fc) for different time periods from 1 hour to 20 hours. When the photocurrent was 180 μA or higher, the H_2 peak in the gas chromatograph could be detected. In all cases, after 30 min, the photocurrent decreases to 1/10 of the initial value, and subsequently the response is constant for 20 hours. This behaviour is due to the adsorption of the cobaloxime compounds on the electrode materials with the subsequent loss of electrocatalytic activity. This problem was solved by illuminating the electrode with shuttled light, as showed Figure S4b.



Supplementary Figure S4: a) Shuttered J-V curve for the ITO/PEDOT:PSS/BHJ (red line) and for FTO electrode (black line) in acetonitrile containing 5 mM of cobaloxime, 5 mM HCl, and 0.1 M tetrabutyl hexafluorophosphate recorded at 5 mV s^{-1} (b) Shuttered chronoamperometric curve for the system ITO/PEDOT:PSS/BHJ/cobaloxime in acetonitrile (5 mM HCl, and 0.1 M tetrabutyl hexafluorophosphate) at -0.7 V vs Fc/Fc^{+}.