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High Photocurrent Generation by Photosystem I on Artificial Interfaces Composed of π-System-Modified Graphene

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Experimental Section

Graphene electrodes: The graphene electrodes used in this study have been constructed and characterized as follows: graphene has been deposited on a polished silicon wafer with 300 nm thermal grown SiO_2 by filtered High Current Arc (Φ-HCA) in noble gas atmosphere using solid-graphite target as carbon source at a deposition temperature of 1050 °C. The coating consists of graphene flakes with a lateral size of about 5 nm. The upper layers of the coating consist of mostly flat graphene-flakes with a thickness of about 2 nm. Between this graphene structure and the substrate material (polished silicon wafer with 300 nm thermal grown SiO_2), there is a sub-layer of mostly perpendicular grown graphene-flakes. Consequently, the overall carbon thickness is about 25 nm with technological relevant 2 nm flat graphene on top. The optical and electrical properties of these graphene electrodes are: optical transmission 81 % at 600 nm, sheet resistance of 7 $kOhm_{sqr}$ and an electron mobility of 20 cm^2/Vs.

Carbon coating on QCM-chips: Due to the low temperature tolerance of the used QCM-chips, these carbon coatings were made using a substrate temperature of 300°C. All other parameters (gas pressure, arc current, tilt angle of the substrate) were constant as described above.

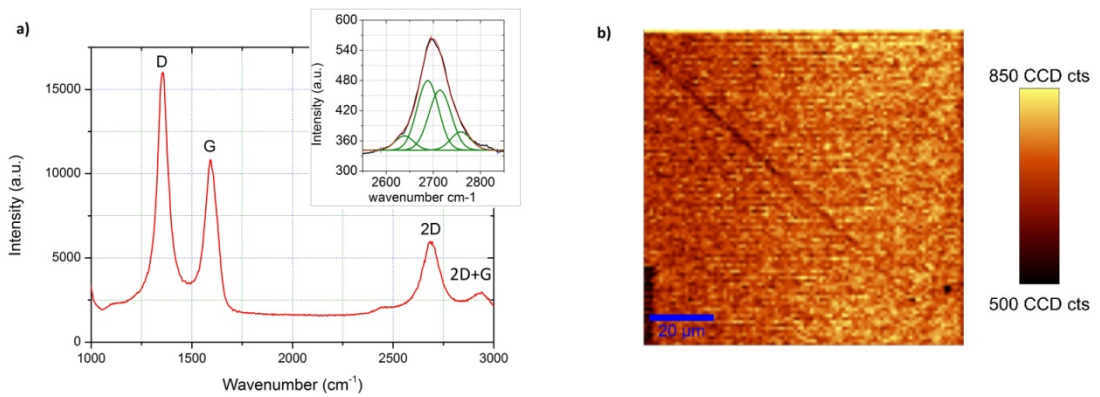

Fig. S1 a) Raman spectrum of a graphene-based coating on bare quartz; inset: The 2D peak, split into four components: $2D_{1B}$, $2D_{1A}$, $2D_{2A}$, $2D_{2B}$, b) False color picture of I_{2D} (100 µm x 100 µm).

Figure S1a shows the Raman spectrum (WITec alpha 300, λ =488 nm) of a graphene-based carbon coating on bare quartz with an optical transmission of 87%. The well resolved and narrow D and G peaks are present together with the 2D band at ~2700 cm^{-1}. These are the

typical signatures of a graphene-like coating. The high D band centered at ~1350 cm^{-1} shows the presence of disordered carbon atoms as well as a high density of grain boundaries. For that reason, the G+D band at ~2950 cm^{-1} is also visible. The I_D/I_G ratio of 1.5 shows a distance between the defects (grain size) of about 5 nm.[1] The 2D peak (Figure S1a, inset) is a convolution of four components: $2D_{1B}$, $2D_{1A}$, $2D_{2A}$, $2D_{2B}$. Moreover, the position of the 2D-peak at 2690 cm^{-1} has shifted to a higher wavenumber with respect to what is expected for monolayer graphene on silicon oxide.[2,3] The homogeneity of the deposition was investigated by measuring the intensity of the 2D-band over an area of (100 µm x 100 µm) (Figure S1b).

Photosystem preparation form T. elongatus: Trimeric PSI has been isolated from *T. elongatus* essentially as described previously.[4,5] The PSI containing fraction has been further purified by one or two sucrose gradient ultracentrifugation steps as required. Functionality of PSI has been assessed as light-driven electron transport from ascorbate reduced 2,6-dichloro-indophenol to methyl viologen (1,1'-dimethyl-4,4'-bipyridinium, MV^{2+}) with a Clark-type electrode (Oxyview-1, Hansatech, King's Lynn, UK). Typical light-induced oxygen consumption rates were on the order of 3.5 µmol mg^{-1}Chl a * min^{-1}. Fluorescence emission spectra measured at RT and 77 K indicated the integrity of the excitation energy transfer chain in PSI.

Preparation of graphene/Π-system/PSI electrodes: Graphene chip electrodes have been modified by incubation in a π-system containing ethanolic solution (0.25 – 0.5 mM) for 24 h at RT. After modifying the graphene chip via π-π-stacking, the chip has been incubated in a solution of PSI (0.5 µM, phosphate buffer 5 mM, pH 7) for 48 h at 4°C, followed by a final rinsing step with buffer.

Photoelectrochemical investigations set up: Photoelectrochemical measurements have been performed using an integrated system (CIMPS, Zahner) containing a white LED light source (4300 K, Zahner) with a continuous change of intensity (max. 100 mW cm^{-2}), an electrochemical cell and a photodiode with feedback control to the light source via a potentiostat (PP211, Zahner). Electrochemical investigations have been carried out through a coupled potentiostat (Zennium,Zahner). In all experiments a Pt counter electrode and an Ag/AgCl (1 M KCl) reference electrode has been used in an aqueous solution containing phosphate buffer (5 mM, pH 7). As a soluble electron mediator MV^{2+} was used at a final concentration of 250 µM. Photochronoamperometric experiments have been performed at RT and different potentials (vs. Ag/AgCl), while using an illumination time of 30 s. Chopped light voltammetry experiments have been carried out at a scan rate of 2 mV s^{-1} from 700 mV to -700 mV vs. Ag/AgCl with a light intensity of 60 mW cm^{-2} and a light period time of 15 s.

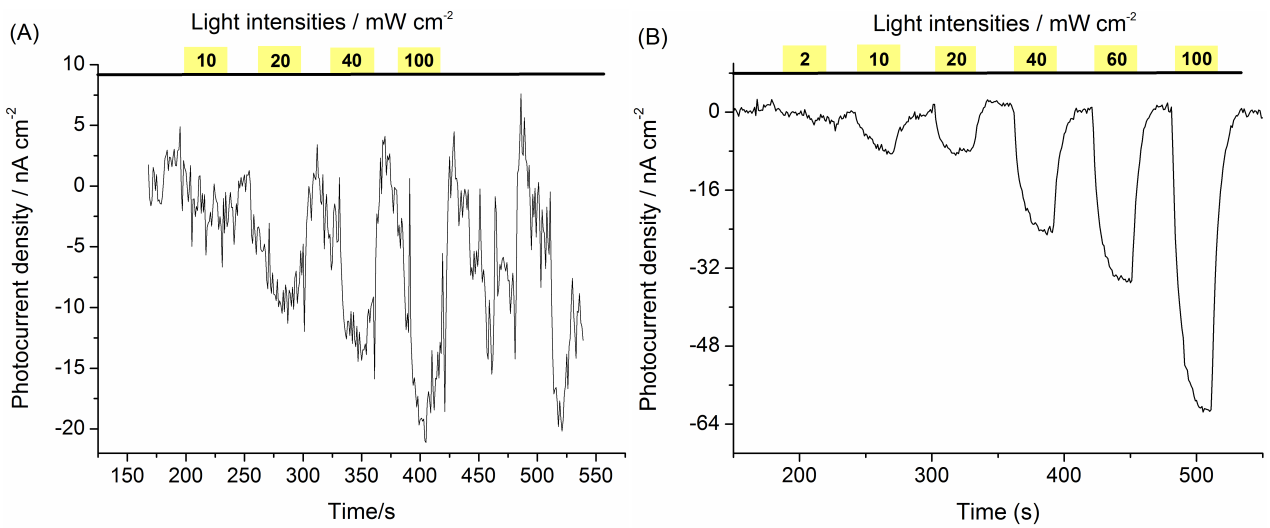

Fig. S2 Photochronoamperometric measurements of blank graphene electrode modified with π-system 2 at different light intensities (2, 10, 20, 40, 60, 100 mW cm^{-2}). A) Maximum photocurrent recorded at OCP (-100 mV vs. Ag/AgCl). B) Maximum photocurrent at an overpotential of – 600 mV vs. Ag/AgCl.

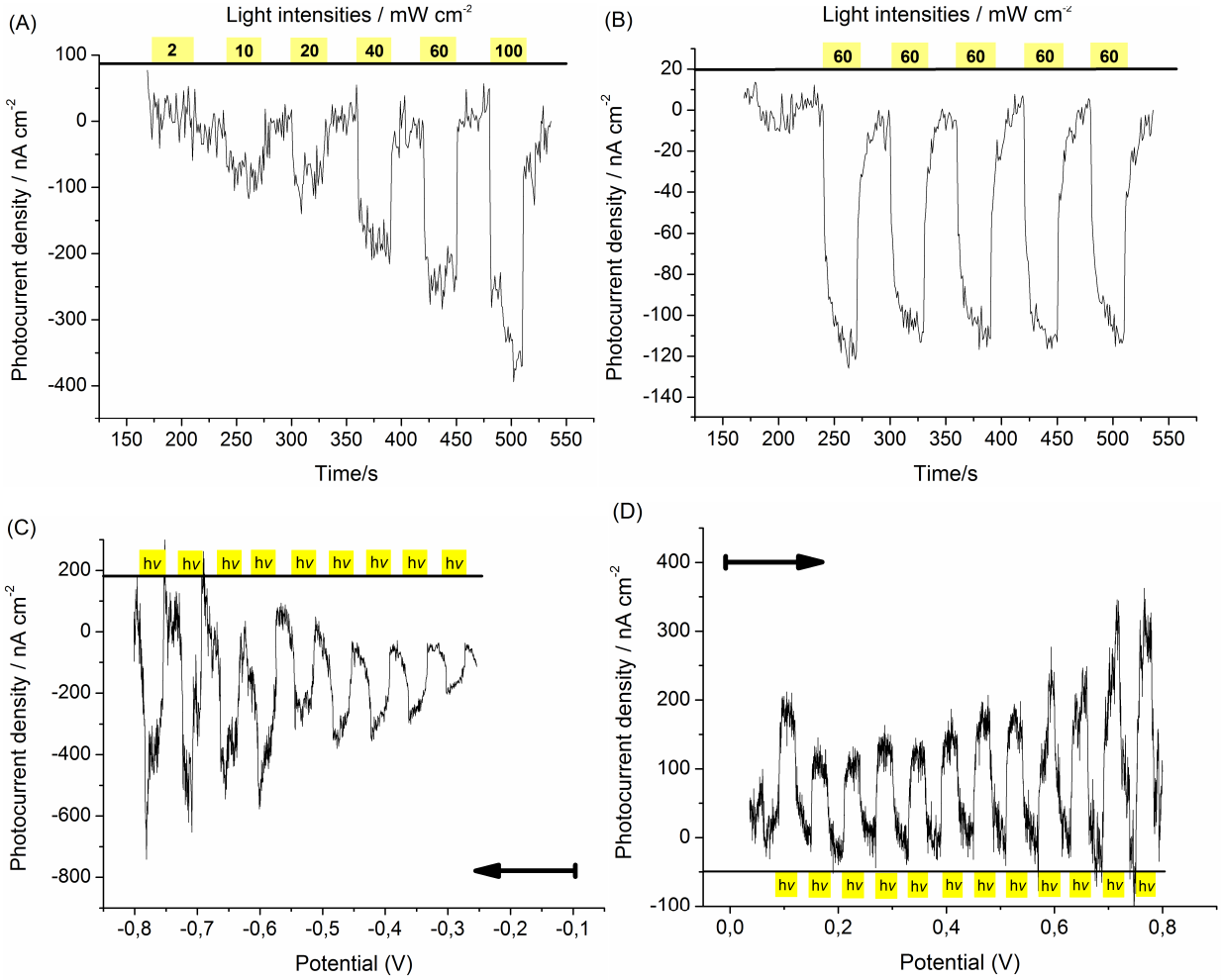

Fig. S3 Photochronoamperometric measurements of graphene/carboxyl-anthracene(π-1)/PSI electrode at different light intensities (2, 10, 20, 40, 60, 100 mW cm^{-2}). A) Measured at an over-potential (-450 mV vs. Ag/AgCl). B) Photocurrent stability measured at an overpotential (-250 mV vs. Ag/AgCl), with a constant light intensity of 60 mW cm^{-2}. Chopped light voltammetry measurements at a constant light intensity of 60 mW cm^{-2}. C) A negative potential scan (cathodic current). D) A positive potential scan (anodic current).

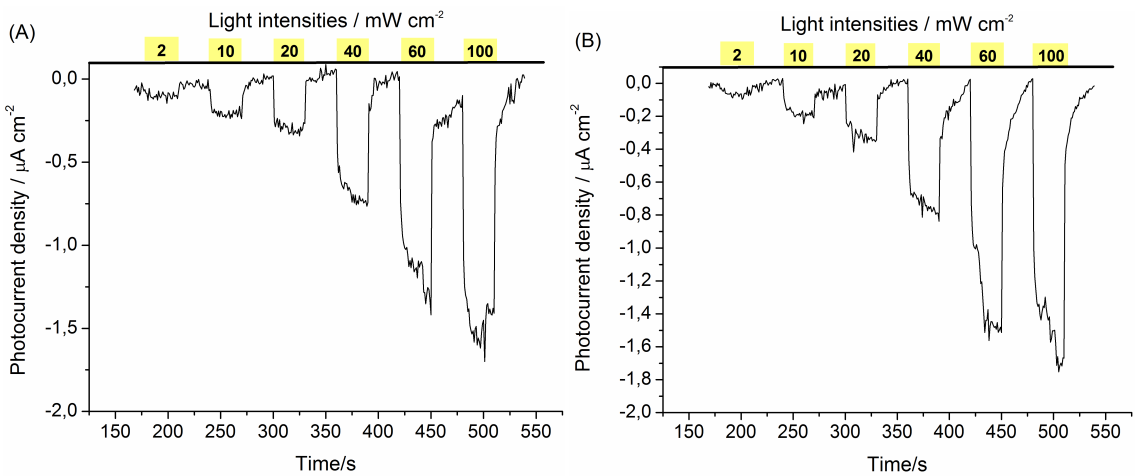

Fig. S4 Photochronoamperometric measurements of graphene/hydroxyl-keto-pyrene (π-3)/PSI electrode at different light intensities (2, 10, 20, 40, 60, 100 mW cm^{-2}). A) Measured at an overpotential (-250 mV vs. Ag/AgCl). B) Addition of MV^{2+} (250 µM).

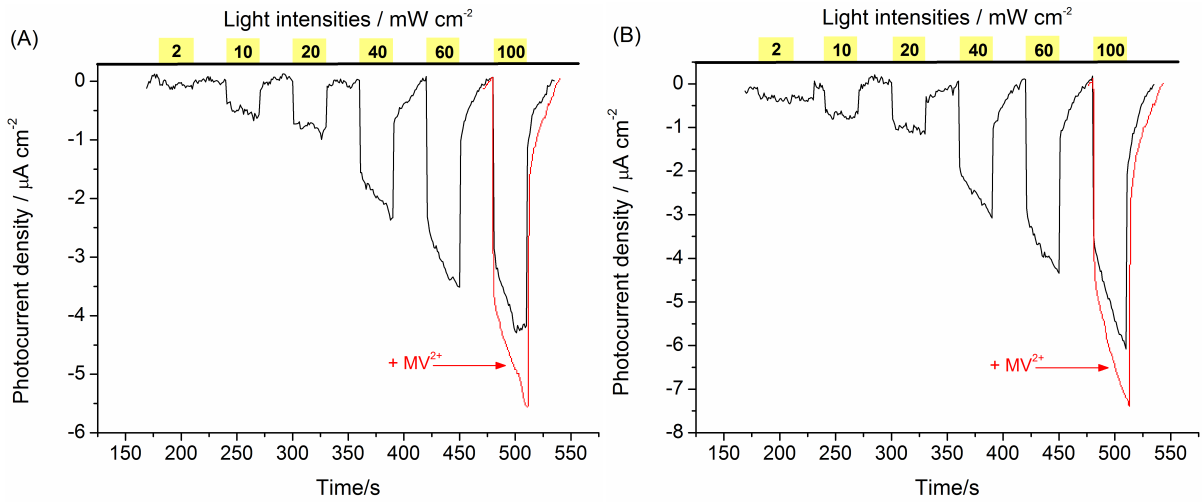

Fig. S5 Photochronoamperometric measurements of graphene/carboxyl-pyrene (π-4)/PSI electrode at different light intensities (2, 10, 20, 40, 60, 100 mW cm^{-2}). A) Measured at an overpotential of -480 mV vs. Ag/AgCl; overlay (red line): addition of MV^{2+} (250 µM). B) At an overpotential of -580 mV vs. Ag/AgCl; overlay (red line): addition of MV^{2+} (250 µM).

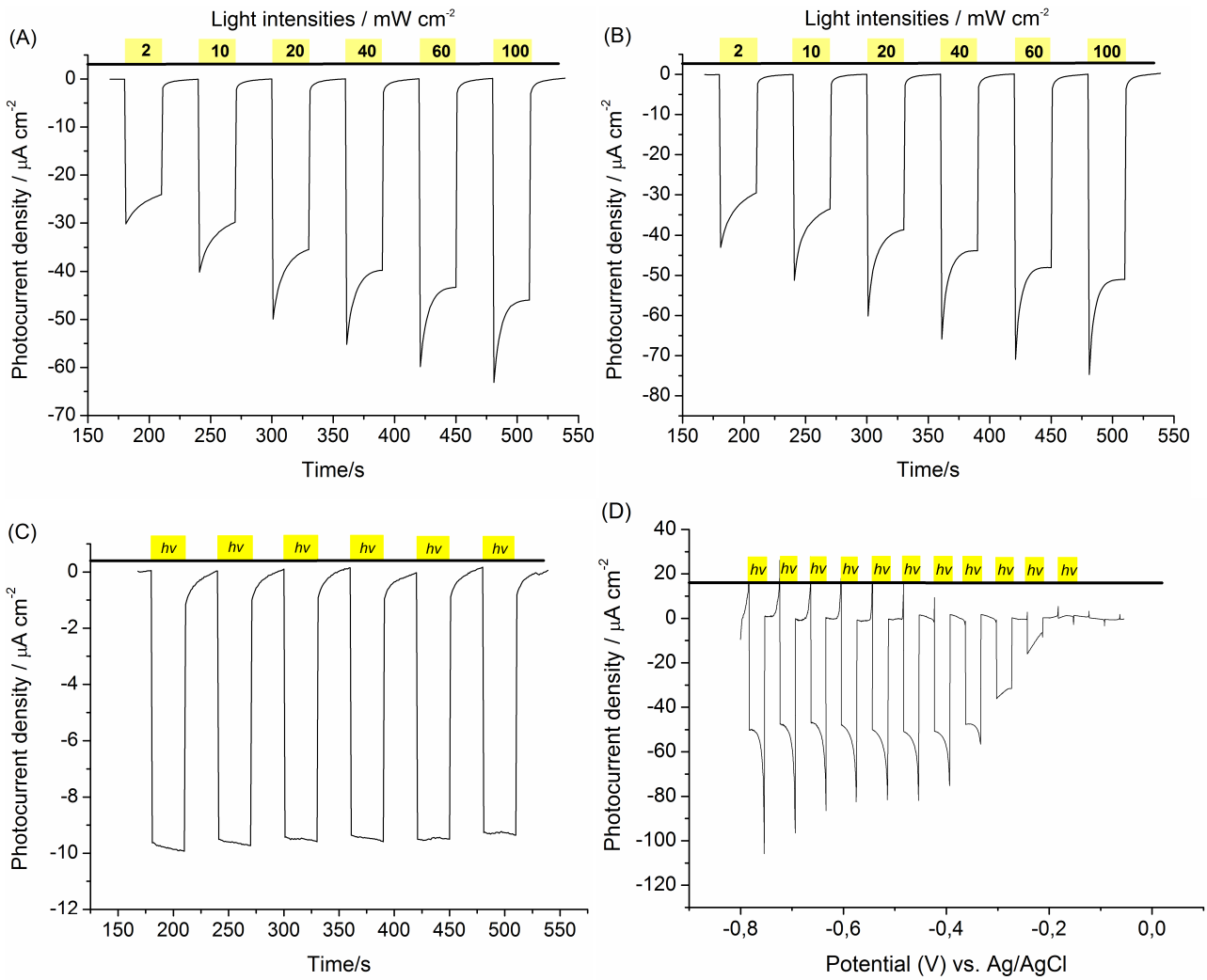

Fig. S6 Photochronoamperometric measurements of graphene/NHS-pyrene (π-5)/PSI electrode at different light intensities (2, 10, 20, 40, 60, 100mW cm^{-2}). A) Measured at an overpotential (-400 mV vs Ag/AgCl). B) Measured at an overpotential (-450 mV vs Ag/AgCl). C) *Stability*

investigations after two weeks storage measured at OCP (-260 mV vs Ag/AgCl) with a constant light intensity of 60 mW cm^{-2}. D) Chopped light voltammerty measurements at a constant light intensity of 60 mW cm^{-2} in the presence of MV^{2+} (250 µM).

Contact Angle measurements: Contact angles with Milli-Q water were measured applying the sessile drop method using a Rame-Hart100-00 goniometer. Each contact angle value reported here is the average of at least three measurements per substrate.

Quartz crystal microbalance: A Q-Sense-D E4 piezoelectric instrument (QSense, Vaestra Froelunda, Sweden) was used for the quartz crystal microbalance measurements. A carbon coated quartz sensor chip (5 MHz, QSense, Vaestra Froelunda, Sweden) was incubated in ethanolic solution containing 0.25 - 0.5 mM of the corresponding π-system (4 & 5) for 24 h at RT, then rinsed with ethanol, water and mounted into the QCM flow system. The solution containing PSI of the above given concentration were pumped through the cell for 60 minutes with 5 minutes of buffer flow at the end (to remove loosely bound material), at a flow rate of 25 µL/min.

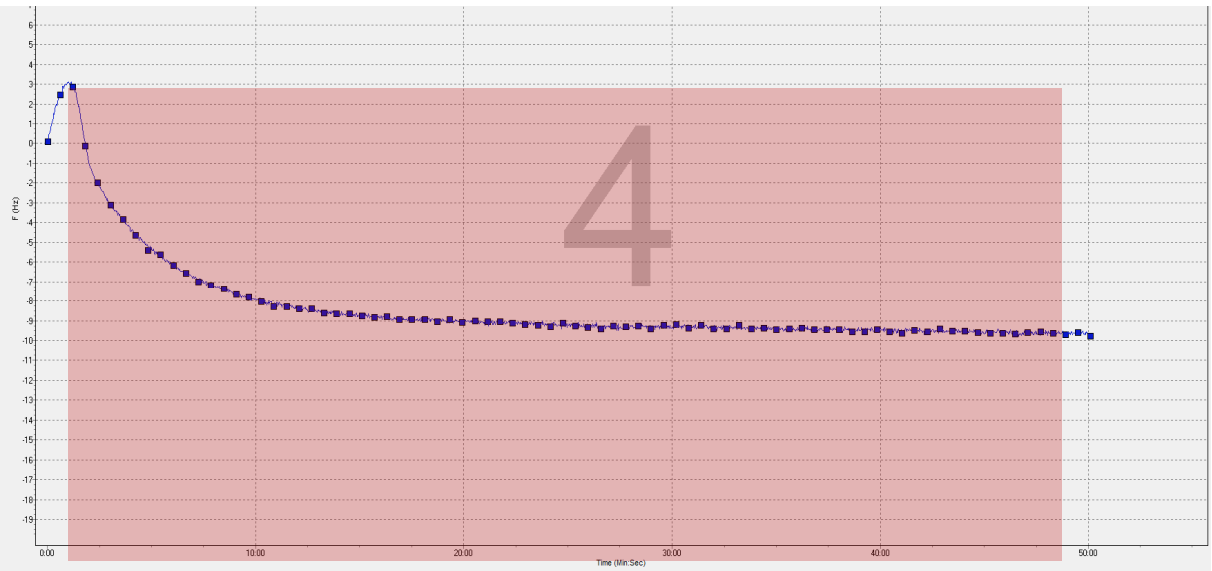

Fig. S7 *QCM of a blank graphene electrode* (**Δ*f* = 9 Hz**): Unspecific assembly of PSI on a unmodified chip. The PSI (0.5 µM) solution was pumped through the cell for 45 min (red) at a constant flow rate of 25 µL min^{-1}.

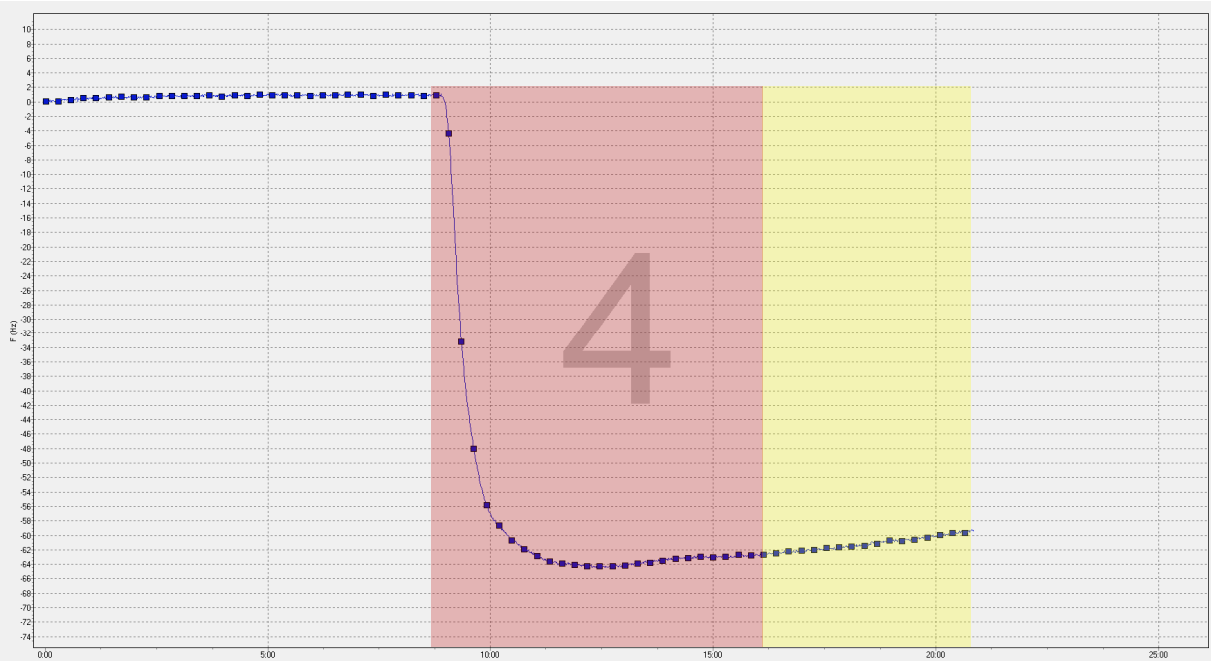

Fig. S8 *QCM of a graphene/carboxyl-pyrene (π-4)/PSI electrode* (**Δf = 60 Hz**): Assembly of PSI on a Π-4 modified chip. The PSI (0.5 µM) solution was pumped through the cell for 20 min (red) with 5 min of buffer flow after assembly (yellow), at a constant flow rate of 25 µL min^{-1}.

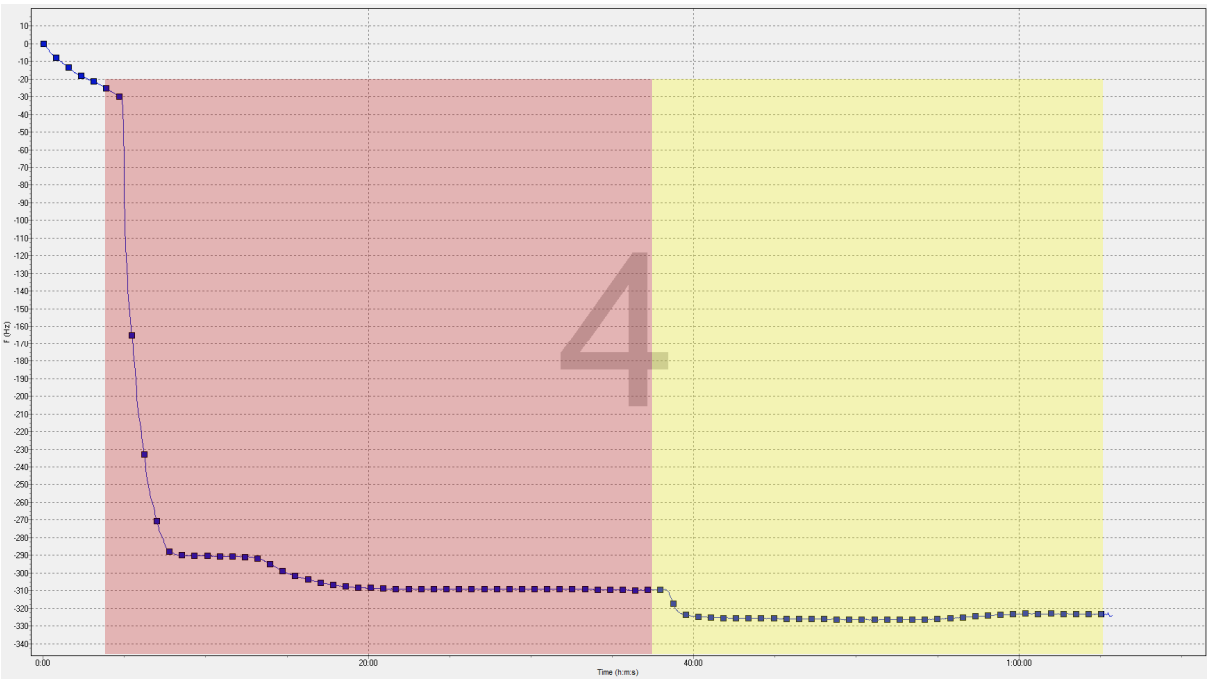

Fig. S9 *QCM of a graphene/NHS-pyrene (π-5)/PSI electrode* (**Δ*f* = 330 Hz**): Assembly of PSI on a Π-5 modified chip. The PSI (0.5 µM) solution was pumped through the cell for 30 min (red) with 20 min of buffer flow after assembly (yellow), at a constant flow rate of 25 µL min^{-1}.

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