Electronic supporting information (ESI) for

SPONTANEOUS GRAFTING OF 9,10-PHENENTREQUINONE ON POROUS CARBON AS ACTIVE ELECTRODE MATERIAL IN ELECTROCHEMICAL CAPACITOR IN ALKALINE ELECTROLYTE

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1. CHARACTERIZATION OF THE COMPOUNDS BY NMR AND IR

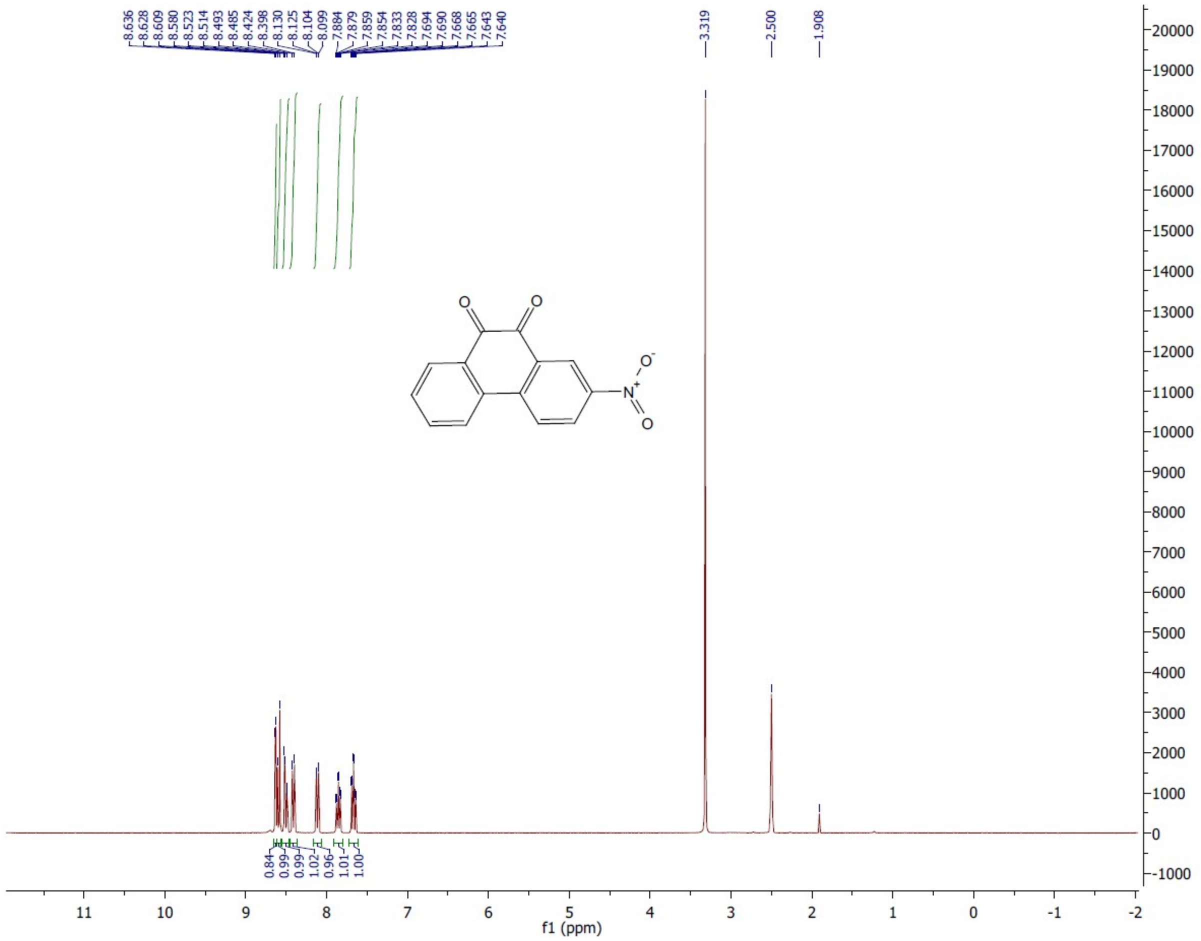

Figure S1. ^{1}H NMR spectrum of 2-nitro-9,10-phenanthrenequinone

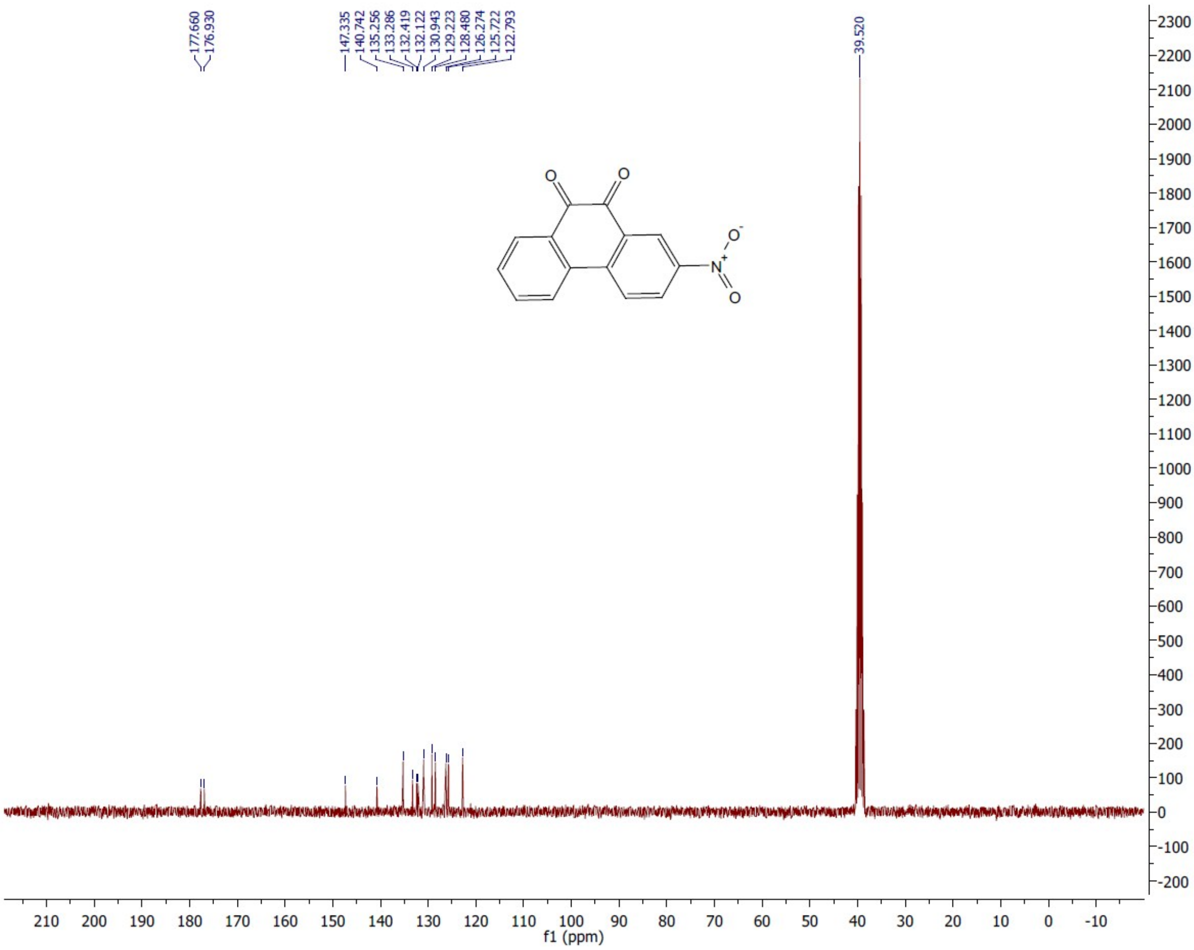

Figure S2. ^{13}C spectrum of 2-nitro-9,10-phenanthrenequinone

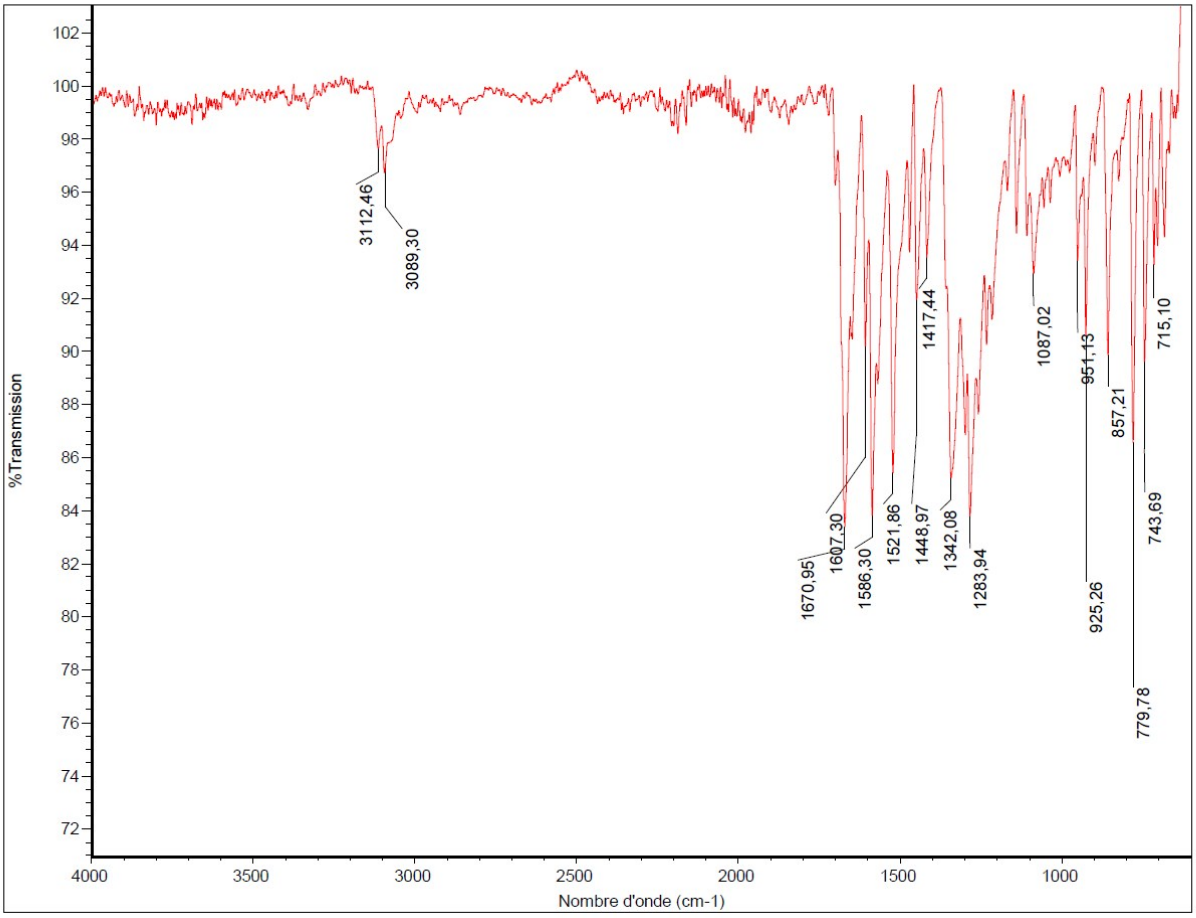

Figure S3. FT-IR spectrum of 2-nitro-9,10-phenanthrenequinone

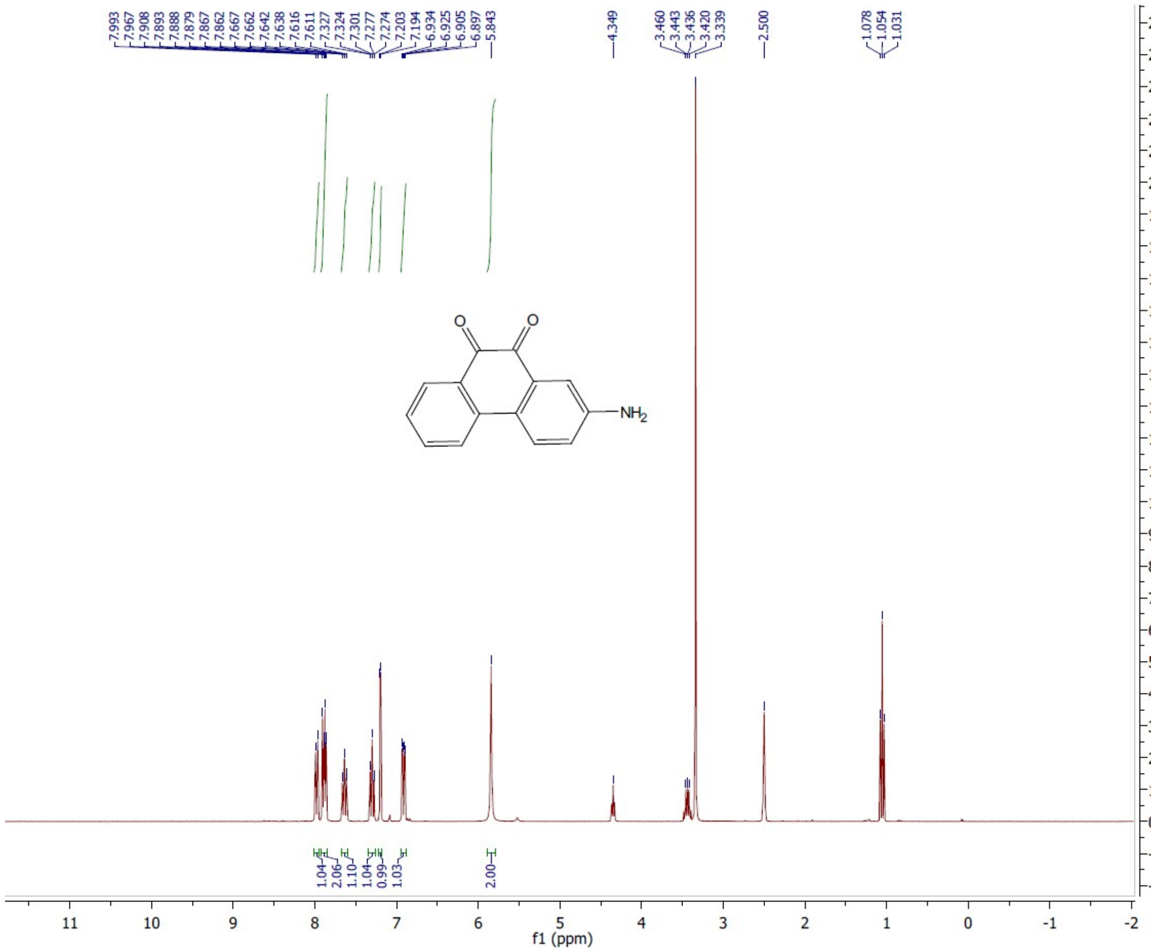

Figure S4. ^{1}H NMR spectrum of 2-amino-9,10-phenanthrenequinone

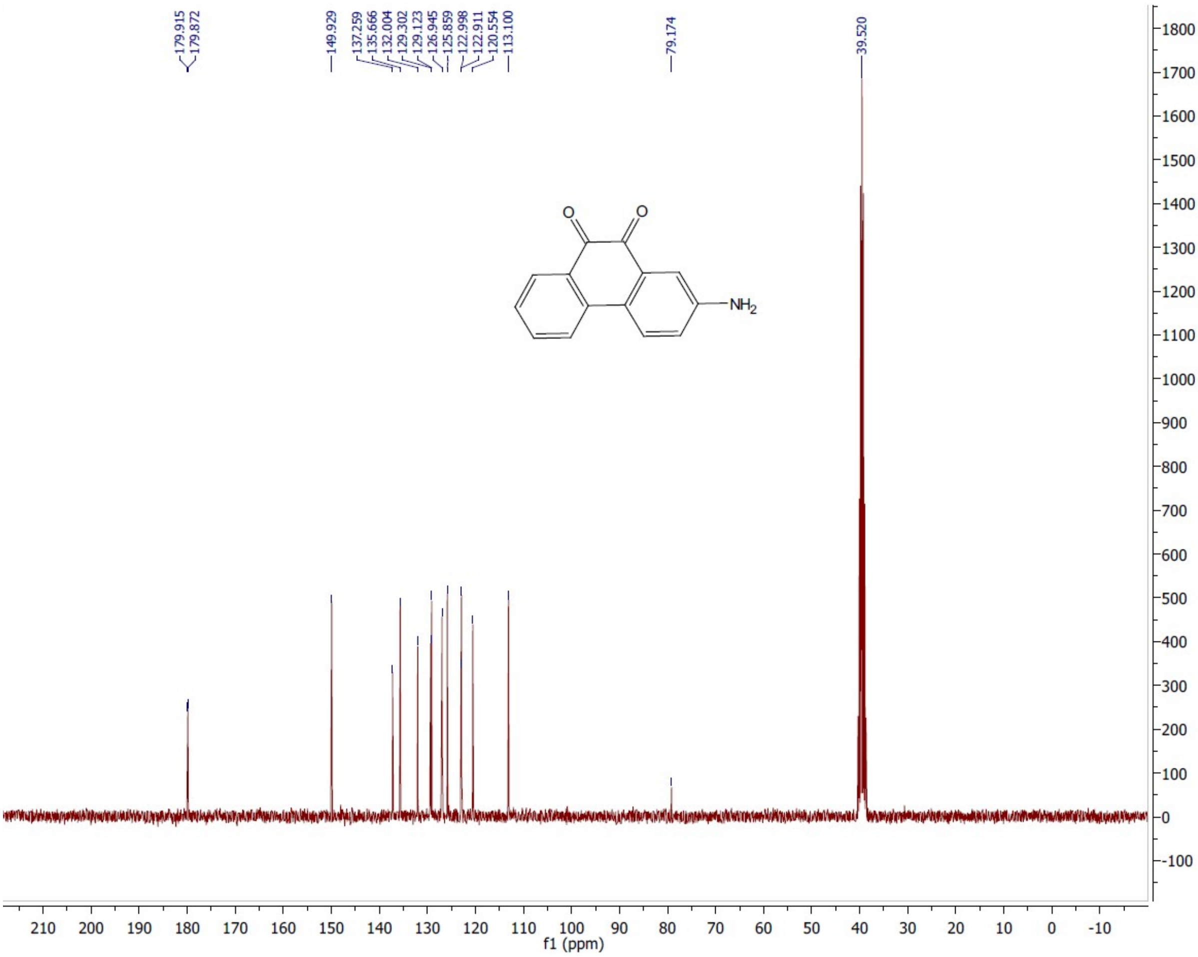

Figure S5. ^{13}C **NMR spectrum of 2-amino-9,10-phenanthrenequinone**

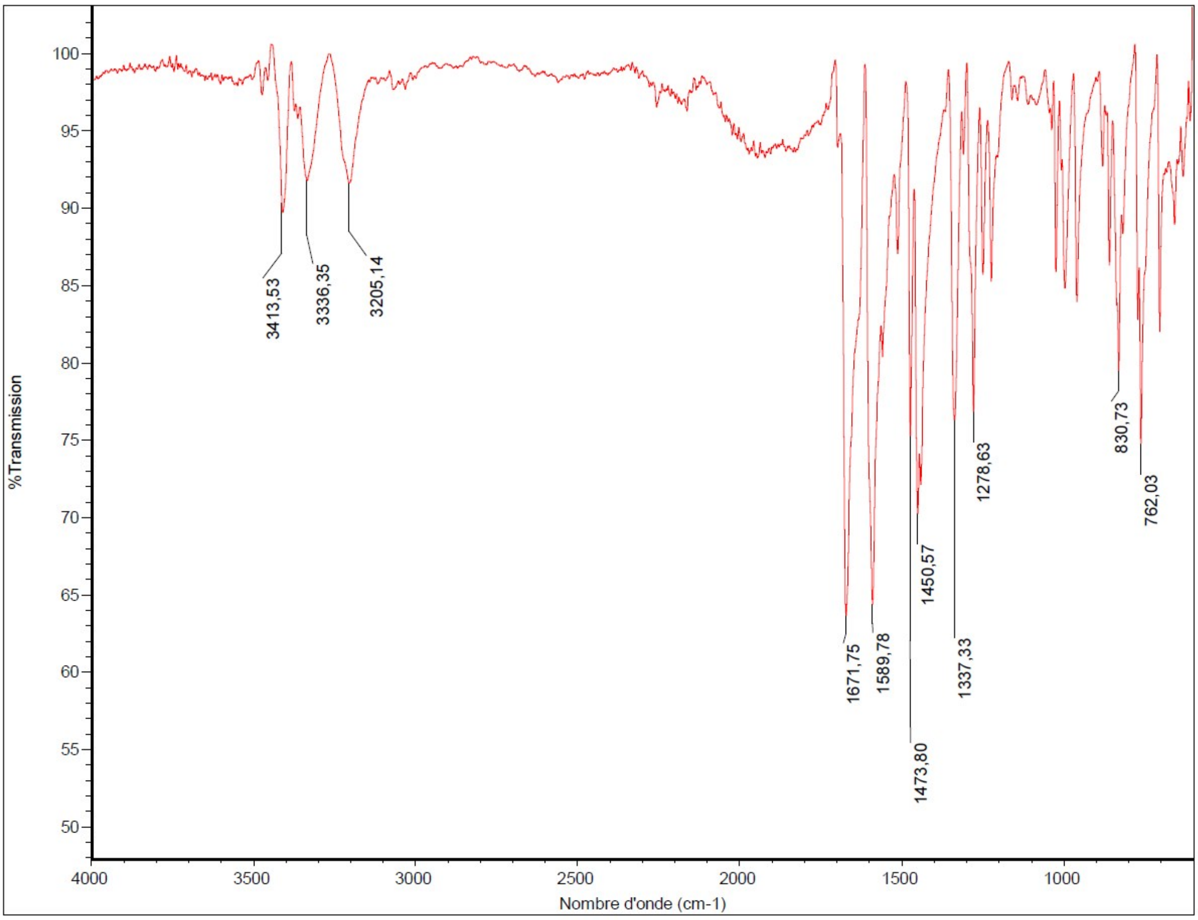

Figure S6. FT-IR spectrum of 2-amino-9,10-phenanthrenequinone

2. GRAFTING EFFICIENCY : EFFECT OF POWDER CLEANING

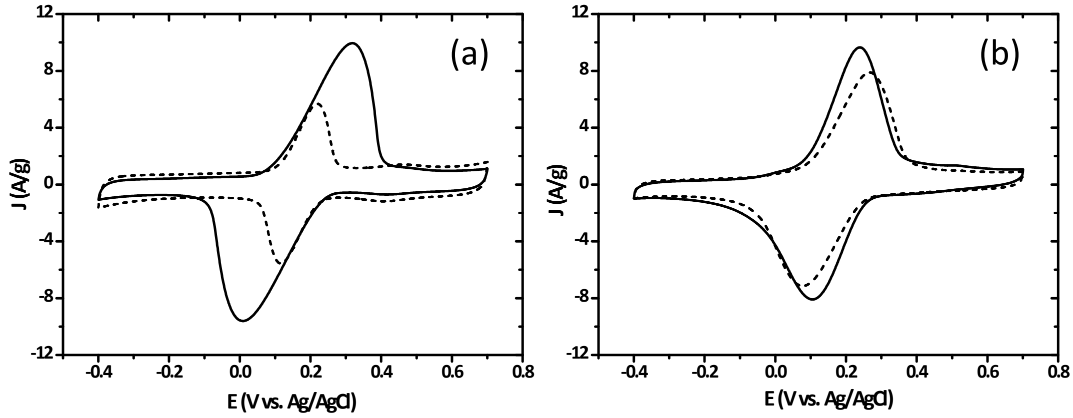

Figure S7. Cyclic voltammetry of unwashed powder (solid line) and washed powder (dashed line) for (a) PQ-adsorbed carbon and (b) PQ-grafted carbon in 0.1 M H_2SO_4 at a scan rate of 10 mV s^{-1}

Figure S7 exhibits the cyclic voltammograms of adsorbed and grafted BP powder modified with 0.1 equiv. of precusor before and after washing with successive aliquots of acetonitrile, DMF, acetone and methanol. The same procedure was used in both cases. In the case of adsorption the Faradaic capacity associated to the PQ molecules drops from 215 to 63 C g^{-1} after washing which corresponds to a loss of 71% of Faradaic contribution. On the other hand, in the case of PQ-grafted BP electrodes the Faradaic capacity after washing remains equal to 176 C g^{-1} which represents 86 % of the initial value (201 C g^{-1}).

3. XPS SURVEY SPECTRA

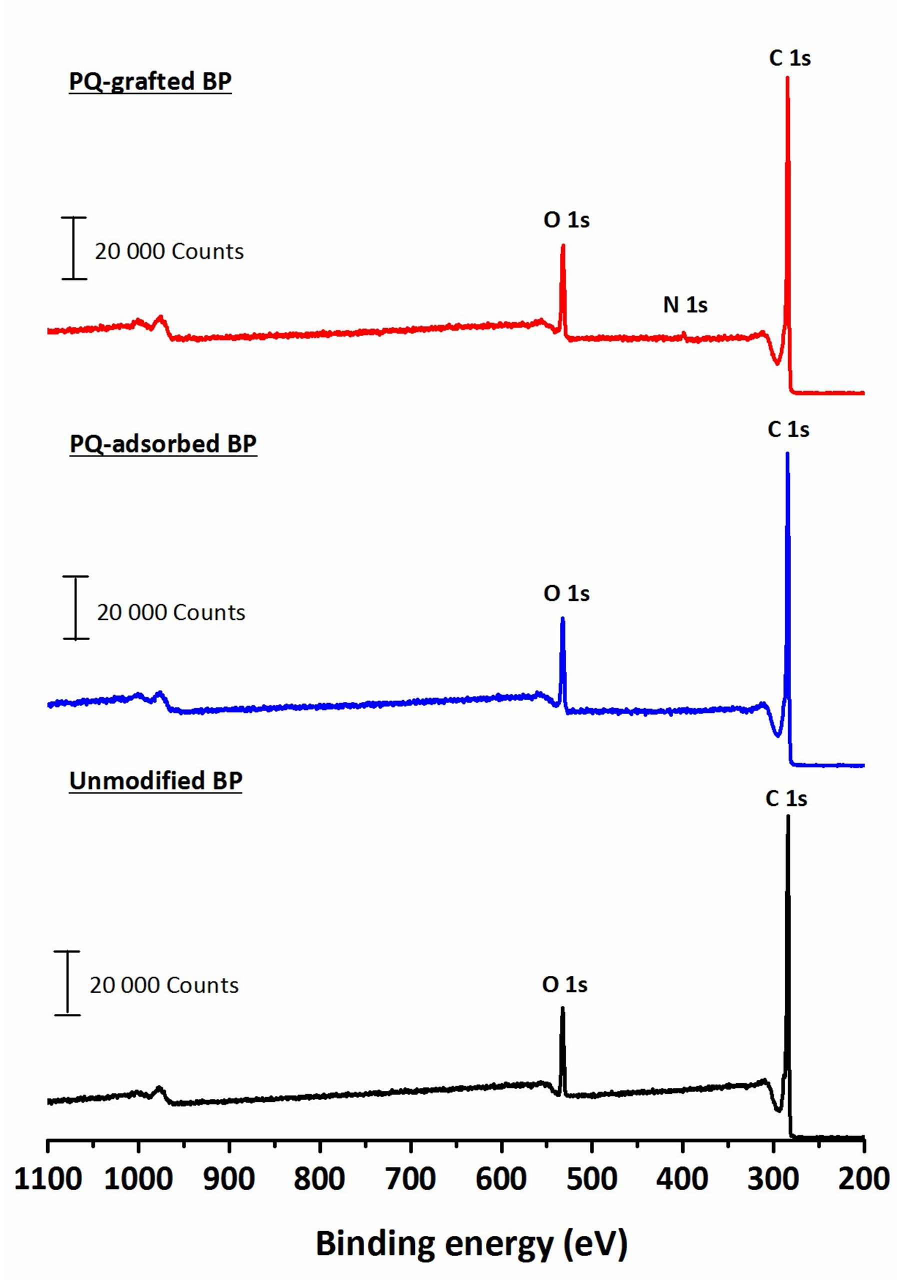

Figure S8. XPS survey spectra of unmodified BP (black squares), PQ-adsorbed (blue triangles) and PQ-grafted (red circles) BP powder modified with 0.1 equiv. of precursor.

4. NORMALIZATION OF THE XPS CORE LEVEL SPECTRA

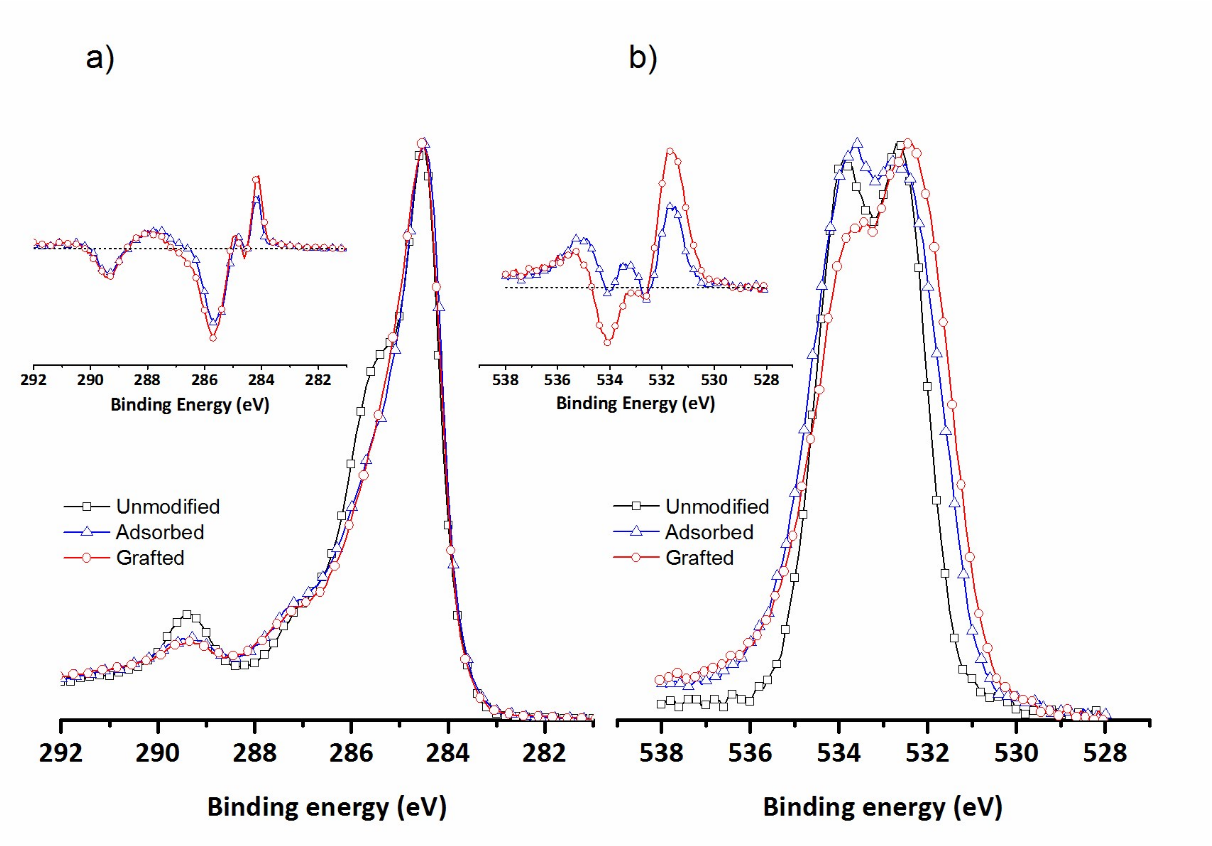

Figure S9 a) C 1s and b) O 1s XPS core level spectra of unmodified (-□-), PQ-adsorbed (-Δ-) and PQ-grafted (-○-) BP powder. Adsorbed and grafted spectra are normalized according to the maximum intensity of unmodified spectrum. The inset present the subtracted signal obtained by difference between PQ-adsorbed (-Δ-) or PQ-grafted (-○-) spectra and unmodified BP spectra.

In order to confirm the attribution of each components and especially their appearance or disappearance after modification, C 1s and O 1s core level spectra of unmodified, PQ-adsorbed and PQ-grafted BP powder were normalized. In the case of C 1s spectra, after adsorption and grafting one can indeed observe the decrease of the components at 285.4 and 284.4 eV attributed to carbon atoms attached to oxidized carbon atoms and –COOH carbons, respectively. Moreover an additional component at 287.7 eV related to quinone moieties arises after carbon modification. Those results are confirmed by O 1s spectra where the appearance of quinone component at 531.9 eV is very obvious. The decrease of C-O and C=O components located at 534.0 and 532.6 eV respectively is also in good agreement with the decrease of the –COOH component on C 1s spectra.

5. XPS CORE LEVEL SPECTRA CURVE FITTING

	Unmodified BP			PQ-adsorbed BP			PQ-grafted BP		
	BE (eV)	**FWHM (eV)**	**Area (%)**	**BE (eV)**	**FWHM (eV)**	**Area (%)**	**BE (eV)**	**FWHM (eV)**	**Area (%)**
C sp^2	284.5	0.9	48.1	284.5	1	55.1	284.5	1	56.5
β-carbon	285.5	1.0	30.5	285.3	1.2	22.3	285.3	1.2	22.9
C-O	286.2	1.0	8.6	286.1	1.2	8.7	286.1	1.2	8.7
C=O	287.1	1.0	6.5	287.0	1.2	6.81	287.1	1.2	5.8
Quinone	-	-	-	287.5	1.2	2.2	287.5	1.2	2.4
-COOH	289.4	1.0	6.4	289.4	1.2	4.8	289.4	1.2	3.7

Table S1. Curve fitting parameters for the C 1s photoelectron region.

	Unmodified BP			PQ-adsorbed BP			PQ-grafted BP		
	BE (eV)	**FWHM (eV)**	**Area (%)**	**BE (eV)**	**FWHM (eV)**	**Area (%)**	**BE (eV)**	**FWHM (eV)**	**Area (%)**
Pollution	530.5	1.4	1.0	529.7	1.6	1.3	529.7	1.6	0.9
Quinone	-	-	-	531.9	1.6	12.0	531.9	1.6	20.9
C=O	532.6	1.4	48.5	532.5	1.6	37.4	532.5	1.6	35.5
C-O	534.0	1.4	50.5	534.0	1.6	45.2	534.0	1.6	38.8
H_2O	-	-	-	535.4	1.6	4.2	535.4	1.6	3.9

Table S2. Curve fitting parameters for the O 1s photoelectron region.

	Unmodified BP			PQ-adsorbed BP			PQ-grafted BP		
	BE (eV)	**FWHM (eV)**	**Area (%)**	**BE (eV)**	**FWHM (eV)**	**Area (%)**	**BE (eV)**	**FWHM (eV)**	**Area (%)**
Amine	-	-	-	-	-	-	399.2	1.4	44.2
Azo	-	-	-	-	-	-	400.0	1.4	40.2
Amide	-	-	-	-	-	-	401.0	1.4	15.6

Table S3. Curve fitting parameters for the N 1s photoelectron region.

6. XPS CORE LEVEL SPECTRA

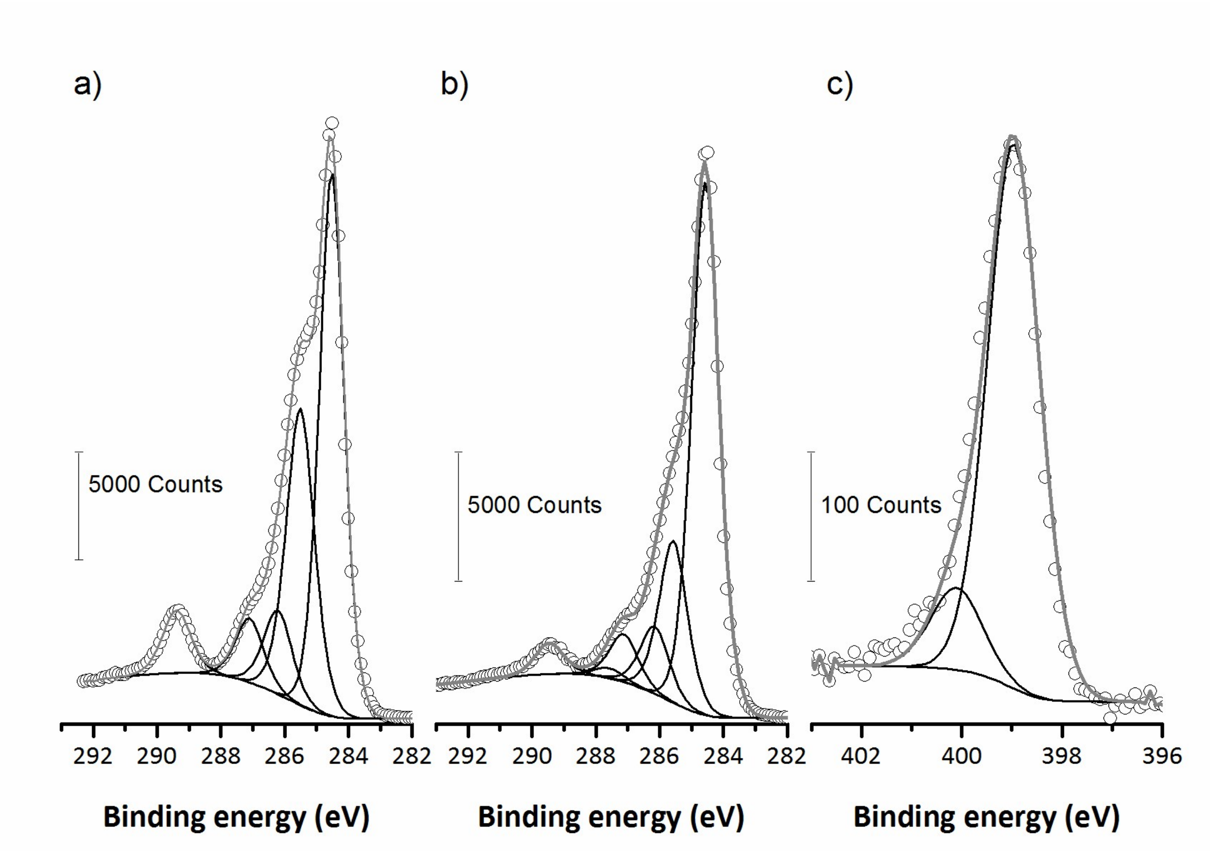

Figure S10. C 1s XPS core level spectra of a) unmodified and b) APQ-adsorbed BP powder and c) N 1s XPS core level spectrum of APQ-adsorbed BP powder

N 1s core level spectrum of APQ-adsorbed BP powder shows to major components centered at 399.0 and 400.1 eV respectively. The more intense contribution (399.0 eV) can be assigned to the amine functionalities of the adsorbed molecules. Since the second peak (400.1 eV) is not observed in the case of unmodified BP powder, it cannot be attributed to nitrogen functional groups present at the BP carbon surface. The presence of this component could be explained by amide linkage due to peptidic reaction between between the amine functionalities in the aminoPQ molecules and carboxylic groups present at the carbon surface.

7. THERMOGRAVIMETRIC ANALYSIS

The weight loss is estimated from the thermogram at 700°C and are average of three measurements. The subtracted weight loss is determined by taking into account the weight loss of unmodified carbon, it corresponds to the difference between the weight loss of the modified sample and the weight loss of unmodified carbon at 700°C.

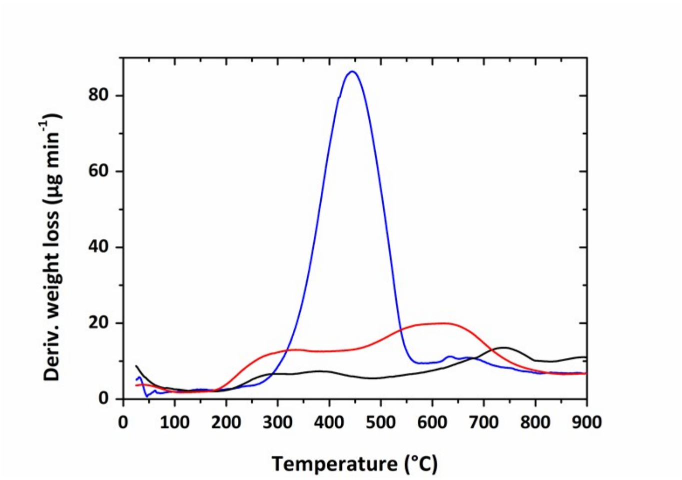

Figure S11. Derived thermogravimetric analysis curve performed under nitrogen at a temperature rate of 10 °C min^{-1} for unmodified BP (solid black) ; PQ-adsorbed BP with 0.1 equiv. of PQ (blue) and PQ-grafted BP (red) with 0.1 equiv. of APQ.

8. CYCLIC VOLTAMMETRY OF PQ-ADSORBED AND PQ-GRAFTED BP ELECTRODES

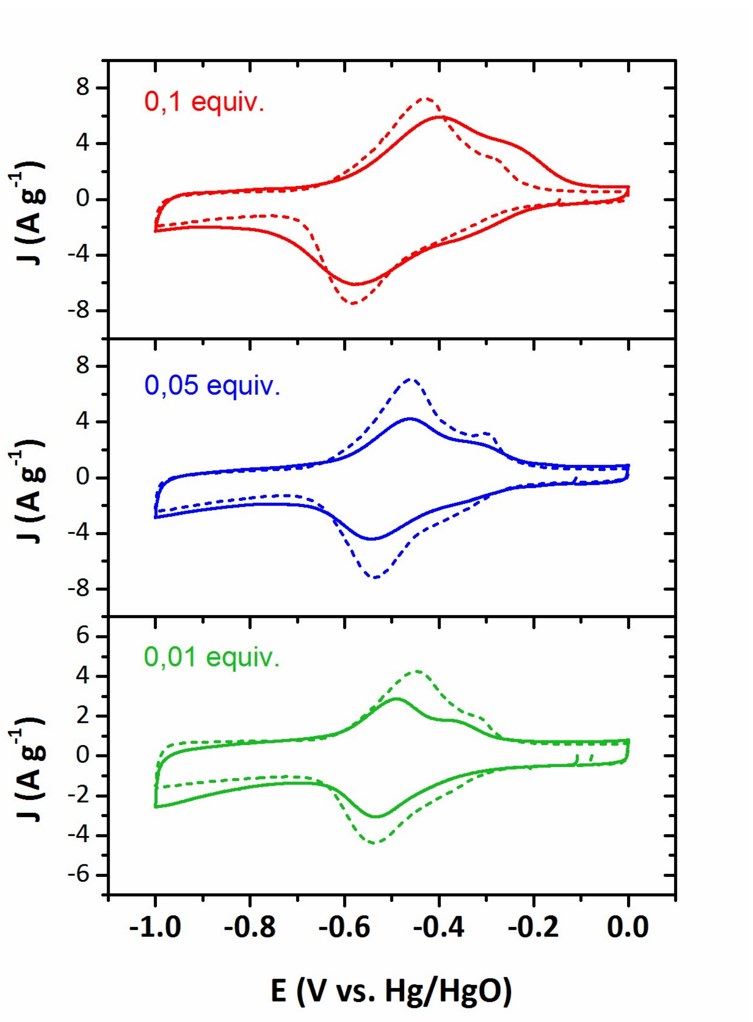

Figure S12. Cyclic voltammograms in 1M KOH at a scan rate of 10 mV s^{-1} of PQ-adsorbed (dashed line) and PQ-grafted (solid line) BP electrodes modified with (green) 0.01, (blue) 0.05 and (red) 0.1 equiv. of the precursor.

9. MAXIMUM THEORETICAL SURFACE COVERAGE

The maximum theoretical surface coverage is calculated taking into account that the molecules are in parallel orientation with the carbon substrate. The area occupied by a PQ molecule is equal to 94 Å². The maximum theoretical surface coverage is obtained using the following calculation:

$$\frac{1}{94.10^{-16}\times N_A} = \frac{1}{94.10^{-16}\times 6.02.10^{23}} = 1.77\ x\ 10^{-10}\ mol.cm^{-2}$$

10. CYCLIC VOLTAMMETRY OF ANTHRAQUINONE-GRAFTED AND PHENANTHRENEQUINONE-GRAFTED CARBON ELECTRODES

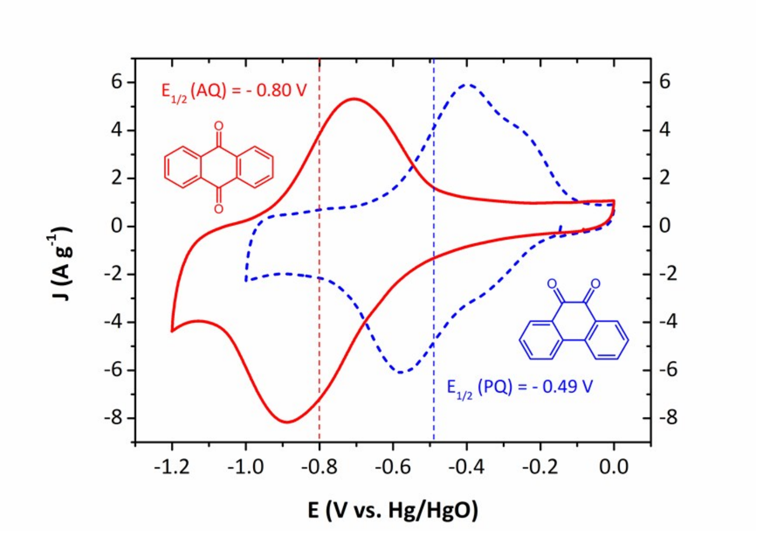

Figure S13. Cyclic voltammetry of AQ-grafted (red) and PQ-grafted (blue) carbon electrodes in 1 M KOH at a scan rate of 10 mV s^{-1}

Figure S13 displays the cyclic voltammograms of AQ-grafted and PQ-grafted BP electrodes. The same grafting procedure was used in both cases. One can clearly observe that the cyclic voltammogram of the PQ-modified electrode is shifted by about 300 mV to more positive value in comparison to that of the AQ-modified electrode. Moreover, the cyclic voltammogram of the AQ-grafted electrode shows the onset of the hydrogen evolution at – 1.2 V. This would have negative impact on long-term cyclability of AQ-grafted electrodes in alkaline electrolyte.