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SUPPLEMENTARY MATERIAL

Conjugated redox polymer with poly(3,4-ethylenedioxythiophene) backbone and hydroquinone pendant groups as the solid contact in potassium-selective electrodes

Iryna Ivanko^{a,§}, Tom Lindfors^{a,*}, Rikard Emanuelsson^b, Martin Sjödin^b

^a Åbo Akademi University, Johan Gadolin Process Chemistry Centre (PCC), Laboratory of Molecular Science and Engineering (Analytical Chemistry Group), Biskopsgatan 8, 20500 Åbo, Finland; tom.lindfors@abo.fi

^b Nanotechnology and Functional Materials, Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden; martin.sjodin@angstrom.uu.se, rikard.emmanuelsson@kemi.uu.se

* Corresponding author

[§] Permanent address: Institute of Macromolecular Chemistry AS CR, Czech Academy of Sciences, Heyrovsky Sq. 2, 162 06 Prague 6, and Charles University, Faculty of Science, Prague 2, 128 00 Czech Republic; ivanko@imc.cas.cz

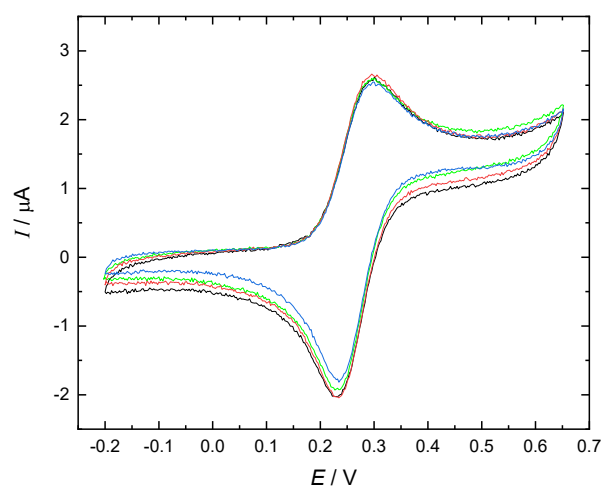


Figure S1. Cyclic voltammograms of four identical GC electrodes measured with the scan rate of 5 mV s^{-1} in $2 \text{ mM K}_4\text{Fe(CN)}_6$ with 1.0 M KNO_3 as the supporting electrolyte. RE: Ag/AgCl/3 M KCl.

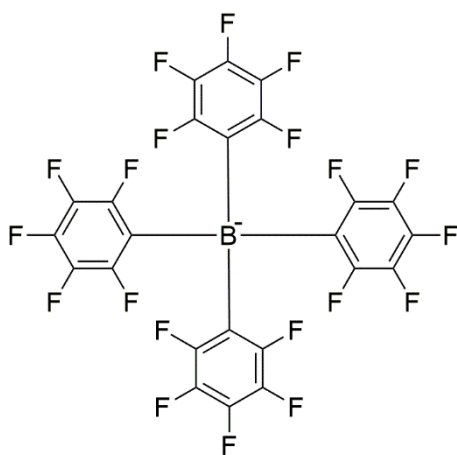


Figure S2. The chemical structure of potassium tetrakis(pentafluorophenyl)borate (KTFAB).

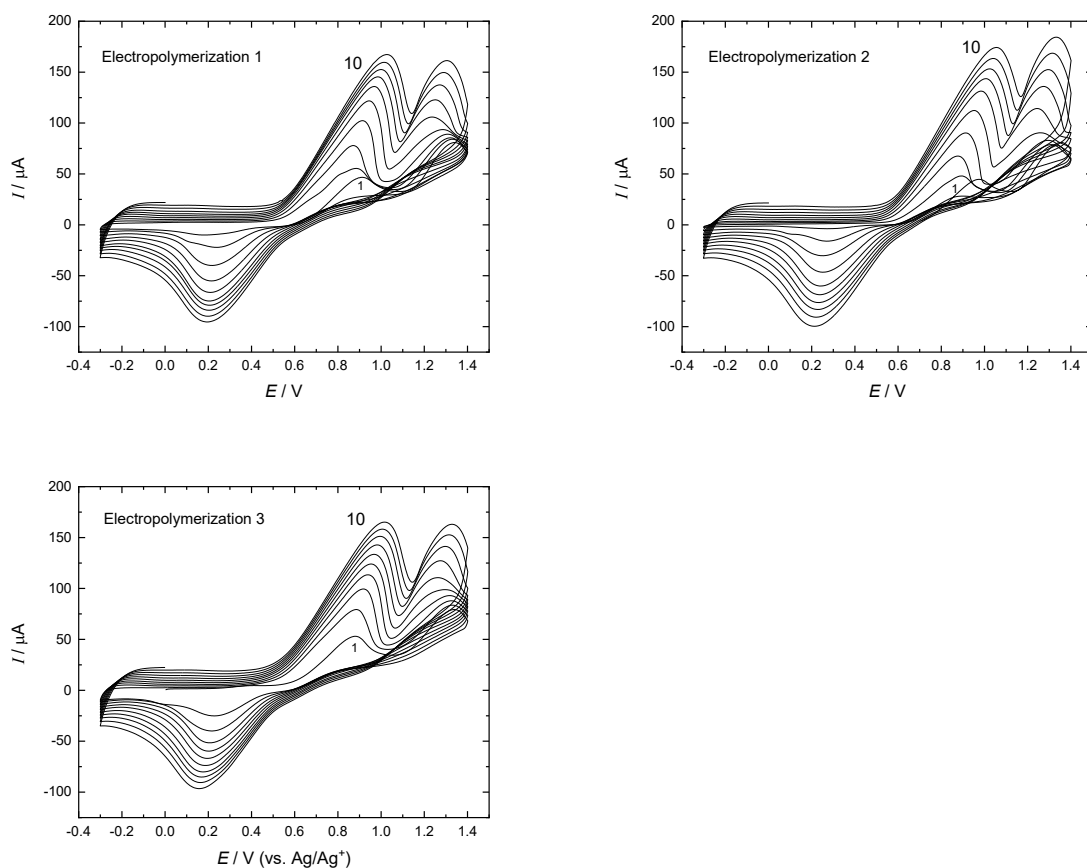


Figure S3. Electropolymerization of 5 mM EDOT-HQ on GC in acetonitrile containing 0.01 M KTFAB. Three PEDOT-HQ films were electropolymerized from the same monomer solution with cyclic voltammetry by cycling the potential ten times ($v=50 \text{ mV s}^{-1}$) between -0.3 V and 1.4 V vs. Ag/Ag⁺ (0.01 M AgNO₃ and 0.1 M TBAPF₆ dissolved in acetonitrile).

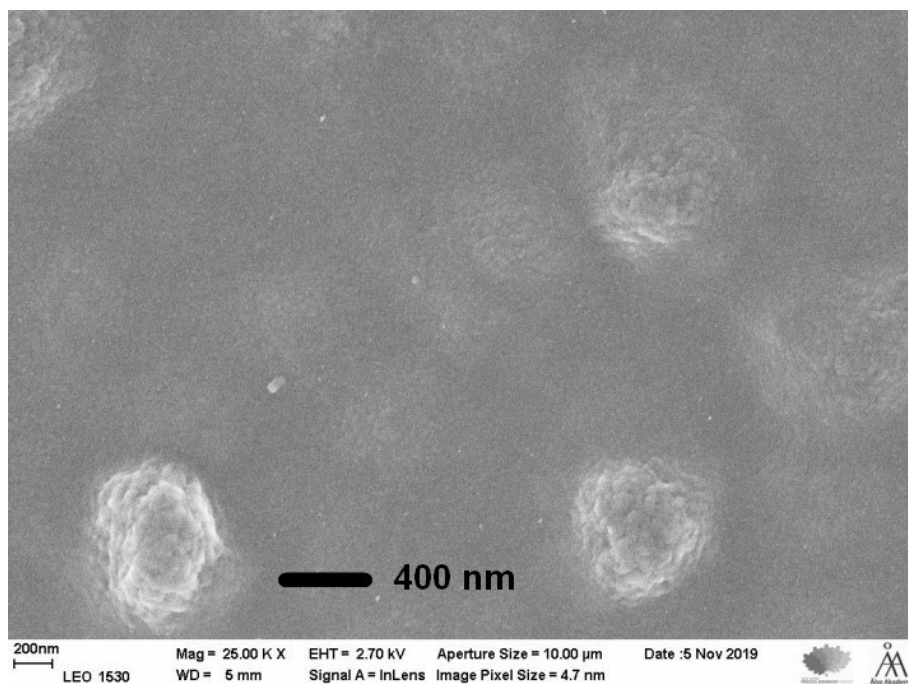
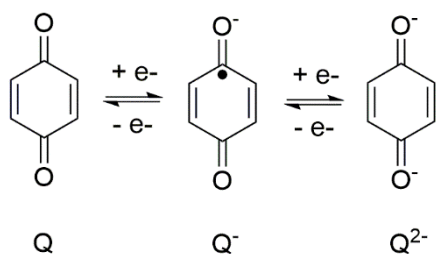


Figure S4. SEM image of the surface of the PEDOT-HQ film that was electropolymerized by cyclic voltammetry from acetonitrile containing 5 mM EDOT-HQ and 0.01 M KTFAB (see Figure S3). Magnification: 25000 times.



Scheme S1. The redox reaction of benzoquinone (BQ) in aprotic solvents [1].

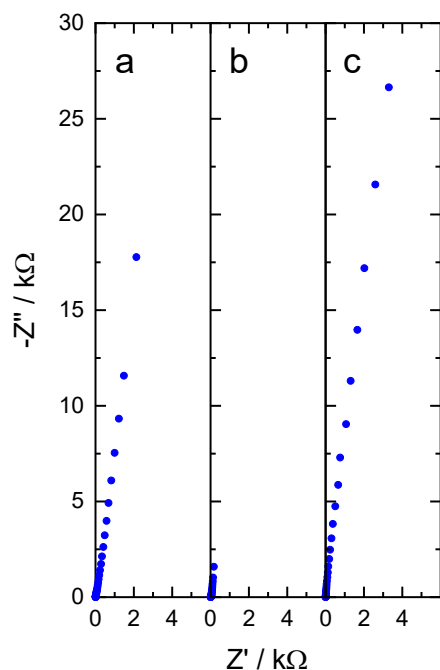


Figure S5a. Electrochemical impedance spectrum of the PEDOT-HQ solid contact measured at (a) 0.30 V, (b) 0.55 V and (c) 0.70 V in an aqueous buffer solution at pH=0; $f=0.01$ Hz – 10 kHz (0.30 V and 0.55 V) 0.01585 Hz – 10 kHz (0.70 V); $\Delta E_{ac}=0.005$ V. RE: Ag/AgCl/3 M KCl.

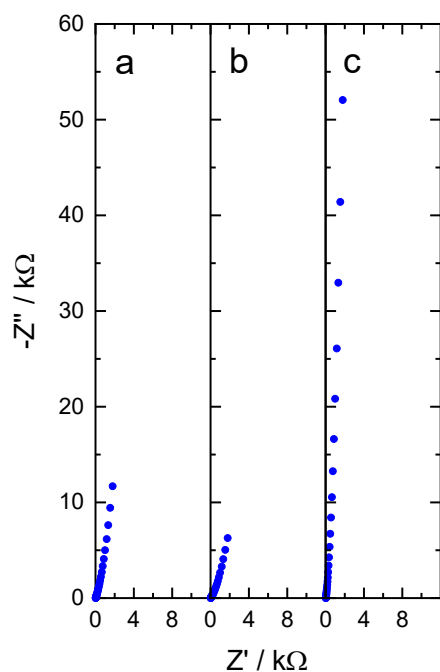


Figure S5b. Electrochemical impedance spectrum of the PEDOT-HQ solid contact measured at (a) 0.00 V, (b) 0.30 V and (c) 0.55 V in an aqueous buffer solution at pH=5.5; $f=0.01$ Hz – 10 kHz and $\Delta E_{ac}=0.005$ V. RE: Ag/AgCl/3 M KCl.

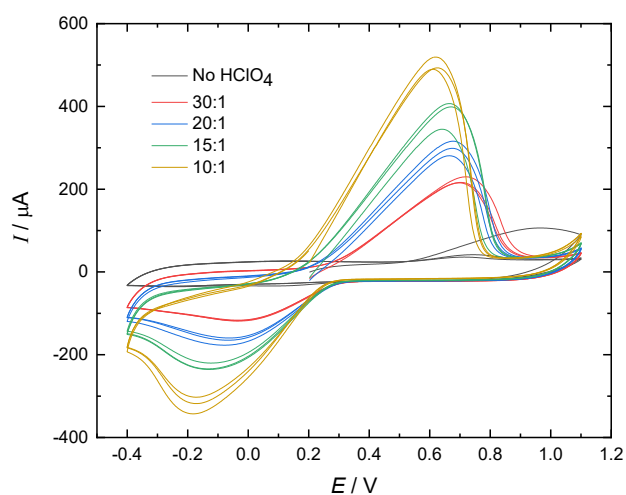


Figure S6. Cyclic voltammograms of the PEDOT-HQ film recorded in 0.01 M KTFAB-acetonitrile with no HClO_4 added and in 30:1, 20:1, 15:1 and 10:1 mixtures (v/v %) of 0.01 M KTFAB-acetonitrile and 0.2 M HClO_4 . Three first cyclic voltammograms recorded in each mixed solution are shown in the figure. RE: Ag/Ag^+ .

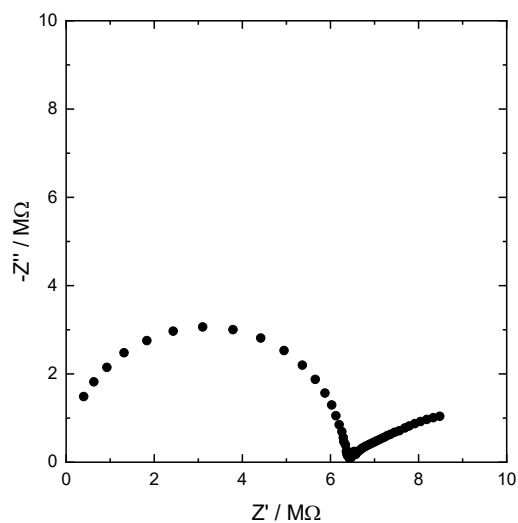


Figure S7. A typical electrochemical impedance spectrum of $\text{K-SCISE}_{\text{mix}}$ measured in 0.1 M KCl; $f=10\text{ kHz} - 25\text{ kHz}$, $E_{\text{dc}}=0.74\text{ V}$ (vs. $\text{Ag}/\text{AgCl}/3\text{ M KCl}$), $\Delta E_{\text{ac}}=0.10\text{ V}$.

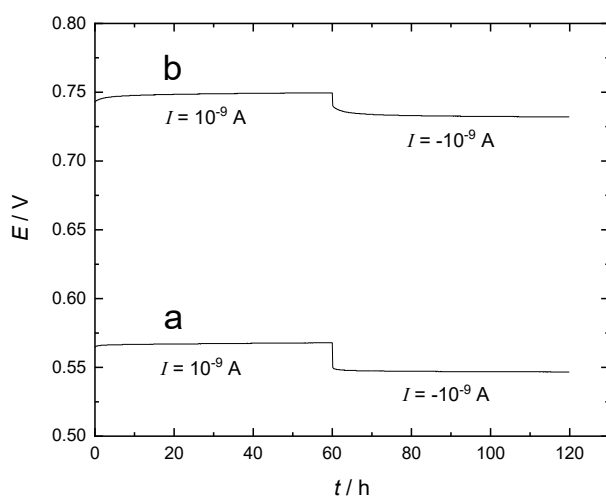


Figure S8. Typical chronopotentiograms of the (a) K-SCISE_{org} and (b) K-SCISE_{mix} measured in 0.1 M KCl. Applied current: $+10^{-9}$ A for the first 60 s and -10^{-9} A for the next 60 s. RE: Ag/AgCl/3 M KCl.

Table S1. E_{pa} , E_{pc} and ΔE for four new GC electrodes shown in Figure S1.

| Electrode # | E_{pa} (mV) | E_{pc} (mV) | ΔE (mV) |
|-------------|------------------|------------------|--------------------|
| 1 | 300.2 | 234.5 | 65.6 |
| 2 | 300.4 | 232.0 | 68.4 |
| 3 | 300.4 | 227.8 | 72.6 |
| 4 | 300.4 | 229.6 | 70.8 |
| Mean | 300.4 ± 0.1 | 231.0 ± 2.5 | 69.4 ± 2.6 |

Table S2. Selectivity coefficients for the K-SCISE with PEDOT-HQ as the solid contact ($n=5$).

| J | $\log K_{K^+, J}^{\text{pot}}$ |
|------------------|--------------------------------|
| NH_4^+ | -1.92 ± 0.02 |
| Na^+ | -4.46 ± 0.05 |
| Li^+ | -5.56 ± 0.05 |
| H^+ | -5.80 ± 0.01 |
| Mg^{2+} | -5.57 ± 0.15 |
| Ca^{2+} | -5.96 ± 0.05 |

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[1] M. Quan, D. Sanchez, M.F. Wasyliw and D.K. Smith, Voltammetry of Quinones in Unbuffered Aqueous Solution: Reassessing the Roles of Proton Transfer and Hydrogen Bonding in the Aqueous Electrochemistry of Quinones, J. Am. Chem. Soc., 129 (2007) 12847-12856.