

Supplementary Information

Direct electrochemical co-polymerization of EDOT and hydroquinone

Alexey I. Volkov, Alexander S. Konev,* Elena V. Alekseeva, Oleg V. Levin*

St. Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, Russian Federation

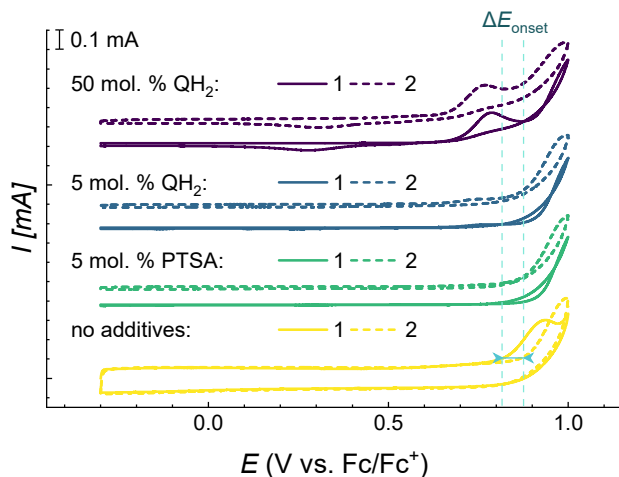


Figure S1. The first and the second cycle for potentiodynamic electropolymerization of EDOT in the presence of QH_2 or PTSA.

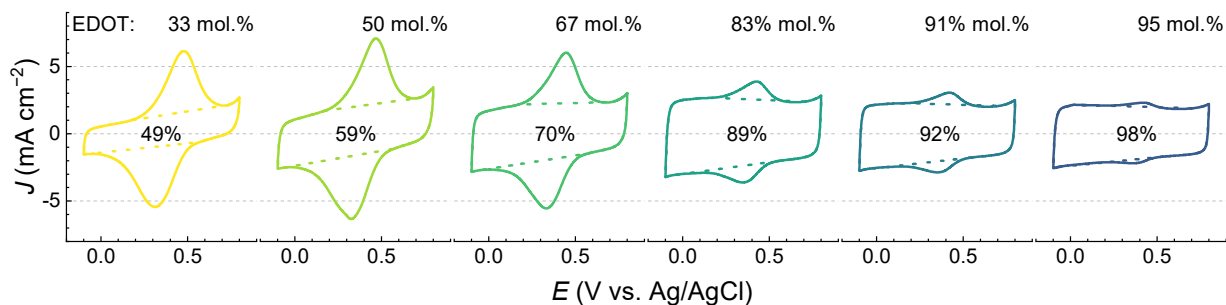


Figure S2. CVs of co-PEDOT- QH_2 films synthesized via cyclic voltammetry deposition from EDOT: QH_2 solution with various EDOT to QH_2 ratios. Molar share of QH_2 with respect to EDOT is shown next to each CV. CVs are recorded in -0.2 V to 0.9 V at 50 mV s^{-1} in 0.1 M HClO_4 . The percentage values indicated inside CVs show contribution of PEDOT-related capacity towards total recorded capacity.

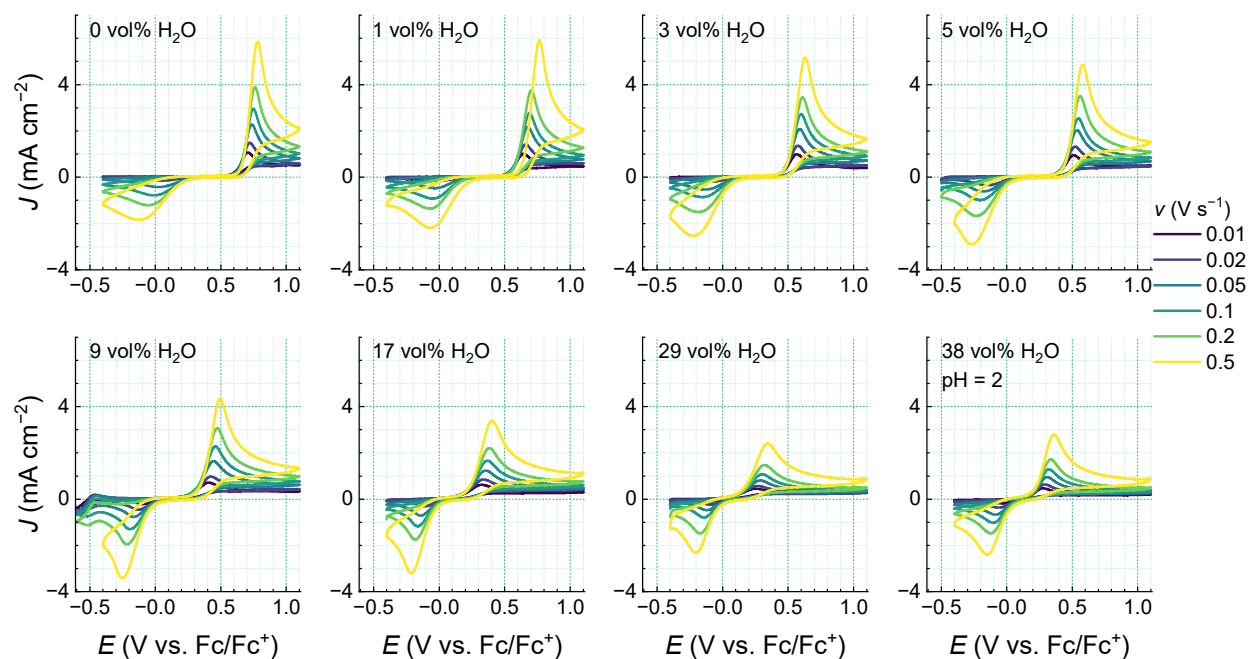


Figure S3. Cyclic voltammograms of QH_2 in MeCN (1 M LiClO_4) at different scan rates with variable water content.

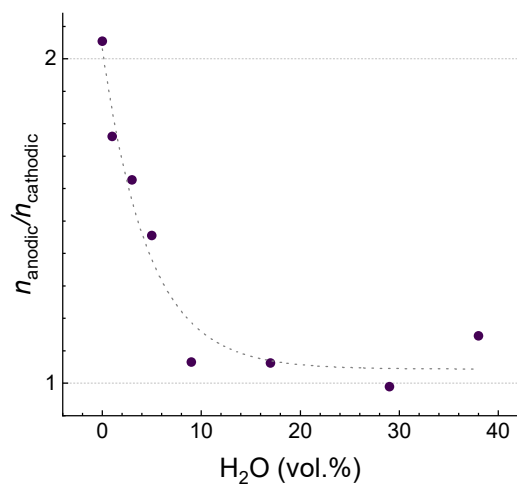


Figure S4. The ratio of the number of electrons involved in the anodic and cathodic reactions depending on the water content in the solution based on the peak analysis in the cyclic voltammograms of QH_2 (MeCN, 1 M LiClO_4) via the Randles–Ševčík equation.

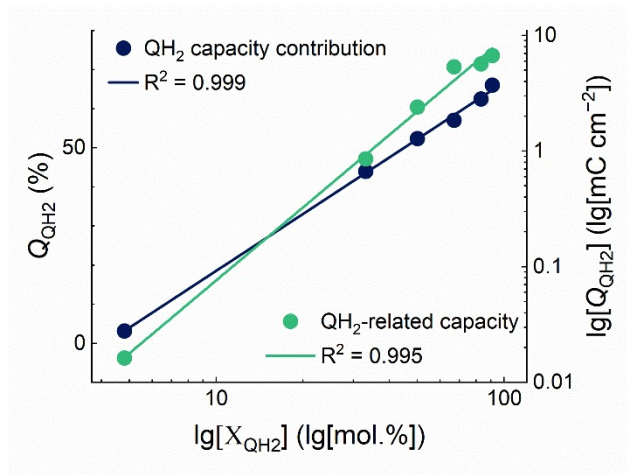


Figure S5. The relation of the capacity contribution of QH_2 towards total capacity of co-PEDOT- QH_2 films in relative (% , left) and absolute ($mC \cdot cm^{-2}$, right, logarithmic) values on the logarithm of molar share of QH_2 in the polymerization feed.

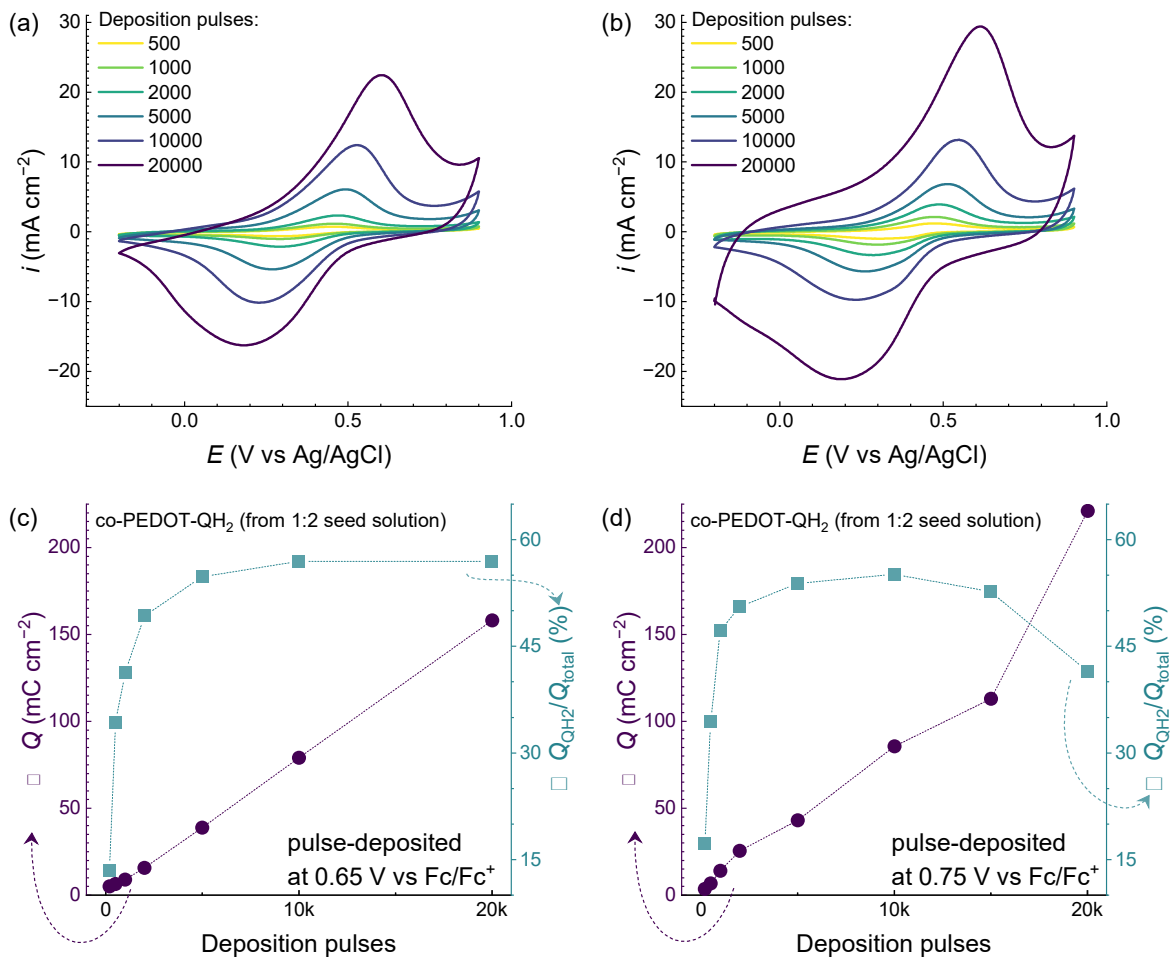


Figure S6. CVs (a, b) of co-PEDOT:QH₂ films synthesized on a 0.07 cm² glassy carbon electrode in pulse potentiostatic mode (0.65 V vs. Fc/Fc⁺ (a) or 0.75 V vs. Fc/Fc⁺ (b), $t_{dep} = 100$ ms, $t_{rest} = 5$ ms) by applying different numbers of pulses from the solution containing 67% QH₂ molar fraction, and (c, d) the total film specific capacity and the QH₂ contribution to the total capacity as functions of the number of synthesis pulses for films deposited at 0.65 V vs. Fc/Fc⁺ (c) or 0.75 V vs. Fc/Fc⁺ (d). CVs are recorded in -0.2 V to 0.9 V range at 50 mV s⁻¹ in 0.1 M HClO₄.

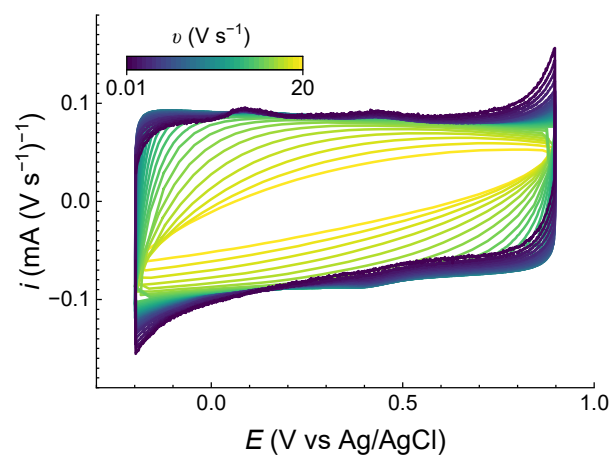


Figure S7. Normalized cyclic voltammograms of a PEDOT film synthesized potentiodynamically ratio at different scan rates indicated in a color bar (V s^{-1}).

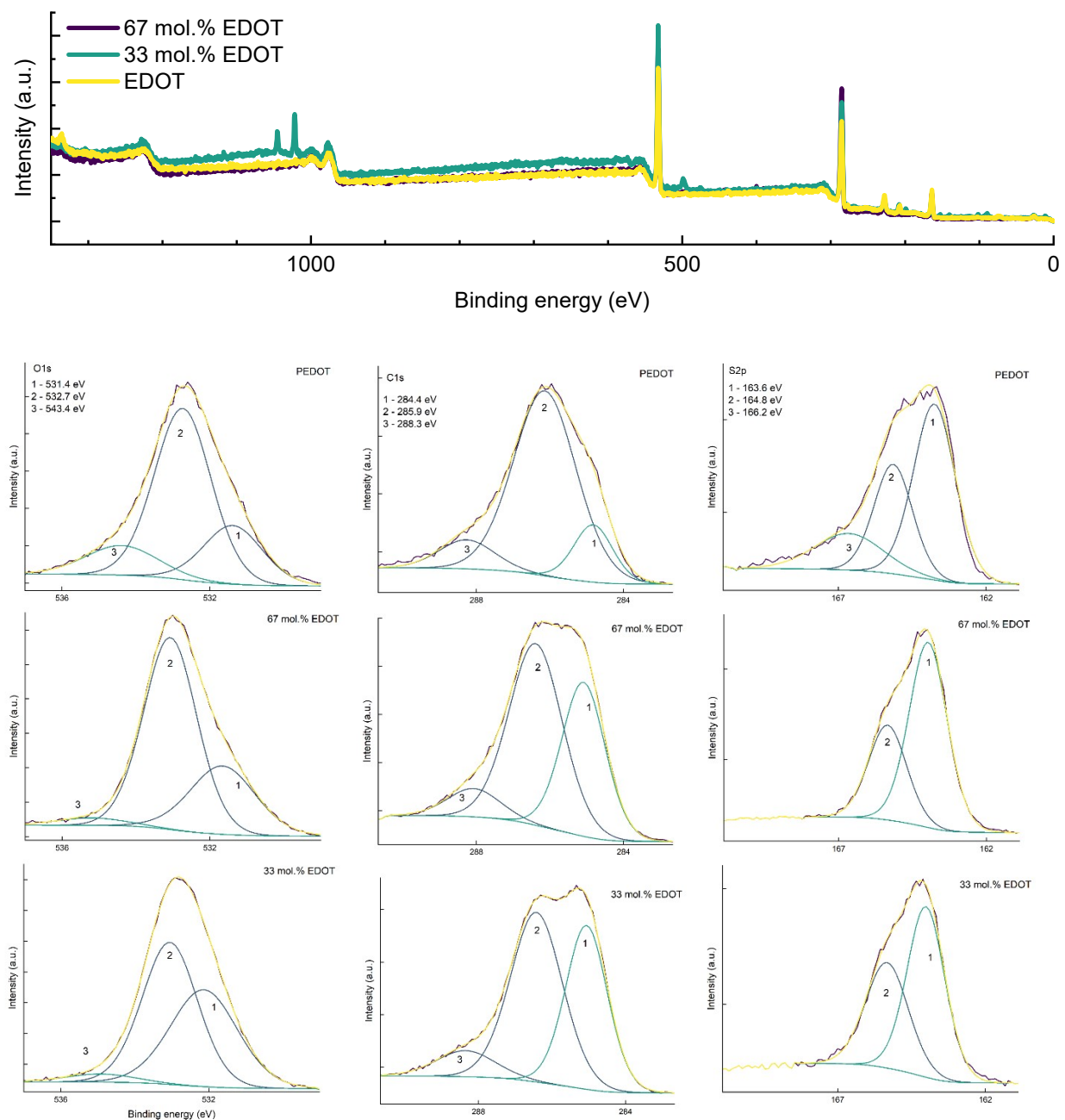


Figure S8. XPS spectra of co-PEDOT-QH₂ films synthesized from the EDOT:QH₂ solutions with 67 mol. % and 33 mol. % QH₂, and PEDOT film. Survey spectra (top), and background-subtracted (Shirley algorithm) O1s (left), C1s (middle) and S2p (right) spectra.

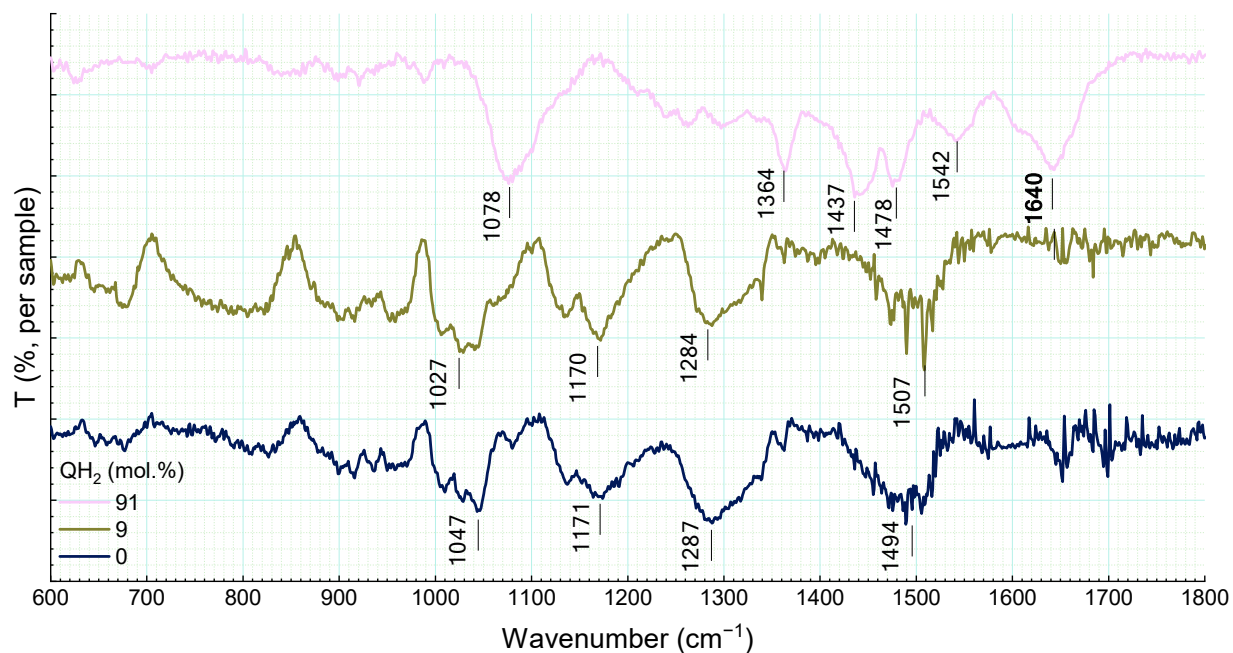


Figure S9. ATR FT-IR spectra of the films synthesized from EDOT:QH₂ solutions with various QH₂ concentration and from EDOT solution, as well of a PEDOT film.

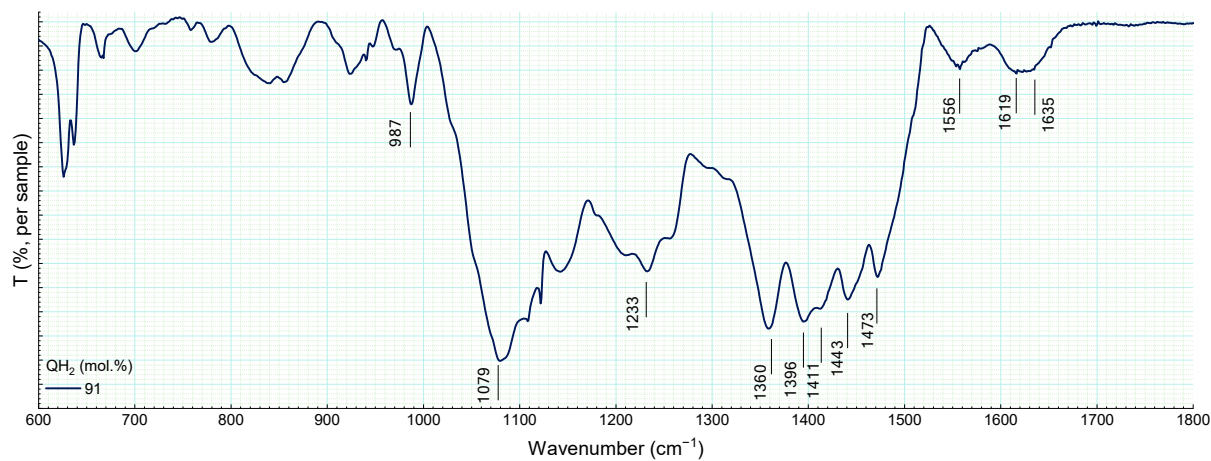


Figure S10. FT-IR (KBr) spectrum of the film synthesized from the solution with 1:10 EDOT:QH₂ ratio.

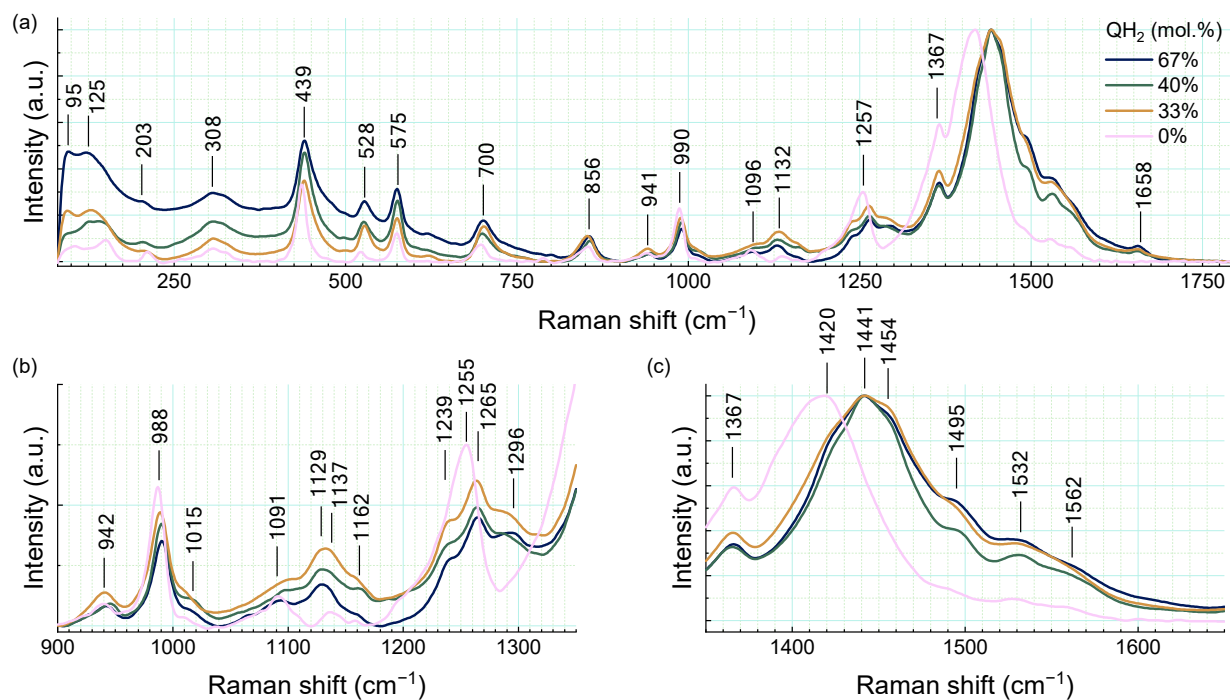


Figure S11. Raman spectra of the films synthesized from EDOT:QH₂ solutions with various QH₂ concentration and from EDOT solution: (a) in 80–1800 cm⁻¹ range, (b) in 900–1350 cm⁻¹ range, and (c) in 1350–1650 cm⁻¹ range.

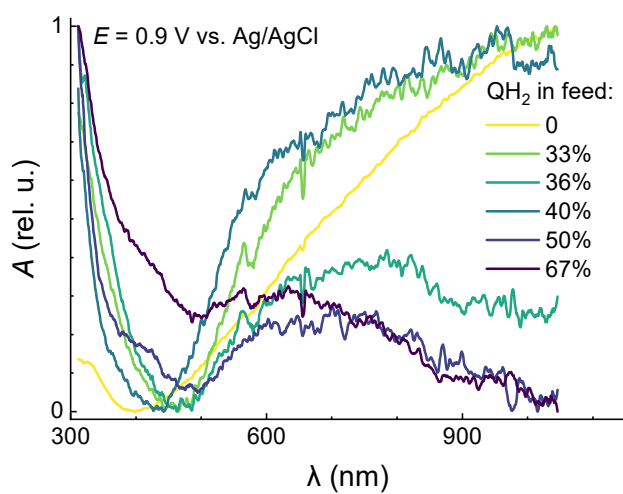


Figure S12. UV-Vis spectra of co-PEDOT-QH₂ films synthesized from feed solutions with different QH₂ content recorded at 0.9 V vs. Ag/AgCl.

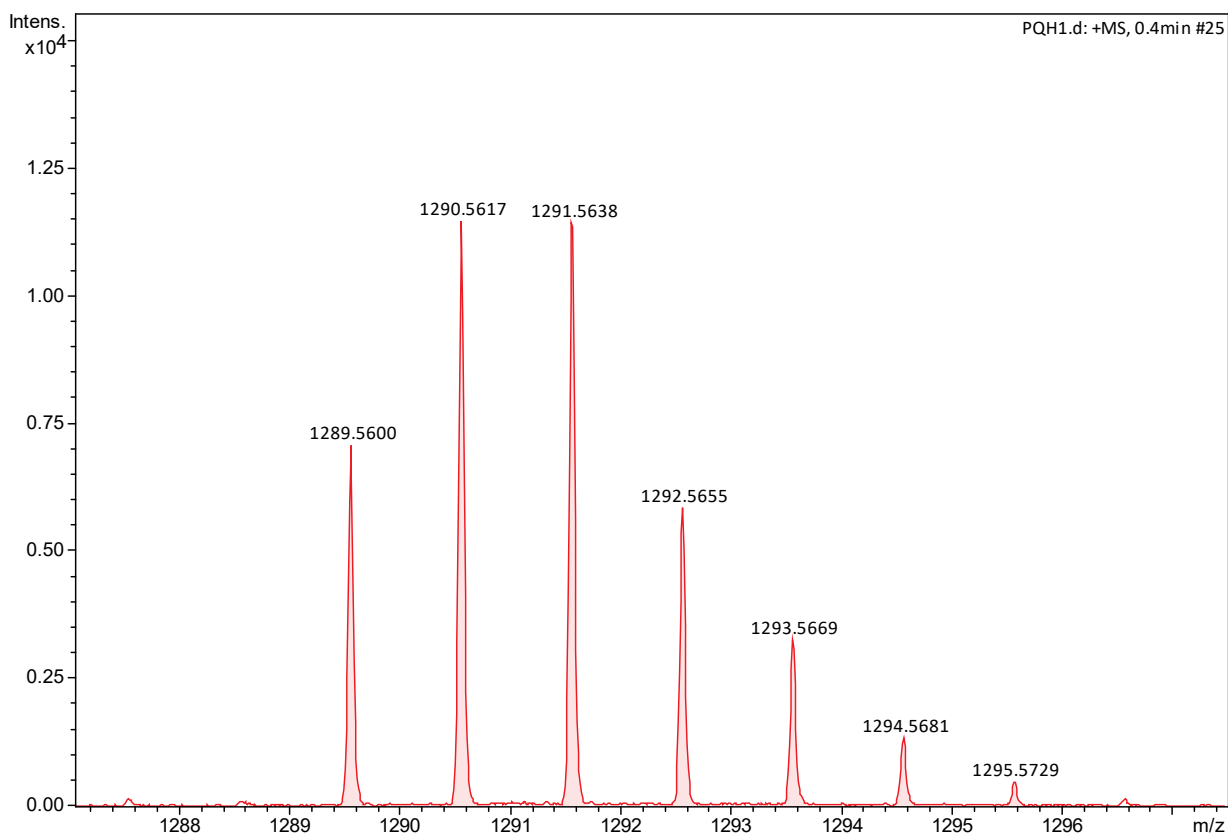


Figure S13. Mass-spectrum of the molecular ion of $(\text{QH}_2)_4(\text{EDOT})_6$ oligomer found in co-PEDOT- QH_2 film synthesized from seed solutions with 1:2 EDOT: QH_2 ratio. $(\text{QH}_2)_4(\text{EDOT})_6$ appears as $[\text{M}+\text{Na}^+]$, the mass distribution is caused by both isotopic distribution and quinone protonation distribution. The least M/e value of 1289.6 corresponds to fully deprotonated $\text{Q}_4(\text{EDOT})_6\cdot\text{Na}^+$ form (calc. M_w 1289.0). The connectivity of the co-monomers in the schematic chemical sketch of $\text{Q}_4(\text{EDOT})_6\cdot\text{Na}^+$ is arbitrary.

Table S1. Fitting parameters used for the analysis of electrochemical impedance spectra of the films.

Parameter	9 mol.% QH ₂	67 mol.% QH ₂
R_s (Ω)	76.0	138
R_1 (Ω)	13.9	18.6
CPE_1^T ($S \cdot s^{p1}$)	$2.11 \cdot 10^{-5}$	$7.32 \cdot 10^{-5}$
$p1$	0.68	0.95
R_2 (Ω)	2020	5660
CPE_2^T ($S \cdot s^{p2}$)	$5.80 \cdot 10^{-4}$	$6.10 \cdot 10^{-4}$
$p2$	1.0	0.60
CPE_{lf}^T ($S \cdot s^{Plf}$)	$5.83 \cdot 10^{-5}$	$5.43 \cdot 10^{-4}$
Plf	0.93	0.88
W ($S \cdot s^{1/2}$)	$1.35 \cdot 10^{-2}$	$4.25 \cdot 10^{-3}$

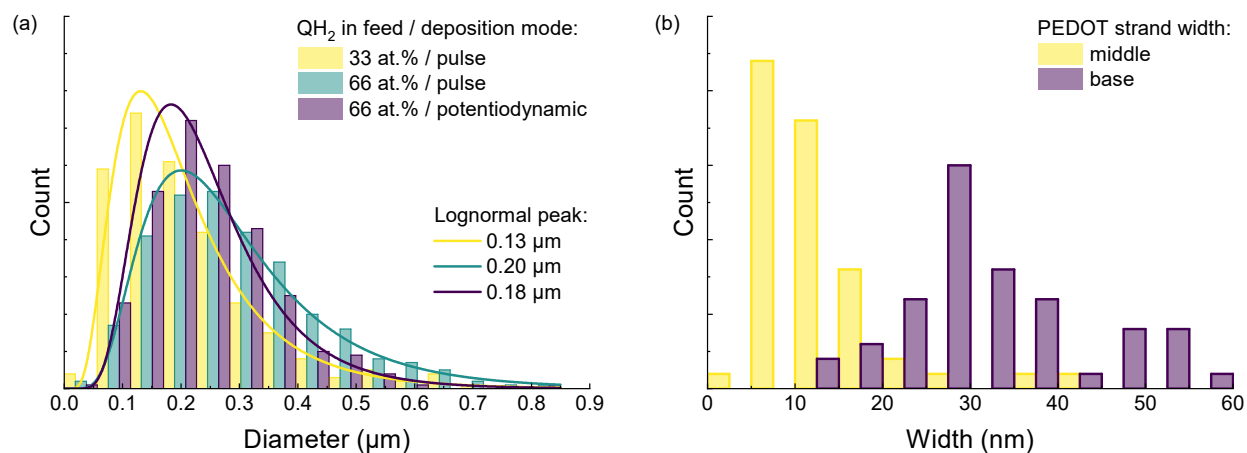


Figure S14. Spherical particles diameter distribution for co-PEDOT-QH₂ films synthesized from feed solutions with different QH₂ content and in various deposition modes (a), and distribution of widths of the PEDOT strands in PEDOT films at the base and in the middle (at the narrowest) (b), according to SEM images.

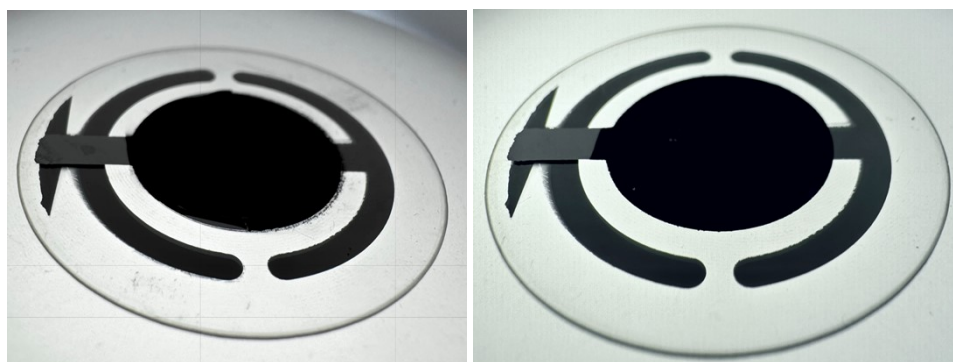


Figure S15. Photo images of the films of QH₂-EDOT co-polymers on platinum plate deposited by pulse voltammetry from EDOT-QH₂ 1:2 (left) and 10:1 (right) solutions.

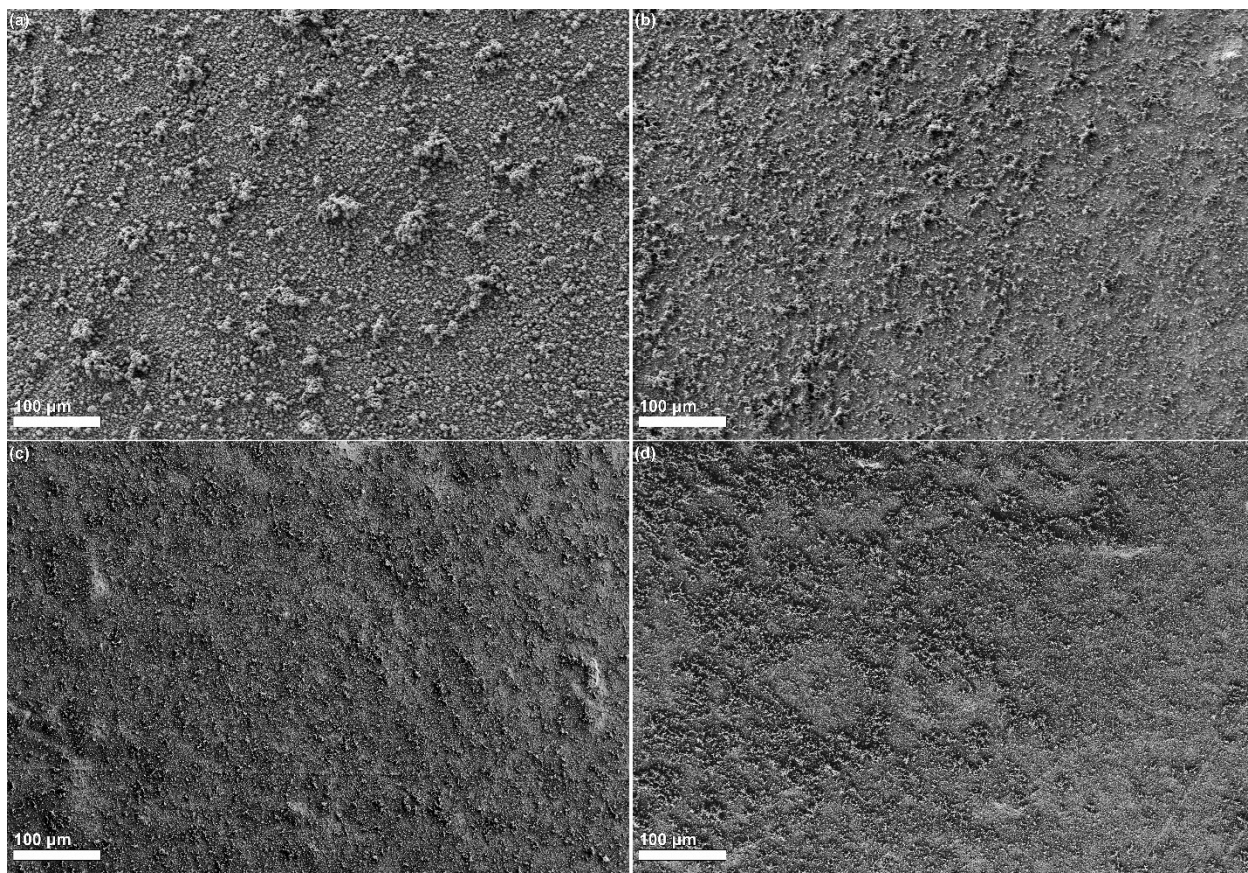


Figure S16. Survey SEM images at low (300x) magnification in SE2 mode of the following films: (a) PEDOT (CV-deposited), (b) co-PEDOT-QH₂ (67 mol.% QH₂) (CV-deposited), (c) co-PEDOT-QH₂ (33 mol.% QH₂) (pulse-deposited), (d) co-PEDOT-QH₂ (67 mol.% QH₂) (pulse-deposited).