

Electrochemical copolymerization-fabricated hybrid photosensitive layers based on poly-3,4-ethylenedioxythiophene and thiophene-substituted nickel porphyrinates

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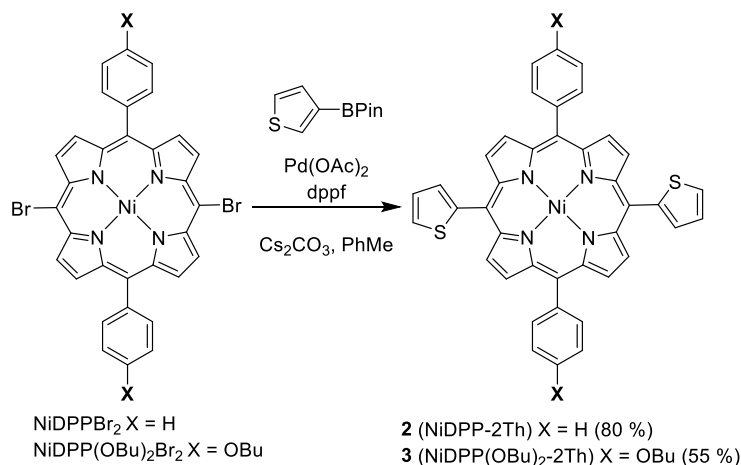
Experimental details

Equipment

The electrochemical copolymerization of EDOT with thiophene-substituted nickel porphyrinates and subsequent studies of the energetic (HOMO and LUMO levels) and electrochemical characteristics of the resulting layers were conducted in a glovebox (MBraun) with a controlled atmosphere of dry argon. Electrochemical experiments were performed using an Autolab PGSTAT302N potentiostat/galvanostat (Metrohm, Utrecht, the Netherlands). Electronic absorption spectra of the porphyrinates in solutions and the resulting layers in air were recorded on a Shimadzu UV3101PC spectrophotometer (Shimadzu GmbH, Duisburg, Germany).

Synthesis of thiophenyl-substituted di- and tetraphenylporphyrins and their Ni-complexes

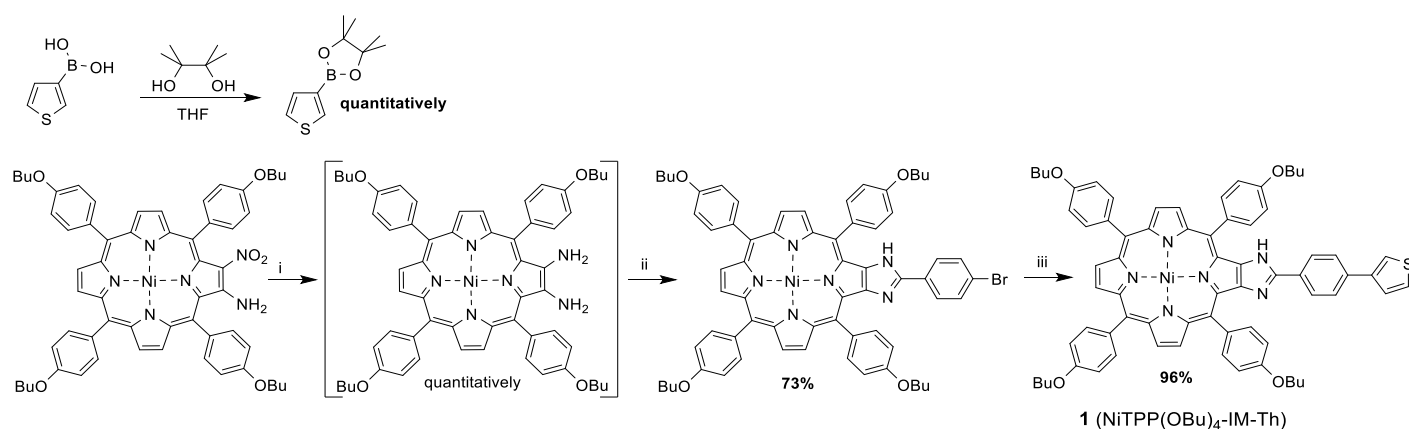
Porphyrins NiDPP-2Th **2** and NiDPP(OBu)₂-2Th **3** were prepared from previously described nickel(II) diarylporphyrinates.^{S1,S2} Porphyrins NiDPPBr₂ and NiDPP(OBu)₂Br₂ were prepared following the reported method.^{S3}



Scheme S1. Synthesis of thiophene-substituted porphyrins **2,3**.

Thiophene-substituted porphyrins NiDPP-2Th **2** and NiDPP(OBu)₂-2Th **3** were synthesized using Suzuki cross-coupling reaction from corresponding nickel(II) dibromoporphyrinates NiDPPBr₂ and NiDPP(OBu)₂Br₂ (Scheme S1). These porphyrins were subjected to the reaction with thiophen-3-ylboronic acid pinacol ester in the presence of Pd(OAc)₂, 1,1'-bis(diphenylphosphino)ferrocene (dppf), Cs₂CO₃ in toluene under argon atmosphere. The synthesis procedure allowed one to prepare target thiophene-substituted porphyrins.

Imidazolyl-substituted porphyrin NiTPP(OBu)₄-IM-Th **1** was also synthesized using Suzuki cross-coupling reaction from 4-bromophenyl-substituted precursor. The precursor was synthesized from β -nitro- β' -aminoporphyrin and 4-bromobenzaldehyde. Thiophen-3-ylboronic acid pinacol ester was also used for the cross-coupling reaction due to its higher reactivity compared to aryl boronic acids.



Scheme S2. Synthesis of thiophene-substituted nickel(II) imidazolylporphyrinate **1**: i, NaBH₄, 10% Pd/C, CH₂Cl₂/MeOH; ii, 4-bromobenzaldehyde (1 equiv.), 1,2-dichlorobenzene, 120°C; iii, thiophen-3-ylboronic acid pinacol ester (5 equiv.), Pd(PPh₃)₄ (13 mol%), CsF (4 equiv.), 1,2-dimethoxyethane, reflux.

Reaction of 4-bromophenyl-substituted imidazoporphyrin with thiophen-3-ylboronic acid pinacol ester allowed one to prepare the target compound NiTPP(OBu)₄-IM-Th **1** with nearly quantitative yield. It is worth to mention that no reductive debromination product was observed during the reaction course, though formation of the product is typical for this type of reaction. An alternative synthetic route could involve borylation of nickel(II) dibromoporphyrinate and subsequent cross-coupling with 3-bromothiophene. However, we found that borylation of the nickel(II) dibromoporphyrinate proceeds with low yield and requires additional optimization.

Electronic absorption spectra of thiophene-substituted Ni-porphyrinates are presented in Figure S1.

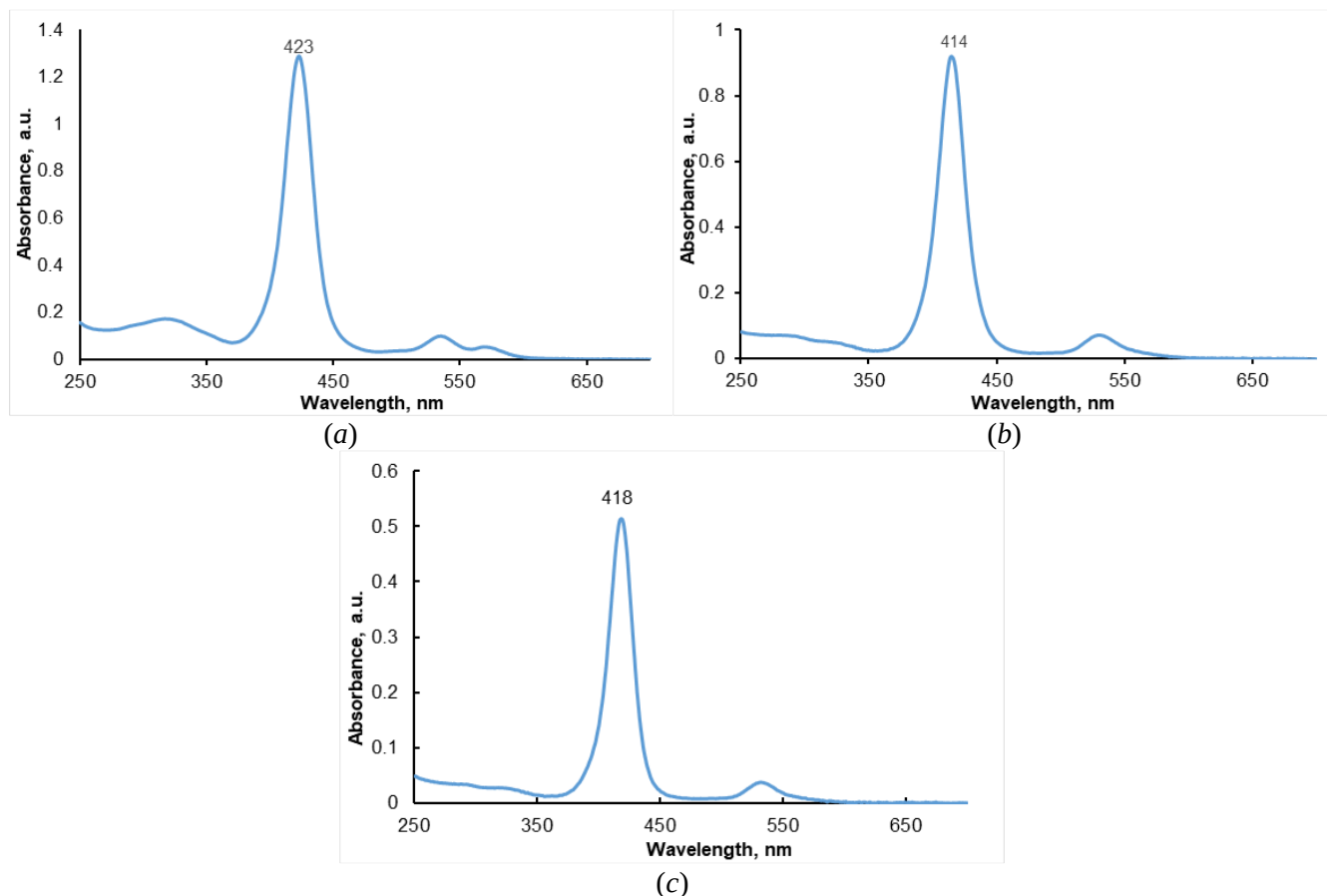


Figure S1. Electronic absorption spectra (chloroform solutions) of thiophene-substituted porphyrinates used in the work: (a) NiTPP(OBu)₄-IM-Th 1; (b) NiDPP-2Th 2; (c) NiDPP(OBu)₂-2Th 3.

References

- S1 A. Wiehe, Y. M. Shaker, J. C. Brandt, S. Mebs and M. O. Senge, *Tetrahedron*, 2005, **61**, 5535; <https://doi.org/10.1016/j.tet.2005.03.086>.
- S2 J. V. S. Krishna, N.V. Krishna, S. K. Singh, P. K. Shaw, V. M. Dhavale, A. K. Vardhaman and L. Giribabu, *Eur. J. Inorg. Chem.*, 2018, 1549; <https://doi.org/10.1002/ejic.201701427>.
- S3 X.-Q. Lu, Y. Guo and Q.-Y. Chen, *Synlett*, 2011, 77; <https://doi.org/10.1055/s-0030-1259101>.

Electrochemical copolymerization of EDOT with thiophene-substituted nickel porphyrinates

Electrochemical copolymerization of EDOT with thiophene-substituted nickel porphyrinates (Figures S2 *a,b*, S3 *a,b*, S4 *a,b*) was carried out in a 0.4 M Bu₄NBF₄ solution in a 1:1 mixture of acetonitrile (AN) and dichloromethane (DCM) as a supporting electrolyte. The addition of DCM is necessary to ensure the solubility of the porphyrin monomer. To measure the energy characteristics by cyclic voltammetry (CV), copolymer films were deposited in the potential cycling mode on Pt electrodes in a glass three-electrode cell with volumes for the working (Pt), auxiliary (Pt) electrodes and pseudo-reference electrode (Ag/Ag⁺) – an Ag wire in a background electrolyte solution with the addition of AgNO₃, isolated by glass valves. The electrolyte for the volume of the cell with the working electrode (working volume) was prepared separately according to the following procedure: 1) a weighed portion of the porphyrin monomer, required to obtain a solution with a concentration of 0.5 mM, was dissolved in a volume of pure DCM equal to half the working volume; 2) a solution of 2 mM EDOT in an electrolyte based on

pure AN was added in an amount necessary to ensure the ratio of EDOT:porphyrinate concentrations equal to 2:1, 1:1, 1:2; 3) a calculated amount of pure AN was added to ensure the composition of the solvent mixture was 1:1.

Determination of HOMO and LUMO energy values by cyclic voltammetry

Cyclic voltammograms (Figures S2 c, S3 c, S4 c) for measuring the HOMO and LUMO levels of the prepared films on Pt electrodes were recorded in the same electrochemical cell in the monomer-free background electrolyte of 0.2 M Bu₄NBF₄ in AN. The HOMO and LUMO energy levels were determined by plotting tangents to the oxidation (HOMO) or reduction (LUMO) current fronts until they intersected the axis of potential.

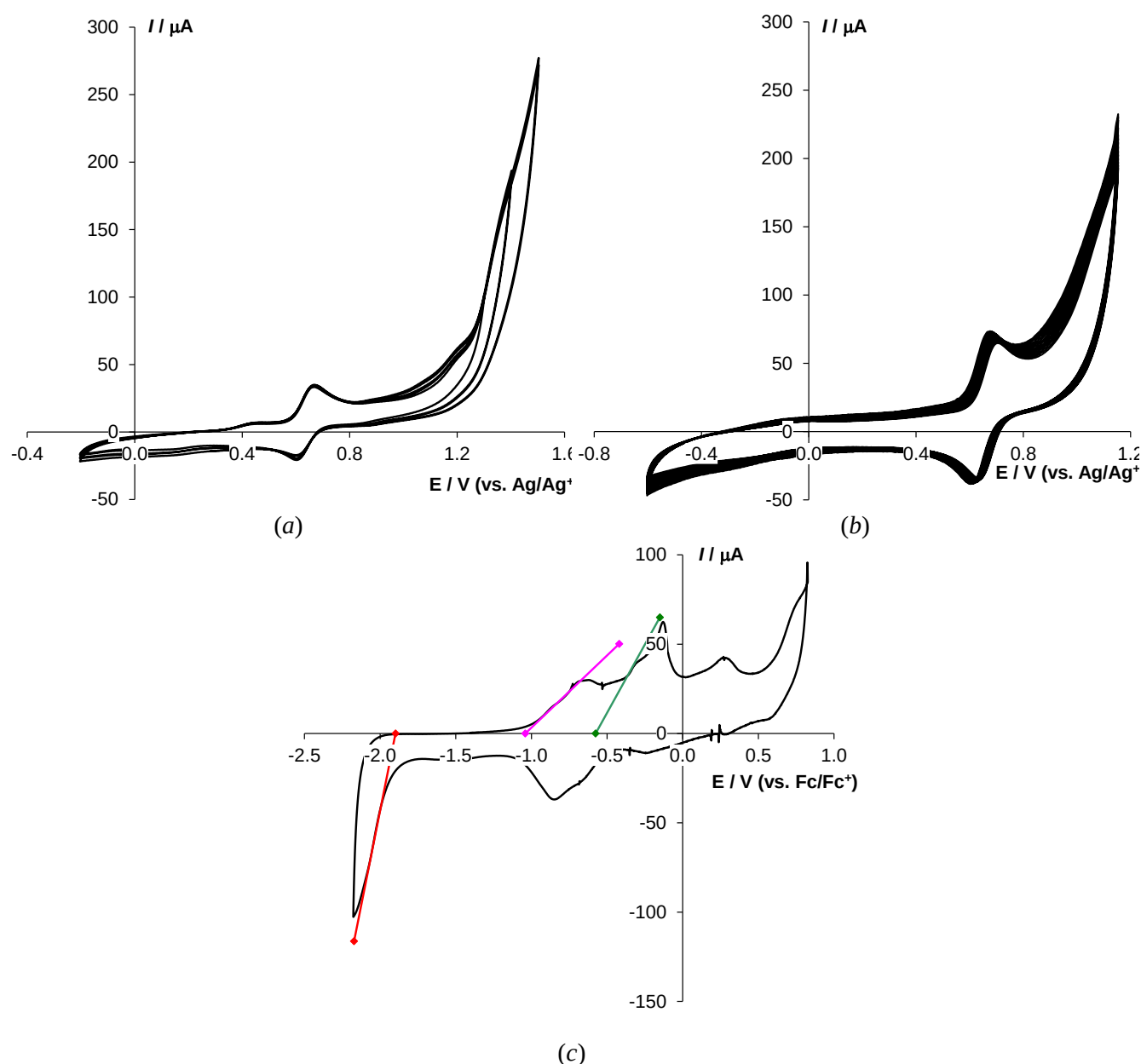


Figure S2. Cyclic voltammograms recorded during electrosynthesis (a), (b) and cycling in monomer-free electrolyte (c) of the poly(EDOT+**1**) films obtained in solutions of the following compositions: (a) 0.5 mM **1**; (b),(c) 0.5 mM EDOT and 0.5 mM **1** (1:1).

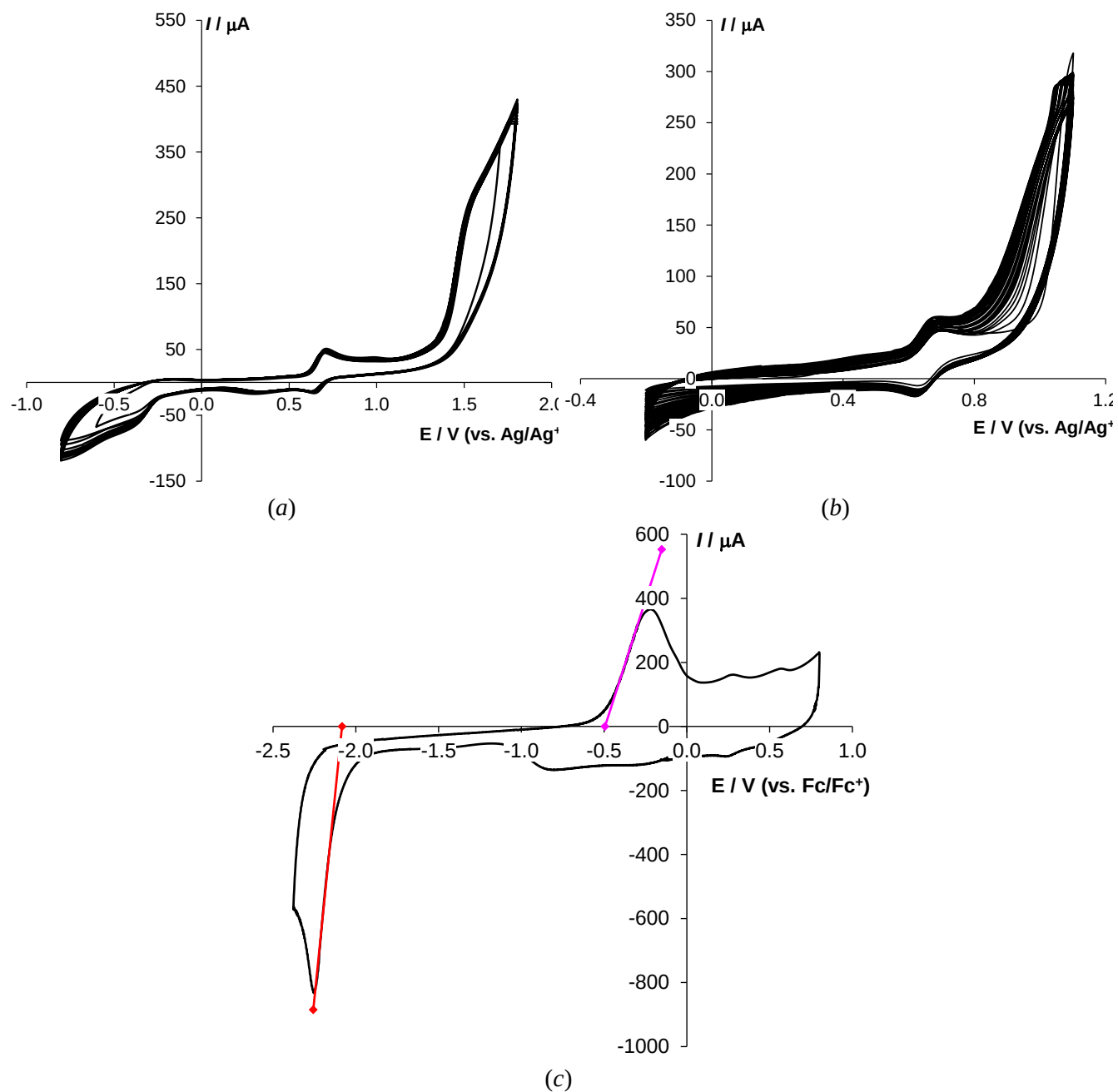


Figure S3. Cyclic voltammograms recorded during electrosynthesis (a),(b) and cycling in monomer-free electrolyte (c) of the poly(EDOT+**2**) films obtained in solutions of the following compositions:
 (a) 1 mM **2**; (b),(c) 0.5 mM EDOT and 0.5 mM **2** (1:1).

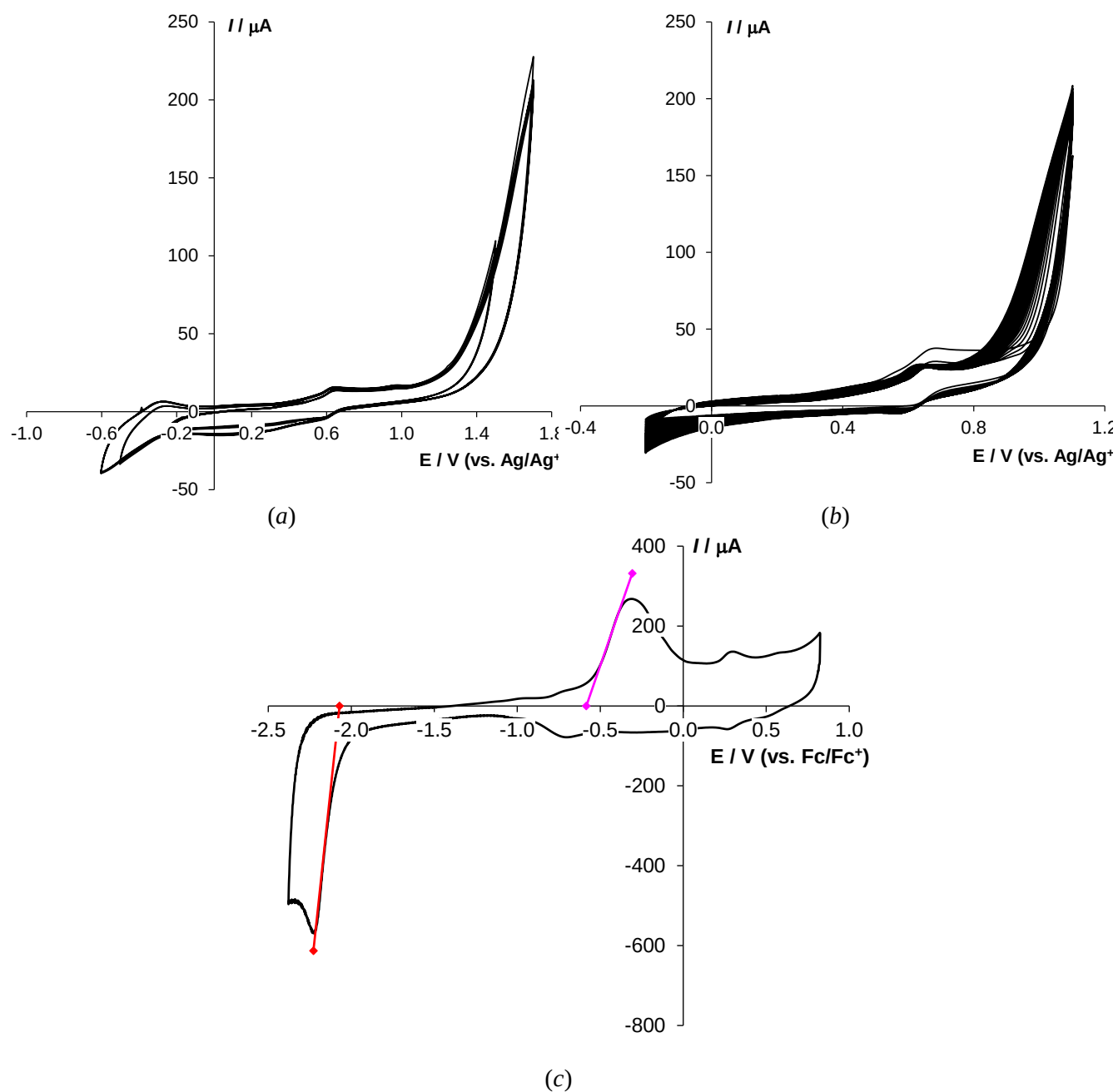


Figure S4. Cyclic voltammograms recorded during electrosynthesis (a),(b) and cycling in monomer-free electrolyte (c) of the poly(EDOT+3) films obtained in solutions of the following compositions: (a) 1 mM 3; (b),(c) 0.5 mM EDOT and 0.5 mM 3 (1:1).

To fabricate photodiode samples, the electrochemical copolymerization of EDOT with thiophene-substituted nickel porphyrinates was carried out in a Teflon two-volume three-electrode cell, the working volume of which contained a clamped working (FTO, 7 Ohm per square, Solaronix SA, Aubonne, Switzerland) and auxiliary (Pt-ring) electrodes, while the volume for the pseudo-reference electrode was separated from the working volume by a fritted glass filter. An organic silver-silver-chloride electrode ($\text{Ag}/\text{AgCl}_{\text{org}}$) was used as a pseudo-reference electrode, which consisted of an Ag wire with an anodic coating of AgCl immersed in the background electrolyte. The pseudo-reference electrode in this cell was also calibrated relative to ferrocene. For ease of comparison, the values of potential in the cyclic voltammograms recorded on Pt and FTO are given relative to the redox potential of the Fc/Fc^+ pair. Before copolymerization, the FTO electrode was coated with a layer of a complex of PEDOT with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) using galvanostatic (GS) electrodeposition (Figure S5) at the current density of $50 \mu\text{A cm}^{-2}$ in an aqueous solution of 0.01 M EDOT and PAMPSA (0.02 g-eq. SO_3^-). Reproducibility of the sublayer thickness was achieved by monitoring the charge spent on electropolymerization (7 mC cm^{-2}). The PEDOT:PAMPSA layer in the photodiode served as a hole-transport layer (HTL), which will be used for its designation below). After application of the HTL layers, they were rinsed with deionized water, air dried and then vacuum dried before application of the hybrid layers.

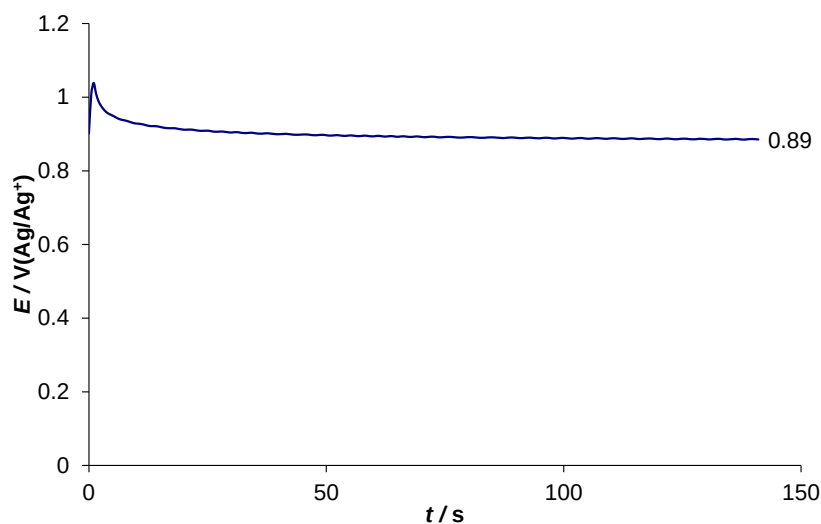


Figure S5. Change of potential in time during GS ($50 \mu\text{A cm}^{-2}$) electrosynthesis of HTL PEDOT-PAMPSA. Electropolymerization charge 7 mC cm^{-2} .

To obtain PEDOT-porphyrinate hybrid layers, electrochemical copolymerization of EDOT with thiophene-substituted porphyrinates was carried out on FTO/HTL substrates from a 0.4 M Bu₄NBF₄ solution in AN:DCM (1:1), to which 1 mM EDOT and 1 mM or 2 mM of porphyrinate were added to obtain 1:1 or 1:2 composition, respectively. The process was carried out in the GS mode at the current densities of 40 or 50 $\mu\text{A cm}^{-2}$ (adjusted in order to exclude growth of the potential during electrodeposition) until a charge of 50 $\mu\text{C cm}^{-2}$ was reached (Figure S6).

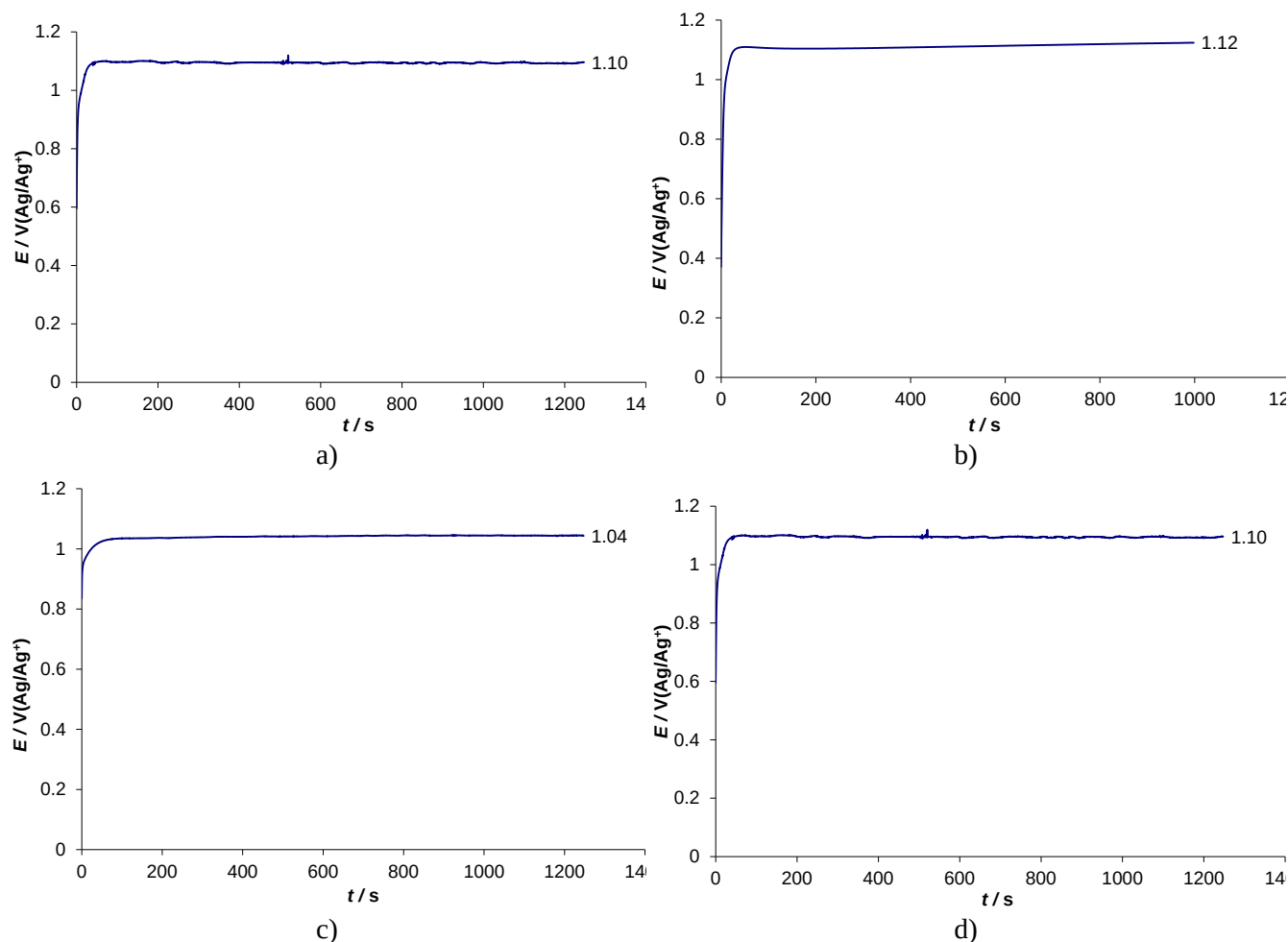


Figure S6. Change of potential in time during GS (50 $\mu\text{A cm}^{-2}$) electro-synthesis of PEDOT-porphyrinate hybrid layers on FTO/HTL substrates in the solution containing: (a) 1 mM EDOT and 1 mM NiTPP(OBu)₄-IM-Th **1**; (b) 1 mM EDOT and 1 mM NiDPP-2Th **2**; (c) 1 mM EDOT and 2 mM NiDPP-2Th **2**; (d) 1 mM EDOT and 1 mM NiDPP(OBu)₂-2Th **3**. Electropolymerization charge 50 mQ cm^{-2} .

After the electro-synthesis, the electrochemical cell with hybrid layers was washed with the full volume of DCM (15 min) and the full volume of AN (15 min). To register the CV of hybrid layers, the cell was filled with a 0.2 M solution of Bu₄NBF₄ in AN. The CV were recorded at the scan rate of 20 mV/s (Figure S7). The HOMO energy levels were determined by plotting tangents to the oxidation current fronts until they intersected the axis of potential (Table S1).

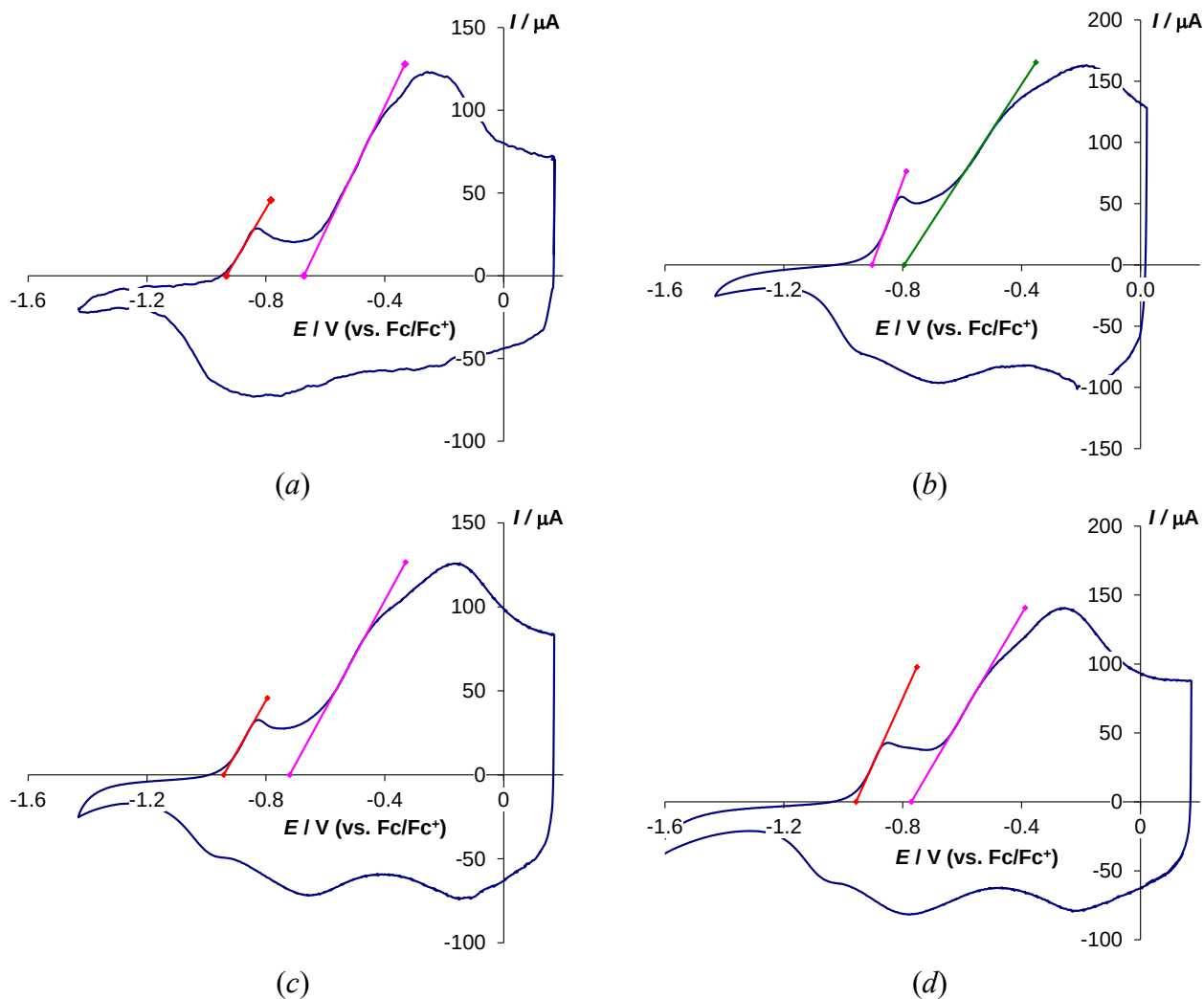


Figure S7. Cyclic voltammograms of PEDOT-porphyrinate hybrid layers deposited on FTO/HTL substrates: (a) PEDOT-1 (1:1); (b) PEDOT-2 (1:1); (c) PEDOT-2 (1:2); (d) PEDOT-3 (1:1).

Table S1. Values of the potential at the end of the GS synthesis (E_{GS}), potential of the peak current on CV curve (E_{max}) and the energy of HOMO level (E_{HOMO2}) of PEDOT-porphyrinate hybrid layers.

PEDOT-porphyrinate	$E_{GS} / V (Ag/Ag^+)$	E_{HOMO2} / eV	$E_{max} / V (Ag/Ag^+)$
PEDOT-1 (1:1)	1.25	-4.22	0.18
PEDOT-2 (1:1)	1.12	-4.19	0.25
PEDOT-2 (1:2)	1.04	-4.27	0.27
PEDOT-3 (1:1)	1.10	-4.22	0.17

Study of photoelectric properties of the hybrid layers

The photoelectric characteristics of PEDOT-Ni-porphyrinate hybrid layers were studied as part of FTO/HTL/PEDOT-Ni-porphyrinate/C₆₀/BCP/Al photodiode structures. On top of the electrodeposited layers the C₆₀ (20 nm thick), bathocuproine (BCP, 8 nm), and Al (80 nm) layers were deposited successively by vacuum thermal evaporation at a residual pressure of 10^{-5} Pa. Current-voltage characteristics of the photodiode structures in the dark and under illuminated conditions were measured using a setup including a standard Keithley 2400 source-measure unit and a xenon lamp (Newport 66028 solar simulator) with the radiation power of $P=0.1 \text{ W cm}^{-2}$. The electrical measurements were performed in a glovebox with a dry argon atmosphere. The integral photosensitivity was determined as $S = I_{ph}/P \text{ [A/W]}$, where I_{ph} is the photocurrent density $\text{[A cm}^{-2}\text{]}$.