Supporting Information

Thiophene-based Microporous Polymer Networks via Chemical and Electrochemical Oxidative Coupling

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Materials and Methods

Monomers and bulk polymers

All reagents and chemicals were purchased from commercial companies, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance III 600 machine. APLI mass spectra were recorded on a Bruker Daltronik micrOTOF system (KrF*-Laser ATLEX-SI, ATL Wermelskirchen). Elemental analyses were obtained on a Perkin Elmer 240 B. Thermogravimetric analyses were recorded under argon flow on a Mettler Toledo TGA/DSC1 STAR System. Solid state ^{13}C{^{1}H} cross-polarization magic-angle spinning (CPMAS) spectra were measured at 50.33 MHz using a Bruker AVANCE III 200 NMR spectrometer with a contact time of 2.5 ms, averaging 32768 transients at a relaxation delay of 2 s. All experiments were carried out at room temperature using a standard Bruker 2.5 mm double resonance MAS probe spinning at 20 kHz, typical $\pi/2$-pulse lengths of 2.5 μs and SPINAL64 proton decoupling (200.15 MHz; $10\pi/12$ pulse set to 4.2 μs) at rather modest power levels of 46.5 Watt (^{13}C) and 19 Watt (^{1}H), respectively. The ^{13}C spectra were referenced with respect to tetramethylsilane (TMS) using solid adamantane as secondary standard (29.46 ppm for ^{13}C). FT-IR and UV-vis spectra were recorded on a JASCO FT/IR-4200 and V-670, respectively. Photoluminescence spectra were obtained on a HORIBA Scientific FluoroMax-4 Spectrofluorometer. A Tousimis Samdri-795 system was used for washing the bulk polymers with supercritical carbon dioxide. Nitrogen and krypton adsorption-desorption isotherms were recorded on a BEL Japan Inc Belsorp-max system at 77 K. A maximum relative pressure of 0.6 was set for measurements with Kr gas. All samples were dried on a Belprep-vac II at 140 °C and ~ 2 Pa overnight prior to the gas sorption measurements.

Synthesis of 2,2’,7,7’-tetra(thien-2-yl)-9,9’-spirobifluorene (SpTh)

2,2',7,7'-Tetrabromo-9,9'-spirobifluorene[S1] (1.00 g, 1.58 mmol) and tributyl(thien-2-yl)stannane (2.36 g, 6.33 mmol) were placed in a 20 mL microwave vial and carefully degassed. Dry toluene (20 mL) and tetrakis(triphenylphosphine)palladium(0) (0.09 g, 0.08 mmol) were added as solvent and catalyst, respectively. The mixture was stirred under argon atmosphere and exclusion of light at 140 °C for 2 hours. After evaporation of the solvent, the crude product was purified by column chromatography on silica (eluent: hexane/dichloromethane 7:3) and recrystallized from a chloroform/ethanol mixture. The product was isolated as yellow crystals, yield: 0.65 g (64 %). ^{1}H NMR (600 MHz, $C_2D_2Cl_4$)

δ: 7.89 (d, *J* = 7.9 Hz, 4H), 7.68 (dd, *J* = 8.0, 1.7 Hz, 4H), 7.20 (dd, *J* = 5.0, 1.1 Hz, 4H), 7.18 (dd, *J* = 3.7, 1.1 Hz, 4H), 7.01 (d, *J* = 1.4 Hz, 4H), 6.97 (dd, *J* = 5.0, 3.7 Hz, 4H); ^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ: 149.16, 143.84, 140.48, 133.96, 127.92, 125.96, 124.76, 123.34, 121.11, 120.54, 65.75; MS (APLI) 644.046 [644.076] (M^+). Elem. Anal. for $C_{41}H_{24}S_4$, found: C 76.03, H 3.39, S 20.4; calc: C 76.36, H 3.75, S 19.89.

Synthesis of 2,2’,7,7’-tetra(thioen-3-yl)-9,9’-spirobifluorene (Sp3Th)

2,2',7,7'-Tetrabromo-9,9'-spirobifluorene[S1] (2.00 g, 3.16 mmol), thien-3-ylboronic acid (1.66 g, 13.0 mmol), and sodium carbonate (3.00 g, 28.3 mmol) were placed in a 250 mL two-necked round flask and carefully degassed. Toluene (35 mL), n-butanol (20 mL) and water (15 mL) were added as degassed solvents. Tetrakis(triphenylphosphine)palladium (0) (0.18 g, 0.16 mmol) in toluene (10 mL) was added and the mixture was stirred under argon atmosphere and exclusion of light under reflux for 24 hours. After cooling down the mixture to rt, chloroform (50 mL) was added and the resulting organic phase was washed 5 times with aqueous 2N HCl. The collected organic phases were dried with $MgSO_4$. After solvent evaporation, the crude product was purified by column chromatography on silica (eluent: hexane/dichloromethane 7:3) and recrystallized from chloroform. The product was isolated as white powder, yield: 1.19 g (58 %). ^{1}H NMR (600 MHz, THF-d8) δ: 7.96 (d, *J* = 8.0 Hz, 4H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.46 (dd, *J* = 2.9, 1.4 Hz, 4H), 7.30 (dd, *J* = 5.1, 2.9 Hz, 4H), 7.27 (dd, *J* = 5.1,1.3 Hz, 4H), 7.06 (d, *J* = 1.4 Hz, 4H); ^{13}C NMR (151 MHz, THF-d8) δ: 150.86, 142.89, 141.54, 136.79, 127.15, 127.01, 126.66, 122.49, 121.26, 79.48; MS (APLI) 644.053 [644.076] (M^+). Elem. Anal. for $C_{41}H_{24}S_4$, found: C 76.01, H 3.50, S 20.07; calc: C 76.36, H 3.75, S 19.89.

Synthesis of tetra[4-(thien-2-yl)phenyl]methane (TPTTh)

Tetra(4-bromophenyl)methane[S2] (1.00 g, 1.57 mmol) and tributyl(thien-2-yl)stannane (2.93 g, 7.86 mmol) were placed in a 20 mL microwave vial and carefully degassed. Dry THF (10 mL), toluene (10 mL) and tetrakis(triphenylphosphine)palladium (0) (0.18 g, 0.16 mmol) were added as solvents and catalyst, respectively. The mixture was stirred under argon atmosphere and exclusion of light at 140 °C for 24 hours. After evaporation of the solvent, the crude product was purified by column chromatography on silica, (eluent: hexane/dichloromethane 8:2). The product was isolated as white powder, yield: 0.18 g (18 %). ^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ: 7.56 (d, *J* = 8.5 Hz, 8H), 7.35 (dd, *J* = 3.6, 0.9 Hz, 4H), 7.30 (m, 12H), 7.10 (dd, *J* = 5.0, 3.6 Hz, 4H); MS (APLI) 648.102 [648.107] (M^+). Elem. Anal. for $C_{41}H_{28}S_4$, found: C 75.89, H 4.35, S 19.77; calc: C 75.49, H 4.46, S 19.92.

Synthesis of tetra[4-(thien-3-yl)phenyl]methane (TPT3Th)

Tetra(4-bromophenyl)methane[S2] (2.00 g, 3.14 mmol), thien-3-ylboronic acid (1.66 g, 13.0 mmol), and sodium carbonate (3.00 g, 28.3 mmol) were placed in a 250 mL two-necked round flask and carefully degassed. Toluene (35 mL), n-butanol (20 mL) and water (15 mL) were added as degasified solvents. Tetrakis(triphenylphosphine)palladium (0) (0.18 g, 0.16 mmol) in toluene (10 mL) was added and the mixture was stirred under argon atmosphere and exclusion of light under reflux for 24 hours. After cooling down the aqueous mixture to rt, chloroform (50 mL) was added and the resulting organic phase was washed 5 times with aqueous 2N HCl. The collected organic phases were dried with $MgSO_4$. After solvent evaporation, the crude product was purified by column chromatography on silica (eluent: hexane/dichloromethane 7:2) and recrystallized from hexane/chloroform mixture. The product was isolated as white powder, yield: 0.40 g (20 %). ^1H NMR (600 MHz, THF-d8) δ: 7.58 (m, 12H), 7.43 (m, 8H), 7.33 (m, 8H); ^{13}C NMR (101 MHz, THF-d8) δ 146.67, 142.89, 134.80, 132.48, 127.13, 126.98, 126.45, 121.17, 65.34; MS (APLI) 648.107 [648.107] (M^+). Ele. Anal. for $C_{41}H_{28}S_4$, found: C 75.89, H 4.18, S 20.03; calc: C 75.89, H 4.35, S 19.77.

Synthesis of bulk polymers by oxidative coupling with $FeCl_3$

All monomers were chemically polymerized using the same methodology, which is here described for the SpTh monomer: 2,2’,7,7’-Tetra(thien-2-yl)-9,9’-spirobifluorene (300 mg, 0.47 mmol) was dissolved in anhydrous chloroform (30 mL) and transferred dropwise to a 250 mL round flask which contains a suspension of iron(III)chloride (415 mg, 2.56 mmol) in anhydrous chloroform (20 mL). The resulting mixture was stirred at room temperature for one day under argon atmosphere. After addition of methanol (100 mL), the mixture was stirred for one more hour. The resulting precipitate was collected by filtration and washed with methanol. The powder was treated with aqueous hydrochloric acid (37 %) for 2 h, filtered off and washed with water and methanol. After Soxhlet extraction with methanol and THF for 24 h, the product was treated with ethanol (p.a.) for three days and finally washed with supercritical carbon dioxide. PSpTh was isolated as yellow powder, yield: 261 mg (84 %), PSp3Th as slightly orange powder (92 %), PTPTTh as slightly green powder (45 %), and PTPT3Th as orange powder (99 %).

Electrochemical polymerization and characterization

Dichloromethane (HPLC grade) was refluxed over phosphorus pentoxide for 3 h and distilled. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, ≥ 99 %) was purchased from Alfa Aesar; boron trifluoride diethyl etherate (BFEE, ≥ 46.5 % BF_3) and phosphate buffered saline (PBS, pH 7.4) from Sigma-Aldrich; 1,3,5-trinitrobenzene (TNB, neat) from Supelco; and potassium chloride (KCl, ≥ 99.5 %, ACS) from Roth. Indium tin oxide-coated transparent electrodes on glass (ITO, ≤ 20 Ohm m^{-2}) were purchased from pgo. For electrochemical polymerization and characterization a Potentiostat/Galvanostat PAR VersaSTAT 4 was used with a three-electrode cell. The AFM images were recorded on an atomic force microscope Bruker diInnova operated in tapping mode. The average surface roughness values were extracted from the topography images. The thickness of the films was measured with a surface profilometer Vecco Dektak 150.

Electrochemical polymerization and characterization on Pt electrodes

10 mL of 0.1 mM solutions of the monomers were prepared in dichloromethane or BFEE/DCM (1:4) using 0.1 M $TBABF_4$ as supporting electrolyte. The solutions were placed in a three-electrode cell under argon atmosphere at 25 °C. A platinum disc electrode (Pt, 1 mm diameter) was used as working electrode (WE); a platinum wire as counter electrode (CE); and Ag°/$AgNO_3$ (0.01 M $AgNO_3$/ 0.1 M TBAP in acetonitrile, 0.53 V vs. NHE) as reference electrode (RE). For Figure S4, twenty cyclic voltammograms were repeatedly recorded in a potential range 0 – 1.2 V for SpTh, Sp3Th and TPTTh, and 0 – 1.3 V for TPT3Th with a scan rate of 0.1 Vs^{-1}. For recording CVs of the resulting products, the deposits on Pt disc electrodes were placed as WE in a monomer-free 0.1 M solutions of $TBABF_4$ in dichloromethane. Cyclic voltammograms at different scan rates from 0.005 to 0.20 Vs^{-1} were recorded in the potential range 0 – 1.0 V (Figure S5).

Electrochemical polymerization on ITO electrodes for porosity measurements, as well as for optical, and morphological characterization

10 mL of the monomers solutions were placed in a three-electrode cell. ITO (~ 1.5x1.2 cm deposit area) on glass and a platinum gauze (2.5x1.2 cm area), separated by 1 cm, were used as WE and CE, respectively; Ag°/$AgNO_3$ as RE. For krypton gas sorption measurements, thick films were produced by applying an oxidative potential of 1.2 V (SpTh, Sp3Th and TPTTh) or 1.3 V (TPT3Th) for 20 min. A potential of 0 V was applied after the electropolymerization for 60 s in order to discharge (dedoped) the deposits. After rinsing the

deposits with acetonitrile and dichloromethane, they were dried for 20 min at 100 °C. The collection of ca. 2 mg of material was necessary for reliable BET measurements. For optical and thickness measurements, MPN films on ITO were prepared by applying ten cyclic voltammograms in the same potential range as the used for Pt disc electrodes. After rinsing the films with acetonitrile and dichloromethane, they were dried for 20 min at 100 °C.

Electrochemical polymerization of TPTTh on glassy carbon (GC) electrodes and electrochemical sensing of TNB.

10 mL of a 0.1 mM TPTTh solution were prepared in dichloromethane or BFEE/DCM (1:4) using 0.1 M $TBABF_4$ as supporting electrolyte. The solutions were placed in a three-electrode cell under argon atmosphere at 25 °C. A glassy carbon disc electrode (GC, 1 mm diameter) was used as working electrode (WE); a platinum wire as counter electrode (CE); and $Ag°/AgNO_3$ as reference electrode (RE). Potentiostatic polymerization of TPTTh was achieved by applying a potential of polymerization of 1.2 V until the required oxidative charge (0.01 – 0.50 mC) was accumulated. A potential of 0 V was applied after polymerization during 30 s in order to discharge (dedope) the deposits. After rinsing the deposits with acetonitrile and dichloromethane, the MPN-modified GC electrodes were used as WE in a 10 mL of aqueous 0.2 M KCl and 0.1 M PBS under argon atmosphere at 25 °C. A platinum wire and Ag°/AgCl(sat.) (NaCl 3M, 0.21 V vs NHE) were used as CE and RE, respectively. After 5 min of stirring, a prepotential of 0 V was applied for 30 s. Linear scan voltammograms were recorded from 0 to −1 V with a scan rate of 0.01 Vs^{-1}. For 1,3,5-trinitrobenzene (TNB) detection, 5 μL of 1 mM TNB solution in acetonitrile were added sequentially in order to adjust the TNB concentration from 0 to 3 μM.

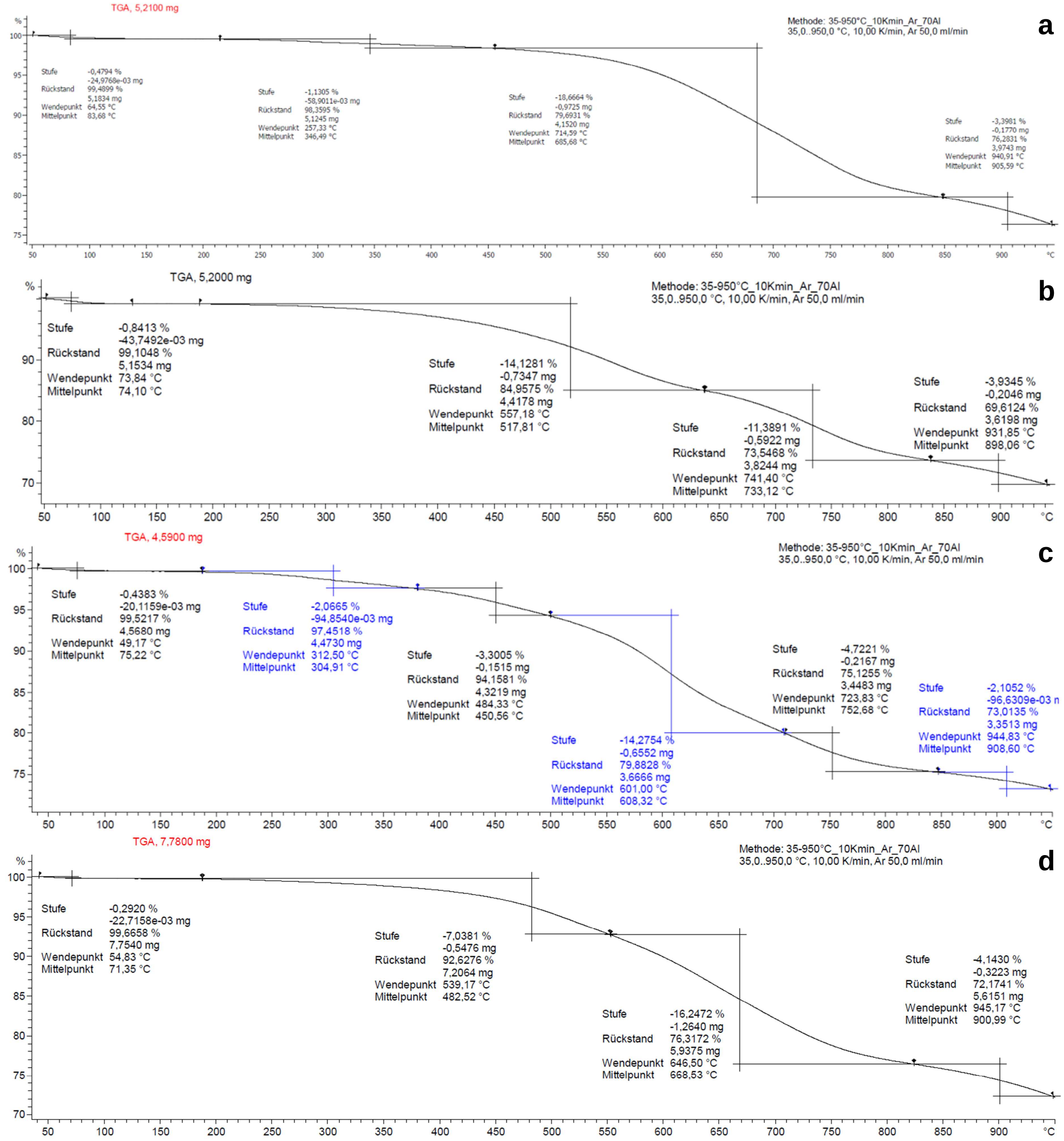

Figure S1. TGA curves of the bulk polymers: (a) PSpTh, (b) PSp3Th, (c) PTPTTh and (d) PTPT3Th.

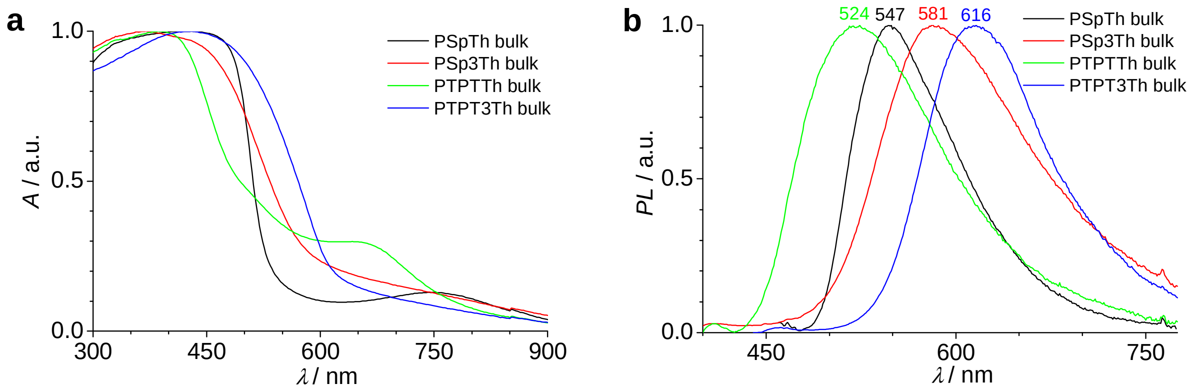

Figure S2. UV-vis (diffuse reflection mode) and PL spectra of the bulk polymers: (a) PSpTh, (b) PSp3Th, (c) PTPTTh and (d) PTPT3Th.

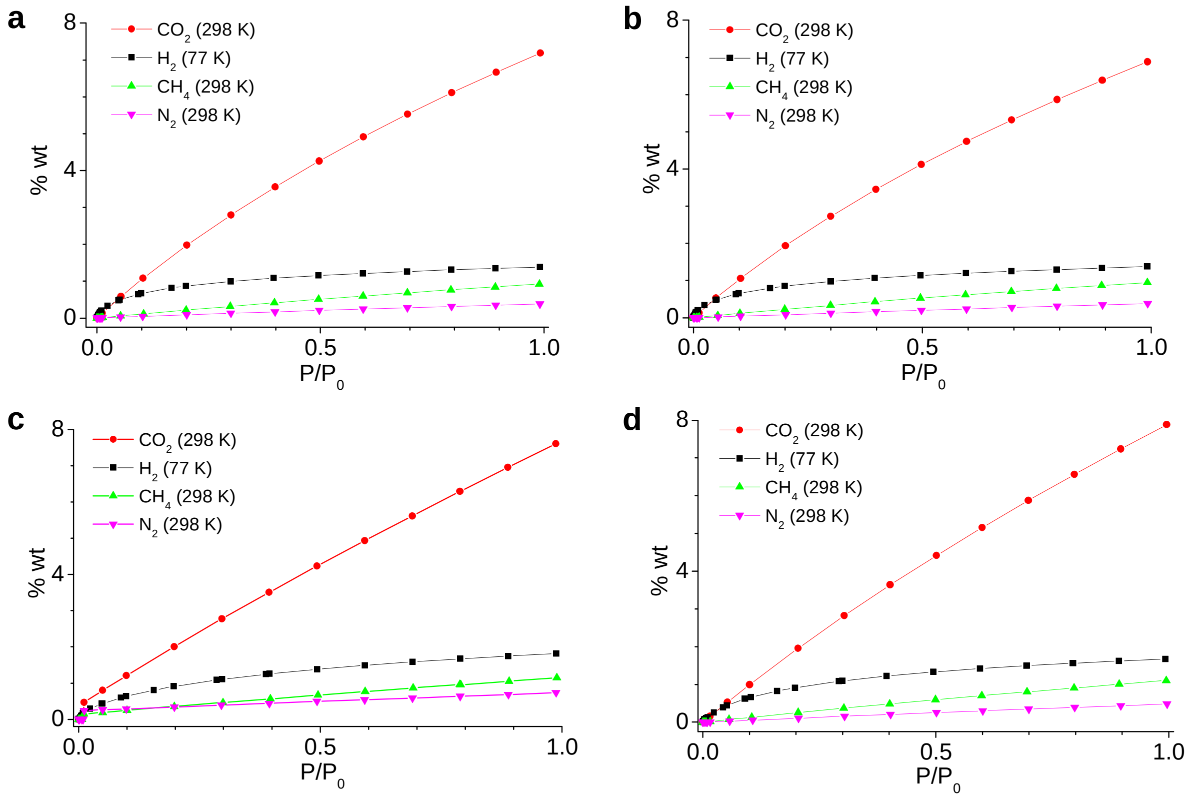

Figure S3. Gas adsorption isotherms for the bulk polymers: (CO_2, circle; H_2, square; CH_4, triangle; N_2, inverted triangle) for (a) PSpTh, (b) PSp3Th, (c) PTPTTh and (d) PTPT3Th.

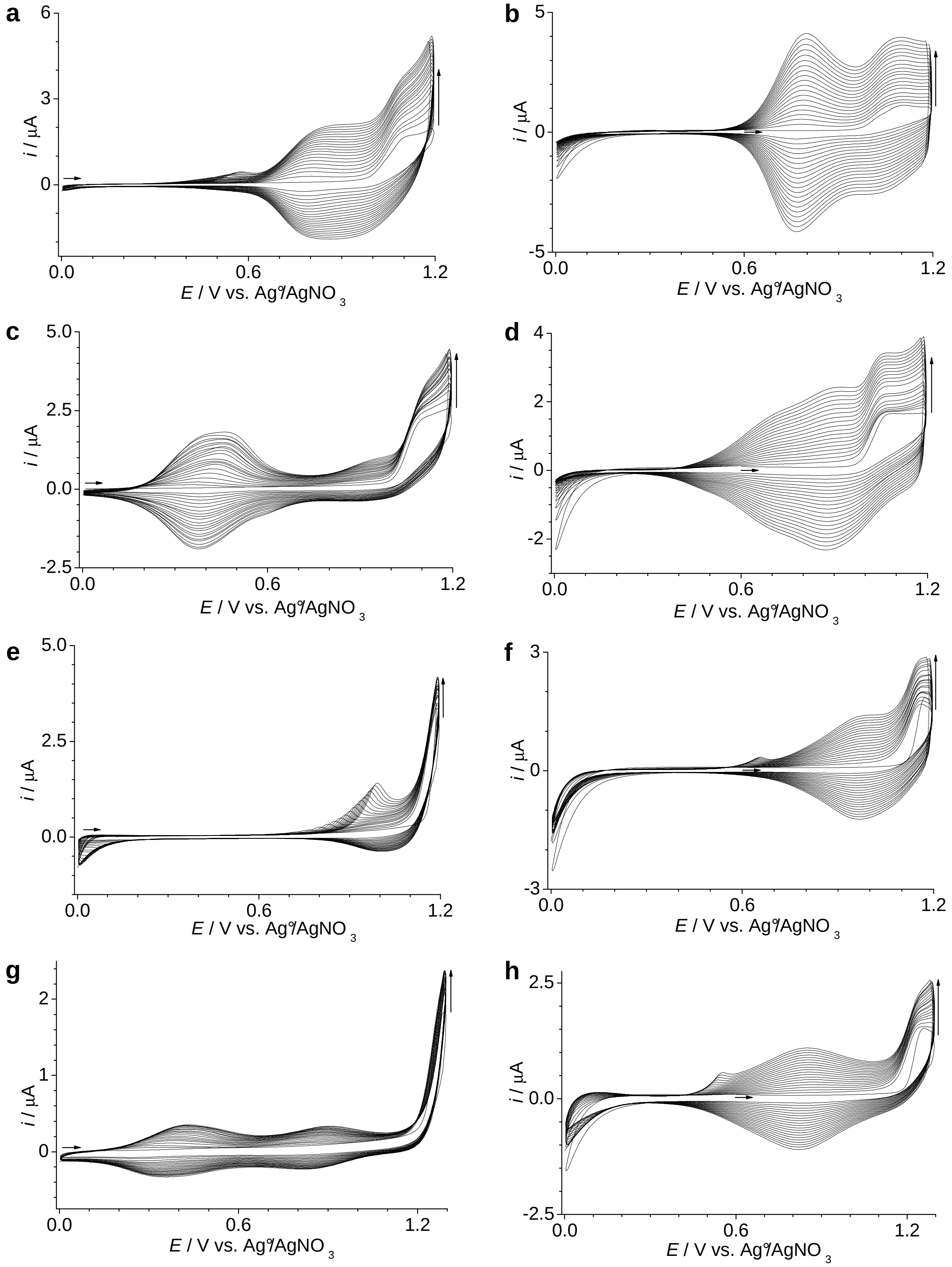

Figure S4. Twenty consecutive cyclic voltammograms during electropolymerization of (a, b) SpTh, (c, d) Sp3Th, (e, f) TPTTh; potential range: 0 to 1.2 V, and (g, h) TPT3Th; potential range: 0 to 1.3 V, scan rate: 0.10 Vs^{-1}, at Pt disc electrodes, 0.1 mM monomer solutions in DCM (a,c,e,g) BFEE/DCM (1:4) (b,d,f,h), 0.1 M TBAP as supporting electrolyte.

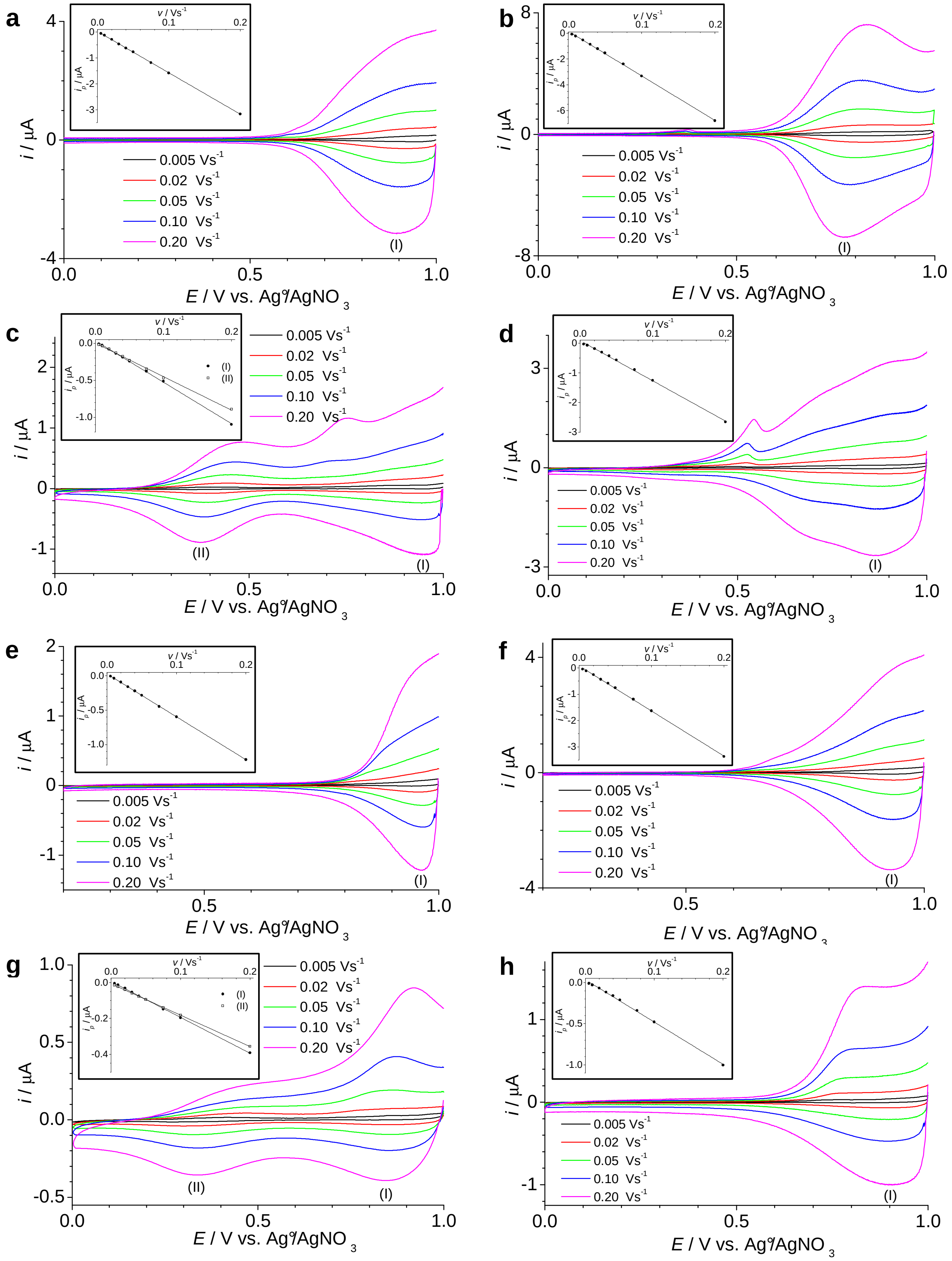

Figure S5. Cyclic voltammograms of (a, b) PSpTh, (c, d) PSp3Th, (e, f) PTPTTh and (g, h) PTPT3Th on Pt disc electrodes within the potential range of 0-1 V at different scan rates from 0.005 to 0.20 Vs^{-1}, in monomer-free DCM containing 0.1 M TBAP. The films were prepared as shown in Figure S4. Insets show linear dependence of cathodic peak current and scan rate.

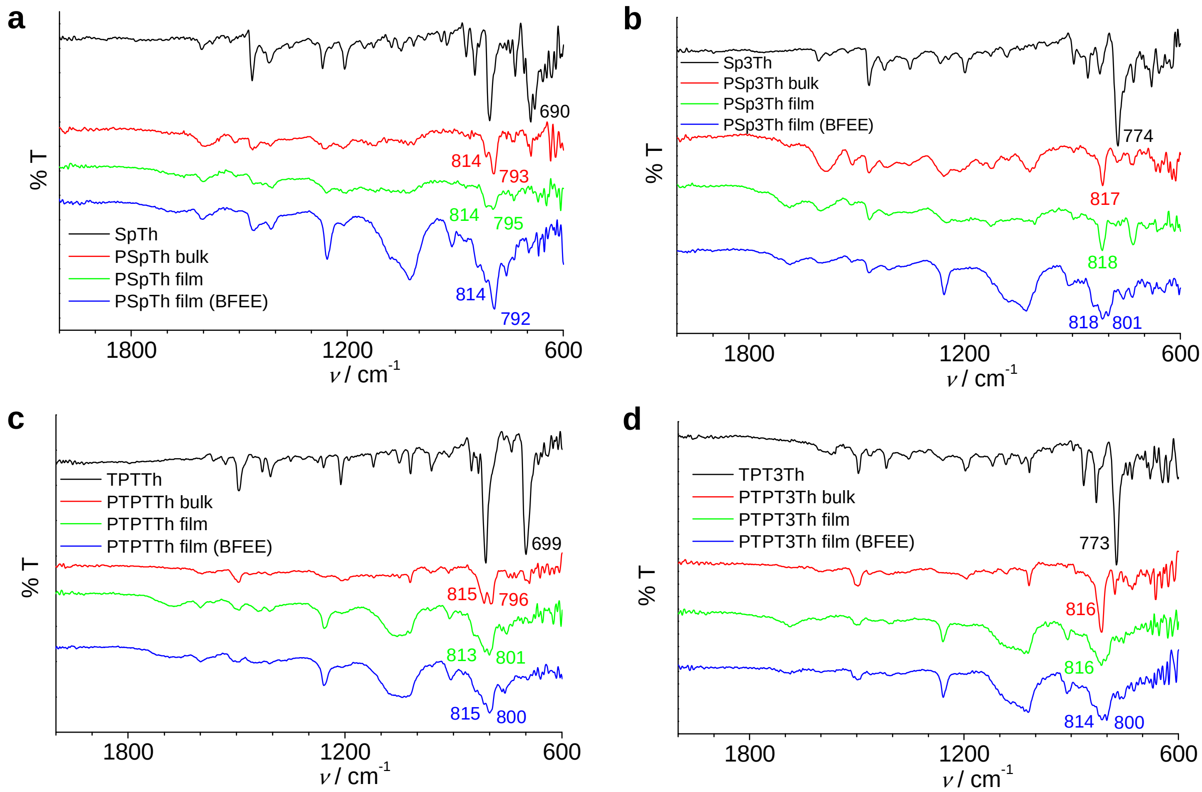

Figure S6. FT-IR spectra of monomers: (a) SpTh, (b) Sp3Th, (c) TPTTh and (d) TPT3Th (black lines); the resulting bulk polymers (a-d, red lines); the resulting MPN films prepared by electropolymerization in pure DCM (a-d, green lines); and the resulting MPN films prepared by electropolymerization in BFEE/DCM (1:4) (a-d, blue lines).

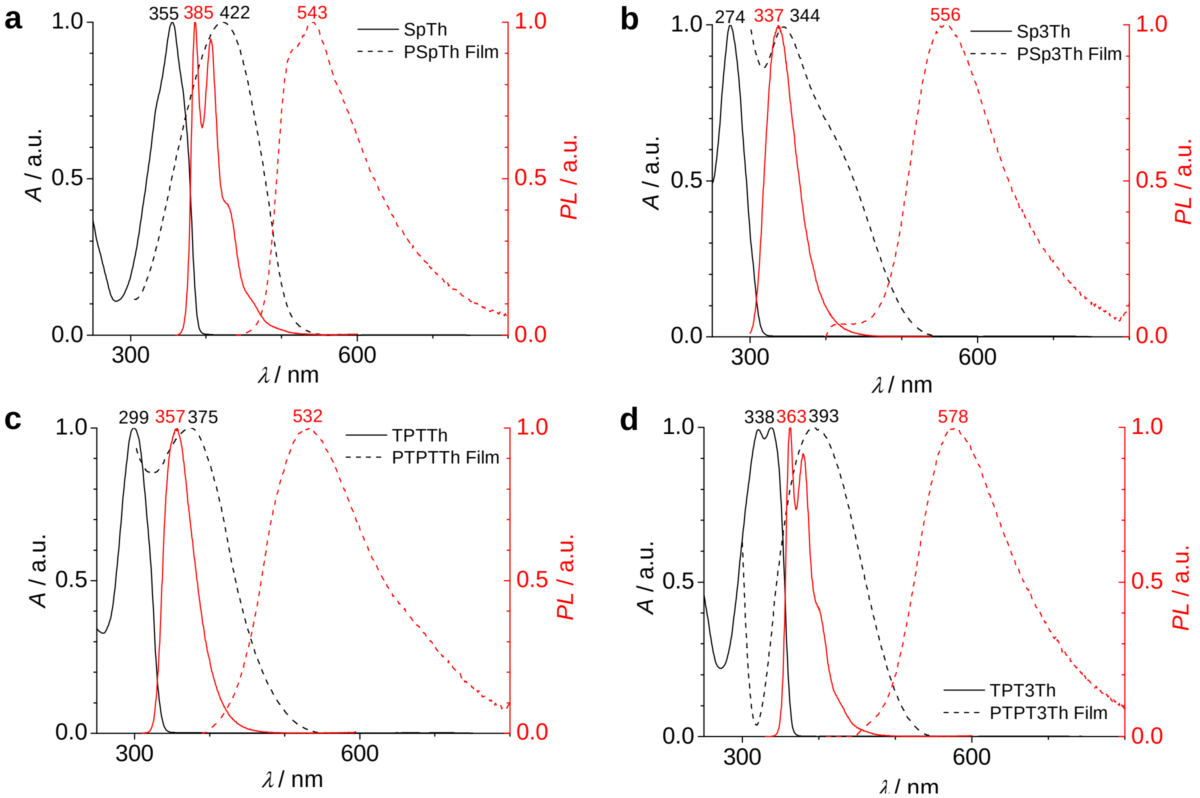

Figure S7. UV-vis (black lines) and PL (red lines) spectra of monomers: (a) SpTh, (b) Sp3Th, (c) TPTTh and (d) TPT3Th (solid lines) and the resulting MPN films prepared by electropolymerization in BFEE/DCM (1:4) (a-d, dashed lines).

Table S1. Average surface roughness (Rq) and thickness of MPN films on ITO made by electrochemical polymerization in BFEE/DCM (1:4), as described on page S5.

MPN films	Rq (nm)	Thickness (nm)
PSpTh	2.5	50.3
PSp3Th	3.6	51.6
PTPTTh	3.5	44.4
PTPT3Th	5.3	32.8

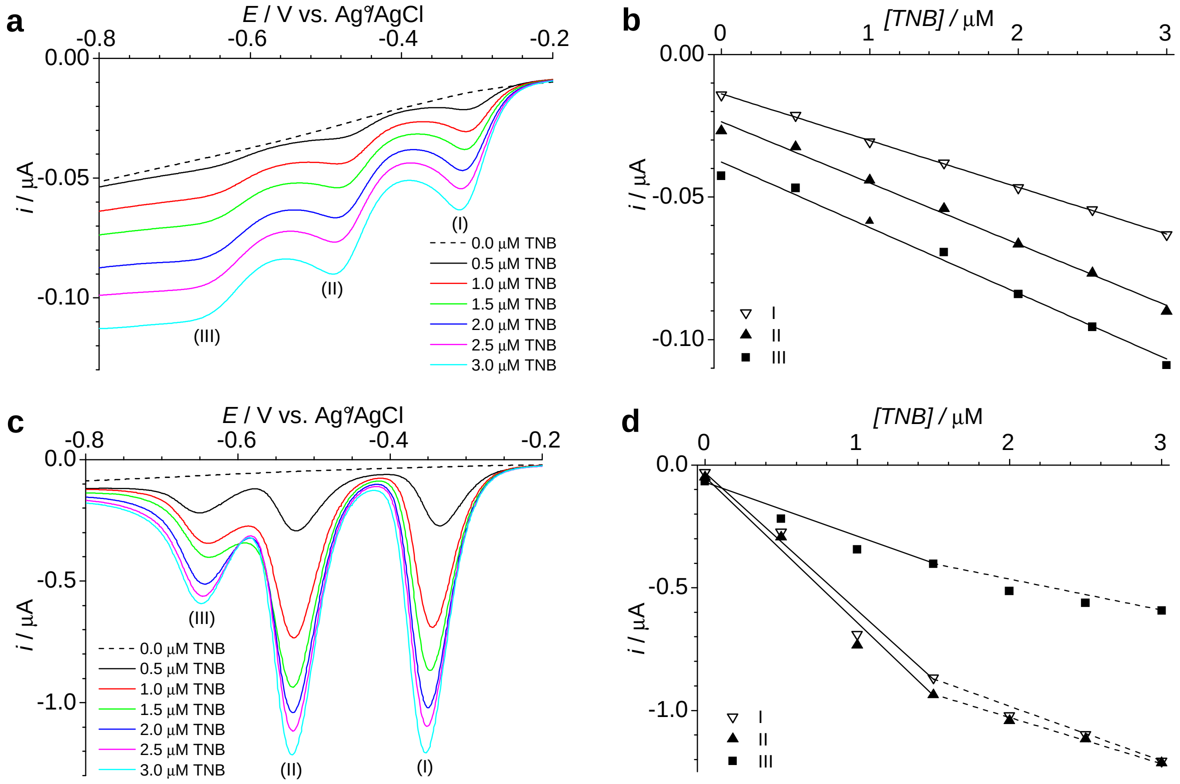

Figure S8. Linear scan voltammograms for the reduction of 0 – 3 µM TNB in aqueous 0.2 M KCl and 0.1 M PBS solution at (a) non-modified, and (c) PTPTTh-modified GC electrodes with a scan rate of 0.01 Vs^{-1}. Plots of peak current vs. [TNB] for (c) non-modified, and (d) PTPTTh-modified GC electrodes for the three different reduction waves (see a and c).

References

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