Supplementary Materials

Highly Photoactive Polythiophenes Obtained by Electrochemical Synthesis from Bipyridine-Containing Terthiophenes.

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Organic Synthesis

Scheme of the 4-bromo-2,2′-bipyridine synthesis:

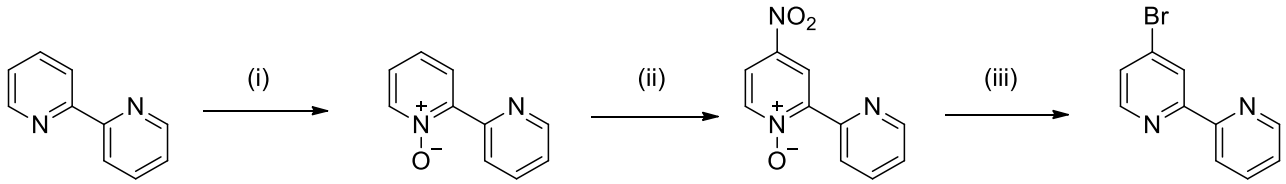


Figure S 1. Scheme of 4-bromo-2,2′-bipyridine preparation. (i) H_2O_2, TFA, rt, 24h; (ii) oleum 60%, fuming HNO_3, reflux, 16h; (iii) acetyl bromide, PBr_3, acetic acid, reflux, 1h.

(2,2'-bipyridine) 1-oxide In a three-necked 500 mL round bottom flask, 2,2'-bipyridine (49.05 g., 314 mmol, 1 eq.) was introduced and TFA (236 mL) was added as the solvent, cooling with ice bath, due to the exothermic reaction of the acid with the bipyridine base. The solution was cooled to rt and hydrogen peroxide 35% (16.02 g.; 40.5 mL, 471 mmol, 1.5 eq.) was added dropwise over 5-10 minutes. A check was performed after 2h by TLC (Silica, EtAc-MeOH 80:20) and it revealed that the reaction was complete.

The solution was partially neutralized adding approximately 200 mL of NaOH 6 N and extracted three times with $CHCl_3$ (300, 100 and 100 mL). From a control, the water contained a lot of product and it was transferred into a 2 L beaker and 6 N NaOH was added (CAUTION: a lot of heat was developed) into an ice bath to cool the solution. When the solution was basic it was extracted three times with $CHCl_3$ (3 × 150 mL). The organic phases were collected and washed 3 times with about 200 mL of 6N NaOH each. The organic phase was dried with Na_2SO_4, filtered, evaporated and further kept overnight in an oven at 50°C obtaining an oil (53.33 g, 99%).

Elemental analysis: (Found: C, 69.72; H, 4.71, N 16.22, Calc. for $C_{10}H_8N_2O$: C, 69.76; H, 4.68, N 16.27%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.97 – 8.81 (m, 1H), 8.73 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.34 (ddd, *J* = 6.3, 1.4, 0.6 Hz, 1H), 8.20 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.84 (ddd, *J* = 8.1, 7.6, 1.8 Hz, 1H), 7.50–7.26 (m, 3H). MS (Electrospray ionization, ESI+) *m*/*z* 173 ($M + H^+$).

4-nitro-[2,2'-bipyridine] 1-oxide In a 1 L one-necked flask the [2,2'-bipyridine] 1-oxide was transferred (50.0 g, 290 mmol, 1 eq.). The flask was mounted on the rack and concentrated sulfuric acid (200 mL) was added slowly, while the solution was cooled with an ice bath. When the temperature was about 10°C, the oleum (40 mL) was added slowly, under vigorous stirring. The

flask was fitted with a dropping funnel and fuming nitric acid (120 mL) was charged directly into the dropping funnel. Nitric acid was dropped in 30–45'. A condenser was connected to the flask, the reaction was brought to reflux and left to react overnight.

The reaction was stopped and cooled to room temperature. The solution was dropped slowly (CAUTION: a lot of red fumes develop!) into a convenient quantity of ice (3 L beaker filled with ice at the 1000–1500 mL mark). The pH was made basic by careful addition of NaOH pellets under stirring. The precipitated material was filtered and it was still moderately acid (pH = 2–3). The water obtained after filtration was made basic by the addition of more NaOH, until pH = 12. The suspension was filtered and the solid was collected and washed with water until neutrality. Inorganic salts precipitated with the organic material; the solid was suspended in chloroform (600 mL), dissolving great part of the product and evidencing that a certain amount of water was still present. If some brown solid is still present this can be filtered away. The solution was dried with Na_2SO_4, and filtered again washing thoroughly the solid on the filter to recover the product. The organic phase was finally evaporated, giving a product that was crystallized from 500 mL of EtOH. The solid that did not dissolve completely was separated by filtration and was found pure by TLC (Silica, EtAc): 16.20 g. The crystallized solid was obtained by filtration: 7.60 g. The mother liquid was evaporated to about 300 mL, and other two crops were recovered by mother liquid concentration for a total of 4.54 g of a slightly impure product. The impure product could be purified by chromatography on Biotage, on silica, with EtAc. The final product was a dark yellow solid. (26.90 g, 42%).

m.p.: 180–181°C (lit. (ref 29) 178–180°C). Elemental analysis: (Found: C, 55.26; H, 3.28, N 19.31, Calc. for $C_{10}H_7N_3O_3$: C, 55.30; H, 3.25, N 19.35%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.16 (d, *J* = 3.1 Hz, 1H), 8.84 (dd, *J* = 19.2, 6.0 Hz, 2H), 8.36 (d, *J* = 7.2 Hz, 1H), 8.06 (dd, *J* = 7.1, 3.3 Hz, 1H), 7.88 (t, *J* = 7.9 Hz, 1H), 7.43 (dd, *J* = 7.5, 4.8 Hz, 1H). MS (Electrospray Ionization, ESI+) *m*/*z* 218 ($M + H^+$).

4-bromo-2,2'-bipyridine A 100 mL flask with magnetic stirring bar was assembled with a condenser, a stopper and a 50 mL dropping funnel with equilibrating arm. The glassware was purged with argon for 3 times. The 4-nitro-2,2′-bipyridine N-oxide (15.0 g., 69.1 mmol, 1 eq) was introduced and the glassware was carefully purged with a gentle Ar flux. The acetic acid (300 mL) was introduced and the N-oxide was dissolved under stirring. Acetyl bromide (125 g, 75 mL, 1014 mmol, 14.69 eq.) was introduced with a syringe. At the end of the introduction the solution became turbid and a yellow precipitate appeared. The suspension was left to stir for about 10 min. The PBr_3 (216 g., 75 mL, 798 mmol, 11.55 eq.) was slowly added dropwise and the solution was warmed at 40° C. At about 30–31°C the solution was a bit turbid and at 40 °C the product was dissolved giving an orange solution. The reaction was refluxed (95 °C), becoming more turbid. The magnetic stir bar stuck at the bottom of the flask since the precipitate became viscous and stuck onto the flask walls. The reaction was stopped after 1 h at reflux and allowed to cool to rt. The product was stuck on the flask in great quantity. The liquid was decanted and poured, slowly and carefully, into a beaker with ice to quench the reactants. The gummy precipitate was dissolved in water by adding concentrated NaOH, and subsequently NaOH pellets, until pH was approximately 11. The solution was extracted with $CHCl_3$ (3 × 300 mL), until the entire product

was extracted, along with minor impurities. The organic phase was dried with Na_2SO_4 and filtered. The organic phase was evaporated, giving an orange solid and an orange oil which, once separated, crystallized upon standing. The product was purified by chromatography on Biotage (portions of 4-5 g on a Silica, 100 g column), with petroleum ether: ethyl acetate 80:20, giving a white solid (12.49 g, 78%).

m.p. 52 °C (lit. (ref 29) 51–52 °C), Elemental analysis: (Found: C, 51.13; H, 2.95, N 11.95, Br 33.84. Calc. for $C_{10}H_7N_2Br$: C, 51.09; H, 3.00, N 11.92, Br 33.99%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.7 Hz, 1H), 8.55 (s, 1H), 8.40 (d, *J* = 5.2 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.47–7.33 (m, 1H), 7.24 (dd, *J* = 13.1, 6.2 Hz, 1H), MS (Electrospray Ionization, ESI+) *m*/*z* 236 ($M+H^+$).

The preparation of the starting 4-bromo-2,2′-bipyridine followed known methods, by applying the best performing steps found in the literature.[1,2]

3'-bromo-2,2':5',2''-terthiophene (1)

In a 20 mL vial, previously flushed with argon for 20 min and closed with rubber stopper, the 2,3,5-tribromothiophene (0.512 g, 1.6 mmol, 1 eq) 2-thiopheneboronic acid (0.497 g, 3.89 mmol, 2.4 eq) and $Pd(PPh_3)_4$ (14.4 mg, 0.0125 mmol, 0.078 eq.) were added. The vial was purged with argon. The DME and 1 M $NaHCO_3$ were degassed with argon for 20 min. The DME (8 mL) was added and the vial was maintained under argon and finally the $NaHCO_3$ solution (5.58 mL, 5.58 mmol, 3.5 eq) was added and the vial was crimped. The solution was stirred under argon for 10 min and then reacted under microwave (MW) irradiation at 120 °C for 30 min. The organic solvent was evaporated at the rotavapor and water (20 mL) was added. The suspension was extracted with diethyl ether (3 × 30 mL); the organic phase was dried with sodium sulfate, filtered and evaporated, giving a dark yellow oil that was purified by chromatography on a Biotage 25 g. column with petroleum ether, giving a yellow oil. (235 mg, 43%).

Elemental analysis: required for $C_{12}H_7BrS_3$, C 44.04, H 2.16, S 29.39, found: C 44.09, H 2.11, S 29.41. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.37 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.27 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.19 (dd, *J* = 3.6, 1.2 Hz, 2H), 7.07 (m, 5H). Mass spectrometry (MS) (Electron ionization, EI) *m*/*z* 327 (M^+, 100%).

4-([2,2':5',2''-terthiophen]-3'-yl)-2-methylbut-3-yn-2-ol (2)

In a 20 mL vial, previously flushed with argon for 20 min and closed with rubber stopper, the oily product 1 (0.323 g, 0.989 mmol, 1 eq.), the solid Pd(PPh3)4 (114 mg, 0.098 mmol, 0.1 eq.) and CuI (19 mg, 0.098 mmol, 0.1 eq.) were introduced. The vial was closed and flushed under argon for 20 min. Freshly distilled diisopropylamine (8 mL) was added along with 2-methylbut-3-yn-2-ol (91 mg, 0.111 mL, 1.086 mmol, 1.1 eq) and the vial was flushed for 15 min with argon. The reaction was warmed with an oil bath at 85 °C for 24 h. The reaction was stopped and dichloromethane (25 mL) was added. The solution was extracted with NaHCO3 saturated solution (2 × 25 mL) and with water (20 mL). The organic phase was dried with sodium sulfate, filtered and evaporated. The crude dark brown oil was purified by chromatography on a Biotage 50 g column, with dichloromethane, obtaining a yellow oil, (279 mg, 85%).

Elemental analysis: required for $C_{17}H_{14}OS_3$, C 61.78, H 4.27, S 29.11, found: C 61.74, H 4.31, S 29.07. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.24 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.17 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.09 (s, 1H), 7.04 (m, 2H), 1.68 (s, 7H). MS (EI) *m*/*z* 330 (M^+, 100%).

3′-ethynyl-2,2′:5′,2″-terthiophene (3)

The glassware was kept in an oven overnight. A 50 mL three-necked round bottom flask, equipped with a Schlenk arm, was mounted with a condenser, closed with stopper and flushed with argon for 20 min. The KOH (804 mg, 13.4 mmol, 5 eq.) was introduced quickly into the reaction flask and the apparatus was flushed with argon. Methanol and toluene were flushed separately with argon for 20 min. The compound 2 (883 mg, 2.68 mmol, 1 eq.) was diluted in a vial with MeOH (5 mL) and introduced in the reaction flask through the Schlenk arm. Further MeOH (5 mL) was used to wash the vial and was introduced in the reaction flask. Toluene (10 mL) was added to the reaction. The reaction was started and stirred at 110°C for 22 h, after which the reaction was stopped and cooled to rt. The solvents were evaporated under reduced pressure and the crude was treated with water (50 mL) and extracted with dichloromethane (3 × 50 mL). The organic phase wash dried with sodium sulfate, filtered and evaporated under reduced pressure. The crude, 0.55 g was purified with a Biotage 100 g column with petroleum ether:ethyl acetate 80:20. After evaporation of the solvent, the product was obtained as a yellow oil, (408 mg, 56%).

Elemental analysis: required for $C_{14}H8S3$, C 61.73, H 2.96, S 35.31, found: C 61.67, H 2.98, S 35.26. 1H NMR (CDCl3, ppm): δ 7.50 (dd, 1H), 7.26 (d, 1H), 7.19 (d, 1H), 7.13-7.07 (m, 2H), 7.07–6.95 (m, 2H,), 3.34 (s, 1H). MS (EI) m/z 272 (M+, 100%).

4-([2,2:5,2-Terthiophen]-3-ylethynyl)-2,2-bipyridine, TABP (4)

In a 100 mL round bottom flask equipped with a condenser, a magnetic stirrer and an Ar inlet, 4-bromo-2,2′-bipyridine (0.302 g, 1.285 mmol), $Pd(PPh_3)_4$ (0.074 g, 0.064 mmol), CuI(0.024 g, 0.1284 mmol), 3′-ethynyl-2,2′:5′,2″-terthiophene (0.350 g, 1.285 mmol) (**3**) were added and dissolved with 1,4-dioxane/H_2O 3 : 1 (32 mL). Finally triethylamine (0.260 g, 2.57 mmol) was added. The reaction mixture was then refluxed under Ar for 17–22 h and checked with TLC (petroleum ether:ethyl acetate 7:3 + TEA 0.1%) to monitor the disappearance of the starting material. After cooling to RT, the mixture was filtered off, and 1,4-dioxane evaporated under reduced pressure. The crude was diluted with water (40 mL) and the solution was washed with dichloromethane (3 × 20 mL). The combined organic phase was dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was purified by medium pressure flash chromatography (Biotage) with a 50 g column, using petroleum ether: ethyl acetate (8:2) and 0.1% TEA as an additive. The final product was obtained as a yellow oil, (164 mg, 30%).

m.p.: 153-156°C. Elemental analysis: required for $C_{24}H_{14}N_2S_3$, C 67.57, H 3.31, N 6.57, S 22.55, found: C 67.60, H 3.28, N 6.62, S 22.50. 1H NMR (200 MHz, CDCl3) δ 8.70 (m, 2H), 8.56 (s, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 7.83 (td, *J* = 7.8, 1.8 Hz, 1H), 7.51 (dd, J = 3.7, 1.2 Hz, 1H), 7.44 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.37 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.34–7.29 overlapping (m, J = 7.5 4.8, 1.1, 1H), 7.26 (dd, *J* = 5.1, 1.1

Hz , 1H), 7.20 (m (dd + s), 3.5, 1.2 Hz, 2H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H).7.06 (dd, *J* = 5.1, 3.7 Hz, 1H). MS (EI) m/z, 426 (M+, 100%).

2,2:5,2-Terthiophen-3-ylboronic acid (5)

In a Schlenk 20 mL round bottom flask, a solution of **1** (0.668 g, 2.04 mmol) and trimethylborate (0.276 g, 0.296 mL, 2.65 mmol) in 8 mL THF was treated with n-BuLi (1.6 M in hexane, 1.658 mL, 2.65 mmol) at −78 °C over a period of 20 minutes. The resulting solution was stirred at −78 °C for an hour. The solution was then warmed up to −20 °C in 1 h, quenched slowly using 2 N HCl (1.326 mL, 2.65 mmol) and then stirred for 4 h. The product was precipitated out as a white solid, washed with water and dried under reduced pressure. The crude compound was directly used for the next step.

4-([2,2:5,2-Terthiophen]-3-yl)-2,2-bipyridine, TBP (6)

To a degassed solution of 4-bromo-2,2′-bipyridine (0.177 g, 0.431 mmol, 0.9 eq.) and $Pd(PPh_3)_4$ (55 mg, 0.1 mmol) in dimethoxyethane (DME, 5 mL), 7 mL of a solution of **5** (0.140 g, 0.479 mmol, 1 eq.) in dimethoxyethane were added. The reaction mixture was heated at 120 °C for 30 min under MW irradiation. The reaction was controlled by TLC (dichloromethane:ethyl acetate 4:6 + TEA 0.1%) (Rf = 0.26). When the starting material was fully consumed, the solvent was removed at low pressure. Water (5 mL) was added and the product was extracted with ethyl acetate (5 × 5 mL). The organic phases were collected, dried over Na_2SO_4, and filtered. The crude reaction product (0.496 g) was purified by medium pressure flash chromatography (Biotage) on a 50 g column, with dichloromethane:ethyl acetate 70:30 + 0.5% TEA as an additive, obtaining a yellow oil (74 mg, 43%).
Elemental analysis: required for $C_{22}H_{14}N_2S_3$, C 65.64, H 3.51, N 6.96, S 23.90, found: C 65.61, H 3.52, N 6.91, S 23.94. ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ 8.65 (d, *J* = 4.4 Hz, 1H), 8.57 (d, *J* = 5.0 Hz, 1H), 8.47 (d, *J* = 0.9 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.80 (td, *J* = 7.9, 1.8 Hz, 1H), 7.38–7.12 (m, 6H), 7.08–6.97 (m, 2H), 6.93 (dd, *J* = 5.0, 3.6 Hz, 1H). MS (Electrospray ionization) *m*/*z*, 403.28 [M + H^+].

Electrosynthesis

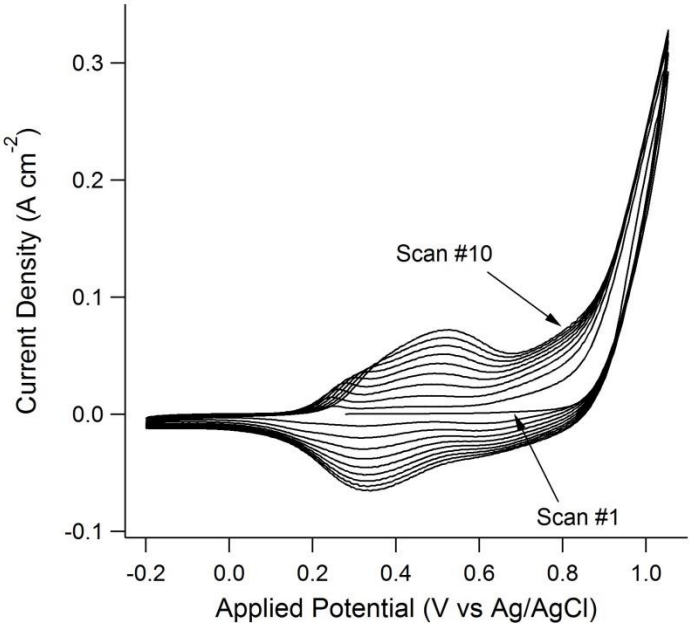


Figure S 2: Electropolymerization of 1 mM TABP and 1 mM T in 0.1 M $TBAPF_6$ in acetonitrile/CH_2Cl_2 1:1; transferred charge: 2.87 mC, P(TBP-co-T) mass deposited : 11.2 µg, estimated average film thickness : 31 nm.

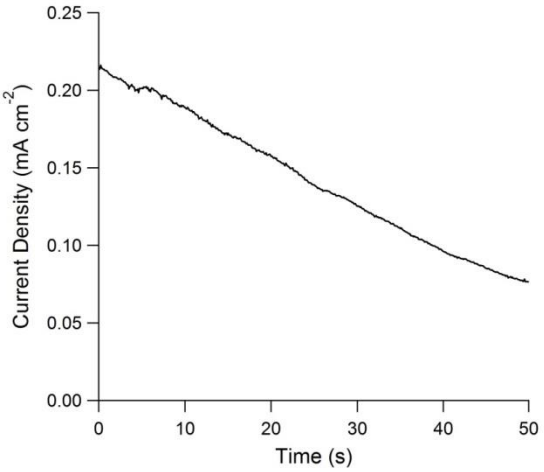
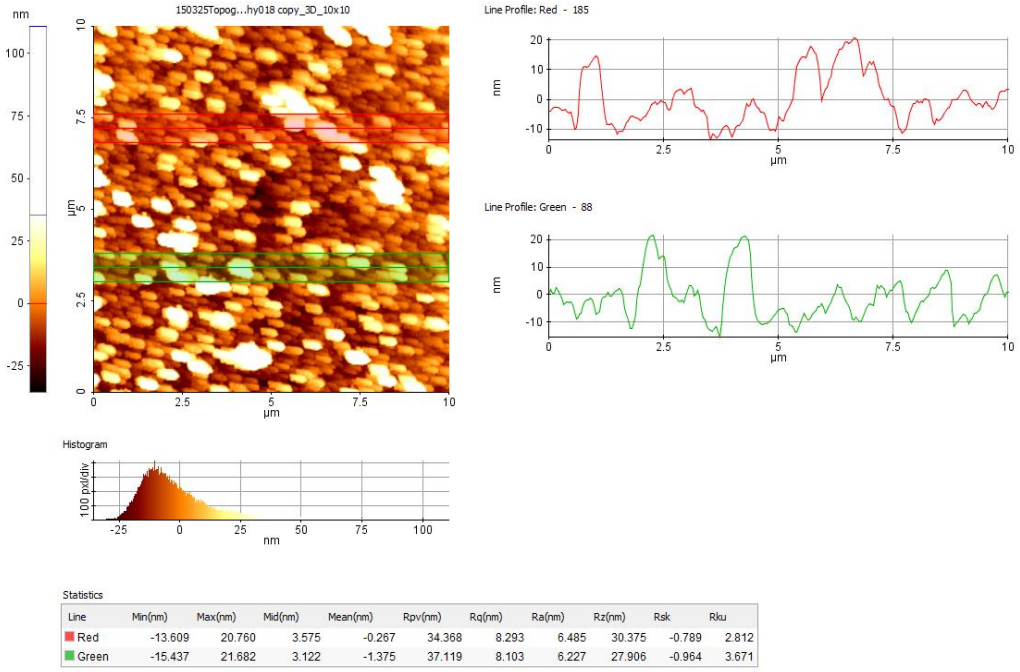


Figure S 3: Electropolymerization of TBP 2 mM in 0.1 M $TBAPF_6$ in acetonitrile/CH_2Cl_2 1:1; electrode potential 1.1 V vs Ag/AgCl/TEACl (0.1 M in acetonitrile); transferred charge : 28.5 mC, PTBP mass deposited : 119 µg, estimated average film thickness : 330 nm.

During TABP and T copolymerization the charge transferred is 2.87 mC. To estimate the mass of the copolymer deposited and the film thickness we must know the amounts of reacted TABP and T. Since in the same conditions, but in the presence of TABP 1 mM only, the transferred charge is 2.47 mC, the resulting excess of charge of 0.40 mC can be ascribed to T polymerization, leading to a molar ratio T:TABP in the copolymer around 0.16, corresponding to a mass ratio of only 0.03, owing to the lower molar mass of T compared to TABP.

Morphology

PT



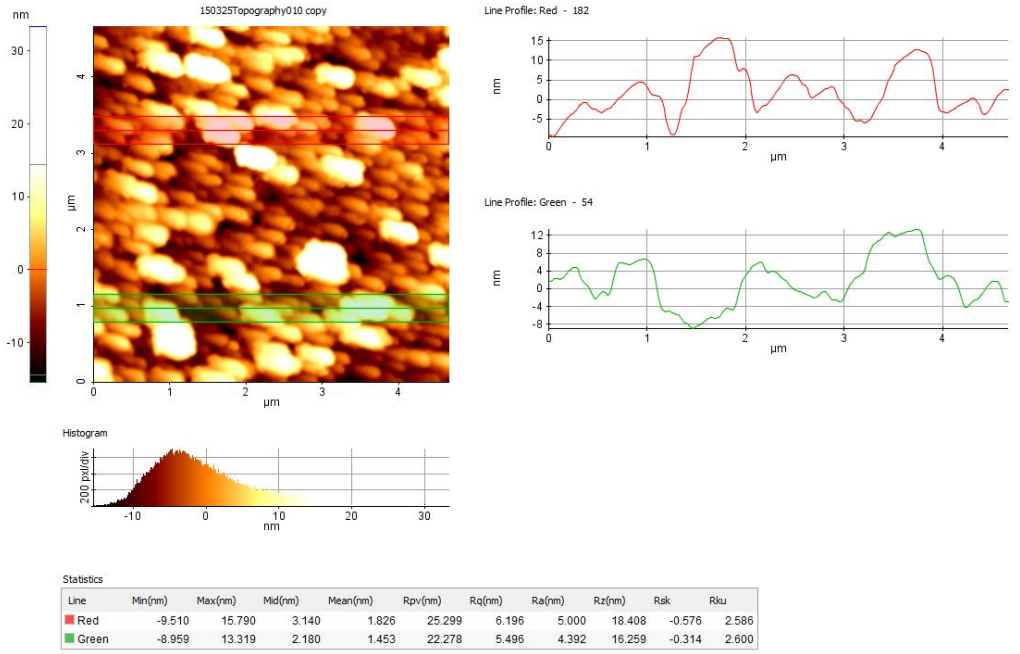
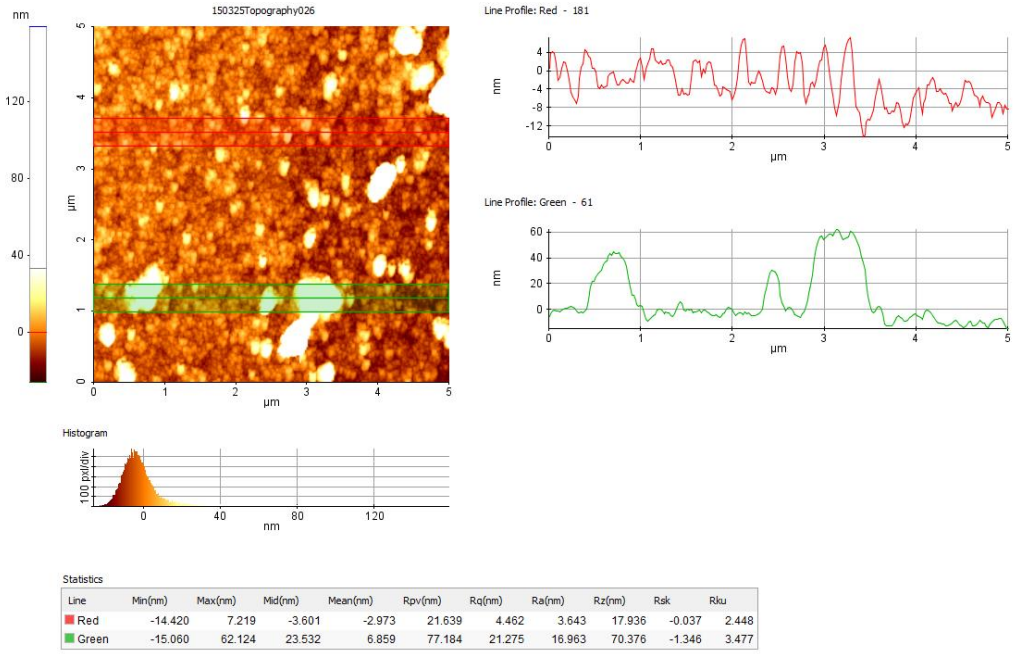


Figure S 4. Supplementary AFM topographies of a PT film electrosynthesized in potentiodynamic conditions.

PTABP



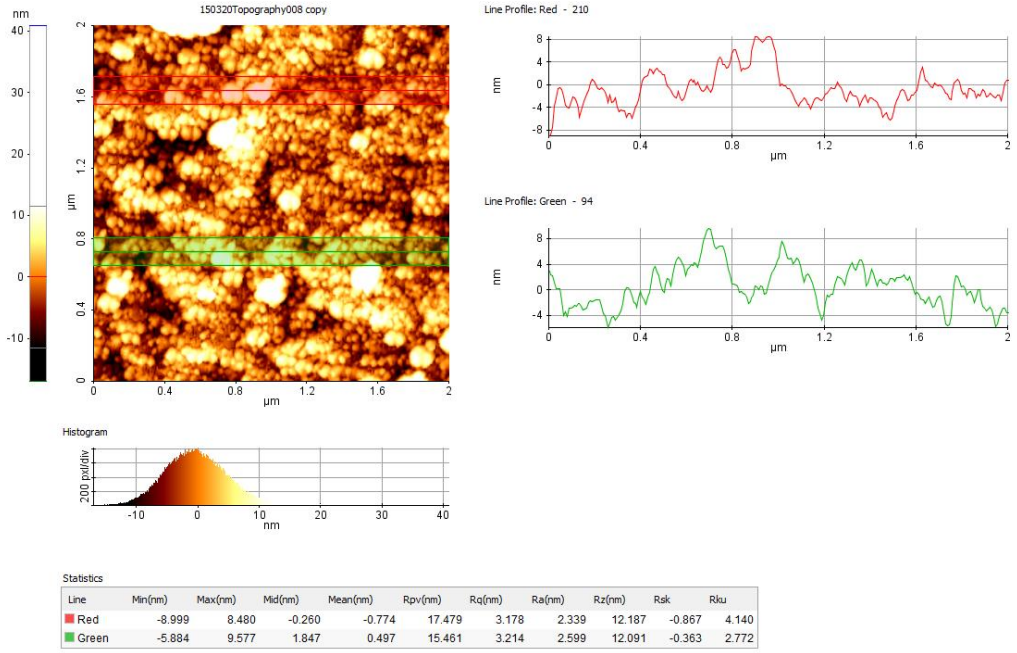
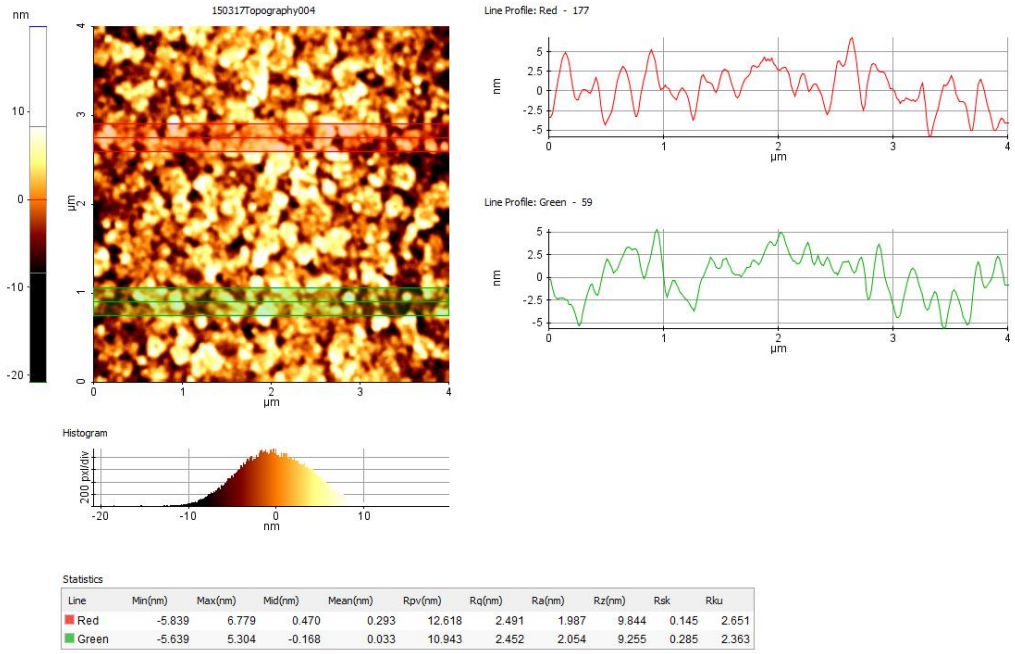


Figure S 5. Supplementary AFM topographies of a PTABP film electrosynthesized in potentiodynamic conditions.

P(TABP-co-T)

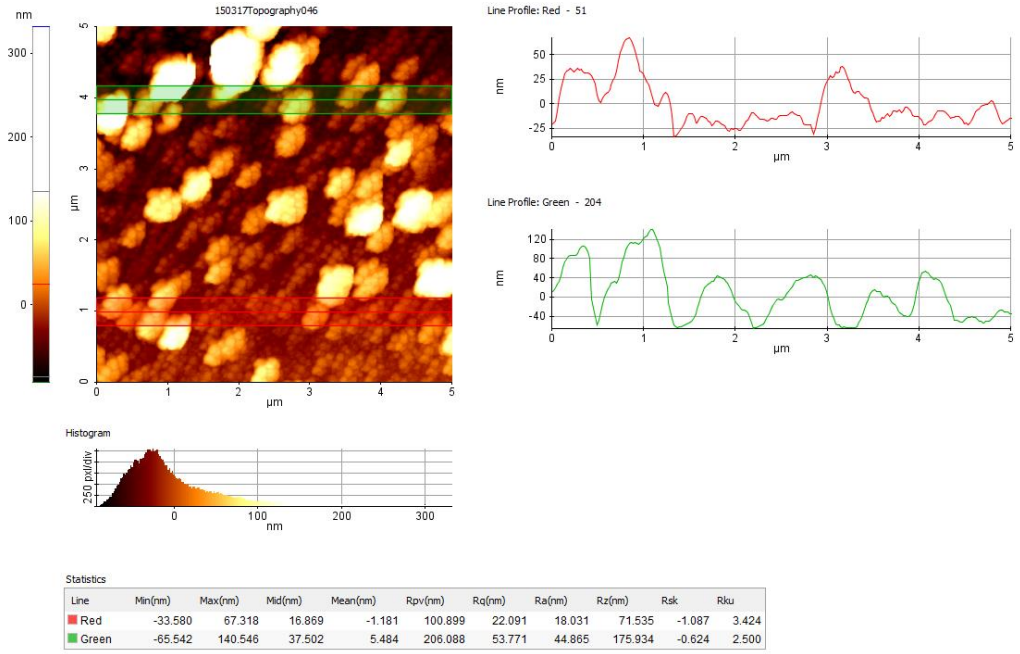


Statistics

Line	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-5.839	6.779	0.470	0.293	12.618	2.491	1.987	9.844	0.145	2.651
Green	-5.639	5.304	-0.168	0.033	10.943	2.452	2.054	9.255	0.285	2.363

Figure S 6. Supplementary AFM topography of a P(TABP-co-T) film electrosynthesized in potentiodynamic conditions.

PTBP



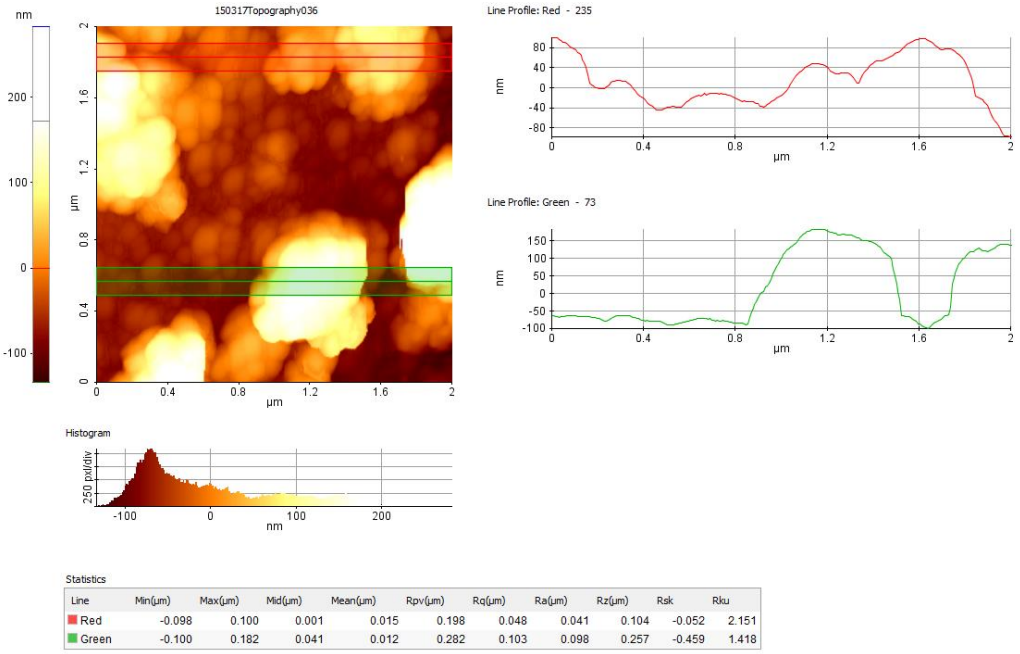
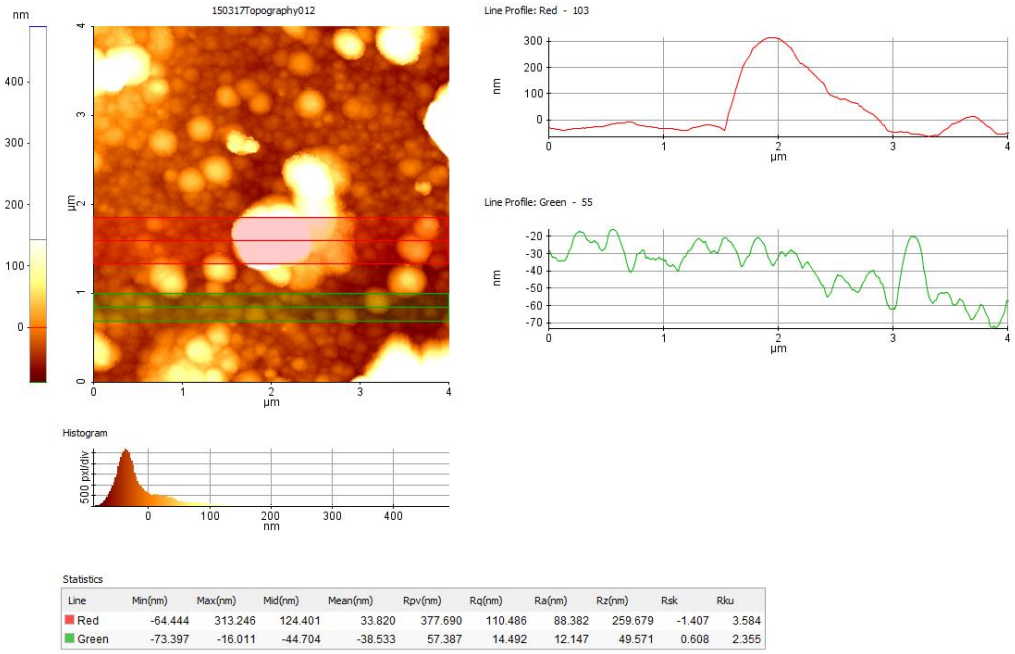


Figure S 7. Supplementary AFM topographies of a PTBP film electrosynthesized in potentiodynamic conditions.

P(TBP-co-T)



Line	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-64.444	313.246	124.401	33.820	377.690	110.486	88.382	259.679	-1.407	3.584
Green	-73.397	-16.011	-44.704	-38.533	57.387	14.492	12.147	49.571	0.608	2.355

Figure S 8. Supplementary AFM topography of a P(TBP-co-T) film electrosynthesized in potentiodynamic conditions.

Supplementary Electrochemical Results

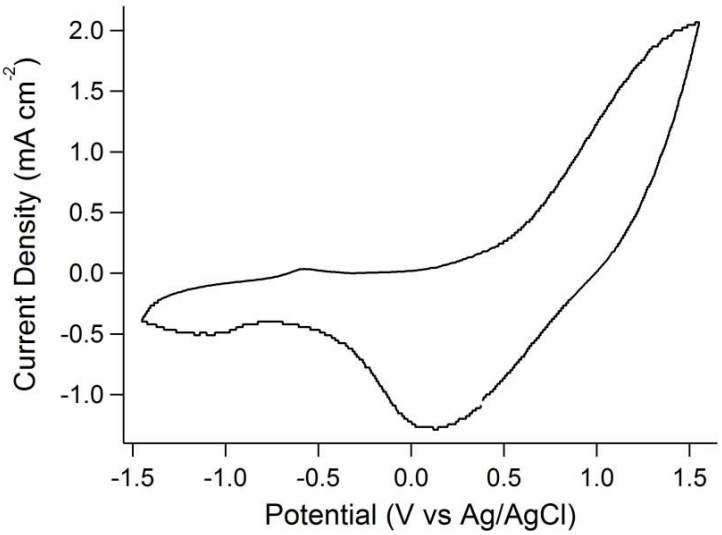


Figure S 9: Cyclic voltammetry of electropolymerized PT at 0.5 V s^{-1} scan rate in 0.1 M $NaClO_4$ in acetonitrile.

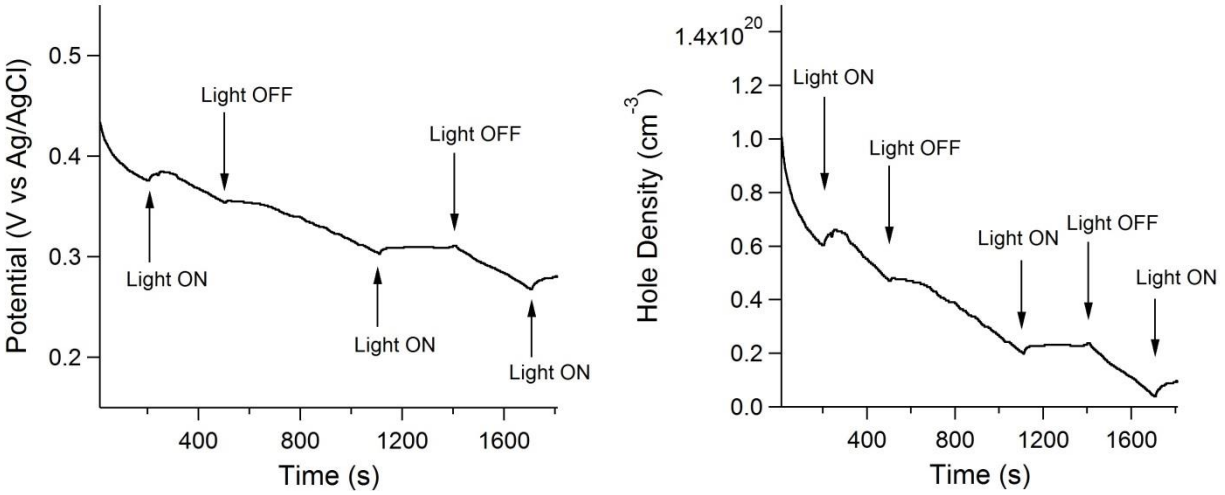


Figure S 10: a) Chronopotentiometry of electropolymerized PT in 0.1 M $NaClO_4$ in acetonitrile and b) corresponding hole polaron density.

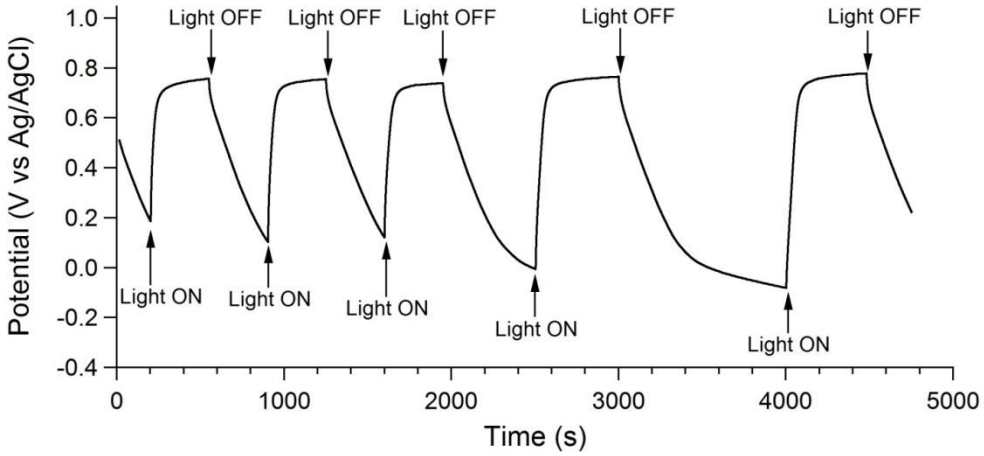


Figure S 11: Chronopotentiometry of electropolymerized PTBP in 0.1 M $NaClO_4$ in acetonitrile.

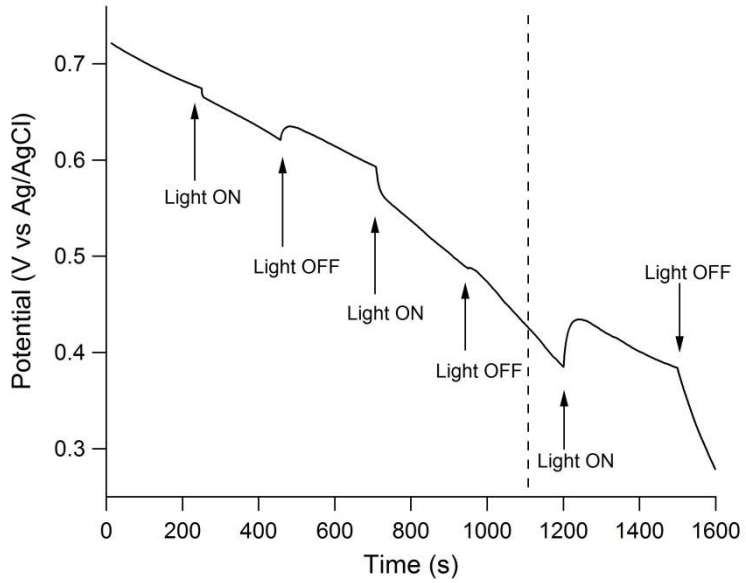


Figure S 12: Chronopotentiometry of electropolymerized P(TABP-co-T) in 0.1 M $NaClO_4$ in acetonitrile recorded immediately after electrosynthesis.

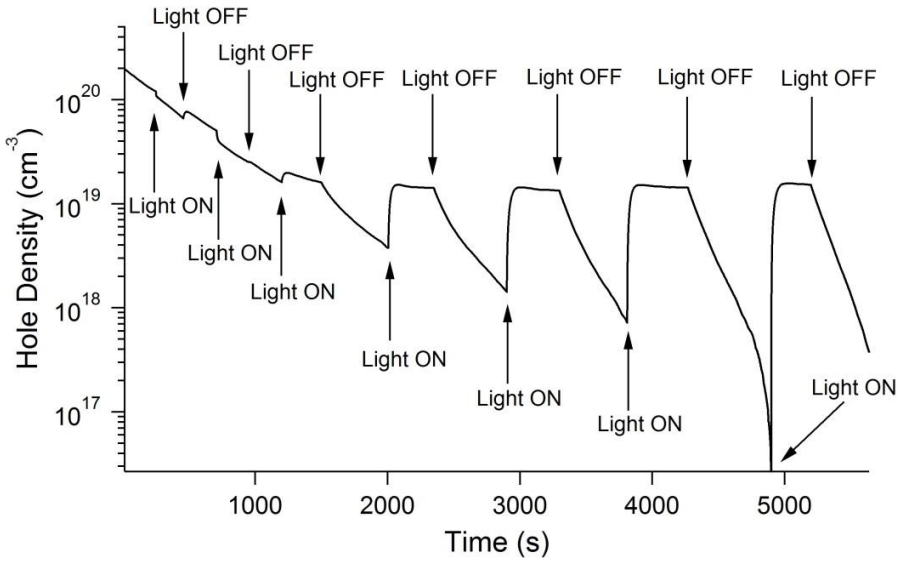


Figure S 13: Hole density as a function of time corresponding to the CP measurement of Figure S 12 and Figure 10 on P(TABP-co-T).

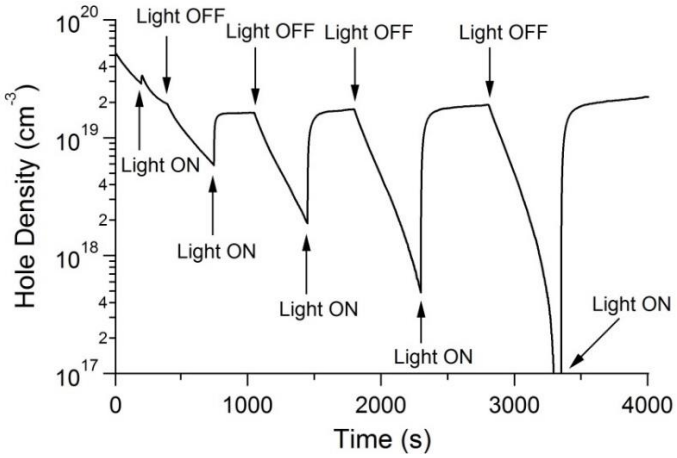


Figure S 14: Hole density as a function of time corresponding to a CP measurement on PTBP performed immediately after its electropolymerization.

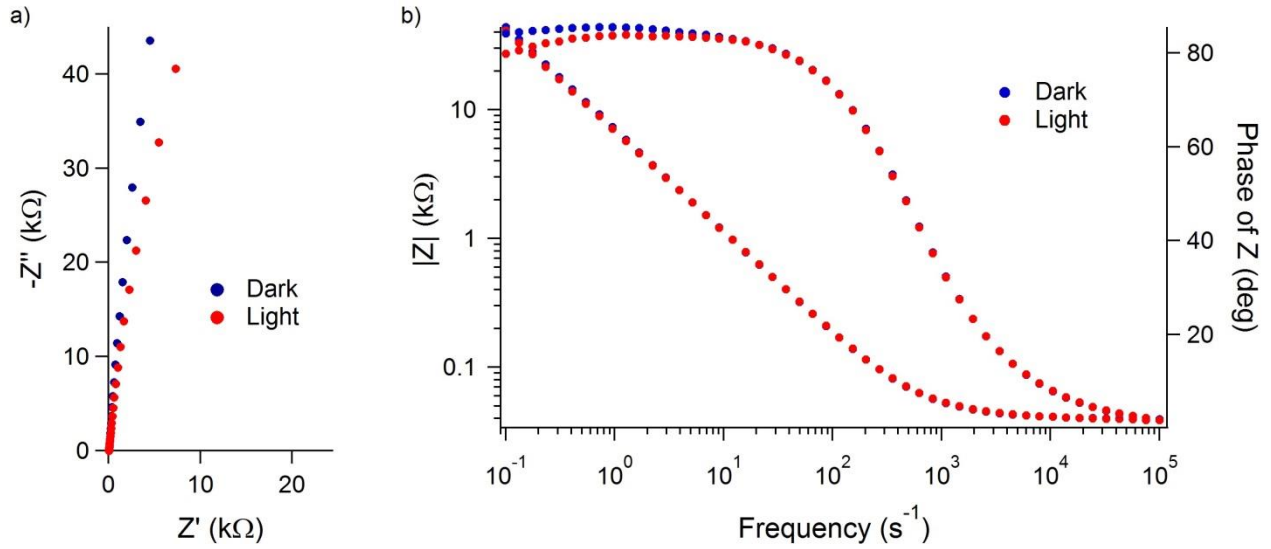


Figure S 15: a) Nyquist and b) Bode plots of electropolymerized TBP at 0 V vs Ag/AgCl in 0.1 M $NaClO_4$ in acetonitrile recorded between 100 kHz and 100 mHz.

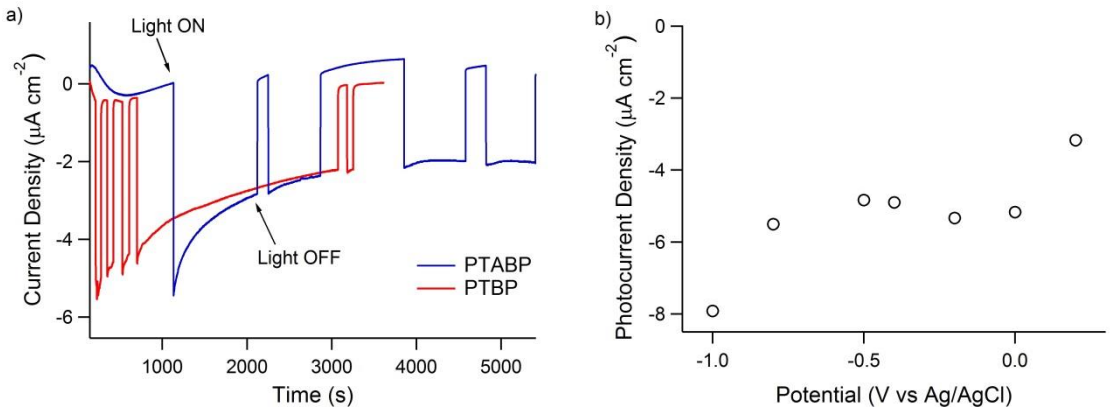


Figure S 16: a) Current density as a function of the time for PTABP and PTBP during sequential cycles of irradiation and b) photocurrent density as a function of the potential for PTBP.

References

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2. Demnitz, F.W.J.; D'Heni, M.B. A HIGH YIELDING PREPARATION OF 2,2′-BIPYRIDINE-1-OXIDE. *Org. Prep. Proced. Int.* **1998**, *30*, 467–469, doi:10.1080/00304949809355313.