

***On-substrate* polymerization – a versatile approach for preparing conjugated polymers
suitable as electrochromes and metal ion sensing**

Monika Wałęsa-Chorab¹ and W.G. Skene^{1*}

¹Laboratoire de caractérisation photophysique des matériaux conjugués
Département de chimie
Université de Montréal
CP 6128, Centre-ville
Montreal, QC

Corresponding author: w.skene@umontreal.ca

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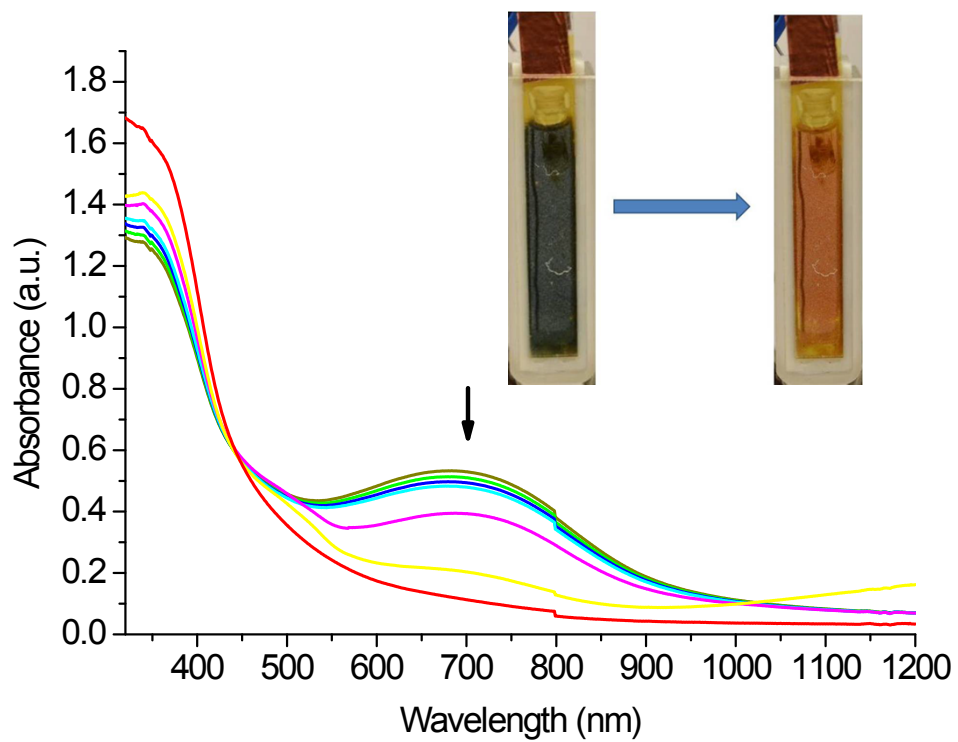


Figure S1. Spectroelectrochemistry of **P1** with applied voltages of 2000 (—), 1900 (—), 1800 (—), 1700 (—), 1500 (—), 1000 (—) and 100 (—) mV for 30 sec.

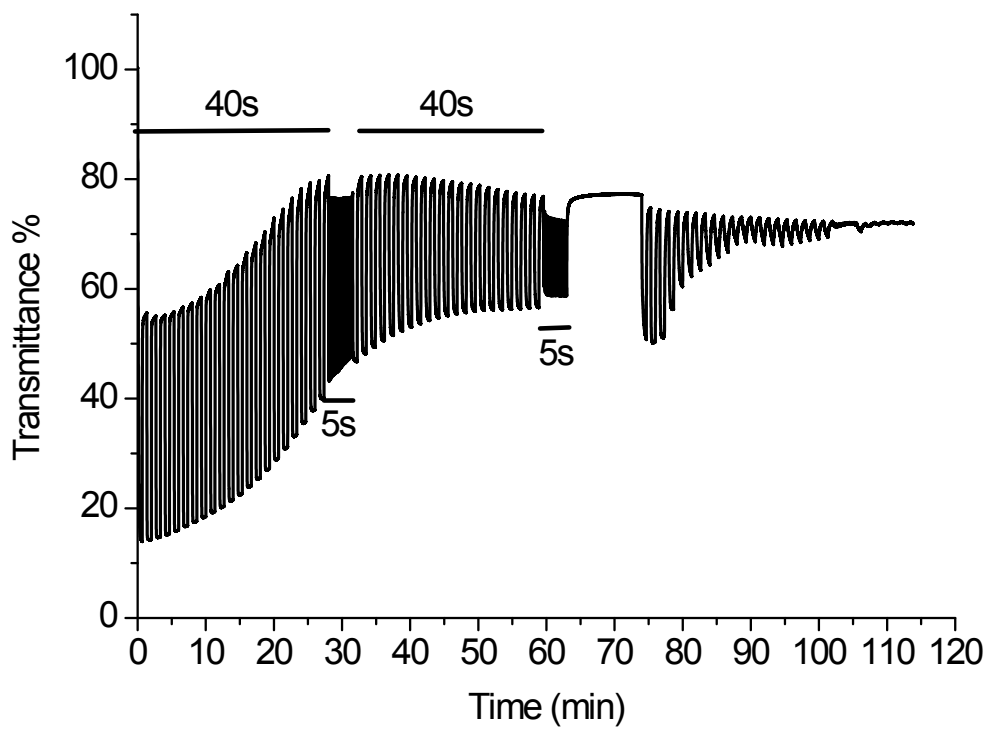


Figure S2. Percent transmission of **P1** monitored at 690 nm with switching potentials of 1500 and 100 mV for 40 and 5 sec.

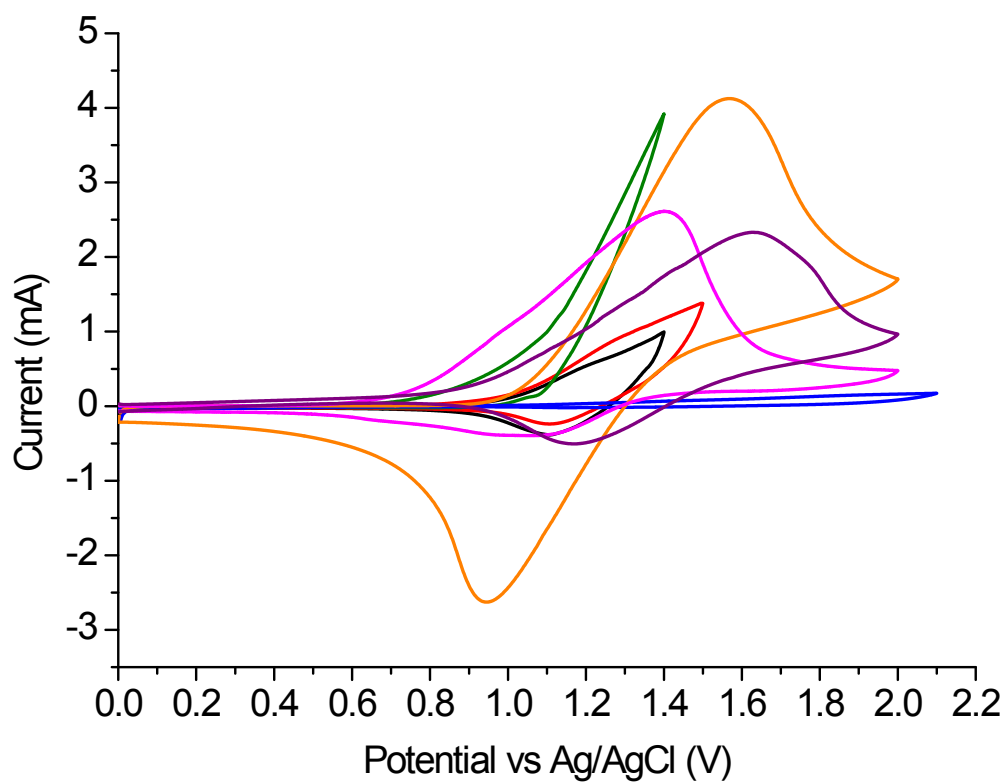


Figure S3. Cyclic voltammograms of P1 (—), P2 (—), P3 (—), P4 (—), P5 (—), P6 (—) and P7 (—).

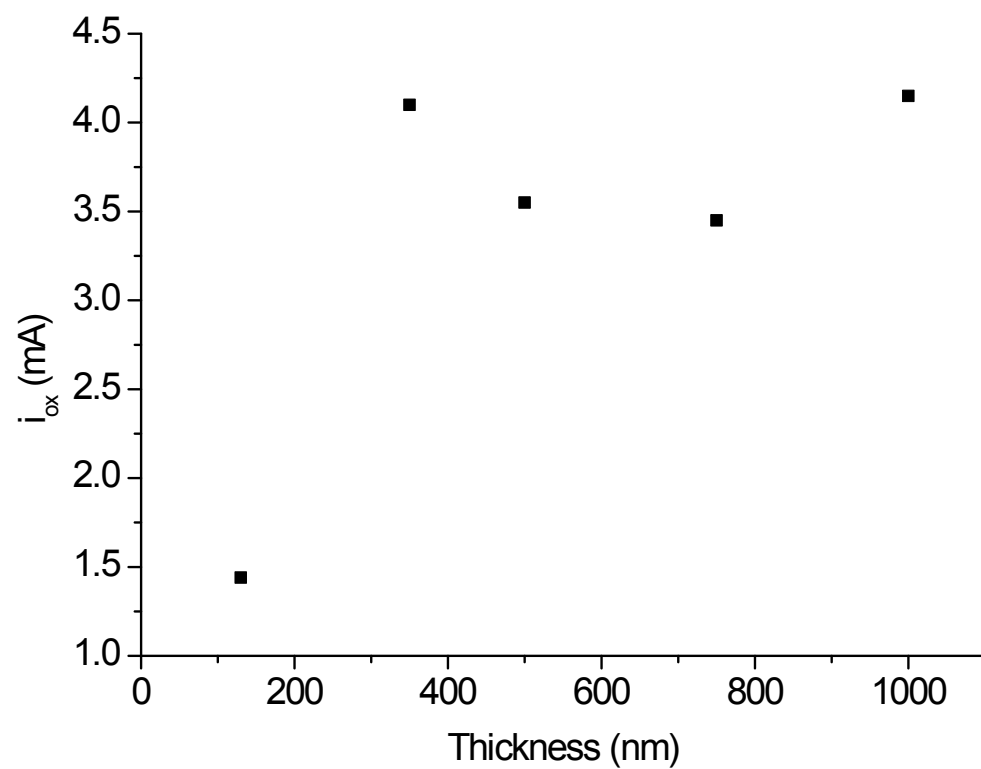


Figure S4. Dependence of i_{ox} on the thickness of the layer of **P1**.

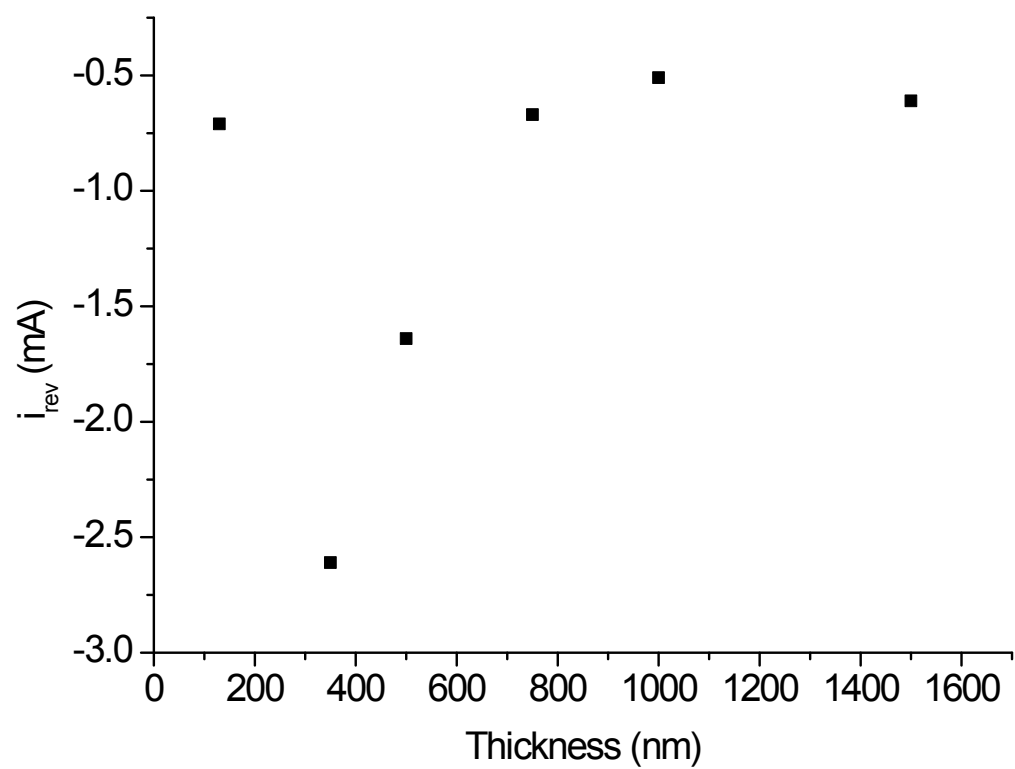


Figure S5. Dependence of i_{rev} on the thickness of the layer for **P1**.

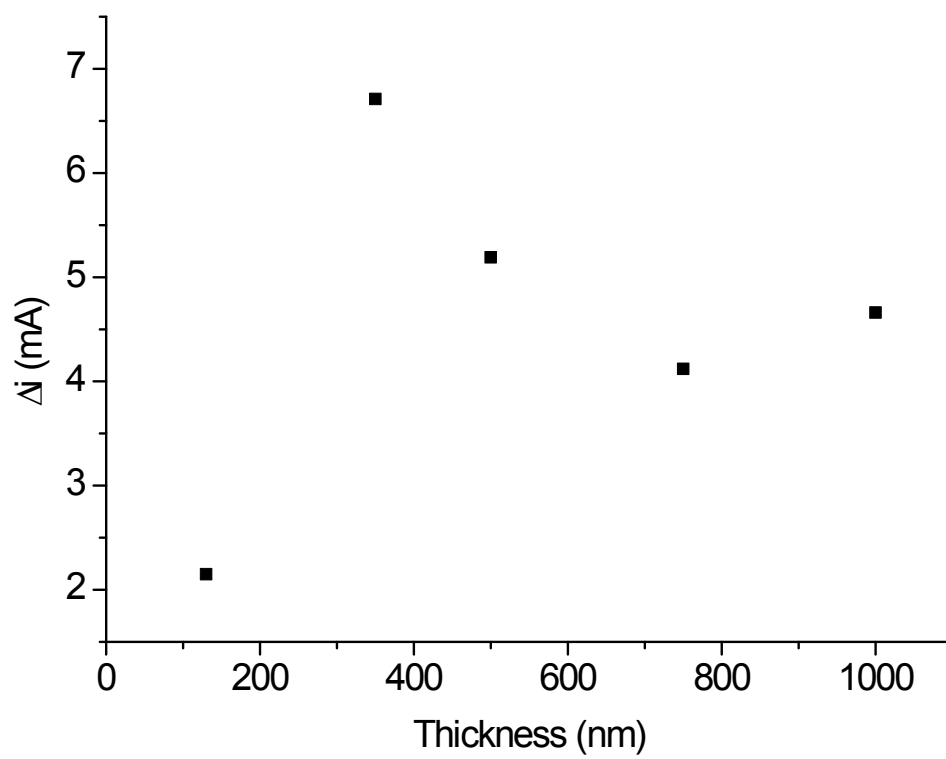


Figure S6. Dependence of Δi on the thickness of the layer of **P1**.

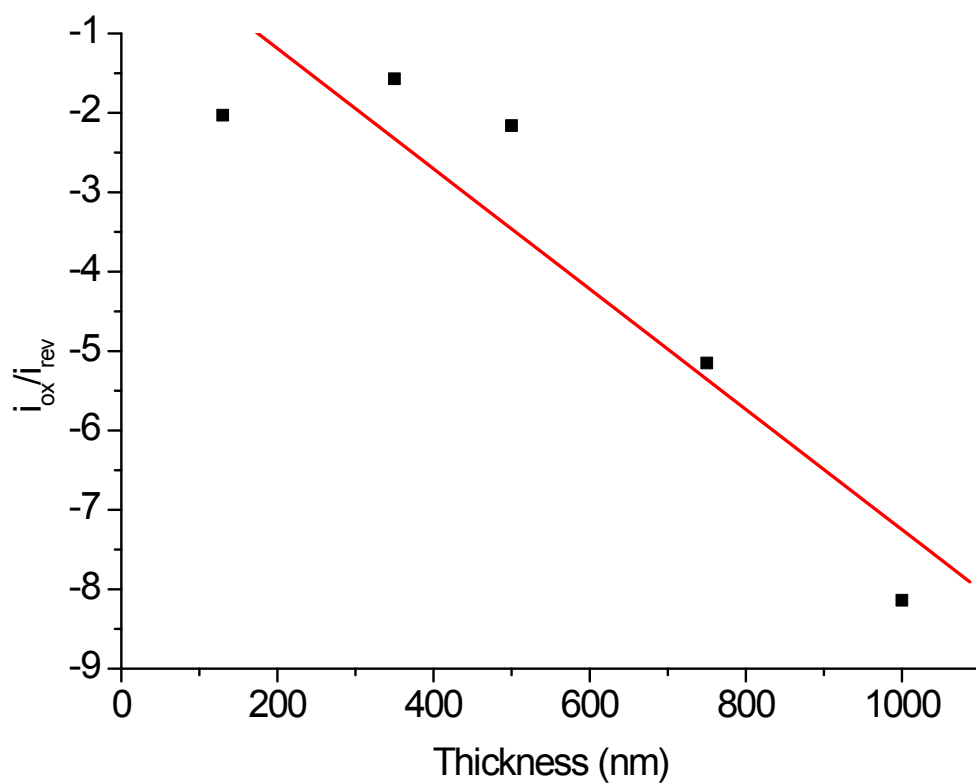


Figure S7. Dependence of i_{ox}/i_{rev} on the thickness of the layer of **P1** ($R = -0.92$).

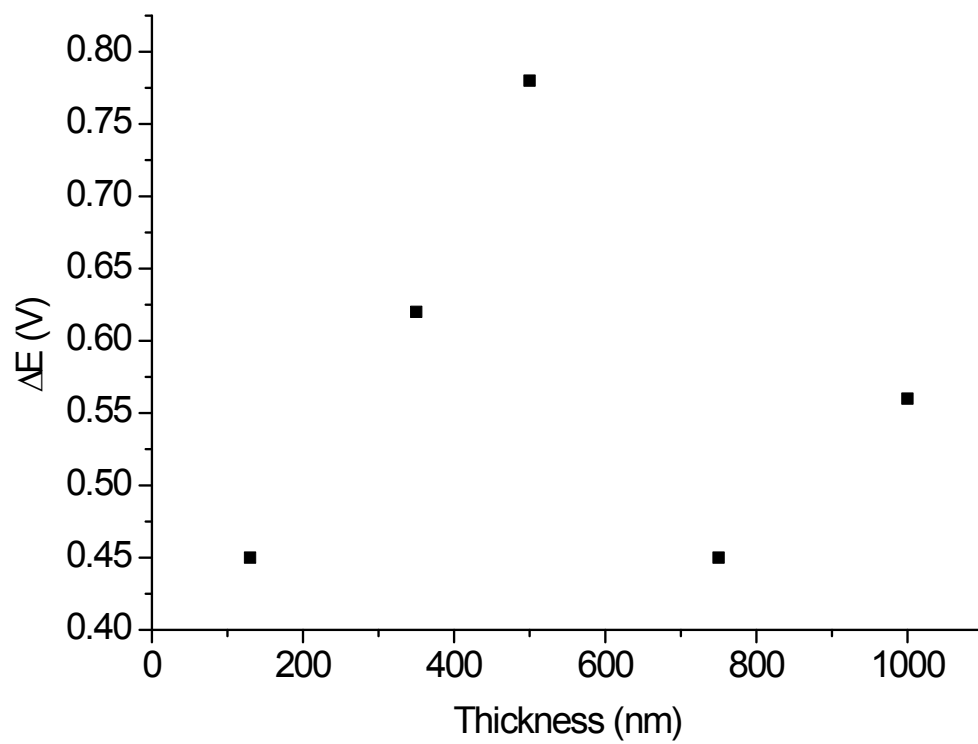


Figure S8. Dependence of ΔE on the thickness of the layer of P1.

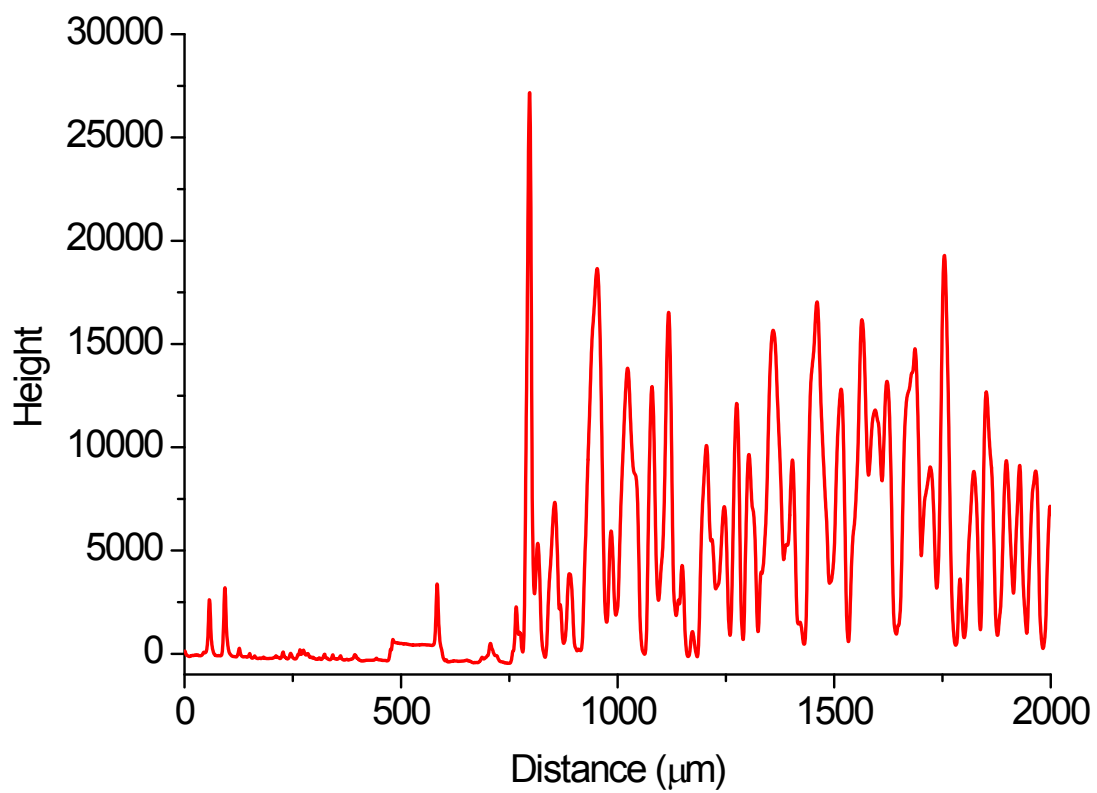


Figure S9. Profilometry trace of **P1** immobilized on glass having a thickness of 1500 nm.

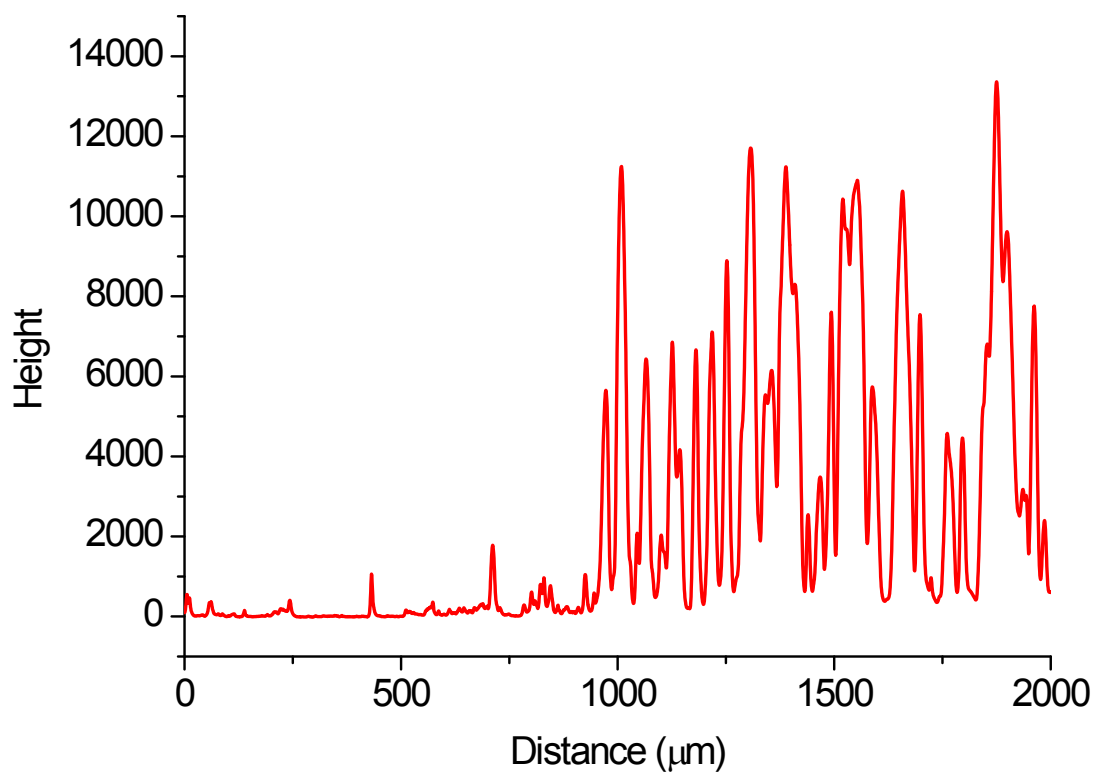


Figure S10. Profilometry trace of **P1** immobilized on glass having a thickness of 1000 nm.

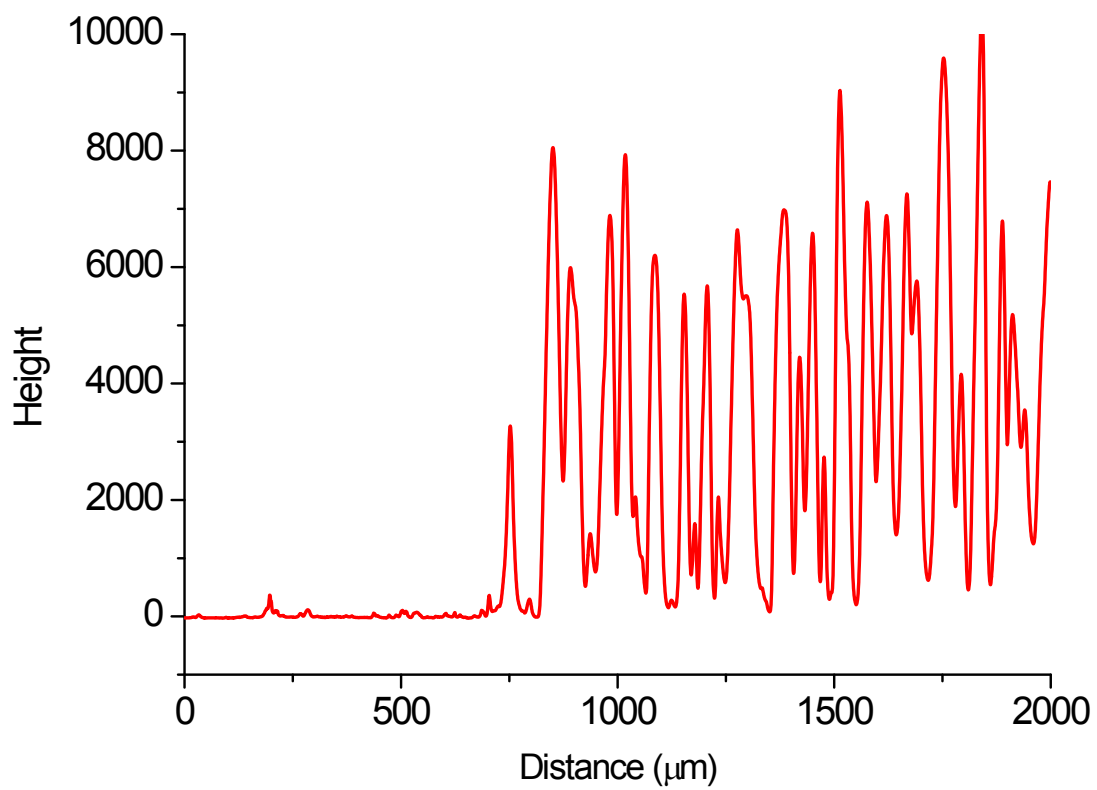


Figure S11. Profilometry trace of **P1** immobilized on glass having a thickness of 750 nm.

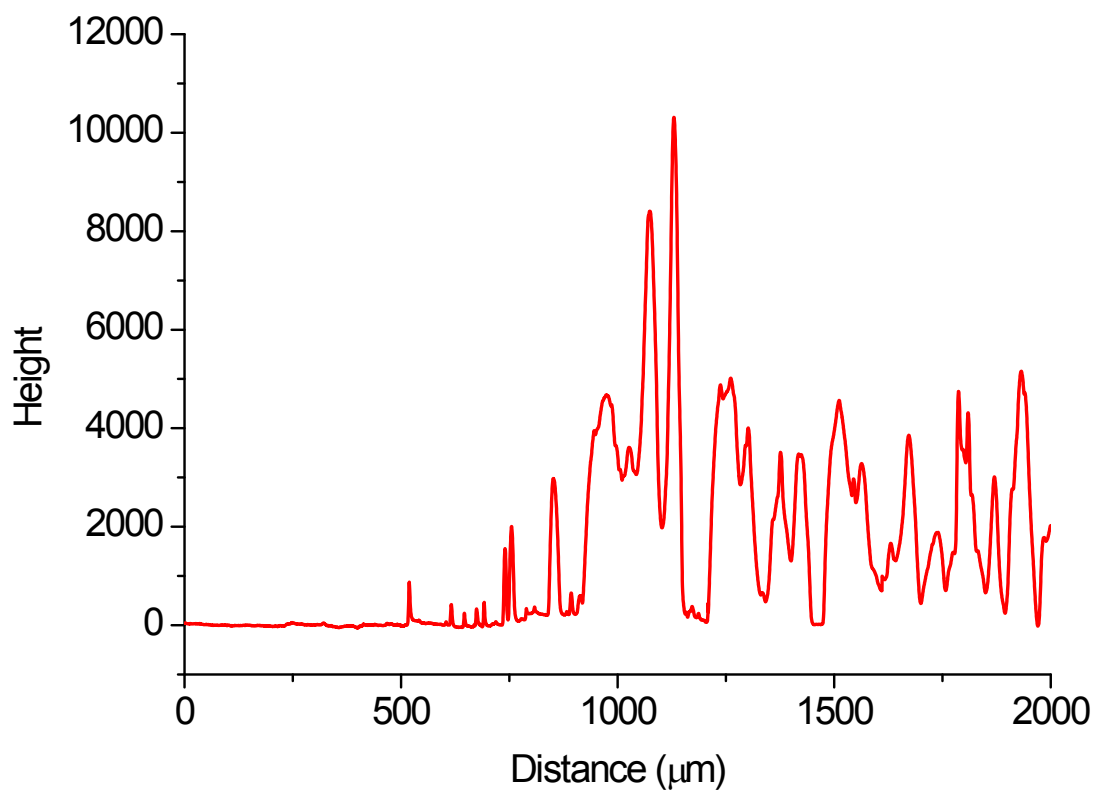


Figure S12. Profilometry trace of **P1** immobilized on glass having a thickness of 500 nm.

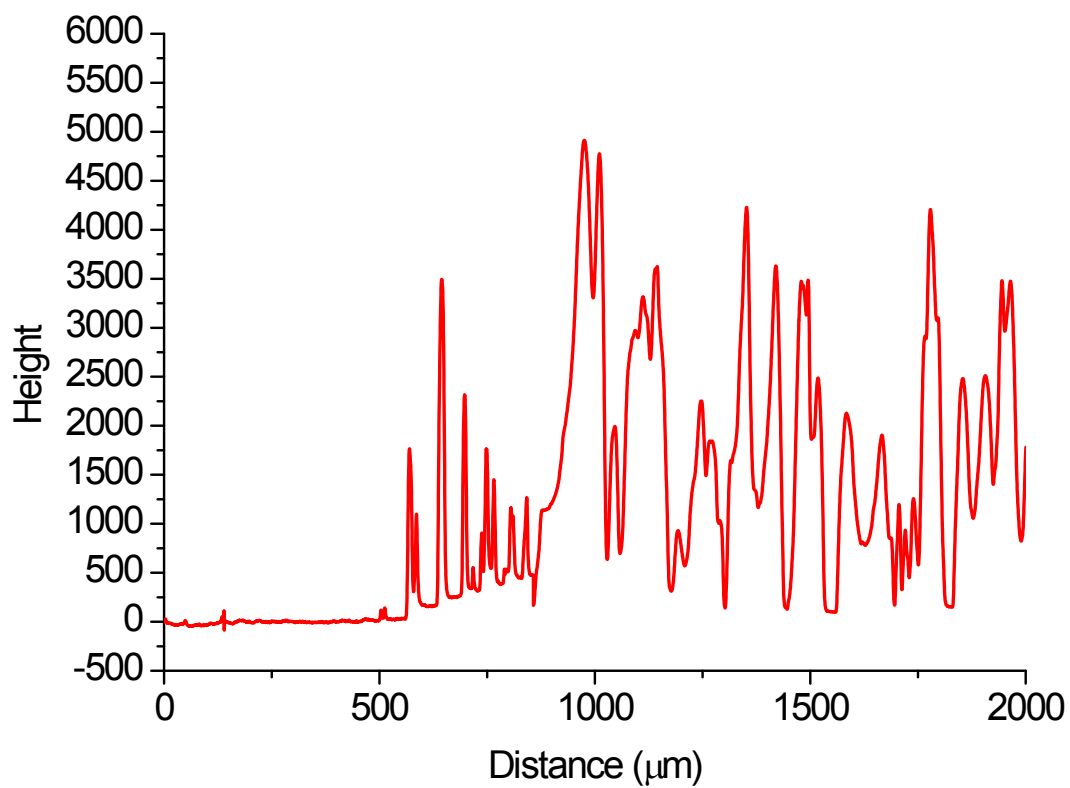


Figure S13. Profilometry trace of **P1** immobilized on glass having a thickness of 350 nm.

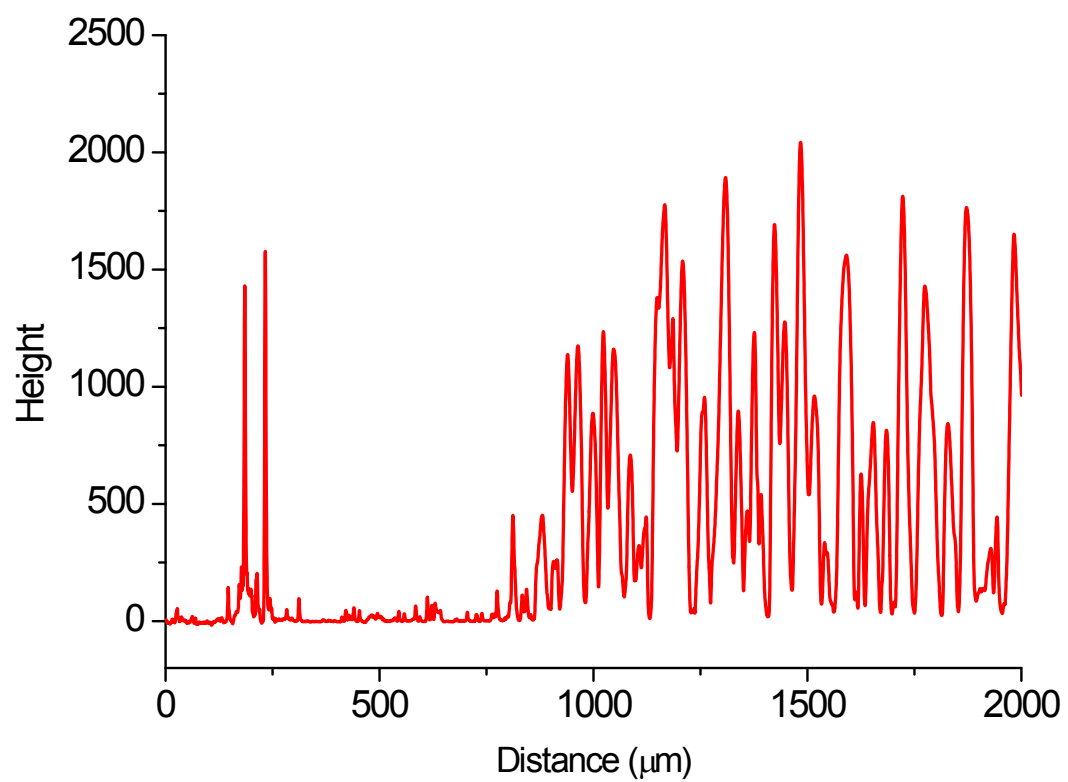


Figure S14. Profilometry trace of **P1** immobilized on glass having a thickness of 130 nm.

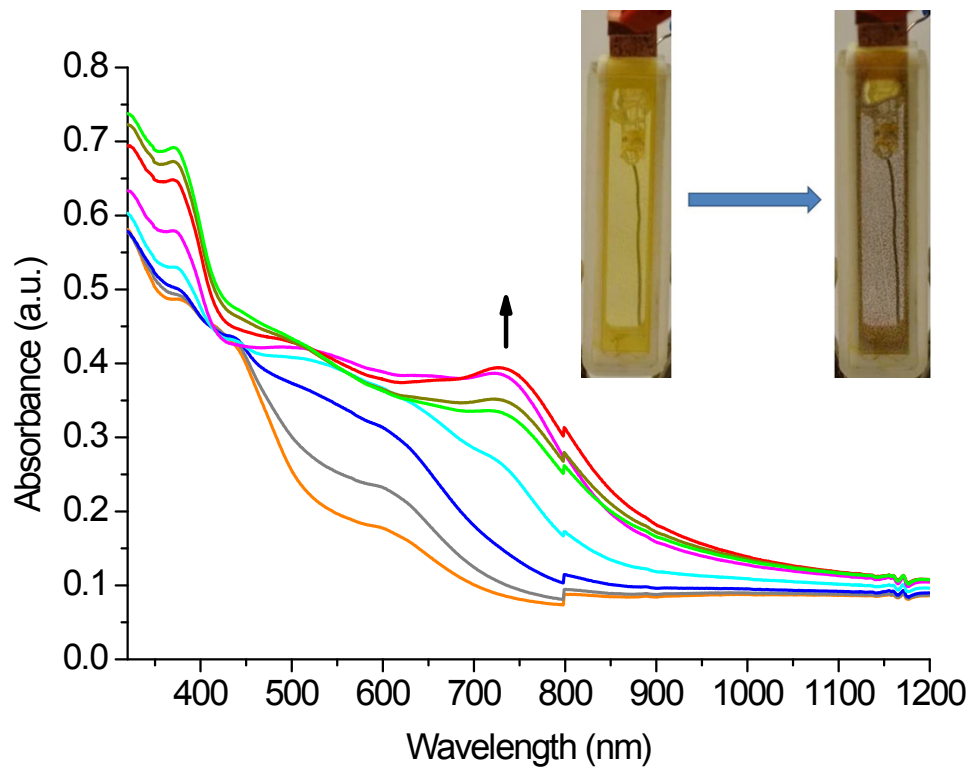


Figure S15. Spectroelectrochemistry of **P2** with applied voltages of 0 (—), 800 (—), 1000 (—), 1100 (—), 1200 (—), 1300 (—), 1400 (—), and 1500 (—) mV for 30 sec.

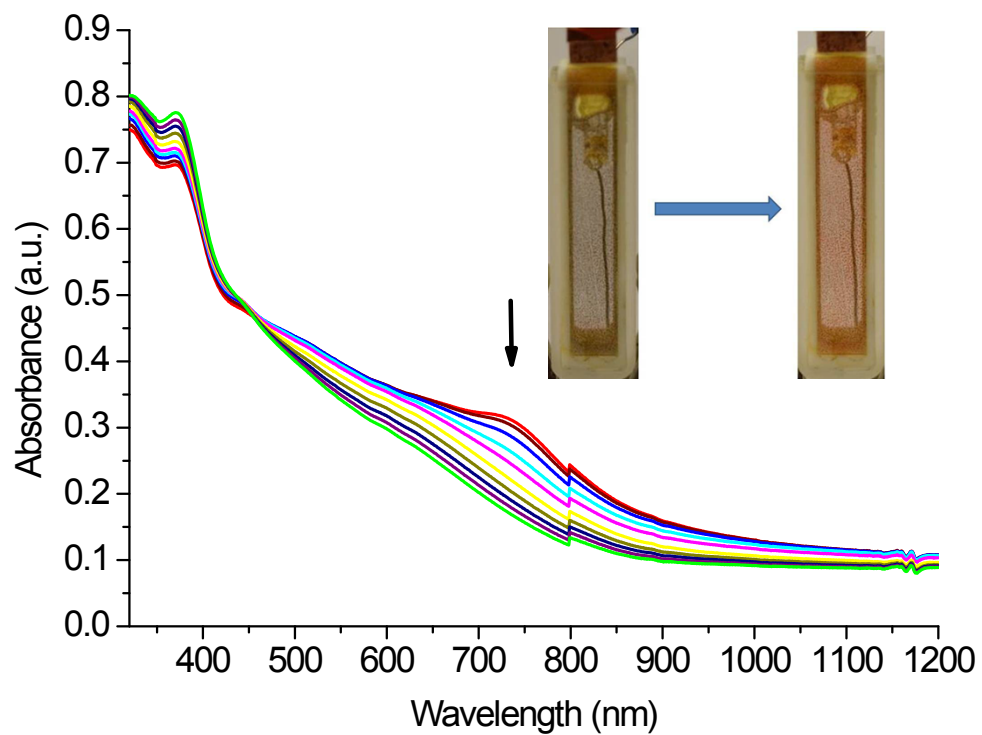


Figure S16. Spectroelectrochemistry of **P2** with applied voltages of 1500 (—), 1400 (—), 1300 (—), 1200 (—), 1100 (—), 1000 (—), 800 (—), 600 (—), 400 (—), and 0 (—) mV for 30 sec

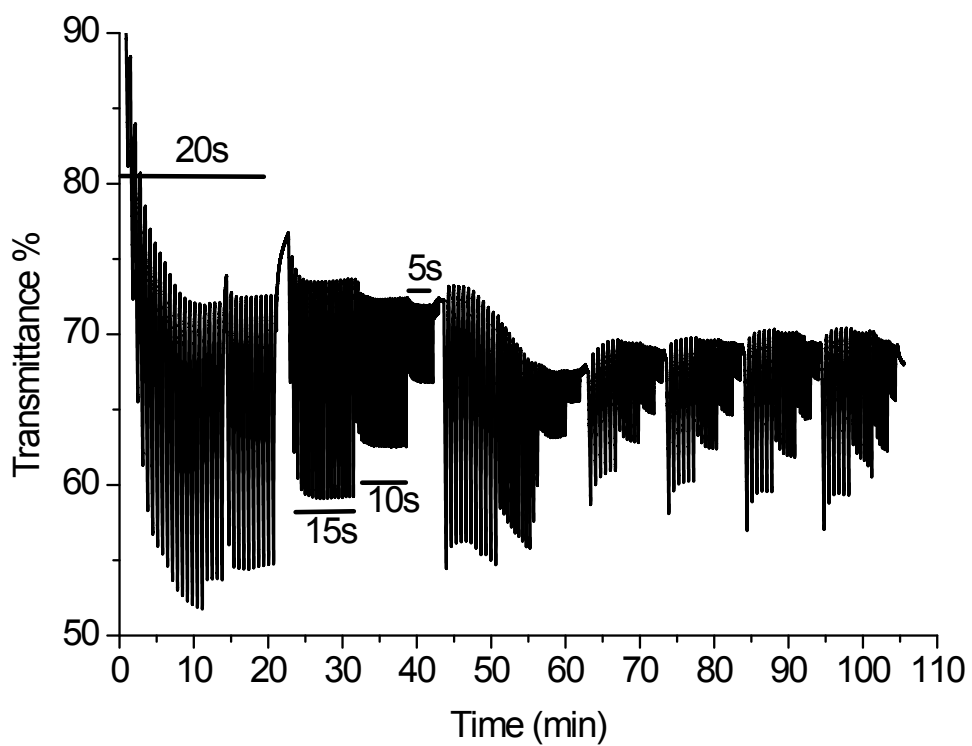


Figure S17. Transmission percent with switching potentials of 1300 and 100 mV for 20, 15, 10, 5 and 1 sec monitored at 720 nm for **P2**.

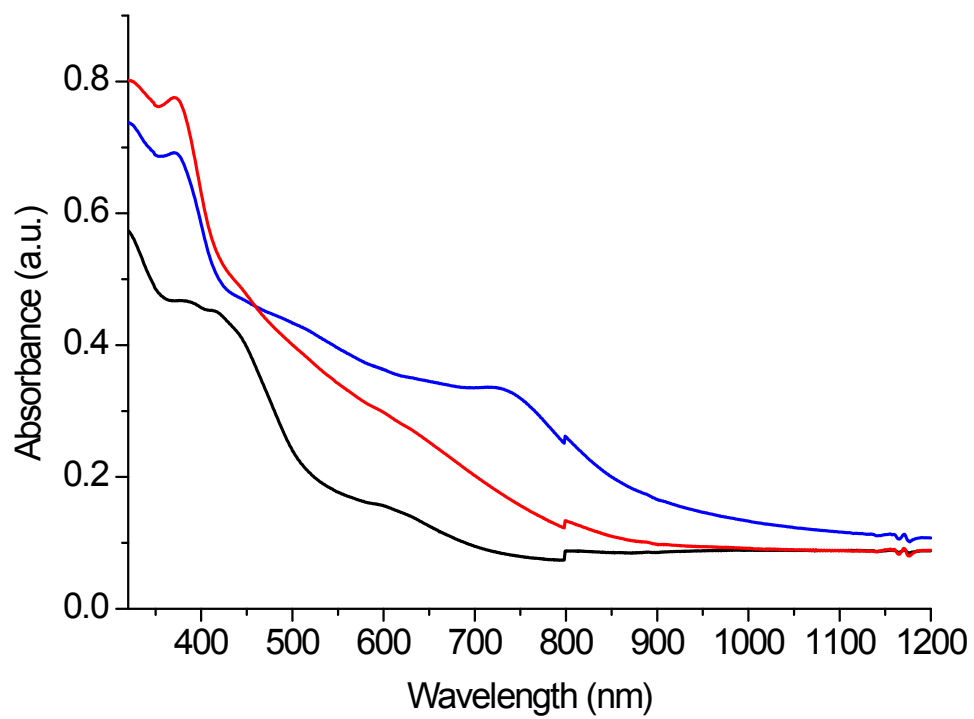


Figure S18. The UV-Vis spectra of polymer **P2** in its original (—), oxidized (—) and neutral (—) states.

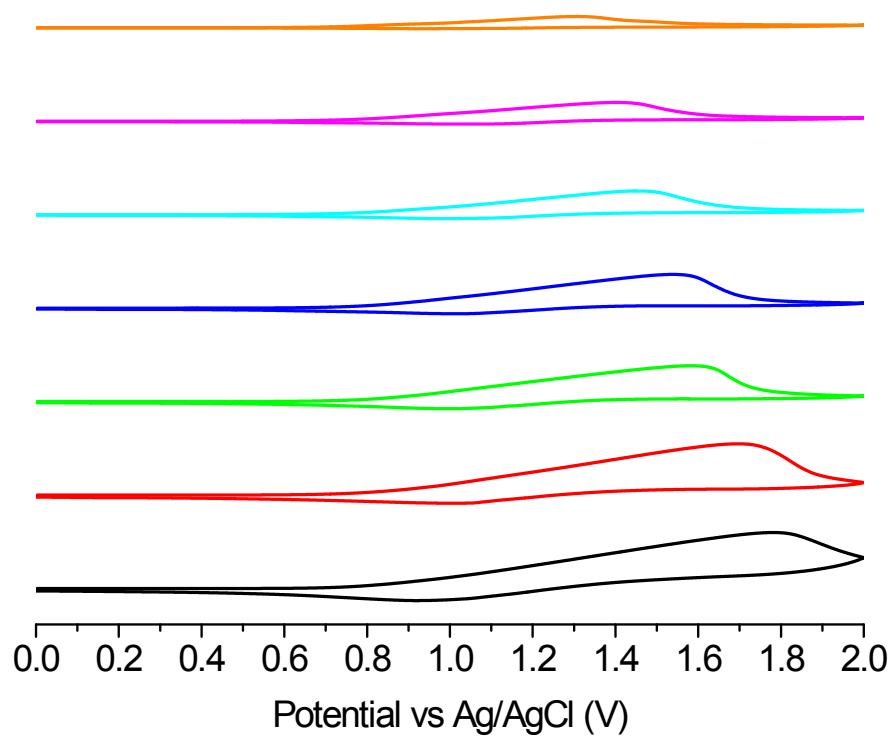


Figure S19. Dependence of cyclic voltammograms on the thickness of the layer of **P2** immobilized on ITO glass slides: 2000 (—), 1500 (—), 900 (—), 500 (—), 400 (—), 280 (—) and 130 (—) nm measured in anhydrous deaerated acetonitrile with 0.1 M TBAPF₆.

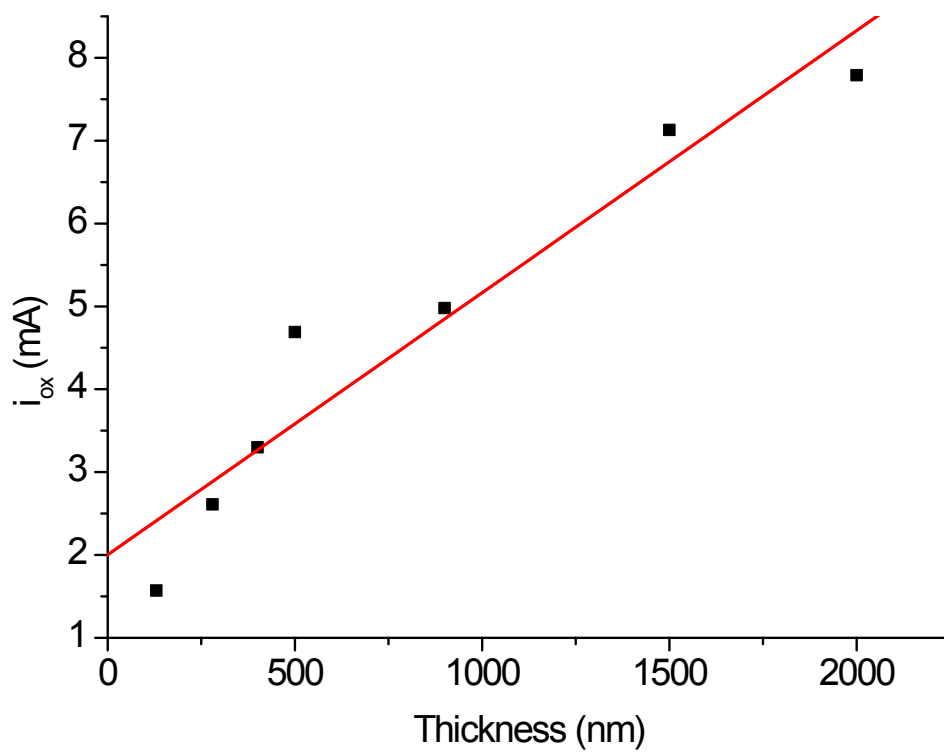


Figure S20. Dependence of i_{ox} on the thickness of the layer for **P2** ($R = 0.96$).

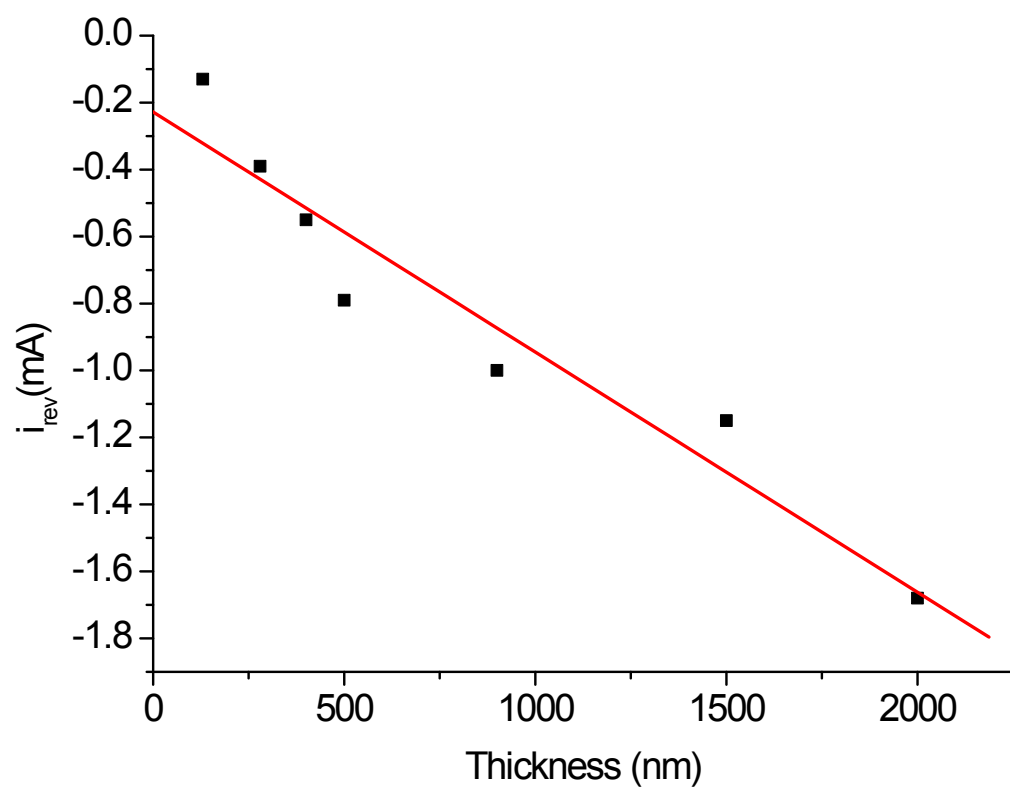


Figure S21. Dependence of i_{rev} on the thickness of the layer for **P2** ($R = -0.96$).

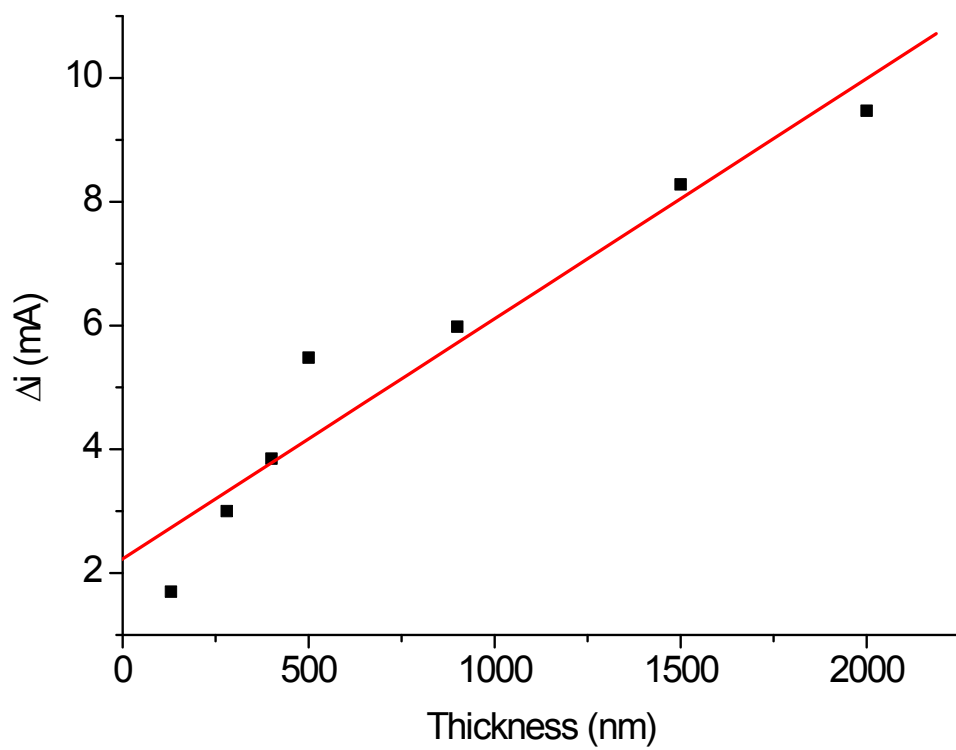


Figure S22. Dependence of Δi on the thickness of the layer of **P2** ($R = 0.96$).

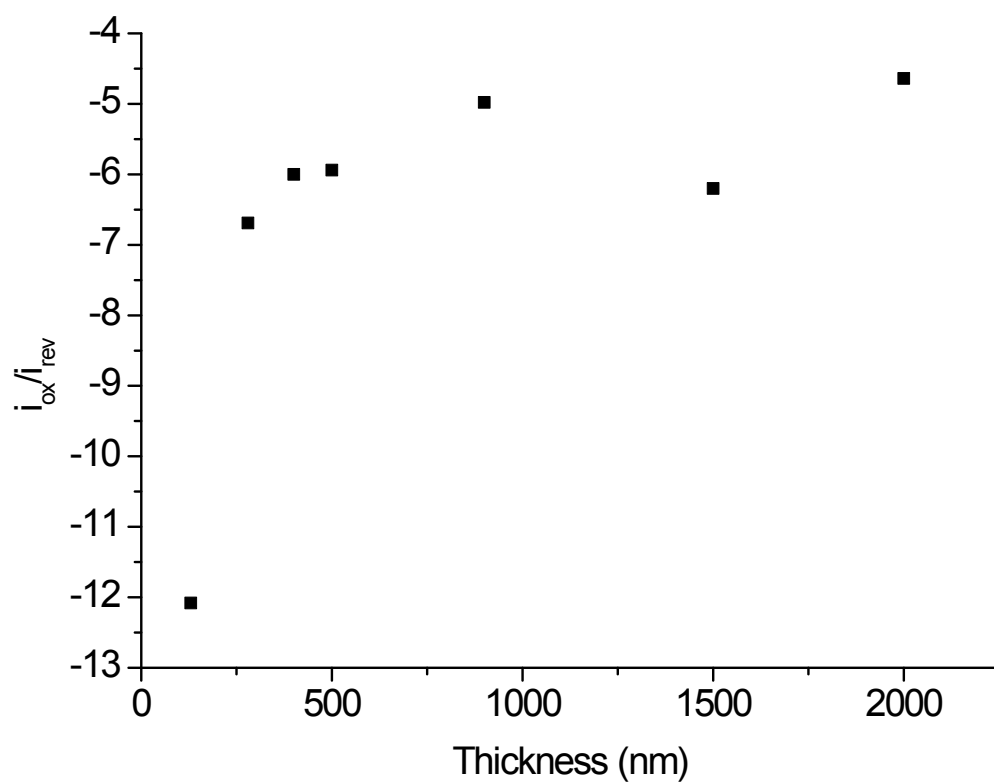


Figure S23. Dependence of i_{ox}/i_{rev} on the thickness of the layer of **P2**.

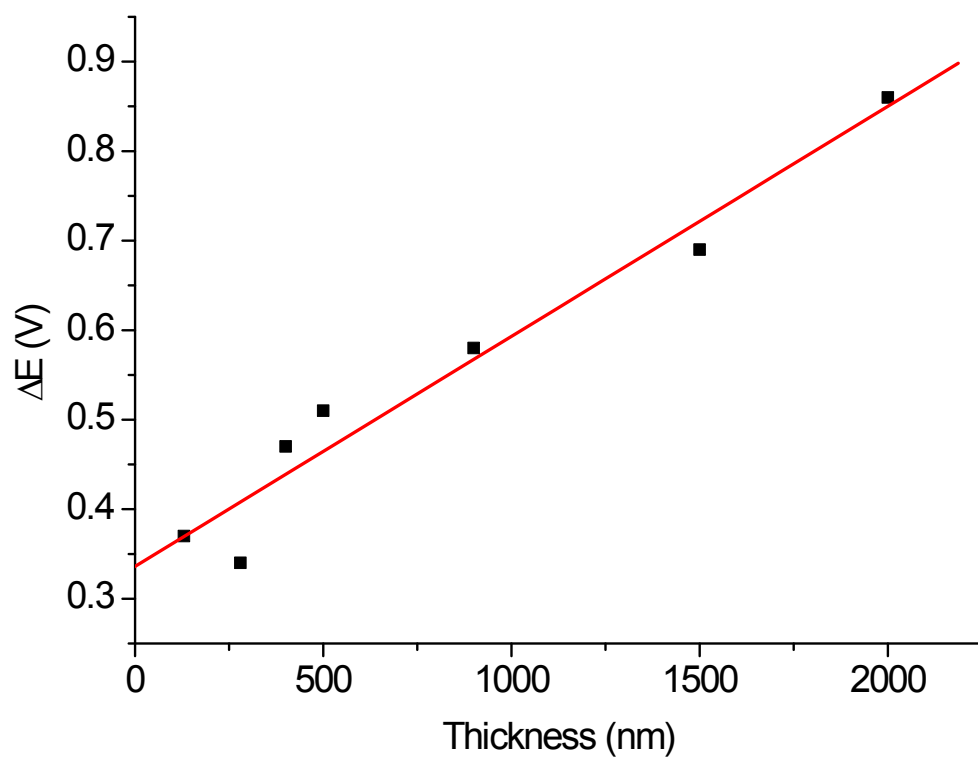


Figure S24. Dependence of ΔE on the thickness of the layer of **P2** ($R = 0.98$).

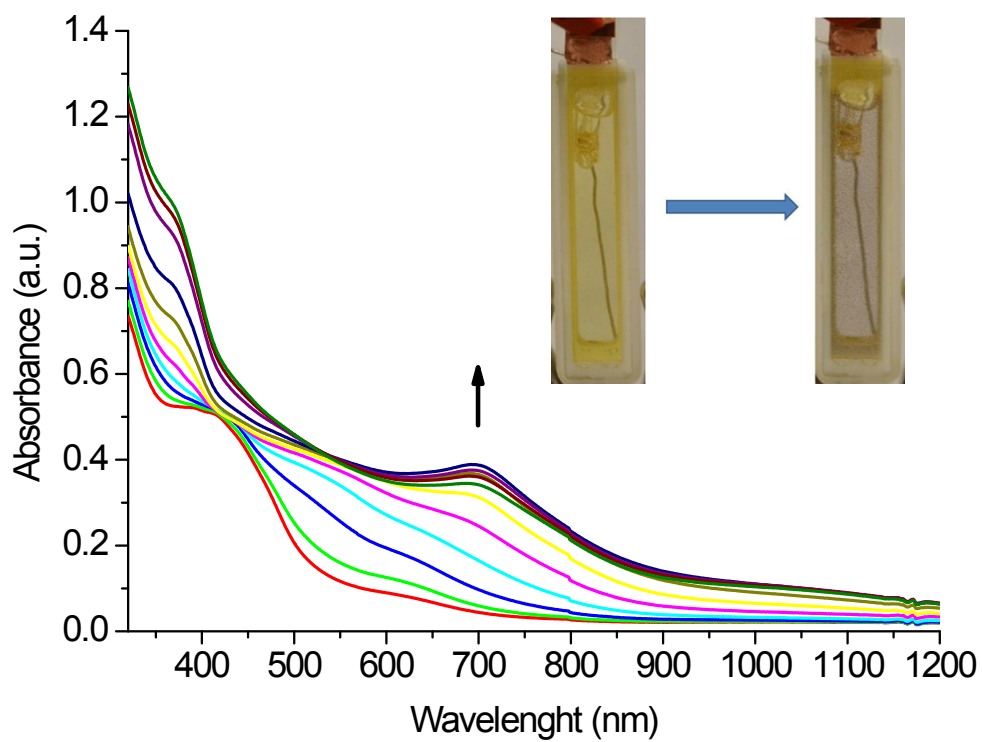


Figure S25. Spectroelectrochemistry of **P3** with applied voltages of 0 (—), 900 (—), 1000 (—), 1100 (—), 1200 (—), 1300 (—), 1400 (—), 1500 (—), 1600 (—), 1700 (—) and 1800 (—) mV for 30 sec.

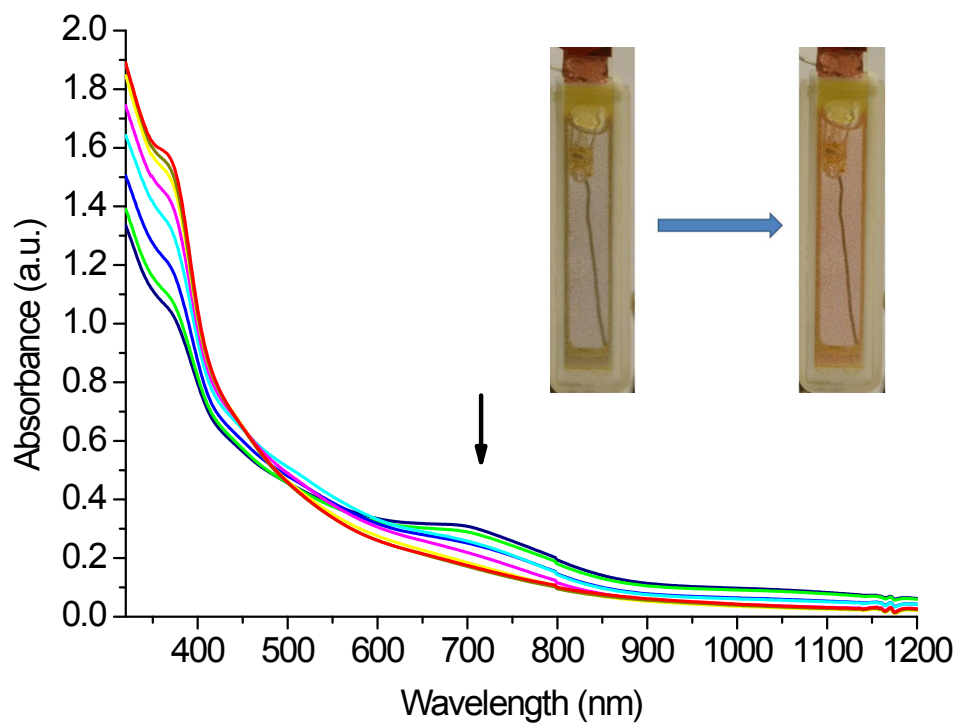


Figure S26. Spectroelectrochemistry of **P3** with applied voltages of 1800 (—), 1600 (—), 1400 (—), 1200 (—), 1000 (—), 800 (—), 600 (—), and 0 (—) mV for 30 sec.

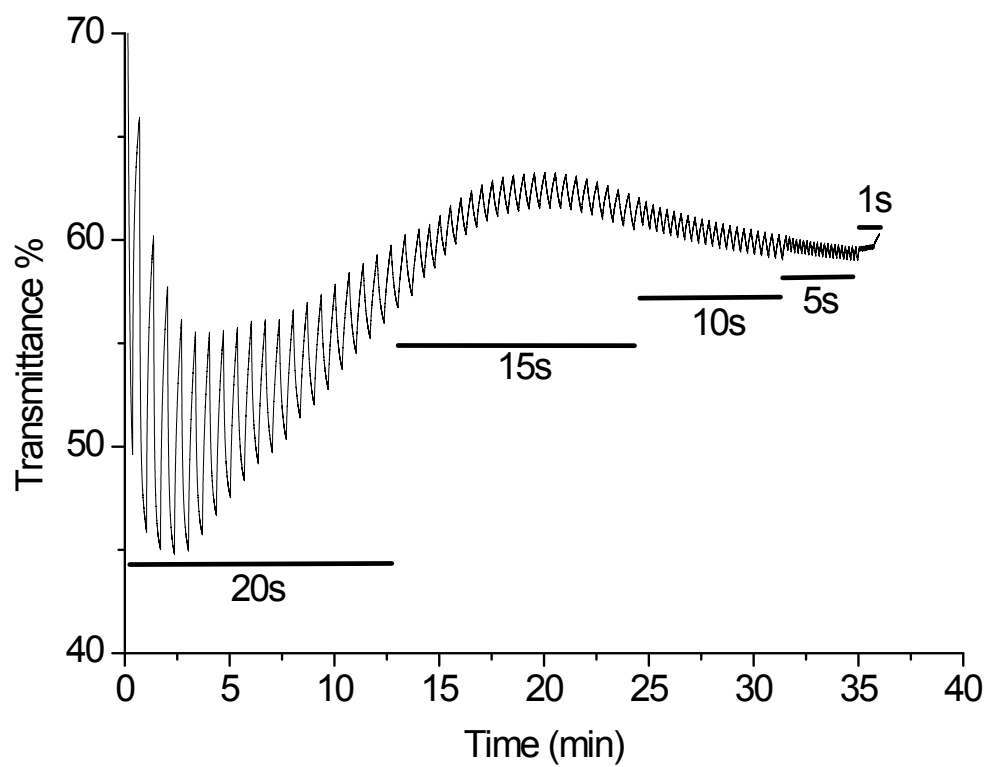


Figure S27. Percent transmission of **P3** monitored at 700 nm with switching potentials of 1500 and 100 mV for 20, 15, 10, 5 and 1 sec.

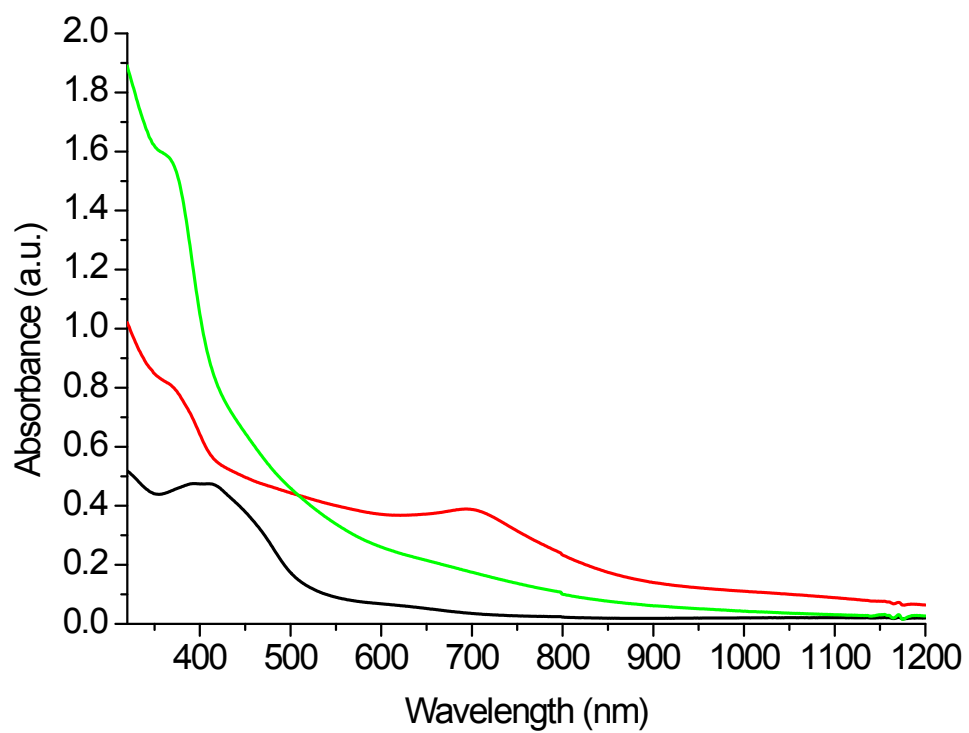


Figure S28. Absorbance spectra of **P3** in its original (—), oxidized (—) and neutral (—) states.

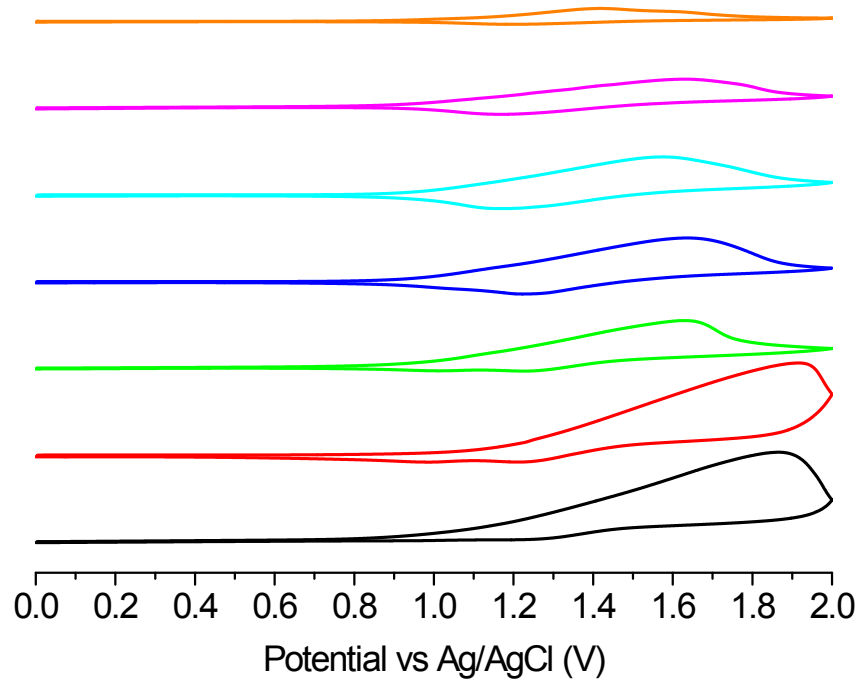


Figure S29. Dependence of cyclic voltammograms on the thickness of the layer of **P3** immobilized on ITO glass slides: 2500 (—), 1000 (—), 720 (—), 400 (—), 300 (—), 200 (—) and 120 (—) nm measured in anhydrous degassed acetonitrile with 0.1 M TBAPF₆.

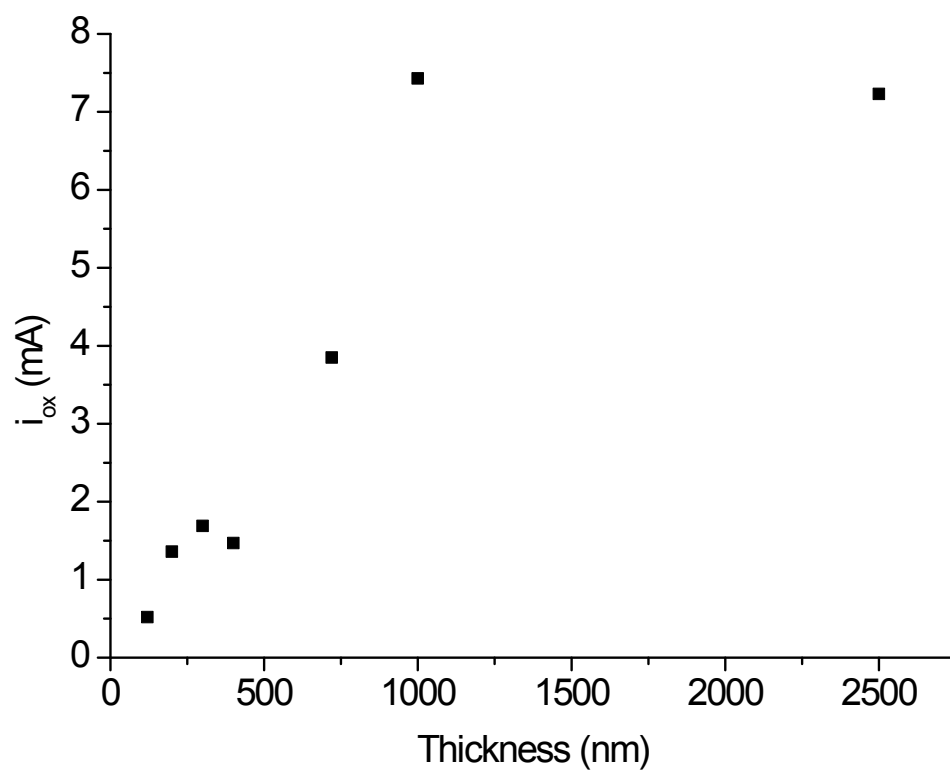


Figure S30. Dependence of i_{ox} on the thickness of the layer for **P3**.

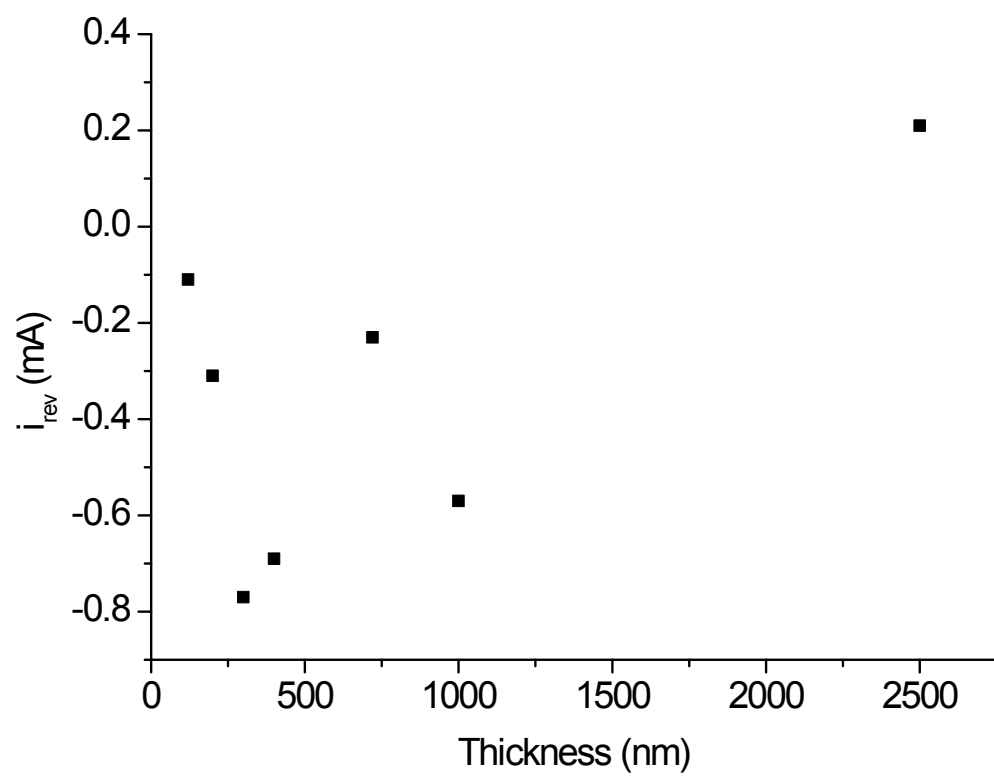


Figure S31. Dependence of i_{rev} on the thickness of the layer for **P3**

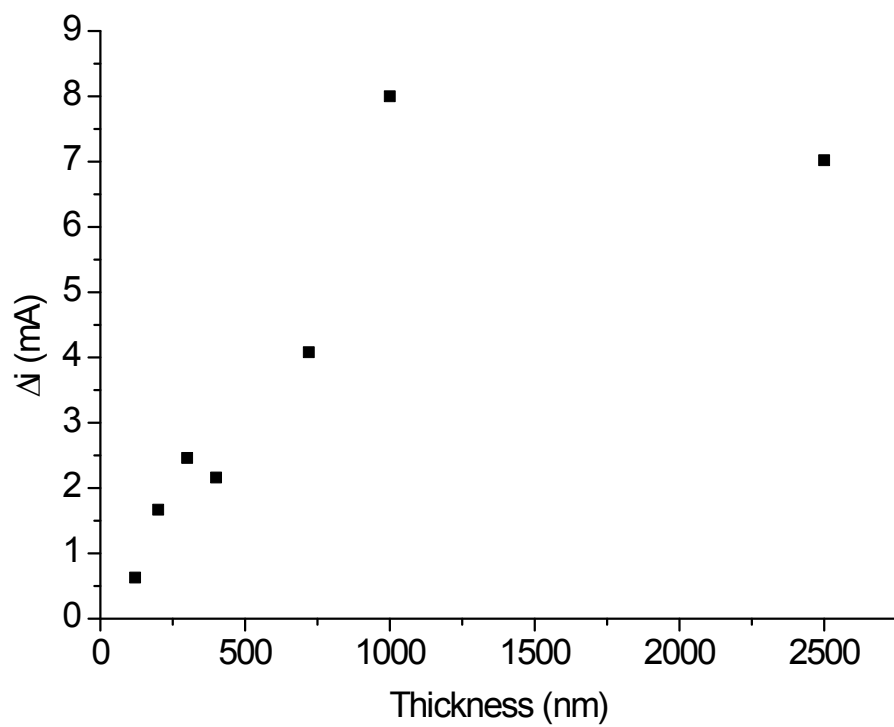


Figure S32. Dependence of Δi on the thickness of the layer of **P3**.

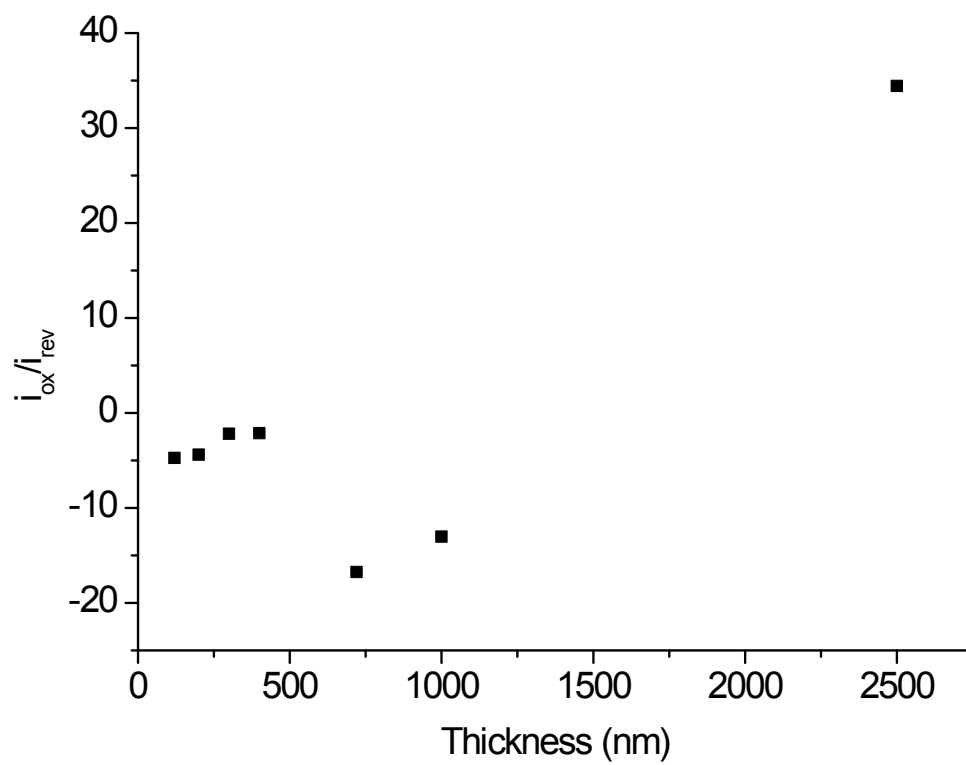


Figure S33. Dependence of i_{ox}/i_{rev} on the thickness of the layer of **P3**.

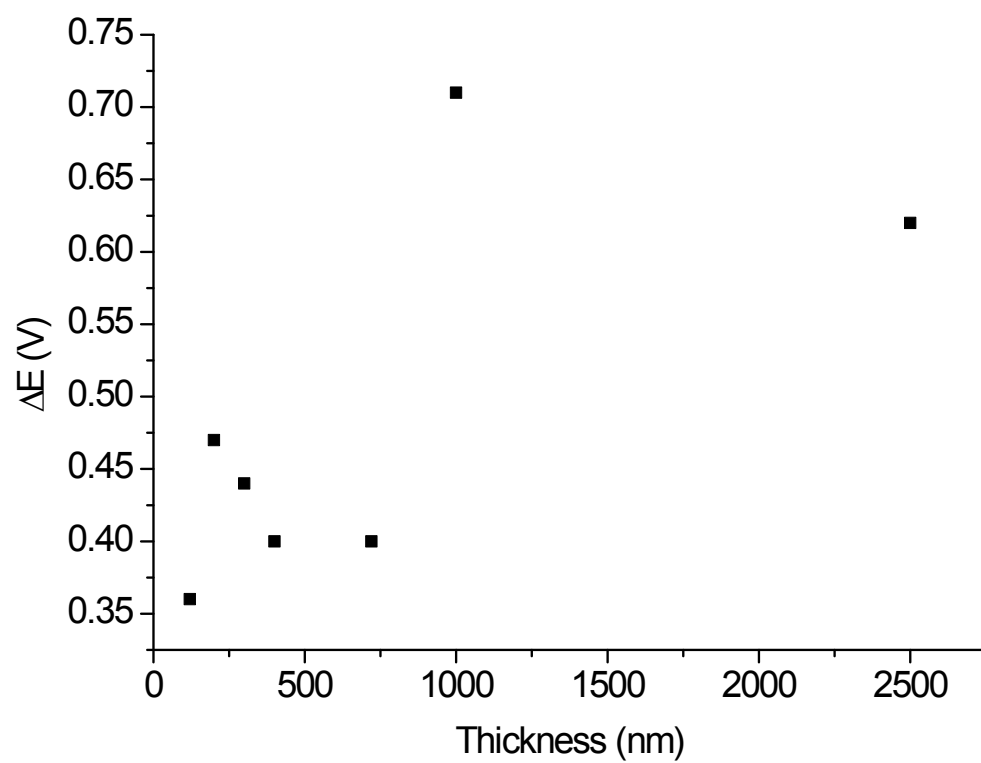


Figure S34. Dependence of ΔE on the thickness of the layer of P3.

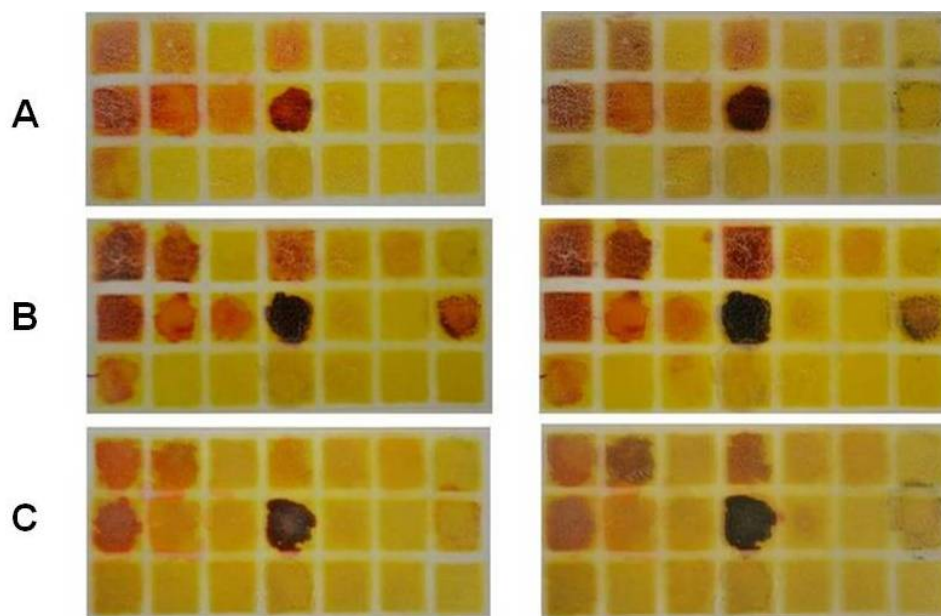


Figure S35. Complexation of **P1** (top), **P2** (middle) and **P3** (bottom) with various transition metal ions before (left) and after heating at 65°C for 2h (right).

$\text{Cu}(\text{BF}_4)_2$	$\text{Cu}(\text{ClO}_4)_2$	$\text{Cu}(\text{OAc})_2$	ZnCl_2	$\text{Zn}(\text{CF}_3\text{SO}_2)_2$	$\text{Zn}(\text{ClO}_4)_2$	RuCl_2
$\text{Fe}(\text{BF}_4)_2$	$\text{Fe}(\text{CF}_3\text{SO}_2)_2$	FeBr_3	$\text{Fe}(\text{ClO}_4)_3$	$\text{Co}(\text{ClO}_4)_2$	CoCl_2	AgBF_4
AgPF_6	EuCl_3	$\text{Ni}(\text{NO}_2)_2$	CuI	$\text{Pb}(\text{OAc})_2$	$\text{Hg}(\text{OAc})_2$	Original polymer

Figure S36. Corresponding legend of metal ion complexes drop-casted onto polymers from Figure 29.

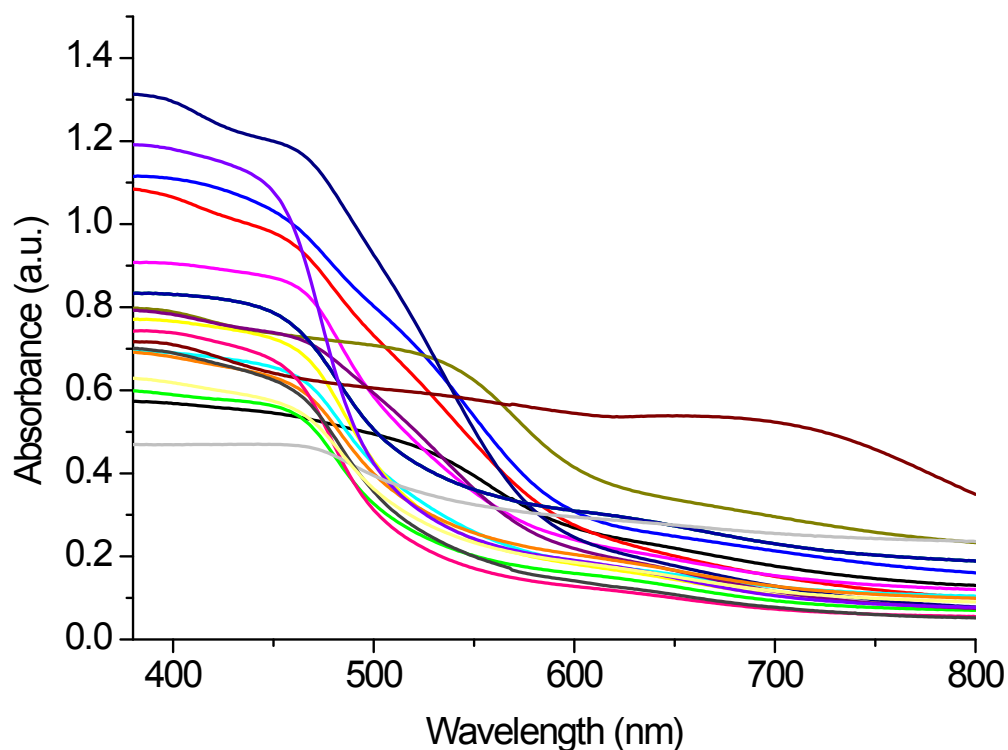


Figure S37. Absorbance spectra of complexes of **P1** immobilized on ITO coated glass with drop-cast $\text{Cu}(\text{BF}_4)_2$ (—), $\text{Cu}(\text{ClO}_4)_2$ (—), $\text{Cu}(\text{OAc})_2$ (—), ZnCl_2 (—), $\text{Zn}(\text{OTf})_2$ (—), $\text{Zn}(\text{ClO}_4)_2$ (—), RuCl_3 (—), $\text{Fe}(\text{BF}_4)_2$ (—), $\text{Fe}(\text{OTf})_2$ (—), FeBr_3 (—), $\text{Fe}(\text{ClO}_4)_3$ (—), $\text{Co}(\text{ClO}_4)_2$ (—), CoCl_2 (—), AgBF_4 (—), AgPF_6 (—), EuCl_3 (—), $\text{Ni}(\text{NO}_3)_2$ (—), CuI (—), $\text{Pb}(\text{OAc})_2$ (—) and $\text{Hg}(\text{OAc})_2$ (—) measured after heating at 65°C for 2h.

Table S1. Absorbance maximum of **P3** immobilized on ITO coated glass with various metal salts.

metal salt	λ_{abs} (nm)	metal salt	λ_{abs} (nm)	metal salt	λ_{abs} (nm)
$\text{Cu}(\text{BF}_4)_2$	504	$\text{Fe}(\text{BF}_4)_2$	535	AgPF_6	458
$\text{Cu}(\text{ClO}_4)_2$	459	$\text{Fe}(\text{OTf})_2$	466	EuCl_3	439
$\text{Cu}(\text{OAc})_2$	444	FeBr_3	468	$\text{Ni}(\text{NO}_3)_2$	452
ZnCl_2	451	$\text{Fe}(\text{ClO}_4)_3$	696	CuI	467
$\text{Zn}(\text{OTf})_2$	460	$\text{Co}(\text{ClO}_4)_2$	442	$\text{Pb}(\text{OAc})_2$	455
$\text{Zn}(\text{ClO}_4)_2$	460	CoCl_2	448	$\text{Hg}(\text{OAc})_2$	458
RuCl_3	459	AgBF_4	445		

Table S2. Dependence of anodic cyclic voltammograms on the thickness of the layer of **P1**.

	i_{ox} (mA)	i_{rev} (mA)	Δi (mA)	i_{ox}/i_{rev}	E_{ox} (V)	E_{rev} (V)	ΔE (V)
1500 nm	-	-0.61	-	-	-	1.40	-
1000 nm	4.15	-0.51	4.66	-8.14	1.70	1.14	0.56
750 nm	3.45	-0.67	4.12	-5.15	1.64	1.19	0.45
500 nm	3.55	-1.64	5.19	-2.16	1.83	1.05	0.78
350 nm	4.10	-2.61	6.71	-1.57	1.57	0.95	0.62
130 nm	1.44	-0.71	2.15	-2.03	1.50	1.05	0.45

Table S3. Dependence of cyclic voltammograms on the thickness of the layer of **P2**.

	i_{ox} (mA)	i_{rev} (mA)	Δi (mA)	i_{ox}/i_{rev}	E_{ox} (V)	E_{rev} (V)	ΔE (V)
2000 nm	7.79	-1.68	9.47	-4.64	1.78	0.92	0.86
1500 nm	7.13	-1.15	8.28	-6.20	1.70	1.01	0.69
900 nm	4.98	-1.00	5.98	-4.98	1.58	1.00	0.58
500 nm	4.69	-0.79	5.48	-5.94	1.54	1.03	0.51
400 nm	3.30	-0.55	3.85	-6.00	1.45	0.98	0.47
280 nm	2.61	-0.39	3.00	-6.69	1.40	1.06	0.34
130 nm	1.57	-0.13	1.70	-12.08	1.30	0.93	0.37

Table S4. Dependence of cyclic voltammograms on the thickness of the layer of **P3**.

	i_{ox} (mA)	i_{rev} (mA)	Δi (mA)	i_{ox}/i_{rev}	E_{ox} (V)	E_{rev} (V)	ΔE (V)
2500 nm	7.23	0.21	7.02	34.43	1.87	1.25	0.62
1000 nm	7.43	-0.57	8.00	-13.03	1.92	1.21	0.71
720 nm	3.85	-0.23	4.08	-16.74	1.63	1.23	0.40
400 nm	1.47	-0.69	2.16	-2.13	1.53	1.13	0.40
300 nm	1.69	-0.77	2.46	-2.19	1.52	1.08	0.44
200 nm	1.36	-0.31	1.67	-4.39	1.54	1.07	0.47
120 nm	0.52	-0.11	0.63	-4.73	1.40	1.04	0.36

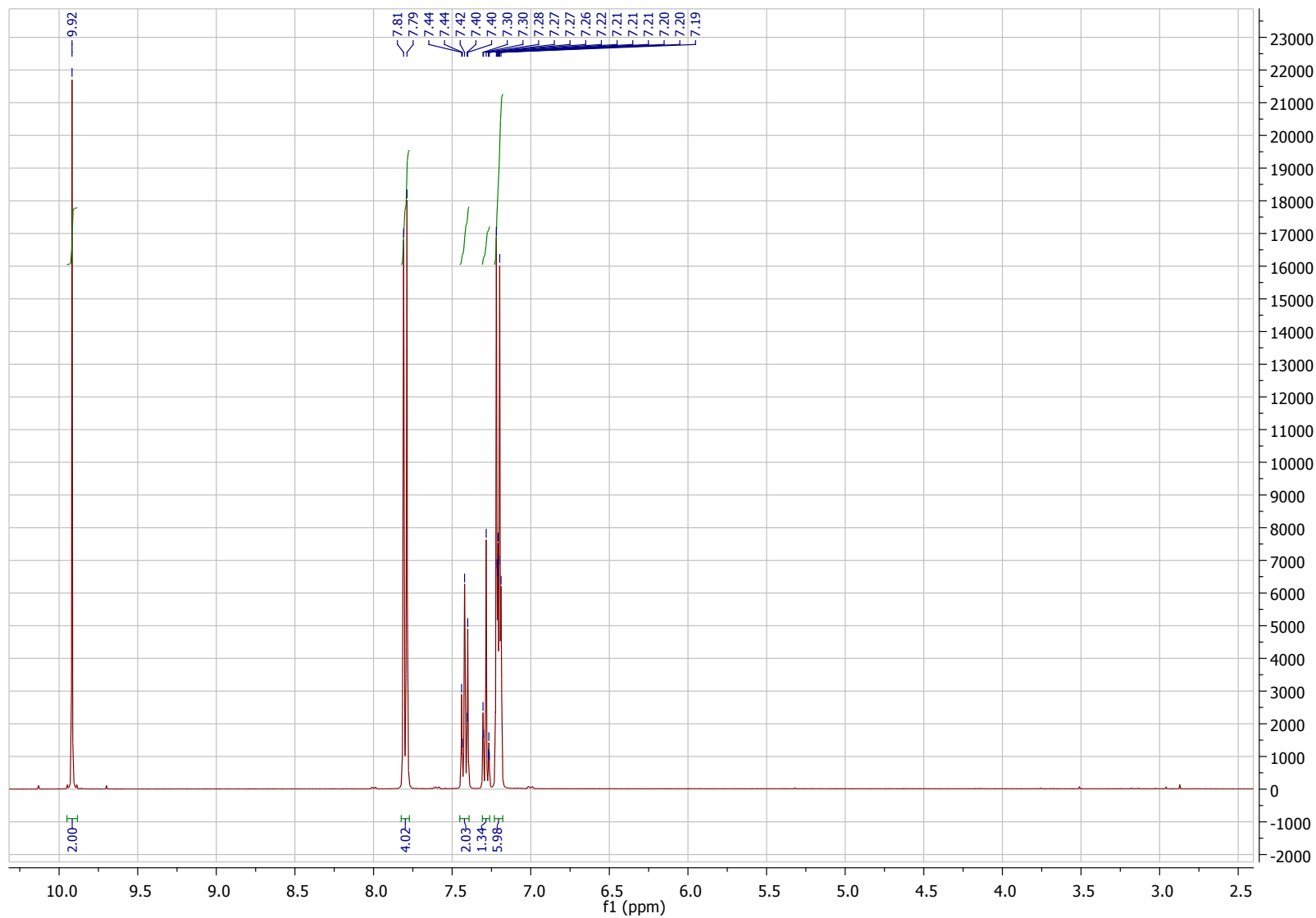


Figure S38. ¹H NMR spectrum of 1.

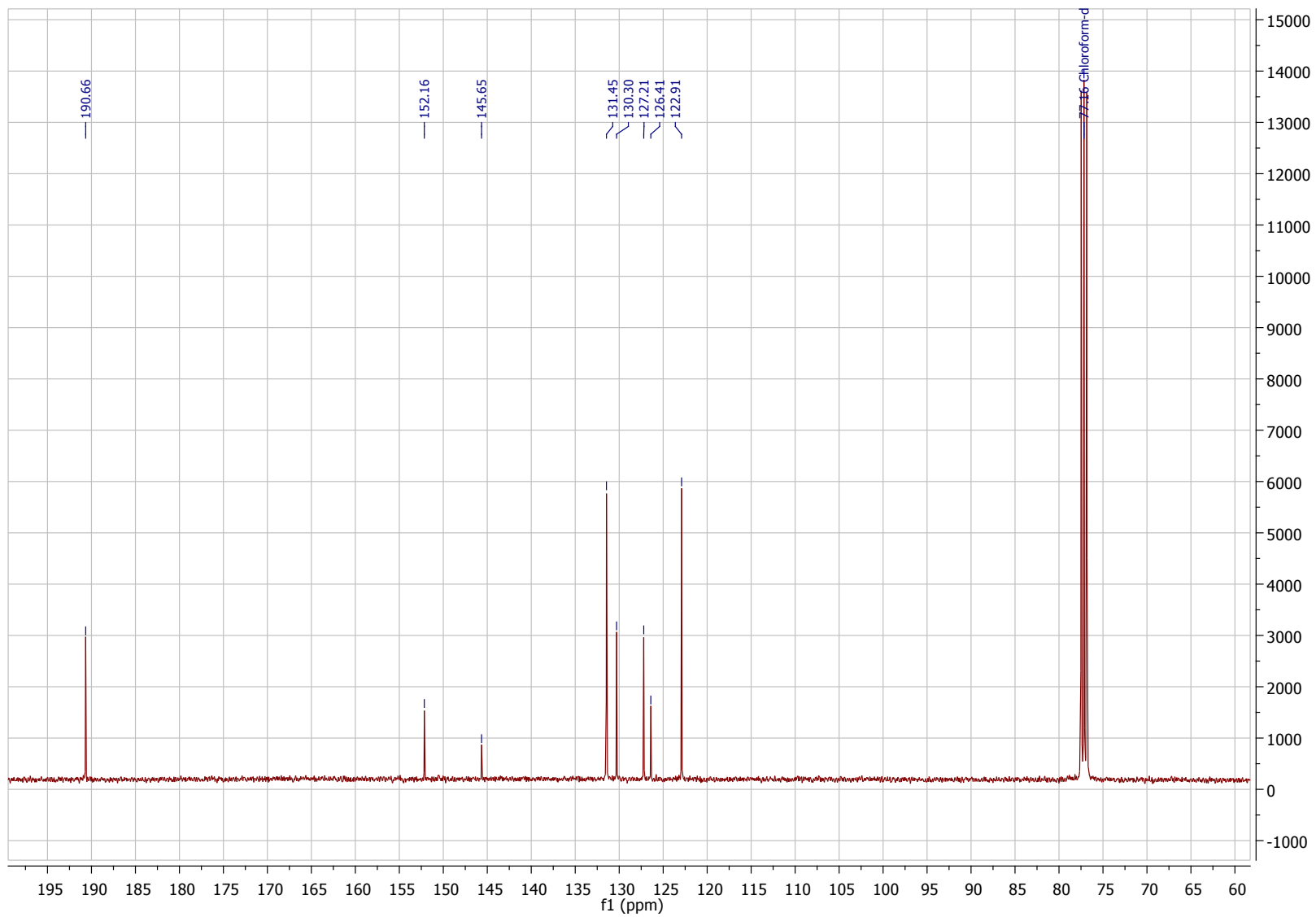


Figure S39. ^{13}C NMR spectrum of 1.

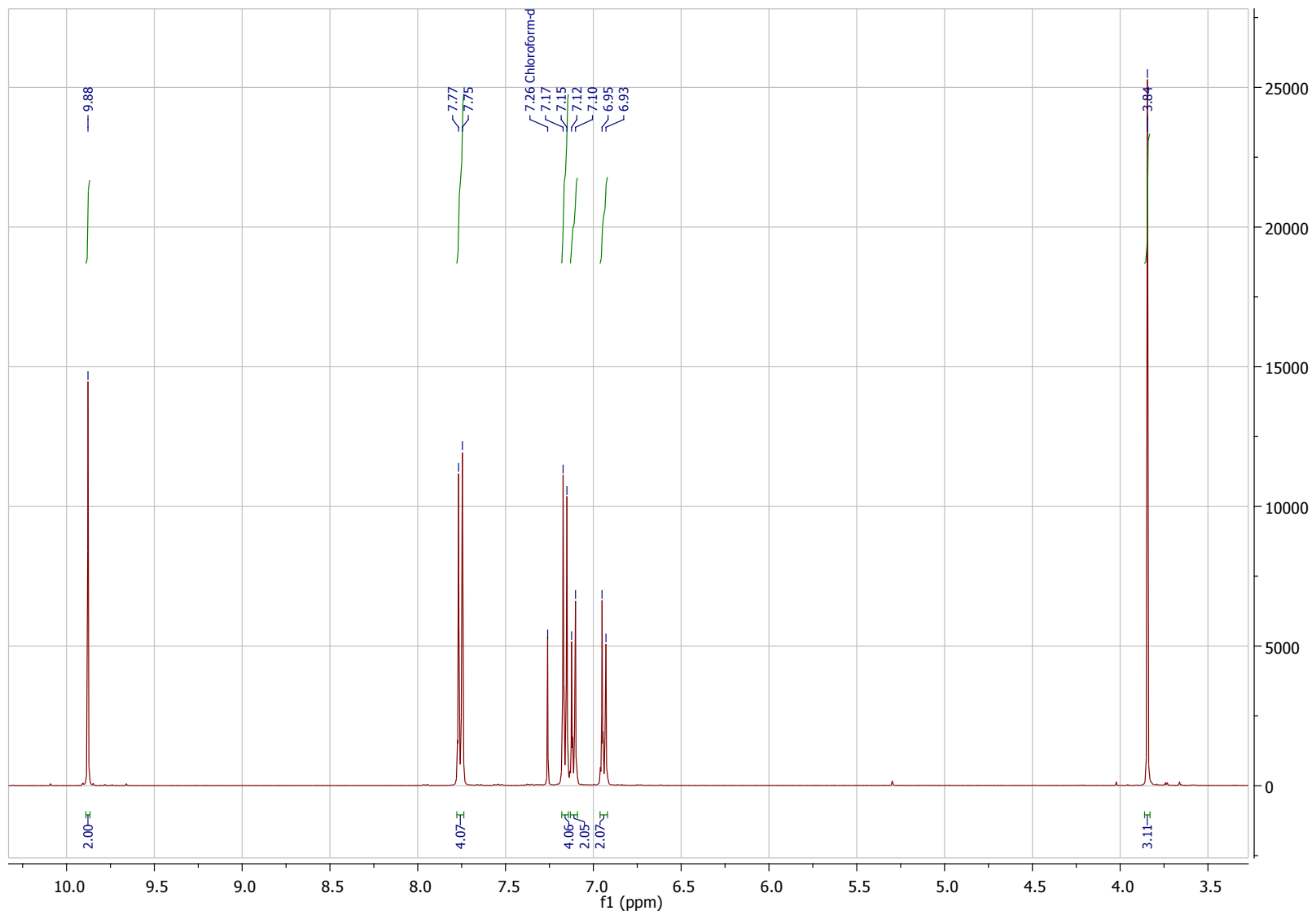


Figure S40 ^1H NMR spectrum of **2**.

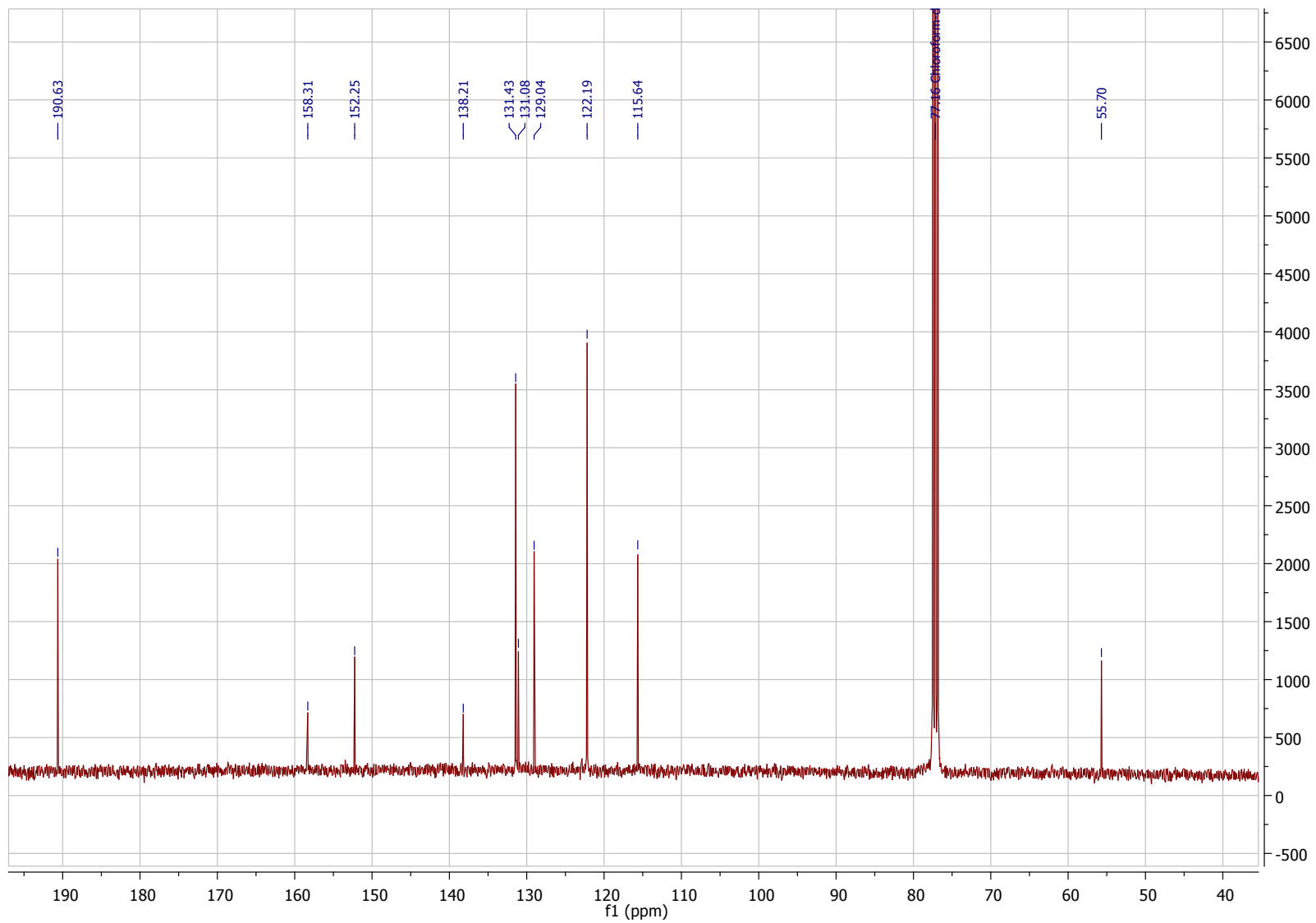


Figure S41. ^{13}C NMR spectrum of **2**.

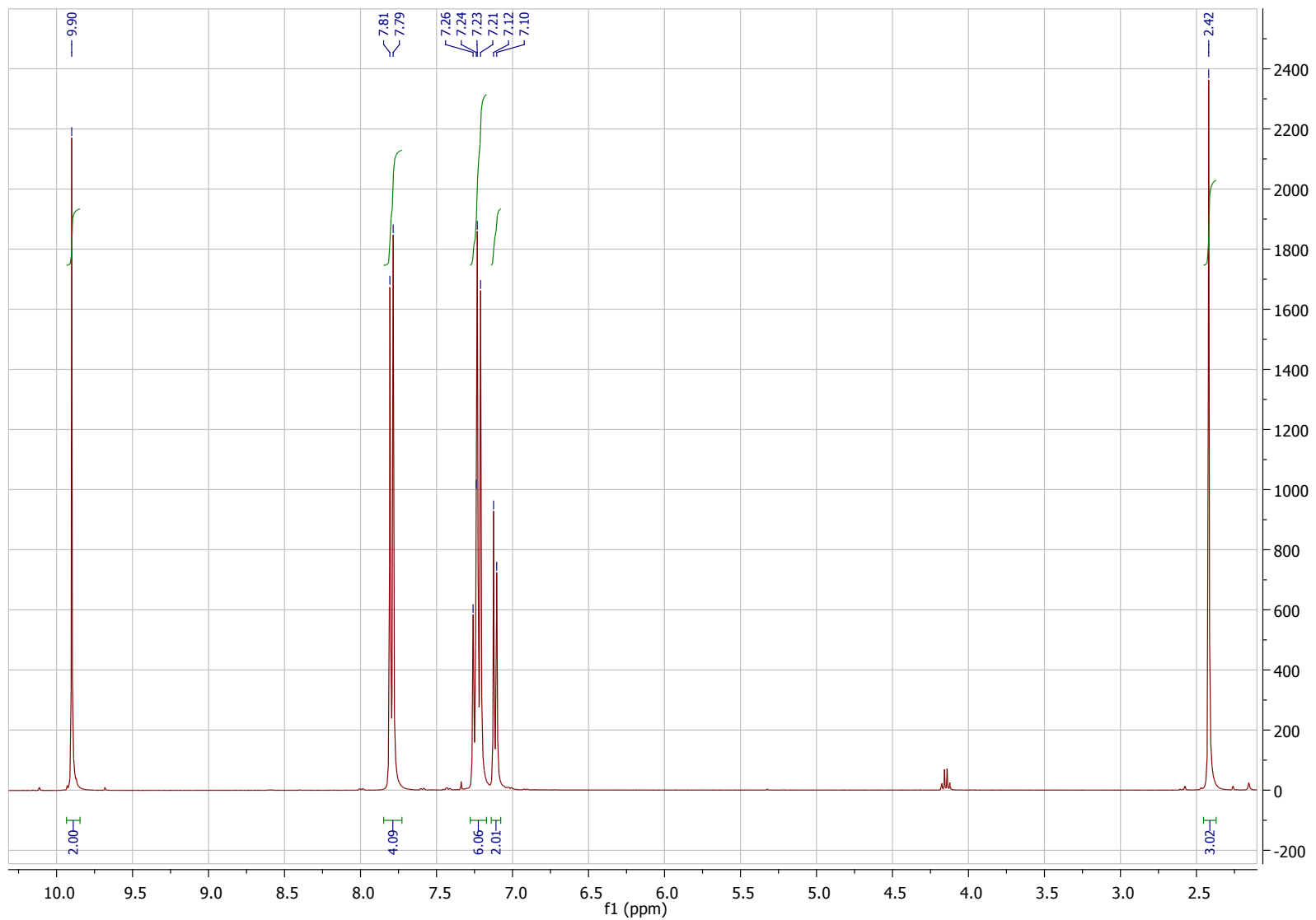


Figure S42. ¹H NMR spectrum of 3.

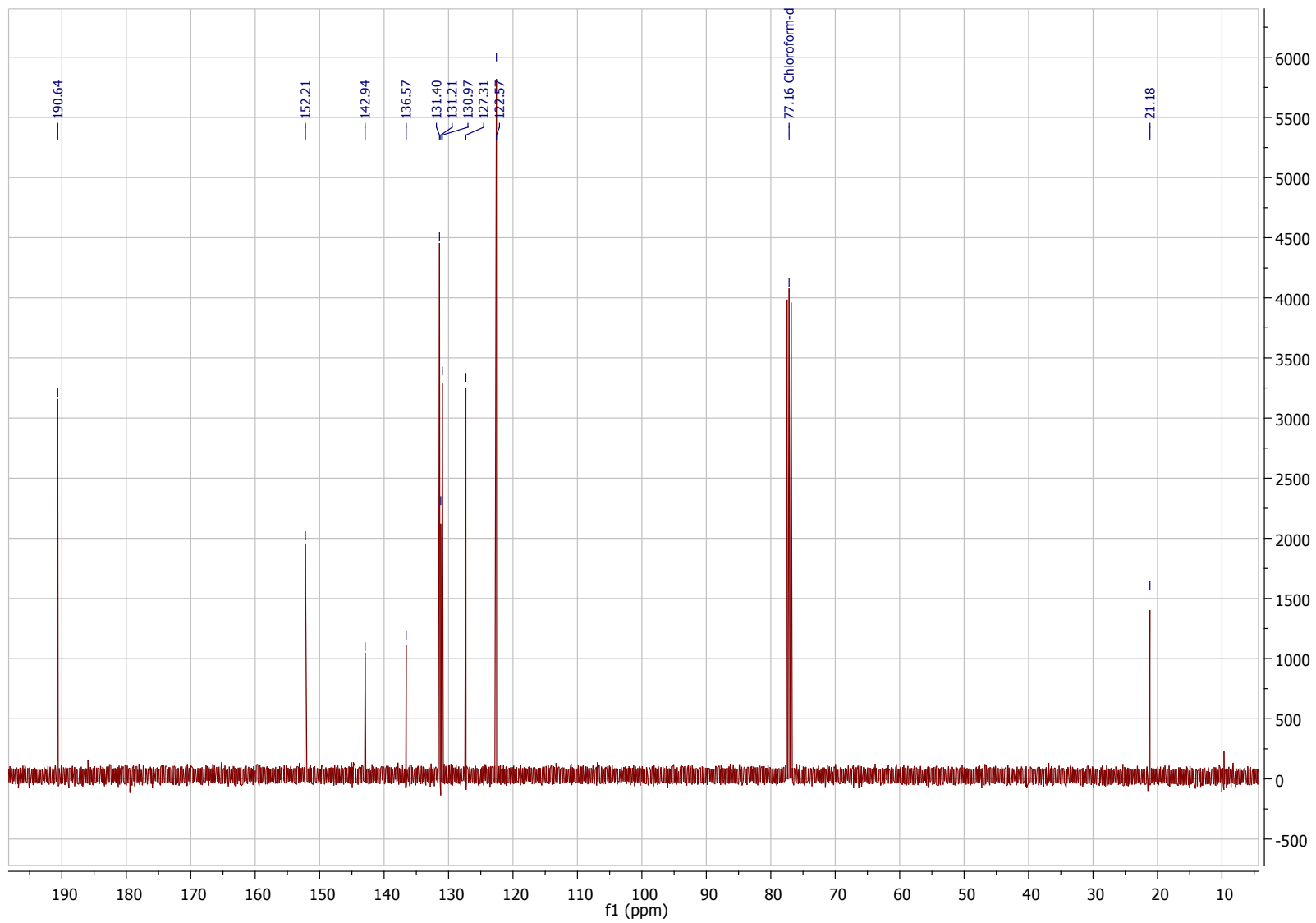


Figure S43 ^{13}C NMR spectrum of 3.