SUPPORTING INFORMATION

A New "ONE-STEP" Thiol Functionalization Procedure for Ni by Self-Assembled Monolayers

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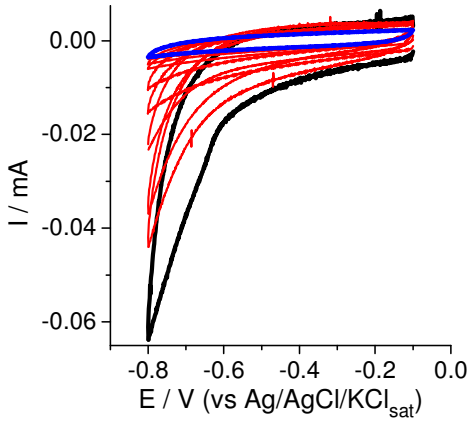
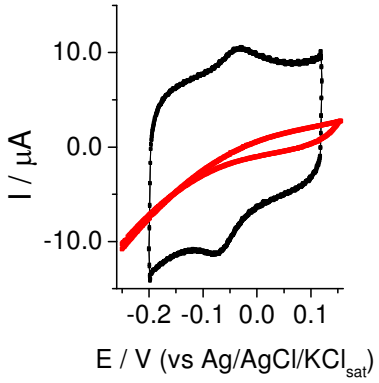


Figure S1. Electrochemical deposition of PCT-L polymer on nickel electrode. Current vs voltage graph, 10 subsequent CV cycles (E_{ini} = -0.1 V, $E_{inversion}$ = -0.8 V), with a scan rate of 0.05 V s^{-1}. Solution composition: 0.5 mM PCT-L containing 0.1 M TBATFB in dry chloroform.



FigureS2. Cyclic voltammograms of Ni/L-cysteine/TBO interface (Black line) and Ni/L-cysteine (red line). The voltammograms were recorded in 10 mM phosphate buffer containing 0.1 M KCl water solution, pH =7. The scan rate used was 0.1 V s^{-1} for each case.

Electrochemistry of Au/L-Cysteine/TBO

The hybrid Au/L-Cysteine/TBO CVs, recorded in the -0.35 to 0.25 V potential ranges, show a quasi-reversible pattern in Figure S2. Reduction/oxidation peaks feature a peak-to-peak potential

separation of about 0.18 V at a scan rate of 0.1 V s^{-1}, showing a CV pattern analogous to the results obtained using the nickel instead of gold.

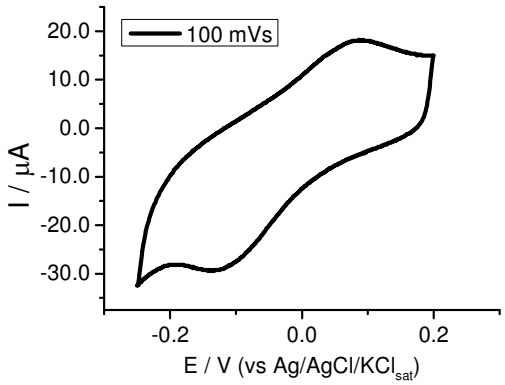


Figure S3. CV of the Au/L-cysteine/TBO interface (working electrode), 10 mM phosphate buffer of 0.1 M KCl water solution, pH =7. The scan rate used was 0.1 V s^{-1}.

XPS *1-Hexadecanethiol*

Table I SI sets out values of atomic concentrations (%), elemental ratios and film thickness collected in the case of four different samples: two different pristine Ni surfaces (Pristine entry) and two different functionalized Ni surfaces (SAM sample1 and 2). Eventually data are shown for measurements carried out at SAM 60° incident X-ray grazing angle. The first four columns show atomic elemental ratios, Ni(3p)/Ni(2p) is the ratio between the Ni(3p) and Ni(2p) intensities, Sox/S and represent the ratios in intensities concerning the sulphur in the oxidized/reduced oxidation states, Oinner/O the oxygen signal recorded at 100 Å depth and on the surface, C/S the atomic carbon to sulfur ratio, d_C the estimated SAM thickness.

Table I SI. ***XPS atomic concentrations (%), elemental ratios and film thickness; see text for entry details.***

	Ni 3p	**O**	**C**	**S**	**Ni(3p)/Ni(2p)**	**S_{ox}/S**	**O_{inner}/O**	**C/S**	**d_C/Å**
Pristine	26.0	29.5	22.9		1.203		0.195		11.4
SAM sample 1	27.6	7.2	46.4	3.9	1.843	0.36	0.09	11.9	26.0
SAM sample 2	29.2	6.6	44.5	3.8	1.840	0.39	0.073	11.9	24.8
SAM 60° grazing angle	23.4	8.65	50.1	4.0	1.679	0.22	0.06	12.6	14.4

POLYMER CHARACTERIZATION[1]

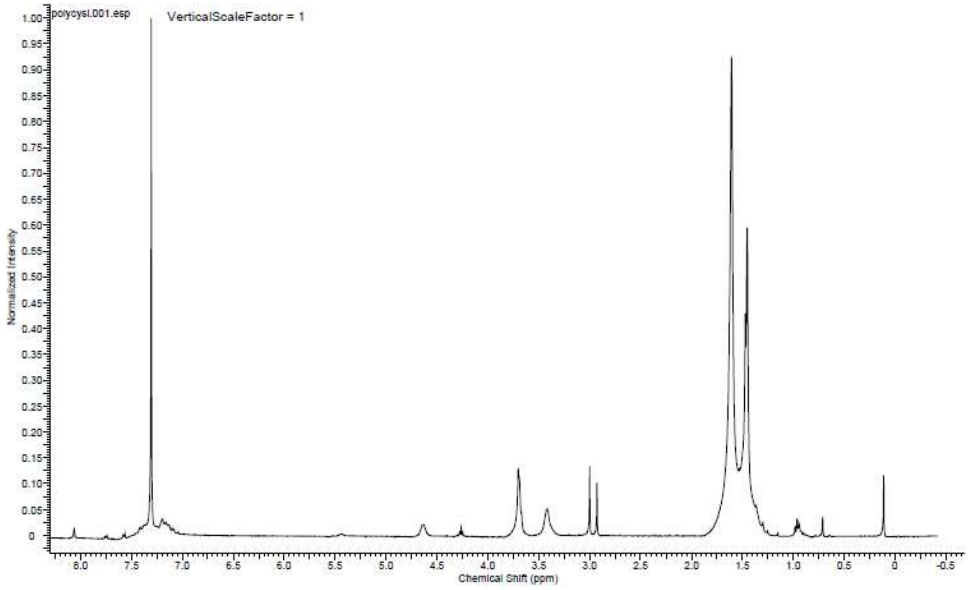


Figure S4. ^{1}H-NMR spectrum of the PCT-L in $CDCl_3$ (400 MHz).

GPC

GPC was carried out on a Hewlett–Packard system equipped with a Hewlett–Packard 5m mixed PL gel column and a diode-array UV detector, using THF as the eluent, with a flow rate of 1.0 mL minK1, at room temperature. The GPC system was calibrated using a series of monodisperse polystyrene standards. The GPC data of PCT-L (Figure S5) shows two major peaks, one with molecular weight (Mw)=24036 and polydispersity index (PDI) = 1.15 and the other with Mw = 4683 and PDI = 1.5.

The first peak of the GPC is attributed to an interchain aggregated form of the polymer, while the second peak is attributed to the free standing chain.

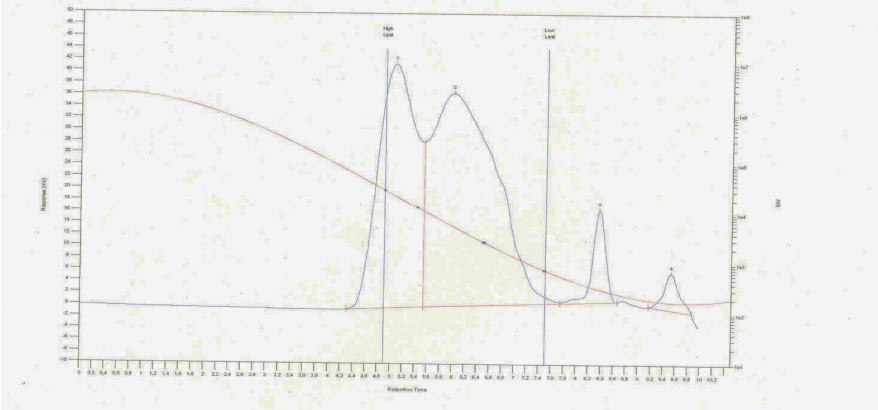


Figure S5. GPC monitoring graph PCT-L polymer.

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	23373	20833	24036	27704	31503	23518	1.15375
2	5782	3122	4683	6312	7587	4441	1.5
3	321	323	327	331	337	326	1.01238
4	0	0	0	0	0	0	0

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	4.30	5.07	5.53	41.727	0	1802.03	100
2	5.53	6.00	7.75	36.5427	0	2666.91	100
3	7.75	8.37	8.67	15.8558	0	230.943	100
4	9.17	9.53	9.87	6.33069	0	109.682	100

UV-Vis and Circular Dichroism Spectra

The UV-Vis and CD spectra of a PCT-L drop casted film on quartz are shown in Figure S6 and S7 respectively.

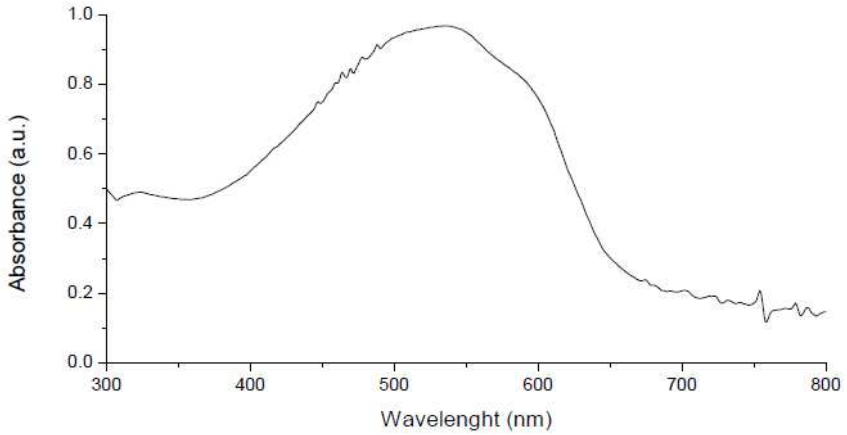


Figure S6. UV-Vis spectrum of PCT-L polymer film on quartz.

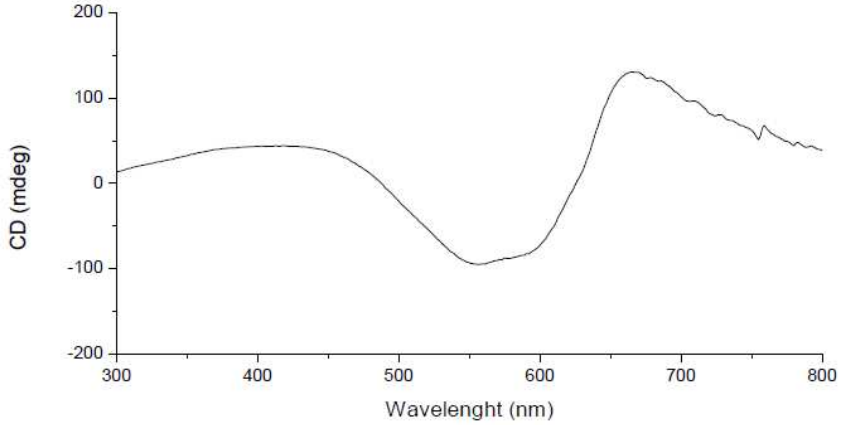


Figure S7. CD spectrum of PCT-L polymer film on quartz.

References

(1) Cagnoli, R.; Lanzi, M.; Mucci, A.; Parenti, F.; Schenetti, L. Polymerization of Cysteine Functionalized Thiophenes. *Polymer* **2005**, *46*, 3588–3596.