

Photochromism and electrochemistry of a dithienylcyclopentene electroactive polymer

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Electronic Supplementary Information

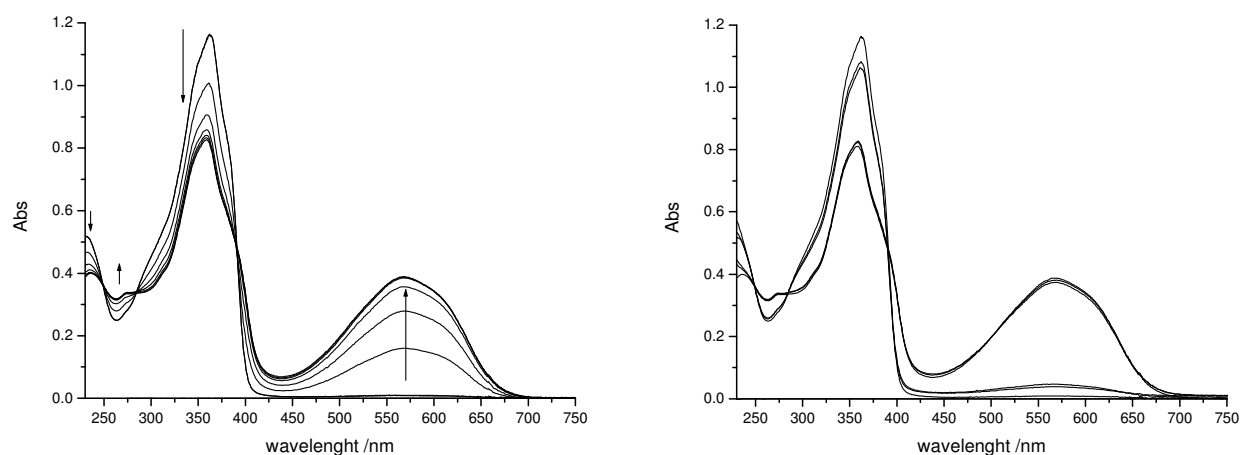


Figure S 1 Left) Conversion of **2o** to **2c** by irradiation at λ_{exc} 365 nm in CH₂Cl₂. Right) sequential irradiation of **2o** at 365 nm to form **2c** followed by irradiation at >450 nm to reform **2o** over three cycles.

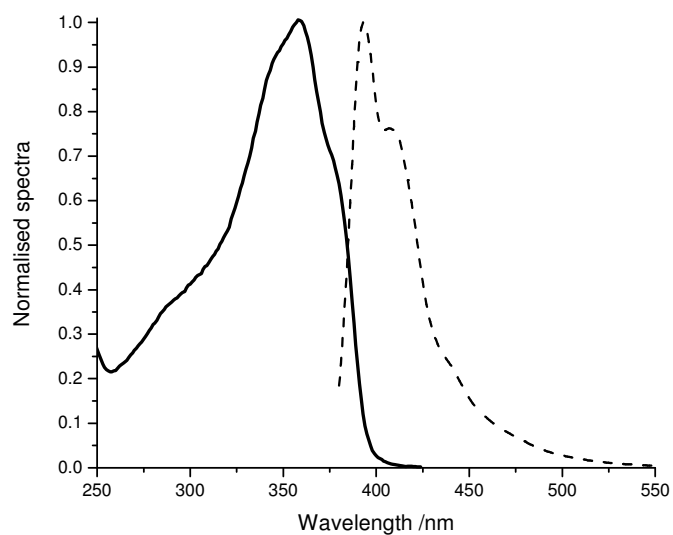


Figure S 2 Absorption and fluorescence spectra of **2o** in CH₂Cl₂. $\lambda_{\text{exc}} = 362 \text{ nm}$

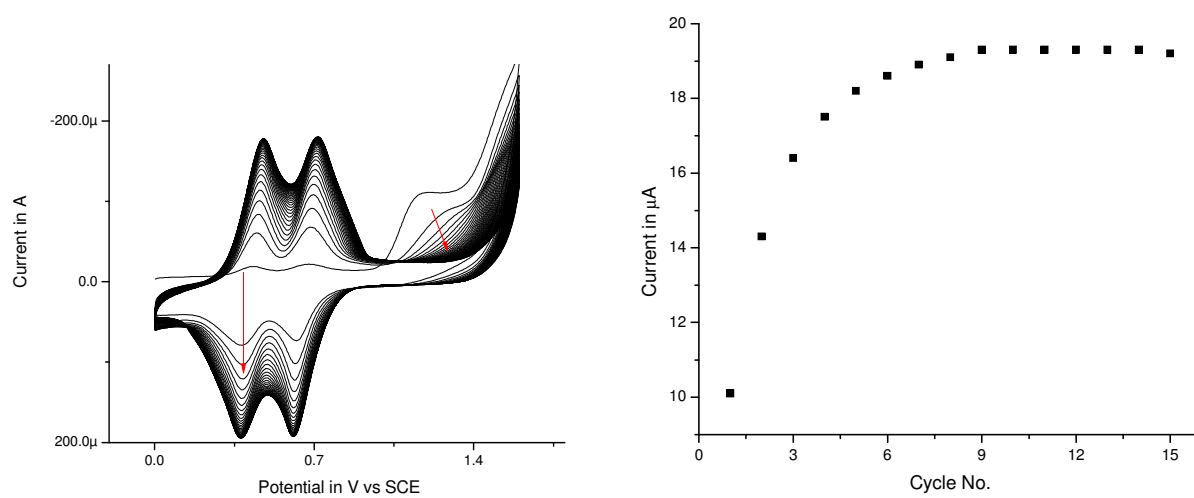


Figure S 3 Top: poly-**2c** electrochemical deposition on an ITO electrode by cyclic voltammetry (Scan rate, 0.5 V s^{-1} during repetitive cycles between 0-1.6 V vs SCE) and bottom: increase in current at 0.3 V vs SCE with number of cycles.

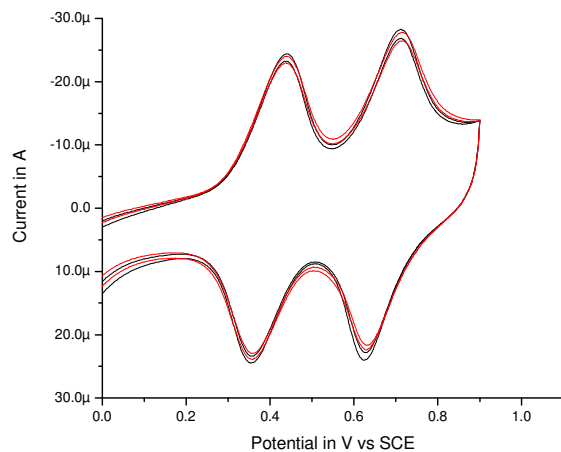


Figure S 4 Cyclic voltammetry (0.5 V s^{-1}) of poly-**2c** deposited on a glassy carbon electrode potentiostatically at 1.55 V for 60 s (black) and 120 s (red).

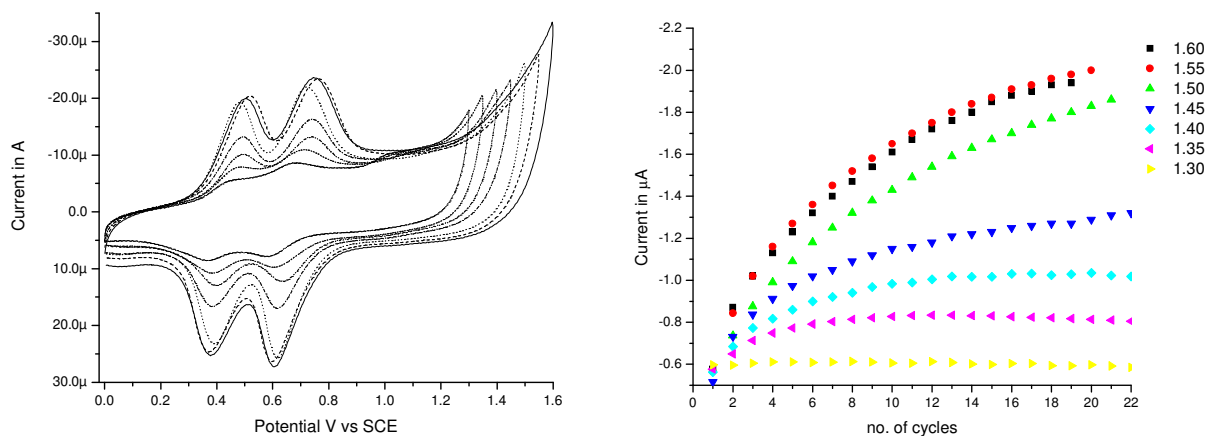


Figure S 5 Electropolymerization of **2o** as a function of switching potential in 0.5 V increments between 1.35 and 1.6 V, at a GC electrode in CH_2Cl_2 (0.1 M TBAClO_4) at 0.75 V s^{-1} . Left: Cyclic voltammograms of the 25th cycle measured for different maximum anodic potentials, right: change in faradic current of $E_{p,a1}$ of poly-**2c**.

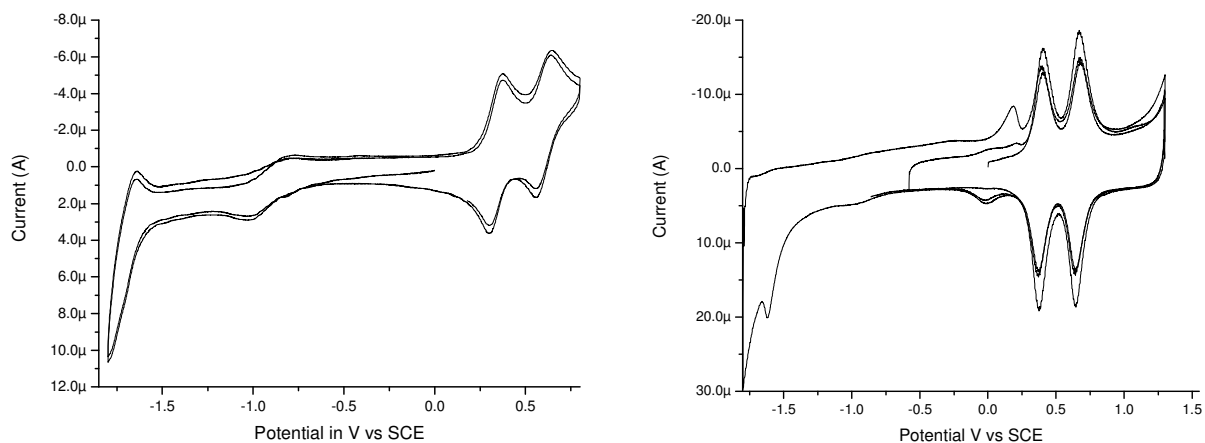


Figure S 6 Cyclic voltammetry of left: **2c** and right: poly-**2c** in CH_2Cl_2 (scan rate 0.5 V s^{-1} , 0.1 M TBAPF_6).

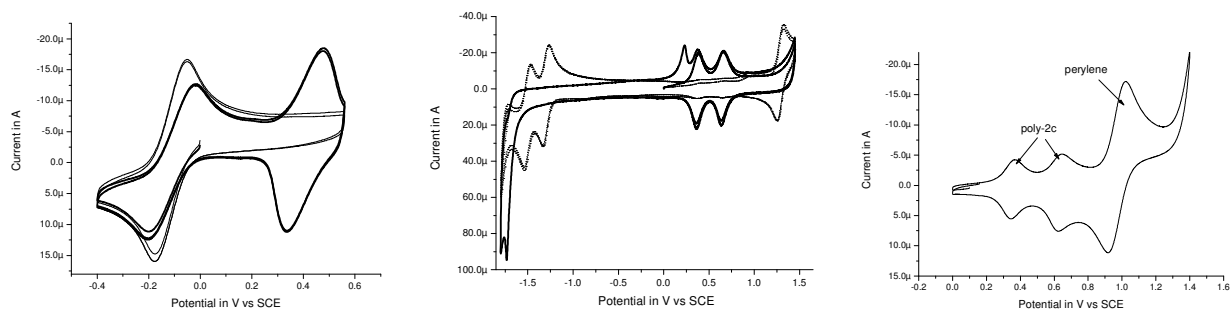


Figure S 7 Left: Clean (thin line) and poly-**2c** modified (thick line) glassy carbon electrode in an electrolyte solution ($\text{CH}_2\text{Cl}_2/\text{TBAClO}_4$) containing dekamethylferrocene. centre: Clean (dotted line) and poly-**2c** modified (solid line) glassy carbon electrode in an electrolyte solution ($\text{CH}_2\text{Cl}_2/\text{TBAClO}_4$) containing $\sim 1 \text{ mM}$ $[\text{Ru}(\text{II})(4,7\text{-diphenyl-}1,10\text{-phenanthroline})_3](\text{PF}_6)_2$ (scan rate 0.5 V s^{-1}). Right: poly-**2c** modified (solid line) glassy carbon electrode in an electrolyte solution ($\text{CH}_2\text{Cl}_2/\text{TBAClO}_4$) containing $\sim 1 \text{ mM}$ perylene (scan rate 0.1 V s^{-1}).

Atomic force microscopy

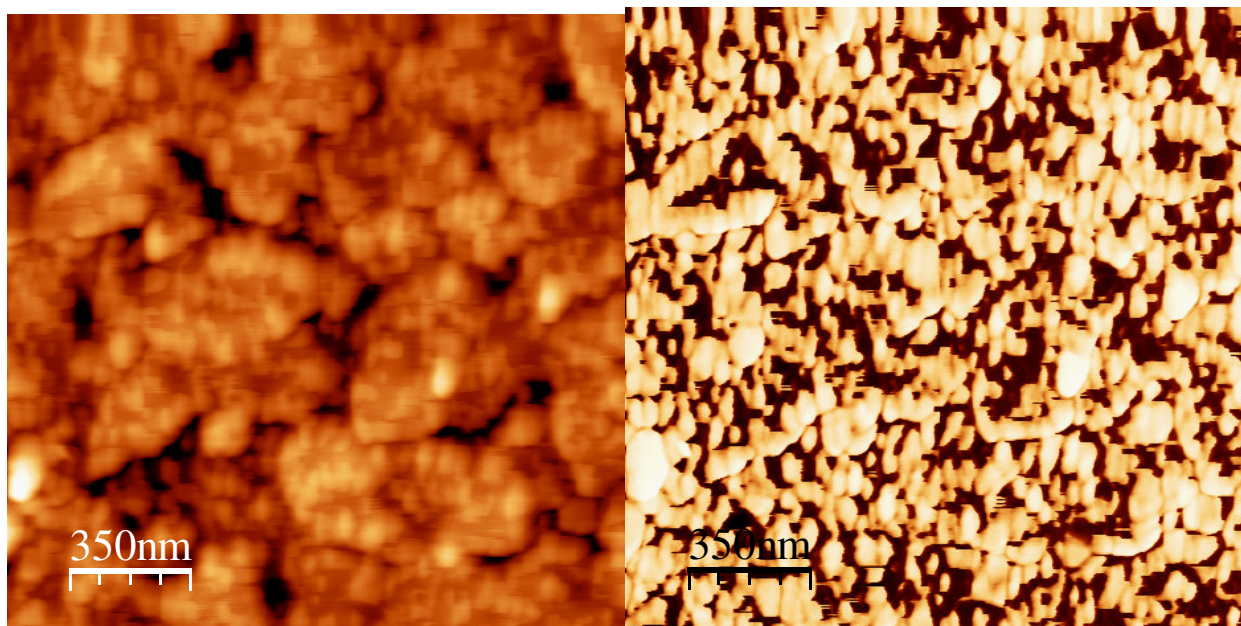


Figure S 8 AFM (intermittent contact mode, in air) of poly-**2c** on ITO. a) $4.5\ \mu\text{m} \times 4.5\ \mu\text{m}$. The RMS roughness of this area is 2.6 nm. b) $1.7\ \mu\text{m} \times 1.7\ \mu\text{m}$.

Photo- and electrochemical switching of Poly-**2c**

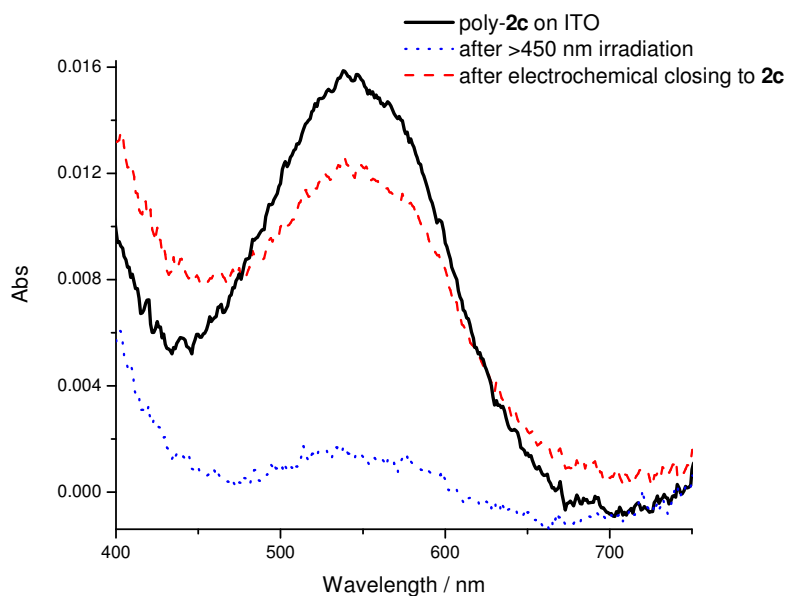


Figure S 9 Visible absorption spectrum of poly-**2c** on an ITO electrode before (solid line) and after (dotted line) irradiation with visible light ($> 420\ \text{nm}$) to form poly-**2o** and after subsequent electrochemical ring closure to reform poly-**2c**.

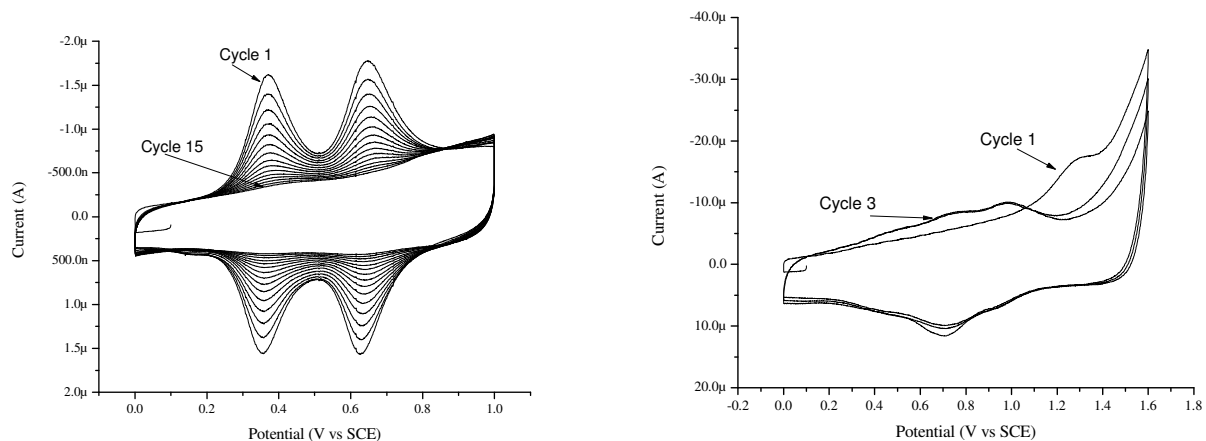


Figure S10 Cyclic voltammetry (a) (15 cycles) of a Poly-2c modified GC electrode in DCM (0.1 M TBAPF₆) at 0.05 V s⁻¹. (b) over a wider potential window after (a). Note that although the electrode remains modified by the polymer cyclic voltammetry at > 0.5 V s⁻¹ leads to irreversible loss of the redox response of poly-2c.

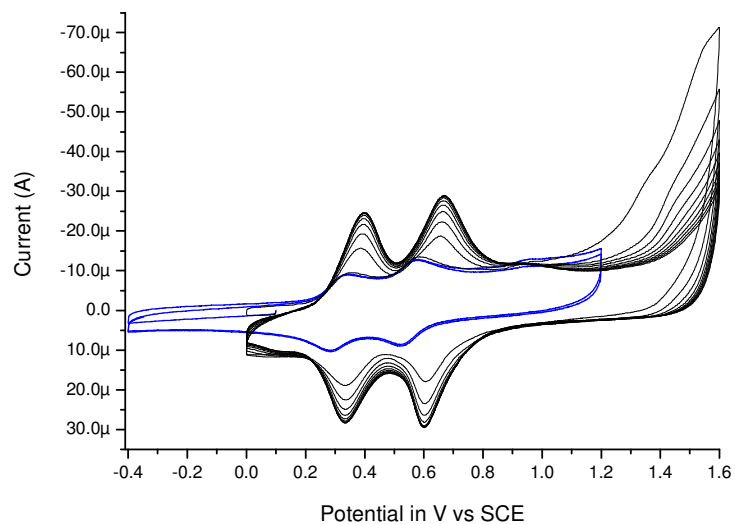


Figure S11 Cyclic voltammetry (a) **2c** in DCM (0.1 M TBAPF₆) at 0.5 V s⁻¹ with a GC working electrode and (b) over a wider potential window showing electropolymerisation.

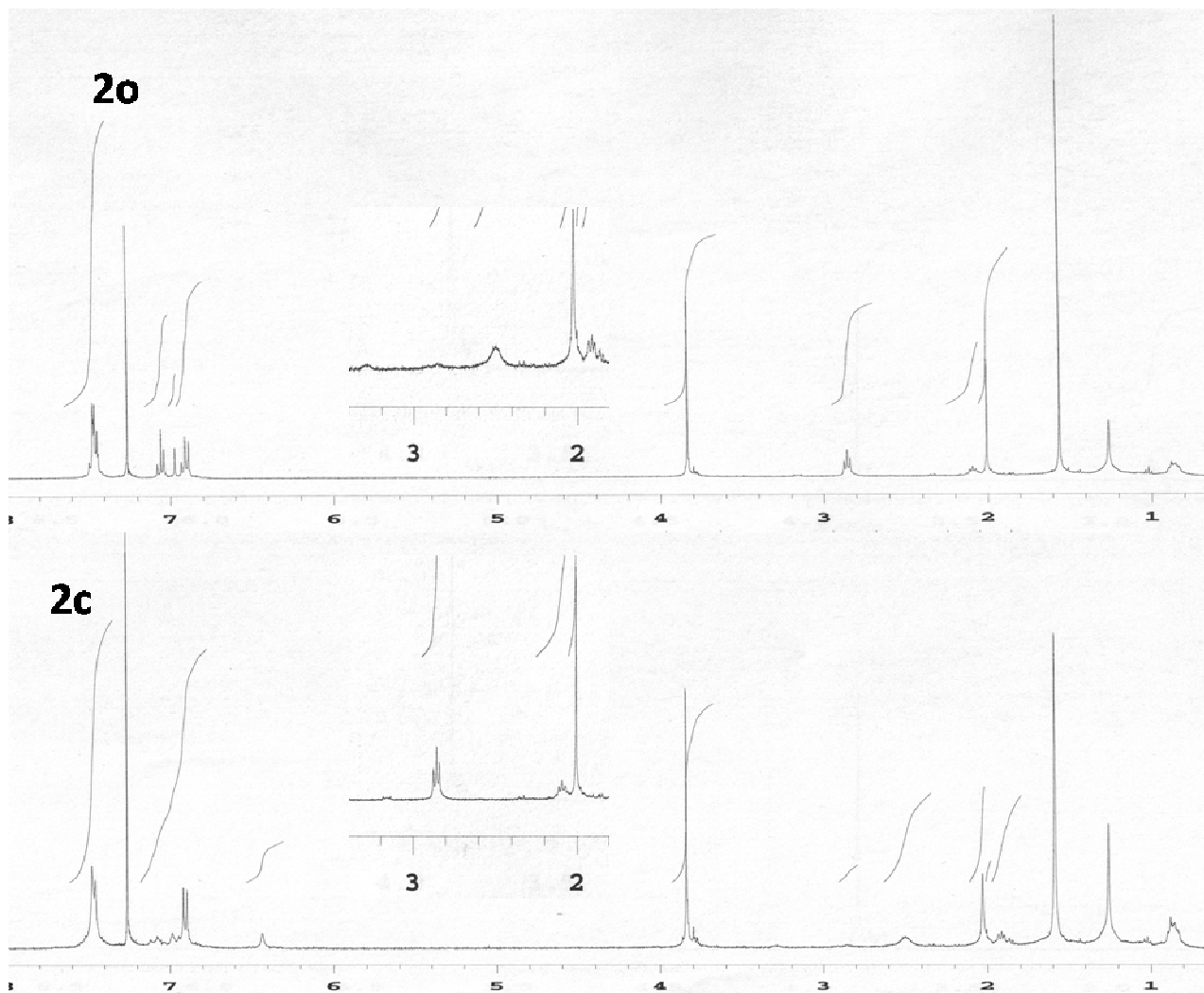


Figure S12 ^1H NMR spectra of open (**2o**) and at PSS (**2c**) at 365 nm in CDCl_3 . The PSS is >90% by integration.