Electrochromic Properties of Spiropyran-Terthiophene adaptive polymers.

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INTRODUCTION

Terthiophene-Spiropyran polymers (**TTT-BSP**) are members of the family of conducting polymers and can be classified as 'adaptive materials' that can be switched between two or more states (each with their own distinct characteristics) using an external stimulus (in our case electrochemical). The photochromic properties of the monomers have also been analyzed and their physico-chemical profile has been studied and described. In this work we have studied the potential applications in the field of sensors actuators.
Switchable or adaptive surfaces made with molecular switches can be externally controlled by switching between an active and passive state, enabling or inhibiting their capability to, for example, bind a target molecule (for example Cu^{2+}, Co^{2+}, small amino acids and, for some particular spiropyran derivatives, also DNA). The materials here presented can show different physical states directly related with specific chromism. Particular interesting is the analysis of the conduction band generated and studied with spectroelectrochemistry experiments: the behavior is unique and repeatable.

PHOTOCHROMIC PROPERTIES OF THE MONOMERS

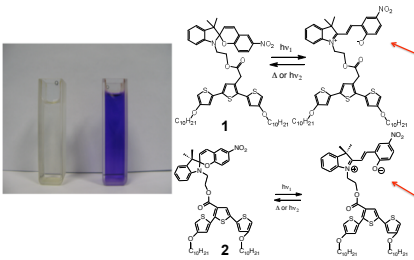

Figure 1a: Structures of the two monomers analysed from the photochemical point of view. In the picture it is possible to appreciate the conversion of the chromophore into its active **MC** zwitterionic isomer, characterized by intense purple coloration.

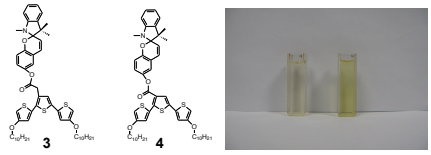

Figure 1a: Structures of the two monomers containing **BSPOH** chromophore, **BSPOHacetoTTh** (**3**) and **BSPOHcarboxyTTh** (**4**). In the picture it is possible to appreciate the conversion of the chromophore into its active **MC** zwitterionic isomer, characterized by intense yellow coloration.

The **kinetics** of closing of the ring in derivatives containing $BSPNO_2$ chromophore was studied. The samples were irradiated with UV-vis light at 254nm to induce ring opening and merocyanine (**MC**) formation. Upon removal of the light source the thermal relaxation first order decay curves were then examined using the Arrhenius equation, **A**. The rates of thermal relaxation were recorded in a range of temperatures included between 298 K and 308 K. The thermodynamic parameters and the dependence of the rate of thermal relaxation with temperature were investigated using eqs **B** and **C** to find the activation energy (**Ea**), entropy of activation (**ΔS≠**), enthalpy of activation (**ΔH≠**) and Gibbs energy of activation (**ΔG≠**). An alternative form of the Eyring equation (eq **D**) was also used to derive the equilibrium of the activated complex of the transition state theory.

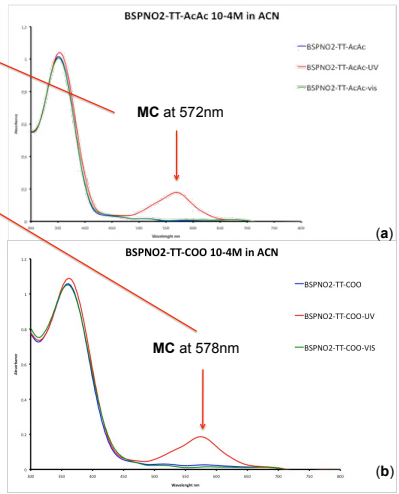

Figure 2: Spectra of two of the four monomers synthesized and characterized: (**a**) **$BSPNO_2$-aceto-terthiophene;** (**b**) **$BSPNO_2$carboxyTTh**. They are composed by two functional units: spiropyran (**BSP**), the chromophore, and terthiophene (**TTh**), the conducting backbone. They exhibit a nitro-**BSP** moiety. At 572nm (**a**) and at 578nm (**b**) can be detected the presence of correspondent **MC**.

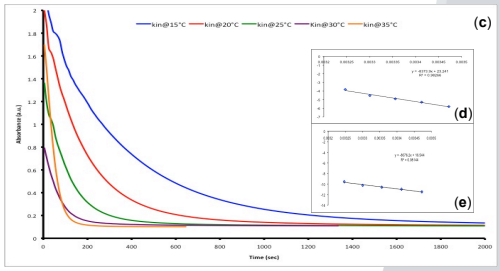

Figure 3a: (**c**) Kinetics of conversion from **MC** to **BSP** of **$BSPNO_2$-aceto-terthiophene** measured from 15°C to 35°C. (**d**) Arrhenius plot. (**e**) Eyring plot.

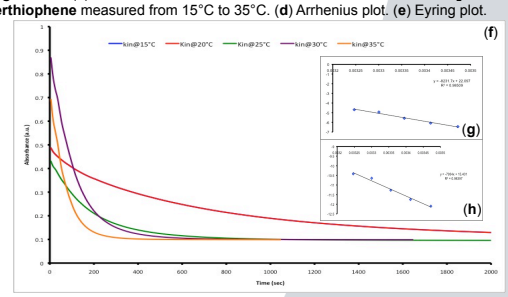

Figure 3b: (**f**) Kinetics of conversion from **MC** to **BSP** of **$BSPNO_2$carboxyTTh** measured from 15°C to 35°C. (**g**) Arrhenius plot. (**h**) Eyring plot.

			Arrhenius		Eyring		
	λ max (MC nm)	k (at 298K) x $10^{-2}/s^{-1}$	Ea (KJ • mol^{-1})	A	ΔS≠ (J • K^{-1} • mol^{-1})	ΔH (KJ • mol^{-1})	ΔG_{25} (KJ • mol^{-1})
$BSPNO_2$	567	0.0058	90,42	$2,19 \times 10^{13}$	-57,12	69,30	86,03
$BSPNO_2$-aceto-terthiophene	572	0.0107	69,62	$1,24 \times 10^{10}$	-99,07	54,74	83,77
$BSPNO_2$-carboxy-terthiophene	578	0.0072	68,44	$3,95 \times 10^{9}$	-113.46	52,14	85,39

$$\ln \frac{[A]}{[A_0]} = -kt \quad \text{A}$$

$$\ln k = E_a/RT + \ln A \quad \text{B}$$

$$\ln(k/T) = -\Delta H^{\ddagger}/RT + \ln(k_B/h) + \Delta S^{\ddagger}/R \quad \text{C}$$

$$k = (k_B T/h)K^{\ddagger} \quad \text{D}$$

Figure 4: Values resulting from Arrhenius and Eyring's plot. The higher negative Entropy for the **carboxy** derivative indicates faster conversion from its **MC** to the steady state. [1]Thermal relaxation rate constant calculated from plotting $\ln(A_0/A_t)$ *vs.* time where *k* = slope.

ELECTROCHROMIC PROPERTIES OF THE POLYMERS

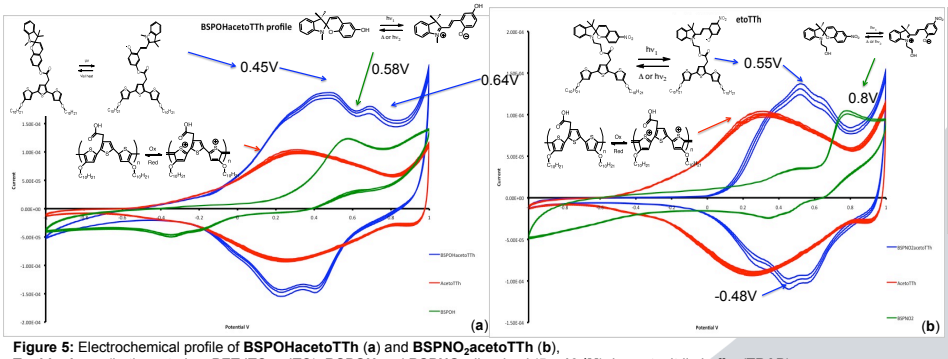

Figure 5: Electrochemical profile of **BSPOHacetoTTh** (**a**) and **$BSPNO_2$acetoTTh** (**b**), **Terthiophene** (both coated on PET-ITO or ITO), **BSPOH** and **$BSPNO_2$** dissolved (**5 x 10^{-4}M**) in acetonitrile buffer (**TBAP**).

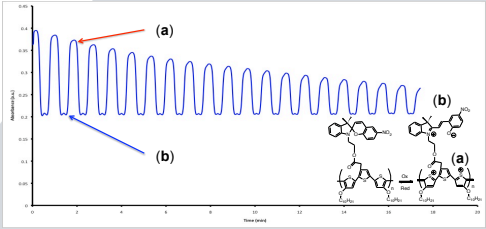

Figure 6: Live Kinetics acquirement of **$BSPNO_2$carboxyTTh** while excited by cyclic Voltammetry. Small peaks generated by the chromophore (**b**), whilst the higher are due to the backbone (**a**).

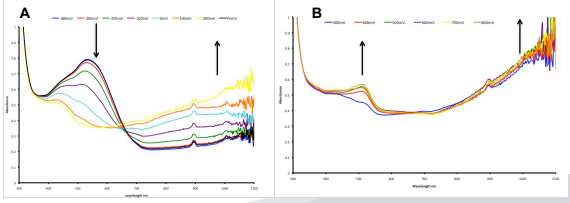

Figure 7: UV-*vis* Spectroelectrochemistry of **BSPOHacetoterthiophene**. **(A)** spectra obtained while increasing electrode potential from -0.4V to 0.2V. **(B)** spectra obtained while increasing electrode potential from 0.3V to 0.8V. E vs. Ag wire/ [V].

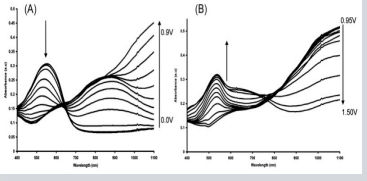

Figure 8: UV-*vis* Spectroelectrochemistry of **$BSPNO_2$acetoTTh**. **(A)** spectra obtained while increasing electrode potential from 0.0V to 0.9V. **(B)** spectra obtained while increasing electrode potential from 0.95V to 1.50V. E vs. Ag wire/ [V].

CONCLUSIONS

An important progress in the field of conducting polymers was achieved with this project: the full profile, electrochemical and photochemical, of a new family of adaptive molecules was described. Several potential applications are under accurate analysis especially in the field of optoelectronics and energy harvesting systems. An important possible development could be found in the field of chemical and biological sensors, thanks to the specific properties of benzospiropyran functional unit.

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