# PHOTO/ELECTRO – RESPONSIVE HYBRID MATERIALS BASED ON SPIROPYRAN DYES AND TERTHIOPHENE

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## TERTHIOPHENE-SPIROPYRAN POLYMERS

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. These new materials showed particular propensity to functionalize surfaces especially via electrochemical deposition. In this work have been studied the potential properties and the possible developments, in particular in the field of sensors and new materials capable of conductivity, sector in wide expansion and subject of high and deep interest.

## TARGETS AND GUIDELINES

A fundamental and ambitious target in the sector of the adaptative materials is the direct control of the molecular properties that constitute the structure. Switchable or adaptative surfaces can be externally controlled by changing the state of convertible molecules between an active or passive state, enabling or inhibiting their capability to, for example, bind a target entity. Organic photo-electrochromic compounds are particularly interesting from this point of view, with their highly related physical and chromatic properties: the materials here presented can show different physical states directly associated with specific chromism.

The main target consists in the isolation and characterization of a new family of active compounds able to exhibit photochromic and electrochromic properties comparable with sensible and detectable surface control. A consistent progress in this direction is presented in this work, with the chemical synthesis of the terthiophene-based monomers, their electrochemical polymerization and the activity tests performed to validate their characteristics.

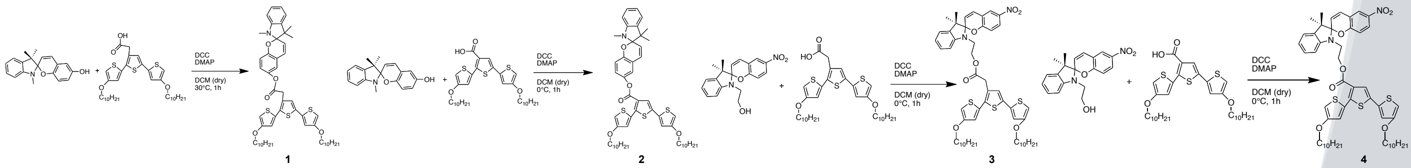



**Figure 1**: Synthesis pathways leading to the isolation of the first two monomers belonging to this family of moieties. The process was developed and tested by the authors and afforded 80% yields average. The new materials were characterized by mass spectroscopy, UV-*vis*, $^1$H, $^{13}$C and 2D NMR experiments. (**1**) BSP-aceto-terthiophene; (**2**) BSP-carboxy-terthiophene; (**3**) BSPNO$_2$-aceto-terthiophene; (**4**) BSPNO$_2$-carboxy-tertthiophene

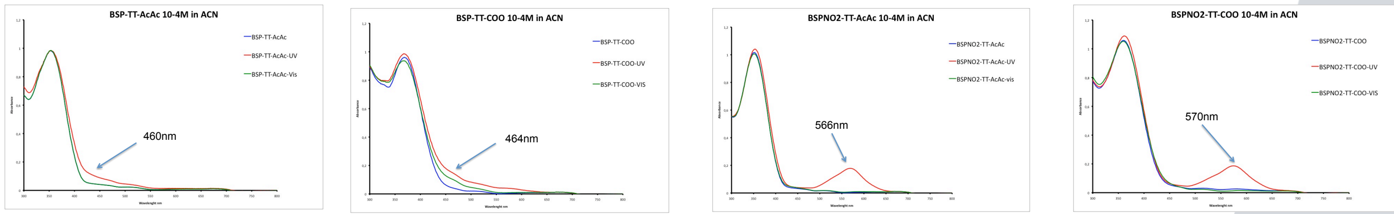



**Figure 2**: UV-*vis* tests on the four monomers were conducted on solutions in ACN at the concentration of $10^{-4}$M. The concentration of the ligands were $10^{-3}$M. The analysis show the potential skill of the new compounds in terms of complexant agents. Hybryd monomers retain the ability to switch optical properties in response to changes in the pH of the solution. Highlighted the wavelengths of **MC** formation.

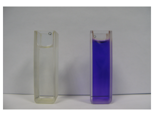


**Figure 3**: BSPNO$_2$–aceto-terthiophene monomer solution before and after exposure to 254nm UV-*vis* light source. The solution switched from colourless to intense purple.

**Figure 4**: BSP – aceto - terthiophene monomer solution before and after exposure to 254nm UV-*vis* light source. The solution switched from colourless to intense yellow.

The kinetics of BSPNO$_2$ derivatives was also studied. The samples were irradiated with UV-vis light 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, ***1***. 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 ***2*** and ***3*** 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 ***4***) was also used to derive the equilibrium of the activated complex of the transition state theory.

$$\ln \frac{[A]}{[A_0]} = -kt \qquad \textbf{1}$$

$$\ln k = E_a/RT + \ln A \qquad \textbf{2}$$

$$\ln(k/T) = -\Delta H^{\ddagger}/RT + \ln(k_B/h) + \Delta S^{\ddagger}/R \qquad \textbf{3}$$

$$k = (k_B T/h)K^{\ddagger} \qquad \textbf{4}$$

| | λ max (MC nm) | Arrhenius: Ea (KJ • mol$^{-1}$) | Arrhenius: A | Eyring: ΔS (J • K$^{-1}$ • mol$^{-1}$) | Eyring: ΔH (KJ • mol$^{-1}$) | ΔG$_{25}$ (KJ • mol$^{-1}$) |
|---|---|---|---|---|---|---|
| BSPNO$_2$ | 567 | 90,42 | 2,19 x $10^{13}$ | -57,12 | 69,30 | 86,03 |
| BSPNO$_2$-aceto-terthiophene | 572 | 69,62 | 1,24 x $10^{10}$ | -99,07 | 54,74 | 83,77 |
| BSPNO$_2$-carboxy-terthiophene | 570 | 68,44 | 3,95 x $10^{9}$ | -113.46 | 52,14 | 85,39 |

## ELECTROCHEMICAL STUDY OF THE MONOMER AND ELECTROPOLYMERIZATION ON ITO AND PET-ITO.

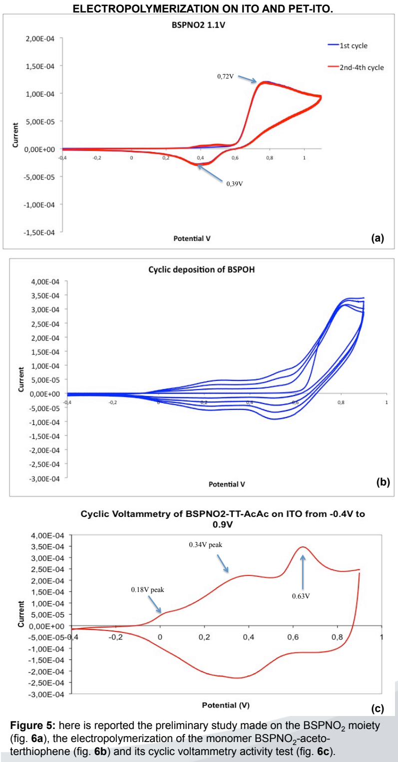
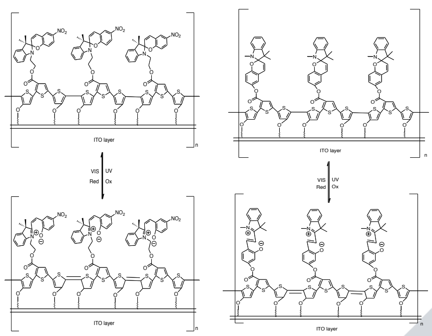



**Figure 5:** here is reported the preliminary study made on the BSPNO$_2$ moiety (fig. **6a**), the electropolymerization of the monomer BSPNO$_2$-aceto-terthiophene (fig. **6b**) and its cyclic voltammetry activity test (fig. **6c**).

## RESULTING POLYMER ON THE COATED SURFACE




## AN IMPORTANT STEP: THE CONTROL OF THE SURFACE WITH EXTERNAL STIMULUS.

This activity has been proved with a study performed on the contact angle: it has been demonstrated that the simple variation of the potential generates a redistribution of the charges on the surface of the material, with a consequent variation of the completive hydrophilicity. To support these observations, AFM images were taken: they showed appreciable differences of conformation.

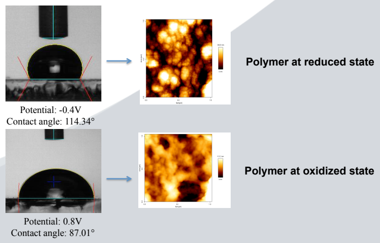



**Figure 6:** Contact angle images and AFM measurements on the BSP-aceto-terthiophene polymer, grown on ITO conducting layer (from monomer **1**).

## ACTIVITY TESTS: SPECTROELECTROCHEMISTRY

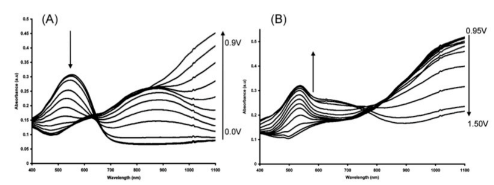



**Figure 7.** UV-vis Spectroelectrochemistry of poly(TT-BSP1). (A) spectra obtained while increasing electrode potential from 0.0V (reduced state, 557 nm) to 0.9V (oxidised state, 1100 nm) of polymer. (B) spectra obtained while increasing electrode potential from 0.95V (oxidised state, 1100 nm) to 1.50V (Merocyanine isomer, 540 nm) . E vs. Ag wire/ [V].

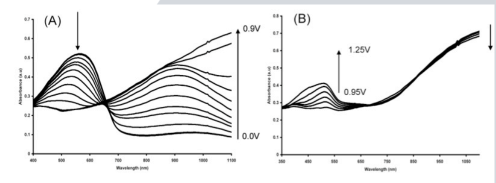



**Figure 8.** UV-vis Spectroelectrochemistry of poly(TT-BSP2). (A) spectra obtained while increasing electrode potential from 0.0V (reduced state, 565 nm) to 0.9V (oxidised state, 1100 nm) of polymer. (B) spectra obtained while increasing electrode potential from 0.95V (oxidised state, 1100 nm) to 1.25V (Merocyanine isomer, 512 nm). E vs. Ag wire/ [V].

## CONCLUSION

Spiropyran has well known optical properties, easily controllable with photonic stimuli. A similar concept is in the background qualities of terthiophene polymers, with a different control coming from an electronic source. In this work a new family of adaptative materials has been synthesized and early characterized. The study exhibits the reliable properties of the new materials and the possibility to control the surface structural conformation with an external source.

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