

Electro- and Photo- chromism of Hybrid Conducting 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 (photonic or electrochemical). These new materials showed particular propensity to functionalize surfaces especially via electrochemical deposition. 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 changing their configuration between an active or 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 spirocyanine derivatives, also DNA). Organic photo-electrochromic compounds are particularly interesting from this point of view, with their highly related physical and strong chromatic properties: 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. The important achievement of this work consists in the isolation and full characterization of a new family of stimuli responsive materials able to exhibit photochromic and electrochromic properties comparable with sensible and detectable surface control (observed with AFM and SEM technology).

EXPERIMENTAL SECTION

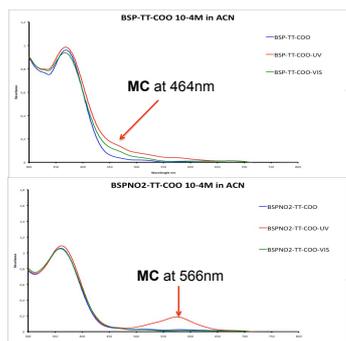


Figure 2: UV-vis analysis of the two monomers bearing the carboxylate-spacer: remarkable differences between hydroxyl- and nitro-BSP.

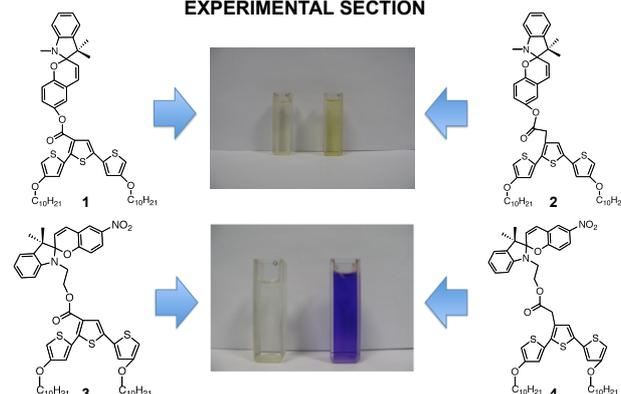


Figure 1: The four monomers synthesized and characterized: (1) BSP-carboxy-terthiophene; (2) BSP-aceto-terthiophene; (3) BSPNO₂-carboxy-terthiophene; (4) BSPNO₂-aceto-terthiophene. They are composed by two functional units: spiropran (BSP), the chromophore, and terthiophene (TTh), the conducting backbone. 1 and 2 carry on their structure an hydroxyl-BSP derivative, while 3 and 4 exhibit a nitro-BSP moiety. They also differ each other for the length of the linker: 2 and 4 have a methyl-bridge between the ester and BSP.

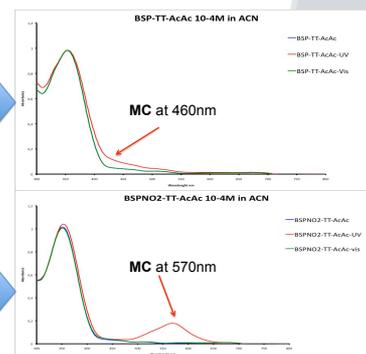


Figure 3: UV-vis characterization of the monomers exhibiting the acetate-spacer: evidence of formation of Merocyanine (MC) isomer only for nitro-BSP monomer.

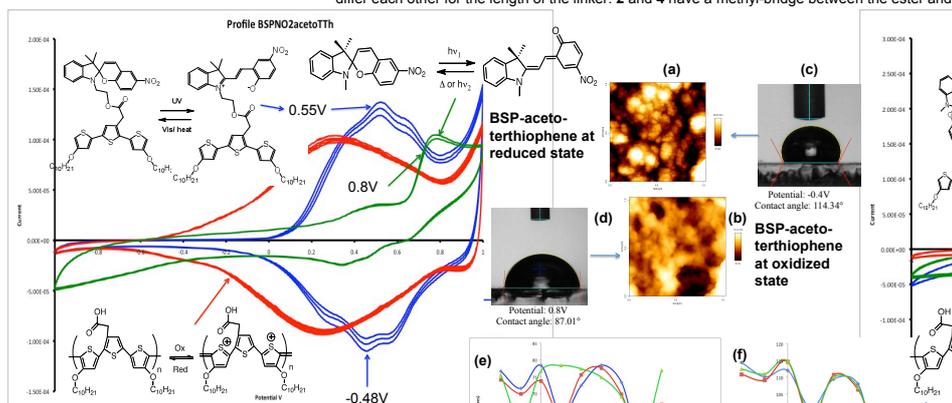


Figure 4: Electrochemical analysis of the three species involved in the study: terthiophene and the hybrid BSPNO₂acetoTTh have been previously electropolymerized on PET-ITO and ITO and then examined BSPNO₂ was dissolved ($5 \times 10^{-4}\text{M}$) in acetonitrile buffer (TBAP). The results obtained allow to establish the electrochemical contribution of each component in the hybrid system.

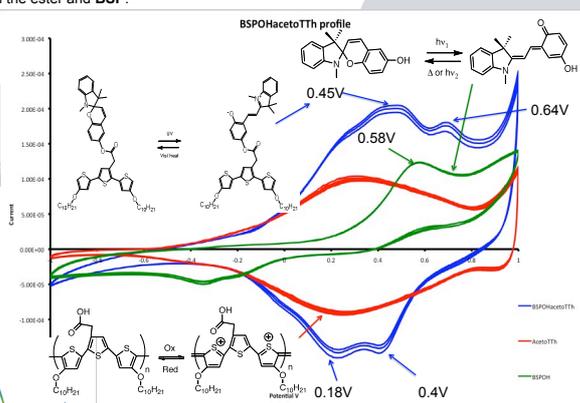


Figure 6: Electrochemical profile of BSP-aceto-terthiophene, Terthiophene (both coated on PET-ITO or ITO) and BSPOH dissolved ($5 \times 10^{-4}\text{M}$) in acetonitrile buffer (TBAP).

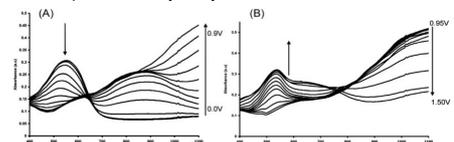


Figure 7: UV-vis Spectroelectrochemistry of BSPNO₂acetoTTh. (A) spectra obtained while increasing electrode potential from 0.0V to 0.9V. (B) spectra obtained while increasing electrode potential from 0.95V to 1.50V. E vs. Ag wire/ [V].

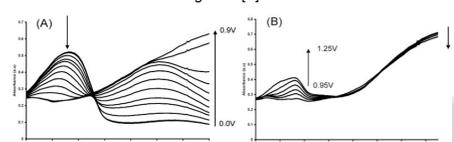


Figure 8: UV-vis Spectroelectrochemistry of BSP-aceto-terthiophene. (A) spectra obtained while increasing electrode potential from 0.0V to 0.9V. (B) spectra obtained while increasing electrode potential from 0.95V to 1.25V. E vs. Ag wire/ [V].

GAINING THE CONTROL OF THE SURFACE WITH EXTERNAL STIMULI. Figure 5: The activity has been proved with a study performed on the contact angle (c) and (d) on both the families: 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 complete hydrophilicity. To support these observations, AFM images (a) and (b) were taken: they showed appreciable differences of conformation at different potentials for both polymers. (e) and (f) show the progression of the contact angle measurements on the three different layers tested. SEM pictures were also acquired (g) BSPNO₂acetoTTh and (h) BSP-aceto-terthiophene.

CONCLUSIONS

The properties of this new hybrid molecules belonging to the family of conducting polymers were described. With the full spectrochemical and electrochemical characterization. Particularly interesting results were obtained with AFM microscopy, technique that showed modification of the molecular conformation of the polymers at different potentials. A further confirmation was observed with the contact angle, with a direct correlation between hydrophilicity/hydrophobicity, potential applied and surface conformation.

REFERENCES

- S. Gambhir, K. Wagner, D. L. Officer, *Towards functionalised terthiophene-based polymers*. Synthetic Metals **154**, 2005: 117-120.
- S. Hammes-Schiffer, A. V.Soudakov. *Proton-coupled electron transfer in solution, Proteins and electrochemistry*. Journal of Physical Chemistry B, 2008, 14108-14123.
- A. Radu, S. Scarmagnani, R. Byrne, C. Slater, K. T. Lau, D. Diamond, *Photonic modulation of surface properties: a novel concept in chemical sensing*. Journal of Physics D: Applied Physics, **40**, 2007, 7238-7244.
- H. Mehenni, L. H. Dao, *Synthesis and characterization of novel conducting homopolymers based on β -styryl terthiophene*. Canadian Journal of Chemistry, **86**, 2008, 1010-1018.

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