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On/Off Photoswitching of the Electropolymerizability of Terthiophenes

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Conductive polymers are a cornerstone of the development of organic electronic devices, such as field effect transistors,¹ electrochromic windows and displays,² actuators,³ and solar cells.⁴ The flexibility of these synthetic polymer systems offered in terms of physical characteristics and processibility sets them apart from nonmolecular semiconducting and conducting materials.⁵

The functionality of both monomers and polymers can be extended by introducing responsive units that can be switched reversibly between two states using external stimuli, e.g., $h\nu$, Δ , or redox switching. For example, the introduction of a photocontrolled switching unit⁶ into a monomer to control its polymerizability could offer considerable opportunities in device fabrication. In this regard the dithienyl cyclopentenes pioneered by Irie and co-workers (Figure 1)⁷ have proven to be excellent platforms on which to build functional molecular based systems, allowing for reversible control of properties as diverse as fluorescence,⁸ redox chemistry,⁹ self-assembly,¹⁰ and molecular conductivity.¹¹ In addition, their high fatigue resistance and thermal stability provide for robust materials with excellent photochromic properties.

Here, we report the ability to switch off and on the electropolymerizability of the monomer **1F** with UV and visible light, respectively (Scheme 1). The design of the present system is based on the combination of alkene bridged terthiophene units and the well-known photoswitchable dithienylethene photochromic unit (Figure 1). The bithiophene substituted photochromic dithienyl perfluorocyclopentene (**1F**) can be switched reversibly by UV and visible light between a colorless open state (**1Fo**) and a colored closed state (**1Fc**), respectively (Scheme 1). In the open state (**1Fo**) electropolymerization yields alkene bridged sexithiophene polymers through oxidative α,α -terthiophene coupling, while in the closed state (**1Fc**) the polymerizability is switched off (Scheme 1).

1Fo was prepared by standard methods.^{12,13} Cyclic voltammetry¹⁴ of **1Fo** between -0.20 and 1.25 V (vs SCE, Figure 2a) results in the formation and deposition of an alkene bridged sexithiophene polymeric material manifested in a cycle dependent linear increase^{15,16} in the intensity of two new redox waves at 0.7 and 1.1 V (Figure S3a).¹³

Electrodeposition of the polymer on ITO yields an adherent yellow film with a surface roughness of ~ 100 nm,¹³ which is mechanically stable (with respect to peeling) and insoluble in CH_2Cl_2 , CH_3CN , and toluene.¹⁷ Remarkably, the formation of the polymer film proceeded smoothly at a monomer concentration > 0.1 mM and was insensitive to air and trace water (i.e. anhydrous conditions and/or Lewis acids were not required).

The cyclic voltammetry of the resulting modified electrode is characteristic of the formation of a sexithiophene based polymer.¹⁸ In a monomer-free electrolyte solution (Figure 3a), a surface

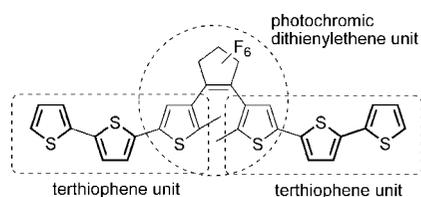
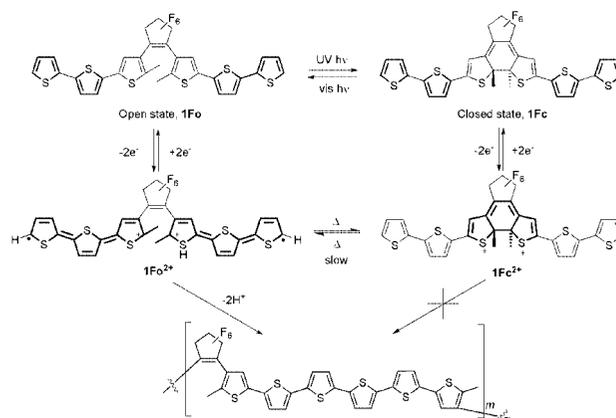


Figure 1. Polymerizable bis-terthiophene and photochromic dithienylethene units of **1Fo**.

Scheme 1. Photochemical Switching between Polymerizable (**1Fo**) and Nonpolymerizable (**1Fc**) States



confined redox process is observed with an apparently quasi-reversible redox wave at ca. 0.7 V and a reversible redox wave at 1.1 V. The electropolymerized film is homogeneous with a thickness of ca. 57 nm (25 cycles, Supporting Information (SI)). FTIR spectroscopy of the monomer and the polymer film shows that the characteristic C–F IR stretching absorptions are present in both spectra. The IR absorptions and Raman scattering of the dithienylethene unit are replaced by bands typical of the sexithiophene unit (see SI for detailed analysis).^{13,19}

In the neutral state the polymer is yellow (λ_{max} 427 nm) with the absorption being assigned to a π – π^* transition of the hexathieryl component of the polymer.¹³ The coloration is easily tuned by varying the thickness of the poly-**1Fo** film.¹³ Upon oxidation at 0.9 V, the polymer film becomes blue with the intensity of the 427 nm absorption band decreasing and the appearance of a new broad absorption band in the NIR region (600 – 1600 nm) assigned to the polaron state of mono-oxidized sexithiophene (λ_{max} 660 , 1084 nm).²⁰ At 1.3 V a further change to a purple colored film is observed with broad features characteristic of a bipolaron state in the 900 – 1300 nm region of the electronic absorption spectrum. The electrochromic switching of poly-**1Fo** between 0.0 to 1.2 V (Figure 3) can be performed over multiple cycles (see SI for movie) as expected for a stable oligothiophene based polymer. The revers-

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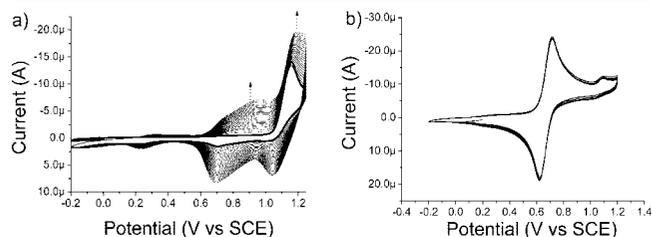


Figure 2. Repetitive scan cyclic voltammogram of (a) **1Fo** and (b) **1Fc** at a Pt electrode in 0.1 M TBAPF₆/CH₂Cl₂. The closed form **1Fc** can be oxidized to **1Fc**²⁺ reversibly (Scheme 1), but in contrast to **1Fo**, electropolymerization is not observed even at high concentrations.

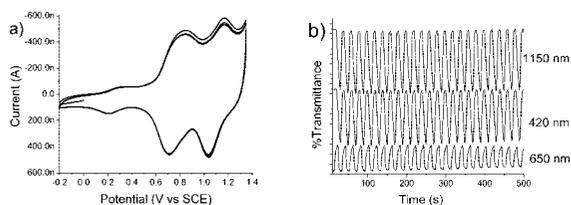


Figure 3. (a) Cyclic voltammogram of a poly-**1Fo** film electrodeposited on a Pt microelectrode. (b) Multicycle redox switching of poly-**1Fo** on an ITO electrode between 0.0 and 1.2 V. 0.1 V s⁻¹ in 0.1 M TBAPF₆/CH₂Cl₂.

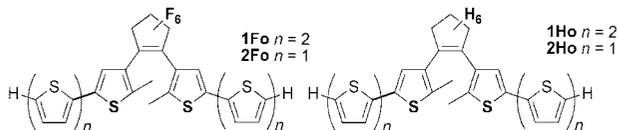


Figure 4. Mono- and bis-thiophene substituted dithienylethenes.

ibility of the changes during redox cycling (Figure 3b) with full recovery of the initial spectrum at 0.0 V and the absence of color change with irradiation with UV light confirms that ring closing does not occur in the redox polymer film.

When the ring closed form (**1Fc**) is oxidized to the dicationic state the positive charge is centered in the dithienylethene core unit. Hence the cationic radical character of the terminal thiophene units is insufficient to permit α,α' -dimerization (Scheme 1). However, as we have shown previously,^{9b} there is a thermal equilibrium between the dicationic open and closed forms of dithienylcyclopentenes (Scheme 1, i.e. between **1Fo**²⁺ and **1Fc**²⁺) with increased electron donating character of both the substituents on the thienyl rings and the cyclopentene bridge moving the equilibrium toward the closed state. Indeed in the case of **1Ho**, **2Ho**, and **2Fo** (Figure 4 and SI), which are structurally analogous to **1Fo**, the electrochemically driven formation of the ring closed isomers **1Hc**, **2Hc**, and **2Fc**, respectively, show that they are, functionally, dithienylethenes. In these systems the rate of thermal ring closure upon oxidation of the open form is much faster, and hence electrochemical ring closing is observed and not electropolymerization. Hence it would be expected that oxidation of **1Fo** would lead to formation of **1Fc**²⁺. However, in this system the rate of ring closure is insufficient to compete with that of the α,α' -coupling of **1Fo**²⁺ giving sufficient time for electropolymerization to proceed. The ability to control electropolymerizability by light allows for localization of polymer growth/deposition through optical patterning. Thus, using **1Fo**, the controlled delivery of polymerizable monomer units to the preferred site for electropolymerization can be achieved.²¹

A solid film of **1Fc** (on ITO glass) was irradiated with visible light through a mask to generate **1Fo** locally. A potential of 1.3 V

was applied to the ITO electrode, which resulted in polymer film formation only where the film was in the open state (**1Fo**).¹³

In conclusion, this remarkable system (**1F**) shows that the inherent character of a molecule (polymerizable terthiophene vs electrochromic dithienylethene) can be switched by light in a fully reversible manner. In the open state **1Fo**, the terthiophene cationic radical formed by oxidation reacts readily via α,α' -dimerization to form perfluorocyclopentene bridged sexithiophene polymers. In the closed state (**1Fc**), oxidation results in the formation of a stable dication, in which the cationic radical character at the α -positions of the two terthiophene units is insufficient for α,α' -coupling to proceed and hence the oxidized **1Fc**²⁺ does not engage in polymerization (Scheme 1). The robustness of the electropolymerization of the monomer with respect to H₂O or O₂ and the stability of the polymer itself makes this system an excellent basis to control electropolymer deposition in a broad range of applications where spatial control is required.

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Supporting Information Available: Experimental details, syntheses, electrochemical and spectroscopic data, AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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