Synthesis and Characterization of Poly(thiophenes) Functionalized by Photochromic Spironaphthoxazine Groups

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ABSTRACT: A photochromic spironaphthoxazine group has been covalently bonded in the 3 position of thiophene (**I**) and in the 3′ position of terthiophene (**II**). The electrochemical and spectroscopic properties of these compounds have been characterized, together with their photochromic properties, associated with the ring opening of the naphthoxazine moiety under light excitation, which occurs in solution and even in the solid state of these compounds. Electropolymerization into spironaphthoxazine functionalized poly(thiophenes) is only successful with **II**, due to the relief of steric hindrance and electronic effects on the thiophene units in this compound. The much lower photochromic properties of poly(**II**) are associated with the compactness of this polymer.

Introduction

Conjugated polymers form an interesting class of materials, owing to the intrinsic conducting properties shown by the polymer chains.[1] These polymers can be further functionalized by the covalent bonding of specific groups, which present specific interactions with external physical or chemical phenomena. In this context, the use of the conjugated chains as routes for the reversible transport of information between such functional groups and an electrode may be exploited for the design of new molecular electronic devices.[2,3] This approach requires first a very careful synthesis of the functionalized precursor monomers, bearing the covalently bonded functional group, and second the polymerization of these monomers into conjugated conducting polymers. Electropolymerization is an elegant route for the elaboration of such conducting polymer films on electrodes, but the steric and electronic effects originating from the substituents have to be taken into account and overcome in order to realize polymers being at the same time functionalized and electronically conducting. Many examples of chemical and even biological recognition have been already developed in conjugated polymers. Thus, the functionalization of these polyheterocycles with crown ethers has led to the observation of specific interactions with alkali cations present in the electrolytic medium.[4] On the other hand, polypyrrole-bearing bioactive peptides as substituents have also been synthesized, which show selective recognition toward enzymes in solution.[5]

The interaction of conjugated polymers with external physical quantities, such as photons, is also of large potential interest, as it should allow a very fast electrical response of a polymer film. As photon-sensing functional groups, photochromic derivatives can be of particular interest for several reasons. Photochromism is a very fast process occurring in the nanosecond to femtosecond time range,[6,7] which induces a reversible modification of the absorption spectrum, linked to a reversible structural modification of the species when submitted to a photon pulse. Photochromism is also accompanied by changes of many physical characteristics of the species, such as the refractive index or the dielectric constant. These intrinsic modifications accompanying photochromic phenomena offer wide possibilities for practical applications, encompassing high-resolution photography, fast electrooptical devices, holographic systems, etc.[8] The covalent bonding of such photochromic moieties on the chains of conjugated polymers is attracting interest, and we report here on the functionalization of conducting poly(thiophene) by photochromic groups.

Results and Discussion

Synthesis. The first step concerned the functionalization of the monomer, realized by the substitution of a spironaphthoxazine either on thiophene or on terthiophene. The 9′-hydroxy-1,3,3-trimethylspiro[indoline-2,3′-naphto[2,1-*b*][1,4]oxazine] was synthesized using a procedure described in the literature.[9] The mild one-pot esterification[10] between 3-thiopheneacetic acid and 9′-hydroxy-1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine] led to compound **I** (thiophene–spironaphthoxazine). The reaction sequence used to prepare the terthiophene derivative, compound **II**, is depicted in Scheme 1. The carboxylic function of the starting commercially available material, 3-thiopheneacetic acid, was protected using an ethyl ester protecting group. Ethyl 2,5-dibromothiophene-3-acetate was obtained in quantitative yield by action of bromine in a chloroform solution. 2-(Tributylstannyl)thiophene was then prepared from a Grignard reagent, derived from 2-iodothiophene and tributylstannyl chloride.[11] Ethyl (2,2′:5′,2″-terthiophene)-3′-acetate is obtained in moderate yield, on the order of 50%, by using the Stille reaction, involving a cross coupling of 2-(tributylstannyl)thiophene and ethyl 2,5-dibromothiophene-3-acetate, in the presence of $Pd(dpp)Cl_2$.[12] The deprotection reaction occurs quantitatively in concentrated HCl, leading to (2,2′:5′,2″-terthiophene)-3′-acetic acid. The monomer **II** (terthienyl–spironaphthoxazine) is obtained in good yield by a mild esterification involving the (2,2′:5′,2″-terthiophene)-3′-acetic acid and 9′-hy-

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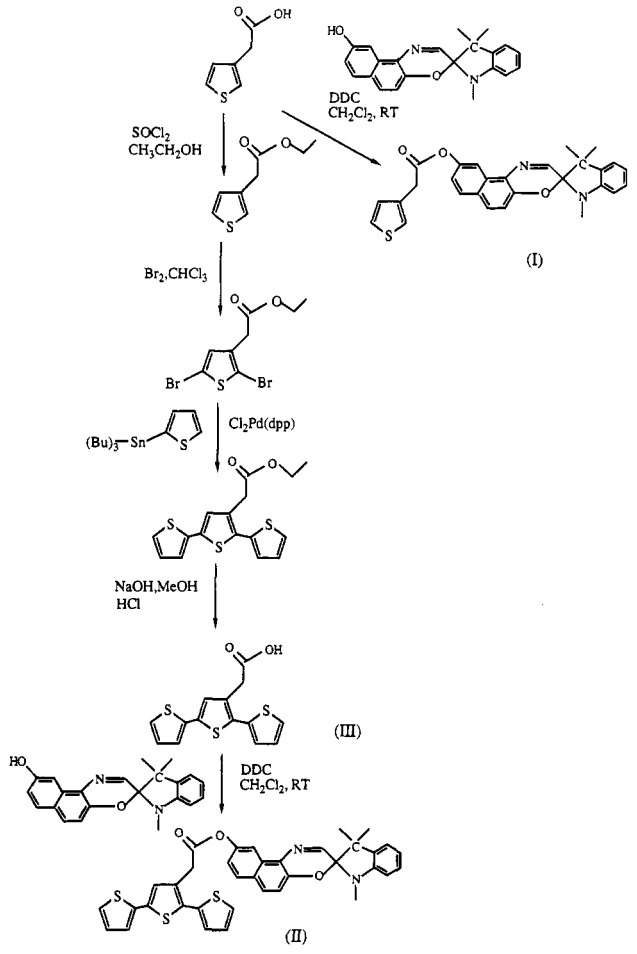
Scheme 1. Reaction Sequences Used for the Synthesis



droxy-1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*]-[1,4]oxazine].

UV–Visible Absorption. The absorption spectra of compounds **I** and **II** in hexane are characterized by two broad bands in the UV range, located at 278 and 321 nm, with a comparable value for the optical density. On the other hand, the molecular extinction coefficient of the band located at low energy, at λ_{max} = 321 nm, is higher for the terthienyl–spironaphthoxazine compound (**II**), as can be expected from the absorption contributions of the terthienyl and of the spironaphthoxazine moieties, respectively. The absorption spectrum of **II** is directly given by the sum of the respective spectra of the oligothiophene and of the spironaphthoxazine, which indicates that these two moieties are electronically uncoupled in **II**. When exciting terthienyl–spironaphthoxazine (**II**) in a dichloromethane solution by a laser flash at 355 nm, the immediate formation of a transient is characterized by two absorption maxima, located at 470 and 600 nm (Figure 1). Taking account of the literature data, the absorption at 470 nm can be attributed to the triplet state of the terthienyl moiety,[13] and the second absorption band, located at 600 nm, can be associated with the opened form of the spironaphthoxazine, originating from the photochromic ring-opening process depicted in Scheme 2.

The absorption spectrum of a thin film of **II** deposited on a glass slide (Figure 2a) shows two broad transitions, peaking at 324 and 260 nm. The most distinctive feature concerns the absence of any vibronic contribution, contrary to what is generally observed for α-conjugated oligothiophene in the solid state, which has been attributed to the quasi planar and rigid-rod conformation of these conjugated molecules.[14] The absence of a hypsochromic shift, between the absorption spectrum of **II** in solution and in the solid state, suggests that the molecules in the film are not arranged in a close packed organization, as classically observed in the case of unsubstituted oligothiophene, which led to the so-called H aggregates.[15] The absence of such close-packed organization clearly indicates that molecular interactions in the solid state are weak. As a consequence of this particular molecular organization, the spironaphthoxazine groups keep a large degree of freedom in the solid state, which allows the photochromic ring opening of spironaphthoxazine to a merocyanine form. This feature is confirmed when exposing a thin film of **II** to UV light excitation (Figure 2b). An immediate formation of a strong absorption peak at 600 nm is observed, which is assigned to the merocyanine type molecule formed by the ring opening of the spironaphthoxazine. This result confirms that the ring-opening photochromism process is still operating in the solid state.

Electropolymerization. The cyclic voltammogram (CV) of an acetronitrile solution containing 10^{-4} M monomer **I** and 0.1 M Bu_4NClO_4, with a saturated calomel reference electrode (Figure 3), exhibits successive redox systems, with anodic peak potential at 1.1 and 1.2 V/SCE, in close agreement with the oxidation potentials reported for spirooxazine derivatives.[16] These redox systems are followed by an intense anodic wave at 1.9 V/SCE, corresponding to the irreversible oxidation of the thiophene moiety. Attempts to electropolymerize **I** in a acetonitrile or nitrobenzene solution, using standard conditions,[1] were unsuccessful. This inhibition of electropolymerization can be explained by two factors. First, the presence of the bulky spironaphthoxazine groups, covalently bonded on the thiophene monomer, induces high steric interactions, which can hinder any coupling of the corresponding thiophene radical cations which are formed by the electrooxidation of the heterocyclic monomers. As a second possible explanation of the inhibition of polymerization, one can also consider the competitive reaction occurring between the thiophene cation radicals, electrogenerated at a working potential of 1.7 V/SCE, and the spironaphthoxazine cation radicals, which are already formed at a lower potential of 1.1 V/SCE. In order to overcome these possible steric and electronic contributions inhibiting the electropolymerization, monomers involving a bithiophene or a terthiophene moiety should be used, owing to the relief of steric hindrance and a decrease of the electroxidation potential offered by the lengthening of the thiophene chain.[15] As a matter of fact, it has been already largely shown that the oxidation potential of oligothiophene derivatives decreases when increasing the chain length of this oligomer. Such a lower oxidation potential of oligothiophene, as compared to that of thiophene, should allow the use of milder electropolymerization conditions and enable the electrochemical elaboration of spironaphthoxazine-functionalized polythiophene films. Following this route, the electrochemical characterization of monomer **II**, based on a terthiophene moiety, reveals an irreversible oxidation wave, located at 0.95 and 1.1 V/SCE (Figure 4). The oxidation potential of terthiophene in compound **II** is comparable to that of (2,2′:5′,2″ terthiophene)-3′-acetic acid (**III**) and appears thus to be not affected by the presence of the spironaphthoxazine. These results clearly show that, whereas the oxidation peak of spironaphthoxazine remains at about 1.1 V/SCE, that of the thiophene moiety has been

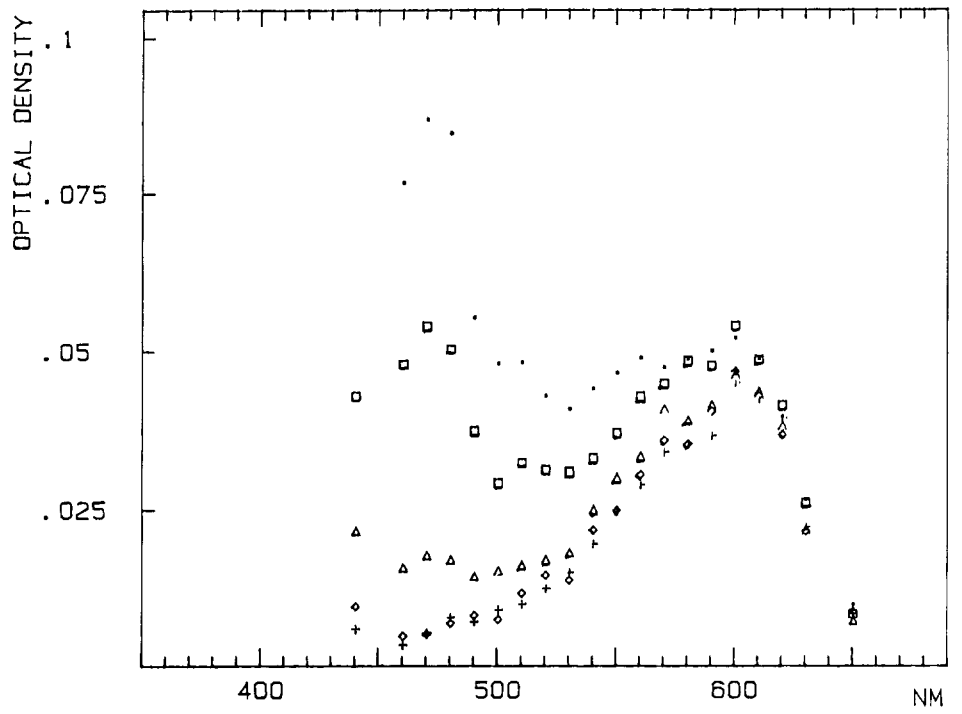
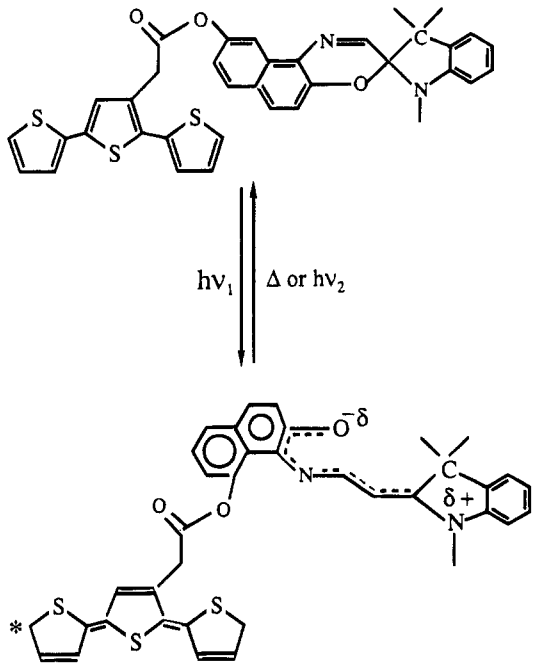


Figure 1. Transient spectra of terthienyl–spironaphthoxazine in dichloromethane obtained at an excitation energy of 355 nm and recorded after 250 (●) 500 (□), 1000 (△), 2000 (◇), 3500 ns (+).

Scheme 2. Structural Modification Induced by Light Excitation of Terthienyl–Spironaphthoxazine[a]



[a] Ground state (top); photoexcitation state in terthienyl and merocyanine form in spironaphthoxazine (bottom).

lowered from 1.7 V/SCE for thiophene in **I** to 0.95 V/SCE in **II**, which should be favorable for electrochemical polymerization of terthiophene units in **II**. This result also indicates that terthienyl and spironaphthoxazine moieties are electronically uncoupled, due to the presence of a methylene spacer. The observed redox process fully accounts for the oxidation of the terthienyl groups into terthienyl radical cations. Figure 5 shows the CVs observed during repetitive potential scans in an electrosynthesis medium containing monomer **II** (0.05 M) and Bu_4NPF_6 (0.1 M) in acetonitrile. The first CV shows an anodic wave at 0.95 V/SCE, followed in the reverse

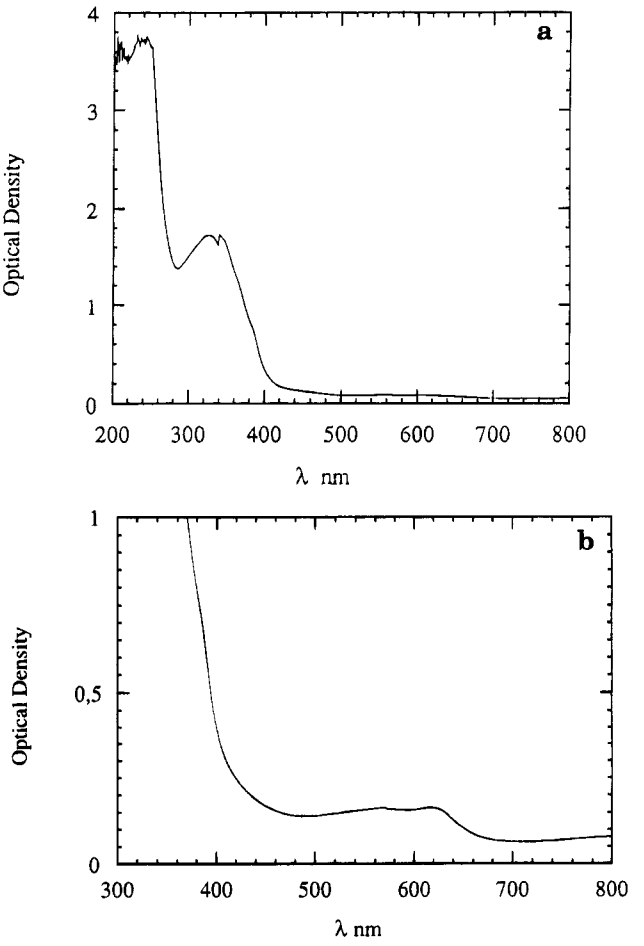


Figure 2. (a) UV–visible absorption spectra of a terthienyl–spironaphthoxazine thin film. (b) UV–visible absorption spectra of a terthienyl–spironaphthoxazine thin film after excitation by UV light.

scan by a reduction wave at 0.9 V/SCE. Contrary to the previous case of compound **I**, repetitive cycling leads

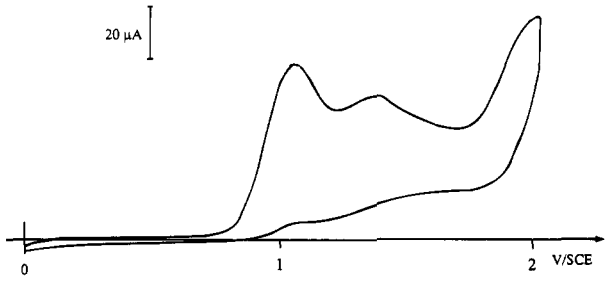


Figure 3. Single voltammogram of thiophene–spironaphthoxazine (10^{-4} M) in 0.1 M Bu_4NClO_4–CH_3CN.

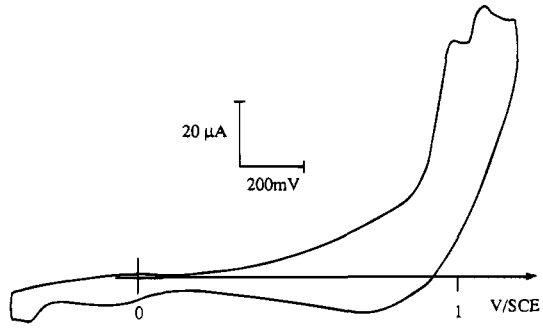


Figure 4. Single voltammogram of terthiophene–spironaphthoxazine (10^{-4} M) in 0.1 M Bu_4NClO_4–CH_3CN.

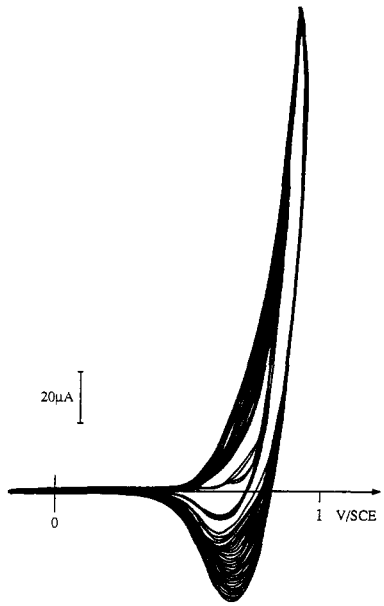


Figure 5. Electropolymerization of terthiophene–spironaphthoxazine, by repetitive potential scans between −0.2 V and 0.95 V/SCE.

to an intensification of the CV waves, which confirms that electropolymerization of the monomers occurs on the electrode.

Films of poly(**II**), obtained by such anodic electropolymerization, have been electrochemically characterized in an electrolytic solution free of monomer. In Figure 6, a set of reversible cyclic voltammograms of poly(**II**) recorded at a 100 mV/s scan rate is depicted. The cyclic voltammogram of poly(**II**) shows one distinct, nearly symmetrical wave, with an oxidation potential at 0.9 V/SCE and a reduction wave at 0.8 V. The peak current varies linearly with the scan rate, indicating that redox-active species are anchored onto the electrode surface. It is well-known in the field of conjugated polymers that the strong π–π interactions between the chains lead to completely unsoluble polymers, which does not allow

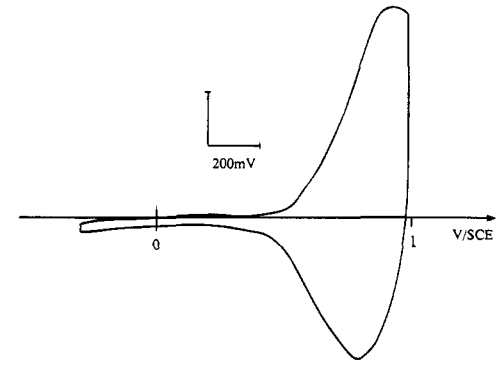


Figure 6. Cyclic voltammogram of poly(terthiophene–spironaphthoxazine) in 0.1 M Bu_4NClO_4–CH_3CN (scan rate 100 mV/s).

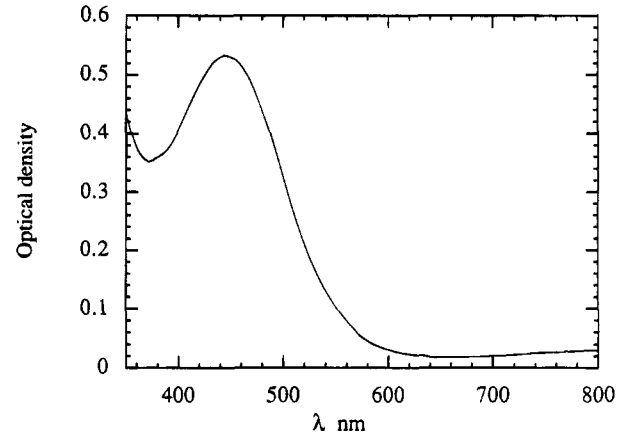


Figure 7. UV–visible absorption spectra of a poly(terthienyl–spironaphthoxazine) thin film.

their characterization by the use of conventional techniques such as NMR or GPC. Even the use of permeation gel chromatography, realized on lower molecular weight soluble fractions of these polymers, has been debated and shows to lead to overestimated molecular weights.[17] Thus, the mainly used criteria concern the appearance of a new electroactive species on the electrode, characterized, when compared to the starting monomer, by a lower redox potential and a lower energy absorption band, which indicate the presence of a longer conjugated material. This is indeed the case of poly(**II**), which shows the same oxidation potential as that of poly(terthienyl),[18] suggesting that this polymer presents a conjugation length comparable to that of poly(terthienyl). Further additional support for this conclusion is provided by the UV–visible absorption spectra of thin polymer films, synthesized on ITO electrodes and electrochemically reduced to their neutral state (Figure 7). Neutral poly(**II**) exhibits an absorption maximum in the UV–visible range, at 450 nm, which is comparable to that of poly(terthienyl)[18] and of poly(perfluorohexylterthiophene).[19] However, this absorption maximum is located at a shorter wavelength than that of poly(alkylterthiophene),[20] $\lambda_{max} = 510$ nm, which can be explained by the weak electron-donating effect of alkyl substituents. These electrochemical and spectroscopic results show thus that, contrary to the thiophene derivative (**I**), the spironaphthoxazine-functionalized terthiophene (**II**) can be electropolymerized into poly(**II**), confirming that steric and electronic effects originating from the spironaphthoxazine substituent can be overcome by lengthening the oligo(thiophene) chain to a trimer.

Preliminary experiments on light excitation of poly-(**II**) did not yet bring definitive evidence concerning the photochromic ring-opening process of the spironaphthoxazine moiety in the polymer. As a matter of fact, the conjugated chains of the poly(thiophene) backbone are themselves converted, under light excitation, into polaronic and bipolaronic states,[21] which are characterized by optical transitions in the same spectral range as the opened form of the spironaphthoxazine. However, the low optical signals recorded in the 600−700 nm range indicate that the photochromic properties of poly(**II**) are much lower than those of a thin film of **II**, which can be explained by a much more entangled and compact morphology of the polymer chains in poly(**II**). The evidence, however, that this photochromic process occurs in the solid state of **II** gives hope that, by controlling the polymerization conditions and mainly the size of the counteranions used as electrolyte, a much looser polymer poly(**II**) will be realized, in which the degree of freedom will be given to the spironaphthoxazine moiety for undergoing the photochromic ring opening. These results appear thus very promising for the development of new materials associating light-sensitive photochromic groups, together with conjugated poly(thiophene) chains showing charge transport properties. Such an approach has been recently attempted in the case of substituted diarylethene, but without success, as the obtained polymer did not show either electrochemical or photochromic activity.[22]

Experimental Section

Ethyl Thiophene-3-acetate. A total of 5.61 cm^3 of thionyl chloride were added at −10 °C to 100 cm^3 of absolute ethanol. The solution was stirred for 10 min. Then 5 g (35 mmol) of thiophene-3-acetic acid was added and the mixture stirred at room temperature for 24 h. The solvent and the excess of thionyl chloride were removed under vacuum. The crude product was distilled, 95−100 °C under 10 mmHg, leading to 5.65 g of the desired compound (yield = 95%). ^{1}H NMR ($CDCl_3$/TMS): δ 7.22 (dd, H_4, J_4 −2 = 2.98 Hz, J_4 −5 = 4.93 Hz), 7.10 (dd, H_2, J_2 −4 = 2.8 Hz, J_2 −5 = 0.76 Hz), 6.99 (dd, H_5, J_5 −4 = 4.9 Hz, J_5 −2 = 1.25 Hz), 3.55 (s, 2H), 4 (q, 2H, J = 7.15 Hz), 1.17 (t, 3H, J = 7.13 Hz).

Ethyl 2,5-Dibromothiophene-3-acetate. A total of 3.94 cm^3 (77 mmol) of bromine was added to a solution of 5.94 g of ethyl thiophene-3-acetate in 100 cm^3 of chloroform. The solution was stirred for 4 h, then quenched with a 10% aqueous sodium hydroxide solution and washed with distilled water, dried with $MgSO_4$, and evaporated. The resulting residue was distilled, 200 °C under 10 mmHg, yielding 10.9 g (95%). ^{1}H NMR ($CDCl_3$/TMS): δ 6.8 (s, 1H), 3.46 (s, 2H), 4.06 (q, 2H, J = 7.15 Hz), 1.18 (t, 4H, J = 7.14 Hz).

Ethyl (2,2′:5′,2″-Terthiophene)-3′-acetate. Ethyl 2,5-dibromothiophene-3-acetate (3.2 g, 10 mmol) and 2-(tributylstannyl)thiophene (7.45 g, 20 mmol) were added to a THF solution of dichlorobis(triphenylphosphine)palladium (0.46 g, 0.4 mmol). The mixture was heated at 80 °C for 24 h. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2, washed with water, and dried with $MgSO_4$. The crude product was purified by chromatography on silica gel with toluene as eluant. A total of 1.68 g of ethyl (2,2′:5′,2″-terthiophene)-3′-acetate was obtained (50%). MS: m/z 334. ^{1}H NMR ($CDCl_3$/TMS): δ 6.8−7.2 (m, 7H), 3.46 (s, 2H), 4.06 (q, 2H, J = 7.15 Hz), 1.18 (t, 4H, J = 7.14 Hz).

(2,2′:5′,2″-Terthiophene)-3′-acetic Acid (III). A total of 3.4 g of ethyl (2,2′:5′,2″-terthiophene)-3′-acetate was dissolved in methanol and added to a 20% aqueous sodium hydroxide solution (300 mL). The mixture was refluxed for 4 h. After concentration the aqueous solution was washed with ether, acidified with concentrated HCl to pH 1 and extracted by ether. The ether solution was washed up to pH 7; evaporation of ether yielded 2.8 g of (2,2′:5′,2″-terthiophene)-3′-acetic acid. MS: m/z 306. ^{1}H NMR ($CDCl_3$/TMS): δ 11.4 (s, 1H, acid) 6.8−7.4 (m, 7H).

3′-Spironaphthoxazine−2,2′:5′,2″-terthiophene (II). A solution of 1g (3.26 mmol) of (2,2′:5″,2″-terthiophene)-3′-acetic acid, 0.741 g (3.59 mmol) of *N,N*-dicyclohexylcarbodiimide, 1.23 g (3.59 mmol) of 9′-hydroxy-1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine], and 0.053 g (0,326 mmol) of 4-pyrrolidinopyridine (DDC) in 50 mL of CH_2Cl_2 was stirred at room temperature for 2 days, and the reaction was monitored by thin layer chromatography. The *N,N*-dicyclohexylurea was filtered off. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using a graduated pentane/ether (100:0 to 50:50) maximum to give 1.64 g (79%) of compound **II**. ^{1}H NMR ($CDCl_3$/TMS): δ 1.25 (s, 6H), 2.66 (s, 3H), 3.96 (s, 2H), 6.58 (d, J = 7.7 Hz, 1H), 6.9 (t, J = 7.4 Hz, 1H), 6.97−7.28 (m, 10H), 7.3 (dd, J = 3.6 and 1.1 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.71 (s, 1H), 7.74 (dd, J = 8.8 and 1.7 Hz, 1H), 8.26 (s, 1H).

9′-(3-Thienylacetoxy)-1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine] (spironaphthoxazine−thiophene) (I) was synthesized following the procedure described for compound **II** (73%). Mp: 118−119 °C. ^{1}H NMR ($CDCl_3$/TMS): δ 1.33 (s, 6H), 2.75 (s, 3H), 3.96 (s, 2H), 6.57 (d, J = 7.7 Hz, 1H), 6.89 (td, J = 7.4 and 0.7 Hz, 1H), 6.98 (d, J = 8.8 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.11 (dd, J = 8.8 and 2.3 Hz, 1H), 7.18 (dd, J = 4.9 and 1.3 Hz, 1H), 7.2 (dd, J = 7.6 and 1.2 Hz, 1H), 7.29−7.3 (m, 1H), 7.35 (dd, J = 4.9 and 3 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H) 7.7 (s, 1H), 7.74 (d, J = 8.8 Hz, 1H), 8.22 (d, J = 2.3 Hz, 1H). Anal. Calcd for $C_{28}H_{24}O_3N_2S$: C, 71.17; H, 5.16; N, 5.97; S, 6.8. Found: C, 71.72; H, 5.21; N, 5.92; S, 6.8.

The laser flash photolysis experiments were performed on an apparatus which has been previously described.[23]

Electropolymerizations were carried out in a three-electrode single-compartment cell containing monomer and tetrabutylammonium hexafluorophosphate as an electrolyte, using the described procedure.[1] The solutions were degassed by argon bubbling prior to electropolymerization. The polymer was grown on a platinum electrode of 7×10^{-3} cm^2 area, a platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as reference. Electropolymerization and cyclic voltammetry were performed with a 273 potentoistat/galvanostat. UV−visible absorption spectra were obtained on a Cary 2415 spectrophotometer.

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