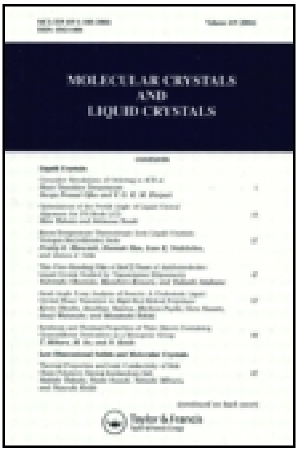

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Conjugated Thiophene Oligomers as Efficient Photochromic Materials for Ultrafast Spatial Light Modulation

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CONJUGATED THIOPHENE OLIGOMERS AS EFFICIENT PHOTOCHROMIC MATERIALS FOR ULTRAFAST SPATIAL LIGHT MODULATION

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Abstract Conjugated oligomers of thiophene have recently become a new class of molecular semiconductors with potential applications in microelectronics. We show here that these compounds are also attractive third-order nonlinear optical materials with potential applications in optical signal processing. We report on the picosecond photoinduced dichroïsm of thiophene oligomers α-nT (n=2-6) in solution and thin film. Spectral concentration in the excited state is identified as the key phenomenon to design a prototype incoherent-to-coherent optical converter (ICOC). Vacuum deposited thin films of the model sexithiophene α-6T meet the material requirements to achieve 1 pJ/pixel exposure sensitivity in the MHz frequency range.

INTRODUCTION

Conjugated thiophene oligomers attract a considerable interest since three years because they form a new class of organic semiconductors with exceptional charge transport properties and potential applications in MIS devices such as thin film transistors[1]. These pseudo-polyenes also have well-defined linear[2] and third order nonlinear[3] optical properties that have been much less investigated but could also have potential applications in optical signal processing.

Spatial light modulators (SLMs) are two-dimensional input devices aimed at fully utilizing the potential speed and parallelism capabilities of light and can be considered as the building blocks of image and beam processors[4]. In conventional real-time optically-addressed SLMs, the active recording material can be a liquid crystal, a photorefractive crystal, a multi quantum well semiconductor or a silver halide film. The comparative performances of various OASLMs based on such materials have recently been discussed by Nunzi et al.[5]. The basic requirements for an optimized OASLM are 1) a uniform response throughout their transverse surface, 2) a pixel size as small as possible in order to reach the resolution limits of optics ($D<1\mu m^2$), 3) a reduced thickness to avoid optical aberrations ($E<D^2/\lambda\approx1\mu m$), 4) a short response time t_r and an ajustable lifetime τ allowing *"real time"* processing, 5) a good write sensitivity ($W\approx1pJ/pixel$) and finally 6) the write (λ_w) and read (λ_r) spectral tunability. But up to now, none of the materials used meet all the requirements necessary for optimizing the SLM performances, in particular spatial resolution which remains limited to $\approx100\ \mu m^2$, exposure sensitivity per pixel (typically 10pJ/pixel) and switching times ($t_r>1\mu s$) because of collective effects in liquid crystals and polarization effects in photorefractives and MQW. In the quest for new materials with high spatial light modulation efficiencies, organics have both advantages of developping instantaneous molecular effects and being easily processible as large area homogeneous thin films.

To this respect, photochromic materials have been intensively studied in view of a number of optical signal processing applications. At the exception of the well-known silver halides which undergo self-darkening when irradiated in the UV-visible, most of the photochromic materials are organic compounds. Organic photochromism usually results from photoinduced isomerism (cis-trans) or molecular re-arrangement (ring closure-opening). In this article, we investigate the transient photochromism of thiophene oligomers and show that these compounds can be the key materials of an ultrafast incoherent-to-coherent optical converter (ICOC), a particular class of optically-addressed SLMs.

2. MATERIALS

The synthesis of unsubstituted α-nT oligothiophenes have already been extensively described according to various routes[6]. Homocoupling of shorter oligomers via organo-metallic intermediates is the most widely used method.

Solutions of α-nT are prepared in dichloromethane. For optical measurements, the solutions are placed in polarimetric-quality fused-quartz cells of thickness 1 mm. The optical densities (OD) of the α-3T, α-4T and α-5T solutions are 1.0 at their respective excitation wavelengths (355 nm for α-3T; 396 nm for α-4T and α-5T). The OD of the α-2T solution is 0.4 at the minimum available excitation wavelength and that of the α-6T one close to saturation is 0.33 at 396 nm.

Thin solid films of α-6T are easily prepared by vapor deposition heating a small quantity of purified powder (melting point=305°C) in a tungsten boat under reduced pressure (10^{-4} Pa). Typical deposition rates are in the range 1-4 nm/sec up to thicknesses in the range 100-300 nm. This procedure affords homogeneous, stable and highly crystalline α-6T thin films. The high optical quality of our samples is due to the extremely small size of the crystallites (30-100 nm). The linear refractive index of the α-6T thin films (n=1.965 at 632.8 nm) has been measured in the transparency region by excitation of evanescent optical waves with a He-Ne laser using the conventional Kretschman configuration[7]. In contrast to poly(3-alkylthiophenes) films, whose high porosity generally results in low refractive indices, the high refractive index of α-6T thin films can be ascribed to the combined effects of a long π-conjugated system (electronic factors) and high film crystallinity and density (morphology factors).

3. TRANSIENT PHOTOINDUCED DICHROISM

Kerr ellipsometry technique

Photoinduced dichroïsm in α-nT solutions and thin films is measured using a modified Kerr ellipsometry technique based on the anisotropy induced by a linearly polarized optical pump in the initially isotropic material[8]. Briefly, it consists in the analysis of the polarization state of a probe beam transmitted by the sample after action of the pump beam. Incoming pump and probe are linearly polarized and their polarization directions make an angle of 45°. This method permits an accurate and sensitive measurement of both the birefringence and dichroïsm induced by the pump.

Dichroïsm is represented by the imaginary part of the complex phase retardation φ which is related to the variation of absorption coefficient at the probe frequency ω_S by:

$$\mathrm{Im}(\varphi)=1/4\, l\, [\Delta\alpha_{/\!/}(\omega_S)-\Delta\alpha_{\perp}(\omega_S)] \qquad (1)$$

where // and ⊥ denote the probe polarization parallel and perpendicular to the pump polarization and l is the optical path length in the sample. The variation of the difference (1) with ω_S reflects the differential spectral properties of the optically excited molecules.

The source is a Nd^{3+}:YAG laser delivering 33ps pulses at 1064 nm with a repetition rate of 10 Hz. Three excitation wavelengths are derived from this source at 532, 396 and 355 nm. The maximum pump intensity is 40 MW/cm^2 at 355 nm and 8 MW/cm^2 at 396 nm. The probe is a weakly chirped continuum generated by focussing the 1064 nm beam in a 5 cm long deuterated-water cell and is detected in the 420-910 nm range.

Measurements in solutions

The spectra of induced dichroïsm in α-nT solutions (n=2 to 6) are given in figure 1. The main feature is a sharp peak for α-3T, α-5T and α-6T at increasing wavelengths, while it is slightly broader for α-2T and α-4T. A similar size dependent behavior has also been observed by Chosrovian et al. but with broader spectra[9]. Our narrow spectra strongly contrast with the smooth and broad photoinduced absorption spectra of polythiophenes and other conjugated polymers. Since these sharp PA peaks are produced by excitation in the broader fundamental absorption band, we call this phenomenon *spectral concentration*.

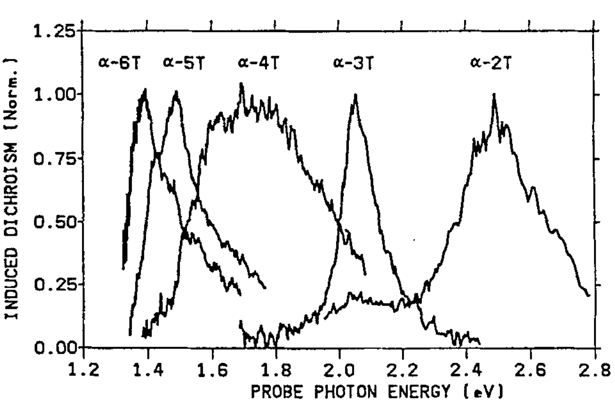

FIGURE 1 Photoinduced dichroïsm spectra of α-nT (n=2-6) oligothiophenes in dichloromethane.

The efficiency of the process is given in Table I in terms of extinction coefficient per absorbed pump photon. As a rule, these spectra are independent of the excitation wavelength. The signal is proportional to the absorbed pump energy, showing that it results from a one-photon absorption process. The rise time is lower than 10 ps and the lifetime of induced anisotropy increases with the oligomer size (18 ps for α-3T and 65 ps for α-5T in dichloromethane).

Oligomer	λ_{max} (nm)	ϵ (10^{-4} M^{-1}cm^{-1})	λ_{PA} (nm)	ϵ_{PA} (10^{-4} M^{-1}cm^{-1})
T	243	0.156		
α-2T	302	1.247	498	9
α-3T	355	2.505	603	25
α-4T	391	4.550	720	28
α-5T	410	5.520	836	39
α-6T	432	≈6	≈890	≈50

TABLE I- Characteristics of linear and photoinduced absorption in α-nT (n=2-6).

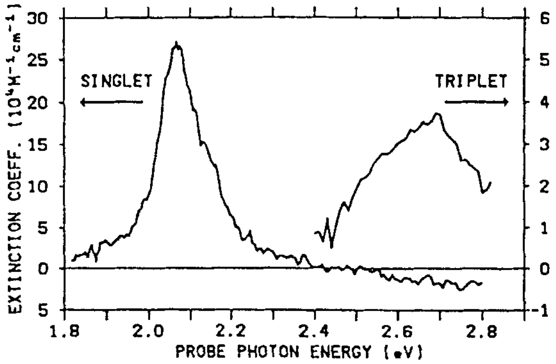

FIGURE 2 Photoinduced absorption of α-3T in a highly viscous solvent at zero (S_1 absorption) and 660 ps (T_1 absorption) probe delay.

The dynamics of the induced dichroïsm also reveals interesting features (figure 2). The nanosecond-lived absorption of α-3T at 460 nm has already been observed[10] and can be assigned to the triplet state absorption ($T_1 \rightarrow T_n$). On the other hand, the picosecond transient peak of α-3T at 600 nm is of different origin. Its line shape and chain length dependence are reminiscent of those of the corresponding radical cations α-nT$^{+\bullet}$as prepared by chemical doping[11]. But owing to its short lifetime and evolution towards the triplet state it should rather be attributed to the lowest singlet state absorption $(S_1 \rightarrow S_n)$. The maximum photoinduced absorption is almost independent on the solvent polarity (methanol, dichloromethane or cyclohexane) which is another argument in favor of a nonpolar species as its origin. Furthermore, as for the α-nT$^{+\bullet}$radical cations, the maximum absorption wavelength fits a linear 1/n progression with the oligomer length n from the trimer to the hexamer (figure 3). But the constant 0.2 eV energy difference between both curves again rules out the possibility for the induced dichroïsm to originate from the respective α-nT$^{+\bullet}$radical cations.

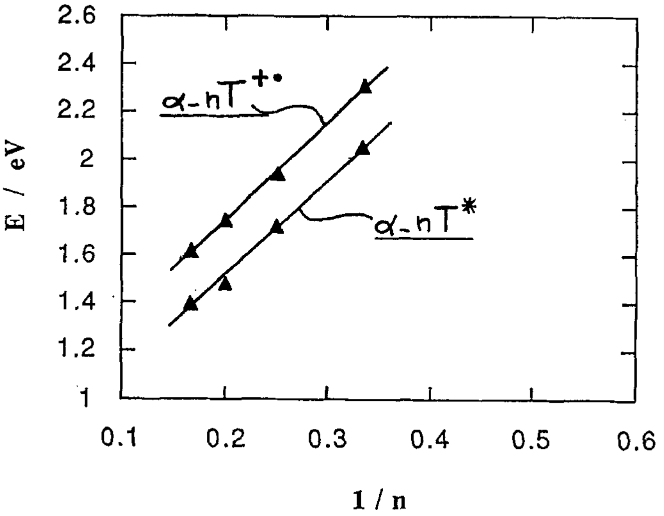

FIGURE 3 Linear 1/n progression of the photoexcited (α-nT*) and radical cations (α-nT$^{+\bullet}$) maximum absorption wavelengths with the oligomer length n.

Measurements in thin films

Spectral concentration is also observed in the solid state as examplified here with α-6T thin film[12]. The linear absorption spectrum of an α-6T thin film is represented in figure 4 (dashed curve) showing the broad and structured π-π^* transition peaking at 398 nm ($\alpha = 2.6 \times 10^6$ cm^{-1}) with three equally-spaced ($\Delta E = 0.194$ eV) vibronic side-bands. The vibronic contributions, which are not observed in solution, are characteristic of the quasi-planar and rigid-rod conformation of α-6T in the solid state[2a]. The left spectrum (solid line) represents the photoinduced dichroïsm in the transparency region 670 ps after excitation at 532 nm (2.33 eV). At a zero time delay, excitation at three different wavelengths (355, 395 and 532 nm) always results in the same photoinduced transient spectrum showing that photoexcitation in the absorption band homogeneously generates the same excited state. It peaks at 790 nm (1.57 eV) instead of 890 nm (1.39 eV) for the $S_1 \rightarrow S_n$ transition observed in solution and has an extremely narrow half-intensity width of 0.1 eV as compared to that of the linear absorption of the film (FWHM≈1.0 eV).

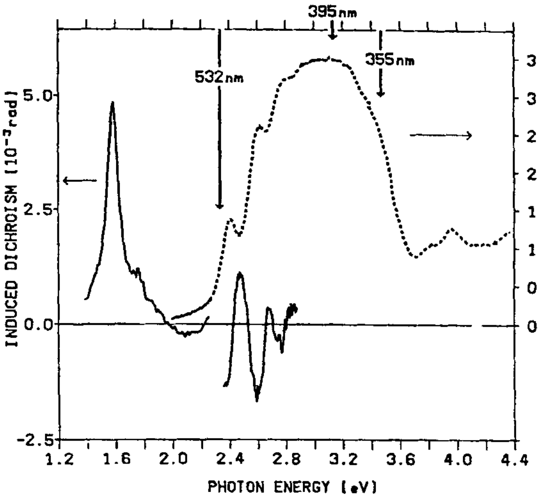

FIGURE 4 Photoinduced dichroïsm spectra (full line on the left) in an α-6T film (thickness 320 nm) excited at 532 nm after a 670 ps probe delay. The dashed curve on the right represents the linear absorption of the film.

The dynamics of photoinduced dichroïsm in a α-6T film after excitation at 2.33 eV by a 50 MW/cm^2 light pulse of 33 ps is shown in Figure 5. The rise time is shorter than 10 ps which is our detection limit. A structureless spectrum extending from 1.35 to 2.1 eV and peaking at about 1.55 eV develops during the first 30-40 ps. Due to its short lifetime (τ=40 ps) and by analogy with what is observed in solution, it can be attributed to the absorption of the lowest singlet excited state S_1. Then, this first spectrum rapidly interconverts into a sharper one peaking at the same energy but with a much longer lifetime (τ=5 ns). We attribute it to absorption by the T_1 triplet state after S_1 relaxation via intersystem crossing (ISC), in agreement with observations on α-3T[10]. The absence of simultaneous absorption in the 0.8 eV near infrared region excludes the possibility to attribute this photogenerated state to the α-6T$^+$ radical cation[11].

The probe-wavelength dependence of the real (birefringence) and imaginary (dichroïsm) parts of the complex phase retardations induced in a α-6T film are displayed in figure 6. It shows that modulation of both phase and amplitude are obtained. The induced optical density at 790 nm is $\delta DO \approx 10^{-2}$ and results of an excitation energy close to 1 mJ/cm^2. The results evidence the Kramers-Kronig relation between birefringence and dichroïsm.

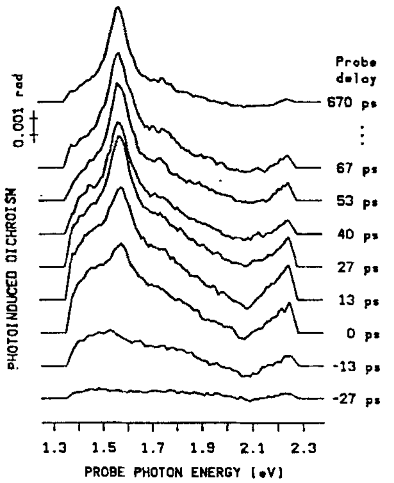

FIGURE 5 Time-resolved spectra of photoinduced dichroïsm in an α-6T film excited at 532 nm by a 50 MW/cm^2 laser pulse of 33 ps.

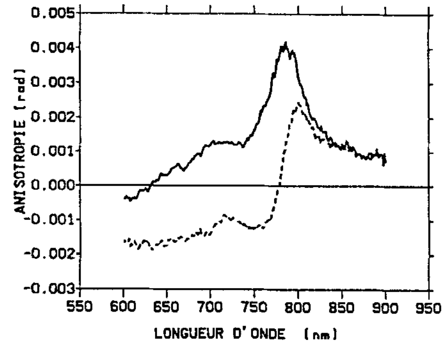

FIGURE 6 Birefringence (dashed line) and dichroïsm (full line) induced in an α-6T film after excitation at 532 nm and a 500 ps probe delay.

From a molecular point of view, spectral concentration may result from a greater contribution of the quinoïd-like electronic configuration (figure 7) inducing an homogeneization of the excited state of the molecule. Molecular engineering rules leading to spectral concentration are discussed elsewhere[5] and consist in identifying the physico-chemical parameters that allow the oscillator strength to be confined in a narrow spectral region close to kT=0.025 eV. Three of them seem essential: (1) damping of vibronic side bands, (2) conservation of the oscillator strength, and (3) homogeneity of the molecule.

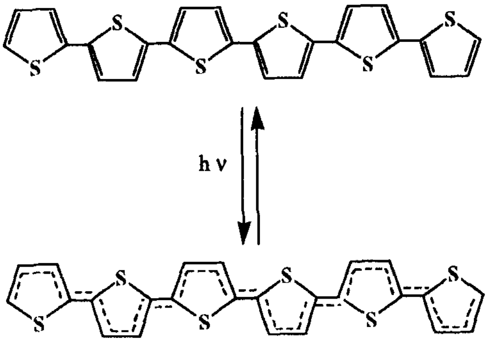

FIGURE 7 Reduction of bond alternance in the quinoïd-like electronic structure of α-6T in its photoexcited state.

4. AN α-6T BASED INCOHERENT-TO-COHERENT OPTICAL CONVERTER

In respect to its short response time (<10 ps), α-6T could be used to design an ultrafast photochromic incoherent-to-coherent optical converter (*ICOC*)[13]. The typical optical arrangement of a prototype ICOC using α-6T as the modulating material is represented in Figure 8. The device itself consists in an α-6T thin film vacuum-deposited on an SiO_2 substrate. A continuous white light source illuminates an object whose image is formed on the surface of the device by mean of an objective. This incoherent writing beam carrying the signal reaches the α-6T film by the x-y front face. The coherent reading beam is produced by a laser diode (λ=800 nm) and successively passes through a spatial filter and a collimation lens before reaching the back x-y face of the ICOC, i.e. the SiO_2 substrate. The laser diode has been selected because its wavelength matches that of the photoinduced absorption of the α-6T film (λ_{max}=790 nm).

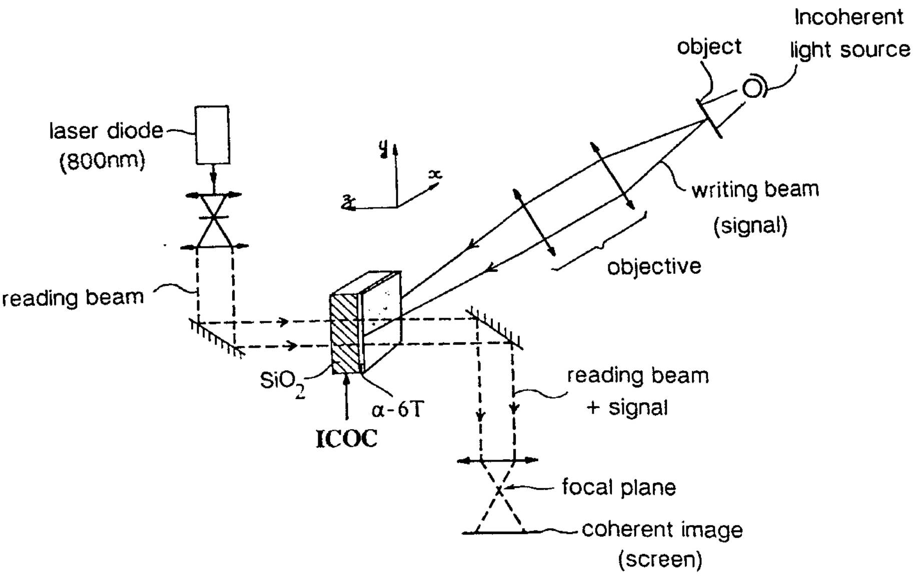

FIGURE 8 Experimental setup of an α-6T based incoherent-to-coherent optical converter (ICOC).

The simultaneous excitation of α-6T by the writing and reading beams finally results in a coherent beam carrying the signal initially contained in the incoherent beam. The coherent image of the illuminated object can then be deflected by a mirror, focussed by a lens on an holographic filter and the correlation result can be displayed on a screen. Such coherent holographic filtering also permits an amplification of the photochromic contrast.

Since the lifetime of the T_1 state responsible of the transient photochromism is $\tau \approx 5$ns under room conditions, it is in principle possible to use the α-6T-based ICOC to process images with frequencies up to 200 MHz. However, such a modulation rate requests a 200 kW/cm^2 continuous white light illumination. This is by far too large and it is better either to dissolve α-6T in an outgazed polymer matrix into which triplet lifetimes can be increased up to microseconds at room temperature or to use pulsed white light exposure. At 1 MHz frequency, exposure energy is reduced to the acceptable value of 1 kW/cm^2. The readout frequency can also be adjusted by selecting the appropriate oligomer length n because of the size dependence of photoinduced absorption.

CONCLUSION

As compared with other ICOC materials such as photorefractive crystals[14], liquid crystal light valves[15] and semiconductor heterostructures[16], α-6T films can improve the speed and spatial resolution of image processing by two orders of magnitude while having the same exposure sensitivity. These performances together with spectral tunability by selecting the appropriate oligomer size make sexithiophene α-6T and other one-dimensional conjugated α-oligothiophenes the "archetype" photochromic materials for ultrafast incoherent-to-coherent optical conversion.

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