Time-resolved spectroscopy of oligothiophenes using the femtosecond fluorescence upconversion technique

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Abstract. In the present work the electronic properties of two oligothiophenes were experimentally studied through the time-resolved fluorescence spectroscopy up-conversion technique. The effect of the substituent at the end of the main chain on the excited state dynamics was investigated. The excited state decay time (τfl), the reorientation time of the emission dipole (τor), the initial fluorescence anisotropy (r0) and the time-dependence of the fluorescence anisotropy r(t) were measured. The results showed that the molecule with the bigger dipole moment has smaller excited state decay time. The other coefficients are almost the same for the two materials because of their similar chemical structure. Also, the angle (α) between the absorption and emission dipoles, µa and µe respectively, was calculated through anisotropy.

1. Introduction

The research in ultra fast phenomena has been intensified during the last decades. These phenomena have to do with the chemical reactions (breakage of the chemical bonds, molecules orientation, transfer energy etc) as well as the behavior of the electrons and nuclei in the molecules. For the study of such phenomena the temporal resolution of the modern electronic systems is inadequate. Thus, new techniques, based on the femtosecond laser pulses, have already developed. The time resolved fluorescence spectroscopy, in femtosecond regime, is based on the frequency mixed phenomenon and presents the best temporal resolution to-date. This technique gives the possibility of measuring the lifetime of the excited state, as well as the temporal evolution of the fluorescence spectrum of a material.

In the present work the above-mentioned technique is applied for the experimental study of two oligothiophenes for a better understanding of their structure and electronics properties. The influence of the change of the substituent, been located at the edge of the main chain, on their excited state dynamics is investigated. The excited state decay time (τfl), the reorientation time of the emission dipole (τor) and the initial fluorescence anisotropy (r0) in directions perpendicular and parallel to the excitation dipole were measured for both materials. The angle (α) between the absorption µa and emission µe dipoles was calculated through anisotropy.
2. Chemical substances
The chemical substances studied are two oligothiophenes with the same main chain but different substituent at its edge. The one is the 5,5’-dicarboxyhaldehyde 2.2’,5’,2’’-Terthiophene having at both edges of the main chain -CHO. The other is the 5-carboxyhaldehyde 2,2’,5’,2’’-Terthiophene where the -CHO at the one edge has been replaced by an -H (figure 1). Solutions of these substances in dichloromethane with concentration 10^{-3} M were studied through up conversion time resolved spectroscopy.

![Figure 1. (a) Molecular structure, (b) The absorption and emission spectra of the two oligothiophenes.](image)

3. Experimental - measurements
The femtosecond time resolved fluorescence spectroscopy used, employs the upconversion technique and its experimental set-up is shown in figure 2. The femtosecond laser pulses are generated by a mode-locked Ti:Sapphire laser pumped by a frequency doubled Nd:YVO4 continuous wave laser (Tsunami, Millennia Vs, Spectra Physics). The laser pulses have a wavelength of 800 nm while their pulse duration and repetition rate are 80 fs and 82 MHz respectively. The laser beam is focused onto a nonlinear BBO crystal (1 mm thickness) generating a second harmonic beam at 400nm. The two beams (fundamental and second harmonic) are separated through a prism. The second harmonic ($P_{PUMP}$=6mW average power), after passing through a half wave plate, excites the polymeric sample contained in a 1 mm thick quartz cuvette. The remaining fundamental laser beam, after passing through an optical delay line, driven by a DC motor (0.1 µm spatial resolution), and plays the role of the “optical gate”. The fluorescence of the polymeric sample is collected and is focused together with the delayed fundamental laser beam onto a second BBO crystal (1.5 mm thickness). As long as the two beams coexist spatially and temporally on the crystal and phase matching conditions are met, an upconversion UV signal beam is generated via a type I phase matching.

![Figure 2. Experimental set-up](image)
spectroscopic technique is given by the full width at half maximum of the cross correlation between the excitation (400 nm) and gate (800 nm) beams and is ~280 fs while the spectral resolution is 2.5 nm.

The frequency mixing acts as an “optical gate” permitting the detection of the radiation only for the time interval of the coincidence of the two pulses with frequencies \( \omega_{IR} \) and \( \omega_{SP} \) in the BBO2 crystal. By this way, the temporal resolution becomes comparable to the duration of the pulses. Finally, the temporal evolution of the fluorescence \( \omega_{SP} \) is detected by varying the delay time of the laser beam \( \omega_{IR} \).

The fluorescence with parallel and vertical polarization as well as the total fluorescence and its anisotropy were measured versus time and these are shown in figure 3.

![Figure 3](image)

**Figure 3.** (a) Fluorescence intensity for parallel and vertical polarization of the \( P_{\text{pump}} \) beam versus time, (b) total fluorescence intensity versus time, (c) anisotropy versus time for both substances.

4. **Theoretical aspects - Results**

The intensity of the up conversion signal (\( I_{\text{ SIGNAL}} \)) for parallel and vertical polarization of the pumping beam \( (P_{\text{PUMP}}) \) is given by the relationships: [1-4]

\[
I_\parallel(t) = (1 + 2r(t)) I(t) \quad , \quad I_\perp(t) = (1 - r(t)) I(t) \\
I(t) = I_0 \exp \left( -\frac{t}{\tau_{\text{fl}}} \right) \quad , \quad r(t) = (r_0 - r_\infty) \exp \left( -\frac{t}{\tau_{\text{or}}} \right) + r_\infty \\
I_\parallel(t) = I_0 \left[ \exp \left( -\frac{t}{\tau_{\text{fl}}} \right) + 2(r_0 - r_\infty) \exp \left( -\frac{t}{\tau_{\text{fl}}} - \frac{t}{\tau_{\text{or}}} \right) \right] \\
I_\perp(t) = I_0 \left[ \exp \left( -\frac{t}{\tau_{\text{fl}}} \right) - (r_0 - r_\infty) \exp \left( -\frac{t}{\tau_{\text{fl}}} - \frac{t}{\tau_{\text{or}}} \right) \right]
\]

where \( I_0 \) is a proportionality constant, \( r_0 \) is the fluorescence initial anisotropy \( r_\infty \) is the anisotropy at long times, \( \tau_{\text{fl}} \) is the fluorescence decay time and \( \tau_{\text{or}} \) is the reorientation time of the molecular dipoles. The dependence of the total fluorescence intensity as well as the dependence of the anisotropy on time was measured through relationship:

\[
I(t) = I_\parallel(t) + 2I_\perp(t) \quad , \quad r(t) = \frac{I_0(t) - I_\parallel(t)}{I_0(t) + 2I_\perp(t)}
\]

By fitting the above relationships with the experimental results shown in figure 3, all the coefficients included in these relationships can be estimated. These are given in the following Table.

In conclusion, the oligothiophene 2 has higher value of dipole moment than the oligothiophene 1. This is the reason for the observed shorter lifetime of the excited state \( \tau_0 \) of the former in comparison to that of the latter.
Table 1

|          | Oligothiophene 1 | Oligothiophene 2 |
|----------|------------------|------------------|
| $I_0$    | $0.64 \pm 0.02$  | $0.62 \pm 0.02$  |
| $\tau_{fl}$ | $254 \pm 10$ps | $220 \pm 10$ps |
| $\tau_{or}$ | $26 \pm 4$ps   | $24 \pm 4$ps    |
| $r_0$    | $0.28 \pm 0.04$  | $0.27 \pm 0.04$  |
| $r_\infty$ | $0.022 \pm 0.004$ | $0.016 \pm 0.004$ |

Figure 4. A schematic of the molecular structure of oligothiophenes. The solid ellipse is an outline of the prolate spheroid used to model this molecule. The double-headed arrows indicate the orientations of the absorption and emission dipoles $\mu_a$ and $\mu_e$ respectively.

A modified Debye-Stokes-Einstein equation is generally used to predict molecular reorientation time, which depends on the size and shape of the solute molecules, the temperature $T$ and the viscosity $\eta$ of the solvent. For a prolate ellipsoid with the emission dipole oriented along its long axis, the reorientation time can be written as: [5]

$$\tau_{or} = \frac{fV\eta}{k_B T}$$

where $V$ is the hydrodynamic volume of the solute molecule, $k$ is the Boltzmann constant, $g$ is the shape factor given by Perrin’s equation and $f$ is the friction term depending on hydrodynamic boundary conditions. The values of the reorientation time $\tau_{or}$ of the molecular dipoles are similar for both substances, as it is expected, because the molecules interact with the solvent in the same manner.

Because of the different geometry of the molecule when it is in the fundamental or in the excited state, its orientation is different during the absorption from that of the emission. The angle ($\alpha$) between the dipole of the absorption and emission has been calculated through the relationship: [1, 2]

$$r_0 = \frac{1}{5} (3\cos^2 \alpha - 1)$$

The angle value for the oligothiophene 1 is ($29^\circ \pm 4^\circ$) while for the oligothiophene 2 is ($30^\circ \pm 4^\circ$)

5. Applications
The present research contributes to the comprehension of the electro-optics properties of the oligothiophenes which constitutes the structural units of the polythiophenes. These substances have wide application in opto-electronics devices as in Light Emitting Diodes (LEDs), transistors circuits, optical modulators e,t,c as well as for the fabrication of 3D optical memories.

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7. References
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