

Study of the Isotropic and Anisotropic Fluorescence of Two Oligothiophenes by Femtosecond Time-Resolved Spectroscopy

Dimitris Anastopoulos, Mihalis Fakis, Ioannis Polyzos, Georgios Tsigaridas, Peter Persephonis, and Vassilis Giannetas*

Department of Physics, University of Patras, 26500 Patra, Greece

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The excited-state dynamics of two oligothiophenes, 5,5'-dicarboxyaldehyde 2,2',5',2''-terthiophene and 5-carboxyaldehyde 2,2',5',2''-terthiophene, were studied by time-resolved fluorescence spectroscopy, in the femtosecond regime. The isotropic and anisotropic parameters of their fluorescence were calculated. The angle (α) between the absorption and emission molecular dipoles was estimated from the initial fluorescence anisotropy. The effect of the chemical substituents, at the ends of the main chain of the molecule, on the temporal behavior of the fluorescence was investigated. Particularly, the nonsymmetric oligothiophene molecule (containing one aldehyde group) exhibits shorter excited-state isotropic decay time than the symmetric one (containing two aldehyde groups). This is due to the higher value of the emission dipole moment of the nonsymmetric oligothiophene in comparison with that of the symmetric one. Additionally, the two materials have almost the same anisotropic fluorescence parameters, and this is attributed to the same rotational motions in the excited state due to their similar molecular structures.

Introduction

Research on the electronic and optical properties of oligothiophenes and polythiophenes has exhibited increased interest, as these have applications in optoelectronic devices, e.g., light-emitting diodes, transistor circuits, optical modulators, three-dimensional optical memories, etc.^{1–5} The advantages of using these organic materials in the above applications are the potentials of extremely low-cost manufacturing and a high degree of flexibility. The suitability of oligothiophenes and polythiophenes for use in such devices depends on their molecular structure and electronic properties. Thus, the study of the excited-state dynamics is very important for the characterization of these materials. Rotational motions of the molecules disturb their initial orientations and also influence the excited-state dynamics leading to fluorescence depolarization. For investigation of these ultrafast processes, taking place in the excited state of molecules, new techniques based on femtosecond time-resolved fluorescence spectroscopy have already been developed and widely used. The main advantage of these techniques is the very short exciting pulse duration in comparison with the fluorescence decay time and the reorientation time of the emission dipole. This allows both of these quantities to be measured accurately without interference from the exciting pulse, in a temporal regime ranging from very short time periods up to a few times the fluorescence lifetime of the molecule.

In this work, two oligothiophenes, 5,5'-dicarboxyaldehyde 2,2',5',2''-terthiophene and 5-carboxyaldehyde 2,2',5',2''-terthiophene, are synthesized and studied by femtosecond time-resolved fluorescence spectroscopy for understanding their excited-state dynamics. The two oligothiophene molecules have the same main chain but different chemical substituents at one of their edges. The influence of this substituent on the time evolution of the isotropic and anisotropic components of the

fluorescence is investigated. The characteristic parameters for these components are calculated for both materials. Finally, the angle (α) between the absorption and emission molecular dipole moments at $t = 0$ is estimated from the initial fluorescence anisotropy.⁶

Theoretical Aspects

When a linearly polarized light pulse with the appropriate wavelength irradiates a fluorophore solution, the light preferentially excites the fluorophores whose absorption dipoles are oriented parallel to the polarization plane of the light. The light from these fluorophores is emitted anisotropically, and any molecular motion (e.g., rotational Brownian motion) changing the direction of the transition dipole reduces the anisotropy leading to the depolarization of the fluorescence. Simultaneously, the initially excited fluorophores decay to the electronic ground state either by isotropic fluorescence or by a nonradiative process. Therefore, when the time evolution of the fluorescence intensity at a fixed polarization plane is recorded, a superposition of rotational diffusion and excited-state population decay is observed.

The pure anisotropic component of the signal is obtained from the definition of the anisotropy $r(t)$, given by the relationship^{7–11}

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\text{is}}(t)} = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (1)$$

where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the fluorescence intensities polarized parallel and perpendicular to the polarization of the excitation beam. The quantity $I_{\text{is}}(t)$ is the isotropic fluorescence intensity, namely, the fluorescence component that does not depend on the molecular rotation. In eq 1, we have also used the relation

$$I_{\text{is}}(t) = I_{\parallel}(t) + 2I_{\perp}(t) \quad (2)$$

according to Gordon's work.¹²

* Author to whom correspondence should be addressed. Fax: +30-2610-996239. E-mail: gianetas@physics.upatras.gr.

Through the use of eqs 1 and 2, the polarized fluorescence intensities $I_{\parallel}(t)$ and $I_{\perp}(t)$ can be written as

$$I_{\parallel}(t) = \frac{I_{\text{is}}(t)}{3}[1 + 2r(t)] \quad (3)$$

and

$$I_{\perp}(t) = \frac{I_{\text{is}}(t)}{3}[1 - r(t)] \quad (4)$$

However, the anisotropy $r(t)$ decays often to zero, and for a molecule whose emission dipole is oriented parallel to its symmetry axis, a single-exponential decay function is applicable.⁷ Thus, we have

$$r(t) = r_0 \exp\left(-\frac{t}{\tau_{\text{or}}}\right) \quad (5)$$

where r_0 is the initial (at $t = 0$) value of anisotropy while τ_{or} is the reorientation time leading to depolarization of the system. In solutions, r_0 is determined by the angle α between absorption and emission dipole moments according to the relationship^{6-8,13}

$$r_0 = \frac{1}{5}(3(\cos^2 \alpha) - 1) \quad (6)$$

For absorption from the ground state to the first excited singlet state ($S_0 \rightarrow S_1$) and the subsequent fluorescence ($S_1 \rightarrow S_0$), these transition moment vectors are often close to parallel, and therefore $r_0 \approx 0.4$. However, for a molecule with $\alpha \approx 54.7^\circ$ (inherent magic angle), the anisotropy $r(t)$ is constantly zero, regardless of its rotational motion, and only the isotropic component of the fluorescence is observed as it can be deduced from eqs 3 and 4.

The pure isotropic component of the signal $I_{\text{is}}(t)$ is attributed only to the decay of the excited-state population and is given by the relationship

$$I_{\text{is}}(t) = I_0 \exp\left(-\frac{t}{\tau_{\text{fl}}}\right) \quad (7)$$

provided that the fluorescence decay is a single-exponential function of time (with a time constant τ_{fl}). By substitution of eqs 7 and 5 into eqs 3 and 4, the two polarized fluorescence intensities I_{\parallel} and I_{\perp} are

$$I_{\parallel} = \frac{I_0}{3} \left[\exp\left(-\frac{t}{\tau_{\text{fl}}}\right) + 2r_0 \exp\left(-\frac{t}{\tau_{\text{fl}}} - \frac{t}{\tau_{\text{or}}}\right) \right] \quad (8)$$

$$I_{\perp} = \frac{I_0}{3} \left[\exp\left(-\frac{t}{\tau_{\text{fl}}}\right) - r_0 \exp\left(-\frac{t}{\tau_{\text{fl}}} - \frac{t}{\tau_{\text{or}}}\right) \right] \quad (9)$$

Both I_{\parallel} and I_{\perp} decay following a double exponential function of time and contain information for the isotropic characteristic time τ_{fl} as well as for the anisotropic parameters r_0 and τ_{or} . Finally, the observed fluorescence for an arbitrary polarization angle γ is given by the formula^{14,15}

$$I_{\gamma}(t) = (\cos^2 \gamma)I_{\parallel}(t) + (\sin^2 \gamma)I_{\perp}(t) \quad (10)$$

and after substituting $I_{\parallel}(t)$ and $I_{\perp}(t)$ from eqs 8 and 9 into eq 10 becomes

$$I_{\gamma}(t) = \frac{I_0}{3} \left[\exp\left(-\frac{t}{\tau_{\text{fl}}}\right) + r_0 \exp\left(-\frac{t}{\tau_{\text{fl}}} - \frac{t}{\tau_{\text{or}}}\right) (3(\cos^2 \gamma) - 1) \right] \quad (11)$$

Obviously, when the polarization angle is the magic angle, $\gamma = \gamma_{\text{m}} = 54.7^\circ$ (γ_{m} magic angle), $\cos^2 \gamma_{\text{m}} = 1/3$, and only the isotropic component of the fluorescence is observed.

Preparation of the Samples

The compounds studied were two oligothiophenes that have the same main chain but different substituents at one edge. Especially, oligothiophene 1 was the 5,5'-dicarboxyhaldehyde 2,2',5',2''-terthiophene, which has CHO substituents at both edges of the main chain. However, oligothiophene 2 was the 5-carboxyhaldehyde 2,2',5',2''-terthiophene, which has CHO substituents at one edge of the main chain and H at the other edge. The preparation of these compounds was realized as follows.

In 10 mL of DMF cooled at 0°C , 450 mg of POCl_3 (3 mmol) was added slowly. The solution was stirred for 30 min at 0°C under an inert atmosphere. Approximately 480 mg (2 mmol) of [2,2';5',2'']terthiophene diluted in 10 mL of DMF was added slowly. The yellow solution was stirred for 15 min at room temperature and heated at 70°C for 1 h. The solution turned dark red. To the above solution, ice and water are added, and the pH is adjusted higher than 6 by the slow addition of 1.3 g of NaOH diluted in 10 mL of H_2O . The solution is cooled in the refrigerator to give a yellow product. The product was filtered and washed repeatedly with water. Chromatographic purification in SiO_2 with CH_2Cl_2 as eluent gave three products; the first is the starting material, the second is 5-carboxyhaldehyde 2,2',5',2''-terthiophene (359 mg, 65% yield), and the third product is 5,5'-dicarboxyhaldehyde 2,2',5',2''-terthiophene (122 mg, 20%).

5,5'-Dicarboxyhaldehyde 2,2',5',2''-terthiophene is an orange crystalline material: mp 224°C . High-performance liquid separation mass spectroscopy results agree with the molecular weight. ^1H NMR (CDCl_3 , ppm): 9.87 (s, 2H, aldehyde groups); 7.70, 7.68 (d, 2H, at positions 4, 4''); 7.31 (s, 2H, at positions 3', 4'); 7.28, 2.29 (d, 2H, at positions 3, 3'').

5-Carboxyhaldehyde 2,2',5',2''-terthiophene is a yellow crystalline product: mp 142°C (141°C in ref 1). ^1H NMR (CDCl_3 , ppm): 9.88 (s, 2H, aldehyde group); 7.66, 7.65 (d, 1H, at position 4); 7.26–7.03 (m, 6H).

The synthesis of the two oligothiophenes is depicted in Figure 1, while their absorption and emission spectra are shown in Figure 2.

Both compounds exhibit broad and structureless spectra, emitting light in the blue-green spectral region. Finally, quantum yield measurements showed that the values for the two oligothiophenes are the same and equal to 0.2. Solutions of these compounds in dichloromethane with a concentration of 10^{-3} M were studied through up-conversion time-resolved fluores-

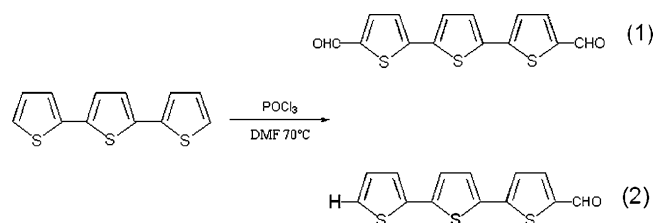


Figure 1. Reaction pathway for the synthesis of the two oligothiophenes.

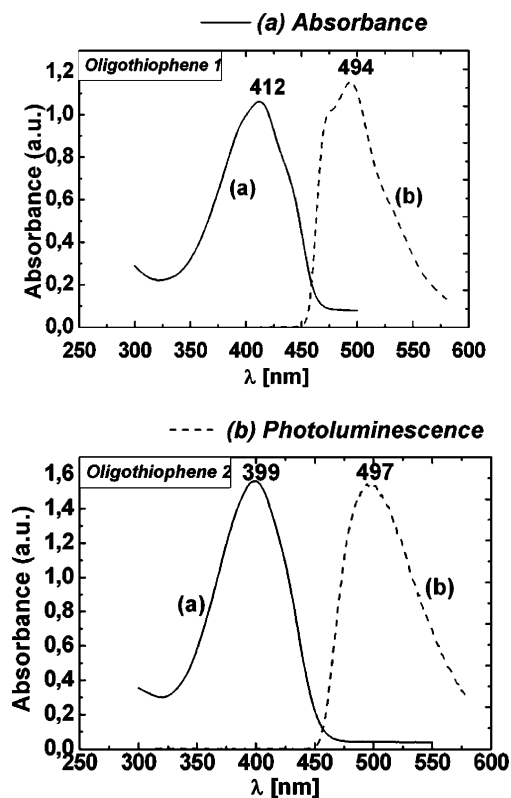


Figure 2. Absorption and emission spectra of the two oligothiophenes.

cence spectroscopy in the femtosecond regime, described in the following section.

Experimental Setup

The experimental setup¹⁶ used for studying the excited-state dynamics of the two oligothiophenes is shown in Figure 3. Femtosecond laser pulses are generated by a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) pumped by a frequency-doubled Nd:YVO₄ continuous-wave laser (Millennia Vs, Spectra Physics). The wavelength of the laser pulses is 800 nm while their pulse duration and repetition rate are 80 fs and 82 MHz, respectively. The laser beam is focused onto a nonlinear β -barium borate (BBO) crystal (1-mm thickness, Fujian Castech),

generating a second harmonic beam at 400 nm. The two beams (fundamental and second harmonic) are separated through a prism. The second harmonic beam ($P_{\text{PUMP}} = 6$ mW average power), after passing through a half-wave plate for rotation of polarization, excites the chemical substance under investigation contained in a 1-mm-thick quartz cuvette. The remaining fundamental laser beam passes through an optical delay line, driven by a direct current motor (Newport ESP300, 0.1- μm spatial resolution), and plays the role of the “optical gate”. The fluorescence of the chemical substance is selected and focused, together with the delayed fundamental laser beam, onto a second BBO crystal (1.5-mm thickness, Fujian Castech). As long as the two beams overlap spatially and temporally on the crystal and phase matching conditions are met, an up-conversion UV signal is generated via type I phase matching. The up-conversion signal is separated from the fluorescence and fundamental laser beams by an iris and a set of filters (UG-11 glass filters) and is directed in the entrance of a 0.25-m monochromator (ORIEL 77200). Finally, the up-conversion signal is detected by a photomultiplier (Becker-Hickie PMH-100-3) connected with a photon counter (Becker-Hickie PMS-400) having an exposure time equal to 1 s at each delay point. The frequency mixing acts as an “optical gate” permitting the detection of the fluorescence only for the time interval of the overlap of the two beams. The temporal evolution of the fluorescence is detected by varying the delay time of the laser gate beam. The resolution of our time-resolved 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.

Measurements and Results

The time evolution of the two polarized fluorescence intensities I_{\parallel} and I_{\perp} were measured for both oligothiophenes (at 500 nm), and the results are shown in Figure 4. The temporal step of the measurements is 932 fs. As predicted from theory (eqs 8 and 9), I_{\parallel} follows a biexponential decay while I_{\perp} initially shows a rise, which is followed by an exponential decay.

The separation of the isotropic and anisotropic contributions to the fluorescence is essential for the interpretation of the transient signals. The isotropic contribution $I_{\text{is}}(t)$ can be either obtained directly, by measuring the fluorescence dynamics under

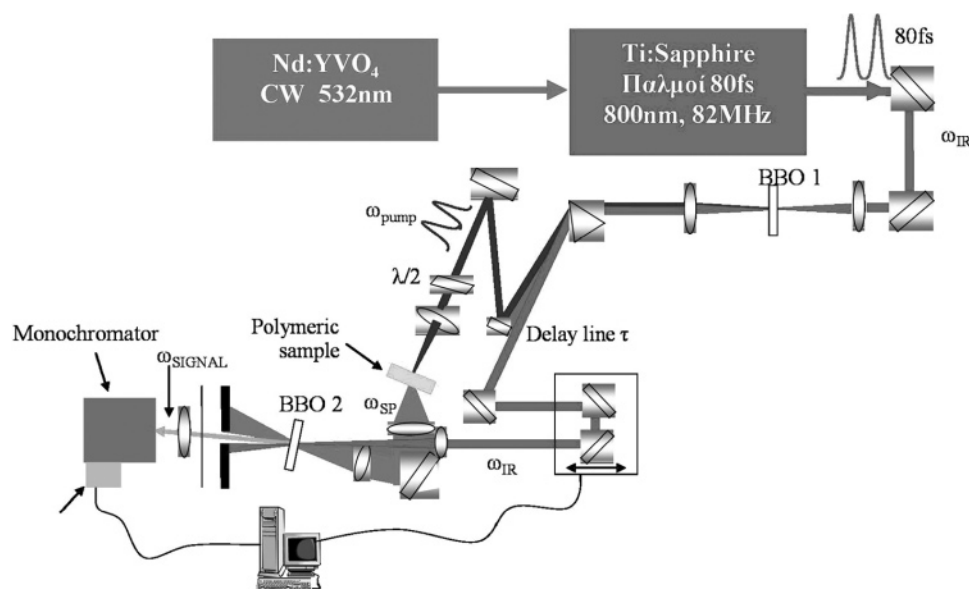


Figure 3. Experimental setup.

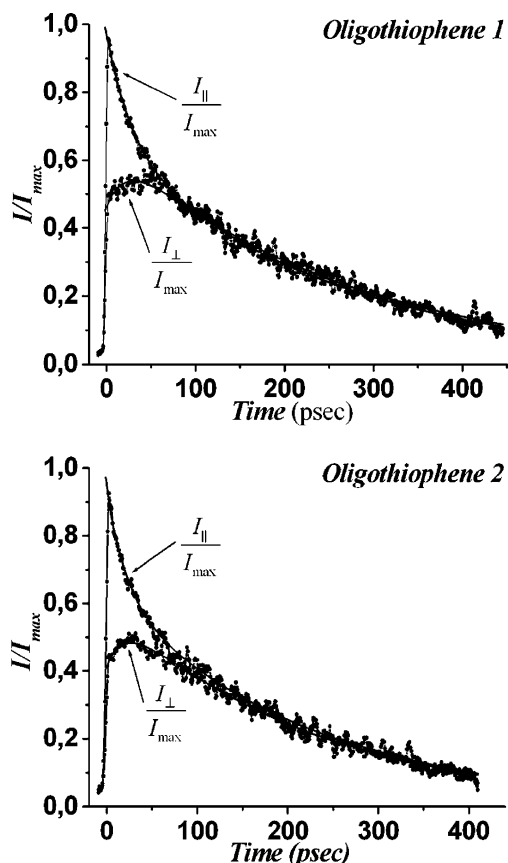


Figure 4. Temporal evolution of fluorescence intensity for parallel and vertical polarization relative to ω_{pump} beam for oligothiophenes 1 and 2 at 500 nm. The correlation coefficient is above 0.99 for all fittings.

magic angle conditions ($\gamma_m = 54.7^\circ$), or constructed from the experimental values of parallel and perpendicular fluorescence intensities I_{\parallel} and I_{\perp} according to eq 2. In our case, both of them were realized, and their results coincide (in the frame of experimental errors), verifying the accuracy of our measurements. These results are shown in Figure 5 for both oligothiophenes at 500 nm. However, the anisotropic contribution can be obtained by substituting the experimental values of I_{\parallel} and I_{\perp} (Figure 4) into eq 1. The results are shown in Figure 6 for both oligothiophenes.

The parameters related to the isotropic and anisotropic contributions to the fluorescence can be obtained by fitting the decay curves shown in Figure 4, 5, and 6 with eqs 5, 7, 8, and 9. Thus, the isotropic decay time τ_{fl} is obtained by fitting the decay recorded in Figure 5 with eq 7. The theoretical fits are also shown in the same figure. The obtained values are $\tau_{\text{fl}} = 254 \pm 10$ ps and $\tau_{\text{fl}} = 220 \pm 10$ ps for oligothiophene 1 and 2, respectively. Through the use of the values of the quantum yields, the radiative and nonradiative lifetimes are calculated and found to be $\tau_{\text{isp}} \approx 1270 \pm 100$ ps and $\tau_{\text{lnr}} \approx 317 \pm 10$ ps for oligothiophene 1 and $\tau_{\text{2sp}} \approx 1100 \pm 100$ ps and $\tau_{\text{2nr}} \approx 275 \pm 10$ ps for oligothiophene 2, respectively.

As is well-known from the literature,^{17,18} the dominant nonradiative decay process of the oligothiophenes in solution, competing with fluorescence, is the triplet formation through intersystem crossing. Although this process is quantum mechanically forbidden and the energy difference between S_1 (singlet) and T_1 (triplet) states is too large, the singlet-to-triplet transition in terthiophene molecules is very efficient.¹⁷ This is attributed to the formation of an intermediate state in the singlet manifold, related to the different geometry of the molecule between the ground and the excited state.¹⁷ The energy of this

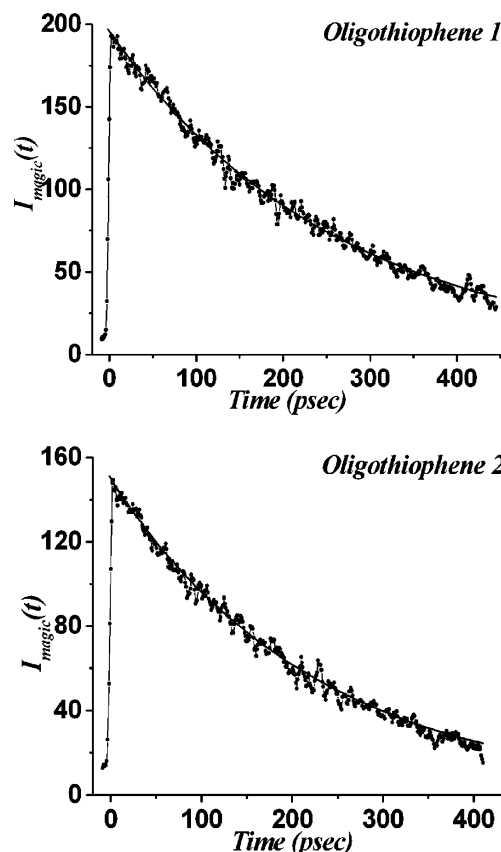


Figure 5. Temporal evolution of isotropic fluorescence intensity at 500 nm, for oligothiophenes 1 and 2. The correlation coefficient is above 0.99 for both fittings.

intermediate state is higher than that of the relaxed S_1 state and very close to that of the T_2 triplet state, facilitating the transition from the singlet to the triplet manifold. For the determination of the anisotropic characteristics r_0 and τ_{or} , we have fitted the experimental decays shown in Figures 4 and 6 with eqs 8, 9, and 5 (τ_{fl} has already been determined). The fitting curves are also shown in these figures. The obtained values for r_0 are 0.26 ± 0.04 and 0.27 ± 0.04 , while for τ_{or} they are 26 ± 4 ps and 25 ± 4 ps for oligothiophene 1 and 2, respectively. The determined isotropic and anisotropic parameters are given in Table 1. Another verification of the validity of our measurements is the very good coincidence of the experimental and theoretical values of the time where a maximum occurs in the $I_{\perp}(t)$ curves. In fact, when the isotropic fluorescence and the anisotropy decays are single-exponential functions of time, the $I_{\perp}(t)$ curves will show a maximum at¹⁵

$$\tau_{\text{max}}^{\perp} = \tau_{\text{or}} \ln \left[\frac{2(\tau_{\text{fl}} + 1)}{5(\tau_{\text{or}})} \right] \quad (12)$$

By substitution of the values of τ_{fl} and τ_{or} into eq 12, the calculated values of $\tau_{\text{max}}^{\perp}$ are 38 and 34 ps for oligothiophene 1 and 2, respectively, in very good agreement with the experimental results (34 and 31 ps). Finally, the temporal evolution of the isotropic fluorescence component (eq 7) as well as of the total fluorescence (eq 11) at every polarization angle (γ) for oligothiophene 1 is shown in Figure 7. The anisotropic component can be extracted by subtracting the isotropic component from the total fluorescence. In this figure, we observe that anisotropy plays an important role at the beginning of the fluorescence process, decaying in a few tens of picoseconds. After this time, the total fluorescence coincides with the isotropic

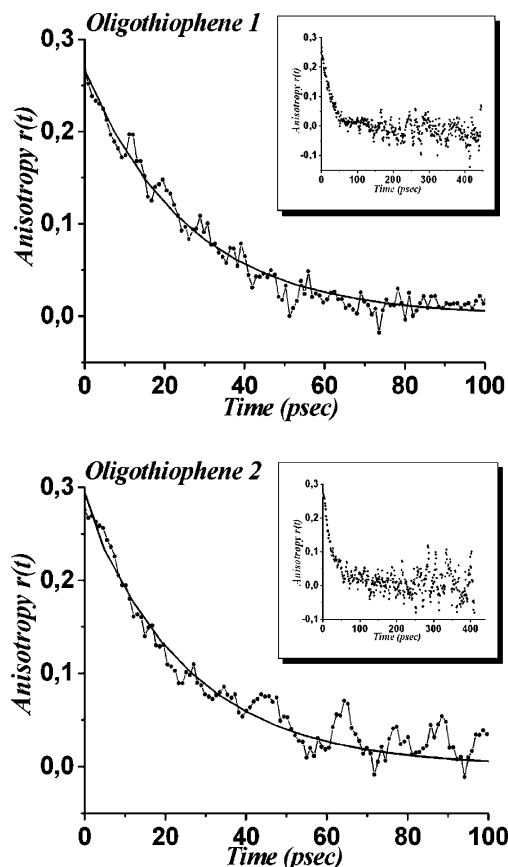


Figure 6. Temporal evolution of anisotropy at 500 nm for oligothiophenes 1 and 2 in the first 100 ps. Inset: The temporal evolution of anisotropy for a longer time scale. The correlation coefficient is 0.98 for both fittings.

TABLE 1: Isotropic Decay Time (τ_{fi}), Radiative and Nonradiative Lifetimes (τ_{sp} , τ_{nr}), Orientation Time (τ_{or}), and Initial Anisotropy r_0 Values of the Fits

| | oligothiophene 1 | oligothiophene 2 |
|--------------------|-------------------|-------------------|
| τ_{fi} | 254 ± 10 ps | 220 ± 10 ps |
| τ_{sp} | 1270 ± 100 ps | 1100 ± 100 ps |
| τ_{nr} | 317 ± 10 ps | 275 ± 10 ps |
| τ_{or} | 26 ± 4 ps | 25 ± 4 ps |
| r_0 | 0.26 ± 0.04 | 0.27 ± 0.04 |

component (circle in the figure), gradually decaying during a few hundred picoseconds.

It seems also clearly in this figure that at the angle of 54.7° (magic angle) there is no anisotropic component while the isotropic one is equal to the total fluorescence. For smaller polarization angles than the magic one, the anisotropic contribution is positive, while for larger angles it is negative. Similar behavior is observed for oligothiophene 2.

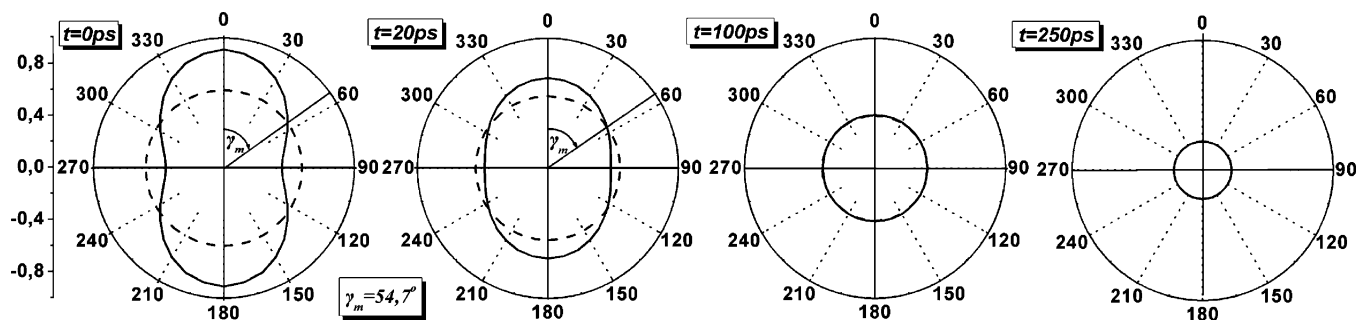


Figure 7. Temporal evolution of the total fluorescence (solid line) for oligothiophene 1 and its isotropic component (dashed line) for every polarization angle (γ).

Discussions

The above-mentioned results show clearly that the change of the chemical substituent at the end of the main chain of the molecule does not affect the anisotropic component of the fluorescence, as its characteristic parameters r_0 and τ_{or} are almost the same for both oligothiophenes. This can be explained as follows. It is well-known in the literature⁷ that the oligothiophene molecule in dichloromethane reorients as a prolate ellipsoid and its emission dipole is directed along the long molecular axis.⁷ In this case, the orientation time τ_{or} is predicted by a modified Debye–Stokes–Einstein equation and can be written as^{6,7,9,19,20}

$$\tau_{\text{or}} = \frac{\eta V f}{K T g} \quad (13)$$

where η is the viscosity of the dichloromethane, V is the hydrodynamic volume of the oligothiophene molecule, K is the Boltzmann constant, T is the temperature, g is the shape factor given by Perrin's equation,²¹ and f is the friction term depending on the hydrodynamic boundary conditions. Equation 13 shows clearly that τ_{or} depends directly on the hydrodynamic volume of the solute molecule. In our case, this volume is the same for both oligothiophenes because they have the same chemical structure. In addition, the two molecules interact with the solvent in the same manner and have the same shape. Thus, it is reasonable that the measured experimental values of τ_{or} for both oligothiophenes are almost the same. Concerning the initial anisotropy r_0 , their values are lower than those obtained for parallel absorption and emission dipole moments (0.4). This indicates that the vectors of the transition moments form an angle (α) that can be calculated using eq 6. The values of this angle were found to be $29^\circ \pm 4^\circ$ and $28^\circ \pm 4^\circ$ for oligothiophene 1 and 2, respectively.

The existence of an angle between emission and absorption dipole moment vectors of oligothiophene molecules may indicate the different molecular conformation and electronic structure between the ground and excited states. This characteristic has also been reported by other groups in the past.²² Further, the values of the initial anisotropy r_0 for the two oligothiophenes are almost equal, indicating that the orientations of the absorption and emission dipoles are not affected by changing the chemical substituent at one edge of the molecular main chain.

However, the values of the isotropic fluorescence decay time τ_{fi} are different for the two oligothiophenes. Thus, in contrast to the anisotropic component of fluorescence, the isotropic one is affected by changing the chemical substituent at the end of the molecular main chain. Particularly, the fluorescence lifetime of oligothiophene 1 is longer than that of oligothiophene 2 ($\tau_{\text{fi1}} > \tau_{\text{fi2}}$). This can be explained as follows. Since the quantum yields of the two oligothiophenes have the same

value we can write

$$\frac{\tau_{1f}}{\tau_{2f}} = \frac{\tau_{1sp}}{\tau_{2sp}} \quad (14)$$

where τ_{sp} is the radiative decay time given by the relationship²³

$$\tau_{sp} = \frac{3\pi\epsilon_0\hbar c^3}{\omega^3 |\mathbf{d}_{fi}|^2} \quad (15)$$

The factor \mathbf{d}_{fi} is the matrix element of the electric dipole moment between the initial and final state of the transition. Substituting eq 15 into eq 14, we finally obtain

$$\frac{\tau_{1f}}{\tau_{2f}} = \frac{|\mathbf{d}_{2fi}|^2}{|\mathbf{d}_{1fi}|^2} \quad (16)$$

Bearing in mind that oligothiophene 1 is a symmetric molecule (having CHO substituents at both edges of the main chain) while oligothiophene 2 is a nonsymmetric molecule (having H and CHO substituents), it is concluded that

$$|\mathbf{d}_{1fi}|^2 < |\mathbf{d}_{2fi}|^2 \quad (17)$$

as the dipole (CHO...H) is stronger than the dipole (CHO...CHO). Combining eq 16 and the inequality in eq 17, we finally have

$$\tau_{1f} > \tau_{2f} \quad (18)$$

in agreement with the experimental results.

Conclusions

Two oligothiophenes have been synthesized and characterized by femtosecond time-resolved spectroscopy. The two oligothiophenes have the same molecular structure but different substituents (H instead of CHO) at one edge of the main chain. The isotropic and anisotropic parameters of their fluorescence have been measured. Comparing the parameters of the two oligothiophenes, we conclude that they have the same anisotropic but different isotropic behaviors. Particularly, the similarity of their anisotropic behaviors is attributed to the fact that the two oligothiophenes have the same main structure (i.e., shape and volume). However, the difference in their isotropic behavior

is attributed to the change in the substituent at one edge of the main chain. The initial anisotropy indicates that the absorption and emission dipoles are not parallel but form an angle. The values of this angle for both oligothiophenes have been calculated.

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