Optical Properties of Quaterthiophenes and Their Dimers End-Capped with Electron-Withdrawing Hexyl-Dicyanovinyl Groups

Yuriy Luponosov, Nikolay Surin and Sergey Ponomarenko

ABSTRACT

In this work the optical properties of novel quaterthiophene-based materials, D1 and D2, having both flexible alkylsiloxane core and electron-withdrawing hexyl-dicyanovinyl (DCV) groups, as well as their model DCV-containing quaterthiophene oligomers 1 and 2 were studied and compared. The results revealed that the number of both DCV and quaterthiophene units influences significantly on absorption and luminescence spectra of the molecules as well as their molar extinction coefficients. As compared to the model α,α′-dihexylquaterthiophene without DCV groups the electronic spectra of the novel molecules are red-shifted up to 100-160 nm.

INTRODUCTION

Macromolecules consisting of thiophene repeating units are of significant interest to researchers from the point of view of their applications as functional materials in organic electronics and photonics.[1] Thiophene-containing oligomers are promising classes of small molecule semiconductors due to their high thermal and thermo-oxidative stability in additional to high charge carrier mobility.[2] However, oligothiophenes poorly absorb sunlight and have emission usually in
short-wave region of the visual spectrum, which limits their application in organic solar cells and organic light emitting devices. In order to shift absorption and luminescent spectra of oligothiophenes to the long-wave region the modification with strong acceptor (A) groups can be used.[3,4] Dicyanovinyl groups are widely used to design various donor-acceptor molecules for organic electronics.[5-8] In this work, we study optical properties of a series of molecules containing quaterthiophene and dicyanovinyl units (Figure 1).

**DISCUSSION**

The optical properties were studied by means of absorption and luminescence spectroscopy and the data are summarized in Figure 2 and Table 1). The spectra were recorded over a range of 250-800 nm in dilute solutions in tetrahydrofurane (THF) (UV-grade) with a concentration of 10^{-5}-10^{-6} M in order to avoid self-absorption. The luminescence measurements were performed on an ALS01M multifunctional absorption-luminescence spectrometer. The absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer (Japan). The synthesis of the molecules will be published elsewhere.

The shape of absorption spectra for all molecules under discussion is quite similar. The low intensive absorption peaks at 330–370 nm usually are ascribed to the π-π* transition of the conjugated backbone, whereas the intense absorption band with absorption maximum (λ_{abs}) close to 500 nm, respectively, are ascribed to the intramolecular charge transfer transition. However, both electronic bands are also suggested to have a mixed character and the intensity of the absorption feature in the short-wave part of the spectrum is a direct measure of the degree of conformational disorder in the molecule.

![Figure 1. Structural formulas of compounds 1, 2, D1 and D2.](image-url)
The molar extinction coefficient ($\varepsilon$) tends to increase with increasing number of DCV groups and quaterthiophene units in the structure of molecules. The number of quaterthiophene units has no influence on the shape of luminescent spectra and their maximums ($\lambda_{\text{lum}}$). In contrast, the number of DCV groups has a pronounced effect on the luminescent spectra. Thus, the molecules with two DCV groups have more broadened and blue-shifted spectra as compared to the direct analogs with one DCV group. The quantum yield of luminescence ($Q_{\text{lum}}$) was found to be a bit higher for molecules 1 and 2 as compared to the dimers D1 and D2. The most interesting thing is a comparison of the optical properties of the molecules 1 and 2 to those of the direct analog without DCV groups – Hex-4T-Hex. One can see that addition of DCV blocks to the quaterthiophene fragment leads to a large enhancement in molar extinction coefficient and shifts the maxima of luminescence and absorption to a long-wave region up to 100 nm and 160 nm, respectively.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$)</th>
<th>$\lambda_{\text{lum}}$ (nm)</th>
<th>$Q_{\text{lum}}$ (%)</th>
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<tr>
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<td>43600</td>
<td>663</td>
<td>15</td>
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<tr>
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<td>498</td>
<td>58000</td>
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</tr>
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<td>497</td>
<td>93800</td>
<td>630</td>
<td>15</td>
</tr>
<tr>
<td>Hex-4T-Hex</td>
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<td>492</td>
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</tr>
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</table>

CONCLUSIONS

DCV derivatives of oligothiophenes have much larger molar extinction coefficients and significantly red-shifted absorption and luminescent spectra as compared to the model $\alpha,\alpha'$-dihexylquaterthiophene. Thus, the combination of number of DCV groups and quaterthiophene blocks can be an efficient tool to
change and finely tune the optical properties of oligothiophenes for various applications in organic electronic devices.

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