Unusual Solvatochromism of a New Conjugated Polymer Containing Oxadiazole

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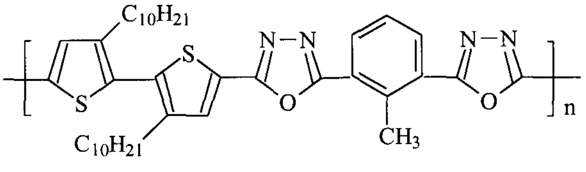
The spectroscopic properties of a new synthesized conjugated polymer constituted of 3,3'-didecyl-2,2'-bithiophene and 2,6-di-1,3,4-oxadiazole-toluene moieties in the mixed solvent system of chloroform (solvent for the polymer) and methanol (non-solvent for the polymer) were studied. An unusual solvatochromism either in absorption or in emission was observed for the first time on conjugated polymers containing oxadiazole.

In the past several years, polymers containing oxadiazoles have attracted more and more attention because they are effective electron-transporting materials and promising *n*-dope type light-emitting polymeric materials used in polymer light-emitting diodes (PLEDs).[1-5] However, to our knowledge, no effort has been devoted to the solvatochromism of this kind of conjugated polymers, which has been widely observed in other soluble conjugated polymers, especially substituted polythiophenes.[6-9] The solvatochromic properties make the conjugated polymers interesting for future applications and offer an effective way to understand their electronic behavior under various external conditions. The unnoticeable solvatochromism of oxadiazole-containing conjugated polymers may be in part ascribable to the poor solubility of most of these polymers in conventional solvents. Recently, a new highly soluble alternated diblock conjugated copolymer of 3,3'-didecyl-2,2'-bithiophene and 2,6-di-1,3,4-oxadiazole-toluene (PDBTDOT) was synthesized in our laboratory.[10] Beside the good light-emitting properties and *n*-dope type feature, unusual solvatochromism was observed on this new conjugated polymer. The brief results of the solvatochromic studies will be reported in this letter.



PDBTDOT

The stock solution of PDBTDOT was prepared by dissolving 10.0 mg sample in 250 cm^3 chloroform. 0.5 cm^3 of the stock solution was put into a volumetric flask with the capacity of 10 cm^3, then calculated amount of chloroform was added, and the rest volume was charged by methanol. Therefore, the concentration of PDBTDOT in all mixed solvents was maintained at 2.0×10^{-3} mg·cm^{-3}. UV-visible and fluorescence spectra were recorded on a Shimadzu UV-1601 and Perkin Elmer PL-50B spectrometers, respectively. All the measurements were carried out with a 1-cm quartz cell at room temperature.

The increase of the volume fraction of methanol (α) in the PDBTDOT solutions causes a progressive color change from colorless to yellow. The UV-visible spectra in $CHCl_3$/MeOH mixtures with different α are displayed in Figure 1. From 0 to 0.35 (curves 1 and 2), no change can be detected in absorption spectrum, characterized by a single structureless band centered at 341 nm. From 0.35 to 0.5 (curves 2, 3, and 4), one can notice a decrease of the absorption at 341 nm, whereas a set of three shoulders emerge around 393, 418, and 445 nm. This spectral change corresponds to disorder to order transformation of the conjugated polymeric chains, which has been widely demonstrated for other substituted conjugated polymers.[6-9] By 0.65 of α, the conformational transformation forced by the addition of the non-solvent of methanol has been completed, indicated by a lack of change upon further increase of α. With this conformational transformation, the absorption maximum of PDBTDOT changes from 341 nm to 389 nm with the appearance of three shoulders around 340, 418, and 445 nm.

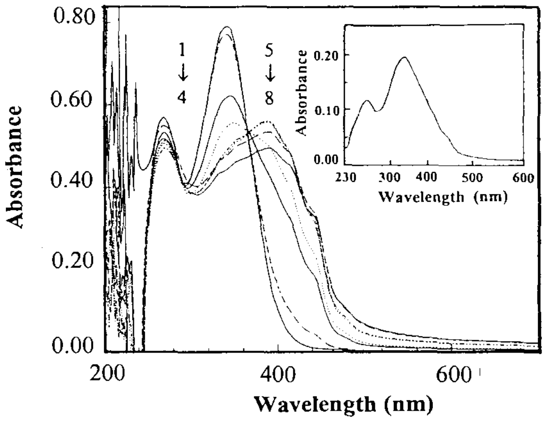


Figure 1. UV-visible absorption spectra of PDBTDOT in the mixture of chloroform and methanol with the volume fractions of methanol α: 0 (1), 0.35 (2), 0.45 (3), 0.50 (4), 0.65 (5), 0.75 (6), 0.85 (7), and 0.90 (8). Inset: UV-visible absorption spectrum of the cast film of PDBTDOT.

Surprisingly, we find that the λ_{max} of PDBTDOT in the mixed solvents with the α being larger than 0.65 is much longer than that in solid state (cast film on quartz plate from the solution of chloroform).[11] The absorption spectrum of PDBTDOT in the cast film is also given in Figure 1 as inset for comparison, which shows the absorption maximum at 352 nm without obvious well-defined vibronic peaks. The results imply that PDBTDOT has more extended structure showing a longer effective average conjugated length in the MeOH-rich mixed solvents than that even in its cast film.

The solvatochromic nature of PDBTDOT is more manifest in emission properties. Figure 2 displays the fluorescence spectra taken with 350-nm excitation in the same solvent systems. In pure chloroform (α = 0), the emission spectrum shows a peak centered at 462 nm with a shoulder at 444 nm. In the mixed solvent with α of 0.35, the emission peak has red-shifted to 491 nm with two shoulders around 444 nm and 525 nm respectively. It indicates that the emission properties are more sensitive to the addition of non-solvent than absorption properties. When the α reaches 0.45, the shoulder at 525 nm grows to an emission peak. Further increase of α induces an increase of the relative intensity of the new emission peak. By 0.75 of α, the intensity of the peak at 525 nm exceeds that at 491 nm. The results indicate that the emission color of PDBTDOT can be tuned from blue to green by controlling the environmental conditions. Like the situation in absorption properties, an unusual red shift of emission peak in MeOH-rich solvents with respect to that in solid states is also observed in emission spectra. The emission spectrum of PDBTDOT taken from its cast film with 380-nm excitation is displayed in the inset in Figure 2, which shows an emission peak at 490 nm and a shoulder at 525 nm.

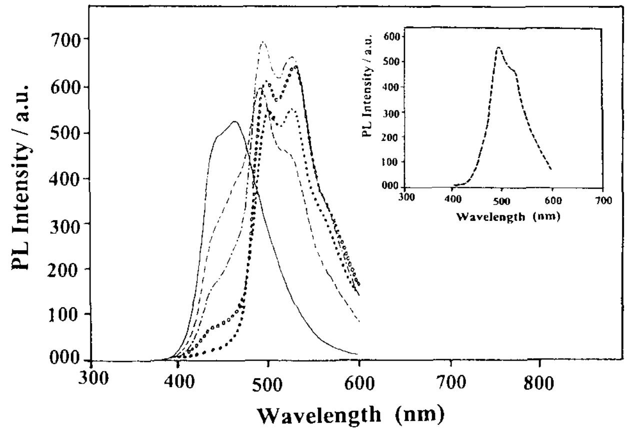


Figure 2. Fluorescence spectra of PDBTDOT in various $CHCl_3$ — MeOH mixtures (excitation at 350 nm). The volume fractions (α) of methanol are 0 (—), 0.35 (----), 0.50 (-·-·), 0.65 (······), and 0.75 (oooooo). Inset: Fluorescence spectrum of PDBTDOT in cast film.

Generally the solvatochromism can be explained by the conformational change of the segment of substituted bithiophene in PDBTDOT with the variation of the solvent condition, which causes the change of effective average conjugated length along the backbones of the molecules. This is supported by the spectral studies for other oxadiazole-containing conjugated polymers. Alternated copolymer of 3-octylthiophene and 1,3,4-oxadiazole and another diblock copolymer with similar chemical structure with PDBTDOT but replacing the substituted bithiophene with 3-octylthiophene were also synthesized by us. Although they were soluble in chloroform, no solvatochromism was found. The unusual red shift both of the absorption spectra and of the emission spectra of PDBTDOT in MeOH-rich solvents compared with those in solid states has not been understood. More detailed studies on the relationship between the chemical structure of the diblock conjugated copolymers and their optical properties are in progress in our laboratory.

References and Notes

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10 PDBTDOT was synthesized as brown powder. Gel permeation chromatography (GPC) measurement with THF as eluent and polystyrene as standard indicated M_w = 35,105 with the polydispersity of 1.41. ^1H NMR ($CDCl_3$), δ 8.17 (2 H), 8.16(2 H), 7.77 (1 H), 3.12 (3 H), 2.64 (4 H), 1.64-1.23 (28 H), 0.9 (6 H) ppm. ^{13}C NMR ($CDCl_3$), δ 163.6, 160.5, 144.6, 138.9, 132.4, 131.4, 126.5, 126.4, 125.2, 124.9, 31.8, 30.5, 29.5, 29.4, 29.2, 29.1, 29.0, 28.9, 22.6, 19.3, 14.0 ppm. Anal. Found: C, 68.34, H, 7.25, N, 7.98, S, 9.30; Calculated for $C_{39}H_{50}N_4O_2S_2$: C, 69.81, H, 7.51, N, 8.35, S, 9.56. The synthesis and characterization of PDBTDOT will be published in a forthcoming article.

11 The cast films were prepared by spin-coating the solution of 1.0 mg sample in 0.5 cm^3 chloroform on a quartz plate at a rate of 2,000 rpm for 2 min. Before spectral measurement, the films were dried under vacuum at room temperature for 2 h.