

PHOTOPHYSICAL BEHAVIORS OF OLIGOMER BASED ON 1,1'-BINAPHTHOL WITH 3,3'-ACETYLENE SPACER*

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Abstract The photophysical behaviors of the oligomer based on 1,1'-binaphthol with 3,3'-acetylene spacer were investigated. The oligomer molecule has a naphthyl-acetylene-naphthyl effective conjugation segment. The atropic of the 1,1'-binaphthyl moiety led to twisted and rigid main chain in the oligomer. With the changes of the external environment such as solvents used, solvent viscosity and ambient temperature, the wavelengths of absorption and the intensities of fluorescence and absorption are changed slightly, but the fluorescent intensity and quantum yield can be influenced. The luminescent behaviors of the oligomer exhibit twisted intramolecular charge transfer characteristics, which could have a potential application in wavelength-stable light emitting material adaptable to ambient temperature and the solvents used in wide range.

Keywords Photophysical behavior; Oligomer based on 1,1'-binaphthol; TICT fluorescence

INTRODUCTION

The conjugated polymers as processable active light-emitting diodes have been extensively developed^[1]. This is because the polymer's properties, such as solubility and emitting property, can be modified by chemical method to meet the desired emission wavelength. Recently, striking thermochromic, solvatochromic and piezochromic phenomena have been observed in some polythiophene derivatives^[2]. All these optical effects have been described in terms of a planar-nonplanar conformational conversion of the conjugated backbone. There is a strong correlation between the molecular structure and its photoluminescence behaviors of conjugated

* This work is supported by the National Natural Science Foundation of China and Tulane University

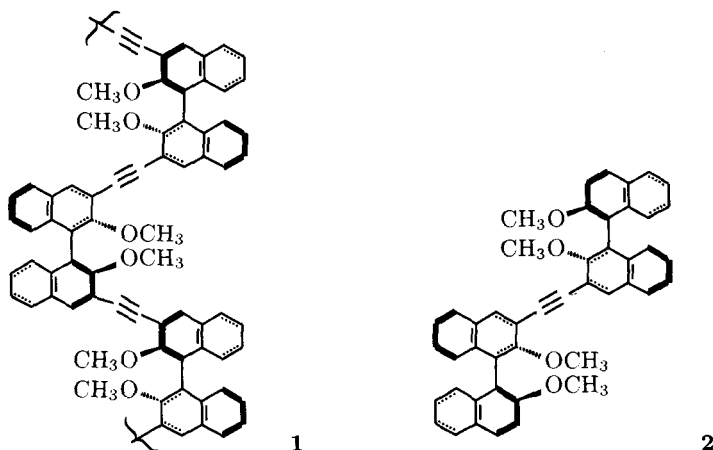
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Received September 6, 1997

polymers. On the basis of the results that the emitting properties can be modulated by the external environment, some thermosensitive devices and molecular or ionic detector have been designed^[3,4]. However, so far all conjugated polymers used for the study of photoluminescent properties only have a linear structure, such as PPV, PPE, etc. Herein, we wish to report the photophysical behaviors of the conjugated oligomer with twisted and rigid main chain, i.e. the oligomer based on 1,1'-binaphthol with 3,3'-acetylene spacer.

EXPERIMENTAL

The conjugated oligomer based on 1,1'-binaphthol with 3,3'-acetylene spacer (**1**)^[5] and corresponding dimer (**2**)^[6] were synthesized by modified Stille reaction, starting from 1,1'-binaphthol. The UV absorption spectra were recorded on a Hitachi 330 UV-Visible absorption spectrophotometer, the fluorescent and excitation spectra were recorded by Hitachi 850 Fluorescent spectrophotometer. The fluorescent quantum yields were determined by the following equation $\phi = \frac{\phi_0(n_x^2 S_F^x OD^R)}{(n_r^2 S_F^R OD^x)}$ with Rhodamine B ($\phi = 0.95$, solvent: ethanol) as reference. ϕ and ϕ_0 are the fluorescent quantum yield of oligomer and reference sample. n_x and n_r are the refractive index, S_F^x and S_F^R are the integral area of the fluorescent spectra of oligomer and reference sample. OD is the optical density of the corresponding absorptions. The solvents used were purified according to the methods described in the reference^[7].



RESULTS AND DISCUSSION

The oligomer **1** was characterized as having main chain chirality, i.e. helical

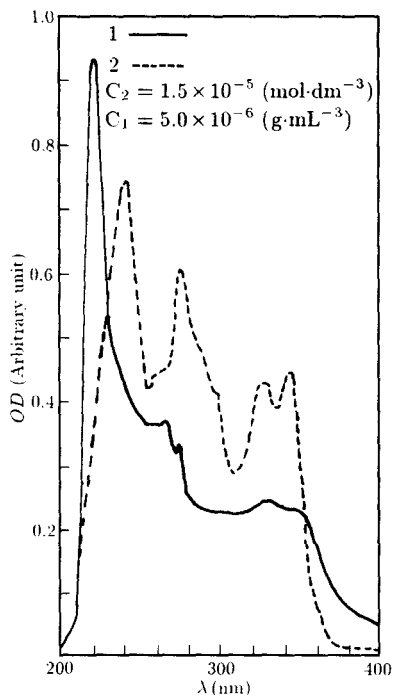


Fig. 1 Absorption spectra of **1** and **2**

tion and emission spectra seems to have a macroscopic symmetry, but with slight differences in detail, which implies that the conformations between ground state and excited state are somewhat different. Compared with to the ground state, some bond twisting, solution relaxation and change of the electronic structure in the excited state probably occur. This exhibits general characteristics of rigid chromophore. Otherwise, the fluorescent quantum yield of **1** in toluene is only 0.14. Obviously, the twisting conformation of the 1,1'-binaphthyl moiety would interfere the extension of the conjugation existing in the NAN segment, reducing the delocalization along the molecule backbone.

structure^[5]. Fig.1 displays the absorption spectra of the oligomer **1** and dimer **2**. The absorptions were observed at 350 nm ($\epsilon_{\max} = 6.9 \times 10^4$) for **1** and 345 nm ($\epsilon_{\max} = 2.0 \times 10^4$) for **2**, respectively. It indicates that although twisting conformation exists in the oligomer molecule, some conjugated characteristics still appear at longer wavelength. The nearly same maximum wavelengths of oligomer and dimer show that they have the same effective conjugation segment, naphthyl-acetylene-naphthyl (NAN) moiety. The excitation spectra (Fig. 2) exhibit vibronic excitations at the same five wavelengths as in the absorption spectra, but with the different intensities for each peak. Under excitation at the different wavelengths, the oligomer **1** has almost the same emission wavelength (Fig. 2). The shape of the absorp-

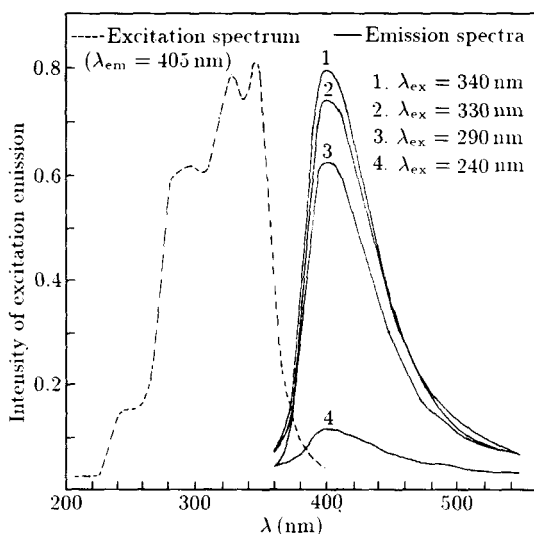


Fig. 2 Excitation and emission spectra of **1**

Fig. 3 is the fluorescent spectra of the oligomer in different solvents. It is inter-

esting to note that the fluorescent wavelength has slight change in different solvents used, excited at 342 nm with emission at 402~406 nm. Table 1 shows that the molar extinction coefficient constant ($\epsilon_{\max}$) and wavelength ($\lambda_{\max}$) of UV absorption at long wavelength are also changed slightly with various solvents. As indicated above, the oligomer **1** has highly ordered and rigid structure, the interaction between the solvents and the oligomer molecules is not great enough to influence the effective conjugation segment in the main chain of **1**. So that the λ_{em} of fluorescence and the $\lambda_{\max}$ and $\epsilon_{\max}$ of absorption spectra are solvent-independent. However, the emission intensities and the quantum yields (ϕ) in fluorescence spectra would change with the solvents used (Fig. 3 and Table 1). It is suggested that there are two main competitive nonradiation pathways for energy relaxation in the oligomer **1** (Fig. 4). One is the rotation of two naphthyl groups around the $C_1-C_{1'}$ bond (path A), which is crucial for the twisted intramolecular charge-transfer the other is the vibration of

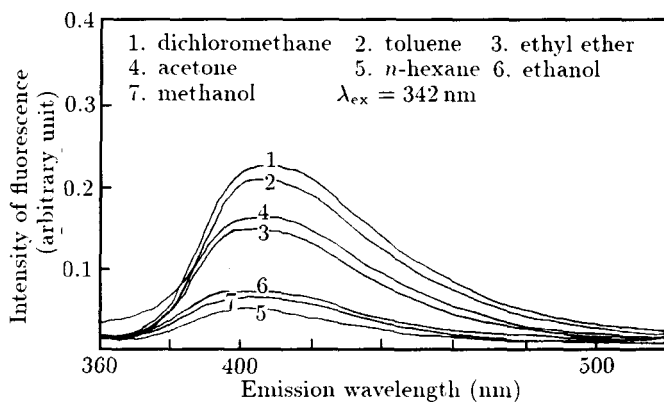
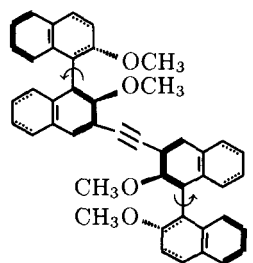


Fig. 3 Fluorescence spectra of **1** in different solvents



Path A: Rotation of naphthyl moieties
Path B: Vibration of MeO groups

Fig. 4 Scheme of two relaxation pathways

Table 1 Absorption and fluorescent data of **1** in different solvents^{a)}

Solvent	$\lambda_{\max}$ (nm) ^{b)}	$\epsilon_{\max} (\times 10^4 \text{ mol}^{-1} \text{ dm}^3)^{\text{c)}}$	λ_{em} (nm) ^{d)}	$\phi^{\text{e)}}$
Hexane	350.0	6.2	402.0	0.080
Toluene	348.0	7.0	406.0	0.14
CH ₂ Cl ₂	348.0	6.9	406.0	0.11
Acetone	348.0	6.4	404.0	0.13
Et ₂ O	346.0	6.8	402.0	0.20
THF	348.0	6.4	404.0	0.14
Ethanol	348.0	6.1	404.0	0.090
Methanol	348.0	6.0	404.0	0.080

a) at 22°C; b) absorption wavelength; c) molar extinction coefficient constants at $\lambda_{\max}$;

d) fluorescent wavelength; e) fluorescent quantum yield

the methoxy group (path B). The change of the ϕ with various solvents used can be ascribed to the solvent molecule clathrating or intercalating into the screwsense structure of the oligomer. Since the screwsense structure could get inclusion with some solvent molecules, this interaction has a great influence on the rotation of the binaphthyl and the vibration of methoxy groups, both of them is directly related to fluorescent intensity and quantum yield. Different solvent molecules have different ability to enter into the screwsense structure of the oligomer molecule, leading to the appearance of solvent-dependence of the fluorescent intensity and the quantum yield.

These twisted intramolecular charge transfer (TICT)^[8] fluorescent characteristics were also confirmed by the dependence of the viscosity of the solvents on the oligomer fluorescent intensity. Fig. 5 shows that the fluorescent intensity of the oligomer **1** decreases with increasing the portion of glycol in the glycol-methanol co-solvent system, i.e. with increasing the viscosity of the co-solvent used. When the solvent system with low viscosity is employed, the fluorescent intensity decreases greatly (cf. CH₃OH/glycol from 1:0 to 9:1). Obviously, viscose solvent system would slow down the rotation of 1,1'-binaphthyl group (path A) and reduce the interaction between oligomer and solvent molecules, leading to lower fluorescent intensity. However, the structure of oligomer is so rigid that the interaction between oligomer and solvent molecules does not change significantly with the increase of solvent viscosity, once the solvent system became viscous enough.

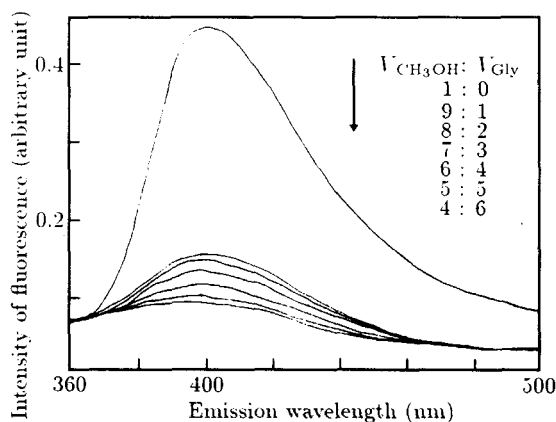


Fig. 5 Viscosity-dependence of intensity in fluorescent spectra of **1**

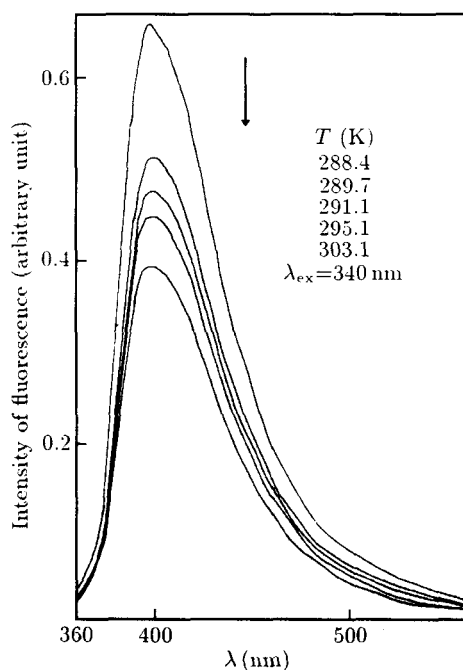


Fig. 6 Temperature-dependence of intensity in fluorescent spectra of **1**

The temperature-dependence of the fluorescent intensity in the oligomer **1** was examined. The λ_{em} does not change with temperature employed, but only fluorescent intensity changes with the ambient temperature. Experimental results show that when the ambient temperature increases from 0°C to 15°C, the fluorescent intensity enhances. However, when the temperature is over 15°C, the fluorescent intensity decreases with the increase of temperature of the system (Fig. 6). For the photophysical behavior of TICT state, under temperature below 15°C, increasing the temperature could promote the rotation of twisted moieties (path A), which results in enhancing the fluorescent intensity. However, when the temperature overpasses a critical point (over 15°C), increasing the temperature would be more favorable to the vibration of the methoxy group (path B) and enhancing the collision between molecules of the solvents and oligomer. It is suggested that path B, as well as enhancement of the collision would lead to decrease of the fluorescent intensity.

It is clear from the results of this investigation that as a twisted conjugated oligomer, the photophysical properties of **1** are very different from that of linear conjugated polymer, such as polyphenylethylene^[9] and polythiophene^[2,3]. For linear conjugated polymers, their effective conjugation segments are sensitive to the external environment. This is ascribed to that the changes of external elements are able to induce the planar-nonplanar conversion along the conjugated chain, leading to the change of absorption and fluorescent wavelength. However, for oligomer **1**, the NAN segments are connected with each other at 1,1'-position of 1,1'-binaphthyl moiety, forming twisted and rigid structure, which results in TICT luminescent characteristics of oligomer **1**. Therefore, the NAN segment is not able to be changed with external environment, such as the changes of solvents used, solvent viscosity and ambient temperature. This TICT luminescent characteristic could have a potential application as a light emitting material adaptable to the ambient temperature and solvents used in wide range.

CONCLUSION

The oligomer based on 1,1'-binaphthol with 3,3'-acetylene spacer has twisted and rigid conjugated structure. The effective conjugation segment is NAN moiety. With the change of external environment, such as solvents used, solvent viscosity and ambient temperature, the effective conjugated segment is changed slightly, leading to a minute change in the fluorescent and absorption wavelengths. However, external environment would influence the rotation of 1,1'-binaphthyl group around C₁—C_{1'} bond, resulting in a change of the fluorescent intensity and quantum yield. On the

basis of the photophysical behaviors of **1**, a TICT luminescent pathway is suggested, which could have a potential application in wavelength-stable light emitting material adaptable to the ambient temperature and solvents used in wide range.

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