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Spectroscopic investigations of a novel tricyanofuran dye for nonlinear optics

Likun Han, Yadong Jiang *, Wei Li, Yuanxun Li, Peng Hao

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

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Abstract

A novel tricyanofuran dye was synthesized and the dye-in-polymer films were fabricated by spin-coating process. The spectroscopic properties of the dye in the solutions and polymer films were investigated by the absorption spectra and fluorescence emission spectra. It is found that the absorption and fluorescence maxima are largely red-shifted along with the increase of the solvent polarity. And the low values of fluorescence quantum yield in higher polarity solvents suggest the presence of twisted intramolecular charge transfer states of the dye. Moreover, the second order polarizability value of the novel dye was estimated based on the quantum-mechanical two-level model.

Keywords: Spectroscopic properties; Quantum yield; Stocks shift; Second order polarizability

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1. Introduction

Conjugated organic dyes with electron donor (D) and acceptor (A) substituents have attracted considerable attention because of their remarkable intramolecular charge transfer (ICT) properties and their related second order nonlinear optical (NLO) response, with potential applications for optical data storage, optical signal processing and optical switches [1–3].

In this paper, a novel D-π-A type organic dye (DCDHF-2-V) containing a tricyanofuran acceptor was synthesized and the spectroscopic properties of the dye in different solutions and polymer films were investigated. The spectroscopic studies indicate that the DCDHF-2-V molecule is sensitive to the polarity of the medium and the polarity dependence may be explained in terms of twisted intramolecular charge transfer (TICT) processes. The second order polarizability (β) was calculated based on the quantum-mechanical two-level model, which provides a firm basis for the potential applications of the dye to nonlinear optical devices.

2. Experimental

2.1. Materials

All chemicals were purchased from Alfa Aesar, and poly methylmethacrylate (PMMA) was purified by recrystallization before use. All solvents used were of spectroscopic grade.

2.2. Synthesis and characterization

According to the method reported in Ref. [4], a new tricyanofuran dye (DCDHF-2-V) was synthesized and its reaction scheme is shown in Fig. 1. Crude products were recrystallized from methanol/dichloromethane (1:1).

DCDHF-2-V: dark green, yield: 78%, mp: 243–245 °C. ^{1}H-NMR ($CDCl_3$): δ: 1.25 (t, 6H), 1.74 (s, 6H), 3.49 (q, 4H), 6.70 (q, 2H), 7.53 (d, 2H), 7.60 (d, 2H). Anal. calcd for ($C_{22}H_{22}N_4O$): C 73.74, H 6.15, N 15.64; found: C 73.54, H 6.15, N 15.42; IR (KBr disc): γ (cm^{-1}) = 2924, 2378, 2222, 1560, 1522, 1375, 1261, 1190, 1149, 1105, 1078, 974.

2.3. Fabrication of DCDHF-2-V/PMMA films

The mixture of DCDHF-2-V and PMMA was dissolved in 1,2-dichloroethane. After the dye and polymer were dis-

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[*] Corresponding author. Tel.: +86 28 83207027; fax: +86 28 83206123.
E-mail address: jiangyd@uestc.edu.cn (Y.D. Jiang).

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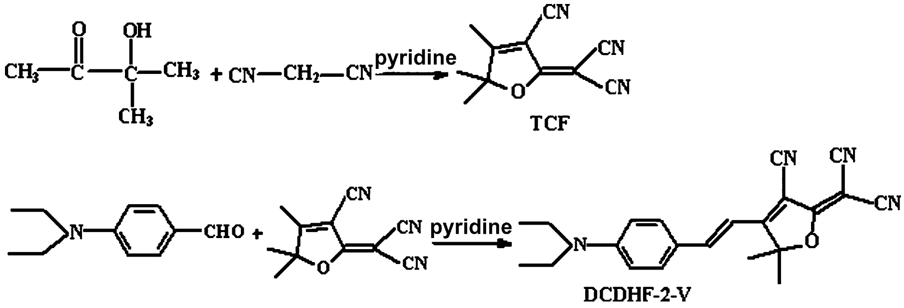

Fig. 1. Synthesis of DCDHF-2-V.

solved completely, the solution was filtered using 0.45 μm millipore filter. The polymeric thin films were prepared by spin-coating method on polished glass substrates and then heated at 70 °C overnight to remove any residual solvent.

2.4. Spectroscopic measurements

The absorption spectra were recorded using a Shimadzu UV-1700 spectrophotometer. The fluorescence emission spectra were recorded on a Hitachi F-4500 spectrofluorimeter at room temperature and the excitation wavelength is 550 nm. The fluorescence quantum yields Φ_f of DCDHF-2-V in organic solvents were calculated from the corrected fluorescence spectra using the following equation [5]:

$$\Phi_f = \Phi_{ref}\left(\frac{I_{dye}A_{ref}}{I_{ref}A_{dye}}\right)\left(\frac{n_{dye}}{n_{ref}}\right)^2 \quad (1)$$

where I_{dye} and I_{ref} are the integrated areas of the corrected fluorescence spectra, A_{dye} and A_{ref} are the absorbances at the excitation wavelength, n_{dye} and n_{ref} are the refractive indices of the solvents for the dye and reference, respectively. Rhodamine B in ethanol ($\Phi_{ref} = 0.97$ [6]) was used as the reference for quantum yield determination. The spectra of solutions were recorded at a dye concentration of 1×10^{-6} g cm^{-3} using a 1 cm thick cell.

3. Results and discussion

3.1. Spectroscopic properties of DCDHF-2-V in polymer film

The absorption spectrum of the tricyanofuran dye-in-polymer film is shown in Fig. 2. The dye has strong absorption in the visible region peaking at 554 nm. The absorption band is attributed to π–π^* transition in the conjugation system formed by the benzene ring, alkene group, diethylamino and tricyanofuran ring.

Fig. 3 shows the fluorescence spectrum of the tricyanofuran dye-in-polymer film at room temperature. In this figure, in addition to the main emission peak near 648 nm, an additional emission peak appears around 833 nm, which should be assigned to the photoisomerization process of DCDHF-2-V molecules in a PMMA matrix. Most of the organic conjugated molecules are expected to exist in a trans form in a rigid matrix, whereas the illumination of the molecules causes the trans form to isomerize to a cis form [7]. In a photostationary condition, it is possible to see the emission from a cis and trans isomer. The 648 nm band is attributed to the fluorescence from the excited state S_1 of a cis isomer and the 833 nm band is attributed to the fluorescence from S_1 state of a trans isomer [8].

3.2. Spectroscopic properties of DCDHF-2-V in different solvents

The absorption and fluorescence spectra of DCDHF-2-V in dioxane and dimethyl formamide (DMF) shown in Fig. 4

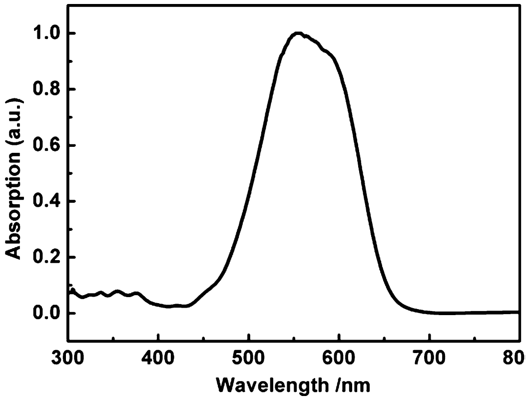

Fig. 2. Absorption spectrum of the spin-coated film.

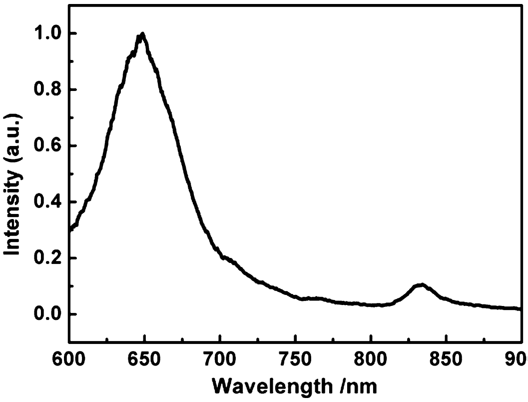

Fig. 3. Fluorescence spectrum of the spin-coated film.

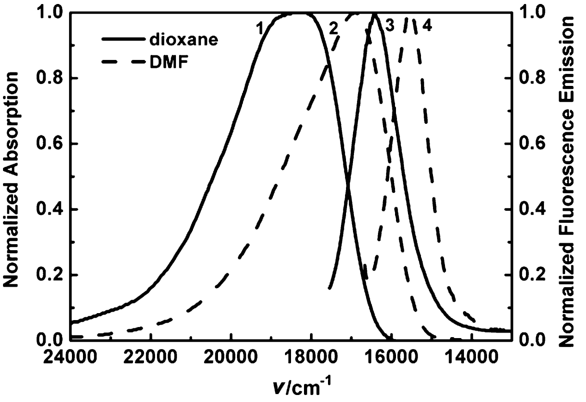

Fig. 4. Absorption (1, 2) and fluorescence (3, 4) spectra of DCDHF-2-V in dioxane and DMF.

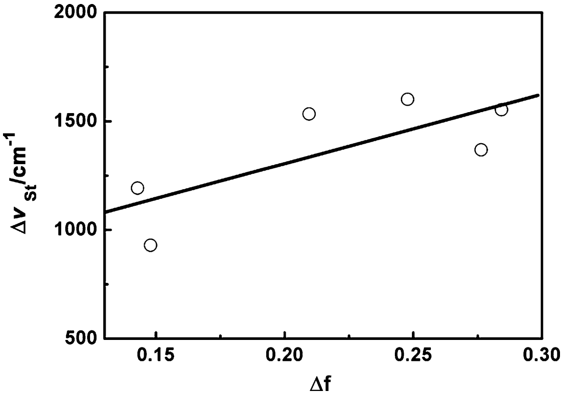

Fig. 5. Plot of Stocks shift Δv of DCDHF-2-V against the solvent polarity function Δf.

reveal a bathochromic shift (positive solvatochromism) when going from low polar dioxane to high polar DMF. The maximum values of bathochromic shifts are $1361\,\mathrm{cm}^{-1}$ for the absorption spectra and $814\,\mathrm{cm}^{-1}$ for the fluorescence ones (Fig. 4 and Table 1). This means that the dipole moment of the DCDHF-2-V molecule is higher in the excited state than in the ground state. The high intensity broad absorption band is assigned to transition from the ground state S_0 to the first excited singlet state S_1. The solvent dependency of the maximum of red-shifted emission band is the characteristics of the excited state charge transfer process. This type of excited state behavior is explained as intramolecular charge transfer (ICT) accompanied by a structural reorganization [9,10].

To understand spectral shifts with solvent polarity, it is important to correlate Stocks' shifts ($\Delta v_{\mathrm{St}} = v_{\mathrm{max}}^{\mathrm{abs}} - v_{\mathrm{max}}^{\mathrm{f}}$) with solvent parameter (Δf), which are expected to follow linear Lippert–Mataga relationship as [11,12]

$$\Delta v_{\mathrm{St}} = \Delta v_0 + \frac{2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})^2}{hcr^3}\Delta f \tag{2}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{3}$$

where μ_{e} and μ_{g} are the excited and ground state dipole moments, respectively, h is the Planck's constant, c is the velocity of light and r is the radius of the Onsager interaction sphere. ε and n are the dielectric constant and the refractive index of the solvent. Fig. 5 shows the Δv_{St} versus Δf plot for the dye in different polarity solvents. The plot is linear within experimental error. The slope k of the resulting straight line is equal to the term $2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})^2/hcr^3$ in Eq. (2). The value of k is obtained as $3397\,\mathrm{cm}^{-1}$. As a result of these calculations, it is found that $\Delta\mu = \mu_{\mathrm{e}} - \mu_{\mathrm{g}} = 33.09 \times 10^{-30}$ C m. Such a large change in the excited state dipole moment of the molecule seems to suggest corresponding large changes in the excited state configuration. One possible cause could be the geometrical distortion of the molecule in the excited state [13].

Fluorescence quantum yields (Φ_{f}) of DCDHF-2-V in different solvents at room temperature are listed in Table 1. It is seen that the fluorescence quantum yields are lower in high polar solvents as compared to low polar solvent like dioxane, which is assigned to the participation of non-emissive TICT states of the dye in higher polarity solvents [14]. According to this model, on electronic excitation, the molecule initially forms a moderately non-polar state with a geometry similar to that in the ground state. The transfer of an electron from an electron donor to an electron accepter group results in a twisted configuration of the molecule, in which the donor and accepter groups are oriented almost perpendicular to each other [13,15]. The stabilization of the excited state in polar solvents indicates that large extent of twisted intramolecular charge transfer is involved which results in the rapid radiationless decay of the excited state.

However, the quantum yield values in chlorinated solvents are significantly large, which may be due to the restriction in the formation of the TICT state, because of some specific interaction [16].

Table 1
The solvent parameters and spectral characteristics of DCDHF-2-V in different solvents

Solvent	ε	n	Δf	$\lambda_{\mathrm{max}}^{\mathrm{abs}}$ (nm)	$\varepsilon_{\mathrm{max}}$ ($\mathrm{L\,mol^{-1}\,cm^{-1}}$)	$\Delta v_{1/2\mathrm{h}}^{\mathrm{abs}}$ (cm^{-1})	f	$\lambda_{\mathrm{max}}^{\mathrm{f}}$ (nm)	Φ_{f}	β ($\mathrm{m^4/V}$, 1.9 μm) (mean value)
Dioxane	2.22	1.4224	0.0213	547	8.045×10^4	3312	1.2253	611	0.065	908.9×10^{-40}
Chlorobenzene	5.62	1.5248	0.1429	586	6.805×10^4	2682	0.7689	630	0.165	
Chloroform	4.81	1.4467	0.1479	588	8.683×10^4	2457	0.9811	622	0.113	
THF	7.58	1.4073	0.2095	572	7.442×10^4	3106	0.8409	627	0.057	
Cyclohexanone	18.2	1.4507	0.2478	583	14.211×10^4	2956	1.606	642	0.052	
DMF	38.3	1.4269	0.2764	591	12.758×10^4	2797	1.3054	643	0.027	
Acetone	20.7	1.3588	0.2843	578	11.553×10^4	2992	1.4416	635	0.024	

3.3. Evaluation of the second order polarizability β

On the basis of the data obtained, one can estimate the second order polarizability β of DCDHF-2-V, which is an important microcosmic data for NLO chromophores. The value of β can be derived from a two-level model [17]:

$$\beta = \frac{3e^2\hbar^2}{2m} \frac{W}{[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]} f\Delta\mu \tag{4}$$

Here e is the electron charge, $\hbar$ is the Planck's constant, m is the electron mass, W ($W = \hbar\omega_{\mathrm{eg}}$) is the energy difference between the ground and the first excited states of the dye, ω is the laser radiation frequency, f is the oscillator strength and $\Delta\mu$ is the difference between the dipole moment of the excited and the ground states. f is related to the intensity of the transition and can be gotten from the area under the band by means of Eq. (5) [18]:

$$f = 4.32 \times 10^{-9} \int \varepsilon(\omega)\mathrm{d}\omega \approx 4.32 \times 10^{-9} \times 1.0645 \varepsilon_{\max} \Delta v_{1/2} \tag{5}$$

where $\varepsilon_{\max}$ is the maximum of molar extinction coefficient and $\Delta v_{1/2}$ is the half-width of the absorption spectra in different solvents. The experimental values of DCDHF-2-V are listed in Table 1. It can be found that the second order polarizabilities of DCDHF-2-V is about 908.9×10^{-40} m^4/V at the wavelength of 1.9 μm.

4. Conclusions

In this paper, we have synthesized a novel tricyanofuran dye (DCDHF-2-V) and investigated the absorption spectra and fluorescence emission spectra of the dye in different solutions and a polymer matrix. A large bathochromic shift in the absorption spectra and emission spectra was observed when increasing solvent polarity, which is related to a difference between the dipole moments of a molecule in the ground and the excited states. Moreover, an increase in the solvent polarity leads to a decrease in the fluorescence quantum yield, which is explained by TICT. The second order polarizability β is calculated according to the two-level model and the high value of β allows to consider DCDHF-2-V as a promising material for NLO applications.

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