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Synthesis and characterization of a new fluorinated nonlinear optical chromophore

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Abstract

A new fluorinated azobenzene chromophore and its non-fluorinated analogue have been synthesized and characterized by UV–vis spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The hyperpolarizabilities were characterized through solvatochromic method and the dispersions of hyperpolarizabilities were studied in terms of the quantum-mechanical two-level model. In contrast with its non-fluorinated analogue, the new fluorinated chromophore exhibits a considerable hypsochromic shift of the absorption maximum and cut-off absorption wavelength, which could lead to a better transparency in operating wavelength of electronic devices. The results also show that the fluorinated chromophore possesses higher thermal stability and the same order of the hyperpolarizability comparing with its non-fluorinated analogue.

Keywords: Fluorinated chromophore; Hyperpolarizability; Solvatochromic method; Nonlinear optical materials

1. Introduction

Organic polymeric second-order nonlinear optical (NLO) materials have attracted steady attention for several decades because of their potential application in integrated optical devices such as optical switching, frequency conversion, and high-speed electro-optic (EO) devices [1–5]. Materials for electro-optic and frequency doubling applications must not only have high nonlinearity, but also require good thermal and chemical stability and low optical loss. Unfortunately, organic chromophores synthesized for incorporation into nonlinear optical polymers typically exhibit tradeoffs between nonlinearity and each of the other properties. For example, some of chromophores have extremely high optical nonlinearities, but only limited thermal stabilities (decomposition temperatures <250 °C) [6–8]. Furthermore, the low energy tails of the electronic absorption bands can extend several hundreds of nanometers into the long wavelength region. Because the long tails of absorption is the primary source of optical loss in NLO materials, even a small absorption at the operating wavelength of electro-optical devices (typically 1.3 or 1.5 μm) can be detrimental. Therefore, it is very important to make NLO chromophores as transparent as possible. Fluorinated materials exhibit a comprehensive combination of high thermal stability, chemical inertness and low dielectric constant. Pitois et al. [9] reported that incorporation of fluorine into the chromophores could offer promising opportunities for increasing transparency. Furthermore, the results from ZINDO-SOS theoretical calculation strongly suggested that the electronegative fluorine substituted systems that are weak π-donors and strong δ-acceptors can be used to produce highly efficient chromophores [10]. Recently, Jen and co-workers [11,12] and Qin and co-workers [8] reported that some fluorinated chromophores were incorporated into polymer as guests and exhibited good

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properties. However, these fluorinated chromophores have less reactive functional group, so that it is difficult to incorporate them into polymer through covalent bond. The guest–host NLO polymer materials have some fatal disadvantages such as fast decay of nonlinear optical activity due to orientational relaxation. In order to optimize the transparency, thermal stability, and nonlinearity for the application of NLO chromophores, we designed a new fluorinated chromophore containing amine groups, which can be easily incorporated into polymer through covalent bond. This paper reports this new fluorinated chromophore that exhibits a comprehensive combination of good transparency, high thermal stability, and nonlinearity.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich, Merck, and Clariant and were used without further purification.

2.2. Synthesis and characterization

A new fluorinated chromophore, 2,4-diamino-2′-fluoro-5′-nitroazobenzene (2R-2F-5N-DIAMINE), was synthesized via the one-step diazonium coupling reaction of 2-fluoro-5-nitrobenzene diazonium salt with 1,3-phenylenediamine. Sodium nitrite (1.41 g, 0.0205 mol) was added to 30 ml of 98% sulfuric acid at a temperature below 10 °C and stirred for 10 min, the solution was then heated in a water bath to 65 °C until the solution was clear. 2-Fluoro-5-nitroaniline (3.20 g, 0.0205 mol) was added to the above solution at a temperature between 0 and 5 °C, stirred for 2 h and filtered. The filtrate was coupled with 1,3-phenylenediamine (2.18 g, 0.0202 mol) dissolved in 200.0 ml of water at a temperature between 0 and 5 °C for 30 min. Then sodium acetate (23.0 g, 0.28 mol) was added, the solution was left in an ice bath for 1 h. After that, additional sodium acetate (23.0 g, 0.28 mol) was added, and the reaction mixture was left for 0.5 h. Once the temperature was raised to room temperature, a 20% sodium hydroxide solution was added until the pH value of the solution reached 7 and the mixture was stirred at room temperature for 1 h. The resultant 2R-2F-5N-DIAMINE was then washed with water and recrystallized twice. For comparison, the non-fluorinated analogue, 2,4-diamino-4′-nitroazobenzene (2R-DIAMINE) was synthesized and purified as described elsewhere [13].

^{1}H NMR spectrum was measured in dimethyl sulfoxide-d_6 (DMSO-d_6) using Bruker 400 MHz instrument. Elemental analysis was performed by Eurovector elemental analyzer. Analytical calculation for $C_{12}H_{10}N_5O_2F$: C, 52.36; H, 3.64; N, 25.45; O, 11.64; F, 6.91. Found: C, 52.31; H, 3.62; N, 25.37; O, 11.71; F, 6.99. The decomposition temperature was studied using a Hi-Res TGA 2950 thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen atmosphere (50 cc/min). Melting point was determined through DSC analysis that was performed by a TA Instruments 2010 at 5 °C/min in nitrogen atmosphere (50 cc/min). The UV–vis spectra were measured with a Shimadzu model UV-2501PC spectrophotometer. The hyperpolarizabilities of the chromophores were measured by solvatochromic method.

3. Results and discussion

The structures of designed 2R-2F-5N-DIAMINE and its non-fluorinated analogue 2R-DIAMINE are shown in Fig. 1. 2R-2F-5N-DIAMINE was characterized by ^{1}H NMR spectrum and element analysis. ^{1}H NMR spectrum of 2R-2F-5N-DIAMINE is shown in Fig. 2 and its structure was confirmed. From Fig. 1, it can be seen that there are two amine groups in both chromophores. It is the amine groups in the chromophores that make the chromophores to be easily incorporated into polymer matrix through covalent bond and therefore avoid orientational relaxation and increase the thermal and chemical stability. The UV–vis absorption spectra shown in Fig. 3 were measured in a solvent of DMSO. The absorption between 300 and 700 nm is mainly due to the π–π* and n–π* electronic transitions of the azobenzene chromophore [14]. It can be found that the maximum absorption wavelengths, λ_{max}, of 2R-2F-5N-DIAMINE and 2R-DIAMINE are 478 and 524 nm, respectively, and their cut-off absorption wavelengths are about 678.5 and 745 nm, respectively. The dramatically blue-shifted λ_{max} of 46 nm and $\lambda_{cut\text{-}off}$ of 66.5 nm can be obtained. The results indicate that 2R-2F-5N-DIAMINE has better transparency than 2R-DIAMINE. Both incorporation of fluorine into the chromophore and the NO_2 group in the meta position could be attributed to the better transparency of 2R-2F-5N-DIAMINE. Generally, the fluorine group is a strong electron withdrawing group in inductive effect and also a weak electron donating group in resonance effect. And the NO_2 group in meta position cannot form the conjugated system. It might be the NO_2 group in meta position and the fluorine group that

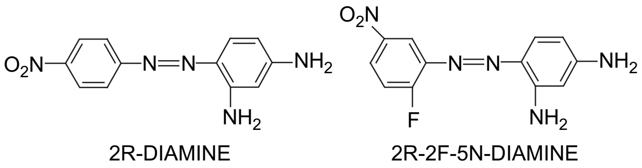

Fig. 1. Structures of 2R-DIAMINE and 2R-2F-5N-DIAMINE.

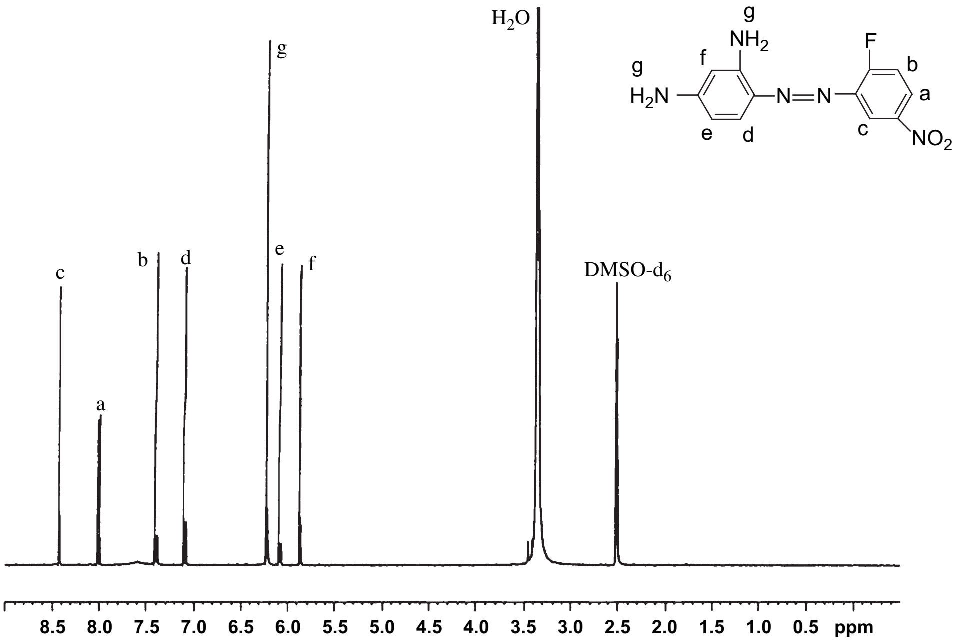

Fig. 2. ^{1}H NMR spectrum of 2R-2F-5N-DIAMINE measured at DMSO-d_6.

increase the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LOMO), leading to a decrease of the λ_{max} and $\lambda_{cut\text{-}off}$. UV–vis absorption results suggest that 2R-2F-5N-DIAMINE could lead to a low optical loss when it was incorporated into polymers. As 2R-2F-5N-DIAMINE can be dissolved in chloroform, tetrahydrofuran, ethanol, acetone, and DMSO etc., 2R-2F-5N-DIAMINE can be easily incorporated into NLO polymer through covalent bond.

TGA results of the 2R-DIAMINE and 2R-2F-5N-DIAMINE shown in Fig. 4 reveal that the initial decomposition temperature of 2R-2F-5N-DIAMINE is 270 °C, which is 28 °C higher than that of 2R-DIAMINE. This indicates that the fluorinated chromophore 2R-2F-5N-DIAMINE can effectively improve the thermal stability. 2R-2F-5N-DIAMINE has better thermal stability because the bond energy of the C–F bonds (456–486 kJ/mol) is higher than that of the C–H bonds (356–435 kJ/mol). It is the stronger C–F bonds that contribute to the higher thermal and oxidative stabilities of organofluorine compounds [15].

The hyperpolarizability was determined using solvatochromic method, as described in previous literatures

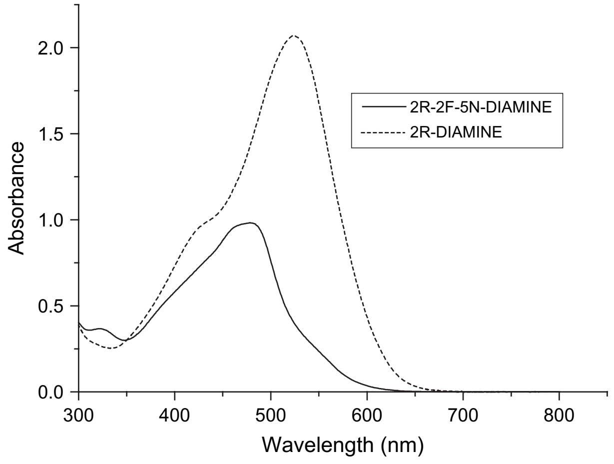

Fig. 3. UV–vis absorption spectra of 2R-DIAMINE and 2R-2F-5N-DIAMINE.

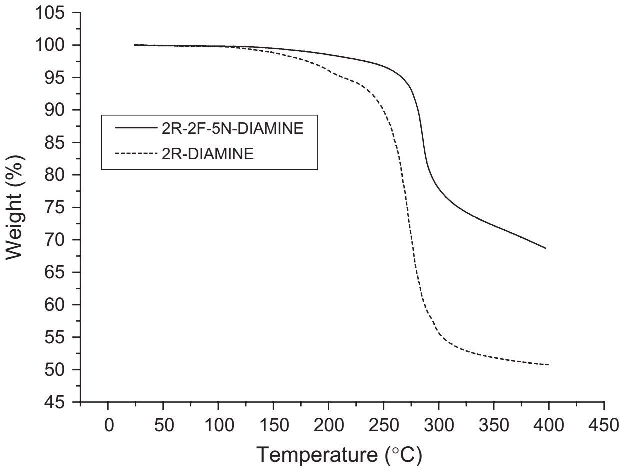

Fig. 4. TGA of 2R-DIAMINE and 2R-2F-5N-DIAMINE.

Table 1
Physical and NLO properties of 2R-2F-5N-DIAMINE and 2R-DIAMINE(1 D = 10^{-18} esu = 3.3564×10^{-30} C m, $\beta_{esu} = (c/4\pi)\beta_{SI} = 2.386 \times 10^9\beta_{SI}$)

	λ_{max}[a] (nm)	M_p (°C)	T_d (°C)	μ_g ($\times 10^{-29}$ C m)	μ_e ($\times 10^{-29}$ C m)	β_0 ($\times 10^{-40}$ m^4/V)
2R-2F-5N-DIAMINE	478	194	270	4.31	5.42	78.6
2R-DIAMINE	524	229	242	3.31	5.1	126

[a] Measured in dimethyl sulfoxide.

[16,17]. The two-level model yields the following expression for the hyperpolarizability β:

$$\beta = \frac{3}{2h^2c^2}\frac{\nu_{eg}^2\gamma_{eg}^2\Delta\mu_{eg}}{\left(\nu_{eg}^2-\nu_L^2\right)\left(\nu_{eg}^2-4\nu_L^2\right)}$$

where ν_{eg} and γ_{eg} are, respectively, the transition frequency (cm^{-1}) and transition dipole moment, $\Delta\mu_{eg}$ is the difference between the excited state (μ_e) and the ground state (μ_g) molecular dipole moment, ν_L is the frequency of the incident radiation, to which the β value is referred, h and c are Planck's constant and velocity of light, respectively. Above parameters were determined by spectroscopic measurements and the results are listed in Table 1. Results show that the static hyperpolarizability (β_0) of 2R-2F-5N-DIAMINE is about 78.6×10^{-40} m^4/V, which is lower than that of 2R-DIAMINE. Fig. 5 shows the dispersions of the hyperpolarizabilities calculated in terms of the quantum-mechanical two-level model. From Fig. 5, it is possible to estimate the hyperpolarizability of the chromophore in a specific wavelength. Generally, when fluorine is incorporated into the molecule structures, the hyperpolarizabilities will decrease [8]. The decrease in β may be attributed to several factors, such as the NO_2 group located in meta position, the weaker π electron donating, and the stronger δ electron withdrawing ability of fluorine group.

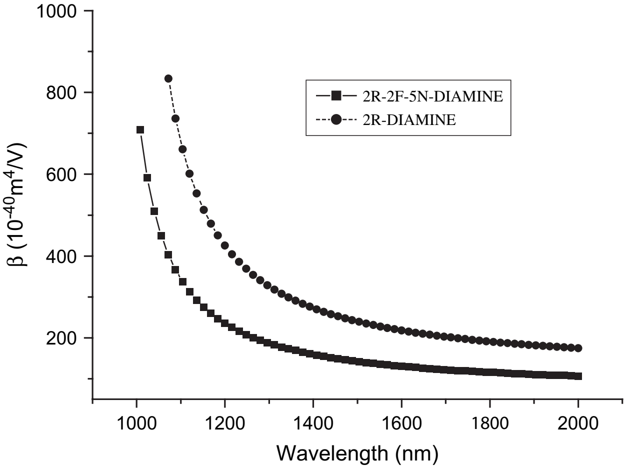

Fig. 5. Dispersions of the hyperpolarizabilities of 2R-DIAMINE and 2R-2F-5N-DIAMINE.

4. Conclusions

In summary, a new fluorinated chromophore 2R-2F-5N-DIAMINE is successfully synthesized. In comparison with its non-fluorinated analogue, the fluorinated chromophore displays a significant blue-shift of 46 nm for λ_{max} and 66 nm for $\lambda_{cut\text{-}off}$, a 28 °C higher decomposition temperature, and about the same order of high hyperpolarizability of its non-fluorinated analogue. The developed new chromophore shows a comprehensive combination of very good transparency, high thermal stability, and nonlinearity.

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