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Synthesis and characterization of fluoronitroaryl azo diaminobenzene chromophores

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Abstract—The novel fluoronitroaryl azo diaminobenzene chromophores for potential NLO applications were synthesized and the effects of the position of the fluorine group on the properties of the chromophores were investigated. These chromophores exhibit high decomposition temperatures whilst keeping molecular hyperpolarizabilities similar to those of the non-fluorinated analogues. The chromophore 2,4-diamino-4′-fluoro-3′-nitroazobenzene (2R-4F-3N-DIAMINE) shows a significant UV blue shift and a combination of good transparency, high thermal stability and nonlinearity in comparison with 2,4-diamino-2′-fluoro-5′-nitroazobenzene (2R-2F-5N-DIAMINE) and its non-fluorinated analogue 2,4-diamino-3′-nitroazobenzene (2R-3N-DIAMINE).

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] Organic nonlinear optical chromophores, which exhibit good properties such as high thermal and chemical stability, high nonlinearity, and transparency as well the capability to be incorporated easily into polymers through covalent bonds, are currently being pursued for the next generation of high-performance photonics devices. This letter reports the synthesis and characterization of fluoronitroaryl azo diaminobenzene chromophores (Fig. 1), which exhibit a combination of good transparency, high thermal stability, and nonlinearity.

Organic chromophores synthesized for incorporation into nonlinear optical polymers typically exhibit trade-offs between nonlinearity and each of the other properties.[2] For the application of organic nonlinear optical materials, it is very important to optimize the comprehensive properties, especially the transparency, because the low energy tails of the electronic absorption bands can extend several hundreds of nanometers into the long wavelength region.[3] The long tails of absorption is the primary source of optical loss in NLO materials so that even a small absorption at the operating wavelength of electro-optical devices (typically 0.8, 1.3, and 1.5 μm) can be detrimental. Fluorinated materials were reported to exhibit a combination of high thermal stability and optical transparency, chemical inertness, and low dielectric constant.[4] The results from ZINDO-SOS theoretical calculations also strongly suggested that the electronegative fluorine substituted systems that possess weak π-donors and strong δ-acceptors could be used to produce highly efficient chromophores, for example, the β value of the chromophores containing a pentafluorophenyl acceptor are approximately half as potent as those with a 4-nitrophenyl acceptor.[5] Recently, Jen[6] and Qin[7] reported that some highly fluorinated chromophores can be incorporated into polymers as guests and exhibit good properties. However, these highly fluorinated chromophores have fewer reactive functional groups and so it is difficult to incorporate them into polymers through covalent bonds. Guest–host NLO polymer materials have some fatal disadvantages such as the fast decay of nonlinear optical activity due to orientational relaxation. In order to find better chromophores for application in nonlinear optics, we designed and synthesized two new fluorinated chromophores containing amino groups and a non-fluorinated analogue through a simple azo coupling reaction, which can be easily

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Keywords: Chromophore; Fluorine; Hyperpolarizability; Nonlinear optical materials.

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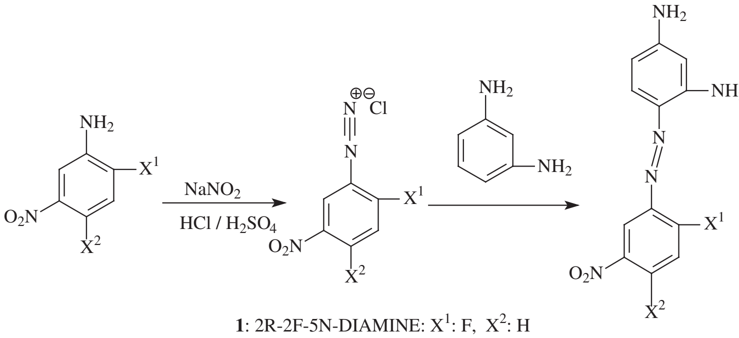

1: 2R-2F-5N-DIAMINE: X^1: F, X^2: H
2: 2R-4F-3N-DIAMINE: X^1: H, X^2: F
3: 2R-3N-DIAMINE: X^1: H, X^2: H

Figure 1. Reaction scheme for the syntheses of fluoronitroaryl azo diaminobenzene chromophores and non-fluorinated analogue.

incorporated into polymers through covalent bonds. The effects of the position of the fluorine group in the isomers on their properties have also been investigated.

The syntheses of chromophores **1**–**3** are schematically depicted in Figure 1. Chromophores **1**–**3** were synthesized through diazotization and coupling with 1,3-phenylenediamine in 70%, 65%, 80% yields, respectively. All the chromophores were isolated as pure compounds as evidenced by ^{1}H NMR, ESI, and elemental analysis.[8] From the structures of the chromophores, it can be seen that there are two amino groups so that they can be reacted easily with other functional groups such as carboxyl groups, isocyanates, esters, anhydrides, acid chlorides, hydroxyls, etc., which gives these chromophores broad applications. Chromophores incorporated into a polymer matrix by covalent bonds through amino groups can avoid orientational relaxation, and hence increase the thermal and chemical stability of the NLO polymer. Solubility experiments showed that the compounds are soluble in common organic solvents such as THF, 1,4-dioxane, and acetone.

Experimental results showed that the incorporation of fluorine into 2R-3N-DIAMINE and the position of the fluorine significantly influenced the properties of the chromophores. Table 1 lists the density, UV–vis absorption maxima (λ_{max}), second order NLO properties, and thermal decomposition temperatures of the new chromophores. The hyperpolarizabilities were determined using the solvatochromic method as described in previous literature[9] and the well-known β_0 value for *p*-nitroaniline (*p*-NA) in 1,4-dioxane (40×10^{-40} m^4/V)[10] was used as the external reference. The hyperpolarizabilities of the fluorinated chromophores decreased in comparison with their non-fluorinated analogue, 2R-3N-DIAMINE as expected. However, it is interesting to note that 2R-4F-3N-DIAMINE almost has the same hyperpolarizability as 2R-3N-DIAMINE. Generally, the incorporation of fluorine into a molecule structure will lead to a decrease in the hyperpolarizability because fluorine substituted systems are weak π-donors and strong δ-acceptors.[5] Our results also show that 2R-4F-3N-DIAMINE has a higher hyperpolarizability than 2R-2F-5N-DIAMINE. This may be because the fluorine group is in different position and may lead to different intramolecular charge transfer between the donor and the acceptor. Levine[11] reported that the intramolecular charge transfer is stronger in the *para*- than in the *ortho*-nitroaniline isomer so that the hyperpolarizability of *p*-nitroaniline is higher than that of the *o*-nitroaniline. Comparing the positions of the fluorine group in our fluorinated chromophores shown in Figure 1, it can be seen that the fluorine group is located in the *ortho*-position (X^1) in 2R-2F-5N-DIAMINE and in the *para*-position (X^2) in 2R-4F-3N-DIAMINE. Therefore, 2R-4F-3N-DIAMINE has stronger intramolecular charge transfer and possesses higher hyperpolarizability than 2R-2F-5N-DIAMINE. Figure 2 shows the dispersions of the hyperpolarizabilities calculated in terms of the quantum-mechanical two-level model. From Figure 2, it is possible to estimate the hyperpolarizability of the chromospheres at a specific wavelength.

Table 1. Physical properties of 2R-2F-5N-DIAMINE, 2R-4F-3N-DIAMINE, and 2R-3N-DIAMINE ($\beta_{esu} = (c/4\pi)$, $\beta_{SI} = 2.386 \times 10^9 \beta_{SI}$)

Chromophore	λ_{max}[a] (nm)	T_d (°C)	β_0[b] ($\times 10^{-40}$ m^4/V)	ρ[c] (g/cm^3)
2R-2F-5N-DIAMINE	467	270	78.6	1.67
2R-4F-3N-DIAMINE	434.5	245	116.7	0.966
2R-3N-DIAMINE	447.5	243	124.1	2.467
p-NA	354.5	379	39.2	1.44

[a] λ_{max} in 1,4-dioxane.
[b] Dispersion-corrected β values calculated using an approximate two-level model.
[c] Density measured using pycnometric method.

The decomposition temperatures T_d of the chromophores were measured by thermogravimetric analysis under nitrogen with a heating rate of 10 °C/min. The chromophores **1**–**3** exhibited T_d is ranging from 241 to 270 °C as listed in Table 1. The fluorinated chromophores had higher thermal decomposition temperatures than their non-fluorinated analogues, possibly due to the presence of fluorine.

Their UV–vis absorption spectra in 1,4-dioxane are shown in Figure 3. The results show that the maximum absorption wavelengths, λ_{max}, of 2R-2F-5N-DIAMINE, 2R-4F-3N-DIAMINE, and 2R-3N-DIAMINE are 467,

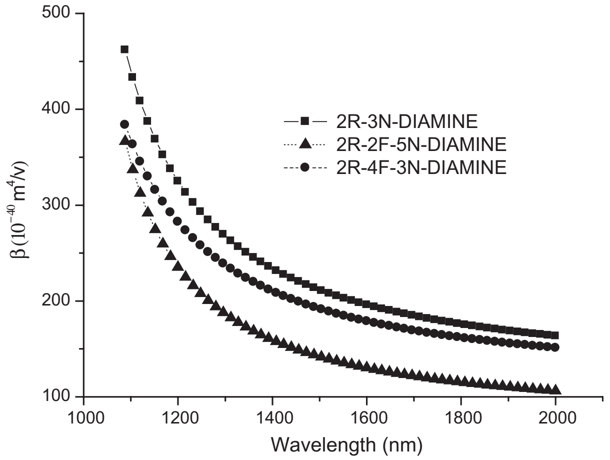

Figure 2. Dispersions of hyperpolarizabilities of 2R-3N-DIAMINE, 2R-4F-3N-DIAMINIE, and 2R-2F-5N-DIAMINE.

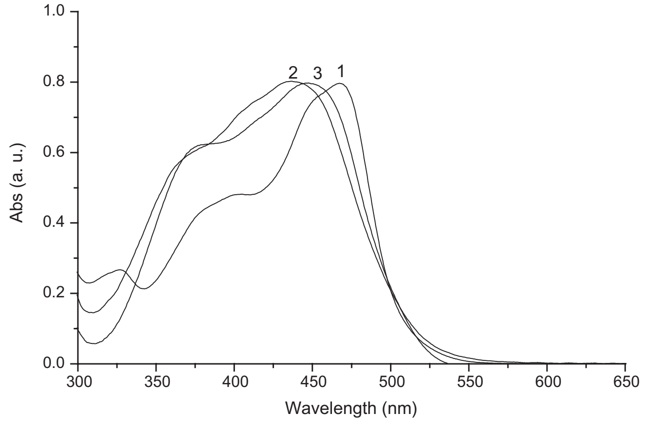

Figure 3. UV–vis absorption spectra (1,4-dioxane) of 2R-2F-5N-DIAMINE **1**, 2R-4F-3N-DIAMINE **2**, and 2R-3N-DIAMINE **3**.

434.5, and 447.5 nm, respectively. The results reveal that 2R-4F-3N-DIAMINE displays a significant blue shift of λ_{max} compared with 2R-3N-DIAMINE. However, 2R-2F-5N-DIAMINE displays a bathochromic shift of λ_{max}. The theoretical calculations of Liu et al.'s showed that fluorine in different positions in the fluoroazulene isomers could lead to different UV absorbances.[12] Our results confirm that the position of the fluorine in the structures can significantly influence the absorbance because the position of fluorine group affects the energy levels of the chromophores.

In summary, we have synthesized two new fluorinated functional chromophores and their non-fluorinated analogue for potential NLO applications. The fluorinated functional chromophores display different properties due to the different positions of the fluorine group. The chromophore 2R-4F-3N-DIAMINE shows a combination of good transparency, high thermal stability, and nonlinearity compared with 2R-3N-DIAMINE and 2R-2F-5N-DIAMINE.

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8. ^{1}H NMR (400 MHz), MS (ESI), elemental analysis data for 1–3 chromophores are as follows: **1** (2R-2F-5N-DIAMINE): ^{1}H NMR (DMSO) δ (ppm) 8.43 (s, 1H), 8.00 (d, $J = 8$ Hz, 1H), 7.60 (s, 2H), 7.40 (d, $J = 8$ Hz, 1H), 7.09 (d, $J = 8$ Hz, 1H), 6.22 (s, 2H), 6.08 (d, $J = 8$ Hz, 1H), 5.87 (s, 1H). MS (ESI) *m*/*z*: 276.2 (M+1), 274.4 (M−1). Anal. Calcd 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. **2** (2R-4F-3N-DIAMINE): ^{1}H NMR (DMSO) δ (ppm) 8.15 (s, 1H), 7.93 (d, $J = 8$ Hz, 1H), 7.35 (d, $J = 8$ Hz, 1H), 7.17 (d, $J = 8$ Hz, 1H), 6.95 (s, 2H), 6.01 (d, $J = 8$ Hz, 1H), 5.95 (s, 2H), 5.86 (s, 1H). MS (ESI) *m*/*z*: 276.1 (M+1), 274.3 (M−1). Anal. Calcd 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, 52.29; H, 3.65; N, 25.43; O, 11.69; F, 6.94. **3** (2R-3N-DIAMIEN): ^{1}H NMR (DMSO) δ (ppm) 8.40 (s, 1H), 8.10 (d, $J = 8$ Hz, 1H), 8.06 (d, $J = 8$ Hz, 1H), 7.69 (t, $J = 8$ Hz, 1H), 7.41 (d, $J = 8$ Hz, 1H), 7.40 (s, 2H), 6.21 (s, 2H), 6.07 (d, $J = 8$ Hz, 1H), 5.87 (s, 1H). MS (ESI) *m*/*z*: 258.2 (M+1), 256.3 (M−1). Anal. Calcd for $C_{12}H_{11}N_5O_2$: C, 56.03; N 27.22; H 4.31; O, 12.44. Found: C, 55.94; H, 4.31; N, 26.97; O, 12.78.
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