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Second-Order Optical Nonlinearity of 6-(Perfluoroalkyl)benzothiazolylazo Dyes

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ABSTRACT

The perfluorobutyl derivative showed a large second-order nonlinear optical coefficient (d_{33}) *and improved relaxation behavior in a series of 6-substituted benzothiazolylazo nonlinear optical chromophores (NLOphores).* *© 1998 Elsevier Science Ltd. All rights reserved*

Keywords: Second-order nonlinearity, perfluoroalkyl, benzothiazolylazo, relaxation, poled polymer.

INTRODUCTION

Organic compounds having electron-donating and -withdrawing moieties through π-conjugation such as Disperse Red 1 (DR1) have been proposed as electro-optic (E-O) materials [1]. The NLOphores are required to have both high second-order coefficients (d_{33}) and improved relaxation behavior in doped polymers. Thiazolylazo- and benzothiazolylazo dyes, having a strong intramolecular push-pull system, a bathochromic shift and an intense ε value, have been reported to show large second-order optical nonlinearity [2–6]. The perfluoroalkyl (R_f) group has both the electron-withdrawing nature

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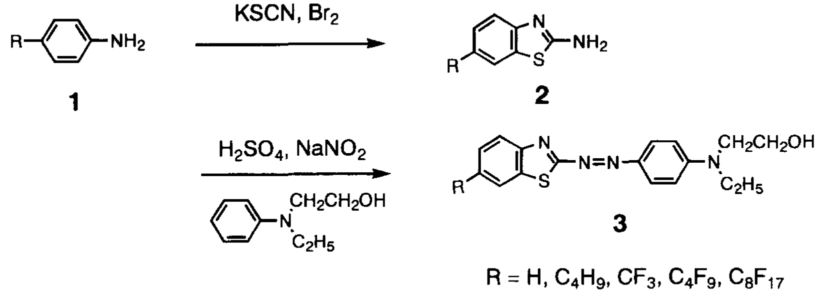
($\sigma_p CF_3 = 0.54$) and rigidity due to the large van der Waals radius of the fluorine atom (F: 1.3 Å, H: 1.1–1.2 Å). These suggest that the introduction of an R_f group in the benzothiazolylazo NLOphore could enhance second-order nonlinearity and improve relaxation behavior of the poled molecule. R_f-substituted dyes have been synthesized and reported to show interesting properties. A series of fluorine-containing cyanine dyes have been prepared by Yagupolskii *et al.* [7] R_f-substituted coumarins [8] and azopyridones [9] are more photostable than the unsubstituted analogues. Disazo dyes [10], perylenes, [11], anthraquinones [12], and naphthalocyanines [13] having R_f group(s) have been reported to be soluble in organic solvents. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate is highly lipophilic. This compound has been used as an anion-catalyzed phase-transfer catalysis and a solvent-extraction material [14, 15]. R_f-fullerene [16] and -phenylboronic acid [17] have been prepared by using bis(perfluoroalkanoyl) peroxides. The chemistry of fluorine has been recently reviewed [18]. We report here the second-order optical nonlinearity of benzothiazolylazo NLOphores substituted with an R_f group.

RESULTS AND DISCUSSION

Benzothiazolylazo NLOphores **3** were prepared as shown in Scheme 1. 6-Substituted 2-aminobenzothiazoles **2** were synthesized by the reaction of 4-substituted anilines **1** with potassium thiocyanate in the presence of bromine. The compounds **2** were diazotised with nitrosylsulfuric acid and coupled with 2-(*N*-ethylanilino)ethanol to afford **3**.

The physical and second-order NLO properties of **3** are indicated in Table 1. The absorption maximum in ethanol of the NLOphores was in the order: **3c**, **3d**, **3e** > **3a**, **3b** > DR1, suggesting the large d_{33} values of the R_f derivatives [1]. No significant difference in the absorption maximum among



Scheme 1

TABLE 1
Physical and Second-order NLO Properties

Compd	*R*	$\lambda_{max}(\varepsilon)^a$ *(nm)*	Td^b *(°C)*	$\lambda_{max}{}^c$ *(nm)*	*Film thickness (μm)*	*Refractive index*		$d_{33}{}^d$ *pm* V^{-1}
						532 nm	*1064 nm*	
3a	H	511 (44 400)	277	505	0.93	1.53	1.50	18
3b	C_4H_9	512 (44 000)	282	506	0.95	1.54	1.50	22
3c	CF_3	525 (31 200)	239	518	0.82	1.53	1.50	39
3d	C_4F_9	528 (31 100)	247	521	0.80	1.55	1.50	36
3e	C_8F_{17}	529 (46 000)	240	519	0.92	1.54	1.50	17
DR1	—	483 (32 100)	299	492	0.96	1.53	1.50	14

[a] Measured in ethanol.
[b] Measured by TG-DTA analysis (heating rate: 10°C min^{-1}, under air),
[c] Doped in PMMA.
[d] 2.0 mol% in PMMA.

the NLOphores **3c**–**3e** was observed, indicating the similar electron-withdrawing nature of the R_f substituents.

The decomposition temperatures (Tds) of the R_f derivatives **3c**–**3e** were low (239–247°C) compared with those of **3a**, **3b** and DR1 (277–299°C). However, the NLOphores **3c**–**3e** were sufficiently stable under poling conditions (110°C, 2 min).

The absorption maxima of PMMA film doped with the NLOphores **3** showed a slight hypsochromic shift compared with those in an ethanol solution. The films of the R_f-benzothiazolylazo derivatives **3c**–**3e** were more bathochromic than those of the other NLOphores **3a**, **3b** and DR1.

The benzothiazolylazo NLOphores **3c** and **3d** showed larger d_{33} values than **3e**. A long and rigid C_8F_{17} group might depress the alignment of the molecule under the corona poling.

A typical result of the change in the absorption spectra of the PMMA film doped with the NLOphore before and after poling is shown in Fig. 1. The absorption maximum of **3e** around 521 nm was decreased by poling. This indicated the alignment of the chromophore (order parameter = 0.07) [19]. No notable change in the absorption maxima before and after poling (120 h) was observed. This result showed that the NLOphore was not decomposed during the poling and relaxation process.

The relaxation behavior of the poled film is shown in Fig. 2. Interestingly, the NLOphores **3d** and **3e** were more stable than the others, suggesting that the long and rigid C_4F_9 and C_8F_{17} groups were effective in improving the relaxation behavior.

In conclusion, the 6-CF_3 and 6-C_4F_9 benzothiazolylazo NLOphores showed large d_{33} values. The relaxation behavior of the 6-C_4F_9 and 6-C_8F_{17} derivatives was improved. These results indicated that the 6-C_4F_9 benzothiazolylazo NLOphore **3d** was the best compound among the 6-substituted

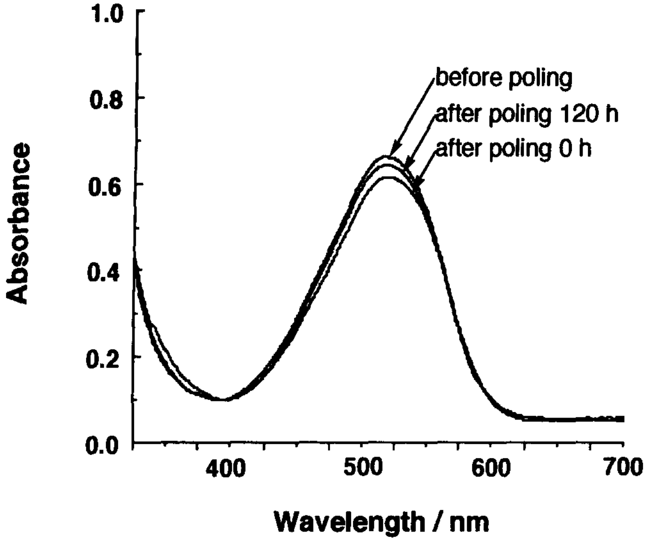


Fig. 1. Change in UV spectra of NLOphore **3e** before and after poling.

benzothiazolylazo NLOphores to show both a large d_{33} value and improved relaxation behavior. These could be attributed to the strong electron-withdrawing and rigid nature of the long R_f group.

EXPERIMENTAL

Instruments

Melting points were measured with a Yanagimoto MP-S2 micro melting point apparatus. NMR spectra were obtained by a Jeol α-400 spectrometer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer. UV spectra were taken on Shimadzu UV-160A and Hitachi U-4000 spectrometers. Thermal analysis was performed with Perkin-Elmer DSC-7 and Rigaku TA-200 instruments. Refractive index was determined by a Mizojiri Kogaku DVA-36VWLD ellipsometer. Film thickness was measured with a Dektak 3030 surface profile measuring system.

Materials

4-Butylaniline (**1b**) 4-(trifluoromethyl)aniline (**1c**), 2-(*N*-ethylanilino)ethanol, and 2-aminobenzothiazole (**2a**) were purchased from Tokyo Kasei Co., Ltd. 4-(Perfluorobutyl)aniline (**1d**) and 4-(perfluorooctyl)aniline (**1e**) were synthesized as described in the literature [7].

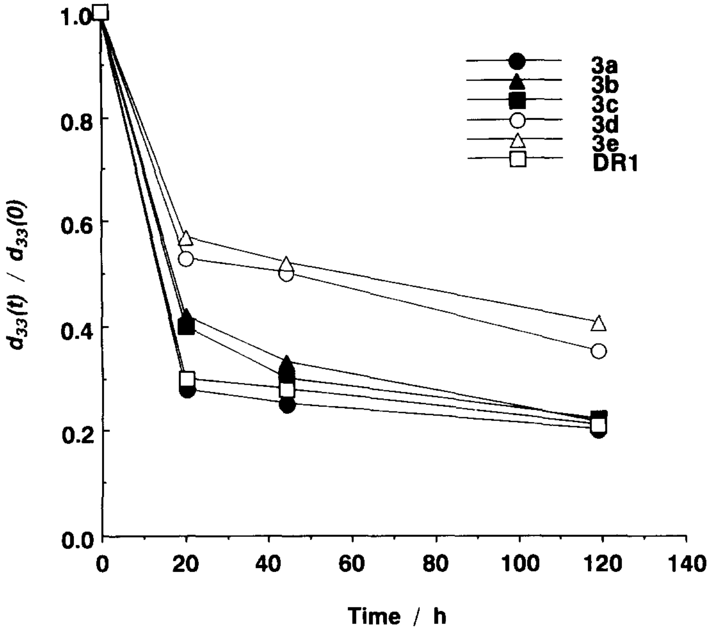


Fig. 2. Relaxation behavior of NLOphores doped in PMMA at 50°C.

Synthesis of 6-substituted 2-aminobenzothiazoles (2)

To an acetic acid solution (9 ml) of an aniline **1** (5 mmol) and potassium thiocyanate (1.95 g, 20 mmol) was added an acetic acid solution (4 ml) of bromine (0.8 g, 5 mmol) below 35°C and the mixture was then stirred for 15 h. After the reaction was complete, the resulting precipitate was filtered and washed with water. The filtrate was neutralized with ammonium hydroxide. The resulting precipitate was filtered, dried, and purified by column chromatography. Pertinent physical and spectral data are given below:

*2-Amino-6-butylbenzothiazole (**2b**)*
Yield 69%; M.p. 115.5–116.0°C; ^{1}H NMR ($CDCl_3$) δ 0.13 (t, J = 8.6 Hz, 3H), 1.36 (sextet, J = 8.6 Hz, 2H), 1.61 (quintet, J = 8.6 Hz, 2H), 2.65 (t, J = 8.6 Hz, 2H), 7.13 (d, J = 8.1 Hz, 1H), 7.40 (s, 1H), 7.45 (d, J = 8.1 Hz, 1H); MS (EI, 70 eV) m/z (%) 206 (23) [M^+], 163 (100), 136 (28).

*2-Amino-6-(trifluoromethyl)benzothiazole (**2c**)*
Yield 64%; M.p. 121.5–122.5°C; ^{1}H NMR ($CDCl_3$) δ 5.68 (br s, 2H), 7.56 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 1H), 7.87 (s, 1H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ 16.65 (3F); MS (EI, 70 eV) m/z (%) 218 (100) [M^+], 171(20), 164 (20).

*2-Amino-6-(perfluorobutyl)benzothiazole (**2d**)*
Yield 77%; mp 124–126°C; ^{1}H NMR ($CDCl_3$) δ 6.11 (br s, 2H), 7.51 (dd, $J = 8.4$ and 1.3 Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 1.3$ Hz, 1H); MS (EI, 70 eV) m/z (%) 368 (37) [M$^+$], 199 (100).

*2-Amino-6-(perfluorooctyl)benzothiazole (**2e**)*
Yield 41%; mp 157–158°C; ^{1}H NMR ($CDCl_3$) δ 5.40 (br s, 2H), 7.52 (dd, $J = 8.4$ and 1.3 Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.82 (d, $J = 1.3$ Hz, 1H); MS (EI, 70 eV) m/z (%) 568 (12) [M$^+$], 199 (100), 172 (20), 69 (22).

Synthesis of 4-(6-substituted 2-benzothiazolylazo)-*N*-ethyl-*N*-(2-hydroxyethyl)aniline 3

Sodium nitrite (0.69 g, 10 mmol) was added to conc. sulfuric acid (7.5 ml) and the mixture heated to 60–70°C. A propionic acid-acetic acid (1:5) solution (5 ml) was added to the solution, which was then cooled to room temperature. The nitrosylsulfuric acid was added to a propionic acid-acetic acid (1:5) solution of the benzothiazole **2** (10 mmol) and the liquor stirred for 2 h at 0–5°C. This mixture was added to an ethanol-propionic acid-acetic acid-water (20:3:15:5) solution (45 ml) of 2-(*N*-ethylanilino)ethanol (10 mmol) and sodium acetate (12 g), and the mixture was stirred overnight at 0–5°C. The liquor was neutralized with aq. sodium hydroxide and extracted with dichloromethane. The product was isolated by column chromatography (SiO_2–$CH_3COOC_2H_5$). Physical and spectral data are given below:

*4-(2-Benzothiazolylazo)-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (**3a**)*
Yield 14%; M.p. 214°C; ^{1}H NMR ($CDCl_3$) δ1.27 (t, $J = 7.1$ Hz, 3H), 1.78 (br s, 1H), 3.59 (q, $J = 7.1$ Hz, 2H), 3.65 (t, $J = 5.7$ Hz, 2H), 3.93 (t, $J = 5.7$ Hz, 2H), 6.81 (d, $J = 9.3$ Hz, 2H), 7.39 (t, $J = 8.1$ Hz, 1H), 7.47 (t, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 9.3$ Hz, 2H), 8.08 (d, $J = 8.1$ Hz, 1H); MS (EI, 70 eV) m/z (%) 328 (23) [M$^+$], 295 (73), 133 (100).

*4-(6-Butyl-2-benzothiazolylazo)-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (**3b**)*
Yield 34%; M.p. 132°C; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.18 (t, $J = 6.6$ Hz, 3H), 1.32 (sextet, $J = 7.3$ Hz, 2H), 1.62 (quintet, $J = 7.3$ Hz, 2H), 2.50 (br s 1H), 2.71 (t, $J = 7.3$ Hz, 2H), 3.58 (q, $J = 6.6$ Hz, 2H), 3.64 (t, $J = 5.4$ Hz, 2H), 3.91 (t, $J = 5.4$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 1H), 7.83 (d, $J = 8.7$ Hz, 2H), 7.84 (s, 1H), 7.89 (d, $J = 8.3$ Hz, 1H); MS (EI, 70 eV) m/z (%) 382 (40) [M$^+$], 351 (94), 323 (94), 133 (100), 104 (32).

*4[6-(Trifluoromethyl)-2-benzothiazolylazo)-*N*-ethyl-*N*-(2-hydroxyethyl)aniline (3c)*

Yield 5%; M.p. 194°C; ^{1}H NMR ($CDCl_3$) δ1.29 (t, $J=7.2\,$Hz, 3H), 1.77 (br s, 1H), 3.61 (q, $J=7.2\,$Hz, 2H), 3.67 (t, $J=5.4\,$Hz, 2H), 3.94 (t, $J=5.4\,$Hz, 2H), 6.83 (d, $J=9.3\,$Hz, 2H), 7.69 (d, $J=8.9\,$Hz, 1H), 7.99 (d, $J=9.3\,$Hz, 1H), 8.12 (s, 1H), 8.13 (d, $J=8.9\,$Hz, 1H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ 16.5 (3F); MS (EI, 70 eV) *m/z* (%) 394 (25) [M^+], 363 (100), 133 (57).

*4-[6-(Perfluorobutyl)-2-benzothiazolylazo]-*N*-ethyl-*N*-2-(hydroxyethyl)aniline (3d)*

Yield 2%; M.p. 149°C; ^{1}H NMR ($CDCl_3$) δ 1.29 (t, $J=7.2\,$Hz, 3H), 3.61 (q, $J=7.2\,$Hz, 2H), 3.67 (t, $J=5.6\,$Hz, 2H), 3.94 (t, $J=5.6\,$Hz, 2H), 6.82 (d, $J=9.0\,$Hz, 2H), 7.65 (d, $J=8.4\,$Hz, 1H), 7.99 (d, $J=9.0\,$Hz, 2H), 8.08 (s, 1H), 8.14 (d, $J=8.4\,$Hz, 1H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ 3.2 (3F), -32.0 (2F), -44.6 (2F), -47.8 (2F); MS (EI, 70 eV) *m/z* (%) 544 (20) [M^+], 513 (100), 133 (100).

4-[6-(Perfluorooctyl)-2-benzothiazolylazo]-N-ethyl-N-2-hydroxyethylaniline (3e)

Yield 1%; M.p. 163°C; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, $J=7.1\,$Hz, 3H), 1.64 (s, 1H), 3.59 (q, $J=7.1\,$Hz, 2H), 3.67 (t, $J=5.7\,$Hz, 2H), 3.94 (t, $J=5.7\,$Hz, 2H), 6.81 (d, $J=9.2\,$Hz, 2H), 7.65 (d, $J=8.4\,$Hz, 1H), 7.97 (d, $J=9.2\,$Hz, 2H), 8.08 (s, 1H), 8.14 (d, $J=8.4\,$Hz, 1H); ^{19}F NMR ($CDCl_3$, ext CF_3COOH) δ -2.96 (3F), -31.72 (2F), -43.61 (4F), -44.10 (4F), -44.92 (2F), -48.32 (2F); MS (EI, 70 eV) *m/z* (%) 744 (17) [M^+], 713 (100), 164 (23), 133 (82), 104 (28).

PMMA film formation doped with NLOphores

The NLOphore (0.01 mmol) was dissolved in a chloroform solution (1 ml) of PMMA (50 mg), and sonicated for 1 min at room temperature. The solution was filtered (0.5 μm), put onto an ITO glass and spin coated (1000 rpm, 20 s). The film was dried under reduced pressure for 3 h. The film was then poled (6.0 kV cm^{-1}, 2 min) at 110°C. After cooling the film to room temperature, the applied high voltage was removed.

Second harmonic generation (SHG) measurement

SHG of the film was measured by a Maker fringe method using a Q-switched Nd: YAG laser ($\lambda = 1064\,nm$). A 1 mm-thick y-cut quartz ($d_{11} = 0.33\,\mathrm{pm\,V^{-1}}$) was used as a reference. The second-order NLO coefficient (d_{33}) was determined by the mean square method using the relationship of SH light intensity and an incident angle of the poled film as described in our previous paper [20–22].

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