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Synthesis of azo chromophores containing a perfluorocyclo-alkenyl moiety and their second-order optical nonlinearity

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Dedicated to the 75th birthday of Prof. Yoshiro Kobayashi

Abstract

1,2-Bis[4-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclopentene, having two independent intramolecular push-pull chromophores in a molecule, showed the highest second-order nonlinear coefficient (d_{33}) among the cyclobutenyl, -pentenyl, -hexenyl, and cyclopentenyl nitro derivatives in both doped poly(methyl methacrylate) (PMMA) and polycarbonate (PC). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Second-order optical nonlinearity; Perfluorocycloalkenyl; Azo dyes

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1. Introduction

Much attention has been paid to prepare nonlinear optical chromophores (NLOphores) having large second-order nonlinearity. To design the NLOphores, π-conjugated compounds possessing large dipole moment, bathochromicity, and intense absorptivity (molar absorption coefficient (ϵ)) are required [1]. Many compounds such as Disperse Red 1 (4-(4-nitrophenylazo)-*N*-ethyl-*N*-(2-hydroxyethyl)aniline, DR1) [2], 4-(dimethylamino)-4′-nitrostylbene (DANS) [3], disazo dyes [4–7], cyanine dyes [8–11], benzopyrilium salts [12] and azomethine dyes [13] being largely dipolar and bathochromic compounds, have been proposed as excellent NLOphores. However, little attention has been paid to prepare the compounds having intense ϵ values. When a NLOphore consists of independent chromophores, an intense ϵ value of the compounds is expected. In this paper, we report the synthesis of azo chromophores linked with the perfluorocycloalkenyl moiety and their second-order optical nonlinearities.

2. Results and discussion

Scheme 1 shows the synthesis of NLOphores **3a–c** and **5b**. The NLOphores **3a–c** were prepared by the reaction of 1,2-dichloroperfluorocycloalkenes with 4-aminothiophenol in the presence of sodium hydride to give dianilino intermediates **2a–c**, followed by diazotization-coupling reaction. The nitro derivative **5b** was obtained by way of monoanilino intermediate **4b**.

Since little is known about the electronic effect of perfluorocyclopentenylthio moiety, intramolecular push–pull chromophoric azobenzene derivatives were prepared. Their absorption maxima were plotted against Hammett's σ_p constants. The result is shown in Fig. 1. The perfluorocyclopentenylthio substituent showed similar electron-withdrawing nature to a trifluoromethyl group (σ_p: 0.54).

The molecular structure of **3b** is shown in Fig. 2. Crystallographic data and selected bond lengths and various angles are given in Tables 1 and 2, respectively. The molecule was V-shaped: two long azo chromophores protruded from roughly planar cyclopentene (CP) ring via the sulfur atoms S1 and S2. The conformations around S1 and S2 were different each other: C2–C1–S1–C7 linkage was assumed

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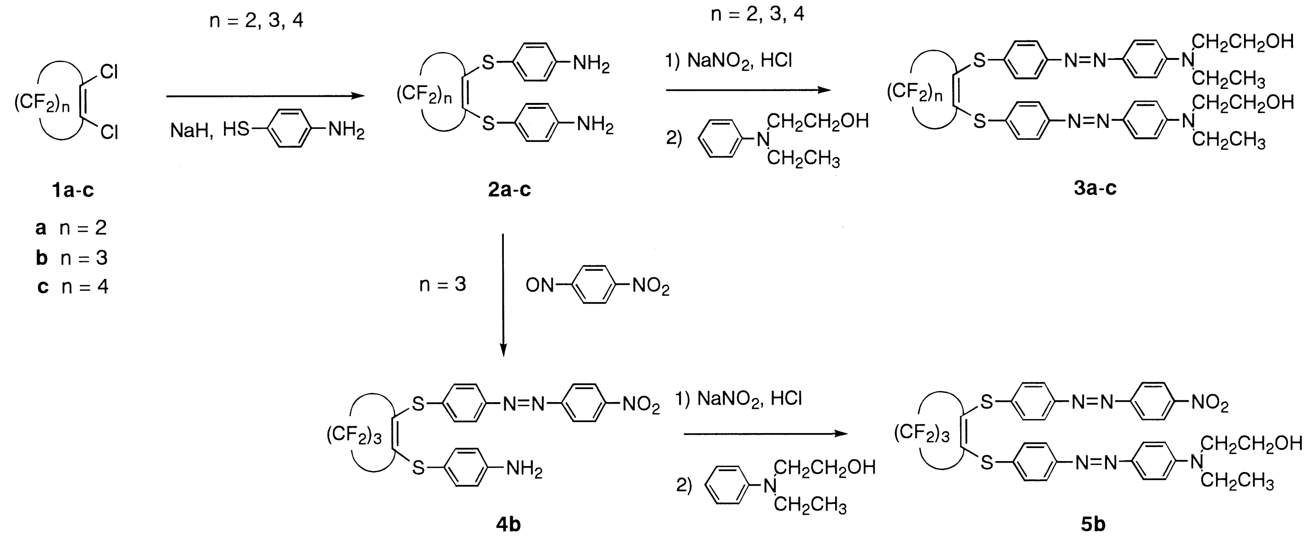


Scheme 1. Synthesis of NLO phores.

trans, while that of C1–C2–S2–C27 nearly gauche. Both azo groups, Azo1 and Azo2, took *trans* configuration. Two phenyl groups bonded to the azo groups were twisted in opposite direction each other: 7.2 and 8.2° in Azo1 and 16.8 and 19.7° in Azo2. All the bond lengths and angles were in the range of empirical values, except a few bond lengths. The C–N distances of 1.51–1.55 Å were longer than the generally accepted value of 1.43–1.46 Å. The S–C(CP) bonds of 1.733 and 1.757 Å were somewhat shorter than the S–C(Ph) bonds of 1.783(7) and 1.783(8) Å, indicating slight differences of double-bond character for the bonds. The van der Waals interaction was dominant among the molecules, except that two hydrogen bonds were formed to link the molecules: O11–H–O21=2.72(1) Å and O21–H–N21=2.90(1) Å.

The physical data of NLOphores are summarized in Table 3. NLOphores **3a–c** (λ_{max}; 438–441 nm in EtOH) and **5b** (442 and 351 nm) were more hypsochromic than DR 1 (482 nm), due to the less electron-withdrawing nature of perfluorocycloalkenylthio moieties than the nitro group. As expected, NLOphores **3a–c** showed more intense ϵ value (46 000–77 000 in ethanol) than DR 1 (27000). The decomposition temperature (Td) of **3b** was observed to be 290°C by TG-DTA analysis, indicating that these compounds were stable enough under poling conditions. Interestingly, these NLOphores were soluble in organic solvents such as ethanol, acetone, and chloroform.

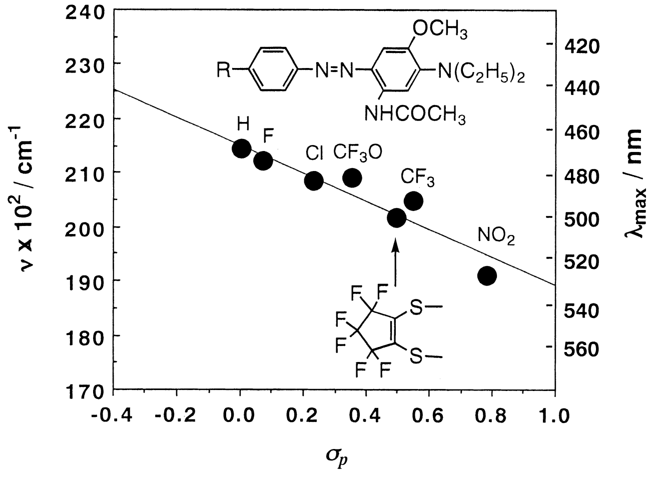


Fig. 1. Hammett's plot for the absorption maxima of azobenzenes. [a]The absorption bands were measured in hexane.

A dichloromethane solution of the polymer matrix containing the NLOphores was put on an ITO glass, spin-coated, dried, and corona-poled at the transition temperature of the polymers. The second-harmonic generation (SHG) of the film was measured by the Maker fringe method using a Q-switched Nd:YAG laser (λ=1064 nm). The second-order NLO coefficient (d_{33}) was then determined by the mean square methods using the relationship of the second harmonic light intensity and the incident angle of the poled film. The d_{33} values of **3a–c** and **5b** in doped PMMA and PC are also shown in Table 3. The hypsochromic NLOphores **3a–c** showed higher second-order nonlinearity than DR 1,

Table 1
Crystallographic data for **3b**

Formula	$C_{37}H_{36}F_6N_6O_2S$
Mol. wt	774.12
Crystal color, habit	Red, Plate-like
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions[a]	
a=14.631(3) Å	b=17.667(5) Å
c=7.586(7) Å	α=99.36(4)
β=99.51(4)	γ=79.72(4)
V=1884(2) Å^3	

[a] Throughout this paper the standard deviation in the least significant digit of the proceeding value is given in parenthesis.

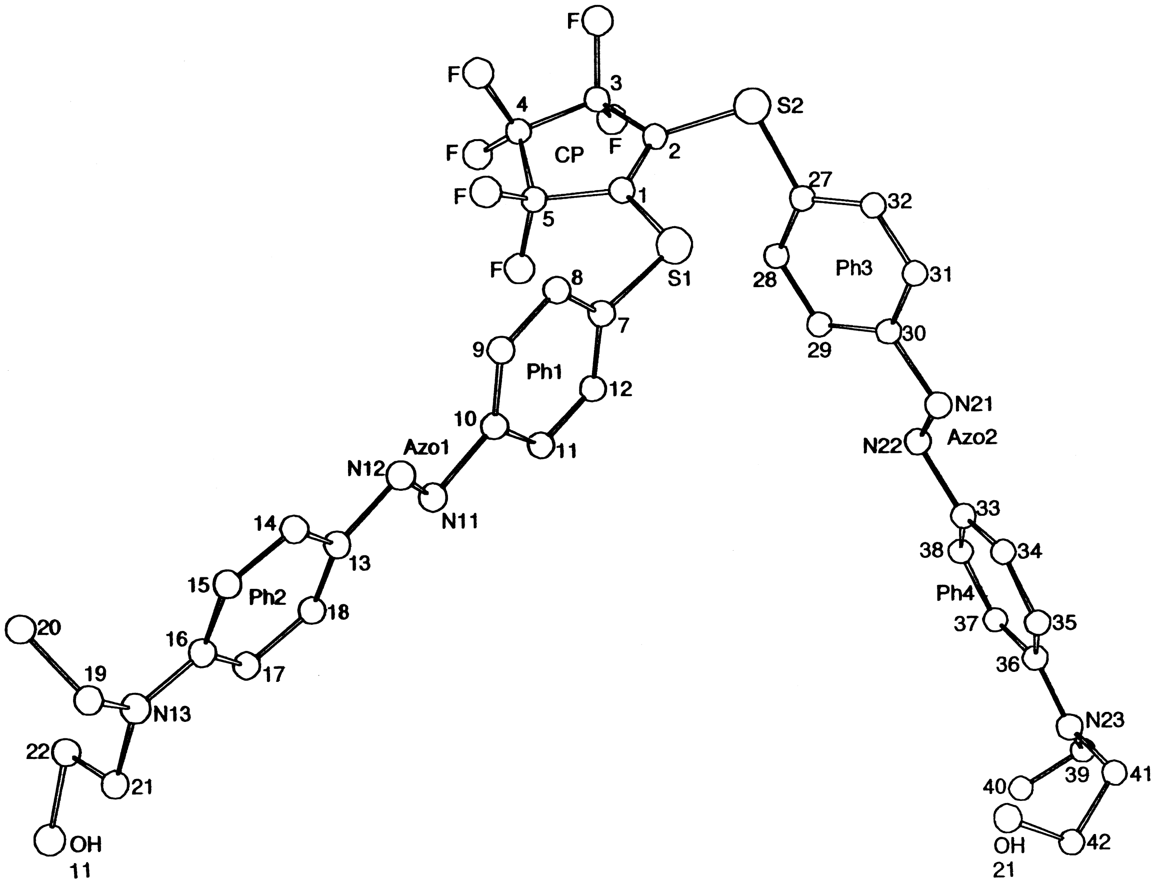


Fig. 2. Perspective drawing of the molecular structure of **3b** (the carbon atoms are shown only by numbers)

due to their intense ϵ values. The NLOphore **3b** also showed larger d_{33} value than the nitro derivative **5b**. The NLOphore **3b** showed the largest d_{33} value among **3a–c** and **5b**.

In conclusion, azo NLOphores containing a perfluorocycloalkenyl moiety have been synthesized. The second-order nonlinearity of 1,2-bis[4-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)-amino]phenylazo]phenylthio]perfluorocyclopentene showed the highest d_{33} value among four-, five-, and six-membered symmetrical and five-membered nitro derivatives.

3. Experimental

Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were taken on a Jeol α-400 spectrometers. Mass spectra were measured with Shimadzu QP-1000 and 9020-DF spectrometers. UV spectra were taken on Shimadzu UV-160A and Hitachi U-4000 spectrometers. A thermal analysis was performed with a Perkin-Elmer DSC-7 instrument. The refractive index was determined by a Mizojiri Kogaku DVA-36VWLD ellipsometer. The film thickness was measured with Dektak 3030 surface profile measuring system.

3.1. Synthesis of 5-acetyl-4-arylazo-2-methoxy-N,N-diethylanilines

To an acetone–water mixed solution (1:1, 20 ml) of conc. hydrochloric acid (1.35 ml, 15.1 mmol) was added an aniline (5.4 mmol). The mixture was stirred for 1 h at room temperature and cooled to 0°C. To the mixture was added an aqueous solution (10 ml) of sodium nitrite (5.5 mmol) and the mixture was stirred for 30 min at 0°C. To the mixture was added an acetone solution (15 ml) of 5-acetylamino-2-methoxy-*N,N*-diethylaniline (1.3 g, 5.5 mmol) and the mixture was stirred for 1 h. The pH value of the solution was adjusted to 7.0 with an aqueous sodium hydroxide solution. The resulting precipitate was filtered, purified by column chromatography (SiO_2, CH_2Cl_2), and recrystallized from hexane. Physical and spectral data are shown below.

5-Acetyl-2-methoxy-4-phenylazo-*N,N*-diethylaniline yield 38%; mp 105–107°C; ^1H NMR ($CDCl_3$) δ=1.19 (t, J=6.7 Hz, 6H), 2.25 (s, 3H), 3.40 (q, J=6.7 Hz, 4H), 3.90 (s, 3H), 7.36 (s, 1H), 7.40–7.50 (m, 3H), 7.76–7.80 (m, 2H), 8.25 (s, 1H), 10.11 (s, 1H); EIMS (70 eV) m/z (rel. intensity) 340 (M^+; 83), 325 (100), 77 (19).

5-Acetyl-2-methoxy-4-(4-nitrophenylazo)-*N,N*-diethylaniline yield 82%; mp 163–165°C; ^1H NMR ($CDCl_3$)

Table 2
Selected bond lengths, angles, torsion angles and dihedral angles for **3b**

Bond	Length (Å)	
(a) Bond lengths		
C1–C2	1.326(8)	
S1–C7	1.783(7)	
S2–C27	1.783(8)	
C30–N21	1.523(12)	
N21–N22	1.168(11)	
N22–C33	1.513(11)	
C1–S1	1.733(6)	
C2–S2	1.757(7)	
C10–N11	1.552(11)	
N11–N12	1.153(10)	
N12–C13	1.514(11)	
Bond	Angle (°)	
(b) Bond angles		
C1–S1–C7	105.1(3)	
C10–N11–N12	104.6(7)	
N11–N12–C–13	104.8(7)	
C2–S2–C27	102.1(3)	
C30–N21–N22	106.9(7)	
N21–N22–C33	107.3(7)	
Bond	Angle (°)	Configuration
(c) Torsion angles		
S1–C1–C2–S2	0.1(6)	*cis*
C2–C1–S1–C7	−178.0(6)	*trans*
C1–C2–S2–C27	51.9(7)	*gauche*
C10–N11–N12–C13 (Azo1)	177.0(8)	*trans*
C30–N21–N22–C33 (Azo2)	−177.3(9)	*trans*
Plane[a]	Angle (°)	
(d) Dihedral angles		
CP–Ph1	85.9	
Ph1–Azo1	7.2	
Azol–Ph2	8.2	
Ph1–Ph2	15.4	
Cp–Ph3	69.1	
Ph3–Azo2	16.8	
Azo2–Ph4	19.7	
Ph3–Ph4	36.4	

[a] Constitution atoms of the planes. CP: C1, C2, C3, C4, C5; Ph1: C7, C8, C9, C10, C11, C12; Ph2: C13, C14, C15, C16, C17, C18; Ph3: C27, C28, C29, C30, C31, C32; Ph4: C33, C34, C35, C36, C37, C38; Azo1: C10, N11, N12, C13; Azo2: C30, N21, N22, C33.

δ=1.25 (t, J=7.0 Hz, 6H), 2.28 (s, 3H), 3.50 (q, J=7.0 Hz, 4H), 3.89 (s, 3H), 7.33 (s, 1H), 7.83 (d, J=9.1 Hz, 2H), 8.21 (s, 1H), 8.34 (d, J=9.1 Hz, 2H), 10.13 (s, 1H); EIMS (70 eV) *m/z* (rel. intensity) 385 (M^+; 58), 370 (100).

5-Acetyl-4-(4-chlorophenylazo)-2-methoxy-*N*,*N*-diethylaniline yield 71%; mp 117–119°C; ^{1}H NMR ($CDCl_3$) δ=1.19 (t, J=7.1 Hz, 6H), 2.26 (s, 3H), 3.41 (q, J=7.1 Hz, 4H), 3.89 (s, 3H), 7.33 (s, 1H), 7.46 (d, J=8.5 Hz, 2H), 7.72 (d, J=8.5 Hz, 2H), 8.23 (s, 1H), 10.13 (s, 1H); EIMS (70 eV) *m/z* (rel. intensity) 376 (M^++2; 26), 374 (M^+; 79), 361 (35), 359 (100).

5-Acetyl-4-(4-fluorophenylazo)-2-methoxy-*N*,*N*-diethylaniline yield 29%; mp 76–78°C; ^{1}H NMR ($CDCl_3$) δ=1.19 (t, J=7.0 Hz, 6H), 2.25 (s, 3H), 3.40 (q, J=7.0 Hz, 4H), 3.89 (s, 3H), 7.33 (s, 1H), 7.78–7.90 (m, 2H), 8.24 (s, 1H), 9.99 (s, 1H); EIMS (70 eV) *m/z* (rel. intensity) 358 (M^+; 91), 343 (100), 95 (43).

5-Acetyl-2-methoxy-4-[4-(trifluoromethyl)phenylazo]-*N*,*N*-diethylaniline yield 18%; mp 113–114°C; ^{1}H NMR ($CDCl_3$) δ=1.22 (t, J=7.0 Hz, 6H), 2.26 (s, 3H), 3.45 (q, J=7.0 Hz, 4H), 3.89 (s, 3H), 7.35 (s, 1H), 7.73 (d, J=8.4 Hz, 2H), 7.83 (d, J=8.4 Hz, 2H), 8.23 (s, 1H), 10.06 (s, 1H); EIMS (70 eV) *m/z* (rel. intensity) 408 (M^+; 83), 393 (100), 145 (16).

5-Acetyl-2-methoxy-4-[4-(trifluoromethoxy)phenylazo]-*N*,*N*-diethylaniline yield 85%; mp 109–110°C; ^{1}H NMR ($CDCl_3$) δ=1.20 (t, J=7.1 Hz, 6H), 2.26 (s, 3H), 3.42 (q, J=7.1 Hz, 4H), 3.89 (s, 3H), 7.32 (s, 1H), 7.33 (d, J=8.5 Hz, 2H), 7.80 (d, J=8.5 Hz, 2H), 8.24 (s, 1H), 9.99 (s, 1H); EIMS (70 eV) *m/z* (rel. intensity) 424 (M^+; 77), 409 (100).

1,2-Bis[4-[2-acetyl-4-(diethylamino)-3-methoxy]phenylazo]phenylthio]perfluoro-1-cyclopentene yield 32%; mp 103–107°C; ^{1}H NMR ($CDCl_3$) δ=1.21 (t, J=7.0 Hz, 12H), 2.26 (s, 6H), 3.44 (q, J=7.0 Hz, 8H), 3.88 (s, 6H), 7.32 (s, 2H), 7.59 (d, J=8.5 Hz, 4H), 7.75 (d, J=8.5 Hz, 4H), 8.22 (s, 2H), 10.08 (s, 2H); EIMS (70 eV) *m/z* (rel. intensity) 916 (M^+; 1), 443 (16), 250 (100).

3.2. Synthesis of 1,2-bis(4-aminophenylthio)-perfluorocycloalkenes **2**

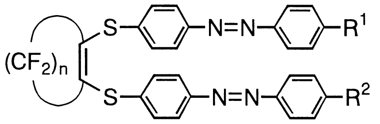
To a DMF (10 ml) solution of 4-aminothiophenol (1.25 g, 10 mmol) was added 60% sodium hydride (0.4 g, 10 mmol). The mixture was stirred for 30 min at −78°C under a nitrogen atmosphere. To the mixture was added 1,2-dichloroperfluorocycloalkene (5 mmol) and the mixture was stirred overnight under a nitrogen atmosphere. After the reaction was completed, the mixture was poured into water (100 ml) and extracted with dichloromethane (100 ml×2). The extract was washed with water (100 ml×6) and dried. After evaporation of the solvent, the product was isolated by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from hexane. Physical and spectral data are shown below.

1,2-Bis(4-aminophenylthio)perfluorocyclobutene (**2a**). Yield 23%; mp 71–72°C; ^{1}H NMR ($CDCl_3$) δ=3.77 (s, 4H), 6.59 (d, J=8.5 Hz, 4H), 7.26 (d, J=8.5 Hz, 4H); EIMS (70 eV) *m/z* (rel. intensity) 372 (M^+; 6), 248 (100), 124 (94).

1,2-Bis(4-aminophenylthio)perfluorocyclopentene (**2b**). Yield 20%; mp 117–118°C; ^{1}H NMR ($CDCl_3$) δ=3.87 (s, 4H), 6.63 (d, J=8.7 Hz, 4H), 7.35 (d, J=8.7 Hz, 4H); EIMS (70 eV) *m/z* (rel. intensity) 422 (M^+; 73), 149 (32), 124 (100).

1,2-Bis(4-aminophenylthio)perfluorocyclohexene (**2c**). Yield 17%; mp 122–123°C; ^{1}H NMR ($CDCl_3$) δ=3.86 (s, 4H), 6.62 (d, J=8.3 Hz, 4H), 7.32 (d, J=8.3 Hz, 4H); EIMS (70 eV) *m/z* (rel. intensity) 472 (M^+; 100), 184 (27), 124 (38).

Table 3
Absorption band and d_{33} values of NLOphores doped in polymers



NLOphore	n	R^1	R^2	λ_{max}^{a} (nm)	ϵ^{a}	In PMMA^b		In PC^c	
						λ_{max} (nm)	d_{33} (pm)	λ_{max} (nm)	d_{33} (pm)
3a	2	$N(C_2H_5)C_2H_4OH$	$N(C_2H_5)C_2H_4OH$	438	46 000	444	11	431	27
3b	3	$N(C_2H_5)C_2H_4OH$	$N(C_2H_5)C_2H_4OH$	441	53 000	443	32	430	48
3c	4	$N(C_2H_5)C_2H_4OH$	$N(C_2H_5)C_2H_4OH$	440	77 000	447	19	442	20
5b	3	NO_2	$N(C_2H_5)C_2H_4OH$	442 351	32 000 28 700	457	6	d	d
DR1	–	–	–	482	27 000	491	16	487	19

[a] Measured in ethanol.
[b] 1.5 Mol% of NLOphore.
[c] 3.0 Mol% of NLOphore.
[d] Not measured.

3.3. *Synthesis of 1,2-bis[4-[4-[N-ethyl-N-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocycloalkenes* **3a–c**

To an acetone–water mixed solution (1:1, 20 ml) of conc. hydrochloric acid (1.13 ml, 13.6 mmol) was added 1,2-bis(4-aminophenylthio)perfluorocycloalkenes **2** (1.5 mmol). The mixture was stirred for 1 h at room temperature and then cooled to 0°C. To the mixture was added an aqueous solution (10 ml) of sodium nitrite (0.25 g, 3.6 mmol) and the mixture was stirred for 30 min at 0°C. After the reaction was completed, to the mixture was added an acetone solution (15 ml) of *N*-ethylanilinoethanol (0.56 g, 3.4 mmol) and the mixture was stirred for 1 h. The pH value of the mixture was adjusted at 7.0 with an aqueous sodium hydroxide solution. The resulting precipitate was filtered, purified by column chromatography (SiO_2, $CH_3COOC_2H_5$), and recrystallized from dichloromethane. Physical and spectral data are shown below.

1,2-Bis[4-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclobutene (**3a**). Yield 25%; mp 174–177°C; ^{1}H NMR ($CDCl_3$) δ=1.24 (s, *J*=7.1 Hz, 6H), 1.60 (t, *J*=5.6 Hz, 2H), 3.55 (q, *J*=7.1 Hz, 4H), 3.60 (t, *J*=5.6 Hz, 4H), 3.87 (q, *J*=5.6 Hz, 4H), 6.80 (d, *J*=9.2 Hz, 4H), 7.56 (d, *J*=8.4 Hz, 4H), 7.80 (d, *J*=8.4 Hz, 4H), 7.86 (d, *J*=9.2 Hz, 4H); EIMS (70 eV) *m/z* (rel. intensity) 724 (M^+; 38), 693 (44), 664 (17), 649 (31), 548 (32), 517 (100), 331 (88), 301 (18), 270 (58), 149 (23), 133 (73). Found: C, 59.58; H, 4.86; N, 11.75. Calcd. for $C_{36}H_{36}F_4N_6O_2S_2$: C, 59.65; H, 5.01; N, 11.59.

1,2-Bis[4-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclopentene (**3b**). Yield 22%; mp 147–149°C; ^{1}H NMR ($CDCl_3$) δ=1.24 (t, *J*=7.1 Hz, 6H), 1.64 (t, *J*=5.7 Hz, 2H), 3.56 (q, *J*=7.1 Hz, 4H), 3.60 (t, *J*=5.7 Hz, 4H), 3.88 (q, *J*=5.7 Hz, 4H), 6.80 (d, *J*=9.2 Hz, 4H), 7.56 (d, *J*=8.6 Hz, 4H), 7.81 (d, *J*=8.6 Hz, 4H), 7.86 (d, *J*=9.2 Hz, 4H); EIMS (70 eV) *m/z* (rel. intensity) 774 (M^+; 13), 743 (27), 715 (17), 599 (18), 568 (59), 358 (100) 134 (28). Found: C, 57.42; H, 4.61; N, 10.82. Calcd. for $C_{37}H_{36}F_6N_6O_2S_2$: C, 57.35; H, 4.68; N, 10.85.

1,2-Bis[4-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]phenylthio]perfluorocyclohexene (**3c**). Yield 28%; mp 138–143°C; ^{1}H NMR ($CDCl_3$) δ=1.24 (t, *J*=7.1 Hz, 6H), 1.67 (t, *J*=5.6 Hz, 2H), 3.54 (q, *J*=7.1 Hz, 4H), 3.59 (t, *J*=5.6 Hz, 4H), 3.88 (q, *J*=5.6 Hz, 4H), 6.78 (d, *J*=9.2 Hz, 4H), 7.51 (d, *J*=8.5 Hz, 4H), 7.80 (d, *J*=8.5 Hz, 4H), 7.85 (d, *J*=9.2 Hz, 4H); EIMS (70 eV) *m/z* (rel. intensity) 824 (M^+; 10), 793 (23), 764 (20), 617 (30), 381 (95),133 (100). Found: C, 55.67; H, 4.52; N, 10.22. Calcd. for $C_{38}H_{36}F_8N_6O_2S_2$: C, 55.33; H, 4.40; N, 10.19.

3.4. *Synthesis of 1-(4-aminophenylthio)-2-[4-(nitrophenylazo)phenylthio]perfluorocyclopentene (***4b***)*

To an acetic acid solution (10 ml) of 1,2-bis(4-aminophenylthio)perfluorocyclopentene **2b** (1.06 g, 2.5 mmol) was added 4-nitrosonitrobenzene (0.38 g, 2.5 mmol) and the mixture was stirred overnight at room temperature. After the reaction was completed, the mixture was poured into water. The resulting precipitate was filtered, dried, purified by column chromatography (SiO_2, CH_2Cl_2), and recrystallized from a chloroform–hexane mixed solution. Yield 38%; mp 134–135°C; ^{1}H NMR ($CDCl_3$) δ=3.93 (s, 2H), 6.63 (d, *J*=8.3 Hz, 2H), 7.31 (d, *J*=8.5 Hz, 2H), 7.58 (d, *J*=8.5 Hz, 2H), 7.96 (d, *J*=8.3 Hz, 2H), 8.05 (d, *J*=8.5 Hz, 2H), 8.40 (d, *J*=8.5 Hz, 2H); EIMS (70 eV) *m/z* (rel. intensity) 556 (M^+; 99), 373 (26), 298 (35), 199 (100).

*3.5. Synthesis of 1-[4-[4-[N-ethyl-N-(2-hydroxyethyl)amino]phenylazo]phenylthio]-2-[4-(4-nitrophenylazo)phenylthio]perfluorocyclopentene (**5b**)*

To an acetone–water mixed solution (1:1, 20 ml) of conc. hydrochloric acid (0.34 ml, 4.1 mmol) was added 1-(4-aminophenylthio)-2-[4-(nitrophenylazo)phenylthio]perfluorocyclopentene **4b** (0.50 g, 0.9 mmol). The mixture was stirred for 1 h at room temperature and then cooled to 0°C. To the solution was added an aqueous solution (10 ml) of sodium nitrite (0.077 g, 1.1 mmol) and the mixture was stirred for 30 min at 0°C. After the reaction, to the mixture was added an acetone solution (15 ml) of *N*-ethylanilinoethanol (0.165 g, 1.0 mmol) and the mixture was stirred for 1 h. The pH value of the mixture was adjusted at 7.0 with an aqueous sodium hydroxide solution. The resulting precipitate was filtered, purified by column chromatography (SiO_2, $CH_3COOC_2H_5$), and recrystallized from a chloroform–hexane mixed solution. Yield 47%; mp 136–138°C; ^{1}H NMR ($CDCl_3$) δ=1.25 (t, J=7.1 Hz, 3H), 1.60 (t, J=5.8 Hz, 1H), 3.55 (q, J=7.1 Hz, 2H), 3.61 (t, J=5.8 Hz, 2H), 3.89 (q, J=5.8 Hz, 2H), 6.80 (d, J=9.1 Hz, 2H), 7.56 (d, J=8.5 Hz, 2H), 7.59 (d, J=8.5 Hz, 2H), 7.81 (d, J=8.5 Hz, 2H), 7.86 (d, J=9.1 Hz, 2H), 7.96 (d, J=8.5 Hz, 2H), 8.05 (d, J=9.1 Hz, 2H), 8.40 (d, J=9.1 Hz, 2H); EIMS (70 eV) *m/z* (rel. intensity) 732 (M^+; 13), 701 (60), 133 (100). Found: C, 54.13; H, 3.42; N, 11.44. Calcd. for $C_{33}H_{26}F_6N_6O_2S_3$: C, 54.09; H, 3.58; N, 11.67.

3.6. Film preparation

The NLOphores (1.5 mol% in PMMA, 3.0 mol% in PC) were dissolved in a dichloromethane solution of the polymer matrix. The mixture was put on an ITO glass and spin-coated (600 rpm, 20 s). After drying the film under reduced pressure overnight, the films were poled (6 kV cm^{-1}, 2 min) at 110 (PMMA) and 150°C (PC). The thickness of the films were about 2000 (PMMA) and 1500 (PC) Å, respectively. After cooling the film, the applied high voltage was removed.

3.7. Second harmonic generation (SHG) measurement

The SHG of the film was measured by the Maker fringe method using a Q-switched Nd:YAG laser (λ=1064 nm). A 1 mm thick y-cut quartz (d_{11}=0.33 pm V^{-1}) was used as the reference. The second-order NLO coefficient (d_{33}) was determined by the mean square methods using the relationship of the second harmonic light intensity and the incident angle of the poled film as described in our previous papers [14–16].

3.8. X-ray crystallographic analysis

Single crystals of suitable quality for X-ray diffraction were obtained from a mixed solution of chloroform and hexane at room temperature. Intensity data were collected on a MAC SCIENCE diffractometer by use of Mo K_α radiation (λ=0.71073 Å) in the range of 2θ less than 53°. Altogether 6785 independent reflections were measured. 3498 Reflections of these intensities were exceeded their standard deviations three times and considered as observed to use in the structure determination. Throughout the structure determination the program package CRYSTAN GM (MAC SCIENCE) was used. Anisotropic thermal vibrations were assumed for the non-hydrogen atoms. All the hydrogen atoms, except the hydroxy hydrogen atoms, were found from a difference Fourier map and refined isotropically. The final residual index R and weighted index R_w were 0.072 and 0.064, respectively. The goodness-of-fit was 1.246.

Table of the atomic coordinates and the temperature factors will be obtained from the author with asterisk on request.

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