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A new class of second-order non-linear optical material: stilbazolium benzimidazolate derived from alkylsulfonyl substituted stilbazole

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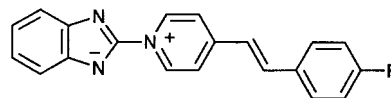
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A novel stilbazolium benzimidazolate derivative, *i.e.* 2-(4-{2-[4-(octylsulfonyl)phenyl]ethenyl}pyridinio)benzimidazolate **4a**, was prepared by the quaternization reaction of 4-{2-[4-(octylsulfonyl)phenyl]ethenyl}pyridine with 2-chlorobenzimidazole, followed by deprotonation with aqueous ammonia. Poly(methyl methacrylate) (PMMA) thin films containing 10 or 20 mass% of **4a** were obtained by spin-coating from their THF solutions on an ordinary cover glass substrate. Second-harmonic generation (SHG) measurements of the obtained thin films were carried out by the Maker fringe method using a Q-switched Nd:YAG laser (1064 nm) as an exciting beam after corona-poling. A poled PMMA film containing 10 or 20 mass% of **4a** exhibited a second-order non-linear optical (NLO) coefficient, d_{33} , of 7.6 or 11 pm V⁻¹, respectively, which was much larger than the d_{33} value of a PMMA thin film containing 10 mass% of 2-[4-(2-phenylethenyl)pyridinio]benzimidazolate **4c** (d_{33} 1.6 pm V⁻¹) or 2-{4-[2-(4-octyloxyphenyl)ethenyl]pyridinio}benzimidazolate **4d** (d_{33} 0.51 pm V⁻¹). There were no significant differences in linear absorption properties of PMMA films containing **4a**, **4c** or **4d**. The introduction of an octylsulfonyl group at the 4'-position of the stilbazole moiety increases the second-order NLO coefficient.

Second-order non-linear optical organic molecules, which have been the subject of many reports, are aromatic compounds with a pair of electron-donor and electron-acceptor groups at π -conjugating sites, so-called classical D- π -A system molecules.^{1,2} Recently, various types of NLO molecules classified into non-classical molecular systems have been developed³ for the improvement of the physical properties of NLO molecules and for solving the problem of the trade-off between optical non-linearity and cutoff wavelength, which is generally defined as the wavelength where the value of the first deviation for the absorbance becomes 0. Heterocyclic betaines have received much attention because of their unusually high dipole moments, which are ascribed to their zwitterionic character; this is confirmed by the fact that they exhibit negative solvatochromism.⁴ Pyridinium or stilbazolium benzimidazolates, which consist of a negatively charged aromatic donor group and a positively charged aromatic acceptor group, are heterocyclic betaines. The NLO activities of the present pyridinium or stilbazolium benzimidazolates are attributed to short-range charge transfer through the σ -bond from the charged aromatic donor group to the charged aromatic acceptor group. We have revealed that some pyridinium or stilbazolium benzimidazolates classified as non-classical molecular systems are applicable as second-order non-linear optically active molecules from theoretical investigations⁵ and hyper-Rayleigh scattering measurements.⁶ One distinct characteristic of pyridinium betaine compounds is that the value of the first hyperpolarizability, β , is enlarged with decreasing dipole moment.⁷ Namely, from theoretical calculations,⁸ the introduction of an electron-acceptor substituent at the 4'-position of the stilbazole moiety in stilbazolium benzimidazolate decreased the dipole moment in the ground state, but increased the β value compared with stilbazolium benzimidazolate without a substituent at the 4'-position of the stilbazole moiety. In many cases, an increase in β for classical D- π -A system molecules is accompanied by an increase in the dipole moment.² A large polarizability often brings temporal or thermal relaxation to the noncentrosymmetric alignment of NLO-phores in a poled

polymer film due to dipole-dipole interactions, which results in the temporal or thermal relaxation of second-order NLO activity. It may be possible for pyridinium betaine compounds to overcome this problem, due to their characteristics as mentioned above. We have also investigated poled thin films of some pyridinium or stilbazolium benzimidazolates dispersed in poly(methyl methacrylate) (PMMA) *via* Maker fringe measurements.⁹ However, the limited solubility and centrosymmetric aggregation of pyridinium betaines in polymeric matrixes seemed to inhibit the increase of their second-order NLO susceptibility.

To solve these problems, we have prepared two kinds of novel stilbazolium benzimidazolates **4a** and **4b**, the phenyl groups of which are substituted by electron-acceptor groups, *i.e.* octylsulfonyl or perfluorooctylsulfonyl groups, which would cause not only an increase in the β value but also render them more soluble in organic solvents owing to their decreased dipole moment in the ground state. Additionally, a poly(methyl methacrylate) (PMMA) thin film containing **4a** was prepared, the linear optical and second-order NLO properties of which are described.



	R
4a	-SO ₂ (CH ₂) ₈ H
4b	-SO ₂ (CF ₂) ₈ F
4c	-H
4d	-O(CH ₂) ₈ H

Experimental

Materials

N,N-Dimethylformamide (DMF) was distilled over CaH₂ under reduced pressure. Butan-1-ol and triethylamine (Wako Pure Chemical Industries, Ltd.) were used after distillation over CaH₂. 4-Bromobenzenethiol, 1-bromooctane (Tokyo

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Kasei Kogyo Co., Inc.), palladium(II) acetate, 30% aqueous hydrogen peroxide and acetic acid (Kanto Chemical Co., Inc.) were commercially available and used as received. 4-Vinylpyridine was distilled under reduced pressure just before use. 2-Chlorobenzimidazole was prepared by modifying the method reported by Harrison *et al.*¹⁰ PMMA (M_n : 4.3×10^5 , determined by gel permeation chromatography; T_g 101 °C determined by differential scanning calorimetry) was purchased from Nacalai Tesque, Inc. and used as received.

Instrumentation

UV-VIS absorption spectra were measured by transmission on a Shimadzu Model U-2100 spectrophotometer. ¹H NMR spectroscopy was conducted with a Hitachi R-90H FT NMR (90 MHz) spectrometer or a Bruker AM-400 FT NMR (400 MHz) spectrometer; *J* values are given in Hz. IR Spectra were measured by transmission on a Jasco A-202 IR spectrometer. Mass spectrometry was conducted on a Hitachi Mass Spectrometer M-80B by electron ionization method. Differential scanning calorimetry (DSC) measurements were carried out on a Shimadzu Model DSC-50 under a helium flow rate of 20 ml min⁻¹ and a heating rate of 10 °C min⁻¹.

4-(Octylthio)bromobenzene 1a

Under an argon atmosphere, 4-bromobenzenethiol (9.45 g, 50.0 mmol) in dry DMF (10 ml) was added dropwise to sodium hydride (2.40 g, 60.0 mmol, 60% in mineral oil) suspended in dry DMF (30 ml) in an ice bath. The reaction mixture was stirred at ambient temperature for 1 h, and 1-bromooctane (10.62 g, 55.0 mmol) was added dropwise. After the reaction mixture was stirred at ambient temperature for 2 h, DMF was evaporated under reduced pressure. Water and ethyl acetate were added to the residue, and the organic layer was washed with water. The organic layer was dried with anhydrous sodium sulfate, and the solvent was evaporated to dryness. The crude product was purified by column chromatography, using a column packed with silica gel with hexane as eluent. The product yield was 14.97 g (99%) as a colourless liquid: δ_H (CDCl₃, 90 MHz) 0.88 [t, *J* 7.0, 3H, CH₃(CH₂)₇], 1.1–2.0 [m, 12H, CH₃(CH₂)₆CH₂], 2.88 (t, *J* 7.0, 2H, CH₂S), 7.22 (dt, *J* 2.2, 8.8, 2H, phenylene protons), 7.39 (dt, *J* 2.2, 8.8, 2H, phenylene protons); ν_{\max} /cm⁻¹ 2955, 2925, 2855, 1885, 1630, 1565, 1475, 1385, 1305, 1265, 1240, 1180, 1095, 1070, 1005, 805, 725, 505, 480; *m/z* 302 ($M^+ + 2$), 300 (M^+), 203 [($M^+ + 2$) - (C₇H₁₅)], 201 [$M^+ - (C_7H_{15})$], 188, 186, 122, 108, 82, 71, 57, 55, 43, 41, 29 (Found: C, 55.6; H, 7.1. Calc. for C₁₄H₂₁BrS: C, 55.81; H, 7.03%).

Compound **1b** was prepared *via* a similar method as for **1a** using perfluorooctyl iodide instead of 1-bromooctane. The product yield was 86% as colourless crystals. δ_H (CDCl₃, 90 MHz) 7.54 (s, 4H, phenylene protons); ν_{\max} /cm⁻¹ 2925, 1905, 1640, 1570, 1475, 1385, 1370, 1325, 1245, 1200, 1150, 1115, 1100, 1090, 1070, 1010, 935, 820, 800, 780, 745, 730, 710, 675, 655, 600, 560, 530, 510, 490; *m/z* 608 ($M^+ + 2$), 606 (M^+), 589 [($M^+ + 2$) - F], 587 ($M^+ - F$), 508, 239 [(BrPhSCF₂⁺) + 2], 237 (BrPhSCF₂⁺), 189 [(BrPhS⁺) + 2], 187 (BrPhS⁺), 169 [(C₃F₇)⁺], 158, 131, 119 (C₂F₇⁺), 108, 82, 69 (CF₃⁺), 55, 43, 28 (Found: C, 27.7; H, 0.7. Calc. for C₁₄H₄BrF₁₇S: C, 27.49; H, 0.43%).

4-(Octylsulfonyl)bromobenzene 2a

A mixture of **1a** (14.19 g, 47.1 mmol), acetic acid (100 ml) and 30% aqueous hydrogen peroxide (16.02 g, 141.3 mmol) was refluxed for 1 h. The reaction mixture was poured into 300 ml of saturated aqueous sodium hydrogen carbonate. The crude product was extracted with ethyl acetate, and the combined ethyl acetate extracts were dried over anhydrous sodium sulfate. The residue resulting from evaporation of the ethyl acetate was purified by column chromatography using a

column packed with silica gel with hexane–ethyl acetate (7:1) as eluent. Evaporation of the solvent afforded the title compound **2a** (14.83 g, 94.5%) as colourless crystals: δ_H (CDCl₃, 90 MHz) 0.86 [t, *J* 6.9, 3H, CH₃(CH₂)₇], 1.1–2.0 [m, 12H, CH₃(CH₂)₆CH₂], 3.0–3.3 (m, 2H, CH₂SO₂), 7.73 (s, 4H, phenylene protons); ν_{\max} /cm⁻¹ 3090, 3065, 2955, 2925, 2850, 1910, 1780, 1650, 1580, 1470, 1410, 1390, 1325, 1315, 1305, 1280, 1245, 1215, 1205, 1180, 1145, 1085, 1065, 1010, 985, 960, 930, 895, 855, 820, 795, 770, 735, 725, 620, 565, 550, 530, 495, 455; *m/z* 334 ($M^+ + 2$), 332 (M^+), 317, 315, 291 [($M^+ + 2$) - (C₃H₇)], 289 [$M^+ - (C_3H_7)$], 249, 247, 234, 232, 223, 221, 203, 201, 197, 195, 185, 183, 171, 169, 157 [($M^+ + 2$) - (C₃H₇SO₂)], 155 [$M^+ - (C_3H_7SO_2)$], 141, 112, 93, 71, 57, 43, 29 (Found: C, 50.45; H, 6.35. Calc. for C₁₄H₂₁BrO₂S: C, 50.29; H, 6.32%).

Compound **2b** was prepared *via* a similar method as for **2a** using **1b** instead of **1a**. The product yield was 87%: δ_H (CDCl₃, 90 MHz) 7.86 (s, 4H, phenylene protons); ν_{\max} /cm⁻¹ 3095, 1575, 1470, 1395, 1365, 1330, 1285, 1205, 1175, 1150, 1080, 1070, 1010, 935, 830, 800, 750, 705, 660, 645, 615, 595, 550, 530; *m/z* (SIMS) 641 ($M^+ + 3$), 639 ($M^+ + 1$) (Found: C, 26.2; H, 0.4. Calc. for C₁₄H₄BrF₁₇O₂S: C, 26.31; H, 0.63%).

4-{2-[4-(Octylsulfonyl)phenyl]ethenyl}pyridine 3a

Under an argon atmosphere, a mixture of **2a** (9.998 g, 30.0 mmol), 4-vinylpyridine (4.206 g, 40.0 mmol), triethylamine (3.036 g, 30.0 mmol), palladium(II) acetate (0.203 g, 0.90 mmol) and 15 ml of dry acetonitrile was degassed, refluxed for 72 h and cooled. To this reaction mixture was added chloroform and water. The crude product was extracted with chloroform, and the organic layer was dried over anhydrous sodium sulfate. The chloroform was evaporated, and the residue was purified by column chromatography, using a column packed with silica gel with hexane–ethyl acetate (2:1) as eluent. Finally, recrystallization of the product from ethyl acetate–hexane afforded the title compound **3a** with a yield of 8.093 g (75.5%) as white crystals: δ_H (CDCl₃, 400 MHz) 0.86 [t, *J* = 7.0, 3H, CH₃(CH₂)₂], 1.2–1.3 [m, 8H, CH₃(CH₂)₂CH₂], 1.36 [quintet, *J* 7.0, 2H, CH₃(CH₂)₄CH₂], 1.7–1.8 [m, 2H, CH₃(CH₂)₂CH₂], 3.1 (m, 2H, CH₂SO₂), 7.16 (d, *J* 16.4, 1H, =CH-pyridyl), 7.33 (d, *J* 16.4, 1H, =CH-phenylene), 7.40 (dd, *J* 1.6, 4.6, 2H, pyridyl protons), 7.71 (dt, *J* 1.7, 8.5, 2H, phenylene protons), 7.92 (dt, *J* 1.7, 8.5, 2H, phenylene protons), 8.63 (dd, *J* 1.6, 4.6, 2H, pyridyl protons); ν_{\max} /cm⁻¹ 3050, 3030, 2980, 2955, 2925, 1930, 1670, 1635, 1595, 1565, 1550, 1495, 1465, 1380, 1300, 1285, 1260, 1245, 1215, 1195, 1140, 1120, 1090, 1045, 1015, 980, 970, 870, 830, 800, 770, 750, 725, 705, 665, 620, 590, 570, 565, 545, 530, 500, 480, 445, 415; *m/z* 357 (M^+), 328 [$M^+ - (C_2H_5)$], 314 [$M^+ - (C_3H_7)$], 292, 270, 265, 245, 228, 208, 195, 181, 160, 152, 138, 127, 69, 57, 43, 28 (Found: C, 70.6; H, 7.6; N, 4.0; S 9.0. Calc. for C₂₁H₂₇NO₂S: C, 70.55; H, 7.61; N, 3.92; S, 8.97%).

Compound **3b** was prepared *via* a similar method as for **3a** using **2b** instead of **2a**. The product yield was 35.9%: δ_H (CDCl₃, 400 MHz) 7.24 (d, *J* 16.4, 1H, =CH-pyridyl), 7.35 (d, *J* 16.4, 1H, =CH-phenylene), 7.41 (dd, *J* 1.5, 4.6, 2H, pyridyl protons), 7.80 (d, *J* 8.5, 2H, phenylene protons), 8.05 (d, *J* 8.5, 2H, phenylene protons), 8.66 (dd, *J* 1.6, 4.6, 2H, pyridyl protons); ν_{\max} /cm⁻¹ 3025, 3010, 1595, 1570, 1555, 1495, 1415, 1375, 1330, 1260, 1230, 1160, 1145, 1120, 1085, 1055, 1015, 990, 975, 955, 940, 880, 860, 830, 805, 750, 710, 695, 680, 660, 605, 585, 555, 515, 480; *m/z* 663 (M^+), 644 ($M^+ - F$), 244 [$M^+ - (C_8F_{17})$], 228, 196 [$M^+ - (C_8F_{17}SO)$], 180 [$M^+ - (C_8F_{17}SO_2)$], 169 [(C₃F₇)⁺], 152, 131, 119 (C₂F₅⁺), 90, 69 (CF₃⁺), 51 (Found: C, 37.9; H, 1.3; N, 2.1. Calc. for C₂₁H₁₀NO₂SF₁₇: C, 38.02; H, 1.52; N, 2.11%).

2-(4-{2-[4-(Octylsulfonyl)phenyl]ethenyl}pyridinio)benzimidazole 4a

Under an argon atmosphere, a mixture of 2-chlorobenzimidazole (1.526 g, 10.0 mmol), **3a** (3.575 g, 10.0 mmol) and 5 ml of

dry butan-1-ol was stirred at 100 °C for 12 h and then cooled. This reaction mixture was poured into 500 ml of diethyl ether, and the resulting precipitate was collected by filtration. The residual solid was washed with diethyl ether and dissolved in 100 ml of methanol at 60 °C. The solution was treated with 10 ml of aqueous ammonia at 60 °C. To this mixture was added 400 ml of water. The resulting precipitate was collected by filtration. The crude product was purified by recrystallization from acetone–methanol affording the title compound **4a** with a yield of 2.77 g (58%) as red–brown crystals: δ_{H} (CDCl₃, 400 MHz) 0.87 [t, *J* 7.1, 3H, CH₃(CH₂)₇], 1.2–1.3 [m, 8H, CH₃(CH₂)₄CH₂], 1.38 [quintet, *J* 7.1, 2H, CH₃(CH₂)₄CH₂], 1.7–1.8 [m, 2H, CH₃(CH₂)₅CH₂], 3.1–3.2 (m, 2H, CH₂SO₂), 7.10–7.16 (m, 2H, benzimidazole protons), 7.18 (d, *J* 16.3, 1H, =CH–pyridyl), 7.55 (d, *J* 16.4, 1H, =CH–phenylene), 7.62–7.68 (m, 2H, benzimidazole protons), 7.72 (d, *J* 7.2, 2H, pyridyl protons), 7.78 (d, *J* 8.4, 2H, phenylene protons), 8.00 (d, *J* 8.4, 2H, phenylene protons), 9.83 (d, *J* 7.2, 2H, pyridyl protons); ν_{max} /cm^{−1} 3125, 3055, 2930, 2855, 1620, 1565, 1555, 1500, 1465, 1410, 1395, 1320, 1310, 1270, 1190, 1145, 1115, 1090, 1045, 1015, 1000, 970, 955, 900, 880, 845, 810, 770, 745, 730, 710, 660, 620, 600, 555, 545, 530; *m/z* 475 (M⁺ + 2), 396, 384, 357, 299, 284, 273, 259, 220, 209, 183, 133, 118, 105, 90, 79, 64, 51, 39 (Found: C, 71.01; H, 6.60; N, 8.87; S, 6.77%). Calc. for C₂₈H₃₁N₃O₂S: C, 71.01; H, 6.60; N, 8.87; S, 6.77%).

Compound **4b** was prepared *via* a similar method as for the preparation of **4a** using **3b** instead of **3a**. The product yield was 63%: δ_{H} (CDCl₃, 400 MHz) 7.14–7.22 (m, 3H, benzimidazole protons and =CH–pyridyl), 7.38 (d, *J* 15.2, 1H, =CH–phenylene), 7.68–7.72 (m, 2H, benzimidazole protons), 7.90 (d, *J* 8.5, 2H, phenylene protons), 7.93 (d, *J* 7.2, 2H, pyridyl protons), 8.14 (d, *J* 8.5, 2H, phenylene protons), 10.02 (d, *J* 7.2, 2H, pyridyl protons); ν_{max} /cm^{−1} 3125, 3075, 3050, 1620, 1590, 1570, 1555, 1500, 1470, 1450, 1410, 1375, 1330, 1305, 1215, 1175, 1150, 1125, 1085, 1055, 1030, 1010, 970, 955, 880, 845, 810, 750, 710, 680, 660, 645, 600, 580, 555, 525, 490; *m/z* 779 (M⁺), 715, 663, 553, 489, 346, 296 [M⁺ − (C₈F₁₇SO₂)], 244, 228, 209, 196, 180, 169 [(C₃F₇)⁺], 152, 131, 119 (C₂F₅⁺), 100, 85, 69 (CF₃⁺), 64, 51, 48 (Found: C, 43.0; H, 1.6; N, 5.3. Calc. for C₂₈H₁₄N₃O₂SF₁₇: C, 43.15; H, 1.81; N, 5.39%).

SHG Measurement

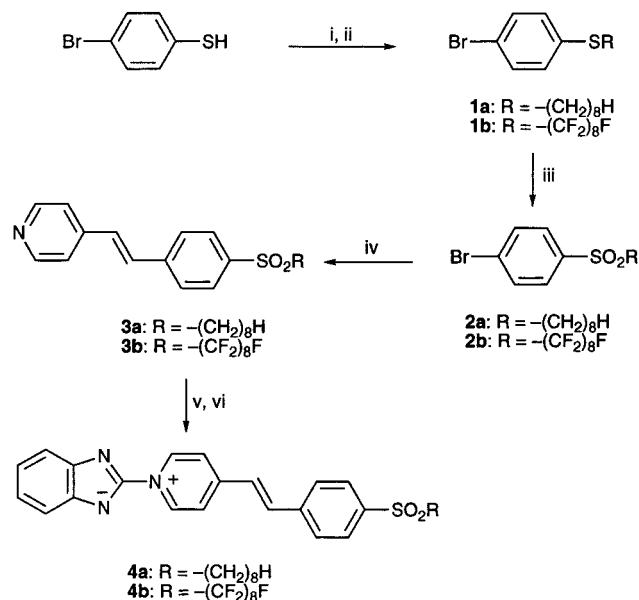
PMMA thin films containing 10 or 20 mass% of **4a** were obtained by spin-coating on an ordinary cover glass plate at a rate of 2000 rpm from a THF solution which contained PMMA and 10 or 20 mass% of **4a** with respect to PMMA. The thickness of the obtained film was determined to be *ca.* 0.5 μm . Poling was normal to the surface by corona discharge. The distance of the tungsten needle from the surface was 25 mm. The needle side was set to 10 kV negative to an aluminum heating plate. After 20 min of poling at 110 °C, the film was cooled to ambient temperature with continuous corona poling.

The second harmonic generation (SHG) at 532 nm was measured in transmission by means of the Maker fringe method,¹¹ using a Q-switched Nd:YAG laser (Spectron SL404G, $\lambda = 1064$ nm, 10 Hz repetition rate, 6 ns pulse duration) as the exciting light source. Detailed experimental and calculating procedures are described in our previous report.¹² As a reference sample we used a 1 mm-thick γ -cut quartz ($d_{11} = 0.46$ pm V^{−1}).

Results and Discussion

Preparation of novel stilbazolium benzimidazolate derivatives

The synthetic pathways to novel stilbazolium benzimidazolate derivatives **4a** and **4b** are described in Scheme 1. Stilbazolium benzimidazolate derivatives **4a** and **4b** were prepared by the formation of the betaine structure between 2-chlorobenzimidazole



Scheme 1 Reagents and conditions: i, NaH, DMF, 0 °C, 1 h; ii, Br(CH₂)₈Br or I(CF₂)₈F, DMF, room temp., 2 h; iii, H₂O₂, AcOH, reflux, 1 h; iv, 4-vinylpyridine, Pd(OAc)₂, Et₃N, CH₃CN, reflux, 72 h; v, 2-chlorobenzimidazole, BuOH, 12–24 h; vi, aq. NH₃, MeOH, 60 °C, 30 min

zole and novel stilbazole derivatives **3a** and **3b**, which were prepared by the Heck reactions of 4-vinylpyridine with 4-(octylsulfonyl)bromobenzene **2a** and 4-(perfluorooctylsulfonyl)bromobenzene **2b**, respectively. Stilbazolium benzimidazolate derivatives **4a** and **4b** are soluble in common polar organic solvents such as chloroform, methanol, ethanol, acetone, THF and so on, however, the solubility of **4a** was much better than that of **4b** in the common organic solvents mentioned above. The decomposition temperatures of **4a** and **4b** were estimated from differential scanning calorimetry (DSC) measurements. Melting was observed from 232 °C in the case of **4a** with thermal decomposition occurring at 235 °C on a heating scan; however, no melting was observed for **4b**, while thermal decomposition occurred at 237 °C. The thermal stability of **4a** and **4b** seems to be compatible with the processing temperatures of promising NLO polymers.¹³

Optical-quality thin films of PMMA containing 10 or 20 mass% of **4a** could be obtained by spin coating on an ordinary glass substrate from a THF solution which contained PMMA and 10 or 20 mass% of **4a** with respect to PMMA. However, optical-quality thin films of PMMA containing 10 mass% of **4b** could not be obtained, because of the poor solubility in organic solvents of **4b**, possibly owing to the effects of the perfluorooctyl moiety. On the other hand, other stilbazolium benzimidazolate derivatives **4c** (4'-position not substituted) and **4d** (4'-position substituted with an octyloxy moiety) could be dissolved in PMMA up to 10 mass% with respect to PMMA. Taking these results into account, it can be seen that the introduction of an octylsulfonyl group at the 4'-position of the stilbazole moiety contributes to an improvement in processability.

Optical properties of PMMA thin films containing stilbazolium benzimidazolate derivatives

The optical properties of betaine **4a** in PMMA are summarized in Table 1. We defined the cutoff wavelength (λ_{cutoff}) as the wavelength where the value of the first deviation for absorbance becomes 0. Fig. 1 shows the UV–VIS spectrum of 20 mass% of **4a** dispersed in a PMMA thin film, λ_{CT} of which is 426 nm. The present λ_{CT} means that the wavelength where the absorbance becomes maximal is in the visible region. The λ_{CT}

Table 1 Linear and non-linear optical properties for spin-coated films of PMMA containing stilbazolium benzimidazolate derivatives

run	compound	content of betaine/mass%	λ_{CT}/nm^a	λ_{cutoff}/nm	$d_{33}/pm\ V^{-1}$
1	4a	10	433	610	7.6
2	4a	20	426	610	11
3	4c^b	10	430	600	1.6
4	4d^b	10	440	600	0.51

^a λ_{CT} = the wavelength in the visible region where the absorbance becomes maximal. ^bFrom ref. 9(b).

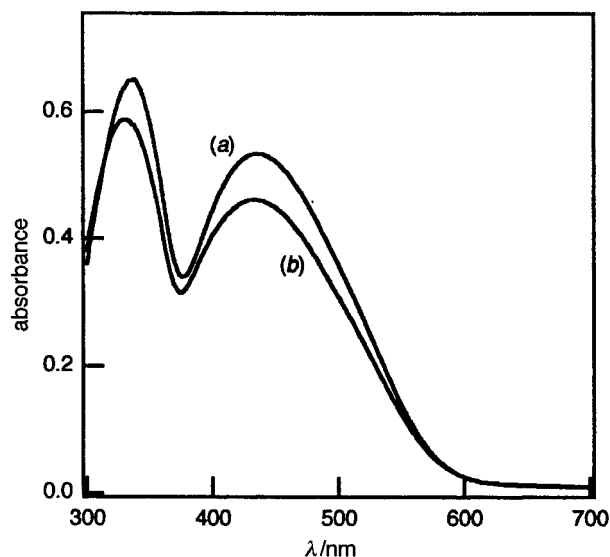


Fig. 1 UV-VIS absorption spectra of 10 mass% of **4a** dispersed in a PMMA thin film; (a) before corona poling, (b) after corona poling at 110 °C

of the PMMA thin film containing 10 mass% of **4a** was 433 nm. The blue-shift of λ_{CT} in the case of the PMMA thin film containing 20 mass% of **4a** is probably due to the increase in the content of **4a** inducing the enlargement of the polarizability around the chromophores. An increase in the polarity of the medium has been known to induce the blue-shift of a maximum absorption band of pyridinium betaines.⁴ The λ_{CT} of the stilbazolium benzimidazolate without a substituent, **4c**, dispersed in a PMMA thin film has been reported^{9b} to be 430 nm, which is comparable to the λ_{CT} of the present stilbazolium benzimidazolate **4a**. Namely, the introduction of an octyl-sulfonyl group at the 4'-position of the stilbazole moiety has no significant effect on λ_{CT} . It is generally accepted that the introduction of a strong electron-acceptor group into classical D- π -A molecular systems is accompanied by the red-shift of the λ_{CT} . Such red-shifts of the λ_{CT} were not observed in the stilbazolium benzimidazolate derivatives investigated. The absorbance around λ_{CT} decreased after the sample was poled at 110 °C for 20 min, applying the voltage of 4 kV cm⁻¹ with the corona poling method as shown in Fig. 1, indicating the promotion of chromophore orientation by electric poling. Similar results were obtained in the case of 20 mass% of **4a** dispersed in a PMMA thin film. Additionally, a blue-shift of the maximum absorption in the visible region was observed, which could be interpreted as resulting from the polarity of the environment around the chromophores being increased due to the noncentrosymmetric alignment of **4a**, as mentioned above. The order parameters of poled samples were estimated using spectroscopic measurements at λ_{CT} and eqn. (1),¹⁴

$$\langle P \rangle = 1 - A/A_0 \quad (1)$$

where $\langle P \rangle$ is the order parameter, and A_0 and A are the absorbance λ_{CT} before and after poling at 110 °C for 20 min, respectively. The order parameters in the cases of runs 1, 3 and 4 (Table 1) were estimated as 0.14, 0.19 and 0.10, respectively.

In the case of run 4, the centrosymmetric aggregation of **4d** in PMMA, which is probably promoted by the large polarizability of **4d**,⁸ provides the lowest order parameter in the present series. The order parameter in the case of run 1 was lower than that in the case of run 3. Our previous study using *ab initio* and INDO/S calculations⁶ revealed that the dipole moment of a stilbazolium benzimidazolate derivative, the 4'-position of which is substituted with a nitro moiety, is smaller than that of **4c** by ca. 7.5 D. According to this finding, the dipole moment of **4a** in the ground state was expected to be smaller than that of **4c**. Thus, the electric poling was more effective in the case of run 3 than in the case of run 1.

The second harmonic generation (SHG) of the thin film was measured in transmission by means of the Maker fringe method.^{11,12} A Q-switched Nd:YAG laser (Spectron SL404G, $\lambda = 1064$ nm, 10 Hz repetition rate, 6 ns pulse duration) was used as the exciting light source. The p-polarized laser beam was chosen using a $\lambda/4$ wave plate and a linear polarizer. Fig. 2 describes the relationship between SH light intensity and the incident angle of the exciting beam for the spin-coated film of PMMA containing 20 mass% of **4a** obtained after corona poling.

The second-order NLO coefficients, d_{33} , of the spin-coated films were determined by the mean-square method¹⁵ using the relationship of SH light intensity and the incident angle of an exciting beam proposed by Jerphagnon and Kurtz.¹¹ It has been reported⁹ that poled films of PMMA containing 10 mass% of **4c** or **4d** exhibit a d_{33} of 1.6 or 0.51 pm V⁻¹, respectively. In the present case, the d_{33} value of PMMA containing 10 or 20 mass% of **4a** is 7.6 or 11 pm V⁻¹, respectively. Namely, the d_{33} value of PMMA containing 10 mass% of **4a** is 5-fold larger than that of PMMA containing 10 mass% of **4c**, although the order parameter in the case of run 1 was lower than that in the case of run 3, as mentioned above. This result is due to the substituent effect of the

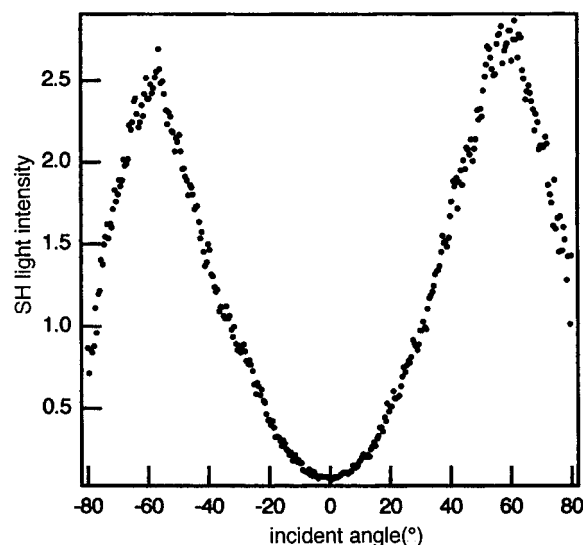


Fig. 2 Relationship between SH light intensity and the incident angle of an exciting beam for 10 mass% of **4a** dispersed in a PMMA thin film after corona poling at 110 °C

octylsulfonyl moiety. The introduction of the octylsulfonyl group at the 4'-position of the stilbazole moiety is of value not only for improving the processability of stilbazolium benzimidazolates but also for increasing their second-order NLO susceptibility. On the other hand, the d_{33} value of a poled PMMA film containing ca. 8 mass% of Disperse Red 1 (DR1, 2- $\{[N$ -ethyl-4-(4-nitrophenyl)azo]anilino}ethanol), which is a typical example of a classical D- π -A molecule (λ_{CT} 490 nm) has been reported¹⁶ to be ca. 8.5 pm V⁻¹ using a Nd:YAG laser (λ = 1064 nm) as an exciting source. The present PMMA film containing 10 mass% of **4a** exhibited a shorter λ_{CT} (433 nm) and a comparable d_{33} value (7.6 pm V⁻¹) using the same exciting light source.

If the preparation of stilbazolium benzimidazolate covalently bound to a polymeric backbone is achieved hereafter, the NLO activity would be expected to increase, because of the uniform distribution of the stilbazolium betaine in the matrix as well as the inhibition of aggregation due to polymeric effects.¹⁷ Studies on this subject are in progress.

Conclusions

The preparation of a novel stilbazolium benzimidazolate derivative, i.e. 2-(4-{2-[4-(octylsulfonyl)phenyl]ethenyl}pyridinio)benzimidazolate **4a**, has been achieved. The introduction of an octylsulfonyl group at the 4'-position of the stilbazole moiety is of value not only in improving the processability of stilbazolium benzimidazolates but also in increasing their second-order NLO susceptibilities without significantly influencing their linear absorption properties. The application of pyridinium heterocyclic betaines in NLO is worthy of notice and should lead to the development of a new class of second-order NLO materials.

References

- Recent books and reviews: (a) *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Miyata, CRC Press, Boca Raton, 1997; (b) *Organic Nonlinear Optical Materials, Advances in Nonlinear Optics*, ed. C. Bosshard, K. Sutter, P. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz and P. Günter, Gordon and Breach Publishers, New York, 1995, vol. 1; (c) *Polymers for Second-Order Nonlinear Optics*, ACS Symposium Series 601, ed. G. A. Lindsay and K. D. Singer, American Chemical Society, Washington, DC, 1995; (d) *Molecular Nonlinear Optics: Materials, Physics and Devices*, ed. J. Zyss, Academic Press, Boston, 1994; (e) D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31; (f) L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, H. Fetterman, Y. Shi, R. V. Mustacich, A. K.-Y. Jen and K. J. Shea, *Chem. Mater.*, 1995, **7**, 1060.
- (a) J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664; (b) J. L. Oudar and J. Zyss, *Phys. Rev. A*, 1982, **26**, 2016.
- (a) J. O. Morley, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 1853; (b) C. Serbutoviez, J. F. Nicoud, J. Fischer, J. Ledoux and J. Zyss, *Chem. Mater.*, 1994, **6**, 1358; (c) M. S. Wong, C. Bosshard, F. Pan and P. Günter, *Adv. Mater.*, 1996, **8**, 677; (d) X.-M. Duan, S. Okada, H. Oikawa, H. Matsuda and H. Nakanishi, *Nonlinear Opt.*, 1996, **15**, 119.
- Typical review: E. Alcalde, *Adv. Heterocycl. Chem.*, 1994, **60**, 197.
- J. Abe and Y. Shirai, *J. Am. Chem. Soc.*, 1996, **118**, 4705.
- J. Abe, Y. Shirai, N. Nemoto, F. Miyata and Y. Nagase, *J. Phys. Chem. B*, 1997, **101**, 576.
- J. Abe, N. Nemoto, Y. Nagase and Y. Shirai, *Chem. Phys. Lett.*, 1996, **261**, 18.
- J. Abe, Y. Shirai, N. Nemoto and Y. Nagase, *J. Phys. Chem. B*, 1997, **101**, 1910.
- (a) N. Nemoto, J. Abe, F. Miyata, M. Hasegawa, Y. Shirai and Y. Nagase, *Chem. Lett.*, 1996, 851; (b) N. Nemoto, J. Abe, F. Miyata, Y. Shirai and Y. Nagase, *Nonlinear Opt.*, in the press.
- D. Harrison, J. T. Ralph and A. C. B. Smith, *J. Chem. Soc.*, 1963, 203.
- J. Jerphagnon and S. K. Kurtz, *J. Appl. Phys.*, 1970, **41**, 1667.
- N. Nemoto, Y. Nagase, J. Abe, H. Matsushima, Y. Shirai and N. Takamiya, *Macromol. Chem. Phys.*, 1995, **196**, 2237.
- P. Boldt, T. Eisenträger, C. Glania, J. Göldenitz, P. Krämer, R. Matschiner, J. Rase, R. Schwesinger, J. Wichern and R. Wortmann, *Adv. Mater.*, 1996, **8**, 672.
- B. Guichard, C. Noël, D. Reyx and F. Kajzar, *Macromol. Chem. Phys.*, 1996, **197**, 2185.
- N. Nemoto, F. Miyata, Y. Nagase, J. Abe, M. Hasegawa and Y. Shirai, *Macromolecules*, 1996, **29**, 2365.
- M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins and A. Dienes, *J. Opt. Soc. Am. B*, 1989, **6**, 733.
- N. Nemoto, J. Abe, F. Miyata, Y. Shirai and Y. Nagase, *J. Mater. Chem.*, 1997, **7**, 1389.

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