Synthesis and Crystal Structures of Fluorinated Chromophores for Second-Order Nonlinear Optics

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Partially fluorinated skeleton of 4-[2-(4-dimethylamino-2,3,5,6-tetrafluorophenyl)ethynyl]-2,3,5,6-tetrafluoro-N,N,N-trimethylanilinium (2) was synthesized as a second-order nonlinear optical (NLO) material to decrease the absorption around 1.3 and 1.5 μm, which deteriorates the device efficiency. Several salts of 2 were prepared, and we found that the trifluoromethanesulfonate salt of 2 had a shorter absorption-wavelength than that of 4-nitroaniline (pNA). From hyper-Rayleigh scattering (HRS) measurement, the β value of 2 was found to be about 8 times greater than that of pNA. We also performed X-ray crystallographic analysis of 2 and estimated NLO coefficient (β) by the oriented gas model. We found that diagonal component of 2 (d11 = 610 pm V⁻¹) was about 14 times greater than that of 2-methyl-4-nitroaniline and off-diagonal component of 2 (d12 = 155 pm V⁻¹) was about 6.5 times greater than that of N-(4-nitrophenyl)l-prolinol. Compound 2 should be an excellent candidate for NLO applications.

A variety of organic chromophores for second-order nonlinear optical (NLO) materials have been studied over the last two decades,1,2 because they have the potential to surpass inorganic materials. Especially, organic ionic chromophores have several advantages compared to non-ionic chromophores, like a large hyperpolarizability (β), derived from charged π-conjugation systems, crystal structure controllability by changing the counter ion, and high melting points and hardness due to Coulombic interaction. However, most organic chromophores have C–H bonds, which cause absorption at wavelengths around 1.3 and 1.5 μm, which are used for optical communications, due to overtones of C–H stretching vibration, limiting the performance in electro-optic (EO) applications. In this work, we investigated an ionic chromophore having C–F bonds instead of C–H bonds, since C–F bond shifts the conjugation systems, crystal structure controllability by changing the counter ion, and high melting points and hardness due to Coulombic interaction. However, most organic chromophores have C–H bonds, which cause absorption at wavelengths around 1.3 and 1.5 μm, which are used for optical communications, due to overtones of C–H stretching vibration, limiting the performance in electro-optic (EO) applications. In this work, we investigated an ionic chromophore having C–F bonds instead of C–H bonds, since C–F bond shifts the absorption to lower energy. Sonoda et al. have synthesized deuterated compounds4–6 for the same reason. However, shift range after C–D substitution is smaller than that after C–F substitution, because fluorine is heavier than deuterium. Thus, we tried to synthesize a chromophore with fluorine instead of hydrogen. In a previous study, we have synthesized 4-[2-(4-dimethylamino-2,3,5,6-tetrafluorophenyl)ethynyl]-N,N,N-trimethylanilinium iodide (1a) (iodide salt of 1 as shown in Fig. 1). We have found that its β value is 7 times greater than 4-nitroaniline (pNA), which is traditionally used as a NLO material, in spite of having almost the same absorption region.7 Therefore, we investigated fluorine substitution of the hydrogen atoms attached to the benzene rings of 1. Namely, 4-[2-(4-dimethylamino-2,3,5,6-tetrafluorophenyl)ethynyl]-2,3,5,6-tetrafluoro-N,N,N-trimethylanilinium (2), as shown in Fig. 1, was synthesized, and its optical properties were studied.

Experimental

Calculated β values (β0calc), excitation energy (E0g), and dipole moment difference between the ground and excited states (Δμ0g) of pNA, 1 and 2 were obtained by semiempirical molecular orbital (MO) calculations using MOPAC94 PM3 (CAChe ver. 4.1.1) on their optimized structure. Compound 2a was synthesized according to Fig. 2. Experimental procedures are described below.

Fig. 1. Chemical structures of 1 and 2.
yellow liquid (47 g, 92%). ¹H NMR (CDCl₃, δ) 2.97 (t, J = 2.2 Hz, 6H); ¹³C NMR (CDCl₃, δ) 43.1 (t, J_C-F = 4.3 Hz), 60.5 (t, J_C-F = 27.9 Hz), 131.8 (tt, J_C-F = 2.5, 10.5 Hz), 141.5 (ddddd, J_C-F = 4.6, 7.1, 13.9, 241 Hz), 147.4 (dddd, J_C-F = 4.6, 7.1, 13.9, 241 Hz); Found: C, 30.04; H, 1.93; N, 4.18%. Calcd for C₈H₁₀F₄N: C, 30.12; H, 1.90; N, 4.39%.

2,3,5,6-Tetrafluoro-4-trimethylsilylethynyl-N,N-dimethylaniline (5). To a mixture of 4 (25 g, 78 mmol), dichlorobis(triphenylphosphine)palladium(II) (1.1 g, 1.6 mmol), CuCl (0.078 g, 0.46 mmol), and triethylamine (150 mL), trimethylsilylacetylene (15 mL) was added, and the mixture was stirred for 6 days at room temperature under a nitrogen atmosphere. Then, the mixture was filtered, and the solvent in the filtrate was removed under reduced pressure. The residue was purified by vacuum distillation (100–110 °C, 0.67 kPa) to give 5 (88 g, 71%) as pale-yellow liquid. ¹H NMR (CDCl₃, δ) 0.27 (s, 9H), 2.99 (t, J = 2.4 Hz, 6H); ¹³C NMR (CDCl₃, δ) −2.3 (t, J_C-F = 6.6 Hz), 89.4 (t, J_C-F = 3.7 Hz), 95.4 (tt, J_C-F = 1.5, 18.5 Hz), 106.0 (t, J_C-F = 3.5 Hz), 132.0 (tt, J_C-F = 2.2, 11.1 Hz), 141.1 (ddddd, J_C-F = 3.9, 6.5, 13.4, 248 Hz), 147.8 (ddddd, J_C-F = 3.9, 6.5, 13.4, 248 Hz); Found: C, 53.94; H, 5.40; N, 4.64%. Calcd for C₁₉H₁₅F₄N₂Si: C, 53.96; H, 5.23; N, 4.84%.

4-Ethynyl-2,3,5,6-tetrafluoro-N,N-dimethylaniline (6). To a mixture of 5 (7.5 g, 26 mmol) and tetrahydrofuran (50 mL), 1 mol L⁻¹ tetrahydrofuran solution of tetrabutylammonium fluoride (52 mL) was added, and the mixture was stirred for 16 h. Then, concentrated hydrochloric acid (20 mL) and water (200 mL) were added, and the mixture was extracted with ether (150 mL × 3). The organic phase was dried over Na₂SO₄ and filtered. Solvent in the filtrate was removed under reduced pressure to give 6 (6.0 g, 88%) as pale-yellow liquid. ¹H NMR (CDCl₃, δ) 3.00 (t, J = 2.4 Hz, 6H), 3.50 (s, 1H); ¹³C NMR (CDCl₃, δ) 42.8 (t, J_C-F = 4.3 Hz), 69.3 (t, J_C-F = 3.6 Hz), 87.2 (t, J_C-F = 3.4 Hz), 93.3 (t, J_C-F = 18.3 Hz), 132.5 (tt, J_C-F = 2.6, 10.4 Hz), 140.8 (ddddd, J_C-F = 4.2, 6.6, 12.7, 248 Hz), 148.0 (ddddd, J_C-F = 4.2, 6.6, 12.7, 248 Hz); Found: C, 55.81; H, 3.64; N, 5.84%. Calcd for C₁₀H₁₅F₄N₂: C, 55.31; H, 3.25; N, 6.45%.

4,4'-Ethylenediylbis(2,3,5,6-tetrafluoro-N,N-dimethylaniline) (7). To a mixture of 6 (10 g, 46 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.64 g, 0.91 mmol), CuCl (0.046 g, 0.46 mmol), and triethylamine (150 mL), 4 (15 g, 47 mmol) was added, and the mixture was stirred for 3 days at room temperature under a nitrogen atmosphere. Then, the mixture was filtered, and solvent in the filtrate was removed under reduced pressure. The residue was recrystallized from chloroform to give 7 (7.0 g, 37%) as yellow crystals. Mp 195 °C; ¹H NMR (CDCl₃, δ) 3.02
A mixture of 7 (4.5 g, 11 mmol) and methyl trifluoromethanesulfonate (6.9 mL) were stirred for 2 days at room temperature. Then, chloroform was added, and the solution was filtered. The solid was washed with chloroform. After dissolving the remaining solid part using ethanol, the precipitate was filtered off. The solvent of the filtrate was removed under reduced pressure. The residue was recrystallized from methanol to give 2b (3.5 g, 55%) as pale-yellow crystals. Mp 238 °C; $^1$H NMR (CD$_2$OD, $\delta$) 3.08 (t, $J = 2.7$ Hz, 6H), 3.94 (t, $J = 1.8$ Hz, 9H). Found: C, 41.52; H, 3.09; N, 4.89%. Calcd for C$_{14}$H$_{21}$N$_2$: C, 41.97; H, 2.64; N, 4.89%. Unfortunately, $^{13}$C NMR data of 2b could not be obtained because of the low solubility.

4-[2-(4-Dimethylamino-2,3,5,6-tetrafluorophenyl)ethyl]ene]-2,3,5,6-tetrafluoro-N,N,N-trimethylsilanilinium Trifluoromethanesulfonate (2b). A mixture of 7 (4.5 g, 11 mmol) and methyl trifluoromethanesulfonate (6.9 mL) were stirred for 2 days at room temperature. Then, chloroform was added, and the solution was filtered. The solid was washed with chloroform. After dissolving the remaining solid part using ethanol, the precipitate was filtered off. The solvent of the filtrate was removed under reduced pressure. The residue was recrystallized from methanol to give 2b (3.5 g, 55%) as pale-yellow crystals. Mp 238 °C; $^1$H NMR (CD$_2$OD, $\delta$) 3.08 (t, $J = 2.7$ Hz, 6H), 3.94 (t, $J = 1.8$ Hz, 9H). Found: C, 41.52; H, 3.09; N, 4.89%. Calcd for C$_{14}$H$_{21}$N$_2$: C, 41.97; H, 2.64; N, 4.89%. Unfortunately, $^{13}$C NMR data of 2b could not be obtained because of the low solubility.

The melting points were determined by a differential scanning calorimeter (Perkin-Elmer Pyres Diamond DSC). The chemical structures of the compounds obtained were confirmed by $^1$H and $^{13}$C NMR spectroscopies (JEOL LAMBDA 400) and elemental analysis (IMRAM, Tohoku University). UV–visible absorption spectra were recorded on a Jasco V-570 spectrophotometer. IR spectra were recorded on a Nicolet AVATAR 360 spectrometer. Hyper-Rayleigh scattering (HRS) measurements$^{21}$ for 1a and 2b were performed by using a nano-second Nd:YAG laser (Coherent Infinity™ 40–100) at 1064 nm. These measurements were executed in methanol and pNA was used as an external standard,$^{22}$ of which the $\beta$ value at 1064 nm in methanol is $3.45 \times 10^{-29}$ esu. According to the two-level model,$^{23}$ the $\beta$ values obtained were adjusted to $\beta$ at zero frequency ($\beta_{\text{expt}}$). The SHG activities of synthesized crystals were confirmed by the emission of green light ($539.5$ nm) after irradiation with a Nd:YAP laser (Elmas L-100) at $\lambda = 1079$ nm. This was conducted only for qualitative purpose to remove the centrosymmetric crystals from further investigation. X-ray crystallographic analysis was performed using a Mac Science MXC3 diffractometer with a Mo Kα source ($\lambda = 0.71073$ Å) for a crystal of 2b grown in methanol solution by the slow evaporation method. Cell parameters were determined from 22 preliminary reflections. The crystal structure was determined by direct methods and refined by full-matrix least-squares procedures using the CRYSTAN program. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were attached to their parent atoms by fixed bond lengths and idealized bond angles and were refined isotropically. Crystallographic data have been deposited in Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-255977. Copies of the data can be obtained free charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).


Results and Discussion

MO calculations were performed on pNA, 1, and 2 as shown in Table 1. The $\beta_{\text{calc}}$ of 2 was estimated to be about 9 times greater than that of pNA, whereas the $E_{\text{ex}}$ values were similar. The iodide salt of 2 (2a) was found to be unstable, and half of it was changed to 7 in a few days at room temperature. This is due to the relatively strong nucleophilicity of iodide anion compared to trifluoromethanesulfonate anion. An ammonio methyl group of 2a is eliminated by nucleophilic attack of the iodide anion to give 7, and the resulting methyl iodide evaporates. Then, in order to estimate the linear and nonlinear optical properties of cation 2, 2b was used instead of 2a. The UV and visible absorption spectra of 2b were measured in a methanol solution and compared with that of pNA. As shown in Fig. 3, absorption maximum wavelength ($\lambda_{\text{max}}$) of 2b was 342 nm, which is 27 nm shorter than that of pNA. However, absorption cutoff was almost the same, because 2b had a shoulder at about 380 nm. In the solid state, the shoulder of 2b disappeared, and the cutoff wavelength of 2b was found to be shorter than that of pNA, as shown in Fig. 4. For $\lambda_{\text{max}}$, a similar tendency between two compounds was observed. The IR spectra of 2b were also measured and compared with trifluoromethanesulfonate salt of 1 (1b) as shown in Fig. 5. Transmittances of 1b and 2b were normalized to each other in relation to the absorption around 2200 cm$^{-1}$, which originates from stretching vibration of the C=C bond. Absorption of C–H stretching vibration around 3000 cm$^{-1}$ of 2b was found to be weaker compared to 1b, because of the reduced number of C–H bonds in 2b. Accordingly, lower absorption of 2b around 1.3 and 1.5 μm than 1b was expected, since absorption around these wavelength regions is assigned to be overtones of C–H stretching vibration. Hyper-Rayleigh scatter-

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<th>ε$^2$</th>
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<td>750</td>
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Table 1. Calculated $E_{\text{ex}}$, $\Delta\mu_{\text{ex}}$, and $\beta_{\text{ex}}$ Values of pNA, 1, and 2
dard, the By comparing these data to those for pNA as an external stan-
of the ion-pair number density in the corresponding solution. shows a linear plot of the quadratic coefficient as function of the data, quadratic coefficients were obtained. The inset before. However, crystals were only obtained for so far. From the X-ray crys-
tallographic analysis, the space group of the crystal of 2b was found to be \( \text{Pc} \), which is noncentrosymmetric, and the polar axis of this crystal was in ac plane. Details of crystallographic data and projection of the crystal structure are shown in Table 2 and Fig. 7, respectively. The angle between the polar axis and molecular long axis was found to be about 14°, if the molecular long axis was taken as a line linking two nitrogen atoms in the cation. Using this information, the second-order NLO coefficient \( (d) \) was estimated by using the oriented-gas model. The local field factors of 2b were set to be the same as those of a crystal of \( \text{4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium p-toluene sulfonate (DAST)} \), which is a known organic ionic chromophore for second-order NLO material. As a result, the diagonal component \( (d_{11}) \) and off-diagonal component \( (d_{12}) \) were estimated to be 610 and

![Fig. 4. UV and visible diffuse reflectance spectra of 2b (solid line) and pNA (dotted line). Spectra were normalized at the maximum.](image)

![Fig. 5. IR spectra of 1b (dotted line) and 2b (solid line). Spectra were normalized using the absorption band around 2200 cm\(^{-1}\).](image)

![Fig. 6. The quadratic dependence between fundamental and second-harmonic intensities of 2b in methanol at different ion-pair number densities: A, \( 5.17 \times 10^{17} \) cm\(^{-3}\); B, \( 1.03 \times 10^{17} \) cm\(^{-3}\); C, \( 1.55 \times 10^{17} \) cm\(^{-3}\); D, \( 2.07 \times 10^{17} \) cm\(^{-3}\); E, \( 2.59 \times 10^{17} \) cm\(^{-3}\). Inset: the linear plot of the quadratic coefficient as function of the number density.](image)

### Table 2. Crystallographic Data of 2b

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<th>Formula</th>
<th>( \text{C}<em>{20}\text{H}</em>{13}\text{F}<em>{11}\text{N}</em>{2}\text{O}_{3} \text{S} )</th>
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<td>11.155(3)</td>
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<tr>
<td>( b/\text{Å} )</td>
<td>14.255(7)</td>
<td>117.4(1)</td>
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<tr>
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<tr>
<td>No. of unique reflections</td>
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are caused by the large greater off-diagonal component than that of NPP. These results with those of MNA and NPP, 3b
d stretching vibration are most prominent, compared with 1b
structure of a compound, 24 the corresponding chromophore

155 pm V−1, respectively. 2-Methyl-4-nitroaniline (MNA)17 and N-(4-nitrophenyl)-1-l-prolinol (NPP)18-20 are known to be
typical second-order NLO materials, and they have a similar absorption to 2b. Thus, the d values of these two crystals were
also estimated by the same manner. MNA was found to have
d11 = 43.9 and d12 = 21.8 pm V−1 and NPP had d22 = 8.9 and
d21 = 24.0 pm V−1. When the d values of 2b were compared
with those of MNA and NPP, 2b was found to have 14 times
greater diagonal component than that of MNA and 6.5 times
greater off-diagonal component than that of NPP. These results are
carried by the large β value, which represents microscopic
efficiency, and efficient cation alignment in the crystal of 2b
compared with MNA and NPP.

In conclusion, we successfully synthesized the partially
fluorinated skeleton 2. From the UV and visible absorption
spectrum, λmax of 2b was shorter than that of pNA, while the
βv value was about 8 times larger. In the IR spectra, absorption
originated from C–H stretching vibration of 2b was less
intense than that of 1b. Therefore, 2b should have a lower
absorption around 1.3 and 1.5 μm, where overtones of C–H
stretching vibration are most prominent, compared with 1b.
By using the oriented-gas model, the diagonal d component of
2b was estimated to be 14 times greater than that of MNA, and
the off-diagonal d component was estimated to be 6.5 times
greater than that of NPP. From these results, we think that
2b is an excellent candidate for second-order NLO device
applications. Since deuteration of hydrogen in methyl group
is not so difficult task and generally does not change the crystal
structure of a compound, 24 the corresponding chromophore
without C–H bonds is being synthesized and investigated.

Fig. 7. Crystal structure of 2b viewed along the a axis.
Hydrogen atoms were omitted.

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