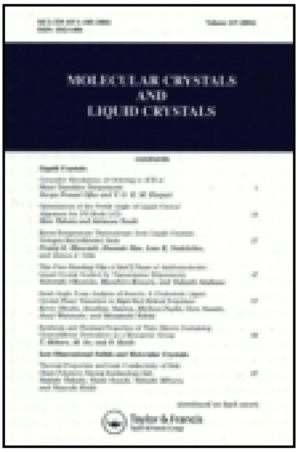

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Aminostilbazolium Derivatives Substituted by Hydroxyethyl Groups for Second-Order Nonlinear Optics

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As DAST (1-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium p-*toluenesulfonate) derivatives for improved crystal stability and inhibition of crystal water inclusion, 1-(2-hydroxyethyl)-4-(2-{4-[bis(2-hydroxyethyl)amino]phenyl}ethenyl)-pyridinium salts* ***2*** *(**2a**–**2l**) and 1-(2-hydroxyethyl)-4-{2-[4-(diethylamino)phenyl]-ethenyl}pyridinium salts* ***3*** *(**3a**–**3l**) were synthesized and their properties were investigated. Salts* ***3*** *were found to have no crystal water, and the cation with one hydroxyethyl group was effective to eliminate water inclusion in the crystals. Although the melting points of* ***2*** *were lower than those of the corresponding* ***3****, decomposition temperatures of these chromophores were above 250°C indicating their good thermal stability. Crystals of* m-*nitrobenzenesulfonate salt* ***3f*** *was obtained without crystal water and showed SHG activity.*

Keywords Aromatic compound; DAST; ionic dye; organic crystal; second-order nonlinear optics

1. Introduction

Utilization of organic second-order nonlinear optical (NLO) crystals as electro-optic devices [1] or terahertz-wave emitters has been extensively investigated [2,3]. Among the organic NLO crystals, 1-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}-pyridinium *p*-toluenesulfonate (DAST) [4–6] is one of the promising materials [1,2,7–10]. However, its crystal growth should be strictly controlled, and the yield of the crystals with both an appropriate size and a good optical quality is not so high. In addition, the obtained crystals are affected by water to be second-order NLO inactive crystals [11]. These points should be improved for the DAST derivatives in the next generation besides enhancement of the NLO susceptibility. In our previous studies, we have investigated synthesis of pure DAST [12], DAST derivatives with different counter anions [13,14] and DAST derivatives with extended π-conjugation in the cation part [15,16]. In this study, we introduced hydroxyethyl

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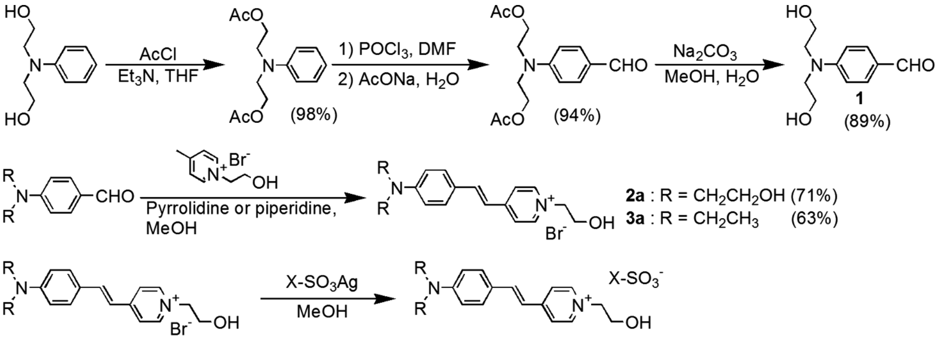
Address correspondence to Shuji Okada, Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan. E-mail: okadas@yz.yamagata-u.ac.jp groups instead of all or a part of methyl groups of the DAST cation to study about the effect of hydroxy groups for crystal stability and crystal water inclusion. Introduced hydroxy groups are also useful for further molecular modification. The bromide salts and the anion-exchanged compounds were prepared and their properties were investigated. Although preparation and luminescent property of the nanocomposite of **2a** with zinc sulfide has been reported [17], crystals of the anion-exchanged salts were not investigated so far.

2. Experimental

Aminostilbazolium derivatives were synthesized according to Figure 1. 4-[*N,N*-bis(2-hydroxyethyl)amino]benzaldehyde **1** was prepared by the Vilsmeier formylation referring to the literature [18]. This reaction starting from 2,2′-(phenylimino)-diethanol gave the targeting aldehyde **1** in 82% yield. Condensation reaction [19] of the resulting aldehyde and 4-(diethylamino)benzaldehyde with 1-(2-hydroxyethyl)-4-methylpyridinium bromide afforded bromide salts **2a** and **3a** in 71% and 63% yields, respectively. Anion-exchange reaction of **2a** and **3a** using silver sulfonates [14] resulted in the corresponding sulfonates in the yields from 9% to almost quantitative. The salts obtained were purified by recrystallization from methanol-ethanol mixed solvent.

^{1}H NMR spectra were recorded for deuterated methanol or chloroform solution on a JEOL ECX-400 spectrometer. IR spectra were obtained for KBr-pelletized samples by using a Horiba FT-210 spectrometer. UV-vis spectra in methanol were recorded on a Jasco V-560 spectrophotometer. Thermogravimetric and differential thermal analyses (TG/DTA) were performed using a Seiko Instruments TG/DTA220 apparatus with heating rate of 10°C/min. Elemental analyses were performed using a Perkin-Elmer 2400II analyzer at Elementary Analysis Laboratory, Department of Polymer Science and Engineering, Yamagata University. X-ray crystallographic analysis was carried out using a Rigaku RAXIS-RAPID diffractometer. Second-order NLO activity of the crystals was verified by



2b, **3b** : X = *p*-tolyl (88%, 9%)
2c, **3c** : X = *p*-hydroxyphenyl (62%, 100%)
2d, **3d** : X = *p*-chlorophenyl (ND, 100%)
2e, **3e** : X = *p*-nitrophenyl (ND, 52%)
2f, **3f** : X = *m*-nitrophenyl (ND, 64%)
2g, **3g** : X = *p*-aminophenyl (50%, 92%)
2h, **3h** : X = *m*-aminophenyl (72%, 78%)
2i, **3i** : X = *p*-ethylphenyl (ND, 9%)
2j, **3j** : X = phenyl (43%, 59%)
2k, **3k** : X = 1-naphthyl (84%, 80%)
2l, **3l** : X = 2-naphthyl (65%, ND)

Figure 1. Synthesis scheme of DAST derivatives with hydroxyethyl groups. Percentages in parentheses are the compound yields, in which ND indicates that the pure compounds were not isolated and the accurate yields could not be determined.

second-harmonic generation (SHG) of green emission at 532 nm when a Q-switched Nd:YAG laser at 1064 nm (Lotis LS-2137U) was irradiated to the powder samples.

3. Results and Discussion

All compounds were successfully synthesized and the structures were confirmed by ^{1}H NMR spectra. When original salts were contained in the anion-exchanged crystals as impurity, recrystallization was repeated and the yield decreased. The yield of the anion-exchanged salts with high solubility was also tend to be low. Figure 2 shows UV-vis absorption spectra of **2a** and **3a**. By replacing the substituents attached to the amino group from ethyl to hydroxyethyl groups, the absorption maximum (λ_{max}) was blue-shifted by 12 nm. This result indicates that the hydroxyethyl groups decrease electron-donating ability of the amino group compared with the ethyl groups.

The data on thermal analyses of **2a** and **3a** are displayed in Figure 3. They only showed one endothermic peak corresponding to the melting points, and there was no weight loss below the melting points. This result suggests that these crystals contained no crystal water, and it was also confirmed by the elemental analysis. These chromophores were found to have high thermal stability because weight loss of these compounds was not observed up to around 250°C. Melting points of the crystals are summarized in Table 1. Crystals of **2d**, **2f** and **2i** were not obtained by recrystallization from methanol-ethanol mixed solvent because of their high solubility for the solvent. Although their recrystallization was also tried using methanol mixed with chloroform or THF or ethyl acetate, oily residues were obtained. Since high affinity for water was considered in these salts, an experiment to remove water from **2f** as an example was performed. The oily residue of **2f** was refluxed in toluene using a Dean-Stark apparatus, and water was eliminated to give solid material. When the resulting solid was exposed in air, solid became wet. Namely, water in air seemed to be easily adsorbed in the compound. For **2e** and **3l**, impurity mainly originated from the silver arenesulfonate salts was confirmed by ^{1}H NMR, and it was hard to remove by the recrystallization process. Among the compounds obtained as crystals, **2b**, **2c**, **2g** and **2l** contained crystal water under ambient recrystallization conditions, and **2b** crystals with crystal water were deliquescent. When these crystals with crystal water were heated at 100°C for 2 h under reduced pressure to dehydrate, crystal water in **2c** and **2g** could be eliminated but that in **2b** and **2l**

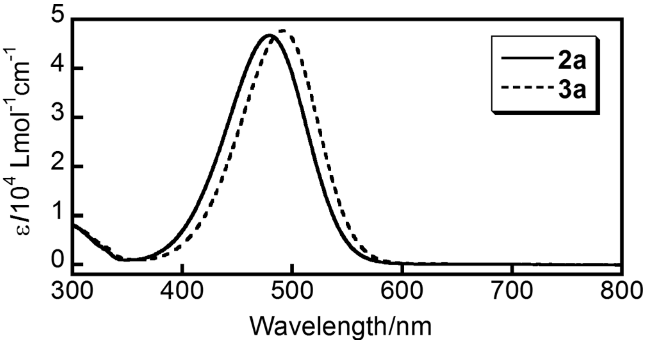


Figure 2. UV-vis spectra of **2a** and **3a** in methanol.

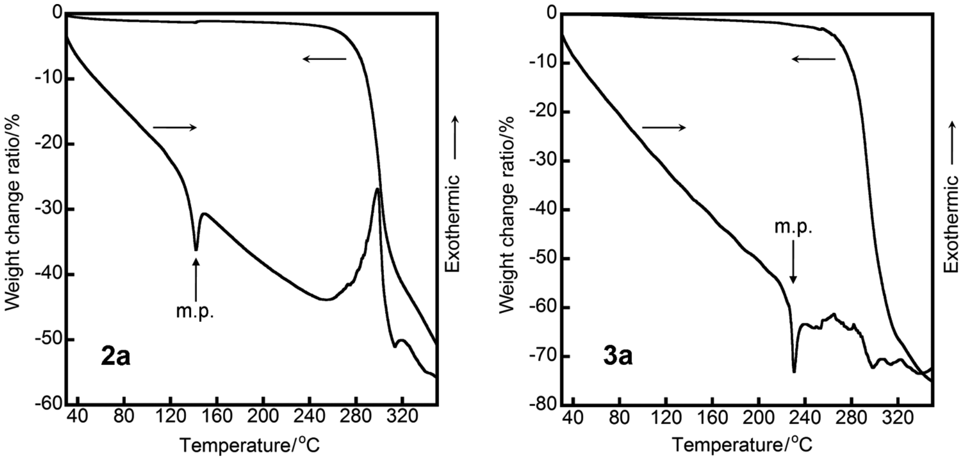


Figure 3. TG/DTA thermograms of **2a** and **3a**.

could not be. The crystals except the above four salts were obtained without crystal water by simple recrystallization. In particular, all obtained crystals of **3a** derivatives were found to have no crystal water, and introduction of one hydroxyethyl group per cation seems to be quite effective to avoid water inclusion in the crystals.

In general, when the number of hydroxy groups increase among compounds with the same structure except the number of hydroxy groups, melting points become high, e.g., the melting points of 1-propanol, 1,3-propanediol and 1,2,3-propanetriol are −127°C, −27°C and 20°C, respectively [20]. This is due to increase in the number of intermolecular hydrogen bonds per molecule. However, in the present case, **2a** with three hydroxy groups showed lower melting point than **3a** with one hydroxy group, and the same relation was found in other salts with the same anion. In IR spectra, peaks for free O-H stretching vibration are generally observed at around $3600\,\mathrm{cm}^{-1}$. Since the peaks of **2a** and **3a** derivatives appeared from $3200\,\mathrm{cm}^{-1}$ to $3300\,\mathrm{cm}^{-1}$, all derivatives were found to form hydrogen bonding. For **3a**, X-ray crystallographic analysis was carried out [21] and the OH group was found to be near a bromide anion to form hydrogen bonding. Sulfonate derivatives of **3a** generally showed the sharper OH peaks in the lower wavenumber region compared with the corresponding **2a** derivatives, indicating that the hydrogen bonds

Table 1. Melting points of crystals

	Melting point/°C											
	a	b	c	d	e	f	g	h	i	j	k	l
2	142	114[a]	141[a]	–[b]	–[c]	–[b]	155[a]	191	–[b]	152	189	113[a]
3	231	130	228	196	189	153	196	225	182	173	205	–[c]

[a] The crystals obtained by recrystallization included crystal water.

[b] The crystals were not obtained by recrystallization from methanol-ethanol mixed solvent.

[c] Purification could not be completed by recrystallization from methanol-ethanol mixed solvent.

of **3a** derivatives were stronger than those of **2a** derivatives. In addition, hydroxyethyl group with three non-hydrogen atoms seemed to have more flexibility than ethyl group with two non-hydrogen atoms, and stabilization by intermolecular hydrogen bonds may be weakened. Therefore, **3a** derivatives showed higher melting points than the corresponding **2a** derivatives. The decomposition temperatures were found to be above 250°C, and all compounds showed good thermal stability as chromophores. Among the synthesized salts with or without crystal water, only *m*-nitrobenzenesulfonate salt **3f** showed SHG activity. The probability to obtain SHG active crystals was not so high in this study. However, it is not a serious problem because SHG activity can be achieved by proper selection of the counter anion.

In conclusion, the aminostilbazolium derivatives having hydroxyethyl groups accompanied by a variety of counter anions **2a**–**2l** and **3a**–**3l** were synthesized and their thermal properties, crystal water inclusion and SHG activity were studied. Obtained crystals of **3a** derivatives do not contain crystal water at all although some derivatives of **2a** include crystal water. When three hydroxy groups were introduced in a cation like **3a** derivatives, hydrophilicity became too large to avoid crystal water inclusion. On the other hand, one hydroxy group in the cation gave good results to exclude crystal water. The melting points of **3a** derivatives were higher than those of the corresponding **2a** derivatives. However, both cationic chromophores have high thermal stability above 250°C without decomposition. Although a similar chromophore with two hydroxyethyl groups has been incorporated in a polymer structure [22], **2a** derivatives are more suitable for the NLO chlomophores in polymer matrixes because there are three crosslinkable parts to fix the poled orientation. Crystals of **3f** have SHG activity and no crystal water. Therefore, by extending conjugated system of **3a** cation, high-performance crystals without crystal water will be prepared.

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