

Engineering of Acentric Stilbazolium Salts with Large Second-Order Optical Nonlinearity and Enhanced Environmental Stability

Zhihua Sun,[†] Xitao Liu,[‡] Xinqiang Wang,[‡] Lina Li,[†] Xiaojun Shi,[†] Shigeng Li,[†] Chengmin Ji,[†] Junhua Luo,^{*,†} and Maochun Hong[†]

[†]Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[‡]State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan, Shandong 250100, China

(5) Supporting Information

ABSTRACT: A series of organic nonlinear optical (NLO) materials based on the stilbazolium derivatives of 4-*N*,*N*-dimethylamino-4'-*N*'-methyl-stilbazolium tosylate (DAST) were synthesized, and the single crystals were grown from the solutions. Single-crystal structure determinations and Kurtz powder tests reveal that replacement of the *p*-toluenesulfonate anion in the DAST crystal, forming 4-*N*,*N*-dimethylamino-4'-*N*'-methyl-stilbazolium 4-aminotoluene-3-sulfonate (1) and 4-*N*,*N*-dimethylamino-4'-*N*'-methyl-stilbazolium *p*-chlorobenzenesulfonate (2), constructs new acentric crystals with quite a large powder second-harmonic generation (SHG) of more than 3 orders of magnitude larger than that of urea around 2.0 μ m, whereas the other two complexes show their centrosymmetric structures without any SHG effects. A possible estimation of the



molecular first hyperpolarizabilities β_{ijk} performed on 2 further confirms its origin of its enhanced NLO merits. Furthermore, both 1 and 2 exhibit even higher environmental stabilities, including the antiwater performance and the formation of anhydrous phases in water-containing solutions. We believe that the findings of the further counterion modification will bring new stilbazolium derivatives with improved optical nonlinearities and the physicochemical performances.

1. INTRODUCTION

Organic nonlinear optical (NLO) materials have greatly attracted much attention owing to their promising and wide applications, such as optical signal processing, integrated photonics, optical switching, and the frequency conversion, including THz-wave generation in the past decades.¹ Among the organic materials, stilbazolium crystals with a high chromophore number density and excellent long-term thermodynamic orientations possess quite prominent second-order (quadratic) NLO properties. Particularly, the crystal of 4-N,N-dimethylamino-4'-N'-methylstilbazolium tosylate (DAST) exhibits remarkable bulk quadratic NLO activities with the powder second-harmonic generation (SHG) efficiency 3 orders of magnitude larger than that of urea at 1907 nm.² Owing to its quite outstanding NLO susceptibilities $(d_{11} > 1000 \text{ pm/V}))$, large electro-optic coefficients $(r_{111} =$ 77 pm/V), and low dielectric constants ($\varepsilon_1 = 5.1$), the DAST crystal has been considered as an excellent candidate for highspeed electro-optic applications, such as THz generators and detectors, electro-optic modulators, optical parametric generators, frequency multipliers, etc.³ Hence, the high-performance properties of DAST have not only accelerated the preparation of bulk high-quality single crystals and thin films⁴ but also promoted the engineering of many stilbazolium derivatives with similar architectures and the improved merit figures,⁵ such as DSTMS with 2,4,6-trimethylbenzenesulfonate anion and DSNS with

2-naphthalenesulfonate anion. However, the major impediment when attempting to engineer NLO stilbazolium materials is still how to orient the chromophores with large molecular first hyperpolarizabilities (β) into a noncentrosymmetric arrangement.^{2d}

Recently, many efforts were extensively made by different research groups to assemble new stilbazolium materials with the enhanced merit figures, including the nonlinear optical properties and the physical performances, such as environmental stability.⁶ Taking DAST crystals as the example, a centrosymmetric monohydrate phase of DAST·H2O is easily formed at the presence of solvent water.⁷ In that case, the air humidity will damage the crystal device, which requires more strict protecting conditions for crystal growth and practical application. Additional measurements should be adopted to protect the crystal devices. To satisfy the requirement of physical properties by crystal engineering, the molecular assembly of a desired structure or crystal symmetry is still most challenging owing to the tendency of imperfect molecular orderings in the crystalline state.⁸ One possible strategy is to design the new acentric molecular complexes with much higher physical stabilities; that is,

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introducing substituted anionic or cationic moieties favors the design of DAST derivatives.^{6b} This strategy has been evidenced to be a simple, but highly successful, approach. Encouraged by the pioneering work, herein, a series of stilbazolium derivatives were synthesized by modifying the structure of DAST counterions through the ion-exchange reaction. Single-crystal structures, environmental stabilities, and optical properties of the obtained derivatives were systematically investigated, which reveal that the anionic modifications of DAST derivatives could assemble new potential NLO materials.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Crystal Growth. All the chemical reagents were purchased as high purity (AR grade) and used without any further purification. Metathesization of the iodide precursor with the corresponding sodium/ammonium or silver anionic salts was used to synthesize the products, as described previously.^{6c} In detail, 4-*N*, *N*-dimethylamino-4'-*N*'-methyl-stilbazolium 4-aminotoluene-3-sulfonate (1), 4-*N*,*N*-dimethylamino-4'-*N*'-methyl-stilbazolium *p*-chlorobenzenesulfonate (2), and 4-*N*,*N*-dimethylamino-4'-*N*'-methyl-stilbazolium *p*-hydroxylbenzenesulfonate hydrate (3) were synthesized by ion-exchange reaction of the respective benzenesulfonate ammonium salts with 4-*N*, *N*-dimethylamino-4'-*N*'-methylstilbazolium iodide, prepared from 4-picoline, methyl iodide, and 4-*N*,*N*-dimethylamino-benzaldehyde in the presence of piperidine. Complex 4 was obtained with trifloromethanesulfonate silver salt (see Scheme 1). Subsequently, the raw materials were purified by

Scheme 1. Molecular Structures of the Synthesized Stilbazolium Derivatives of 1–4



recrystallization three times from methanol solutions. The obtained fine precipitates were dried in a vacuum for 24 h to remove solvents before their characterization.

Crystals were grown using the temperature-lowering method and slow evaporation solution.⁹ All the growth experiments were carried out at constant temperatures with the controlled stability of ± 0.1 °C. Different solvents were chosen according to the solubility of products in those solvents, such as methanol, acetonitrile, and water. Herein, the saturated methanol solutions were prepared at 45–50 °C and then filtered by 0.2 μ m Millipore filters, whereafter, the solutions were slowly preheated and kept about 5–6 °C above their preliminary status, which guarantees the dissolution and homogenization of all ingredients. The temperature-lowering rate was 0.2 °C/day, and crystals with sizes of a few micrometers were obtained after several days (see Figure 1).

X-ray morphology studies indicate that the $(00\overline{1})$ face is dominant to determine the growth of 1 and 2. However, distinctive growth habits are observed owing to their different crystallographic symmetry, that is, the columnar shape of 1 and the plate shape of 2 shown in Figure 1. It is noteworthy that complex 2 presents a quite similar morphology with that of DAST, favoring the subsequent fabrication of THz devices. Moreover, single-crystalline thin films of 2 with a relatively large *c*-plane surface were easily achieved in acetonitrile solution (see Figure S1, Supporting Information), which is quite attractive in the integrated optics applications. The detailed growth and characterization of the thin films are now in progress. Article



Figure 1. Crystals of 1 (a) and 2 (b) grown from the mixed solvents of water/methanol and their growth morphology.

2.2. Structure Determination and Basic Characterization. X-ray single-crystal diffraction data were collected on a Rigaku Saturn 70 diffractometer with a CCD detector (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$) at 293 K. The CrystalClear software package (Rigaku) was used for data collection, cell refinement, and data reduction. All the crystal structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXLTL software package.¹⁰ All non-hydrogen atoms were refined anisotropically, and the positions of hydrogen atoms bound to carbon were generated geometrically. The N-bound and O-bound H atoms were located from a difference Fourier map and refined anisotropically. Table 1 presents the details of data collection and the data summary for 1–4. CCDC 901355–901357 contain the supplementary crystallographic data for this paper.

Purities of the grown crystals of 1 and 2 were confirmed by the X-ray powder diffraction (XRPD) performed on a MiniFlex II X-ray diffraction instrument. Thermogravimetric analysis (TGA) was recorded using a NETZSCH STA 449C unit with the heating rate of 10 °C/min under a nitrogen atmosphere. Nonlinear optical properties were con-firmed by the Kurtz and Perry technique,¹¹ that is, the second-harmonic generation (SHG) powder test. The ground microcrystalline powdered samples were filtrated with different sizes and placed between two glass plates with a thickness of 2 mm. The measured SHG signals were converted into the measurable signal voltage with the fundamental beam being removed by appropriate filters. The collected digital signals were then investigated by a photomultiplier and displayed with a DS1052E digital oscilloscope with respect to the corresponding powdered DAST samples with the same particle sizes of 63–90 μ m as reference. A Q-switching laser with a wavelength of 2.0 μ m was used as fundamental radiation to determine the SHG efficiency. The density functional theory (DFT) was used to optimize the corresponding crystal structure of 2, in order to calculate the first hyperpolarizability tensors by using the hybrid functional B3LYP with the $\overline{6}$ - $\overline{311}$ + G(d) mode with the finite field method.

3. RESULTS AND DISCUSSION

3.1. Analysis of Crystal Structures. All the molecular crystal structures of 1–4 are presented in Figure 2. The crystal structure of 1 belongs to the triclinic crystal system and the space group symmetry *P*1 with one ion-pairing counterpart per unit cell. The three-dimensional packing structure presents a parallel alignment of the chromophore cations with the alternating perpendicular acentric sheets of counterions. The arrangement of stilbazolium chromophores meets the criterion of the possible order parameter $\langle \cos^3 \psi \rangle = 1$, treated as a prerequisite

Table 1. Summary of Crystallographic Data for Complexes 1-4

	1	2	3	4
empirical formula	$C_{23}H_{27}N_3O_3S$	C22H23ClN2O3S	$C_{22}H_{26}N_2O_5S$	$C_{17}H_{19}F_3N_2O_3S$
formula wt	425.54	430.93	430.51	388.40
cryst syst, space group	triclinic, P1	monoclinic, Cc	monoclinic, $P2_1/c$	monoclinic, P2 ₁ /c
cell parameters	a = 7.2651(6)	a = 10.363(5)	a = 14.208(6)	a = 17.508(5)
	b = 8.983(2)	b = 11.163(5)	b = 10.027(4)	b = 7.607(2)
	c = 10.1090(15)	c = 17.892(6)	c = 16.146(7)	c = 13.533(4)
	$\alpha = 97.82(8)^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 110.42(5)^{\circ}$	$\beta = 92.15(3)^{\circ}$	$\beta = 113.042(6)^{\circ}$	β = 93.712(6) °
	$\gamma = 112.30(6)^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
	V = 543.92(54)	V = 2068.2(15)	V = 2116.7(15)	V = 1798.4(10)
Z, $\rho_{\rm cal}$	1, 1.299 g/cm ³	4, 1.384 g/cm ³	4, 1.351 g/cm ³	4, 1.434 g/cm ³



Figure 2. Molecular structures with various symmetries of complexes 1–4.

expected for the possible efficient electro-optic or second-order NLO effects.¹² Crystallographic data indicate that H bonds also play a role in crystal packing and chromophore orientation, in addition to the strong Coulombic interactions between cationic and anionic parts. It is clearly shown that N-H-O type H bonds between the sulfonic oxygen atoms and the neighboring amino groups construct an infinite two-dimensional anionic plane. Furthermore, the perfectly parallel chromophores arrange perpendicular to the anionic planes. The cation layers and the anion layers are linked together through H bonds with the H…O distance of about 2.481 Å. Similar to other stilbazolium derivatives, the weak hydrogen bonds reduce the energy of the whole system and keep it more stable. However, its influence on microscopic and macroscopic nonlinearities may not be negligible. The hydrogen bonds in 1 appear in the π -conjugated bridge part rather at the end of the chromophore, which might diminish the chromophore hyperpolarizability more seriously. The observed smaller bulk second-order optical nonlinearities of 1 would strongly support such a deduction.

Figure 3 presents the packing structure of **2**, which is quite comparative with that of DAST and its derivative, belonging to the monoclinic space group Cc with the point group m. It is noteworthy that there is an isostructural crystal with 4-bromobenzenesulfonate as anion,¹³ which was determined at 100 K without any atomic disorderings. The well-consistent XRPD patterns further confirm their isostructures (Figure S2, Supporting Information). From the packing diagrams, it is clearly shown that the cationic sheets of organic chromophores in **2** are interleaved with that of *p*-chlorobenzenesulfonate anions. The disordered sulfonate moieties are involved with cations into chains by weak C–H…O interactions along the *c* axis (Figure S3,

Supporting Information), accounting for the thin film growth with the large *c*-plane surface. The planes of the *p*-chlorobenzenesulfonate rings are roughly perpendicular to the molecular planes of the cations. Such a crystal packing of flat aromatic molecules, coupled with the electrostatic attraction between the donor of one molecule and the acceptor of an adjacent molecule, is favorable to the formation of the polar cationic sheets.^{2d} The acute angle ψ between the cationic long sheets and the polar *a* axis of the crystal is about 20.5° , giving an order parameter $\langle \cos^3 \psi \rangle = 0.82$ for the projection of molecular nonlinearities to the polar axis. In the case of the DAST crystal, the corresponding ψ value is about 20° and the merit values of $\langle \cos^3 \psi \rangle = 0.83$.^{2a} Therefore, similar nonlinear optical characteristics could be expected for 2 as that of DAST, which is further confirmed by the powder SHG test (about 1.3 times larger than that found in DAST; see Table 2).

The space group symmetries of 3 and 4 are both monoclinic $P2_1/c$ with four ion pairs located per unit cell. The crystal structure and interesting properties of 4 had been described in other work.¹⁴ Herein, we mainly focused on the structure of 3 owing to the planarity of its counterions. Though the cationic chromophores in 3 are arranged almost parallel, their packing directions are totally opposite, which cancels out its SHG activities. Another secondary indicator of its centrosymmetric structure is the assembling participation of the crystal water. Similar with the centrosymmetric crystal structure of DAST·H₂O,⁷ the equilibrium O–H···O hydrogen bonds between water and sulfonate construct a long-chain-like structure and result in the centrosymmetry. Therefore, the results reveal that only DAST and its derivates in the anhydrous phases could possess the possible SHG activities.

3.2. Molecular Hyperpolarizability. To probe the optical nonlinearity of the obtained stilbazolium derivatives at the molecular level, we calculated the first hyperpolarizability tensors by density functional theory (DFT) using the hybrid functional B3LYP with the 6-311+G(d) mode. Here, complex 2 was chosen as the representative because of its bulk larger nonlinearities than that of DAST. The calculated x axis of the coordinate frame was determined along the crystallographic a direction, and the y axis was fixed along the b-axis direction in the ab plane. The z axis was then finally determined to be perpendicular to both x and yaxes according to the right-hand rule. The calculated results of hyperpolarizability tensors for 2 are listed in Table 3 and compared with other stilbazolium salts.¹⁵ When the electron donor and acceptor are exactly located at each end of a chromophore molecule, the long axis of the molecule is assumed to be the main direction of the maximal hyperpolarizability. Though the β_{iik} components present evident diversities owing to the different



Figure 3. (1) Supramolecular interactions of **1** with the triclinic *P*1 symmetry: the H-bonding interactions of N–H···O (1.991 Å) and weak C–H···O bonds (2.481 Å) are illustrated by the dashed black lines. (2) Crystal packing of **2** with a monoclinic *Cc* symmetry viewed along the crystallographic *c* axis showing the chromophores perpendicular to the counterions in the *ab* plane; ψ is the acute angle indicating the orientation of the chromophore relative to the polar *a* axis. (3) Supramolecular interactions of **3** with a monoclinic *P*2₁/*c* symmetry: the selected H-bonds of O–H···O and weak C–H···O are illustrated by the dashed black lines.

Table 2. Powder SHG Efficiencies and Thermal and Environmental Stabilities of 1–4

	thermal stability (°C)	solubility (g/100 g)	antiwater ^c	SHG ^d efficiency
DAST	256 ± 1	4.2 ^{<i>a</i>}	no	1.0
1	192 ± 2	5.7 ^b	yes	0.83
2	297 ± 2	3.5^{b}	yes	~1.3
3	162 ± 2	8.1 ^b	no	0
4	211 ± 2	3.6 ^b	yes	0
^a Methano	al solution at 45 °C	^b Aqueous solu	tion at 45 °C	^c Whether it

"Methanol solution at 45 °C. "Aqueous solution at 45 °C. Whether it stabilizes in water. "Relative to DAST around 2.0 μ m.

determination of coordinates in Table 3, the total hyperpolarizability of **2** is still comparable with the maximal values of DAST and BP3. The results also agree fairly well with their experimental bulk optical nonlinearities. A class of stilbazolium salts were evaluated on the molecular hyperpolarizability β , suggesting that their bulk NLO activities are strongly dependent on the relative arrangement and orientation of the π -conjugated chromophores in the crystalline lattice.^{6b,16} Actually, the maximal component β_{xxx} for **2** is located along the crystallographic *a* axis, which makes an acute angle of 20.5° with respect to the charge-transfer chromophore direction. On the basis of the merit figure $\langle N\beta_{\text{eff}} \rangle^2$, where *N* is the number density of chromophores and

 $\beta_{\rm eff}$ is the quadric effective hyperpolarizability averaged over all possible orientations,¹⁵ it is expected that the relative powder SHG efficiencies of **2** are comparable with those of DAST and BP3 crystals, and the experimental results in Table 2 further confirm this prediction.

3.3. Thermal and Environmental Stabilities. Thermal studies in Figure 4 present that complex 3 starts dehydrating its crystal water at 162 °C, whereas the other three complexes keep their thermal stabilities around or even above 190 °C without any weight loss or solid-solid phase transition. Meaningfully, it is noted that 2 is an organic salt with a much higher thermal stability than DAST crystal (~256 °C). Furthermore, crystal samples of 1 and 2 display no apparent changes in the optical properties after being heated to 100 °C for more than 24 h. The environmental stability of several water-soluble stilbazolium derivatives exhibits some limits for the practical applications and strict requirement for the crystal growth conditions. For example, DAST easily forms a hydrated phase as DAST·H₂O with the centrosymmetric structure $P\overline{1}$.^{7a} Though being preheated above 145 °C could remove the crystal water, crystals grown using the reprocessed anhydrous materials should be completely insulated from water. A similar structural constitution also exists in 3, which crystallizes in the centrosymmetric space group $P2_1/c$ and contains crystal water. Hence, it was proposed that compound 3 would adopt the same pretreatments to that of DAST. However, it failed

Table 3. Calculated Results of the First Hyperpolarizability Tensors β_{ijk} (×10⁻³⁰ esu) with the Optimized (OPT) and the Experimental (EXP) Crystal Structures for 2^b

	DAST		BP3		complex 2	
	OPT	EXP	OPT	EXP	OPT	EXP
β_{xxx}	-0.11	-0.21	3.73	0.61	134.30	151.79
β_{xxy}	-0.04	0.03	8.12	2.85	48.25	50.40
β_{xyy}	0.05	-0.05	16.29	-2.27	14.48	16.05
β_{yyy}	-0.42	-0.06	30.26	-96.43	5.12	6.97
β_{zxx}	0.18	0.25	10.37	-2.57	32.72	-7.57
β_{xyz}	0.00	0.38	23.69	2.40	7.90	-5.70
β_{zyy}	-4.85	-3.89	49.22	86.30	2.26	0.38
β_{xzz}	0.38	-1.28	30.58	-2.16	2.30	-5.29
β_{yzz}	-2.59	-3.86	69.87	-76.69	1.65	1.91
β_{zzz}	158.76	193.60	85.59	65.81	2.33	6.26
$\beta_{\rm total}$	159.05 ^a	193.85 ^a	194.06 ^a	231.78 ^a	165.05	173.03

^{*a*}The maximal hyperpolarizability components along the main chargetransfer direction. ^{*b*}The corresponding data of DAST and BP3 cations are also listed at the B3LYP/6-311+G(d) level cited from ref 15.



Figure 4. Thermal stabilities for complexes 1-4.

to recrystallize in the anhydrous phase using the heated raw materials of 3 above 165 °C. In this case, crystals of DAST and 3 cannot be easily obtained by the slow evaporation method because of their easy formation of the hydrated phases.

Herein, the solubilities of 1 and 2 in water were examined by the gravimetric method in order to investigate their humidity resistance. As shown in Table 2, 1 and 2 exhibit comparative solubilities (5.7 and 3.5 g in 100 g of H₂O) with DAST. However, the crystal growth of 1 and 2 in the water-containing solvents does not form any hydrated phase or other polymorphs (Figure 5), whereas the centrosymmetric hydrated phase of DAST was more easily obtained. These interesting findings suggest that the high environmental stabilities of 1 and 2 without any hydrated polymorphs may favor their practical application and crystal growth process. Moreover, as an estimating figure to indicate the material mechanical resistance, Mohs' hardness experiment of 1 was performed and compared by scratching on the (001) face of DAST. The results indicate that 1 possesses slightly less hardness than DAST, but similar with that of organic salt crystals, such as LAMAD and LYTF,¹⁷ suggesting that 1 may have moderate hardness with a Vickers hardness value of around 36, which is favorable for mechanical processing.

3.4. Linear and Nonlinear Optical Properties. Figure 6 shows the unpolarized visible/near-IR absorption spectra of 1 and 2 crystal samples with the thickness of 0.6-0.8 mm. Below



Figure 5. Respective XRPD patterns of crystals 1 and 2, grown from the methanol solutions without or with H_2O . The results reveal that both crystals did not form any hydrated phase or other polymorphs, showing the identical X-ray diffraction patterns with X-ray structural determination.



Figure 6. Visible/near-IR absorption spectra of crystal samples 1 and 2.

about 700 nm, strong absorption bands are observed, correlating with the charge-transfer process. Both crystal samples are transparent at longer wavelengths down to about 2100 nm with weak absorption around 1700 nm, which is most probably due to the overtones of the C–H stretching vibrations. The magnitude of transparency can be improved by enhancing the crystal qualities and polishing process treatment. Therefore, in the technologically important range with practical applications



Figure 7. Phase-matchable curves for the experimental SHG intensities as a function of particle sizes. The respective insets are comparative SHG signals for the powder samples with particle sizes of 100–150 μ m (up) DAST and 1, and (down) DAST and 2.

of 750-1650 nm, the weak absorption reveals that crystals 1 and 2 can be treated as the potential candidates in nonlinear optics.

SHG activities of complexes 1 and 2 were evaluated at 2.0 μ m using the Kurtz and Perry powder technique. The nonresonant light with the second-harmonic wavelength (1.0 μ m) was observed with a precise photodiode, which was quite resistive to the fundamental wavelength. An appropriate filter was settled for eliminating the contributions of the potential third-harmonic generation ($\lambda = 683$ nm). The detailed results of SHG efficiencies for all the complexes are shown in Table 2, and the experimental SHG intensities as a function of particle sizes for crystalline 1 and 2 are presented in Figure 7. The results indicate that SHG intensities of both 1 and 2 increase with particle sizes and approach almost saturated, suggesting their phasematchable properties of Type I.^{9,18} Furthermore, the oscilloscope

signals reveal that 1 and 2 possess respective SHG efficiencies of 0.83 and 1.3 times that of DAST, approximately equal to 830 and 1300 times that of urea. The experimental absence of SHG signals for 3 and 4 also well agrees with their centrosymmetric crystallographic structures. All the results of SHG tests reveal that the assembling modification of the counteranion can produce novel stilbazolium derivatives with a favorable acentric packing arrangement and the excellent optical second-order nonlinearities.

4. CONCLUSIONS

In summary, a series of organic stilbazolium derivatives were synthesized as nonlinear optical materials. Single-crystal structure determination and the Kurtz powder test were carried out on the obtained derivatives, which indicate that replacing the *p*-toluene sulfonate anion of DAST with *p*-chlorobenzenesulfonate and 4-aminotoluene-3-sulfonate anions built similar crystal

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structures with the comparative optical nonlinearities about 3 orders of magnitude larger than that of urea. However, the other two complexes show their centrosymmetric crystal structures without any SHG effect. These results suggest that the crystal packing of stilbazolium salts is very sensitive to the nature of the counterions, being confirmed by the theoretical results on the molecular hyperpolarizability. Furthermore, both the asymmetric complexes possess higher environmental stabilities, including antiwater performance and the formation of an anhydrous phase, which favor the forthcoming sample processing and practical application. We believe that the further modification of counterions will bring the optimized stilbazolium salts with enhanced NLO properties and physicochemical performances that are essential for crystal growth and further material processing for applications.

ASSOCIATED CONTENT

S Supporting Information

The X-ray crystallographic information files of 1-4 as well as Figures S1–S3. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jhluo@fjirsm.ac.cn.

Notes

The authors declare no competing financial interest.

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