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Noncentrosymmetric Organic Solid and Its Zinc Coordination Polymer with Diamonded Network Prepared from an Ionothermal Reaction: Syntheses, Crystal Structures, and Second-Order Nonlinear Optics Properties

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S Supporting Information

ABSTRACT: An organic ligand 4-(1,2,4-triazol-1-yl) benzoic acid (Htzbc) with a nonlinear optical (NLO) chromophore has been synthesized. Reaction of $Zn(NO_3)_2$ with Htzbc ligand in 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid afforded compound $Zn(tzbc)_2$ (**1**). The Htzbc organic solid and **1** crystallize in the acentric Pn and Cc space groups, respectively. The tetrahedral Zn^{2+} center in **1** coordinates to two triazole nitrogen atoms and two carboxylate oxygen atoms from four $tzbc^-$ ligands, leading to a noncentrosymmetric 5-fold interpenetrating diamondoid network. Second-harmonic generation (SHG) measurements revealed the Htzbc solid and **1** have SHG activities. The Htzbc compound has a large SHG effect, which is approximately 3 times that of KDP and is type-I phase matchable, while **1** also belongs to phase-matchable class with a SHG response of about 1.2 times that of KDP. The SHG active of the organic solid can be derived from the inherently dipolar Htzbc molecule as well as the optimal relative orientation of the molecular NLO-phores in the crystal packing. The odd number-fold interpenetrated diamondoid network with dipolar NLO chromophoric units based on asymmetrical bridging ligands and metal centers results in the SHG activity of **1**. In addition, elemental analysis, IR spectra, powder X-ray diffraction patterns (PXRD), and thermogravimetric analysis of both compounds are described.
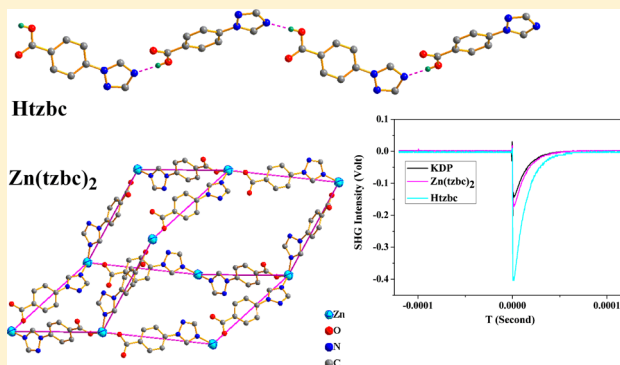
■ INTRODUCTION

The synthesis of new materials possessing crystallographic noncentrosymmetry (NCS) has attracted the interest of both the physicist and chemist communities because of their symmetry-dependent properties such as piezoelectricity, ferroelectricity, pyroelectricity, and second-order nonlinear optics (NLO).[1] In the past few decades, much effort has so far been concentrated on the inorganic oxide crystals based on the octahedral coordinated d^0 transition-metal ions such as Ti^{4+}, V^{5+}, Mo^{6+}, and W^{6+} and lone-pair-containing Te^{4+}, Se^{4+}, and I^{5+} cations because both of them are susceptible to second-order Jahn−Teller (SOJT) distortions.[2] The NCS organic molecules with large first hyperpolarizability β are also highly sought after.[3] Most of the organic molecules with large β values having a good electron donor and acceptor moieties are electronically asymmetric and highly dipolar. However, in their solid states the chromophores tend to pack antiparallel because of the strong dipole−dipole interactions, which induces the formation of centrosymmetric molecular arrangements and leads to centrosymmetric crystals. Therefore, the construction of an organic NLO material remains a significant challenge. By

carefully choosing an organic molecule with appropriate β value and controlling the reaction conditions, the centrosymmetric alignment of molecular dipoles can be avoided, which leads to second harmonic generation (SHG) active materials.[4] Herein a new 4-(1,2,4-triazol-1-yl) benzoic acid compound with a five-membered triazole group and benzoic acid moiety has been synthesized. It shows a SHG response resulting from the inherent NLO chromophore of the organic molecules and the asymmetric arrangement of the dipolar molecules in the crystal lattice.

On the other hand, metal−organic coordination compounds or metal−organic frameworks (MOFs) have currently emerged as a new type of potential NLO material.[5] Using a combination of the well-defined geometry of the metal centers and organic ligands containing appropriate functional groups, NCS coordination compounds can be obtained.[6] By employing the rigid conjugated bridging ligand with unsymmetrical linking

groups that introduce the electronic asymmetric, Lin has successfully demonstrated a useful approach to construction of NCS d[10]-metal-based coordination polymers with diamonded networks.[7] Reaction of the zinc salt with the asymmetrical 4-(1,2,4-triazol-1-yl) benzoic acid (Htzbc) ligand with NLO chromophore under ionothermal conditions yielded a NCS coordination polymer of 1. Compound 1 displaying an odd number-fold interpenetrated diamonded network shows a second-order NLO effect. It should be noted that the ionothermal condition effectively prevents the coordination of solvent molecules from tetrahedral zinc centers, thus forming the NCS structure. Herein we present the syntheses, crystal structures, and SHG properties of the Htzbc compound and the zinc compound.

■ EXPERIMENTAL SECTION

General. All chemicals were reagent grade and used as commercially obtained from Sinopharm Chemical Reagent Co., Ltd., China.

NMR Spectrum, Elemental Analysis, and Infrared Spectroscopy. NMR analyses were recorded on a Bruker Avance 400 spectrometer equipped with an automatic sample holder. Chemical shift data for each signal are reported in ppm units with DMSO as reference, where δ (DMSO) = 2.50 ppm. Elemental analyses were carried out on an Elementar Vario EL III analyzer, and IR spectra (KBr pellets) were recorded on PerkinElmer Spectrum One.

Second-Order NLO Measurements. The measurement of the powder frequency-doubling effect was carried out by means of the method of Kurtz and Perry.[8] The fundamental wavelength is 1064 nm generated by a Q-switched Nd:YAG laser with a frequency doubling at 532 nm. SHG efficiency has been shown to depend strongly on particle size; thus samples of Htzbc and compound 1 were ground and sieved into several distinct particle size ranges (45−53, 53−75, 74−105, 105−150, 150−210 μm). The samples were pressed into a disk with a diameter of 8 mm that was put between glass microscope slides and secured with tape in a 1-mm thick aluminum holder, and a powdered KDP sample used as the reference was sieved into the same size range. No index-matching fluid was used in any of the experiments.

Thermogravimetric Analysis. The thermogravimetric measurements were performed with a Netzsch STA449C apparatus under a nitrogen atmosphere with a heating rate of 10 °C/min in the Al_2O_3 containers. Temperature intervals are 30−400 °C for organic compound and 30−600 °C for compound 1, respectively.

Powder X-ray Diffraction. Powder X-ray diffraction patterns were performed on a Rigaku Miniflex Π powder diffractmeter using Cu−Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 5−60° with a continuous scan step width of 0.05°. The recorded patterns were compared with theoretical patterns calculated from single-crystal structure data (Figure S2 in the Supporting Information).

Synthesis of Htzbc Ligand (Scheme 1). The Htzbc ligand was prepared following a modified known procedure.[9] 0.1 mL of tricaprylylmethylammonium chloride was added dropwise to a 10 mL of DMF containing a mixture of 1H-1,2,4-triazole (2.302 g 0.033

mol) and potassium carbonate (4.6 g 0.033 mol) in 50 mL three-neck flask under stirring. The reaction mixture was heated at 90 °C for 5 min. Then 4-fluorobenzaldehyde (2.302 g 0.033 mol) was gradually added to a stirred solution of the reaction mixture. The resulting mixture was vigorously stirred at 90 °C for 24 h to form a yellow precipitate. After cooling of the mixture to room temperature, 50 mL of ice water was added to the reaction mixture. The resulting yellow precipitate was collected by filtration and washed with Et_2O (5 mL). The product was dried at 60 °C to afford the intermediate 4-(1,2,4-triazol-1-yl) benzaldehyde. 4-(1,2,4-Triazol-1-yl) benzaldehyde (1.74 g 0.01 mol) and $AgNO_3$ (3.4 g 0.02 mol) were added to a 60 mL 70% NaOH solution in 150 mL flask. The reaction mixture was slowly heated to 60 °C and stirred for 24 h at this temperature. After cooling to room temperature, the insoluble material was removed by filtration and then rinsed with H_2O (20 mL). The filtrate was acidified (pH ≈ 2) by addition of concentrated HCl to form a yellow precipitate. The yellow precipitate was collected by filtration and washed with Et_2O (5 mL). The crude product was recrystallized from hot DMF to yield the Htzbc solid as colorless crystals. Yield 1.22 g (65%). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 13.10 (s, 1H), 9.41(s, 1H), 8.29 (s, 1H), 8.12 (d, 2H), and 8.02 (d, 2H). Anal. Calcd. for $C_9H_7N_3O_2$ (189.18): C, 57.14; H, 3.73; N, 22.21%. Found: C, 57.01; H, 3.76; N, 22.14%. IR spectrum (cm^{-1}, KBr pellet): 3444 (m), 3131 (m), 1692 (s), 1641 (w), 1606 (s), 1558 (m), 1525 (m), 1446 (s), 1385 (w), 1346 (w), 1317 (m), 1272 (s), 1224 (m), 1138 (s), 1123 (s), 1067 (s), 973 (w), 953 (m), 823 (w), 801 (w), 772 (m), 692 (w), 671 (m), 644 (w), 619 (w), 562 (w), 538 (w), 516 (w).

Synthesis of Zn(tzbc)$_2$ (1). $Zn(NO_3)_2$·6H_2O (0.0595 g, 0.2 mmol) and 4-(1,2,4-triazol-1-yl)benzoic acid (0.0756 g, 0.4 mmol) were mixed with 0.6 g of 1-n-butyl-3-methylimidazolium tetrafluoroborate in a 15 mL Parr Teflon-lined stainless steel vessel. The vessel was sealed and heated to 160 °C. This temperature was kept for 6 days and then the mixture was cooled naturally to form colorless crystals of 1 (yield: 0.054 g, 62% on the basis of Zn). Anal. Calcd. for $C_{18}H_{12}N_6O_4Zn$ (441.71): C, 48.95; H, 2.74; N, 19.03%. Found: C, 48.91; H, 2.68; N, 19.01%. Main IR features (cm^{-1}, KBr pellet): 3443 (w), 3131 (w), 1687 (s), 1608 (s), 1568 (m), 1542 (m), 1504 (m), 1492 (m), 1462 (w), 1427 (w), 1384 (s), 1297 (s), 1219 (m), 1142 (s), 1045 (s), 1068 (m), 1002 (w), 975 (m), 955 (m), 860 (m), 809 (w), 771 (m), 690 (w), 670 (m), 638 (w), 559 (w), 538 (w), 516 (w).

X-ray Crystallography. Single crystal X-ray diffraction data of Htzbc compound and compound 1 were collected on a Bruker Apex II CCD diffractometer equipped with a graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. Adsorption corrections were applied using the SADABS routine.[10] The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F^2 (SHELXTL, version 5.1).[11] All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms were assigned to calculated positions. The R_1 values are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. The details of the crystal parameters, data collection, and refinement are summarized in Table 1.

■ RESULTS AND DISCUSSION

Syntheses. Ionothermal synthesis, the use of an ionic liquid as solvent in the preparation of crystalline solids, is a new synthetic methodology developed recently. Compared with the traditional hydro(solvo)thermal methods, the change from molecular to ionic reaction media leads to new types of materials with structural properties that are much different than those obtained using a routine synthetic approach. Reaction of $Zn(NO_3)_2$ with Htzbc ligand in 1-n-butyl-3-methylimidazolium tetrafluoroborate solvent afforded compound 1. However, replacing the 1-n-butyl-3-methylimidazolium tetrafluoroborate solvent with aqueous solvent in a similar reaction leads to a mononuclear structure of $Zn(tzbc)_2(H_2O)_4$,[12] where the zinc

Scheme 1. Preparation of Htzbc Ligand
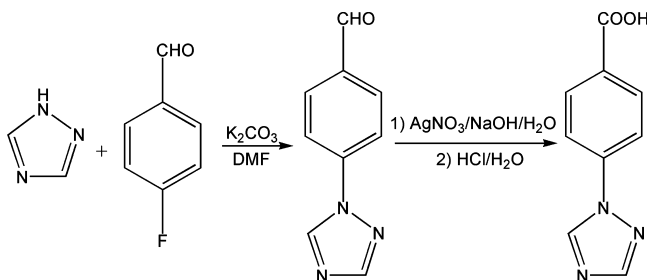
Table 1. Crystallographic Data for Htzbc Ligand and Compound 1^a

	Htzbc	1
formula	$C_9H_7N_3O_2$	$C_{18}H_{12}N_6O_4Zn$
fw	189.18	441.71
temp (K)	296(2)	296(2)
cryst syst	monoclinic	monoclinic
space group	Pn	Cc
Z	2	4
a (Å)	3.96260(10)	12.4567(16)
b (Å)	6.2888(2)	20.188(3)
c (Å)	16.5205(5)	8.1381(10)
α (deg)	90	90
β (deg)	94.462(2)	115.5500(10)
γ (deg)	90	90
V (Å^3)	410.44(2)	1846.4(4)
D_{calcd} (g·cm^{-3})	1.531	1.589
μ (mm^{-1})	0.113	1.370
no. of reflns collected	3628	8434
independent reflns	1428	4116
obsd reflns ($I > 2\sigma(I)$)	1230	3750
F(000)	196	896
Flack parameter	−0.3(15)	0.009(10)
R[int]	0.0194	0.0239
R_1 ($I > 2\sigma(I)$)	0.0331	0.0291
wR_2 (all data)	0.0832	0.0716

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$.

center is six-coordinated by four aqua ligands and two nitrogen atoms of two tzbc$^-$ monoanions. Thus the noncentrosymmetric 3D structure of **1** is much different from the centrosymmetric mononuclear structure of Zn(tzbc)$_2$(H$_2$O)$_4$ synthesized under hydrothermal conditions. The result clearly shows that the ionothermal reaction can effectively prevent the coordination of solvent molecules such as H$_2$O and DMF to the zinc center.

Crystal Structures. Single-crystal X-ray diffraction analyses revealed that the Htzbc solid crystallizes in the noncentrosymmetric monoclinic space group Pn with one molecule in the asymmetric unit. The O−H···N hydrogen bonds between the carboxylic hydrogen and triazole nitrogen atom with an O···N distance of 2.697(3) Å link the Htzbc molecules to form a 1D infinite chain as shown in Figure 1. The 1D chains are stacked parallelly to give a 2D layer spreading out the ac plane. The interchain π−π interactions with a center-to-center distance of 3.96 Å between the parallel aromatic rings are observed (Figure S1 in the Supporting Information). 2D layers are packed along the (010) axis to give a 3D crystal packing in which interlayer C−H···O (C···O = 3.26 Å) interactions are observed (Figure 2).

Compound **1** is crystallized in the noncentrosymmetric space group Cc, as a result of the unsymmetrical nature of organic ligand. There is one zinc(II) ion and two tzbc$^-$ monoanions in the asymmetric unit. As depicted in Figure 3, the Zn1 ion coordinates to two nitrogen atoms and two carboxylate oxygen atoms of four tzbc$^-$ ligands in a distorted tetrahedral geometry, which is different from the octahedral coordination geometry of the zinc center in compound Zn(tzbc)$_2$(H$_2$O)$_4$ obtained under hydrothermal reaction.[12] The Zn−O bond distances are 1.908(2) and 1.9418(19) Å, and the Zn−N bond distances are 2.015(2) and 2.023(2) Å, respectively. The Zn(II) centers are bridged by the tzbc$^-$ ligands in a bidentate bridging fashion through the monodentate carboxylate and triazole groups, to give a 3D framework featuring a diamondoid network (Figure 4). With Zn···Zn separations of 12.24 and 12.31 Å, a large void is generated within a single diamondoid cage. For such an empty framework (Figure 4), structural interpenetration is difficult to avoid. Actually, the void space in **1** is filled by the formation of a 5-fold diamondoid structure, in which five independent diamond nets are mutually interpenetrated in a parallel mode (Figure 5). We have thus demonstrated that acentric polymeric networks based on diamondoid structures can be readily constructed with a judicious choice of unsymmetrical bridging ligands.

IR Spectra, Thermal Analyses and Powder X-ray Diffraction Patterns. The characteristic band at 1692 cm^{-1} in the IR spectrum of compound Htzbc is attributable to the carboxylic acid group. The IR spectrum of compound Htzbc shows the typical asymmetric (1606 cm^{-1}) and symmetric (1446 cm^{-1}) stretching bands of carboxylate group. The strong bands at 1687 and 1608 cm^{-1}, and 1384 cm^{-1}, respectively, correspond to the asymmetric and symmetric stretching bands of the carboxylate groups in the IR spectrum of compound **1**.

Powder X-ray diffraction (PXRD) has been used to check the phase purity of the bulky samples in the solid state. For compounds Htzbc and **1**, the measured PXRD patterns very closely match the simulated patterns generated from the results of single-crystal diffraction data (Figure S2 in the Supporting Information), indicative of pure products.

To study the stability of compounds Htzbc and **1**, thermogravimetric analysis (TGA) studies were performed. The results of the thermal analyses are represented by the curves in Figure S3, Supporting Information. The Htzbc organic compound is stable up to 185 °C and then exhibits two main steps of weight losses. The first step (185−210 °C) corresponds to the release of the carboxyl group (weight loss: measured 22.79%, theoretical 23.81%). The combustion of the aromatic portion of the organic ligand occurs at 225 °C and ends at 320 °C. The TGA trace for compound **1** displays a continual weight loss occurring at 330 °C. Before 330 °C there
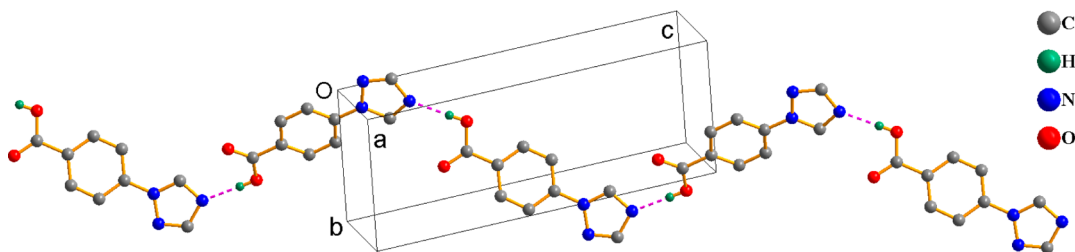
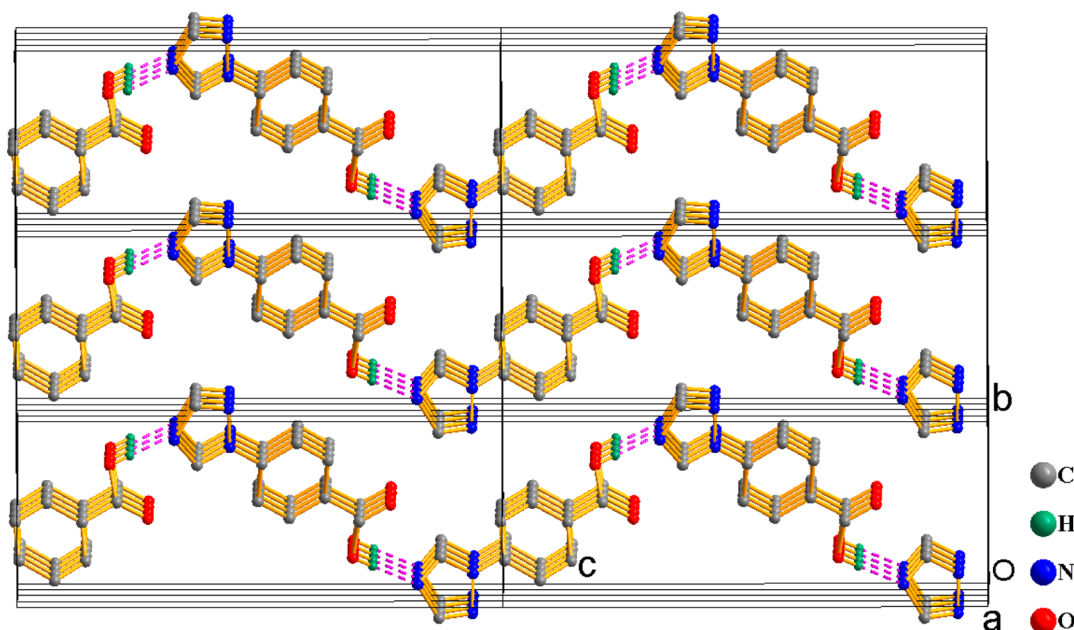**Figure 1.** The Htzbc molecules are linked by hydrogen bonds to give a 1D chain.

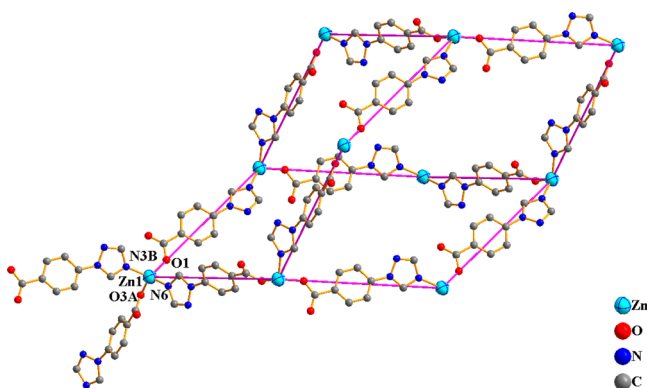**Figure 2.** 3D crystal packing of the Htzbc solid. Dotted lines indicate the hydrogen bonds.

Figure 3. An adamantanoid cage in **1** showing the coordination environment of the Zn(II) center.

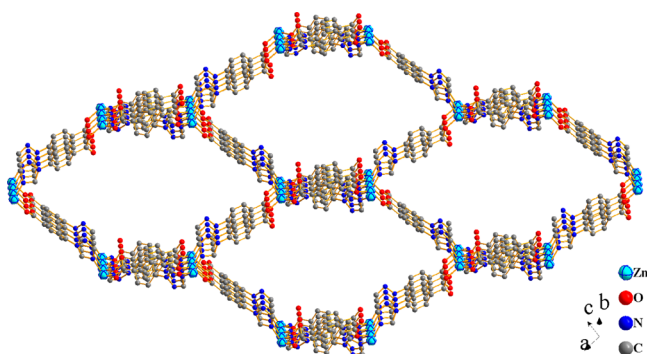**Figure 5.** A schematic view of the 5-fold interpenetrated diamondoid networks in **1**.

Figure 4. A single 3D diamondoid framework in **1**.

is a small gradual mass loss, which can be ascribed to the instability of the electronic balance.

Second-Harmonic Generation (SHG) Properties. Since Htzbc organic solid and compound **1** crystallize in non-centrosymmetric space groups, it is worthy to study their SHG properties. The SHG properties have been measured using the Kurtz−Perry powder SHG technique with a Q-switch Nd:YAG laser of wavelength 1064 nm and KDP as a reference. SHG
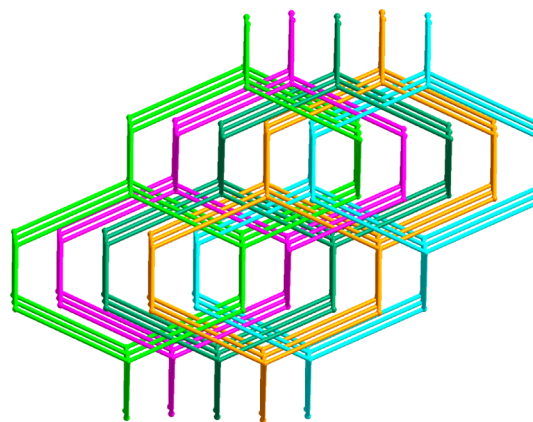
measurements on the sieved powder samples revealed that both compounds display SHG signals. The SHG intensities for Htzbc and compound **1** are about 3 and 1.2 times that of KDP in the particle size of 150−210 μm (Figure 6), which confirms their acentricity as well as to evaluate their potential as second-order NLO materials. The plots of the SHG signals as a function of particle size ranging from 45 to 210 μm measured on ground crystals suggest both compounds are type-I phase-matchable (Figure 6), which is a necessary character for a NLO material to serve for laser frequency converting. The SHG intensity of **1** (1.2 × KDP and 19 × α-quartz) is similar to that of 5-fold interpenetrating diamondoid network Cd(pyb)$_2$·H$_2$O (18 × α-quartz) (pyb = 4-(pyridin-4-yl)benzoate) constructed from the analogous ligands.[13] However, their SHG intensities are lower than those of Zn(4-pya)$_2$ (pya = (*E*)-3-(pyridin-3-yl)acrylate),[14] Zn(imac)$_2$·H$_2$O (imac = (*E*)-3-(imidazol-4-yl)acrylate),[15] and (Me$_2$NH$_2$)[CdLi(odba)$_2$] (odba = 4,4′-oxidibenzoate) with 5-fold interpenetrating diamondoid networks.[16]

As is well-known, the second-order NLO effect from molecular crystals is sensitive to the molecular hyperpolariz-
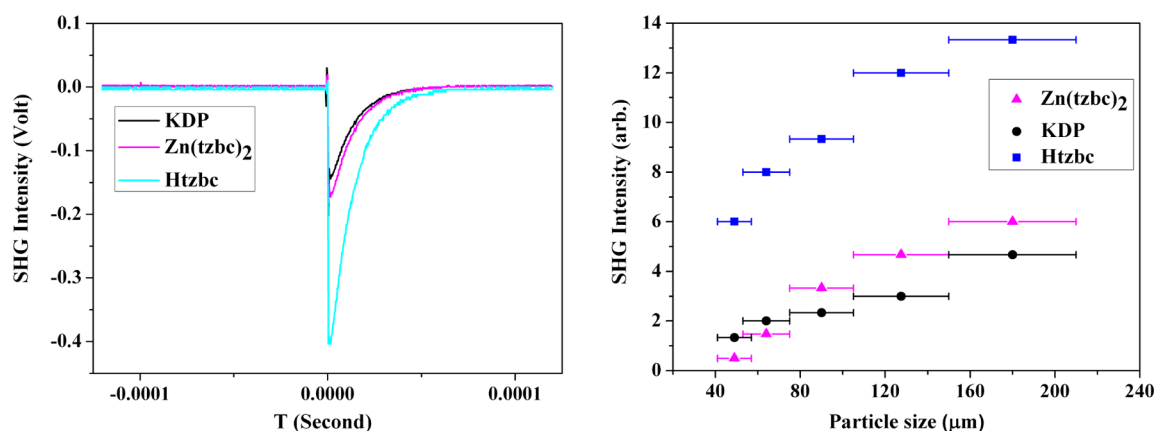
Figure 6. Oscilloscope traces of the SHG signals of KDP, Htzbc, and Zn(tzbc)₂ at the same particle size of 150−210 μm (left) and SHG measurements of ground Htzbc and Zn(tzbc)₂ crystals with KDP as the reference (right).

ability as well as the relative disposition of the molecules in the crystal lattice. The total macroscopic dipolar moment must not be equal to zero, which is essential for a second-order NLO material. As depicted in Figure 1, the Htzbc molecules adopt a head-to-tail alignment in the 1D hydrogen-bonded zigzag chain and the neighboring chains are stacked parallelly along the *ac* plane (Figure S1 in Supporting Information). Moreover, the 2D layers are further stacked parallelly along the *b* axis (Figure 2). It is clear that the magnitudes of dipole moments along the *b* axis are canceled and the vector sum of them is well enhanced along the *ac* plane, which leads to the large SHG response of the Htzbc solid. For **1**, the odd-fold interpenetrated diamondoid networks in a parallel mode with dipolar NLO chromophoric units based on asymmetrical bridging ligands and metal centers contribute the SHG activity of **1**. However, the SHG response of **1** is less intense than that of the organic solid. In **1** the Htzbc ligand is coordinated to the zinc centers. The dihedral angles between the benzoate group and triazole group of the two independent Htzbc ligands in **1** are 29.6 and 39.7°, while in Htzbc solid the dihedral angle between the benzoate group and triazole group is 13.9°, which indicates that the effect of conjugation of the organic ligand is larger in the organic solid than that in compound **1**. That is to say, the molecular hyperpolarizability β of the organic ligand in the organic solid is larger than that in compound **1**. In a microscopic view, the second-order NLO susceptibility is related to the molecular hyperpolarizability β of a molecule. As these results the SHG intensity of **1** is lower than that of the Htzbc organic solid.

CONCLUSIONS

In conclusion, an organic solid of 4-(1,2,4-triazol-1-yl) benzoic acid (Htzbc) with nonlinear optical (NLO) chromophore and its zinc compound with 5-fold interpenetrating diamondoid network prepared under ionothermal condition have been reported. Both compounds crystallize in the acentric space groups. SHG measurements revealed that both compounds are SHG activities and show type-I phase matchable behavior. This demonstrates that ionothermal synthesis can provide a simple and effective approach to the discovery of new nonlinear optics crystalline material.

ASSOCIATED CONTENT

ⓢ Supporting Information

X-ray structure data in CIF format; 2D hydrogen-bonded structure for Htzbc compound; powder X-ray diffraction patterns; TG curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) Unpublished result. Crystal data for compound $Zn(tzbc)_2(H_2O)_4$ ($C_{18}H_{20}N_6O_8Zn$): M_r = 513.79, triclinic, space group $P\bar{1}$, a = 6.1760(7) Å, b = 6.9979(8) Å, c = 12.1225(14) Å, α = 80.6540(10)°, β = 87.9520(10)°, γ = 72.0230(10)°, V = 491.67(10) Å^3, Z = 1, D_{calc} = 1.735 mg/m^3, μ = 1.313 mm^{-1}, $F(000)$ = 264, R_1 = 0.0245, wR_2 = 0.0640.

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