

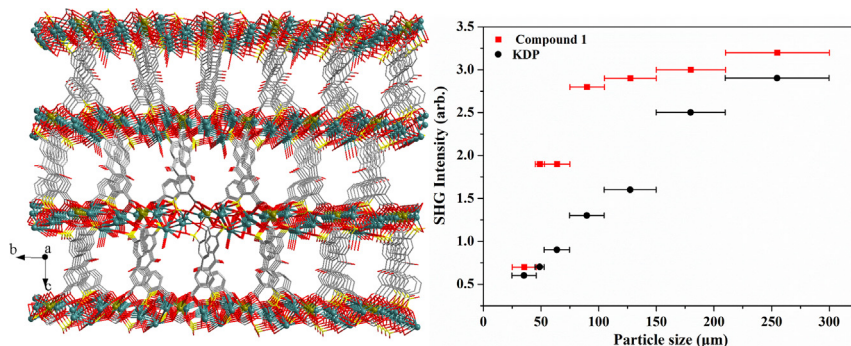
Short communication

A noncentrosymmetric coordination polymer based on the benzophenone-3,3'-disulfonyl-4,4'-dicarboxylate ligand exhibiting second-harmonic-generation responses

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GRAPHICAL ABSTRACT

A 3D coordination polymer $[\text{CdK}_6(\mu_2\text{-H}_2\text{O})_2(\text{BODSDC})_2(\text{H}_2\text{O})]_n$ (**1**) based on the benzophenone-3,3'-disulfonyl-4,4'-dicarboxylate (BODSDC^{4-}) was presented. Compound **1** crystallizes has a large second-harmonic-generation response of 1.3 times that of KDP and is type-I phase-matchable.



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ABSTRACT

A 3D coordination polymer $[\text{CdK}_6(\mu_2\text{-H}_2\text{O})_2(\text{BODSDC})_2(\text{H}_2\text{O})]_n$ (**1**) based on the novel benzophenone-3,3'-disulfonyl-4,4'-dicarboxylate (BODSDC^{4-}) ligand was synthesized and structurally characterized. The carboxylate and sulfonate groups of the organic ligands as well as the bridging water molecules connect the Cd^{2+} and K^+ ions to produce a 2D layer, which is linked by the benzophenone moieties to give a 3D pillared framework. Compound **1** crystallizes in an acentric space group of Cc and has a large second-harmonic-generation (SHG) response of 1.3 times that of potassium dihydrogen phosphate (KDP) in the particle size of 25–210 μm. Further SHG measurements revealed that the material is type-I phase-matchable. The observed SHG efficiency is associated with the unsymmetrical geometry of the organic ligand and the distorted coordination polyhedrons of metal centers.

The crystalline materials possessing crystallographic noncentrosymmetry are an important class of functional materials due to their symmetry-dependent properties such as second-harmonic-generation (SHG) (i.e. second-order nonlinear optics (NLO)),

piezoelectricity, ferroelectricity, and pyroelectricity [1]. It has been reported that the combination of d^0 transition metal ions and lone-pair-containing cations in inorganic oxide crystals can produce noncentrosymmetric (NCS) structures with their inherent unsymmetric

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coordination environments [2]. Recently, coordination polymers or metal–organic coordination compounds are emerging as a new kind of potential NLO materials [3]. Combination of the metal centers with well-defined geometry and functional organic ligands leads to the NCS coordination compounds [4]. The noted examples are the NCS d^{10} -metal-based coordination polymers featuring diamond networks constructed from the rigid conjugated bridging ligand with unsymmetrical linking groups [5]. The NCS coordination compounds can be obtained by using the V-shaped organic ligands due to the unsymmetrical geometry of the ligand [6]. In the present work, a novel sulfonate-carboxylate ligand, benzophenone-3,3'-disulfonyl-4,4'-dicarboxylate (H_4 -BODSDC), is applied for constructing the NCS compound due to its unsymmetrical geometry. The H_4 -BODSDC ligand based on a benzophenone backbone with two carboxylate and two sulfonate groups is expected to be a remarkable organic precursor for preparation of the functional coordination polymers. Here is a NCS cadmium compound with its structure and SHG properties.

One Cd^{2+} ion, six K^+ ions, two tetraanionic BODSDC $^{4-}$ ligands, and three water ligands compose the asymmetric unit of **1** [7]. It is noted that two (O24 and O25) of the water ligands serve as a μ_2 ligand bridging two K^+ ions. As shown in Fig. 1, the Cd^{2+} ion is coordinated by six carboxylate O atoms from four BODSDC $^{4-}$ ligands. The Cd–O bond distances vary from 2.244(10) to 2.423(11) Å (Table S1). The K^+ ions display diverse coordination geometries with the coordination numbers of 5, 6, 7, and 8. The K1 and K2 atoms have the coordination number of 8. The K1 atom is coordinated by two carboxylate O atoms and four sulfonate O atoms from four BODSDC $^{4-}$ ligands, and two water O atoms (Fig. 1). The coordination polyhedron of K2 atom is composed of two carboxylate O atoms and five sulfonate O atoms from four BODSDC $^{4-}$ ligands, and one water O atom. K3 atom is five-coordinated by three sulfonate O atoms and one carboxylate O from three BODSDC $^{4-}$ ligands, and one water O atom. The K4 and K6 atoms have the same coordination number of 7 and both are surrounded by two carboxylate O atoms and five sulfonate O atoms (Fig. 1). K5 is coordinated to six O atoms, five from one carboxylate O atom and four sulfonate O atoms of four BODSDC $^{4-}$ ligands, and one from water molecule. The K–O bond distances range from 2.320(15) to 3.364(16) Å (Table S1). The two independent BODSDC $^{4-}$ ligands exhibit two complicated coordination modes bridging two Cd^{2+} and eleven K^+ ions (Scheme S1). The Cd^{2+} and K^+ ions are interconnected by the

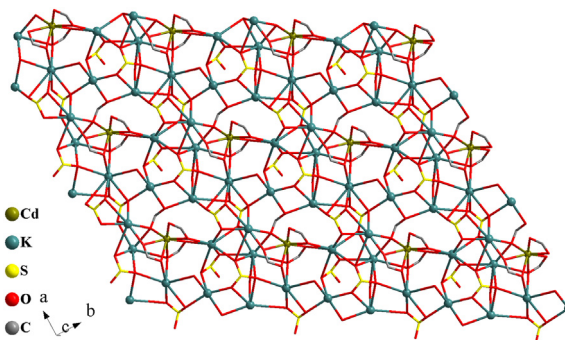


Fig. 2. The 2D layer in **1**.

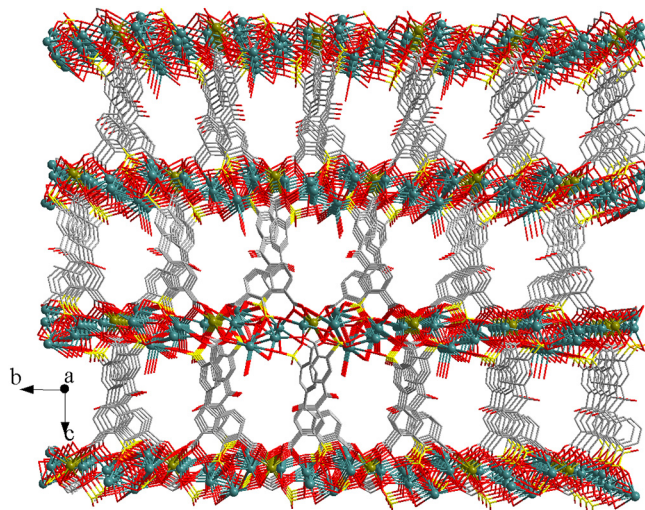


Fig. 3. The 3D framework of **1**.

carboxylate and sulfonate groups and the bridging water ligands to give a 2D layer running along ab plane, as shown in Fig. 2. The 2D layers are further connected by the benzophenone linkers to form a 3D pillared framework (Fig. 3).

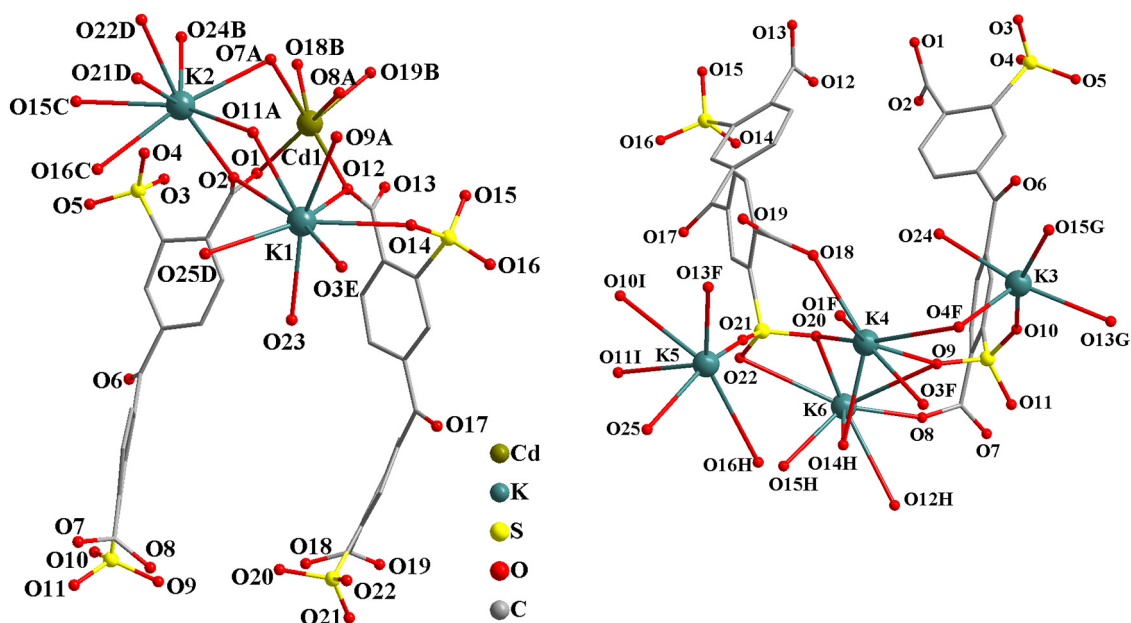


Fig. 1. Coordination environments of Cd(II) and K(I) ions in **1**. Symmetry code: A $x, -y + 1, z - 1/2$; B $x - 1/2, -y + 1/2, z - 1/2$; C $x - 1, y, z$; D $x - 1, -y + 1, z - 1/2$; E $x + 1/2, y + 1/2, z$; F $x + 1/2, -y + 1/2, z + 1/2$; G $x - 1/2, -y + 1/2, z + 1/2$; H $x, -y + 1, z + 1/2$; I $x + 1, y, z$.

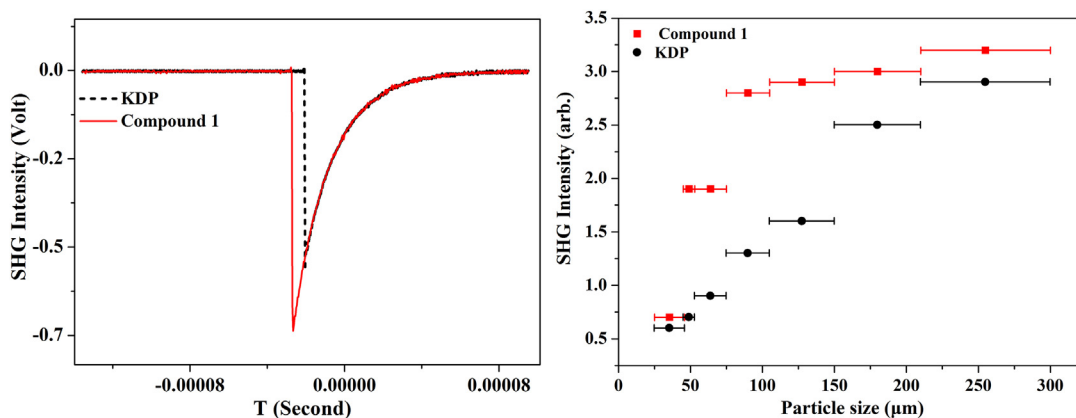


Fig. 4. Oscilloscope traces of the SHG signals of KDP and 1 at the particle size of 150–210 μm (left) and SHG measurements of ground crystals 1 with KDP as the reference (right).

The IR spectrum of **1** shows an absorption at 3465 cm^{-1} , which can be attributed to O–H stretching vibration of water molecule. The absorption peaks at 1662 and 1592 cm^{-1} are the asymmetric stretching bands of carboxylate groups. The symmetric stretching band of carboxylate group is observed in the 1400 cm^{-1} . The characteristic bands of the sulfonate groups are found at 1028 , 1081 , and 1201 cm^{-1} .

Compound **1** is crystallized in the NCS space group *Cc*, thus its SHG properties were investigated. The SHG properties were measured using the Kurtz-Perry powder SHG technique with a Q-switch Nd:YAG laser (1064 nm) and KDP as a reference [8]. The preliminary measurement shows that the SHG intensity of **1** is about 1.3 times that of KDP in the particle size of 150–210 μm (Fig. 4), which indicates that **1** can be potentially as a NLO material. Such a phenomenon confirms the acentricity nature of **1**. The SHG intensity is comparable to that of the Cd (pyb)₂H₂O compound based on the 4-(pyridin-4-yl)benzoate (pyb) ligand [9]. In addition, the SHG responses for **1** at different particle size (from 45 to 300 μm) were measured by sieving of **1** into various particle sizes. The plots of the SHG signals as a function of particle size with the KDP as a reference are depicted in Fig. 4. The SHG intensities of **1** are enhanced with the increasing the particle sizes, suggesting a type-I phase-matchable, which meets a requirement for a NLO material to serve for laser frequency converting. The nonlinear benzophenone-3,3'-disulfonyl-4,4'-dicarboxylate ligand with the sulfonate and carboxylate groups is a unsymmetrical ligand, leading to the NCS structure of **1**. Moreover, from the bond lengths and bond angles around the metal centers (Table S1), we can see that the coordination polyhedrons for all metal centers in **1** are significantly deviated from the ideal coordination geometries, leading to the distorted coordination environments for metal centers. Thus the unsymmetrical bridging ligands arranged in an unsymmetrical relative disposition and distorted coordination environments for metal centers contribute the SHG activity of **1**.

In summary, we demonstrate a cadmium coordination polymer of **1** based on the unsymmetrical ligand of benzophenone-3,3'-disulfonyl-4,4'-dicarboxylate. Compound **1** has a 3D pillared framework featuring the NCS structure, which displays a large SHG signal and has a potential for a NLO crystalline material.

Acknowledgments

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Appendix A. Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC-

1847521). The data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk. PXRD, coordination modes of the ligand, bond distance table, and experiments can be found in the supporting file. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.inoche.2018.07.021>.

References

- (a) K.M. Ok, E.O. Chi, P.S. Halasyamani, Bulk characterization methods for non-centrosymmetric materials: second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity, *Chem. Soc. Rev.* 35 (2006) 710–717; (b) O. Evans, W. Lin, Crystal engineering of NLO materials based on metal–organic coordination networks, *Acc. Chem. Res.* 35 (2002) 511–522; (c) W. Zhang, R.-G. Xiong, Ferroelectric metal–organic frameworks, *Chem. Rev.* 112 (2012) 1163–1195; (d) S.D. Bella, Second-order nonlinear optical properties of transition metal complexes, *Chem. Soc. Rev.* 30 (2001) 355–366; (e) P.S. Halasyamani, K.R. Poeppelmeier, Noncentrosymmetric oxides, *Chem. Mater.* 10 (1998) 2753–2769.
- (a) P.S. Halasyamani, Asymmetric cation coordination in oxide materials: influence of lone-pair cations on the intra-octahedral distortion in d^0 transition metals, *Chem. Mater.* 16 (2004) 3586–3592; (b) S. Zhao, Y. Yang, Y. Shen, B. Zhao, L. Li, C. Ji, Z. Wu, D. Yuan, Z. Lin, M. Hong, J. Luo, Cooperation of three chromophores generates the water-resistant nitrate nonlinear optical material $\text{Bi}_3\text{TeO}_6\text{OH}(\text{NO}_3)_2$, *Angew. Chem. Int. Ed.* 56 (2017) 540–544; (c) L. Chang, L. Wang, X. Su, S. Pan, R. Hailili, H. Yu, Z. Yang, A. Nitrate Nonlinear, Optical crystal $\text{Pb}_{16}(\text{OH})_{16}(\text{NO}_3)_{16}$ with a large second-harmonic generation response, *Inorg. Chem.* 53 (2014) 3320–3325; (d) F.-F. Mao, C.-L. Hu, X. Xu, D. Yan, B.-P. Yang, J.-G. Mao, $\text{Bi}(\text{IO}_3)\text{F}_2$: the first metal iodate fluoride with a very strong second harmonic generation effect, *Angew. Chem. Int. Ed.* 56 (2017) 2151–2155; (e) C. Wu, L. Li, J. Song, G. Yang, M.G. Humphrey, C. Zhang, Facile syntheses of $\text{Ba}_2[\text{B}_4\text{O}_7(\text{OH})_2]$ and $\text{Na}[\text{B}_5\text{O}_7(\text{OH})_2](\text{H}_2\text{O})$ borate salts exhibiting nonlinear optical activity in the ultraviolet, *Inorg. Chem.* 56 (2017) 1340–1348; (f) E.L. Belokoneva, S.Y. Stefanovich, O.V. Dimitrova, A.S. Karamysheva, A.S. Volkov, Iodide-iodates $\text{M}_3[\text{IO}_3]_{12}\text{Ag}_4$, $\text{M} = \text{Bi}, \text{Tb}$, with a framework structure and high second-harmonic generation optical response, *Inorg. Chem.* 56 (2017) 1186–1192.
- (a) H. Zhao, Z.-R. Qu, H.-Y. Ye, R.-G. Xiong, In situ hydrothermal synthesis of tetrazole coordination polymers with interesting physical properties, *Chem. Soc. Rev.* 37 (2008) 84–100; (b) Y. Liu, G. Li, X. Li, Y. Cui, Cation-dependent nonlinear optical behavior in an octupolar 3D anionic metal–organic open framework, *Angew. Chem. Int. Ed.* 46 (2007) 6301–6304; (c) H.-L. Sun, B.-Q. Ma, S. Gao, S.R. Batten, A novel acentric three-dimensional network with complicated topology, *Cryst. Growth Des.* 6 (2006) 1261–1263; (d) Q.-Y. Liu, Y.-L. Wang, Z.-M. Shan, R. Cao, Y.-L. Jiang, Z.-J. Wang, E.-L. Yang, Novel noncentrosymmetric zinc coordination polymer containing an unusual zinc carboxylate-sulfonate substructure with a (10,3)-d topology and its SHG properties, *Inorg. Chem.* 49 (2010) 8191–8193.
- (a) L. Li, J. Ma, C. Song, T. Chen, Z. Sun, S. Wang, J. Luo, M. Hong, A 3D polar nanotubular coordination polymer with dynamic structural transformation and ferroelectric and nonlinear-optical properties, *Inorg. Chem.* 51 (2012) 2438–2442; (b) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B.F. Abrahams, Z. Xue, Novel, acentric metal–organic coordination polymers from hydrothermal reactions involving in situ

- ligand synthesis, *Angew. Chem. Int. Ed.* 41 (2002) 3800–3803;
- (c) X. Feng, Y.H. Wen, Y.Z. Lan, Y.L. Feng, C.Y. Pan, Y.G. Yao, Multifunctional zinc (II) urocanate with rare fivefold interpenetrating diamondoid network, *Inorg. Chem. Commun.* 12 (2009) 89–91.
- [5] (a) C. Wang, T. Zhang, W. Lin, Rational synthesis of noncentrosymmetric metal–organic frameworks for second-order nonlinear optics, *Chem. Rev.* 112 (2012) 1084–1104;
- (b) Y.-L. Wang, J.-H. Fu, J.-J. Wei, X. Xu, X.-F. Li, Q.-Y. Liu, Noncentrosymmetric organic solid and its zinc coordination polymer with diamondoid network prepared from an ionothermal reaction: syntheses, crystal structures, and second-order nonlinear optics properties, *Cryst. Growth Des.* 12 (2012) 4663–4668.
- [6] J.D. Lin, X.F. Long, P. Lin, S.W. Du, A series of cation-templated, polycarboxylate-Based Cd(II) or Cd(II)/Li(I) frameworks with second-order nonlinear optical and ferroelectric properties, *Cryst. Growth Des.* 10 (2010) 146–157.
- [7] Crystal data: **1**: $C_{30}H_{18}O_{25}S_4CdK_6$, $M_r = 1253.68$, Monoclinic, space group *Cc*, $a = 10.840(2) \text{ \AA}$, $b = 18.697(4) \text{ \AA}$, $c = 27.370(3) \text{ \AA}$, $\beta = 98.154(15)^\circ$, $V = 5491.1(17) \text{ \AA}^3$, $Z = 4$, $D_{calc} = 1.516 \text{ mg/m}^3$, $\mu = 1.076 \text{ mm}^{-1}$, $F(000) = 2496$, $R_1 = 0.0773$, $wR_2 = 0.1992$. Single-crystal X-ray diffraction data were collected on a Rigaku Oxford SuperNova Single Source diffractometer with an Eos detector and a Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). CrysAlisPro Agilent Technologies software was used for collecting the frames of data, indexing the reflections, determining the lattice constants, absorption correction, and data reduction. The structure was solved by the direct methods and successive Fourier difference syntheses (SHELXT-2015), and refined by the full-matrix least-squares method on F^2 (SHELXL-2014). All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms attached carbon atoms were assigned to calculated positions. Water hydrogen couldn't be located in the difference Fourier map. The unit cell includes a large region of disordered guest solvent molecules, which could not be modeled and were treated by the SQUEEZE routine of PLATON and refined further using the data generated.
- [8] S.K. Kurtz, T.T. Perry, A powder technique for the evaluation of nonlinear optical materials, *J. Appl. Phys.* 39 (1968) 3798–3813.
- [9] O.R. Evans, R.G. Xiong, Z.Y. Wang, G.K. Wong, W. Lin, Crystal engineering of acentric diamondoid metal–organic coordination networks, *Angew. Chem. Int. Ed.* 38 (1999) 536–538.