



Deliberate design of an acentric diamondoid metal-organic network

Caiqin Yang, Jing Wang*, Wei Wang, Wenhong Zhan

School of Pharmaceutical Sciences, Hebei Medical University, Shijiazhuang, China

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ABSTRACT

Reaction of 2,5-dicarboxy-1-methylpyridinium (DCMP) chloride and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the presence of NaHCO_3 in water gave an expected acentric diamondoid network $[\text{Zn}(\text{DCMP})_2]$ with a three-fold interpenetration. With long Zn–Zn separations, very large cavities are formed within each diamondoid network with high propensity to interpenetration, which makes it show a promising non-linear optical property with SHG efficiency approximately 7 times higher than that of potassium dihydrogen phosphate (KDP). The design strategy of ligand through methylation of the corresponding pyridine-carboxylic acid can be extended to other widely used carboxylic acids, more importantly, to lead to an unsymmetric bifunctional bridging ligand, which is essential for generating polar solids.

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1. Introduction

Second-order nonlinear optical (NLO) materials find practical applications in electrooptic devices [1–7]. This kind of materials requires noncentrosymmetric arrangement of the molecule in the bulk, which is opposite to the favorable centrosymmetric arrangement for most molecules; therefore it is a great challenge for scientists to synthesize those materials. Consequently, several approaches towards alignment of NLO chromophores into an acentric bulk, including poled-polymers, Langmuir–Blodgett films, and self-assembled multilayers [8–12], acentric hydrogen-bonded aggregates [13], antiparallel alignment of ionic sheets [14], head-to-tail alignment of dipolar guests confined in channels of organic host lattices [15], and symmetry control [16] have been explored. Diamondoid networks are of great interest in the field of supramolecular chemistry and crystal engineering because of their predisposition to pack in acentric space groups, which are relevant to NLO properties. Different strategies have been used to prepare such materials through covalent linkage, metal coordination, hydrogen bond, donor–acceptor interactions, or van der Waals forces. The organic diamondoid structures are frequently achieved either directly from homo- or heterogeneous tetrahedral building blocks or through the appropriate linear node connectors [17,18], while the engineering of most inorganic, metal-organic, or organometallic diamondoid networks is achieved by the tetrahedral metal centers with bifunctional bridging ligands [19–21], in which the use of asymmetric pyridinecarboxylate ligands produced a series of acentric diamondoid networks with

interesting SHG properties. This strategy is very efficient to make the NLO materials, and it relies on the design and synthesis of the bifunctional ligand possessing electron pull–push effect. In this context, we modified the widely used 2,5-pyridinedicarboxylic acid for metal-organic frameworks through methylation to produce 2,5-dicarboxy-1-methylpyridinium (H_2DCMP) chloride. The methylation blocks the coordination site of pyridine, which are quite often involved in the coordination [22,23], making the multiple coordination sites easy control. DCMP ligand becomes a linear spacer in contrast to 2,5-pyridinedicarboxylic acid. Moreover, the positive charge after methylation makes the DCMP have a total charge -1 when deprotonated, which is suitable for making diamondoid network with divalent metal center. As expected, the resulting $\text{Zn}(\text{DCMP})_2$ **1** indeed has an acentric diamondoid architecture, which are reported herein.

2. Experimental section

2.1. Materials and general methods

The ligand 2,5-dicarboxy-1-methylpyridinium (H_2DCMP) chloride was prepared according to the literature method [24]. All other chemicals used in this work were of reagent grade. They were commercially available and used as purchased without further purification. Thermogravimetric analysis was performed on an instrument TGA 2050 Thermogravimetric Analyzer with a heating rate of $5^\circ\text{C}/\text{min}$ up to 650°C . A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The back-scattered SHG light was collected using a spherical concave mirror and passed through a filter that

* Corresponding author. Fax: +86 311 86266419.

E-mail address: jingwang@home.ipe.ac.cn (J. Wang).

transmits only 532 nm radiation. Approximate estimations of the second order nonlinear optical intensity were obtained by comparison of the results obtained from a powdered sample in the form of a pellet (Kurtz powder test), with that obtained for KDP.

2.2. Synthesis of compound 1

Preparation of compound 1. 2,5-dicarboxy-1-methylpyridinium (H_2DCMP) chloride (2 mmol, 44 mg) was dissolved in 10 mL water and neutralized by double molar equivalent 1 N NaHCO_3 solution. Then $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 30 mg) aqueous solution was added dropwise. Upon evaporation, the colorless block shaped after a week. Crystal yield based on DCMP is 34%. Anal. Calc. (%) for **1**: C, 45.07; H, 2.82; N, 6.57. Found: C, 45.48; H, 2.32; N, 6.16.

2.3. Crystallography

The crystal data were collected on a SMART CCD 1000 with $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at 150 K. The structures were solved by direction methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program. All hydrogen atoms were located from the difference Fourier maps and refined isotropically. A summary of the crystallographic data and structural determination for **1** is shown in Table 1.

3. Results and discussion

3.1. Single-crystal X-ray diffraction

Single-crystal X-ray diffraction analysis revealed that $\text{Zn}(\text{DCMP})_2$ **1** crystallizes in a noncentric space group $Fdd2$ and forms a 3D diamondoid network as expected. Selected bond lengths and angles are listed in Table 2. An Ortep drawing of the structure of compound **1** is illustrated in Fig. 1. The Zn ions are located on a 2-fold position and coordinated with four oxygen atoms from the monodentate carboxyl group of DCMP ligand. The Zn1–O1 and Zn1–O4^{#2} bond lengths are 1.9583(17) and 1.9596(17) Å, respectively, which are consistent with the corresponding values found in other zinc carboxylate complexes [24,25]. The central Zn ion has a tetrahedral geometry with O–Zn–O angle within the range of 100.7–118.5°, slightly deviated from the ideal tetrahedral geometry. Both carboxyl groups of the DCMP ligand are deprotonated and bridge two Zn ions in a

Table 1
Crystal and refinement data for compound **1**.

Empirical formula	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_8\text{Zn}$
Formula wt.	425.65
Crystal system	Orthorhombic
Space group	$Fdd2$
a (Å)	12.7423 (8)
b (Å)	34.469 (2)
c (Å)	7.2327 (5)
V (Å ³)	3176.7 (4)
Z	8
ρ_{calcd} (mg m^{-3})	1.780
μ (mm^{-1})	1.60
F_{000}	1728
Reflections collected	7234
Unique reflections, R_{int}	1930, 0.054
Observed reflections [$I > 2\sigma(I)$]	1848
Index range (h,k,l)	$-16 \leq h \leq 16, -45 \leq k \leq 45, -9 \leq l \leq 9$
R_1, WR_2 ($F^2 > 2\sigma(F^2)$) ^a	0.029, 0.077

^a Weights during refinement were $w=1/[\sigma^2(F_o^2)+(0.052P)^2+1.5055P]$, where $P=(F_o^2+2F_c^2)/3$.

Table 2

Selected distances (Å) and angles (°) in compound **1**.

Zn1–O1	1.9583 (17)
Zn1–O1 ^{#1}	1.9583 (17)
Zn1–O4 ^{#2}	1.9596 (17)
Zn1–O4 ^{#3}	1.9596 (17)
O1–Zn1–O1 ^{#1}	100.72 (11)
O1–Zn1–O4 ^{#2}	109.74 (7)
O1 ^{#1} –Zn1–O4 ^{#2}	118.46 (8)
O1–Zn1–O4 ^{#3}	118.46 (8)
O1 ^{#1} –Zn1–O4 ^{#3}	109.74 (7)
O4 ^{#2} –Zn1–O4 ^{#3}	100.67 (11)
O2–C1–O1	127.5(2)
O3–C8–O4	128.1(2)

Symmetry codes: (#1) $-x+1, -y, z$; (#2) $x+1/4, -y+1/4, z-3/4$; and (#3) $-x+3/4, y-1/4, z-3/4$;

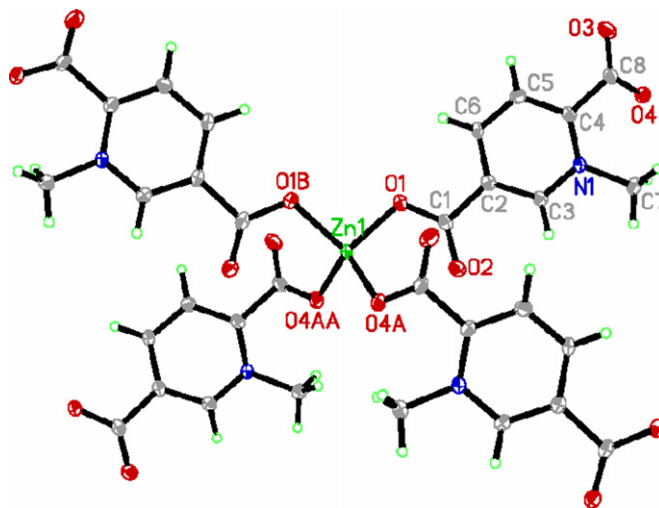


Fig. 1. Molecular structure of $[\text{Zn}(\text{DCMP})_2]$ unit in **1**.

monodentate mode. The carboxyl group O1–C1–O2 is close to be coplanar with the central pyridyl plane with a twisting angle of 10.0°, while the other carboxyl group O3–C8–O4 is more twisted with an angle of 37.3°. Apparently, the carboxyl group O3–C8–O4 has more steric hindrance from the methyl group.

The Zn1 center is connected to four adjacent Zn centers through the DCMP bridges to result in a three-dimensional polymeric network with a diamondoid architecture, in which an equal intraframe Zn...Zn distance is ca. 10.67 Å. Zn...Zn distance in compound **1** is longer than that of bis(isonicotinato) zinc [19] with Zn–Zn separations of 8.78 and 8.81 Å, respectively. With long Zn–Zn separations, very large cavities are formed within each diamondoid network in **1** (Fig. 2). If the DCMP bridge groups are omitted, the Zn–Zn–Zn angles in **1** range from 72.3° to 118.9° and deviate moderately from the 109.45° expected for an idealized diamond network. The same deviation is found in $[\text{Cd}(\text{isonicotinate})_2(\text{EtOH})]$ [20], in which the Cd1 center is connected to four adjacent Cd centers through the isonicotinate bridges to result in a 3-dimensional diamondoid polymeric network with the Cd–Cd–Cd angles ranging from 75.4° to 129.0°. This compound thus adopts a highly distorted diamondoid structure, probably in order to accommodate the coordination of one ethanol molecule. But, in our compound **1**, no solvent molecule has been included; the distortion may result from the steric hindrance of the methyl group.

It is a well-known fact that the diamondoid frameworks have a high propensity to interpenetration [21], which indeed occurs in

compound **1**. Frequently, observed features in interpenetration can be listed: (a) this mode generates large channels of “ideal” square section that run parallel to the direction of interpenetration and usually contain the anions (anionic channels); (b) the adamantanoid cages are stretched in the direction of interpenetration, and, moreover, (c) this direction corresponds to the shortest crystallographic axis. Obviously, compound **1** conforms to all the above points and has effectively avoided the formation of a large void space via a 3-fold interpenetration (Fig. 3). The degree of interpenetration remains difficult to predict and fully explain [26]. It is strongly related to the length of the spacer ligands, which dictates the $M \cdots M$ separations, that is, the length of the edges of the adamantanoid cages, and hence influences the number n of interpenetrating nets. However, even in the presence of rigid ligands, a precise $n/M \cdots M$ correlation does not exist. For example, the $Ag \cdots Ag$ separation in the ninefold diamondoids $[Ag(bpcn)_2]X$ [27,28] is about 16.4 Å, while the corresponding separation in the eightfold interpenetrated network $[Ag(3.3'-dcpa)_2]ClO_4 \cdot H_2O$ is 17.02 Å [29]. In bis(isonicotinato) zinc [19], although with shorter Zn–Zn separations of 8.78 and 8.81 Å than that of compound **1**, three-fold interpenetrated network even forms.

Apart from specific intermolecular noncovalent interactions, the hydrogen bonds with well characterized geometry and robustness are also frequently used in designing supramolecular arrays and amongst hydrogen bonds, C–H \cdots O hydrogen bonds play a dominant role in the stability of organometallic crystals [30]. In compound **1**, the uncoordinated oxygen atoms of carboxyl groups form C–H \cdots O hydrogen bonds $[C3 \cdots O3^{\#1} = 3.364(3) \text{ \AA}; C3-H3A \cdots O3 =$

$152.1^\circ; C7 \cdots O3^{\#1} = 3.288(4) \text{ \AA}; C7-H7D \cdots O3^{\#1} = 163.8^\circ; C5 \cdots O2^{\#2} = 3.193(3) \text{ \AA}; C5-H5A \cdots O2^{\#2} = 149.6^\circ; \#1: x, y, -1 + z; \#2: x, y, 1 + z]$ with the C atoms from the adjacent set of the diamondoid network, stabilizing the 3D network of **1**. C–H \cdots O hydrogen bond, in organic compounds, is assumed to exist in those cases where the C \cdots O distance (D), H \cdots O distance (d), and the C–H \cdots O angle (θ) are such that $2.8 < D < 4.0 \text{ \AA}$, $2.0 < d < 3.0 \text{ \AA}$, and $110 < \theta < 180^\circ$, respectively [31]. Actually, a reliable C–H \cdots O hydrogen bond is considered to be one where the C \cdots O distance, H \cdots O distance, and C–H \cdots O angle are in the ranges 3.10–3.50 Å, 2.00–2.80 Å, and 150–180°, respectively [32]. It is their directionality that makes them important as crystal structure directors [30]. Therefore, it is useful to discuss hydrogen-bond lengths and angles jointly. Very short C–H \cdots O contacts should be viewed with some skepticism. In cases of doubt, angular considerations should take precedence over length considerations. In the present report of compound **1**, the parameters related to C–H \cdots O interactions viz. C \cdots O distance and C–H \cdots O angle lie in the ranges 3.193–3.364 Å and 149.6–163.8°, respectively. They are in close agreement with the above quoted reports of organic and organometallic compounds and consistent with the corresponding values found in organotellurium carboxylate complexes [33]; hence it is concluded that the compound **1** contains C–H \cdots O hydrogen bonds. The oxygen of C–O of carboxylate group acts as acceptor of hydrogen bond from acidic $-CH_3$ and $-CH_2-$ groups resulting in intermolecular $C(sp^3)-H \cdots O$ and $C(sp^2)-H \cdots O$ hydrogen bonds, respectively. Although, on the basis of the above available data, it is difficult to comment on the strength (strong or weak), but it is clear that they do form supramolecular assemblies (Fig. 4).

3.2. SHG efficiency

Requirements for NLO effects are the absence of a center of symmetry and the presence of asymmetric ligands that can introduce electronic asymmetry (push–pull effect). The examples of Zn networks exhibiting NLO effects are $[Zn(ini)_2]_n$ [19], $[Zn(pya)_2]_n$ [34], and $[Zn(bpeb)_2]_n$ [35] that all are of diamondoid type. Owing to the lack of an inversion center at the tetrahedral connectivities diamondoid frameworks are often associated with acentric space groups. Consequently, diamond-related coordination networks based on transparent (tetrahedral) d^{10} metal ions and asymmetric ligands are generally potential candidates for practical second-order NLO applications. $[Zn(ini)_2]_n$, $[Zn(pya)_2]_n$, and $[Zn(bpeb)_2]_n$ possess robust, interpenetrated network structures that are thermally stable up to 360–400 °C. In $[Zn(ini)_2]_n$ each Zn is coordinated by two pyridine nitrogens and two carboxylate oxygens; the 3D structure is 3-fold interpenetrated, while 5-fold interpenetration occurs in the case of $[Zn(pya)_2]_n$. As pointed out in [19], diamond-based frameworks with an odd number-fold interpenetration are necessarily acentric, while those with an even number-fold interpenetration can be either centrosymmetric or

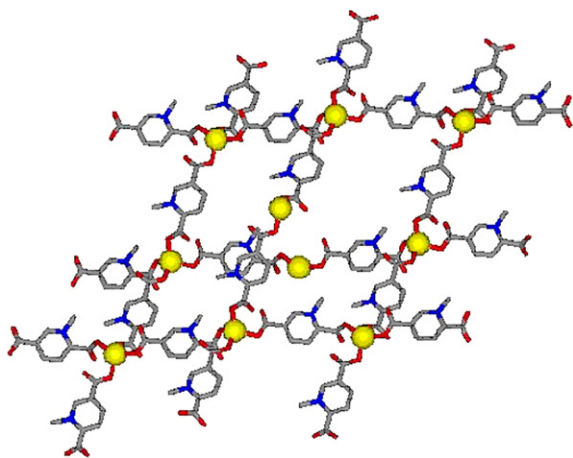


Fig. 2. A single diamondoid network assembled by tetrahedral $[Zn(DCMP)_2]$: carbon, gray; oxygen, red; nitrogen, blue; and zinc, yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

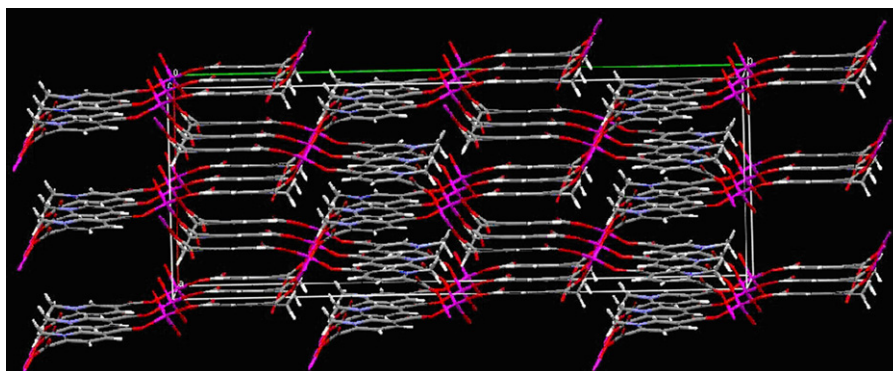


Fig. 3. The packing diagram of diamondoid network with three-fold interpenetration in **1**.

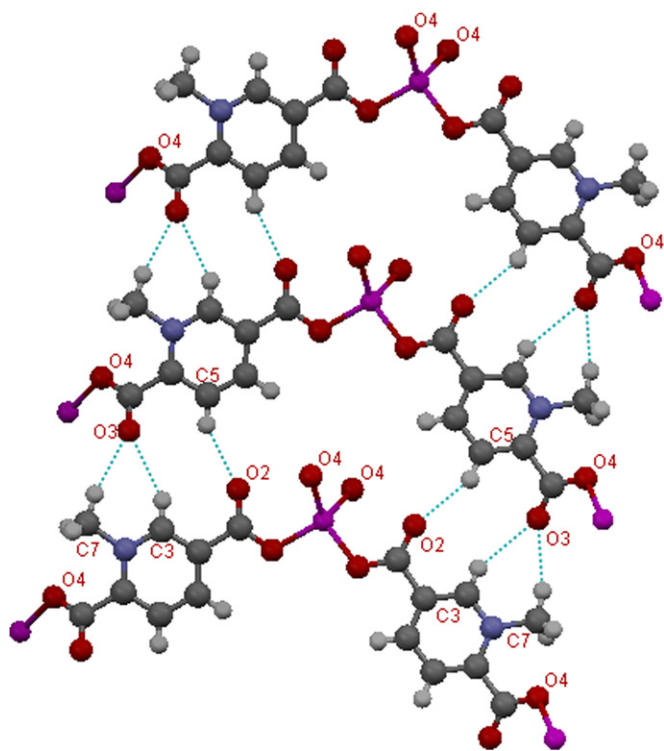


Fig. 4. Molecules of compounds **1** connected through C–H...O hydrogen bonds.

acentric. A preliminary second harmonic generation (SHG) measurement on powdery sample of **1** confirmed its acentricity and odd number-fold interpenetration (3-fold). Compound **1** has a SHG efficiency approximately 7 times higher than that of potassium dihydrogen phosphate (KDP), suggesting that compound **1** be a potential second-order NLO material. The large SHG response is presumably related to the large electronic push–pull effects due to the positive charge of methylpyridinium. Compound **1** also exhibits remarkable thermal stability. Thermogravimetric analysis (TGA) shows no weight loss and the compound is stable up to 410 °C.

The notable feature of this work is deliberate design of the ligand and the structural prediction of its metal complex. A well documented diamondoid networks are based on the divalent Zn and Cd ions with unsymmetrical pyridine-carboxylate ligands [19,20]. Though 2,5-pyridinedicarboxylic acid is unsymmetrical in nature and has been widely used for metal-organic frameworks, no diamondoid network has been reported. Methylation of 2,5-pyridinedicarboxylic acid blocks the coordination site of pyridine, which are quite often involved in the coordination. This makes the DCMP resemble the benzodicarboxylic acid in terms of potential coordination mode, but the charge is reduced from -2 to -1 . More importantly, it leads to an unsymmetric bifunctional bridging ligand, which is essential for generating polar solids. To the best of our knowledge, **1** is defined as the first DCMP metal complex reported so far.

4. Conclusions

A novel metal-organic network with a diamondoid architecture has been obtained through a rational design, which exhibits a promising SHG property. The design strategy of ligand through methylation of the corresponding pyridinecarboxylic acid can be extended to other widely used carboxylic acids. Efforts are currently underway to explore the scope of this new strategy to

form new metal-organic frameworks with useful physicochemical properties.

Supporting information

Crystallographic information files (CIF) and TGA traces. CCDC 743177 contains the supplementary crystallographic data for compound **1**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/deposit>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44)01223336033; or e-mail to deposit@ccdc.cam.ac.uk.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.07.018.

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