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NLO-active zinc(II) and cadmium(II) coordination networks with 8-fold diamondoid structures†

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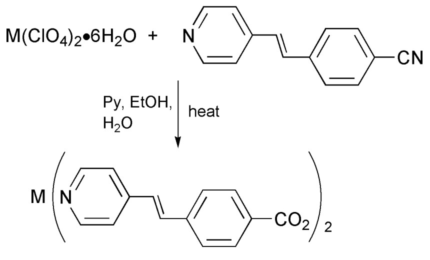
Bis{4-[2-(4-pyridyl)ethenyl]benzoato}-zinc(II) and -cadmium(II) with 8-fold diamondoid network structures have been synthesized under hydro(solvo)thermal conditions and exhibit powder second harmonic generation efficiencies comparable to that of technologically important lithium niobate.

The design and synthesis of extended frameworks *via* metal–ligand coordination has received intense attention over the past few years[1] owing to the propensity of incorporating interesting functions such as zeolitic,[2] magnetic,[3] conducting[4] and non-linear optical (NLO) properties.[5] Our group has been particularly interested in the rational synthesis of non-centrosymmetric coordination networks for second-order NLO applications.[5] By linking conjugated unsymmetrical, bifunctional ligands with transparent d^{10} metals, metal–ligand ligation has been successfully utilized to counteract unfavorable centric dipole–dipole repulsions. In particular, we have recently demonstrated that diamondoid coordination networks with an odd number-fold interpenetration are necessarily acentric[5a] while those with an even number-fold interpenetration can crystallize in centrosymmetric space groups owing to the dipole cancellation of pairs of diamondoid nets.[6] Herein, we report two novel 8-fold diamondoid networks, bis{4-[2-(4-pyridyl)ethenyl]benzoato}zinc(II), **1** and bis{4-[2-(4-pyridyl)ethenyl]benzoato}cadmium(II) **2**, that crystallize in a chiral space group and exhibit powder second harmonic generation efficiencies approaching that of technologically important lithium niobate.[7]

Compound **1** was obtained in 77% yield by treating $Zn(ClO_4)_2 \cdot 6H_2O$ and (*E*)-4-(4-cyanostyryl)pyridine in a mixture of pyridine, ethanol and water at 120 °C [eqn. (1)].‡



(1)

M = Zn, **1**
M = Cd, **2**

Compound **2** was obtained similarly in 61% yield by reacting $Cd(ClO_4)_2 \cdot 6H_2O$ and (*E*)-4-(4-cyanostyryl)pyridine [eqn. (1)].‡ While the IR spectrum of **2** shows a strong symmetric C=O stretch at 1403 cm^{-1} corresponding to bidentate carboxylate groups, the IR spectrum of **1** exhibits two strong C=O stretches at 1416 and 1377 cm^{-1} suggesting the existence of both monodentate and bidentate carboxylate groups.[8] The 4-[2-(4-pyridyl)ethenyl]benzoate (L) groups in both **1** and **2** have evidently resulted from slow hydrolysis of (*E*)-4-(4-cyanostyryl)pyridine under hydro(solvo)thermal conditions.[5,6]

Compound **1** crystallizes in the chiral monoclinic space group *C*2.§ The asymmetric unit of **1** contains two independent Zn centers and two L ligands, with both Zn centers lying on 2-fold axes. While the Zn1 center adopts a distorted octahedral geometry by coordinating to two pyridyl nitrogen atoms and two carboxylate groups in chelating fashion, the Zn2 center exhibits a tetrahedral coordination *via* binding to two pyridyl nitrogen atoms and two carboxylate groups in monodentate fashion (Fig. S1, ESI†). Consistent with the coordination geometry difference, the Zn2–O3 distance of 1.952(5) Å is significantly shorter than the Zn1–O1 distance of 2.237(5) Å and the Zn1–O2 distance of 2.123(4) Å. In spite of the different coordination geometry, both Zn1 and Zn2 centers have a tetrahedral connectivity to their adjacent Zn centers and are linked by the bridging L groups to form a diamondoid network structure (Fig. 1). With the Zn···Zn separations of 15.33 and 15.51 Å, a large cavity is generated within a single diamondoid cage; the void space in **1** has been filled by the interpenetration of 8 independent diamondoid nets (Fig. 2). 8-Fold interpenetration has effectively filled the void space, and **1** contains no included guest molecules.

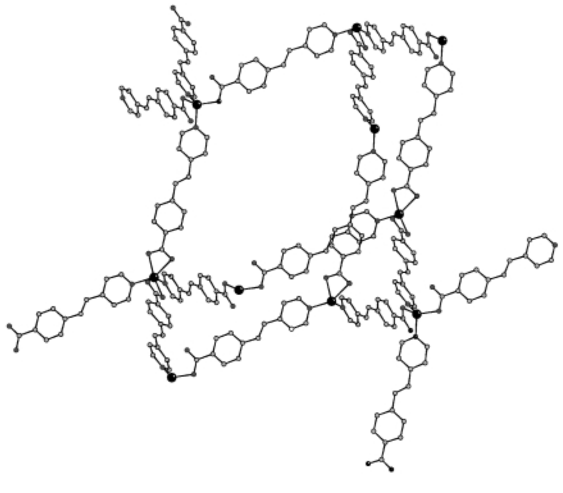


Fig. 1 Diamondoid network structure of **1**. The Zn1 centers have an octahedral coordination geometry while the Zn2 centers have a tetrahedral coordination environment. The Zn–N distances are 2.046 and 2.075 Å.

Compound **2** also crystallizes in the chiral monoclinic space group *C*2.§ The asymmetric unit of **2** contains two independent Cd centers and two L ligands, with the Cd centers lying on 2-fold axes. Both Cd centers in **2** adopt distorted octahedral geometry by coordinating to two pyridyl nitrogen atoms and two carboxylate groups in chelating fashion [Fig. 3, Fig. S2 (ESI)†]. The Cd–O distances range from 2.25 to 2.44 Å. Interestingly, **2** also adopts an 8-fold diamondoid network structure [Fig. S3 (ESI)†] in spite of the very different coordination geometry between the Cd centers in **2** and the Zn centers in **1**. In fact, **2** exhibits exactly the same network topology to that of **1** with slightly longer Cd–Cd separations of 15.65 and 15.77 Å as a result of larger Cd radii (*vs.* Zn radii). These results bear significant implications for the crystal engineering of acentric diamondoid coordination networks: (1)

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† Electronic supplementary information (ESI) available: Zn and Cd coordination environments (Fig. S1 and S2), 8-fold interpenetration in **2** (Fig. S3) and TGA curves of **1** and **2** (Fig. S4). See http://www.rsc.org/suppdata/cc/b0/b007335k/

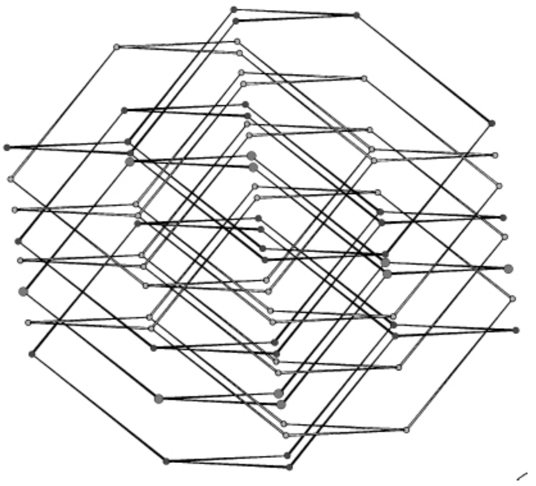

Fig. 2 Interpenetration of 8 independent diamondoid nets in **1**. The Zn centers are represented with circles, while the L ligands are represented with straight lines.

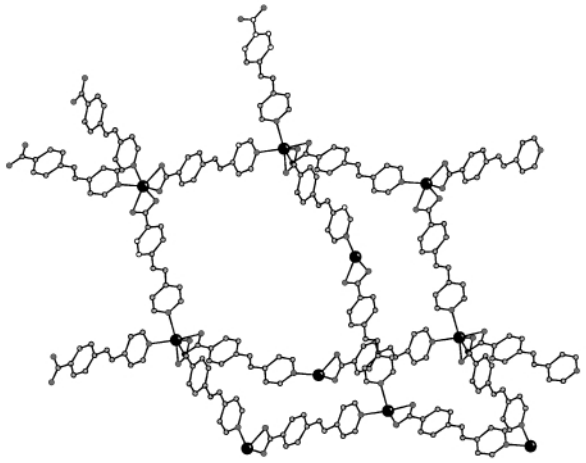

Fig. 3 Diamondoid network structure of **2**. Both the Cd1 and Cd2 centers have an octahedral coordination geometry. The Cd–N distances are 2.259 and 2.301 Å.

an even number-fold interpenetration does not guarantee but can lead to acentric solids; (2) the formation of diamondoid networks only depends on the connectivity of the neighboring metal centers and is not sensitive to the local metal–ligand coordination geometry.

Kurtz powder second harmonic generation (SHG) tests show that **1** exhibits a $I^{2\omega}/\mathrm{I}^{2\omega}$(quartz) of 400 while **2** has a $I^{2\omega}/I^{2\omega}$ (quartz) of 345.[9]¶ These powder SHG efficiencies are comparable to that of technologically important lithium niobate ($I^{2\omega}/I^{2\omega}$ (quartz) of 600). Compounds **1** and **2** also exhibit remarkable thermal stability: TGA analyses [Fig. S4 (ESI)†] show that they both have an onset temperature for decomposition above 400 °C. Both **1** and **2** are insoluble in common solvents owing to their neutral 3-D polymeric structures, and they are thus potential candidates for practical NLO applications. This work clearly illustrates the utility of diamondoid networks as a structural motif for the rational synthesis of novel functional materials.

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Notes and references

‡ *Preparations*: Zn($C_{14}H_{10}NO_2$)$_2$, **1**: a heavy walled Pyrex tube containing Zn(ClO_4)$_2$·6H_2O (0.093 g, 0.25 mmol) and (*E*)-4-(4-cyanostyryl)pyridine (0.126 g, 0.5 mmol) in pyridine (0.3 mL), ethanol (0.3 mL) and H_2O (0.1 mL) was frozen and sealed under vacuum and placed inside an oven at 120 °C. Colorless crystals of **1** were obtained after 72 h of heating. Yield (0.099 g, 77 %).

Cd($C_{14}H_{10}NO_2$)$_2$ **2**: a heavy walled Pyrex tube containing Cd(ClO_4)$_2$·6H_2O (0.125 g, 0.25 mmol) and (*E*)-4-(4-cyanostyryl)pyridine (0.126 g, 0.5 mmol) in pyridine (0.3 mL), ethanol (0.4 mL) and H_2O (0.1 mL) was frozen and sealed under vacuum and placed inside an oven at 130 °C. Colorless crystals of **2** were obtained after 14 days of heating. Yield (0.086 g, 61%).

§ *Crystal data*: for **1**: monoclinic, space group *C*2, a = 21.522(3), b = 8.667(2) c = 13.046(2) Å, β = 95.207(2)°, U = 2479.4(5) Å^3, Z = 4, D_c = 1.377 g cm^{-3}, T = 173(2) K, Mo-Kα radiation (λ = 0.71073 Å). Least-squares refinement based on 3671 reflections with $I > 2\sigma(I)$ and 317 parameters led to convergence, with a final value of $R1$ = 0.064, $wR2$ = 0.142, and goodness of fit = 0.98. Flack parameter χ = 0.03(2).

For **2**: monoclinic, space group *C*2, a = 22.250(4), b = 9.109(2) c = 12.503(3) Å, β = 96.359(3)°, U = 2518.3(8) Å^3, Z = 4, D_c = 1.479 g cm^{-3}, T = 173(2) K, Mo-Kα radiation (λ = 0.71073 Å). Least-squares refinement based on 4405 reflections with $I > 2\sigma(I)$ and 317 parameters led to convergence, with a final value of $R1$ = 0.085, $wR2$ = 0.218, and goodness of fit = 1.04. Flack parameter χ = −0.04(7). CCDC 182/1817. See http://www.rsc.org/suppdata/cc/b0/b007335k/ for crystallographic files in .cif format..

¶ Powder second harmonic generation experiments were carried out on ground samples of **1** and **2** with particle size of 76 ± 13 μm with a Nd:YAG laser at the fundamental wavelength of 1064 nm. Only the transmitted second harmonic signals from the samples inside glass capillaries were collected, and compared to that of α-quartz.

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