

Opto-electronic multifunctional chiral diamondoid-network coordination polymer: bis{4-[2-(4-pyridyl)ethenyl]benzoato}zinc with high thermal stability†

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A novel 8-fold interpenetration diamondoid-like chiral condensed neutral coordination polymer, bis{4-[2-(4-pyridyl)ethenyl]benzoato}zinc [Zn(PEBA)₂] **1**, synthesized by the hydrothermal reaction between Zn(ClO₄)₂·6H₂O and 4-[2-(4-pyridylethenyl)]benzenecarbonitrile (PEBC), displays very strong blue fluorescent emission and SHG response (*ca.* 1.5 × that of urea) as well as high thermal stability (up to *ca.* 430 °C).

Within the family of blue-luminescent compounds previously used in EL devices or light-emitting diodes (LED), most of them are aromatic organic molecules,¹ conjugated organic polymers,² organometallic compounds³ or metal–chelate compounds such as metal complexes based on 8-hydroxyquinoline, 2-methylquinolin-8-ol, azomethine, azaindole, oxadiazole and bipyridyl derivatives.⁴ More recently, boron complexes with 8-hydroxyquinoline derivatives have been shown to display very highly efficient blue-light emission.⁵ However, blue-luminescent emission coordination polymers with high thermal stability (up to 400 °C) are, as far as we are aware, relatively rare. Condensed coordination polymers could play a key role in the development of LED materials because one can tune the emission color and stability of the complex readily by manipulating the ligand and the coordination environment around the central atom. Recently, the crystal engineering strategy has been utilized in the construction of acentric diamondoid metal–organic coordination polymers by using asymmetric bridging ligands as building blocks since the utilization of asymmetric ligands can introduce electronic asymmetry (push–pull effect) which is essential for a second harmonic generation (SHG) response.^{6,7} However, coordination polymers which display both very strong blue fluorescent emission and SHG response in the solid state still remain, to the best of our knowledge, unexplored. The condensed neutral diamondoid-like coordination polymer, bis{4-[2-(4-pyridyl)ethenyl]benzoato}zinc (**1**)[‡] represents the first example of such materials with strong blue-luminescent emission and an SHG response (1.5× as that of urea), as well as high stability up to 430 °C.

The three-dimensional polymeric structure of **1** was revealed by an X-ray single crystal diffraction investigation.§ The local coordination environment around Zn1 and Zn2 ions in **1** can best be described as distorted octahedral and tetrahedral, respectively, as shown in Fig. 1. Each asymmetric unit of **1** contains two Zn atom centers in which the Zn1 center coordinates to four oxygen atoms from two different PEBA groups in bidentate chelating mode and to two pyridine nitrogen atoms of two other PEBA groups, resulting in the formation of

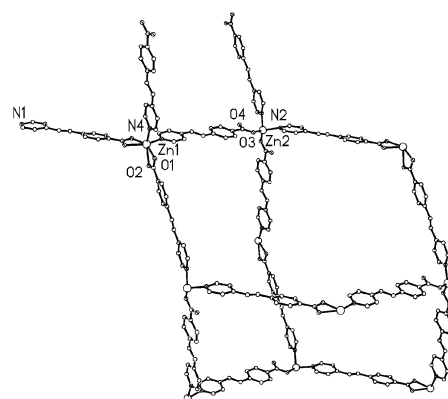


Fig. 1 A chiral diamondoid-like net representation of the coordination polymer [Zn(PEBA)₂] **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) Zn(1)–O(1) 2.088(5), Zn(1)–O(2) 2.297(6), Zn(1)–N(4) 2.085(6), Zn(2)–O(3) 1.953(5), Zn(2)–N(2) 2.077(5).

a distorted octahedral geometry. In contrast to the octahedral coordination of Zn1 centers, the Zn2 center coordinates to two pyridine nitrogen atoms of two PEBA groups and to two carboxylate oxygen atoms of two other PEBA groups in a monodentate fashion. If the chelating carboxylates are treated as one connecting point, Zn1 centers also have a pseudotetrahedral environment. Thus, both Zn1 and Zn2 centers are connected to four Zn centers through PEBA bridges to form a diamondoid-like net (Fig. 1). The crystal contains eight independent interpenetrating diamondoid networks with Zn···Zn separations in each network in the range 15.36–15.49 Å while^{6,7} Zn···Zn···Zn angles are in the range 91.7–128.8° which represents a significant distortion from the ideal tetrahedral angle of 109.5° found in diamond. Thus, although the connectivity of the network is the same as diamond, the symmetry is lower. Two schematic representations of the 3D diamond-like network and the eight interpenetrating nets are shown in Fig. 2(a) and (b), respectively. As a result of the unsymmetrical nature of PEBA, **1** crystallizes in a chiral space group C2, which belongs to the crystal class 2 where optical activity can occur as specific physical effects.⁸ Preliminary experimental results show that **1** displays strong powder SHG efficiencies, *ca.* 1.5× that of urea (see ESI[†]), probably due to its diamondoid structural type which is similar to that of potassium dideuterophosphate (KDP), the only known nonlinear optical (NLO)-active diamondoid network.⁹ On the other hand, the protonated free ligand HPEBA also finds wide applications in second-order NLO films using organic molecular beam deposition techniques. However, because of the absence of strong donor/acceptor substituents in HPEBA, it is unlikely to display a high nonlinearity or substantial SHG response.¹⁰ Thus, **1** combines the advantages of both pure organic and inorganic

† Electronic supplementary information (ESI) available: schematic representation of the 8-fold interpenetrating diamondoid-like network and second harmonic generation (SHG) measurements for **1**. See <http://www.rsc.org/suppdata/cc/b0/b004980h/>

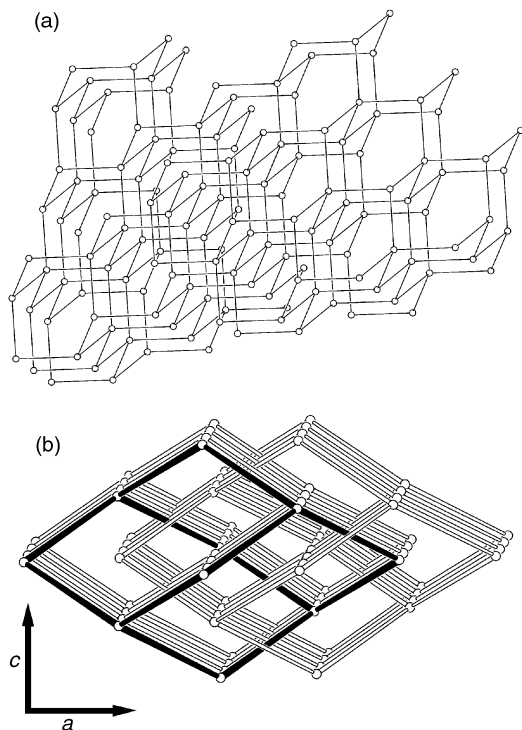


Fig. 2 (a) 3D diamond-like network representation (circles and straight lines denote Zn atoms and PEBA ligands, respectively). The other seven interpenetrating diamondoid nets are omitted for clarity. (b) A schematic representation of the eight interpenetrating diamond nets, with one net highlighted. Three other nets are related by unit cell translations in the *b*-direction. A second set of four nets is related by a translation of $1/2 + x$, $1/2 + y$, z (see also ESI).

NLO materials and such hybrid inorganic–organic NLO materials have recently been widely investigated as NLO materials.¹¹

To study the thermal stability of the compound **1** thermogravimetric analysis (TGA) was performed on a polycrystalline sample, indicating that no strikingly clean weight loss step occurred below 430 °C, indicating that **1** is stable up to this temperature while HPEBA only remains intact up to 350 °C. The most important feature of the structure of **1** is that its three-dimensionally condensed polymeric structure leads to significant enhancement of fluorescent intensity, which is larger than that of free ligand (HPEBA) by a factor of *ca.* 10 (Fig. 3), probably due to the enhanced rigidity of **1**, compared to the free ligand. This phenomenon is similar to that found in Cd(TPT) (PY) (TPT = terephthalato, PY = pyridine).⁴ The emission of **1** with $\lambda_{\text{max}} = 460$ nm is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and can be probably assigned to intraligand fluorescent emission since a weakly similar emission with λ_{max} at 466 nm

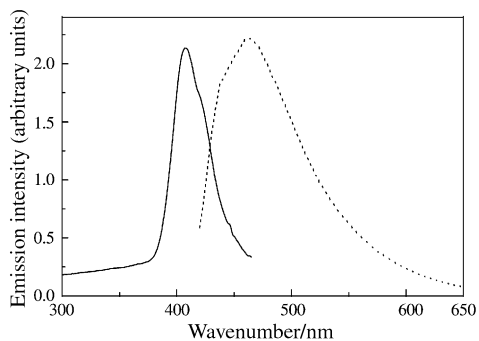


Fig. 3 Fluorescent emission spectrum of **1** in the solid state at room temperature.

is also observed for HPEBA. On the other hand, the diffuse reflectance spectrum of **1** is dominated by an intraligand π – π^* transition at 423 nm. The blue fluorescent emission of **1** suggests that it may be used as an advanced material for blue LED devices. Condensed coordination polymer **1** appears to be an excellent candidate since, in addition to its high thermal stability and SHG response, it is virtually insoluble in most solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene and water.

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Notes and references

‡ Preparation of Zn(PEBA)₂ **1**: hydrothermal treatment of Zn(ClO₄)₂·6H₂O (1.2 mmol), PEBC (1 mmol), pyridine (1 ml) and water (10 ml) for 2 days at 140 °C gave a yellowish platy crystalline product (single pure phase).¹² The yield of **1** *ca.* 35% based on PEBC. Anal. Calc. for C₁₈H₂₀N₂O₄Zn: C, 65.50; H, 3.90; N, 5.46. Found: C, 65.35; H, 4.02; N, 5.62%. IR(KBr, cm⁻¹): 3448br, 3014w, 1737m, 1718m, 1613s, 1549m, 1498w, 1416m (sh), 1373s, 1226m, 1216m, 1177w, 1071w, 1024m, 983w, 854m, 814m, 774m, 684m, 542m.

§ Crystal data for **1**: C₂₈H₂₀N₂O₄Zn, monoclinic, space group C2, *a* = 21.4550(2), *b* = 8.8584(2), *c* = 13.2661(1) Å, β = 93.8150(10)°, *V* = 2515.73(7) Å³, *Z* = 4, *M* = 513.83, *D_c* = 1.357 Mg m⁻³, *R*₁ = 0.0565, *wR*₂ = 0.1638 (4927 reflections). *T* = 293 K, μ = 1.012 mm⁻¹. Flack parameter value χ = 0.08(2). CCDC 182/1776. See <http://www.rsc.org/suppdata/cc/b0/b004980h/> for crystallographic files in .cif format.

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