CHEMISTRY
A EUROPEAN JOURNAL

The First Metal (Nd^{3+}, Mn^{2+}, and Pb^{2+}) Coordination Compounds of 3,5-Dinitrotyrosine and their Nonlinear Optical Properties

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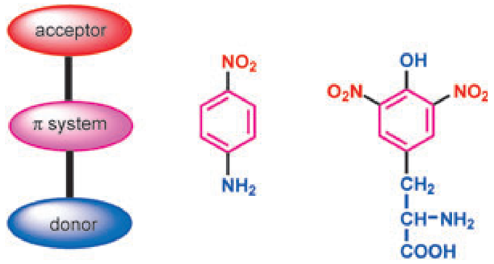
Abstract: The reactions of 3,5-dinitrotyrosine (H_2DNTY) with $Nd(NO_3)_3 \cdot 6H_2O$, $Mn(ClO_4)_2 \cdot 6H_2O$, and $Pb(OAc)_2$ afforded three homochiral compounds: discrete $[Nd(Hdnty)_2(NO_3)(H_2O)_5] \cdot 3H_2O$ (**1**) and two- and three-dimensional coordination polymers, $[Mn(Hdnty)_2]$ (**2**) and $[Pb(dnty)(0.5H_2O)]$ (**3**), respectively. The Nd atom in **1** displays a tricapped trigonal prism and supramolecular weak interactions, such as π–π stacking and H-bonds, between amino and nitro groups result in the formation of a three-dimensional network through these interactions. **2** has a two-dimensional square-grid topological net while **3** has the first three-dimensional homochiral $ThSi_2$ net. To the best of our knowledge, these are the first metal coordination compounds with 3,5-dinitrotyrosine. Preliminary second harmonic generation (SHG) investigations indicated that **1** and **2** are SHG active with estimated responses 5 and 6 times larger than that of urea, respectively, while **3** is SHG non-active (obeying the Klainman symmetry requirement). Strong enhancement of their SHG efficiency, compared with H_2DNTY, may be due to 1) the addition of a good donor–π–acceptor organic chromophore into the compound resulting in superior qualities of both inorganic and organic materials and 2) the H-bonds that persist in them. Crystal data: **1**: $C_{18}H_{32}N_7O_{25}Nd$, $M_r = 890.75\,\mathrm{g\,mol^{-1}}$, monoclinic, $P2_1$, $a = 7.0179(7)$, $b = 27.060(3)$, $c = 8.3097(8)$ Å, $\alpha = \gamma = 90.00$, $\beta = 95.646(2)°$, $V = 1570.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.884\,\mathrm{Mg\,m^{-3}}$, $R_1 = 0.0489$, $wR_2 = 0.1223$, $\mu = 17.67\,\mathrm{mm^{-1}}$, $S = 0.811$, Flack value = 0.003(13); **2**: $C_{18}H_{16}N_6O_{14}Mn$, $M_r = 595.31\,\mathrm{g\,mol^{-1}}$, orthorhombic, $P2_12_12$, $a = 8.4381(14)$, $b = 13.639(2)$, $c = 19.697(3)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 2266.9(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.744\,\mathrm{Mg\,m^{-3}}$, $R_1 = 0.0866$, $wR_2 = 0.2030$, $\mu = 6.72\,\mathrm{mm^{-1}}$, $S = 1.095$, Flack value = 0.02(6); **3**: $C_9H_8N_3O_{7.5}Pb$, $M_r = 485.37\,\mathrm{g\,mol^{-1}}$, tetragonal, $P4_12_12$, $a = 12.8136(12)$, $b = 12.8136(12)$, $c = 14.931(2)$, $\alpha = \beta = \gamma = 90.00°$, $V = 2451.5(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.885\,\mathrm{Mg\,m^{-3}}$, $R_1 = 0.0564$, $wR_2 = 0.1323$, $\mu = 6.942\,\mathrm{mm^{-1}}$, $S = 0.878$, Flack value = 0.03(2). For space group $P4_32_12$: $R_1 = 0.0672$, $wR_2 = 0.1656$, $S = 1.034$, Flack value = 1.02(3); this suggests the chosen space group $P4_12_12$ is correct.

Keywords: coordination compounds · dinitrotyrosine · donor–acceptor systems · homochirality · nonlinear optics

Introduction

Traditional organic nonlinear optic (NLO) materials usually contain donor–acceptor systems (Scheme 1), and, through a push–pull electron effect, have second-order harmonic generation properties.[1] Compared with pure inorganic compounds, these organic chromophores possess some disadvantages such as low environment stabilities, low mechanical proceeding properties, and the absence of optical-electronic



Scheme 1. The prototypical dipolar donor–π–acceptor molecules of *p*-nitroaniline (left) and H_2DNTY (right).

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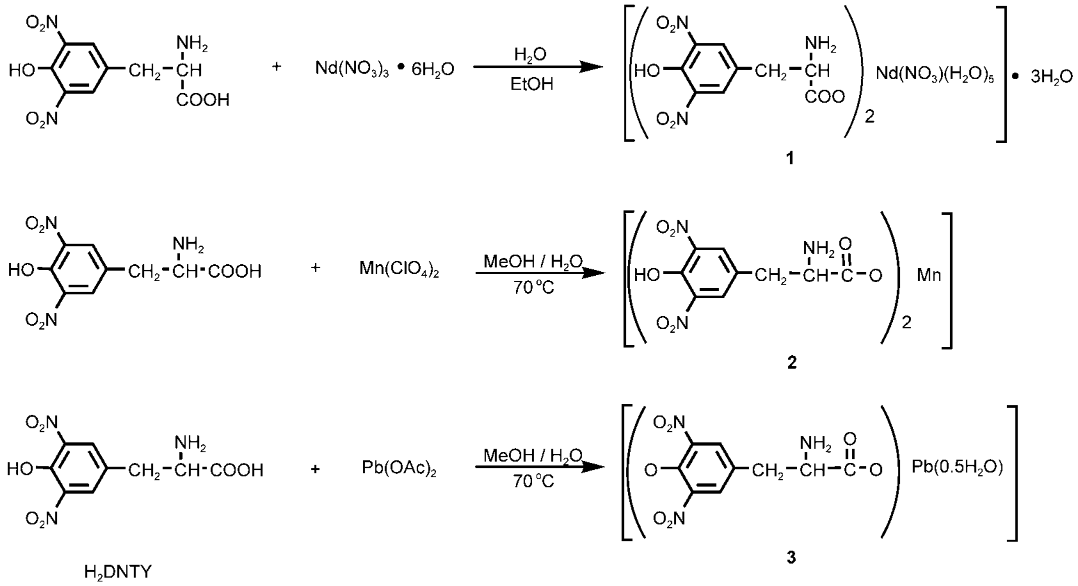
DOI: 10.1002/chem.200400722



Scheme 2. The reactions of $Nd(NO_3)_3{\cdot}6H_2O$, $Mn(ClO_4)_2{\cdot}6H_2O$, and $Pb(OAc)_2$ with H_2DNTY.

properties (without d- or f-orbital electrons).[2] Furthermore, these organic ligands, through coordination to metal ions, can be arranged octahedrally, tetrahedrally, or as geometries that are less frequently observed in organic materials. Such coordination geometries can enable three-dimensional charge transfer. Organic and inorganic hybrids have been shown to overcome the shortcomings of pure organic chromophores.[3] Coordination of organic chromophores to metal ions has resulted in the formation of hybrid inorganic–organic coordination polymers that show superior qualities.[4]

Verbiest and co-workers have pointed out that a strong enhancement of nonlinear optical properties can also be achieved through supramolecular aggregates and chirality.[4c] Furthermore, hydrogen bonding can also be considered as a donor–acceptor system which can significantly enhance the second harmonic generation (SHG) response or be a very useful second way of linking donor and acceptor, because hyperpolarizabilities strongly depend on the number of molecules aggregated through H-bonds.[5]

3,5-Dinitrotyrosine (3,5-dinitro-3-(4-hydroxyphenyl)-D-alanine, H_2DNTY) is a typical donor–π–acceptor organic chromophore ligand (Scheme 1) that displays a weak SHG response (ca. 10% of urea), low decomposition temperature, and is soluble in most solvents. These properties limit its application as a good SHG material. However, the homochiral characteristic of 3,5-dinitrotyrosine, like many amino acids or their derivatives,[6] can ensure the achievement of homochiral metal–organic coordination compounds or polymers if it is used as a building block, because only bulky material with a noncentrosymmetric space group displays an SHG response, in principle. The best way to overcome this disadvantage is by its coordination to metal ions. The reactions of $Nd(NO_3)_3{\cdot}6H_2O$, $Mn(ClO_4)_2{\cdot}6H_2O$, and $Pb(OAc)_2$ with H_2DNTY afford three homochiral coordination compounds: $[Nd(Hdnty)_2(NO_3)(H_2O)_5]{\cdot}3H_2O$ (**1**), $[Mn(Hdnty)_2]$ (**2**), and $[Pb(dnty)(0.5H_2O)]$ (**3**) (Scheme 2). **1** is a discrete molecule with a three-dimensional network through supramolecular interactions. **2** has a two-dimensional square-grid topological net. **3** is the first three-dimensional homochiral $ThSi_2$ network. To the best of our knowledge, these are the first metal coordination compounds with 3,5-dinitrotyrosine, although there have been reports of metal coordination compounds with tyrosine.[7] Preliminary SHG investigations indicate that while **3** is SHG non-active, **1** and **2** are both SHG active and their SHG responses are approximately estimated to be 5–6 times larger than that of urea. Herein we report the preparation of **1**–**3**, their solid-state structures, and preliminary SHG studies.

Abstract in Chinese:

摘要：3，5-二硝基酪氨酸(H_2DNTY)分别与 $Nd(NO_3)_3{\cdot}6H_2O$、 $Mn(ClO_4)_2{\cdot}6H_2O$、以及 $Pb(OAc)_2$ 反应可得到三个单一手性的化合物：单分子的 $[Nd(Hdnty)_2(NO_3)(H_2O)_5]{\cdot}3H_2O$ （1），二维和三维的配位聚合物 $[Mn(Hdnty)_2]$ （2），$[Pb(dnty)(0.5H_2O)]$ （3）。在 **1** 中，钕原子呈现出三帽三棱柱的配位结构，氨基和硝基之间通过微弱的超分子作用力如 π-π 堆积作用和氢键作用连接形成三维的网状结构；**2** 呈现出二维四方格子的拓扑结构，而 **3** 表现出第一个单一手性且类似为 $ThSi_2$ 格子的三维网络结构。据我们所知，它们是首例利用 3，5-二硝基酪氨酸组装的金属配合物。初步的 SHG（二阶谐波产生）检测表明 **1** 和 **2** 具有 SHG 响应，且强度大约分别是尿素 SHG 响应强度的五倍和六倍。而 **3** 没有 SHG 响应（遵循 Klainman 对称要求）。和 H_2DNTY 相比，配合物 SHG 响应强度大大增强的原因大概是由于：在同一化合物中引入优良的π 电子给体-电子受体的有机生色基团可以导致无机和有机部分以及连接它们的氢键电荷分离效果的优化。

Results and Discussion

The reactions of H_2DNTY with $Nd(NO_3)_3{\cdot}6H_2O$, $Mn(ClO_4)_2{\cdot}6H_2O$, and $Pb(OAc)_2$ give pale-red crystals of **1**, yellow crystals of **2**, and yellow crystals of **3**, respectively. The IR spectra of both **1** and **2** display similar peaks at approximately 3426–3007 cm^{-1}, indicating that the phenolic groups are not deprotonated. The IR spectrum of **3** does not show these peaks, and, when compared to the IR spectrum of H_2DNTY, suggests that the phenolic group has been deprotonated and coordinated to Pb^{2+} ions. In addition, the carboxylate groups (1631–1634 cm^{-1}) in **1**, **2**, and **3** appear to be bound to metal ions in non-chelating, monodentate mode, while the carboxylate group in the free ligand looks like a zwitterion (1631–1530 cm^{-1}).

Compound **1**, crystallized in the chiral space group $P2_1$, is in good agreement with the presence of a homochiral ligand.[8] The coordination environment around the neodymium center can be best described as a tricapped trigonal prism (Figure 1a), in which the neodymium(III) ion is nine-coordinate with two carboxylate oxygen atoms from two 3,5-dinitrotyrosine ligands (CO), two oxygen atoms from a nitrate ion (NO), and five water molecules (H_2O). It is interesting to note that the protonated H atom of a phenolic group in **1** forms an intramolecular H-bond (2.777–2.807 Å) with O atoms of one of the nitro groups, while there are moderate intermolecular H bonds between H atoms of the amino group and O atoms of one of the nitro groups from another adjacent molecule. As a result, the two adjacent phenyl rings show weak π–π stacking (Figure 1b and c). Overall, supramolecular weak interactions result in the formation of the three-dimensional network. Thus, $HDNTY^-$ only acts as a monodentate ligand using its O atom of the carboxylate group to coordinate to the Nd^{3+} ion. The bond distances of $Nd{-}O_{H_2O}$, ranging from 2.468 to 2.510 Å, are slightly longer than those of $Nd{-}O_{CO}$ (2.423–2.438 Å), and are comparable to those in $Nd{-}O_{NO}$ (2.495–2.661 Å). The bond lengths of C−C, C−N, C−O, and N−O are unexceptional.

The two-dimensional polymeric structure of **2** was revealed by an X-ray single-crystal diffraction study.[8] There are two crystallographically independent Mn atoms; the local coordination geometry around each Mn^{II} center in **2** is a slightly distorted octahedron (Figure 2a). The Mn^{II} center is bonded to six O atoms from four different HDNTY ligands of which two phenolic atoms (Ph) and one of two O atoms of the nitro groups (NO) chelate to the Mn center to give a stable six-membered ring, while the carboxylate (CO) acts as a mondentate spacer to link the Mn center. Thus, each $HDNTY^-$ serves as a tridentate linker to lead to the formation of a two-dimensional square grid (Figure 2b). A careful investigation indicated that the cavity fails to accommodate any guest molecule. Thus, its packing view also shows that there is no interpenetration of two adjacent layers (Figure 2c). The packing mode among layers is type AAA. The $Mn{-}O_{NO}$ bond distances (2.257–2.207 Å) are the longest among those of $Mn{-}O_{Ph}$ (2.119–2.162 Å) and

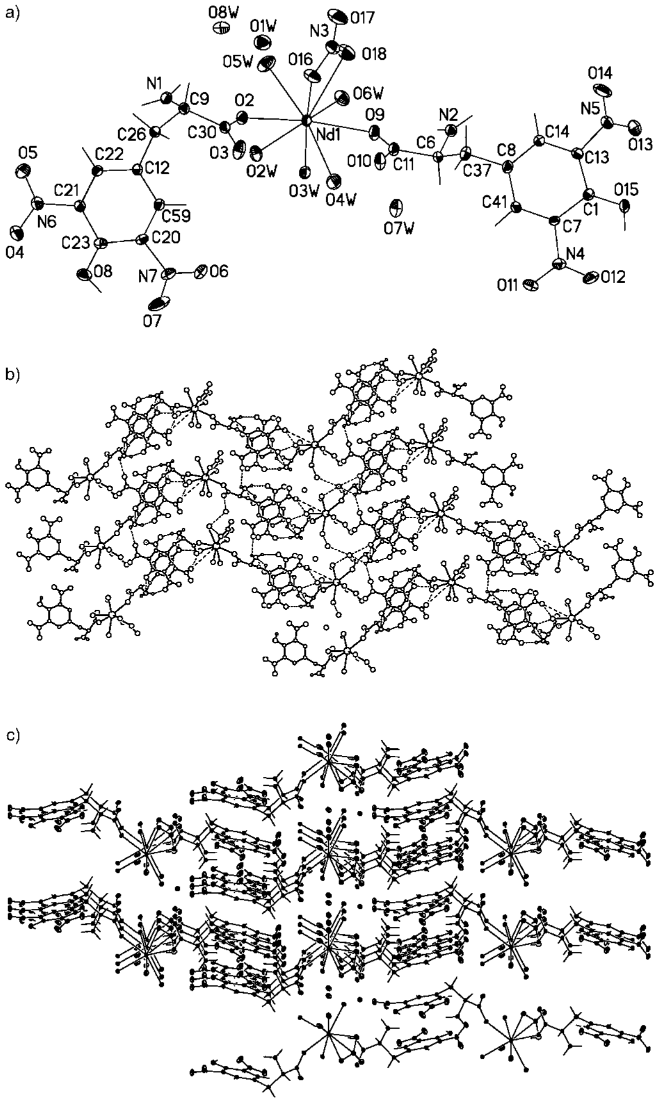


Figure 1. a) An asymmetric unit of **1** showing that the Nd center has a tricapped trigonal prism. Bond distances (Å): Nd1-O9 2.423(4), Nd1-O2 2.438(3), Nd1-O2W 2.468(4), Nd1-O5W 2.477(4), Nd1-O16 2.495(4), Nd1-O3W 2.499(4), Nd1-O6W 2.510(4), Nd1-O4W 2.510(4), Nd1-O18 2.661(5), Nd1-N3 2.989(5); bond angles (°): O9-Nd1-O2 133.67(14), O9-Nd1-O2W 138.29(15), O2-Nd1-O2W 70.78(13), O9-Nd1-O5W 37.99(17), O2-Nd1-O5W 69.35(14), O2W-Nd1-O5W 77.04(19), O9-Nd1-O16 77.19(17), O2-Nd1-O16 71.16(15), O2W-Nd1-O16 140.94(15), O5W-Nd1-O16 81.74(19), O9-Nd1-O3W 71.29(13), O2-Nd1-O3W 71.09(12), O2W-Nd1-O3W 94.73(14), O5W-Nd1-O3W 140.11(14), O16-Nd1-O3W 81.04(15), O9-Nd1-O6W 82.53(15), O2-Nd1-O6W 142.03(14), O2W-Nd1-O6W 89.18(14), O5W-Nd1-O6W 74.98(16), O16-Nd1-O6W 116.47(15), O3W-Nd1-O6W 144.62(14), O9-Nd1-O4W 70.3(2), O2-Nd1-O4W 124.08(19), O2W-Nd1-O4W 68.2(2), O5W-Nd1-O4W 132.1(2), O16-Nd1-O4W 144.83(19), O3W-Nd1-O4W 76.19(16), O6W-Nd1-O4W 72.75(17), O9-Nd1-O18 68.89(18), O2-Nd1-O18 110.40(16), O2W-Nd1-O18 143.06(17), O5W-Nd1-O18 69.8(2), O16-Nd1-O18 49.26(16), O3W-Nd1-O18 121.13(16), O6W-Nd1-O18 67.23(16), O4W-Nd1-O18 125.3(2), O9-Nd1-N3 73.10(15), O2-Nd1-N3 89.94(14), O2W-Nd1-N3 148.25(15), O5W-Nd1-N3 72.53(19), O16-Nd1-N3 24.97(15), O3W-Nd1-N3 102.73(15), O6W-Nd1-N3 91.53(15), O4W-Nd1-N3 141.6(2), O18-Nd1-N3 24.42(16). b) Three-dimensional network representation of **1** formed through supramolecular weak interactions such as π–π stacking and H-bonds. c) Three-dimensional packing view of compound **1** along the *c* axis in which the connections by H-bonds are omitted for clarity.

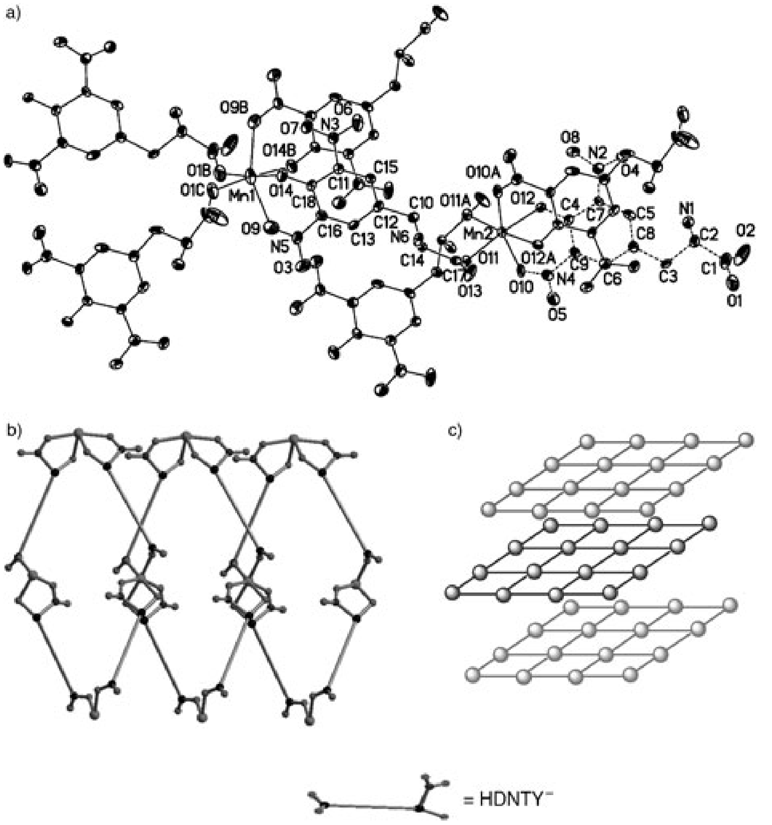


Figure 2. a) An asymmetric unit representation of **2** shows each local Mn ion has a slightly distorted octahedron. The dotted benzene ring is below the un-dotted benzene ring. Bond distances (Å): Mn(1)-O(1)$^{\#1}$ 2.056(8), Mn(1)-O(1)$^{\#2}$ 2.056(8), Mn(1)-O(14) 2.162(6), Mn(1)-O(14)$^{\#3}$ 2.162(6), Mn(1)-O(9)$^{\#3}$ 2.257(8), Mn(1)-O(9) 2.257(8), Mn(2)-O(11)$^{\#4}$ 2.104(6), Mn(2)-O(11) 2.104(6), Mn(2)-O(12)$^{\#4}$ 2.119(6), Mn(2)-O(12) 2.119(6), Mn(2)-O(10)$^{\#4}$ 2.207(6), Mn(2)-O(10) 2.207(6); angles (°): O(1)$^{\#1}$-Mn(1)-O(1)$^{\#2}$ 93.3(5), O(1)$^{\#1}$-Mn(1)-O(14) 87.9(3), O(1)$^{\#2}$-Mn(1)-O(14) 174.7(3), O(1)$^{\#1}$-Mn(1)-O(14)$^{\#3}$ 174.7(3), O(1)$^{\#2}$-Mn(1)-O(14)$^{\#3}$ 87.9(3), O(14)-Mn(1)-O(14)$^{\#3}$ 91.3(4), O(1)$^{\#1}$-Mn(1)-O(9)$^{\#3}$ 109.0(4), O(1)$^{\#2}$-Mn(1)-O(9)$^{\#3}$ 89.7(4), O(14)-Mn(1)-O(9)$^{\#3}$ 85.0(3), O(14)$^{\#3}$-Mn(1)-O(9)$^{\#3}$ 76.1(3), O(1)$^{\#1}$-Mn(1)-O(9) 89.7(4), O(1)$^{\#2}$-Mn(1)-O(9) 109.0(4), O(14)-Mn(1)-O(9) 76.1(3), O(14)$^{\#3}$-Mn(1)-O(9) 85.0(3), O(9)$^{\#3}$-Mn(1)-O(9) 152.9(4), O(11)$^{\#4}$-Mn(2)-O(11) 89.8(3), O(11)$^{\#4}$-Mn(2)-O(12)$^{\#}$4 173.9(2), O(11)-Mn(2)-O(12)$^{\#4}$ 92.5(2), O(11)$^{\#4}$-Mn(2)-O(12) 92.5(2), O(11)-Mn(2)-O(12) 173.9(2), O(12)$^{\#4}$-Mn(2)-O(12) 85.7(3), O(11)$^{\#4}$-Mn(2)-O(10)$^{\#4}$ 96.1(2), O(11)-Mn(2)-O(10)$^{\#4}$ 94.3(2), O(12)$^{\#4}$-Mn(2)-O(10)$^{\#4}$ 78.1(2), O(12)-Mn(2)-O(10)$^{\#4}$ 91.0(2), O(11)$^{\#4}$-Mn(2)-O(10) 94.3(2), O(11)-Mn(2)-O(10) 96.1(2), O(12)$^{\#4}$-Mn(2)-O(10) 91.0(2), O(12)-Mn(2)-O(10) 78.1(2), O(10)$^{\#4}$-Mn(2)-O(10) 165.2(3). Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $z-1$; #2: $x+1$, y, $z-1$; #3: $-x+2$, $-y+1$, z; #4: $-x+1$, $-y+1$, z; #5: $x-1$, y, $z+1$. b) Two-dimensional square-grid view of **2** (HDNTY$^-$ = 3,5-dinitrotyrosine anion). c) Two-dimensional square-grid representation of **2** in which straight lines and balls stand for HDNTY$^-$ and Mn atoms, respectively.

Mn$-$O$_{CO}$ (2.056–2.104 Å). Similarly, the bond lengths of C$-$C, C$-$O, C$-$N, and N$-$O are normal.

In compound **3**, an X-ray single-crystal diffraction study indicated that each ligand (as a tetradentate spacer) coordinates to three Pb centers, and each Pb center is coordinated to three ligands.[8] Almost linear infinite chains extending in both the *a* and the *b* direction are formed when the ligand links lead centers through the phenolic oxygen and a carboxylate oxygen. A third Pb atom is bound to the amine nitrogen and the other carboxylate oxygen resulting in the formation of a five-membered chelate ring (Figure 3). This third Pb center is a member of an equivalent chain that extends in a direction perpendicular to the original chain. Within the crystal structure of **3**, there are two independent interpenetrating networks. From a topological perspective, each ligand serves as a 3-connecting node as does each metal center in each of the interpenetrating nets (Figure 4). Each of the resulting nets is a (10,3)-b net, which is commonly referred to as the ThSi$_2$ net. Although the (10,3)-b net is normally considered to be an open-type network, the interpenetration considerably reduces the volume of network voids. Nevertheless, a water molecule is able to fill a small void between the networks (Figure 5a). Interestingly, two Pb centers from each network surround this water molecule, each making a contact with the oxygen of the guest water molecule at 2.93 Å (Figure 5b). In addition to this interaction, a weak inter-network association between a nitro oxygen atom and a carboxylate oxygen atom (separation 3.19 Å) appears to be an important factor influencing the relative positions of the two nets. To the best of our knowledge, **3** is the first example of a homochiral three-dimensional coordination polymer with a ThSi$_2$ net.[9] The bond distances of Pb$-$O$_{CO}$ (2.305–2.454 Å) are slightly shorter than those of Pb$-$O$_{Ph}$ (2.466 Å). Finally, the C$-$C, C$-$N, C$-$O, N$-$O, and Pb$-$N$_{amino}$ (2.389 Å) bond distances are normal. It is worth noting that only the amino group in DNTY^{2-} of **3** coordinates to the metal ion. The H$_2$DNTY coordination modes are summarized in Scheme 3.

Thermogravimetric analysis (TGA) results of crystalline **1** indicated that its decomposition temperature is about 300 °C while TGA results of crystalline **2** show that no single clear weight-loss step occurred before 360 °C. Finally, compound **3** displays a clear weight-loss step at 150 °C (2.0 %), corresponding to the removal of 0.5 H$_2$O molecules per formula unit (1.85 %). The coordination polymer **3** is stable below approximately 340 °C. Overall, the thermal decomposition temperatures of metal coordination compounds are significantly higher than those of the free ligand (220 °C).[10]

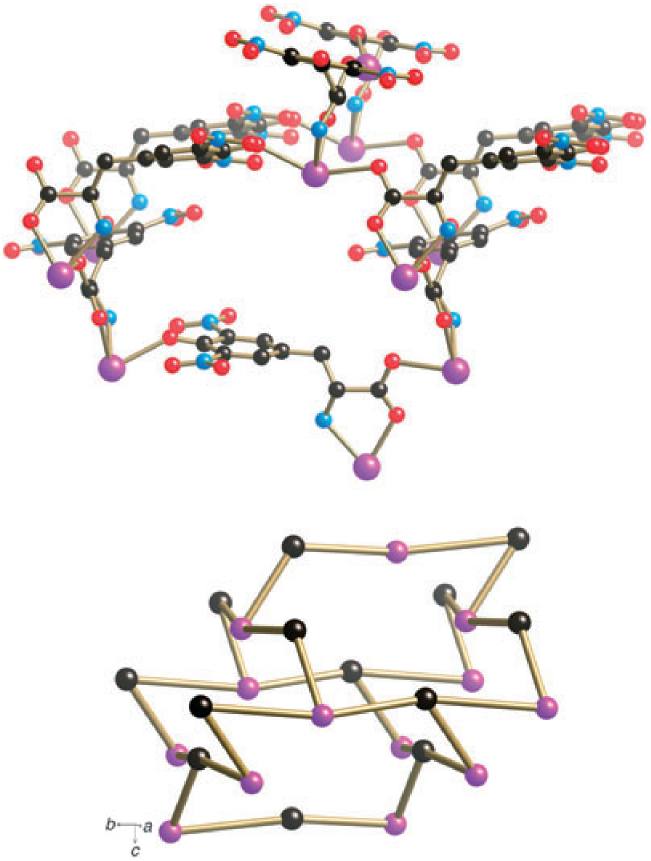


Figure 3. a) An asymmetric unit representation of **3**. Bond distances (Å): Pb(1)-N(1)$^{\#1}$ 2.389(10), Pb(1)-O(2)$^{\#2}$ 2.454(10), Pb(1)-O(3) 2.466(12), O(2)-Pb(1)$^{\#4}$ 2.454(10), O(1)-Pb(1)$^{\#3}$ 2.305(9); angles (°): O(1)$^{\#1}$-Pb(1)-N(1)$^{\#1}$ 70.8(3), O(1)$^{\#1}$-Pb(1)-O(2)$^{\#2}$ 80.2(3), N(1)$^{\#1}$-Pb(1)-O(2)$^{\#2}$ 71.2(4), O(1)$^{\#1}$-Pb(1)-O(3) 82.1(5), N(1)$^{\#1}$-Pb(1)-O(3) 67.8(3), O(2)$^{\#2}$-Pb(1)-O(3) 138.7(4). Symmetry transformations used to generate equivalent atoms: #1: $-y+\frac{1}{2}$, $x+\frac{1}{2}$, $z+\frac{1}{4}$; #2: $x+1$, y, z; #3: $y-\frac{1}{2}$, $-x+\frac{1}{2}$, $z-\frac{1}{4}$; #4: $x-1$, y, z. Purple = lead, black = carbon, blue = nitrogen, and red = oxygen atoms. b) A simplified unique $ThSi_2$ topological-net representation of **3**.

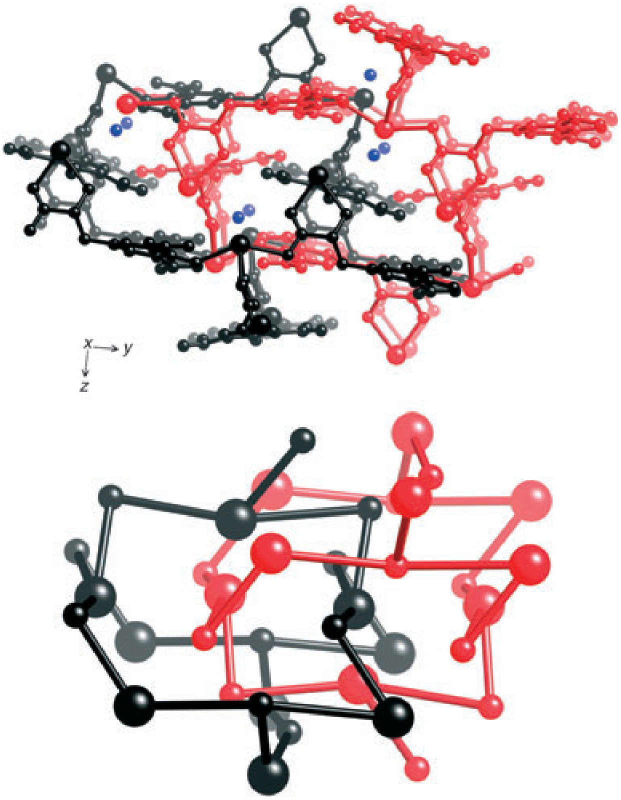


Figure 4. a) A representation of two interpenetrating $ThSi_2$ nets of **3** (top). b) Two simplified interpenetrating $ThSi_2$ nets of **3** (bottom).

When the Kurtz and Perry powder test was performed,[11] crystals of **1** doubled the frequency of an Nd:YAG laser with an efficiency approximately five times that of urea. This is consistent with its chiral space group as determined by an X-ray diffraction study. The significant enhancement of SHG response may be due to the use of a hybrid compound and H-bonds, because the combination (or hybrid) of organic chromophore into the compound favors charge transfer, such as metal-to-ligand or ligand-to metal, and a metal may act as either a strong donor or acceptor of electrons. On the other hand, H-bonds are also a good donor–acceptor system and can increase charge separation which is essential for strong SHG response.[6b] Thus, two synergetic effects of a hybrid and H-bonds result in the strong enhancement of SHG efficiency.

The adoption of the crystal class 222 (point group D_2) in **2** means that a physical property such as SHG can in principle occur, while **3** in the crystal class 422 would obey the Kleinman symmetry requirement.[12] A second-harmonic-generation signal in powders of **2** is approximately equal to 6 times that of urea, probably due to the presence of the good donor–acceptor system in **2**. As the free ligand has an excellent donor–π–acceptor system (Scheme 1), the strong enhancement of SHG efficiency of **2** may be because of the incorporation of the organic chromophore into the metal–organic coordination polymer resulting in the formation of a hybrid.[5] The chirality of H_2DNTY can ensure that in its coordination to metal ions it will crystallize in a noncentrosymmetric space group, an essential requirement for SHG response. On the other hand, intramolecular H-bonds also favor a strong SHG response like that of **1**.

Our experimental results indicate that the powder SHG efficiency of **3** is basically zero because the Kleinman symmetry requirement implies that any permutation of the frequency arguments of the nonlinear susceptibility leaves the tensor unchanged. Under these conditions, the effective nonlinear coefficient (d_{eff}) is always zero regardless of whether waves are ordinary or extraordinary because its matrix is zero under these conditions.[13]

Conclusion

In conclusion, a homochiral organic chromophore with a donor–π–acceptor system can be used as a building block to construct functional metal–organic coordination frameworks

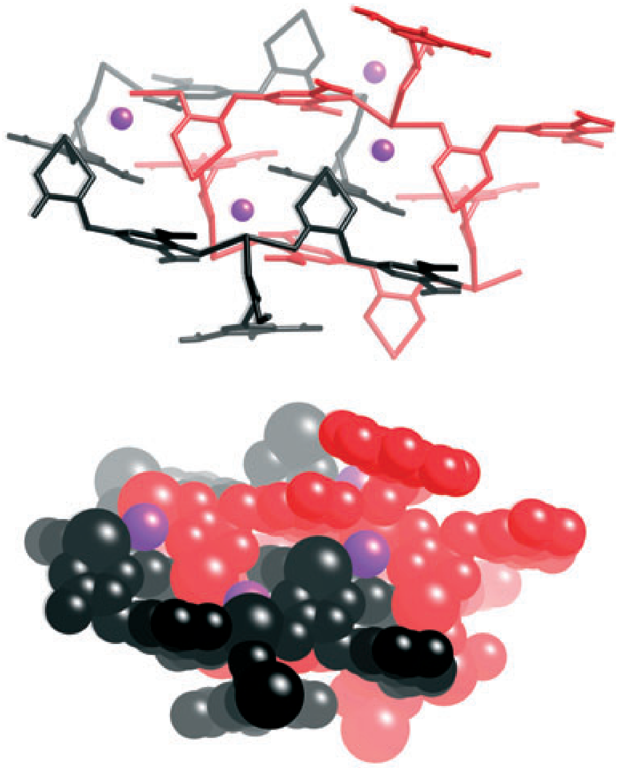
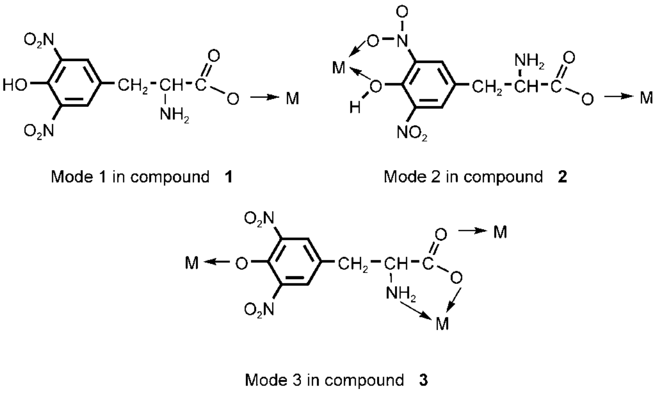


Figure 5. a) Water molecules (in purple) are sited in the cavity of two interpenetrating $ThSi_2$ nets in **3** (top). b) Space-filling diagram of two interpenetrating $ThSi_2$ nets in **3** showing some contacts between the Pb ion and the O atom of a water molecule (bottom).



Mode 1 in compound **1**

Mode 2 in compound **2**

Mode 3 in compound **3**

Scheme 3. Coordination modes of H_2DNTY.

(MOCF). The strong enhancement of SHG response of the hybrid coordination compounds may be due to 1) the addition of the chromophore resulting in the superior qualities of both inorganic and organic components in the compounds and 2) both intramolecular and intermolecular H-bonds.

Experimental Section

Preparation of 1: 3,5-Dinitrotyrosine (0.2 mmol) was dissolved in ethanol, and $Nd(NO_3)_3{\cdot}6H_2O$ (0.1 mmol) was dissolved in water. These two solutions were mixed together and the precipitate was obtained by vacuum filtration. The filtrate was then dissolved in hot ethanol and maintained for 7 days before being slowly allowed to cool to room temperature. Red block crystals were obtained by vacuum filtration, washed with water, and dried at 60 °C to give **1** (65 % yield based on 3,5-dinitrotyrosine). IR (KBr): $\tilde{\nu}=3371$ (br s), 3223 (s), 1629 (s), 1574 (s), 1489 (m), 1413 (w), 1383 (w), 1336 (m), 1260 (s), 1147 (w), 1028 (w), 782 (w), 718 (w), 645 (w), 580 (w), 546 (w), 522 cm^{-1} (w); elemental analysis calcd (%) for $C_{18}H_{32}N_7O_{25}Nd$: C 24.27, H 3.62, N 11.01; found: C 24.30, H 3.52, N 11.09.

Preparation of 2: Hydrothermal treatment of $Mn(ClO_4)_2{\cdot}6H_2O$ (1.0 mmol), H_2DNTY (2 mmol), and mixed solvent (2.5 mL; 0.5 mL H_2O + 2 mL CH_3OH) for 2 days at 70–80 °C yielded pale-red block crystalline **2** (0.25 mmol, 0.148 g in only one pure phase, 25 % yield based on H_2DNTY). IR (KBr): $\tilde{\nu}=3424$ (m), 3237 (m), 3069 (w), 1631 (s), 1543 (w), 1520 (vs), 1450 (w), 1406 (m), 1329 (m), 1257 (s), 1234 (s), 1140 (w), 1112 (w), 1087 (vw), 1075 (vw), 980 (w), 916 (m), 834 (w), 817 (w), 778 (m), 721 (w), 676 (vw), 640 (w), 579 (w), 552 (w), 508 (w), 438 cm^{-1} (w); elemental analysis calcd (%) for $C_{18}H_{16}N_6O_{14}Mn$: C 36.28, H 2.69, N 14.11; found: C 36.35, H 2.53, N 14.01.

Preparation of 3: Hydrothermal treatment of $Pb(OAc)_2{\cdot}3H_2O$ (1.0 mmol), H_2DNTY (1 mmol), and mixed solvent (2.5 mL; 0.5 mL H_2O + 2 mL EtOH) for 2 days at 90–100 °C yielded pale-yellow blocks of crystalline **3** (0.35 mmol, 0.170 g, only one pure phase, 35 % yield based on H_2DNTY). IR (KBr): $\tilde{\nu}=3447$ (br m), 3326 (m), 3267 (w), 1634 (s), 1571 (m), 1534 (vs), 1458 (w), 1403 (m), 1367 (w), 1325 (s), 1213 (s), 1150 (w), 1114 (w), 1075 (m), 1075 (vw), 998 (m), 932 (w), 908 (m), 856 (w), 838 (w), 816 (w), 779 (w), 716 (w), 631 (w), 578 (w), 551 (w), 524 (w), 475 cm^{-1} (w); elemental analysis calcd (%) for $C_9H_8N_3O_{7.5}Pb$: C 22.25, H 1.65, N 8.65; found: C 22.32, H 1.58, N 8.81.

Measurement of SHG responses: Approximate estimations of the second-order nonlinear optical intensity were obtained by comparison of the results from a powdered sample (80–150 μm diameter) in the form of a pellet (Kurtz powder test) with that obtained for KDP. A pulsed Q-switched Nd:YAG laser with a wavelength of 1064 nm was used to generate the SHG signal. The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation.

Acknowledgement

This work was funded by The Major State Basic Research Development Program (Grant No. G2000077500), National Natural Science Foundation of China, Distinguished Young Scholar Fund to XRG from NSFC (No. 2025103 BK2003204), US National Science Foundation, and the Exhibit, Performance and Publication Expenses Fund at the University of Tennessee.

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[8] Crystal data: **1**: $C_{18}H_{32}N_7O_{25}Nd$, $M_r = 890.75\ \mathrm{g\,mol^{-1}}$, monoclinic, $P2_1$, $a = 7.0179(7)$, $b = 27.060(3)$, $c = 8.3097(8)$ Å, $\alpha = \gamma = 90.00$, $\beta = 95.646(2)°$, $V = 1570.4(3)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.884\ \mathrm{Mg\,m^{-3}}$, $R_1 = 0.0489$, $wR_2 = 0.1223$, $\mu = 17.67\ \mathrm{mm^{-1}}$, $S = 0.811$, Flack value $= 0.003(13)$; **2**: $C_{18}H_{16}N_6O_{14}Mn$, $M_r = 595.31\ \mathrm{g\,mol^{-1}}$, orthorhombic, $P2_12_12$, $a = 8.4381(14)$, $b = 13.639(2)$, $c = 19.697(3)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 2266.9(6)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.744\ \mathrm{Mg\,m^{-3}}$, $R_1 = 0.0866$, $wR_2 = 0.2030$, $\mu = 6.72\ \mathrm{mm^{-1}}$, $S = 1.095$, Flack value $= 0.02(6)$; **3**: $C_9H_8N_3O_{7.5}Pb$, $M_r = 485.37\ \mathrm{g\,mol^{-1}}$, tetragonal, $P4_12_12$, $a = 12.8136(12)$, $b = 12.8136(12)$, $c = 14.931(2)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 2451.5(5)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.885\ \mathrm{Mg\,m^{-3}}$, $R_1 = 0.0564$, $wR_2 = 0.1323$, $\mu = 6.942\ \mathrm{mm^{-1}}$, $S = 0.878$, Flack value $= 0.03(2)$. For space group $P4_32_12$: $R_1 = 0.0672$, $wR_2 = 0.1656$, $S = 1.034$, Flack value $= 1.02(3)$; this suggests the space group $P4_12_12$ chosen is correct. The structures were solved with direct methods using the program SHELXTL (Sheldrick, 1997).[14] All non-hydrogen atoms were located from the trial structure and refined anisotropically with SHELXTL using full-matrix least-squares procedures. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. CCDC-244477–244479 contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[13]

$$\begin{pmatrix} P_1^{(2)} \\ P_2^{(2)} \\ P_3^{(2)} \end{pmatrix} = e_0 \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} E_1E_1 \\ E_2E_2 \\ E_3E_3 \\ 2E_2E_3 \\ 2E_3E_1 \\ 2E_1E_2 \end{pmatrix}$$

in which $P_k = \Sigma_{ij} d'_{ijk} E_i E_j$. Under the Kleinman symmetry requirement, we have $d_{ijk} = d_{jki} = d_{kij} = d_{ikj} = d_{kji} = d_{jik}$. Therefore, there are 10 independent coefficients reduced from 18. The first matrix of the right side of the above-mentioned equation becomes as follows:

$$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{pmatrix}$$

Thus, the matrix is equal to zero when solid material crystallizes in crystal class 422, while Kleinman symmetry prevails.

Received: July 14, 2004