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A Second-Order Nonlinear Optical Material Prepared through In Situ Hydrothermal Ligand Synthesis

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The in situ hydrothermal reactions of $ZnCl_2$ with benzonitrile, 2-amino-5-cyanopyridine, and *trans*-2,3-dihydro-2-(4′′-cyanophenyl)-benzo[*e*]indole in the presence of NaN_3 and water afford two 3D-diamond-like networks, $(CN_4–C_6H_5)_2Zn$ (**1**) and $(NH_2–C_5H_3N–CN_4)_2Zn$ (**2**), and one 2D square grid network, $[(CN_4–C_6H_4–C_{12}H_7N–C_5H_4N)_2\text{-}Zn]\cdot 1.5H_2O$ (**3**), in which these ligands gradually involve a noncenter-A–D (acceptor–donor) system, a one-center-A–D system, and a two-center-A–D system, respectively. All three compounds crystallize in noncentrosymmetric space groups ($I\bar{4}2d$ for **1** and **2** and $Fdd2$ for **3**) and display strong second harmonic generation (SHG) responses. Among the three new complexes, **3** shows the largest SHG effect, which is about 50 and 500 times that of urea and KDP (KH_2PO_4), respectively. The two-center-A–D system (multicenter push–pull electronic effect) in **3** may be responsible for it having the largest SHG effect. Interestingly, the three compounds exhibit strong fluorescent emissions at different wavelengths, **1** and **2** with blue fluorescent emissions at 390 and 415 nm and **3** with yellow-green fluorescent emissions at 495 and 532 nm.

Introduction

A main objective of crystal engineering is the design of solid-state structures of molecular solids with specific attributes such as topological features, chemical functions, and physical properties. In recent years, much of this effort has been generally focused on dipolar paradigms (push−pull structures in Scheme 1) wherein electron-donating and -withdrawing substituents interact via conjugated π-electron reservoirs such as *p*-nitroaniline (pNA and its analogues).[1−3] In the polar molecule-based crystal engineering of nonlinear optical (NLO) materials, the establishment of a noncentrosymmetric assembly of molecular dipoles is highly desirable because this is a prerequisite for NLO effects such as second harmonic generation (SHG). The significant ground-state dipole moment in pNA-type dipolar molecules has been recognized as being detrimental toward the establishment of a noncentrosymmetric structure because dipole−dipole interactions tend to favor antiparallel stacking of neighboring molecular units.[4] Consequently, there has been growing interest in reducing the ground-state dipole moment while preserving optical nonlinearity and, thus, the development of push−pull structures.[4] Furthermore, in comparison to organic NLO materials, metal−organic (or inorganic−organic hybrid) complexes offer increased synthetic flexibility for the optimization of hyperpolarizability. The identity of the metal, as well as its oxidation state (d or f orbital electrons), could be altered to tune the electronic properties of surrounding ligands. Thus, these ligands can be arranged in octahedral, tetrahedral, or other geometries

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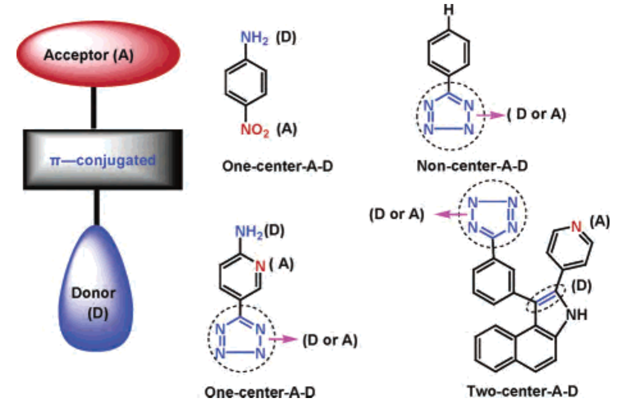
Scheme 1



that are less frequently observed in organic compounds. Such coordination geometries can afford three-dimensional charge-transfer and octupolar materials. On the other hand, the coordination of the pyridyl and tetrazole rings to a metal center results in the donation of the lone pair of electrons on the N atoms to the metal center and the formation of an excellent donor−acceptor (D−A) system (the alkyl group also participates as a donor group) because, via metal-to-ligand or ligand-to-metal charge transfer, a metal may act as either a strong donor or acceptor of electrons. In most D−A systems used as building blocks to construct NLO materials, the organic chromophores usually contain only a one-center-D−A system (i.e., a monocenter-D−A system). More recently, works in our laboratory showed that the SHG responses of organic compounds or metal−organic hybrid coordination polymers (CPs) could be significantly enhanced through the incorporation of multichiral centers into one molecule and metal−ligand coordination.[5,6] In view of these works, we envisioned that the preparation of CPs through the combination of building blocks with *multicenter-A−D systems* and in situ ligand synthesis under hydrothermal conditions should provide convenient access to noncentrosymmetric NLO−CPs because hydrothermal reactions and in situ ligand synthesis have been demonstrated to provide an appealing route to a fascinating variety of noncentrosymmetric and novel CPs.[7,8] Although these reactions are often complicated because of the fact that it is not always possible to exert synthetic control, the types of processes often involved include in situ hydrolysis, oxidation, dehydrogenation, and ligand synthesis. Tetrazole-based ligands, for example, can be produced via an in situ 1,3-polar addition reaction of a cyano group with an azide group in the presence of metal ions.[5,9] It is also worth noting that products generated under hydrothermal conditions are not normally accessible by a direct mixing of solutions of metal ions and ligands. However, over the past decade, there has been a myriad of studies on the synthesis and properties of metal−organic diamondoid networks as a result of the highly robust nature exhibited by such 3D structures.[7] To our knowledge, however, the work of Endo and co-workers describing a low-temperature polymorph of potassium dideuteriophosphate (KDP) remains the only known example of a NLO-active diamondoid network.[10] In view of the above-mentioned synthetic strategies and the advantages a KDP-like network targets, we systematically investigate the following reactions

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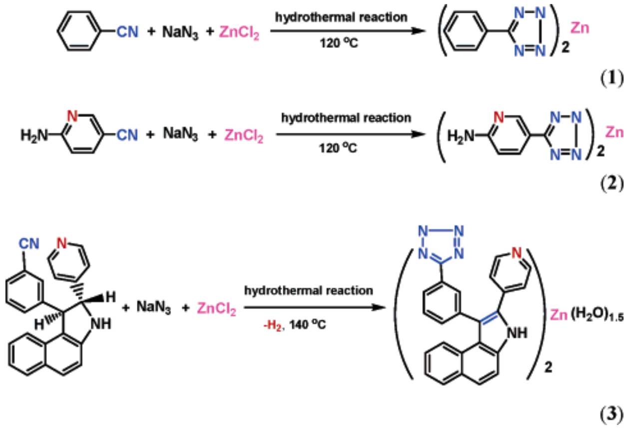
Scheme 2



(Schemes 1 and 2): in situ hydrothermal reactions of cyanobenzene, 2-amino-5-cyanopyridine, and *trans*-2,3-dihydro-2-(4′′-cyanophenyl)-benzo[*e*]indole with $ZnCl_2$ in the presence of NaN_3 to offer two 3D-diamond-like networks, $(CN_4{-}C_6H_5)_2Zn$ (**1**) and $(NH_2{-}C_5H_3N{-}CN_4)_2Zn$ (**2**), and one 2D square grid network, $[(CN_4{-}C_6H_4{-}C_{12}H_7N{-}C_5H_4N)_2Zn]{\cdot}1.5H_2O$ (**3**), in which these ligands gradually involve a noncenter-A−D system, a one-center-A−D system, and a two-center-A−D system, respectively. Among the SHG responses of the three systems, the CP with the two-center-A−D system, as expected, is the largest, whereas the CP with the noncenter-A−D system is the smallest. The SHG responses of **1**, **2**, and **3** are approximately 1, 4, and 50 times that of urea, respectively. Herein, we report their syntheses, solid-state structures, fluorescent properties, and preliminary SHG investigations.

Results and Discussion

In the IR spectrum of **1**, a diagnostic peak of the cyano group at 2200 cm^{-1} disappeared and two peaks at 1500 and 1433 cm^{-1} emerged, suggesting the formation of a tetrazole group, in good agreement with our previous studies.[5,9a−9e] Similarly, IR spectroscopic measurements of **2** reveal the absence of a ν(ZnCN) stretch at ca. 2200 cm^{-1}, suggesting that the cyano group is no longer present in the product complex. Furthermore, the appearance of two peaks at 1630(s) and 1470(s) cm^{-1} implies the probable conversion of the cyano group to a tetrazole, because such stretching frequencies are known to be indicative of tetrazole-containing complexes. Broad peaks at 3123−3484 cm^{-1} also suggest the presence of an amino group in **2**.[7] Interestingly, in the in situ hydrothermal preparation of **3**, two simultaneous reactions occur, dehydrogenation and a 2 + 3 cycloaddition between cyano and azide groups, as the appearance of two peaks at 1544 and 1433 cm^{-1} (tetrazole group) and the absence of a peak 2200 cm^{-1} (cyano group) were also observed.

The 3D polymeric structure of **1** was determined by X-ray crystallography (Figure 1a).[11] In the structure of **1**, there are three crystallographically independent Zn centers, and each Zn center has the same four coordinates and a slightly distorted tetrahedron. But, the direction of the phenyl groups around each Zn center must be different to result in the formation of three different Zn centers. Each 5-phenyl tetrazolato ligand acts as a bidentate bridging linker to connect two Zn centers to lead to the formation of a three-dimensional network. An investigation of the topology of this network reveals that each Zn center has four coordinates, similar to tetrahedral C in a diamond (Figure 1b), and each 10-Zn center consists of just one diamondoid-like net (Figure 1c,d). There are two different diamond nets in **1**, one with tetrahedral angles of 109.4, 109.5, and 109.6° and another with tetrahedral angles of 109.4 and 109.6°. Both nets, thus, show an almost perfect, ideal diamond structure (tetrahedral angle: 109.5°). The Zn−Zn distances of 6.166 and 6.159 Å are almost identical. It is worth noting that there is no interpenetrating in such diamondoid-like networks. The Zn−N bond distances of 1.995(3)∼2.014(3) Å are slightly shorter than those in Zn(OH)(3-ptz) (3-ptz = 3-pyridyltetrazole) [2.042(4)∼2.464(4) Å] and ZnCl(4-ptz)(4-ptz = 4-pyridyltetrazole) [2.026(4), 2.031(3), and 2.036(4) Å][5a] and are comparable to that found in $Zn(3\text{-}ptz)_2$ [1.994(3) Å].[9a] Finally, the bond lengths of C−C and C−N are unexceptional.

Similarly, the three-dimensional polymeric structure of **2** was determined by X-ray crystallography. The coordination geometry around the Zn(II) center in **2** adopts a slightly distorted tetrahedron (Figure 2a) presumably to minimize unfavorable steric interactions between the 5-(4′-amino-3′-pyridyl)tetrazolate (APT) ligands. The Zn(II) center is bonded to the four N atoms of the four APT ligands. Each APT ligand acts as a bidentate spacer, using the two N atoms of the tetrazole ring to bridge two Zn centers to give a 3D network (Figure 2b). It is worth noting that the amino and

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(11) Crystallographical data for **1**: $C_{14}H_{10}N_8Zn$, $M = 335.67$, $T = 293$ K, tetragonal, $I\bar{4}2d$, $a = b = 14.2430(18)$ Å, $c = 28.419(5)$ Å, $V = 5765.2(15)$ Å^3, $Z = 16$, $D_c = 1.639$ Mg/m^3, $\mu = 1.716$ mm^{-1}, GOF = 1.033, $R_1 = 0.0317$, $wR_2 = 0.0929$, Flack value = −0.08(3). For **2**: $C_{12}H_{10}N_{12}Zn$, $M = 387.69$, $T = 293$ K, tetragonal, $I\bar{4}2d$, $a = b = 10.4850(16)$ Å, $c = 13.088(3)$ Å, $V = 1438.9(4)$ Å^3, $Z = 4$, $D_c = 1.790$ Mg/m^3, $\mu = 1.735$ mm^{-1}, $S = 1.084$, $R_1 = 0.0449$, $wR_2 = 0.1196$, Flack value = 0.01(5). For **3**: $C_{48}H_{33}N_{12}O_{1.5}Zn$, $M = 867.23$, orthorhombic, *Fdd*2, $a = 61.594(9)$, $b = 15.968(2)$, $c = 16.590(2)$ Å, $V = 16317(4)$ Å^3, $Z = 16$, $D_c = 1.412$ Mg m^{-3}, $R_1 = 0.0728$, $wR_2 = 0.1597$, $T = 293$ K, $\mu = 0.659$ mm^{-1}, $S = 0.876$, Flack value = 0.05(2). Crystallographic data (excluding structure factors) for the complexes have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 252072, 252073, and 218956.

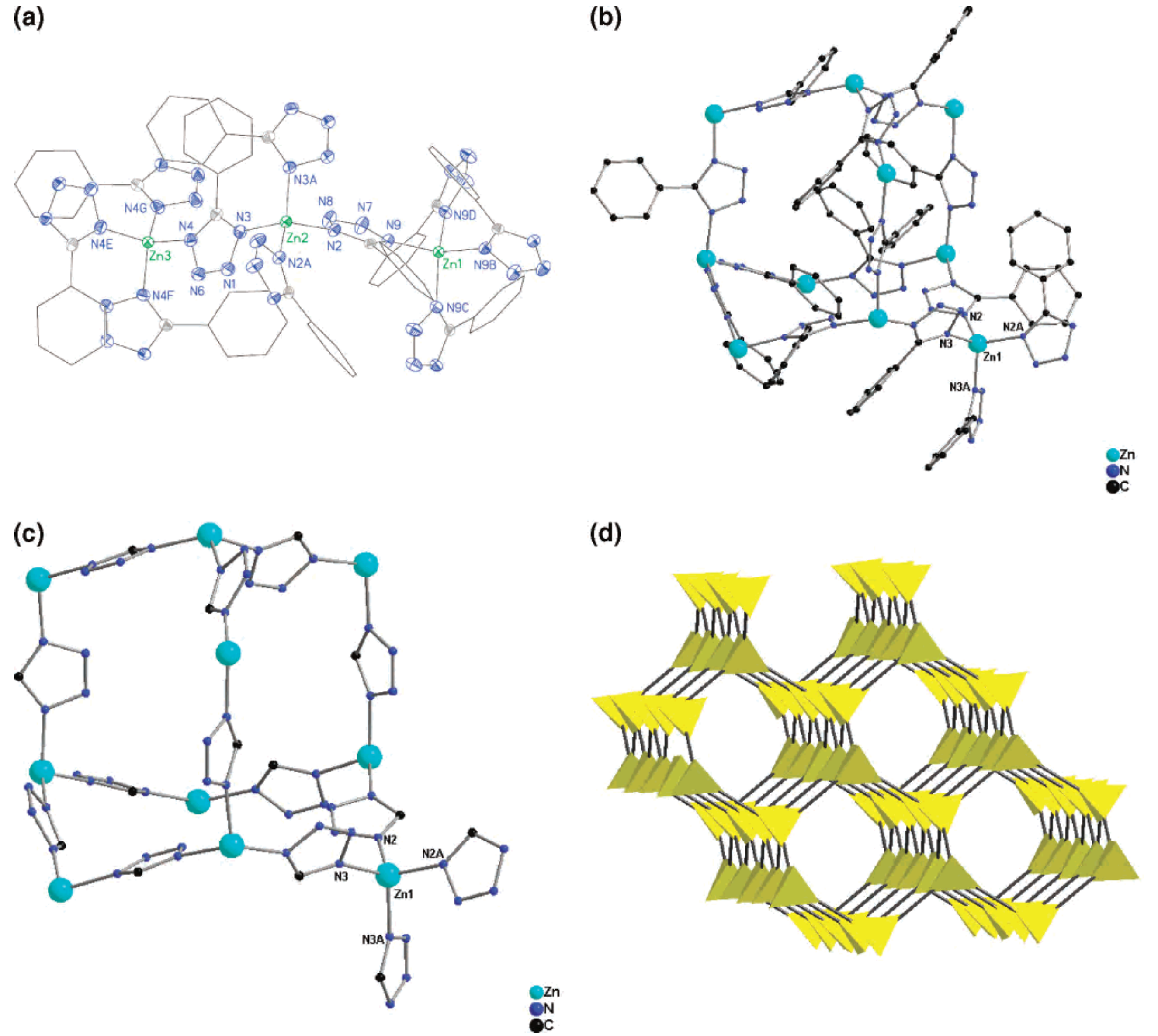

Figure 1. (a) Asymmetric unit representation of **1** in which there are three crystallographically independent Zn centers, although each Zn center displays a tetrahedron with a different direction of the phenyl group on the tetrazole ring. The key bond distances and angles (Å, deg): Zn(2)−N(2) 2.002(3), Zn(2)−N(2)$^{\#1}$ 2.002(3), Zn(2)−N(3) 2.014(3), Zn(2)−N(3)$^{\#1}$ 2.014(3), Zn(3)−N(4)$^{\#2}$ 1.995(3), Zn(3)−N(4)$^{\#3}$ 1.995(3), Zn(3)−N(4)$^{\#4}$ 1.995(3), Zn(3)−N(4) 1.995(3), Zn(1)−N(9)$^{\#5}$ 2.000(3), Zn(1)−N(9)$^{\#6}$ 2.000(3), Zn(1)−N(9)$^{\#7}$ 2.000(3); N(2)−Zn(2)−N(2)$^{\#1}$ 115.47(11), N(2)−Zn(2)−N(3) 108.08(12), N(2)$^{\#1}$−Zn(2)−N(3) 105.58(9), N(2)−Zn(2)−N(3)$^{\#1}$ 105.58(9), N(2)$^{\#1}$−Zn(2)−N(3)$^{\#1}$ 108.08(1), N(3)−Zn(2)−N(3)$^{\#1}$ 114.33(1), N(4)$^{\#2}$−Zn(3)−N(4)$^{\#3}$ 111.68(8), N(4)$^{\#2}$−Zn(3)−N(4)$^{\#4}$ 111.68(8), N(4)$^{\#3}$−Zn(3)−N(4)$^{\#4}$ 105.15(2), N(4)$^{\#2}$−Zn(3)−N(4) 105.15(2), N(4)$^{\#3}$−Zn(3)−N(4) 111.68(8), N(4)$^{\#4}$−Zn(3)−N(4) 111.68(8), N(9)−Zn(1)−N(9)$^{\#5}$ 106.46(6), N(9)−Zn(1)−N(9)$^{\#6}$ 106.46(6), N(9)#5−Zn(1)−N(9)$^{\#6}$ 115.67(1), N(9)−Zn(1)−N(9)$^{\#7}$ 115.67(1), N(9)$^{\#5}$−Zn(1)−N(9)$^{\#7}$ 106.46(6), N(9)$^{\#6}$−Zn(1)−N(9)$^{\#7}$ 106.46(6). Symmetry transformations used to generate equivalent atoms: #1 $x + 0, -y + {}^{1}/_{2}, -z + {}^{1}/_{4}$; #2 $-x + 1, -y + 1, z$; #3 $y, -x + 1, -z$; #4 $-y + 1, x, -z$; #5 $-y, x, -z$; #6 $y, -x, -z$; and #7 $-x, -y, z$. (b) A diamondoid-like net representation of **1** in which each 10-Zn center is composed of one diamond node. (c) A diamondoid-like net representation of **1** in which each 10-Zn center is composed of one diamond node, and the phenyl groups on the tetrazole ring are omitted for clarity. (d) A simplified diamond net representation of **1** in which the highlighted areas represent Zn tetrahedra and the long lines stand for 5-phenyl tetrazolato ligands.

pyridyl ligands present in **2** are uncoordinated to the Zn atom. All of the Zn−N bond distances [2.074(1) and 2.142(1) Å] are similar to those reported in the literature. However, it is worth noting that the bond lengths of Zn−N are slightly longer than those found in **2**. Likewise, the C−C, N−O, and C−N bond distances are comparable to those in analogous systems in the literature. The crystal contains one independent diamondoid network with Zn···Zn separations of 6.180 Å in each network and Zn···Zn···Zn angles in the range of 106.3−111.61° (Figure 2c). This structure represents a slight variation from the ideal tetrahedral angle of 109.5° in a diamond. Thus, although the connectivity of the network is the same as that in a diamond, the symmetry is lower (Figure 2). Similar to the network of **1**, there is also no interpenetrating in such a diamondoid-like network.

As mentioned above, the typical SHG material KH_2PO_4 also displays a diamondoid-like network through P and K atom connections (Figure 2d). This net displays a significant deviation from the ideal diamond net (with a tetrahedral angle of 107.54 and P···K separation distances of 3.0932∼3.1842 Å). KDP crystallizes in a chiral space group ($P2_12_12_1$) and, thus, displays a SHG response. As a result of the twisted

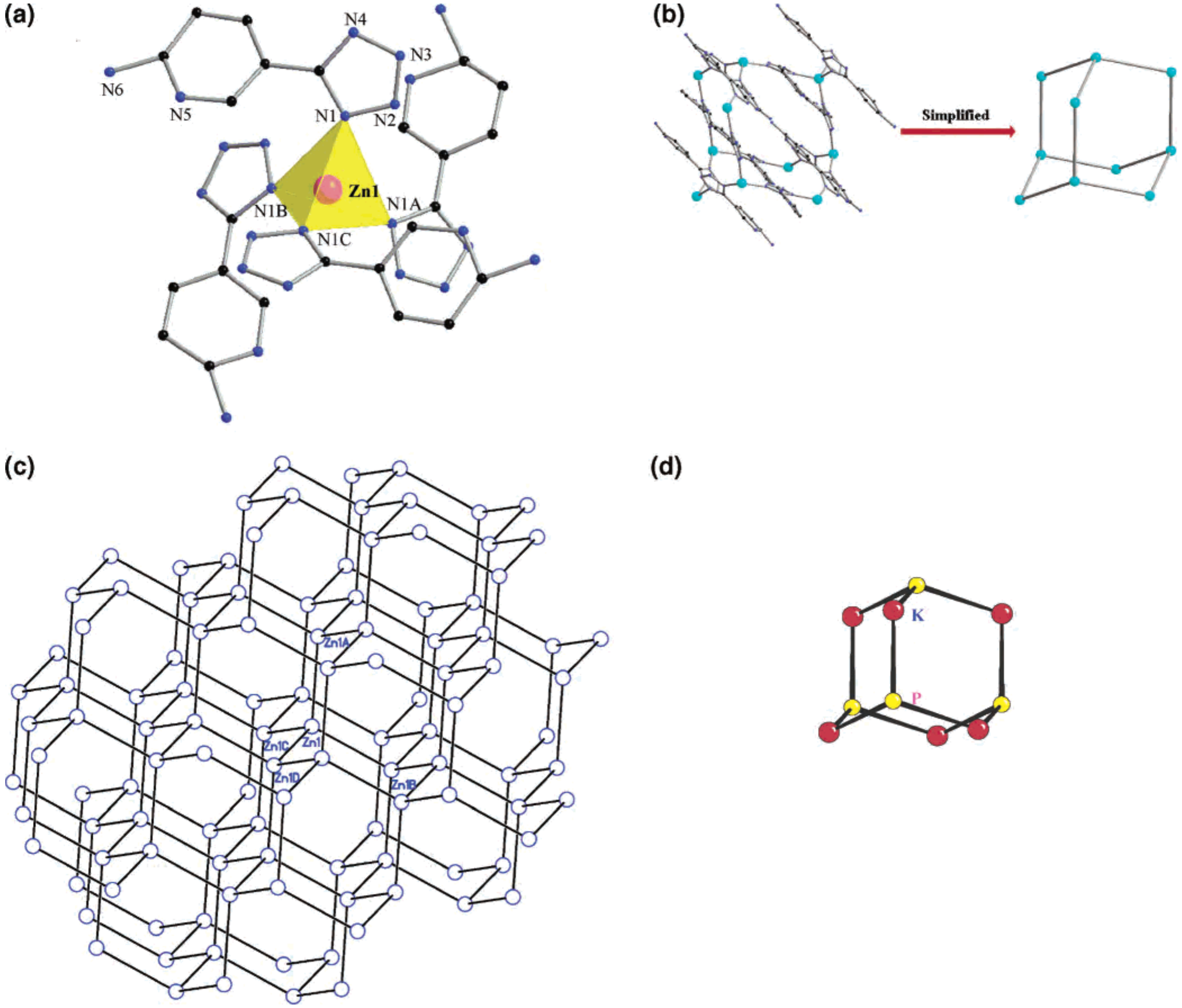

Figure 2. (a) Asymmetric unit representation of **2** showing that the Zn center displays a slightly distorted tetrahedron (the amino group was disordered in two positions, and here, just one is shown). The key bond distances and angles (Å, deg): Zn(1)$-$N(1)$^{\#1}$ 2.023(2), Zn(1)$-$N(1)$^{\#2}$ 2.023(2), Zn(1)$-$N(1)$^{\#3}$ 2.023(2), Zn(1)$-$N(1) 2.023(2); N(1)$^{\#1}-$Zn(1)$-$N(1)$^{\#2}$ 108.40(7), N(1)$^{\#1}-$Zn(1)$-$N(1)$^{\#3}$ 108.40(7), N(1)$^{\#2}-$Zn(1)$-$N(1)$^{\#3}$ 111.64(1), N(1)$^{\#1}-$Zn(1)$-$N(1) 111.64(1), N(1)$^{\#2}-$Zn(1)$-$N(1) 108.40(7), N(1)$^{\#3}-$Zn(1)$-$N(1) 108.40(7), N(2)$^{\#4}-$N(2)$-$N(1) 109.64(2). Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, $-y + 1$, z; #2 $-y + 1$, x, $-z$; #3 y, $-x + 1$, $-z$; and #4 $x + 0$, $-y + {}^{1}/_{2}$, $-z + {}^{1}/_{4}$. (b) A diamondoid-like representation of **2**: (left) a diamond with the free ligand and (right) a simplified diamond net without the free ligand. (c) A 3D diamondoid-like respective view showing that the Zn···Zn···Zn angles are in the range 106.3−111.61°, which represents a slight distortion from the ideal tetrahedral angle of 109.5° found in diamonds. (The long lines stand for the free ligand APT). (d) One diamondoid-like net representation of KDP.

nature, relative to a tetrazole ring, of 5-phenyltetrazolato and the unsymmetrical nature of APT, both **1** and **2** crystallize in a noncentrosymmetric space group, $I\bar{4}2d$, which belongs to the crystal class *42m*, where optical activity can cause specific physical effects. Preliminary experimental results show that **1** and **2** are SHG-active and display strong powder SHG efficiencies, ca. 1 and 5 times that of urea (10 and 50 times that of KDP), respectively, presumably as a result of their diamondoid structures, which are similar to that of KDP, currently the only known NLO-active diamondoid network. Moreover, the presence of strong donor/acceptor substituents in the free ligand in **2** allows for a high nonlinearity or substantial SHG response. Asymmetric ligands have been used to introduce electronic asymmetry (push−pull effect or one-center-A−D system), an essential criterion for a SHG response. The combination of a KDP-like structure and an excellent push−pull effect (or one-center-A−D system) of the free ligand in **2** further optimizes the performance of pure organic and inorganic NLO materials. Such hybrid inorganic−organic NLO materials have also recently been the subject of much investigation as NLO materials. That is why the SHG response of **2** is significantly larger than that of **1**, because there is an absence of such a good one-center-A−D system in **1**. On the other hand, the H atom is also considered to be a very weak donor group. As a result, a very weak one-center-A−D system persists in **1**. The SHG response of **1** is significantly stronger than that of KDP.

As indicated in Scheme 2, **1**, **2**, and **3** are prepared in hydrothermal reactions involving a 2 + 3 cycloaddition of a cyano group {benzonitrile, 2-amino-5-cyanopyridine, and

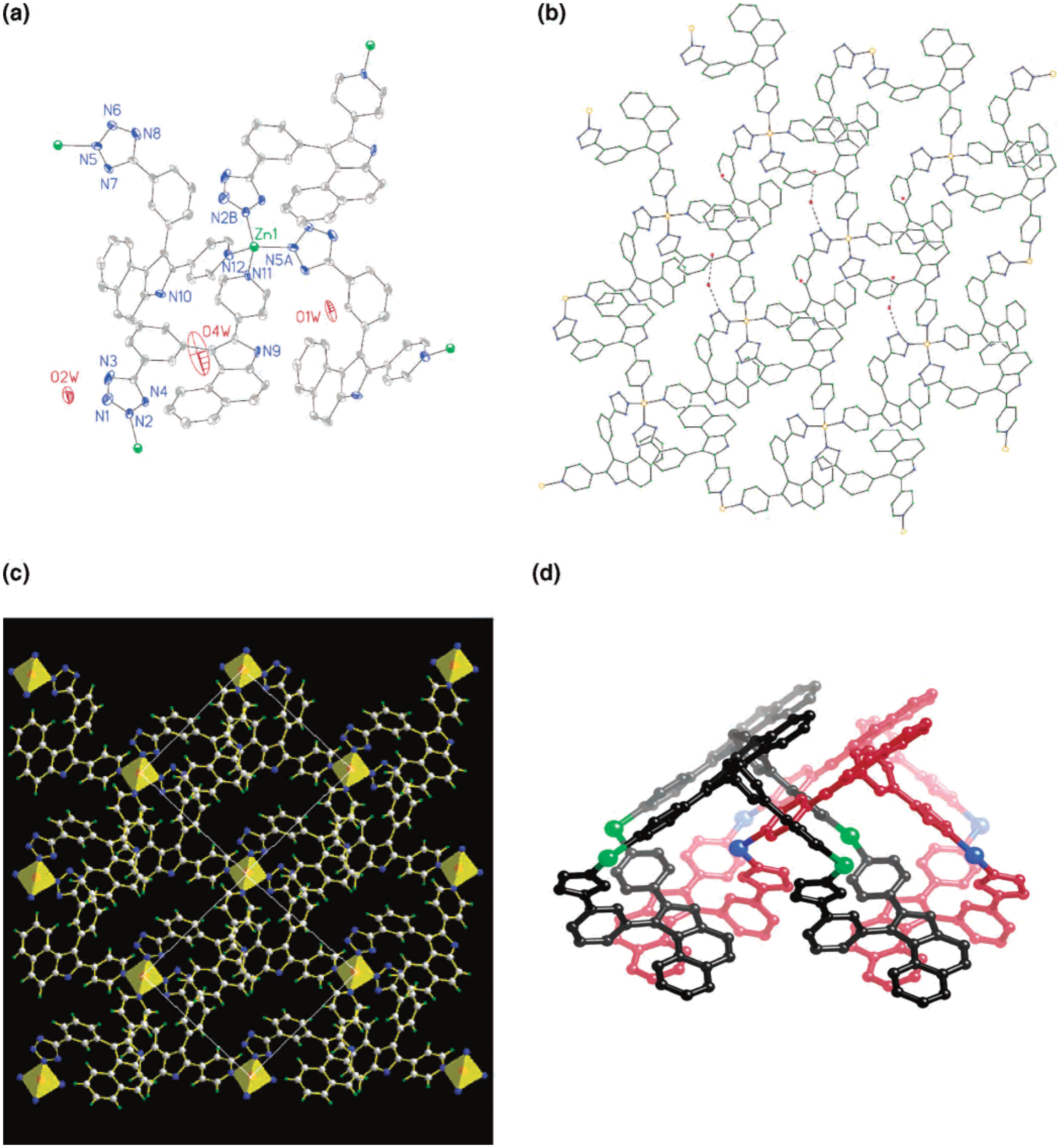

Figure 3. (a) Asymmetric unit representation of **3** in which the coordination geometry around the Zn center has a slightly distorted tetrahedron configuration. The key bond distances and angles (Å, deg): Zn(1)−N(2)$^{\#1}$ 1.968(6), Zn(1)−N(12) 2.002(6), Zn(1)−N(11) 1.998(6), Zn(1)−N(5)$^{\#2}$ 2.013(7); N(2)$^{\#1}$−Zn(1)−N(12) 110.4(3), N(2)$^{\#1}$−Zn(1)−N(11) 107.9(3), N(12)−Zn(1)−N(11) 105.1(2), N(2)$^{\#1}$−Zn(1)−N(5)$^{\#2}$ 111.3(3), N(12)−Zn(1)−N(5)$^{\#2}$ 110.8(2), N(11)−Zn(1)−N(5)$^{\#2}$ 111.2(3), N(6)−N(5)−Zn(1)$^{\#3}$ 125.0(6), N(7)−N(5)−Zn(1)$^{\#3}$123.5(5), N(1)−N(2)−Zn(1)$^{\#4}$ 128.3(5), N(4)−N(2)−Zn(1)$^{\#4}$ 121.2(5). Symmetry transformations used to generate equivalent atoms: #1 $x, y + {}^1/_2, z - {}^1/_2$; #2 $x, y - {}^1/_2, z - {}^1/_2$; #3 $x, y + {}^1/_2, z + {}^1/_2$; and #4 $x, y - {}^1/_2, z + {}^1/_2$. (b) 2D network representation of **3** in which the Zn centers are highlighted as yellow-colored circular balls and water molecules are marked as red-colored balls. The dotted lines stand for H bonds. (c) 2D network representation of **3** in which the Zn center is highlighted as a tetrahedron. The white lines between the Zn centers represent two 4,4 nets. (d) A representation of two interpenetrating square grids in **3**.

trans-2,3-dihydro-2-(4′-pyridyl)-3-(3′-cyanophenyl)benzo[*e*]-indole} with azide.[5f] The reaction to give **3** is followed by dehydrogenation, which has the effect of making the ligand nonchiral. The subsequent generation of a large conjugated system may be expected to make the ligand an excellent chromophore. Similar dehydrogenation was also observed in the reactions of 3-pyridyl-3-aminopropionic acid with $Zn(ClO_4)_2 \cdot 6H_2O$ reported by our group.[5d]

Compound **3** is a 2-dimensional CP (Figure 3a). The local coordination environment around the Zn centers can be best

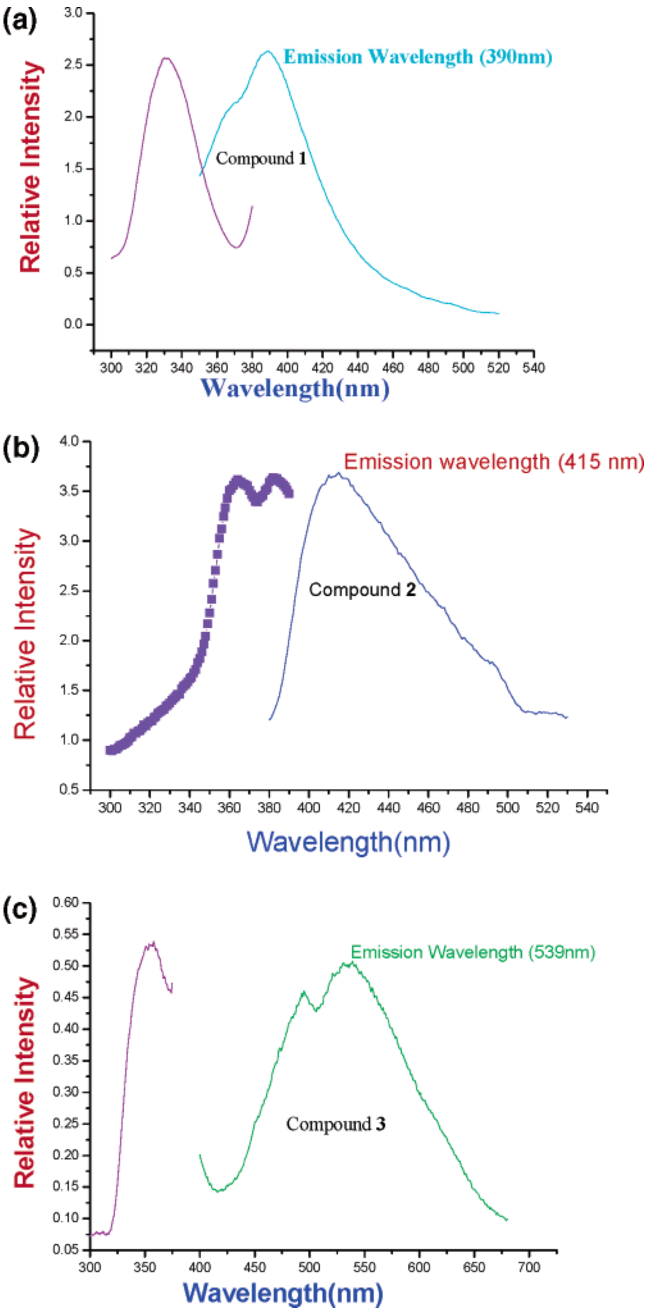

Figure 4. (a) Fluorescent emission spectrum of **1** in the solid state at room temperature (the left spectrum is an excitation spectrum). (b) The fluorescent emission spectrum of **2** in the solid state at room temperature (the left spectrum is an excitation spectrum). (c) The fluorescent emission spectrum of **3** in the solid state at room temperature (the left spectrum is an excitation spectrum).

described as a slightly distorted tetrahedron in which each Zn atom is coordinated by four N donors from four different ligands (L3 = $\mathrm{CN_4{-}C_6H_4{-}C_{12}H_7N{-}C_5H_4N}$). Furthermore, each ligand acts as a bidentate linker (or spacer) to bridge two Zn centers through the N atom of pyridyl and one of the atoms of the tetrazole groups. As such, the tetrazole group in **3** is only used as a monodentate ligand. Overall, each ligand in **3** connects two Zn atoms while each Zn atom is bound by four different ligands to lead to the formation of a 2D square network (Figure 3b). The resulting network has the same topology as a square grid sheet commonly referred to as a 4,4 net (Figure 3c, in which the four highlighted tetrahedral Zn atoms are composed of a 4,4 net). However, the highly irregular shape of the bridging ligands coupled with the tetrahedral coordination of the zinc center results in a severe geometric distortion of the ideal 4,4 net. An interesting aspect of this structure is the interpenetration of this 2D network by a single, identical network. The mean planes of these two networks are coplanar. The interpenetration of a four-membered ring in one sheet by a four-membered ring in another sheet is shown in Figure 3d. Three water molecules are intercalated between two adjacent layers through strong hydrogen-bonding. The bond distances of $\mathrm{Zn{-}N_{tetrazole}}$ [1.968(6)∼2.013(7) Å] are comparable to those of $\mathrm{Zn{-}N_{pyridyl}}$ [1.998(6)∼2.002 Å] and those in **1** but significantly shorter than those in **2**. Moreover, the crystal contains one independent square grid network with Zn···Zn separations of 11.513 Å in each network and Zn···Zn···Zn angles in the range of 92.2°, with a slight variation from the ideal 4,4 net angle of 90.0° found in a square. Finally, the bond lengths of C−C and C−N are unexceptional.

Compound **3** crystallizes in a noncentrosymmetric space group (*Fdd*2) in the crystal class *mm*2, where its optical activity can occur as a specific physical effect. Experimental results indicate that **3** has very strong SHG responses in the powdered state (ca. 50 and 500 times of those of urea and KDP, respectively). As mentioned above, as a result of dehydrogenation in **3**, a large conjugated system is formed in the ligand of **3**. On the other hand, the resulting ligand in **3** is highly asymmetric and can best be induced by the two-functional electronic asymmetry (or the push−pull effect) that is essential for second-order optical nonlinearity. Thus, the building block is an excellent two-A−D chromophore that is essential for strong SHG materials. Furthermore, the presence of two push−pull effect centers (or a two-center-A−D system) is much better in the enhancement of the dipolar moment than the presence of a one-center-A−D system. Thus, among the three new compounds in the current work, the largest SHG response is observed in **3**. As we know, a one-center-A−D system also leads to the noncancellation of the molecular dipolar moment for a compound with a noncentrosymmetric space group (such as in the two cases of **1** and **2** in which they all crystallized in acentric space group $I\bar{4}2d$ and their dipolar moment could not be canceled). Evidently, the two-center-A−D system surely results in the noncancellation of the dipolar moment if the compound crystallizes in an acentric space group. At the same time, the dipolar moment should be larger than that of the one-center-A−D system and is completely aligned in the crystal packing view (see the Supporting Information). Because the SHG responses depend on the charge separation or molecular dipolar moment (hyperpolarizability), the combination of a multicenter-A−D system and metal−ligand coordination could be responsible for a synergistic effect that leads to a strong enhancement of the SHG response.[12]

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Finally, it is interesting to note that the three compounds **1**, **2**, and **3** display strong fluorescent emissions at 390 nm (blue fluorescent emission, Figure 4a), 415 nm (also a blue fluorescent emission, Figure 4b), and 495 and 532 nm (pale yellow-green fluorescent emission, Figure 4c) in the solid states. These fluorescent properties could have potential applications in fluorescent materials.[13] The three CPs may be good multifunctional candidates for blue-to-yellow-fluorescent and SHG-active materials because they are thermally stable with decomposition temperatures of 300∼350 °C, solvent-resistant, and insoluble in most common solvents such as ethanol, chloroform, ethyl acetate, acetone, acentonitrile, benzene, and water.

In conclusion, we have shown, in the current work, that the introduction of a one-A−D center organic chromophore (push−pull electronic effect) into CPs with a KDP-like net and a two-center-A−D system (bi-push−pull electronic effect) into acentric CPs can lead to the significant enhancement of SHG responses. Such a strategy may open up a new avenue for the design and synthesis of multifunctional materials.

Experimental Section

Synthesis of 1. The hydrothermal treatment of benzonitrile (0.4 mmol), $ZnCl_2\cdot6H_2O$ (0.4 mmol), and NaN_3 (0.6 mmol) in water (13 mL) and EtOH (5 mL) for 3 days at 125 °C afforded colorless block crystals of **1** (ca. 0.16 mmol; 40% yield based on benzonitrile). Anal. Calcd for $C_{14}H_{10}N_8Zn$: C, 47.28; H, 2.84; N, 31.50. Found: C, 47.08; H, 2.74; N, 31.35. IR (KBr, cm^{-1}): 3063(m), 1608(w), 1523(m), 1456(s), 1384(s), 1318(w), 1285(m), 1192(w), 1165(w), 1102(m), 1080(m), 1017(m), 929(w), 783(m), 731(s), 689(s), 529(m), 458(m). A strong blue fluorescence emission (λmax = 390 nm) was observed for its solid-state samples at room temperature. A thermogravimetric analysis (TGA) was performed on a polycrystalline sample, indicating that no strikingly clean weight loss step occurred below ca. 310 °C.

Synthesis of 2. The hydrothermal treatment of 2-amino-5-cyanopyridine (2 mmol, 19.1 mg), $ZnCl_2\cdot6H_2O$ (1 mmol), and NaN_3 (5 mmol) in water (3 mL) for 2 days at 130 °C afforded yellow block crystals of **1** (ca. 0.4 mmol; 0.16 g; 40% yield based on 2-amino-5-cyanopyridine). Anal. Calcd for $C_{12}H_{10}N_{12}Zn$: C, 37.18; H, 2.60; N, 43.35. Found: C, 37.28; H, 2.53; N, 43.27. IR (KBr, cm^{-1}): 3484(m), 3421(m), 3284(m), 3123(br, m), 1698(w), 1630(s), 1569(w), 1545(w), 1470(s), 1427(m), 1373(w), 1344(w), 1321(w), 1253(w), 1148(w), 1000(w), 948(w), 856(w), 820(w), 771(w), 642(w), 550(w), 496(m), 446(w). A strong blue fluorescence emission (λmax = 415 nm) was observed for its solid-state samples at room temperature. A TGA was performed on a polycrystalline sample, indicating that no strikingly clean weight loss step occurred below ca. 350 °C, whereas the free ligand only remains intact up to 250 °C.

Synthesis of 3. The hydrothermal reaction of $ZnCl_2\cdot6H_2O$ (1 mmol), NaN_3 (2.25 mmol), and *trans*-2,3-dihydro-2-(4″-cyanophenyl)-benzo[*e*]indole (2 mmol) with 2 mL of water at 160 °C for 4 days afforded ca. 0.5 mmol of **3** based $ZnCl_2$. IR (KBr, cm^{-1}): 3405(br, m), 3054(w), 1616(vs), 1536(w), 1436(w), 1341(w), 1279(w), 1205(w), 1162(s), 1068(w), 1029(w), 975(w), 914(w), 837(w), 805(m), 746(w), 702(w), 674(w), 636(w), 624(w), 536(w), 516(w). A strong yellow fluorescence emission (λ_{max} = 495 and 532 nm, $\tau = 2.2$ ns, and $\Phi \approx 0.42$) was observed for its solid-state samples at room temperature. TGA results indicate that one clean weight loss step occurred at 140 °C (2.80%), corresponding to the removal of 1.5 water molecules per formula unit (3.11% calculated), whereas the polymer can be stable below ca. 300 °C.

Measurement of SHG responses. Approximate estimations of second-order NLO intensity were obtained by a comparison of the results from a powdered sample (80−150-μm diameter), in the form of a pellet (Kurtz powder test),[14] with those obtained for KDP. A pulsed Q-switched Nd:YAG laser at 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.

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Supporting Information Available: X-ray CIF files and a figure showing the dipolar moment direction. This material is available free of charge via the Internet at http://pubs.acs.org.

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