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Introduction

The search for new second-order nonlinear optical (NLO) materials is of great importance because of their applications in photonic technologies, such as laser frequency conversion, signal communication, and optical parameter oscillators.¹ Coordination networks or metal-organic frameworks (MOFs) are an emerging class of crystalline materials with modular structures. The incorporation of second-harmonic generation (SHG) function into the unique MOFs is a challenging but achievable research topic.² Generally, coordination networks possessing remarkable NLO properties are chiral or acentric. However, it is rather difficult to design such networks, particularly from achiral organic tectons. So far, only a few examples have dealt with this aspect.^{3,4} Therefore, systematic research on the generation conditions of chiral or acentric networks with significant SHG function from achiral tectons is of practical significance.

Recently, we have reported spontaneous resolution of the achiral tetrazole-yl acylamide derivatives during the generation of coordination networks.^{5a} Almost at the same time, Bu and co-workers⁶ observed a similar phenomenon from the multi-dentate tetrazolate-based tectons. Interestingly, such acentric

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From achiral tetrazolate-based tectons to chiral coordination networks: effects of substituents on the structures and NLO properties[†]

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Using a hydrothermal synthesis method, the combination of four tetrazolate-yl acylamide tectons bearing substituents of different sizes, 4-nitro-*N*-(1*H*-tetrazol-5-yl)benzamide (H-NTBAN), 4-fluoro-*N*-(1*H*-tetrazol-5-yl)benzamide (H-NTBAF), *N*-(1*H*-tetrazol-5-yl)isonicotinamide (H-NTINA) and *N*-(1*H*-tetrazol-5-yl)thiophene-2-carboxamide (H-NTTCA), with cadmium dichloride led to four crystalline coordination networks, named $Cd_3(NTBAN)_6$ (1), $Cd(NTBAF)_2$ (2), $Cd(NTINA)_2$ (3) and $Cd(NTTCA)_2$ (4), respectively. The X-ray diffraction analysis revealed that compounds 2, 3 and 4 possess a 3D non-interpenetrated diamondoid framework, while compound 1 is of a 0D trinuclear structure. Wherein, compounds 2, 3 and 4 crystallized in chiral space groups with significant second harmonic generation (SHG) efficiencies. The effects of substituents in the semirigid tetrazole-yl acylamide tectons on the structural topologies as well as on the nonlinear optical properties of the generated coordination networks are discussed.

or chiral structures are found to be strongly dependent on the size of the metal ions and the substituents of the tetrazole-yl acylamide.^{5b} In the obtained acentric networks, we noticed that the generated cavities were always filled by the aliphatic acyl substituents of the tetrazole-yl acylamides. Certainly, we wonder whether the coordination patterns could be transformed if the aromatic acyl substituents were too large to be accommodated in the cavities, and how the aromatic acyl substituents affect the formation of chiral networks and thus their NLO properties.

To make it clear, herein we designed four semirigid tetrazole-yl acylamide tectons bearing different aromatic acyl substituents, 4-nitro-N-(1H-tetrazol-5-yl)benzamide (H-NTBAN), 4-fluoro-N-(1H-tetrazol-5-yl)benzamide (H-NTBAF), N-(1H-tetrazol-5-yl)thiophene-2-carboxamide (H-NTTCA), and N-(1H-tetrazol-5-yl)thiophene-2-carboxamide (H-NTTCA), and then combined them with the octahedrally coordinated divalent transition metal ion Cd(II), leading to four novel coordination networks including three chiral structures. As expected, the aromatic acyl substituents in the semirigid tetrazole-yl acylamides are a strong influence on the structural symmetries and NLO properties of the generated coordination networks. In addition, the electron donating/accepting nature of the aromatic acyl substituents and their packing patterns in the crystal structures also greatly contributed to the NLO properties of the chiral structures.

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 $\label{eq:scheme1} \textbf{Synthesis of organic tectons with different-sized substituents}.$

Experimental procedures

Reagents and physical measurements

All chemicals were obtained from commercial sources and used as received without further purification. Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. IR spectra were recorded in the range 4000–400 cm⁻¹ on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Fluorescence spectra were recorded on an Edinburgh Instrument FL/FS-920 fluorescent spectrometer at room temperature. Thermal analyses were performed on a SDT Q600 instrument from room temperature to 650 °C with a heating rate of 10 K min⁻¹ under nitrogen. The second-order NLO intensities were determined with a LAB130 Pulsed Nd:YAG laser.

Synthesis of the tectons and compounds

Synthesis of 4-nitro-*N*-(1*H*-tetrazol-5-yl)benzamide. To a rapidly stirred solution of 5-amino-1*H*-tetrazole (4.3 g, 0.05 mmol) in acetonitrile (20 mL) was added 4-nitrobenzoyl chloride (9.25 g), which was diluted by acetonitrile (20 mL) (Scheme 1), then a few drops of triethylamine were added to this mixture. The suspension was heated to reflux for 4 hours with vigorous stirring and the solid material separated by filtration. The crude product was washed with deionized water, and dried to give 9.36 g (80%) of ligand (H-NTBAN). ESI-MS *m*/*z* calcd for C₈H₆N₆O₃: 234.05; found: 233.0 [M - 1]⁺ (Fig. 1S, ESI†). IR (cm⁻¹): 3237(w), 3041(w), 1670(vs), 1588(s), 1512(m), 1393(m), 1273(m), 1241(m), 1041(s), 858(m), 807(w), 757(m), 612(m).

Synthesis of 4-fluoro-*N*-(1*H*-tetrazol-5-yl)benzamide. The preparation of H-NTBAF was similar to that of H-NTBAN except that 4-fluorobenzoyl chloride was used instead of the 4-nitrobenzoyl chloride (Scheme 1), and the yield was 70%. ESI-MS m/z calcd for C₈H₆FN₅O: 207.05; found: 206.05 [M - 1]⁺ (Fig. 2S, ESI⁺). IR (cm⁻¹): 3238(w), 3061(w), 2853(w), 1670(s), 1594(m), 1506(m), 1399(m), 1279(m), 1033(s), 858(m), 801(m), 681(m), 590(m).

Synthesis of *N*-(1*H*-tetrazol-5-yl)isonicotinamide. The preparation of H-NTINA was similar to that of H-NTBAN except that isonicotinoyl chloride was used instead of the 4-nitrobenzoyl chloride (Scheme 1), and the yield was 77%. ESI-MS *m*/*z* calcd for $C_7H_6N_6O$: 190.06; found: 189.06 [M - 1]⁺ (Fig. 3S, ESI†). IR (cm⁻¹): 3553(w), 3390(w), 3216(w), 3053(w), 2864(w), 1693(s), 1589(vs), 1395(m), 1280(m), 1013(m), 833(m), 749(m), 664(s), 502(w).

	H-NTBAN	Compound 1
C4(II)—	393K, DMF/EtOH	Cd ₃ (NTBAN) ₆
	H-NTBAF 393K, DMF/EtOH	Compound 2 Cd(NTBAF) ₂
Cu(II)	H-NTINA 393K, EtOH	Compound 3 Cd(NTINA) ₂
	H-NTTCA	Compound 4
	393K, H ₂ O	Cd(NTTCA) ₂

Scheme 2 Synthesis of compounds 1 to 4.

Synthesis of *N*-(1*H*-tetrazol-5-yl)thiophene-2-carboxamide. The preparation of H-NTTCA was similar to that of H-NTBAN except that thiophene-2-carbonyl chloride was used instead of the 4-nitrobenzoyl chloride (Scheme 1), and the yield was 86%. ESI-MS *m*/*z* calcd for C₆H₅N₅OS: 195.02; found: 194.02 $[M - 1]^+$ (Fig. 4S, ESI†); IR (cm⁻¹): 3226(s), 3033(m), 3010(m), 2862(w), 1649(vs), 1603(vs), 1543(m), 1417(vs), 1357(m), 1291(s), 1077(m), 1025(s), 858(m), 791(w), 737(s), 417(w).

Synthesis of Cd₃(NTBAN)₆ (1). A mixture of H-NTBAN (0.047 g, 0.2 mmol), CdCl₂ (0.023 g, 0.1 mmol), the mineralization agent dicyandiamide (0.017 g, 0.2 mmol), which was used to facilitate the crystallization of the product, DMF (2 mL), and EtOH (4 mL) was heated in a 25 mL Teflon-lined autoclave at 120 °C for 3 days, followed by cooling to room temperature (Scheme 2). The resulting mixture was washed with water, and colorless block crystals were collected and dried in air. Yield: 35% (based on Cd). Anal. calcd for $C_{48}H_{30}Cd_3N_{36}O_{18}$: C 33.19, H 1.73 N 29.05%. Found: C 33.01, H 1.98, N 29.03%. IR (cm⁻¹): 3230(w), 2841(w), 1659(s), 1563(s), 1525(s), 1355 (s), 1298(m), 1027(m), 1014(w), 896(m), 864(m), 769(w), 711(s).

Synthesis of Cd(NTBAF)₂ (2). The preparation of 2 was similar to that of 1 except that H-NTBAF was used instead of H-NTBAN (Scheme 2). The colorless crystals of 2 were obtained in a 35% yield (based on Cd). Anal. calcd for $C_{16}H_{10}CdF_2N_{10}O_2$: C 36.61, H 1.91, N 26.70%. Found: C 36.44, H 1.98, N 26.53%. IR (cm⁻¹): 3464(w), 3194(w), 3022(w), 2853(w), 1670(s), 1588(s), 1519(m), 1386(w), 1292(s), 1240(m), 1158(m), 1011(w), 896(m), 839(m), 757(s), 606(m).

Synthesis of Cd(NTINA)₂ (3). The preparation of **3** was similar to that of **1** except that H-NTINA was used instead of H-NTBAN and the solvent was ethanol (6 mL). Colorless block crystals of **3** were obtained in a 35% yield (based on Cd). Anal. calcd for $C_{14}H_{10}CdN_{12}O_2$: C 34.26, H 2.04, N 34.26%. Found: C 34.31, H 1.98, N 34.33%. IR (cm⁻¹): 3271(w), 3227(m), 3049(m), 2854(w), 1984(w), 1680(s), 1587(s), 1552(s), 1511(s), 1385(s), 1290(s), 1061(m), 1020(m), 994(w), 905(m), 748(m), 691(m), 659(m), 408(w).

Synthesis of Cd(NTTCA)₂ (4). The preparation of 4 was similar to that of 1 except that H-NTTCA was used instead of H-NTBAN and the solvent was water (6 mL). The colorless crystals of 4 were obtained in a 67% yield (based on Cd). Anal. calcd for $C_{12}H_8CdN_{10}O_2S_2$: C 28.78, H 1.60, N 27.98%. Found:

C 28.84, H 1.48, N 28.03%. IR (cm⁻¹): 3279(w), 3080(w), 2932(w), 1651(vs), 1550(s), 1502(s), 1418(vs), 1353(m), 1280(m), 1091(m), 918(w), 882(m), 761(m), 730(m), 709(m), 572(w), 536(w), 417(w).

X-Ray crystal structure determination

Reflection data of the three compounds **1**, **2** and **4** were collected on a Rigaku Saturn 724 CCD diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature, and compound **3** was collected on a Rigaku R-AXIS-Parid IP diffractometer. The structures were solved by the direct method and subsequent different Fourier syntheses. All calculations were performed by the full-matrix least-squares methods on F^2 by using the SHELX-97 program,⁷ all non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were fixed at calculated positions and refined by a riding mode. Crystal data and the structure refinements are summarized in Table 1.

Crystal structure of compound 1

As illustrated in Fig. 1A, the crystal structure of compound **1** consists of a trinuclear molecule, which contains two crystallographically different Cd(II) cations and three deprotonated tectons. The Cd1(II) cation is six-coordinated by six nitrogen atoms (N4, N4a, N4b, N4c, N4d and N4e) from the tetrazole groups of six deprotonated tectons, while the Cd2(II) cation is six-coordinated by tri-N,O-chelating coordination (N3, O1; N3a, O1a; N3b, O1b) from three of the six mentioned deprotonated tectons. Thus, both of the Cd(II) ion centers form a slightly distorted octahedral geometry. In **1**, the deprotonated tetrazole groups of the tectons are in $\mu_{1,2}$ -bridging mode, the Cd1(II) cation is triply bridged to two Cd2(II) cations by six surrounding tetrazole groups to form a centrosymmetric trinuclear molecule with Cd···Cd separation of 4.104 Å (Fig. 1A). The adjacent trinuclear units interact through hydrogen bonds (N–H···N, 2.983(3) Å) (Fig. 1B), which further stabilize the 3D supramolecular structure of **1** (Fig. 1C). The selected bond lengths and angles for **1** are shown in Table 1S, ESI,† and are similar to the reported values.⁸

Crystal structure of compound 2

The X-ray diffraction experiment reveals that compound **2** is crystallized in the $P4_32_12$ space group. In **2**, the Cd(II) cation that is located in the site with crystallographically imposed twofold symmetry is octahedrally coordinated by *cis*-bis-N,Ochelating coordination (N4a, O1a; N4b, O1b) from two tectons, which connect with another Cd(II), and two N atoms (N1, N1c) from two tetrazole groups, which also coordinate with another metal center (Fig. 2). That is, one metal ion links to four tectons and every ligand bridges two metal centers. Because the two N,O-chelating tectons are in the *cis*-form and the tetrazole group of the ligand is in the $\mu_{1,4}$ -bridging mode, the four neighboring metal ions surrounding the Cd are tetrahedrally arranged (Fig. 3A). Then a non-interpenetrated 3D framework is formed (Fig. 3B).

In Fig. 3B, the purple balls, standing for the fluorine atoms of the substituents, fill in the voids of the framework. That is to say, the voids of the framework should have enough space to accommodate the substituents in order to adopt this structure, otherwise another structure will be formed. The selected bond lengths and angles are listed in Table 1S, ESI,[†] and are similar to reported values.⁸ Crystals with the $P4_12_12$ space group were also found in the product of the same batch synthesis, suggesting the product is a racemic mixture.

Complex **3**, with similar cell parameters to **2**, is crystallized in the $P4_32_12$ or $P4_12_12$ space group. The results of X-ray crystallographic analysis indicate that complex **2** and complex **3** are isomorphous and isostructural. The only difference

Table 1 Crystal data and structure refinement parameters for compounds 1-4^{ab}

Compound reference	Compound 1	Compound 2	Compound 3	Compound 4	
Chemical formula	$C_{48}H_{30}Cd_3N_{36}O_{18}$	$C_{16}H_{10}CdF_2N_{10}O_2$	C ₁₄ H ₁₀ CdN ₁₂ O ₂	$C_{12}H_8CdN_{10}O_2S_2$	
Formula mass	1736.28	524.74	490.74	500.80	
Crystal system	Trigonal	Tetragonal	Tetragonal	Orthorhombic	
a/Å	18.118(3)	10.6882(15)	10.5749(15)	10.877(2)	
b/Å	18.118(3)	10.6882(15)	10.5749(15)	10.898(2)	
c/Å	17.507(3)	16.036(3)	16.256(3)	14.101(3)	
$\alpha/^{\circ}$	90.00	90.00	90.00	90.00	
$\beta/^{\circ}$	90.00	90.00	90.00	90.00	
$\gamma/^{\circ}$	120.00	90.00	90.00	90.00	
Unit cell volume/Å ³	4976.9(14)	1831.9(5)	1817.9(5)	1671.6(6)	
Temperature/K	293(2)	293(2)	293(2)	293(2)	
Space group	RĪ	$P4_{3}2_{1}2$	P41212	$P2_{1}2_{1}2_{1}$	
No. of formula units per unit cell, Z	3	4	4	4	
No. of reflections measured	14 003	15 338	17 521	13 514	
No. of independent reflections	2538	2096	2082	3820	
R _{int}	0.0449	0.0409	0.0846	0.0265	
Final R_1 values $(I > 2\sigma(I))$	0.0435	0.0228	0.0479	0.0209	
Final wR(F^2) values ($I > 2\sigma(I)$)	0.0765	0.0488	0.1112	0.0541	
Final R_1 values (all data)	0.0446	0.0229	0.0581	0.0210	
Final $wR(F^2)$ values (all data)	0.0769	0.0489	0.1159	0.0542	
Goodness of fit on F^2	1.304	1.132	1.066	1.097	
Flack parameter	_	0.00(3)	0.06(8)	0.004(19)	

^{*a*}
$$R_1 = \sum ||F_0| - |F_c|| / \sum |F_o|$$
. ^{*b*} $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)]^{1/2}$.



Fig. 1 A) View of the coordination environment of the Cd(II) cations in **1** with thermal ellipsoids drawn at the 30% probability level. All H atoms are omitted for clarity. Symmetry codes: a) x - y, -y, z; b) -x + y, -x, z; c) -x, -y, 1 - z; d) x - y, x, 1 - z; e) y, -x + y, 1 - z. B) View of the 2D structure of **1**. All H atoms are omitted for clarity. Nitrophenyl groups, which are the same as the segment in the blue ellipse loop, are also omitted for clarity. Hydrogen bonds are shown as red dashed lines. C) View of the 3D structure of **1** along the *c* axis.

between them is that the substituents of them are fluorophenyl and pyridyl, respectively.

Crystal structure of compound 4

Compound 4 crystallizes in the orthorhombic space group $P2_12_12_1$. In 4, the Cd(II) cation is octahedrally coordinated by



Fig. 2 Coordination environment of the Cd(II) cation centre in **2** with thermal ellipsoids drawn at the 30% probability level. All H atoms are omitted for clarity. Symmetry codes: a) -0.5 + x, 1.5 - y, 0.25 - z; b) -0.5 + x, 1.5 - y, -0.25 + z; c) x, y, -z.



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Fig. 3 A) The tetrahedral arrangement in 2 shown by the black solid lines. B) View of the 3D network structure of $\bf 2$. All H atoms are omitted for clarity.

cis-bis-N,O-chelating coordination (N1, O1; N6b, O2b) from two tectons, which connect with another Cd(II), and two N atoms (N4a, N9) from two tetrazole groups of the other two tectons, which also coordinate with other metal centers (Fig. 4A). That is, one metal ion links with four tectons and each ligand bridges two metal centers. Two of the N,Ochelating tectons are in the *cis*-form (Fig. 4A), and the tetrazole group of the ligand adopts the $\mu_{1,4}$ -bridging mode. The result is that the four neighboring metal ions surrounding one Cd are tetrahedral arranged, propagating a 3D chiral structure, which is a typical 6⁶-*dia* network considering the Cd(II) unit as a 4-connected node and the ligand as a linker, respectively (Fig. 4C). The selected bond lengths and angles are shown in Table 1S, ESI.[†] The bond lengths are similar to reported values.⁸

Effect of substituents on the network structures

Four kinds of rigid substituents of different sizes were selected, which is anticipated to find out the effect of the substituents on the topologies and symmetries of the coordination networks. As expected, the tectons in compound **1** adopted a $\mu_{1,2}$ -bridging coordination mode, while those in compounds 2, 3 and 4 possess a $\mu_{1,4}$ -bridging mode to generate a 3D non-interpenetrated chiral diamondoid framework. One way to break the center of symmetry in diamond nets is using unsymmetrical bridging ligands to connect the nodes.² In 2, 3 and 4, the unsymmetrical bridging mode of the ligands and the cis-form of the two N,O-chelating tectons lead to the formation of chiral metal ion centers. Such formed chirality could be further delivered by the unsymmetrical bridging mode to generate the final chiral complexes. Moreover, in these three chiral structures, the substituents of the tectons (fluorophenyl, pyridyl and thiophenyl) could fill in the voids of the framework (Fig. 3B, 4B and S9, ESI[†]), while the nitrophenyl is too large to fill in this dia framework. As a result, the latter cannot form such a dia chiral compound. In other words, the low dimensional trinuclear structure obtained for compound 1 is attributed to the steric hindrance of the nitrophenyl substituents of the H-NTBAN. For the three chiral structures, the remarkable difference is that different space groups resulted from the slightly different substituents, fluorophenyl, pyridyl and thiophenyl moieties, respectively.



Fig. 4 A) Coordination environment of the Cd(II) cation centre in **4** with thermal ellipsoids drawn at the 30% probability level. All H atoms are omitted for clarity. Symmetry codes: a) -0.5 + x, -0.5 - y, -z; b) -1 - x, -0.5 + y, -0.5 - z. B) View of the 3D network structure of **4**. C) Topological view showing the *dia* network for **4**.

Optical properties and substituent effects

The photoluminescent properties of complexes 1-4 were studied in solid state at room temperature. The emission spectra of the complexes 1-4 are shown in Fig. S10 (see ESI[†]). Given that compounds 2, 3 and 4 crystallized in a chiral space group, their solid-state circular dichroism (CD) spectra were measured. The results indicated that no signals were observed for their powder samples, which indicated that the crystals are racemic mixtures. The NLO properties of the crystals for compounds 2, 3 and 4 were measured with a LAB130 Pulsed Nd:YAG laser according to the principle proposed by Kurtz and Perry,⁹ and preliminary studies of the powder samples expectedly showed second harmonic generation (SHG) efficiencies with values of 1.1, 2 and 6 times that of potassium dihydrogen phosphate (KDP), respectively. The plots of the SHG signals as a function of particle size ranging from 40 to 210 µm measured on ground crystals suggest that compound 4 is phasematchable (Fig. S11, see ESI[†]), which is a necessary character for a NLO material to serve for laser frequency converting.

It is known that the NLO properties of organic molecules are closely related to their lengths and polarizabilities.¹⁰ The



Fig. 5 Thermal gravimetric analysis (TGA) diagrams of compounds 2-4.

organic tectons in networks 2, 3 and 4 have similar lengths but different polarizabilities. Considering the electron-deficiency of the tetrazolate moiety, the increased electron-donation by the attached substituents will enhance the polarizability of the organic tecton. This is undoubtedly confirmed by the above preliminary results that complex 4, which contains the thiophenyl group which is the strongest electron-donor, has the highest SHG efficiency (6 fold that of KDP), while networks 2 and 3 bearing the fluorophenyl and pyridyl groups have lower SHG efficiencies. This conclusion is also supported by the theoretical calculations (see ESI[†]), which showed that the calculated value for complex 4 is 8 times that of KDP. However, those for networks 2 and 3 are much smaller than that for compound 4, which is not only attributed to the weak electrondonation by the organic tectons, but also to the packing in the crystal structures. Although the calculated values are different to the experimental values, their orders of SHG efficiency are same. In a word, the polarizability of the tectons as well as the molecular packing plays a key role in the SHG efficiency of coordination networks.

Thermal stability analyses

The phase purity of these compounds is convincingly established by comparison of the powder X-ray diffraction patterns of the as-synthesized products with the simulated ones from the single-crystal date (see Fig. S5–S8 in the ESI†). The thermal stabilities of 3D chiral compounds **2–4** were examined by the thermal gravimetric analysis (TGA) technique from room temperature to 650 °C with a heating rate of 10 K min⁻¹ under an N₂ atmosphere (Fig. 5).

The TG curves for the compounds are similar. No weight losses were observed until about 300 °C for compound **3**, which indicated that the framework is thermally stable. Relative to compound **3**, compounds **2** and **4** have slightly higher temperature stabilities. Sharp weight losses occurred in the temperature range of about 320–350 °C for **2** and **4**. The weight losses for all the compounds are attributed to the decomposition of the organic tectons.

Conclusions

Four coordination networks, including three chiral ones, were obtained from achiral tetrazole-yl acylamide tectons of different substituents with octahedrally coordinated divalent cadmium cations. Of the substituents attached to the organic tectons, the smaller substituents are found to favor the formation of chiral networks. Moreover, the substituents that are stronger electron-donors could also enhance the NLO properties of the generated chiral networks. This result is of practical and heuristic significance in the rational design of chiral coordination networks possessing NLO properties from achiral organic tectons.

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