Controlled Generation of Acentric and Homochiral Coordination Compounds from a Versatile Asymmetric Ligand 4-(1H-1,2,4-Triazol-3-yl)-4H-1,2,4-Triazole

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Experimental Section.

Synthesis of Hbtrz.

The ligand Hbtrz was prepared by the literature method (Reference: R.M. Herbst and J.A. Garrison, *J. Org. Chem.* 1953, **18**, 872.).

Synthesis of [Cd(btrz)₂] (1).

A mixture of CdI_2 (0.366g, 1.0 mmol), Hbtrz (0.136g, 1.0 mmol), and 6 mL of water was placed in a 23 mL Teflon liner. The resulting mixture was stirred for 10 min and was then sealed in a Parr autoclave. The autoclave was placed in a programmable furnace and heated to 160 °C. The temperature was hold for 4 days, and then the reactant mixture was cooled at a rate of 0.5 °C min⁻¹ to form colorless prism crystals of **1**. Yield: 83% (based on Cd(II) salts).

Anal. Calcd (%) for C₈H₈CdN₁₂: C, 24.98; H, 2.10; N, 43.70. Found: C, 24.97; H, 2.11; N, 43.72%. IR (solid KBr pellet, *v*/cm⁻¹) for complex **1**: 3434 (s), 3182 (s), 1638 (m), 1400 (s), 1144 (w), 1058 (w), 633 (w), 615 (w).

Synthesis of [Cd(Hbtrz)Br₂]·(H₂O) (2).

Method A. A mixture of CdBr₂·4H₂O (0.172g, 0.5 mmol), Hbtrz (0.068g, 0.5 mmol), and 8 mL of water was placed in a 23 mL Teflon liner and stirred for 60 min. The resulting mixture was stirred for 3 min and was then sealed in a Parr autoclave. The autoclave was then placed in a programmable furnace and heated to 150 °C. The temperature was hold for 5 days, and then the reactant mixture was cooled at a rate of 1.0 °C min⁻¹ to room temperature. Upon standing and evaporation of the resulting colorless solution under ambient conditions for one month, prism-shaped crystals of **2** were obtained as the product. Yield: 78% (based on Cd(II) salts).

Method B. CdBr₂·4H₂O (0.172g, 0.5 mmol) and Hbtrz (0.068g, 0.5 mmol) were mixed in water (40 mL) with continuous stirring. The resulting colorless solution was allowed to stand at room temperature. After about two months, well prism-shaped

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crystals of 2 were obtained. Yield: 88% (based on Cd(II) salts).

Anal. Calcd (%) for C₄H₆Br₂CdN₆O: C, 11.27; H, 1.42; N, 19.71; Br, 37.48. Found: C, 11.26; H, 1.44; N, 19.70; Br, 37.46%. IR (solid KBr pellet, *v*/cm⁻¹) for complex **2**: 3433 (s), 3134 (s), 1623 (m), 1400 (s), 1165 (w) 1058 (w), 614 (w).

Predominant same enantiomorph of 2

For **2**, a total of seven crystals were randomly picked for single-crystal X-ray diffraction. When the same set of positional coordinates are refined against seven *hkl* data sets, the Flack parameters are -0.014(17), -0.016(7), -0.027(11), -0.005(6), -0.033(4), 0.020(13) and -0.029(9), respectively. If the bulk material was a racemic mixture, the probability of 7 crystals all being of the same chirality is small (1 in 2⁷). This indicates that, at the very least, the bulk samples consist predominantly of the same enantiomorph, and that they are probably chirally pure. The bulk samples of **2** consist entirely of nicely shaped crystals that all look equivalent to the naked eye, which means that any bias in the choice of crystal associated with one enantiomorph having, for example, larger crystals than the other is also unlikely.

Synthesis of 1 from 2:

A mixture of **2** (0.213g, 0.5 mmol) and KI (0.166g, 1.0 mmol) was placed in a 23 mL Teflon liner and stirred for 45 min; 10 mL of water was then added. The resulting mixture was then sealed in a Parr autoclave and placed in a programmable furnace and heated to 180 °C. The temperature was hold for 2 days, and then the reactant mixture was cooled at a rate of 0.5 °C min⁻¹ to form prism crystals of **1**. Yield: 86% (based on **2**).

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X-ray Crystallography.

Suitable single crystals of 1 and 2 were randomly selected under an optical microscope and glued to thin glass fibers. Structural measurements were performed computer-controlled Siemens Smart CCD diffractometer on a with graphite-monochromated Mo K α radiation ($\lambda_{Mo K\alpha} = 0.71073$ Å) at T = 294.15 K. Absorption corrections were made using the SADABS program (Reference: G. M. Sheldrick, SADABS, Program for Area Detector Adsorption Correction, University of Göttingen: Göttingen, Germany, 1996). The structures were solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package (Reference: G. M. Sheldrick, SHELXL-97, Program for Solution of Crystal Structures, University of Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in the calculated positions. Disorders were observed for a triazole ring of 2 with a carbon and a nitrogen atom sharing the same site, and they were refined over this site with occupancies of 0.53(5) and 0.47(5), respectively. Selected bond lengths and angles are given in Table S1.

Nonlinear Optical Properties.

Second-order nonlinear optical effects for the powder samples of **1** and **2** have been investigated by optical second-harmonic generation (SHG) at room temperature. Second-harmonic generation intensity data were obtained by placing the powder sample in an intense fundamental beam from a Q-switched Nd:YAG laser of wavelength 1064 nm. The output ($\lambda = 532$ nm) was filtered first to remove the multiplier and was then displayed on an oscilloscope. This procedure was then repeated using a standard NLO material (microcrystalline KDP), and the ratio of the second-harmonic intensity outputs was calculated. The observed powder second harmonic generation (SHG) efficiency of **1** is 4.0 times that of KDP, and the observed powder SHG efficiency of **2** is 1.5 times that of KDP.

Compound 1						
Cd(1)-N(2)#1	2.239(2)	Cd(1)-N(6)#2	2.431(3)	Cd(1)-N(1)#4	2.510(3)	
Cd(1)-N(2)	2.239(2)	Cd(1)-N(6)#3	2.431(3)	Cd(1)-N(1)#5	2.510(3)	
N(2)#1-Cd(1)-N(2)	176.88(16)	N(6)#2-Cd(1)-N(6)#3	103.32(12)	N(2)#1-Cd(1)-N(1)#5	85.36(9)	
N(2)#1-Cd(1)-N(6)#2	85.74(9)	N(2)#1-Cd(1)-N(1)#4	96.86(8)	N(2)-Cd(1)-N(1)#5	96.86(8)	
N(2)-Cd(1)-N(6)#2	92.32(9)	N(2)-Cd(1)-N(1)#4	85.36(9)	N(6)#2-Cd(1)-N(1)#5	168.61(7)	
N(2)#1-Cd(1)-N(6)#3	92.32(9)	N(6)#2-Cd(1)-N(1)#4	84.14(9)	N(6)#3-Cd(1)-N(1)#5	84.14(9)	
N(2)-Cd(1)-N(6)#3	85.74(9)	N(6)#3-Cd(1)-N(1)#4	168.61(7)	N(1)#4-Cd(1)-N(1)#5	89.89(13)	
N(2)#1-Cd(1)-N(2)	176.88(16)	N(6)#2-Cd(1)-N(6)#3	103.32(12)	N(2)#1-Cd(1)-N(1)#5	85.36(9)	
		Compound	12			
Cd(1)-N(2)	2.349(3)	Cd(1)-Br(1)#1	2.7250(8)	Cd(1)-Br(1)#2	2.7779(9)	
Cd(1)-N(2)#1	2.349(3)	Cd(1)-Br(1)	2.7250(8)	Cd(1)-Br(1)#3	2.7779(9)	
N(2)-Cd(1)-N(2)#1	178.4(2)	N(2)-Cd(1)-Br(1)#2	90.51(9)	N(2)#1-Cd(1)-Br(1)#3	90.51(9)	
N(2)-Cd(1)-Br(1)#1	88.36(9)	N(2)#1-Cd(1)-Br(1)#2	90.63(9)	Br(1)#1-Cd(1)-Br(1)#3	85.82(3)	
N(2)#1-Cd(1)-Br(1)#1	90.59(8)	Br(1)#1-Cd(1)-Br(1)#2	175.469(13)	Br(1)-Cd(1)-Br(1)#3	175.469(13)	
N(2)-Cd(1)-Br(1)	90.59(8)	Br(1)-Cd(1)-Br(1)#2	85.82(3)	Br(1)#2-Cd(1)-Br(1)#3	89.81(3)	
N(2)#1-Cd(1)-Br(1)	88.36(9)	N(2)-Cd(1)-Br(1)#3	90.63(9)	Cd(1)-Br(1)-Cd(1)#4	81.07(3)	
Br(1)#1-Cd(1)-Br(1)	98.58(3)					

Table S1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1 and 2^{a}

^aSymmetry codes: **1**: #1 -x+1, -y+1, z; #2 x+1/2, y, z+1/2; #3 -x+1/2, -y+1, z+1/2; #4 x+1/4, -y+3/4, z-1/4; #5 -x+3/4, y+1/4, z-1/4. **2**: #1 x,-y+1,-z+1/2; #2 -x+1/2, y, -z; #3 -x+1/2, -y+1, z+1/2; #4 -x+1/2, -y+1, z-1/2.



Figure S1. (a) ORTEP drawing of $[Cd(btrz)_2]$ (1) showing the atom-labeling system and 50% thermal ellipsoids. (b) View of the 3D structure of 1.



Figure S2. View of the 3D framework of 1 in a unit cell along the a axis (left), and the b axis (right), showing d glide reflections in 1.



Figure S3. (a) ORTEP drawing of $[Cd(Hbtrz)Br_2] \cdot (H_2O)$ (2) showing the atom-labeling system and 50% thermal ellipsoids. (b) View of the 1D structure of 2.



Figure S4. View of the Cd-N bonds out of the triazole rings (with the Cd-N-plane angles of 5.66° and -5.66°, respectively).



Figure S5. Excitation and emission spectra for 1 and 2 in the solid state at room temperature.



Figure S6. Emission decay traces and the biexponential fits for **1** and **2** at room temperature. (For **1**, $\tau_1 = 1.487$ ns, 47%; $\tau_2 = 3.618$ ns, 53%. For **2**, $\tau_1 = 6.045$ ns, 51%; $\tau_2 = 2.017$ ns, 49%)

(a)



Figure S7. TG coupled with QMS analyses for **1** with ion current signals respectively for (a) m/z = 26, 52 for CN⁺; (b) m/z = 16 for NH₂⁺, m/z = 38 for C₂N⁺.

Compound 1 manifests a high thermal stability with its TG curve unchanged up to 400 °C. Then a steady, moderate to steep weight loss is observed, and detectable ion currents (m/z = 16 for NH₂⁺; m/z = 26, 52 for CN⁺; m/z = 38 for C₂N⁺) are associated with the decomposition of organic ligands. This continuous decomposition is also simultaneously accompanied by the sublimation of residual cadmium products. Therefore, there is no residual composition left behind.



Figure S8. TG coupled with QMS analyses for **2** with ion current signals respectively for (a) m/z = 18 for H_2O^+ , m/z = 17 for H_2O^+ or NH_2^+ , m/z = 16 for NH_2^+ ; (b) m/z = 26, 52 for CN^+ .

Compound **2** manifests the loss of H₂O (m/z = 18, H₂O⁺) (exptl, 4.27%; calcd, 4.23%) occurs below 200 °C, then a steady weight loss without any obvious well defined plateau is observed, and detectable ion currents (m/z = 16, NH₂⁺; m/z = 26, 52 for CN⁺; m/z = 18 for H₂O⁺; m/z = 17 for H₂O⁺ or NH₂⁺) are associated with the decomposition of organic ligands. This continuous decomposition is also simultaneously accompanied by the sublimation of residual cadmium products. Therefore, there is no residual composition left behind.



Figure S9. X-ray powder diffraction patterns of **1** (a) and **2** (b), black, experimental data; blue, simulated from single-crystal X-ray data.

Software

We used DIAMOND 3.1d to draw pictures of crystal structures and schematic presentations of topological nets. Some pictures of helices are generated from 3DMAX 8.0.

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Topology for Sc1

Atom Sc1 links by bridge ligands and has

Common vertex with				R(A-A)			
Cd 1	0.2500	0.2500	1.1229	(-1 0 0)	3.794A	1	
Cd 1	0.5000	0.5000	0.8729	(000)	4.831A	1	
Cd 1	0.0000	0.5000	0.3729	(01-1)	5.093A	1	
Topolo	gy for Cd1						

Common vertex with

R(A-A)

					· · · · · · · · · · · · · · · · · · ·	
Sc 1	0.5170	0.6401	0.5030	(00-1)	3.794A	1
Sc 1	0.4830	0.3599	0.5030	(00-1)	3.794A	1
Sc 1	0.2330	0.3901	0.7530	(000)	4.831A	1
Sc 1	0.7670	0.6099	0.7530	(110)	4.831A	1
Sc 1	0.7330	0.3901	1.2530	(000)	5.093A	1
Sc 1	0.2670	0.6099	1.2530	(010)	5.093A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with CdSc2

Sc1: 1 2 3 4 5 7 8 6 9 10 Num 3 15 24 82 71 197 140 358 235 569 Cum 4 19 43 125 196 393 533 891 1126 1695 _____ Cd1: 1 2 3 4 5 6 7 8 9 10 Num 6 12 48 48 142 106 280 190 470 296 Cum 7 19 67 115 257 363 643 833 1303 1599 ------

TD10=1663

Vertex symbols for selected sublattice

Sc1 Schlafli symbol: {6^3}

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With circuits: [6.6(2).6(3)]

Cd1 Schlafli symbol: {6^10;8^5} With circuits: [6.6.6.6.6.6.6.6.6(2).6(2).8(2).8(2).8(4).8(6).8(8)]

Total Schlafli symbol: {6^10;8^5}{6^3}2 3,6-c net with stoichiometry (3-c)2(6-c); 2-nodal net

New topology, please, contact the authors (23739 types in 6 databases) Elapsed time: 6.11 sec. # Supplementary Material (ESI) for Chemical Communications

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Topology for Sc1

Atom Sc1 links by bridge ligands and has

Common vertex with					R(A-A)		
Sc 1	0.7500	0.2448	0.5000	(100)	3.762A	1	
Sc 1	-0.2500	0.2448	0.5000	(000)	3.762A	1	
Cd 1	0.2373	0.5000	0.7500	(001)	5.105A	1	
Cd 1	0.2627	0.5000	0.2500	(000)	5.105A	1	
Topolo	ogy for Cd1						

Atom Cd1 links by bridge ligands and has

Common vertex with					R(A-A)		
Sc 1	0.2500	0.7448	0.0000	(010)	5.105A	1	
Sc 1	0.2500	0.2552	0.5000	(000)	5.105A	1	
Comm	on edge with	h			R(A-A)		
Cd 1	0.2373	0.5000	-0.2500	(000)	3.577A	2	
Cd 1	0.2373	0.5000	0.7500	(001)	3.577A	2	

Structural group analysis

Structural group No 1

Structure consists of 3D framework with CdBr2ScO

Coordination sequences

_____ Sc1: 1 2 3 4 6 7 8 5 9 10 4 10 22 40 64 88 124 164 198 254 Num Cum 5 15 37 77 141 229 353 517 715 969 _____ Cd1: 1 2 3 4 5 6 7 8 9 10 Num 4 8 20 42 56 96 118 158 208 250 Cum 5 13 33 75 131 227 345 503 711 961 -----

TD10=965

Vertex symbols for selected sublattice

Sc1 Schlafli symbol: {3;8^5} With circuits: [3.8(2).8(2).8(2).8(2).8(2)]

Cd1 Schlafli symbol: {3^2;8^3;9} With circuits: [3.3.8(2).8(2).8(2).9(4)]

Total Schlafli symbol: {3;8^5}{3^2;8^3;9} 4-c net; 2-nodal net

New topology, please, contact the authors (23744 types in 6 databases) Elapsed time: 6.30 sec.

SYSTRE analysis result of 1 (using SYSTRE 1.1.4)

Structure #1 - "6-1".

Given space group is Fdd2. 6 nodes and 12 edges in repeat unit as given.

Given repeat unit is accurate. Point group has 4 elements. 2 kinds of node.

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Coordination sequences:
```

Node Cd1:6 12 48 48 142 106 280 190 470 296Node N1:3 15 24 82 71 197 140 358 235 569

TD10 = 1663.0000

Ideal space group is Fdd2.

Structure is new for this run.

Relaxed cell parameters: a = 2.96514, b = 4.80550, c = 1.73021 alpha = 90.0000, beta = 90.0000, gamma = 90.0000Relaxed positions: Node Cd1: 0.00000 0.00000 0.32639 Node N1: 0.29502 0.09059 0.21220 Edges: 0.00000 0.00000 0.32639 <-> 0.20498 -0.09059 0.71220 0.00000 0.00000 0.32639 <-> 0.29502 0.09059 0.21220 0.00000 0.00000 0.32639 <-> 0.04502 0.15941 -0.03780 Edge centers: 0.10249 -0.04529 0.51929 0.14751 0.04529 0.26929 0.02251 0.07971 0.14429

```
Edge statistics: minimum = 0.99689, maximum = 1.00225, average = 1.00000
Angle statistics: minimum = 54.82601, maximum = 157.13752, average = 107.58462
Shortest non-bonded distance = 0.91977
```

Degrees of freedom: 6

Finished structure #1 - "6-1".