(Supplementary information)

Spontaneous resolution of 3D chiral hexadecavanadate-based frameworks incorporating achiral flexible and rigid ligands

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12. Figure S6. Solid-state CD spectrum of **1** (the mixture of $_{L}$-1 and $_{D}$-1).

Table S1 Crystal data and structure refinement for **1**.

	$_{L}$-1	$_{D}$-1
Empirical formula	C78H75N20Cu5V16O38.5Cl	C78H75N20Cu5V16O38.5Cl
Formula weight	3076.79	3076.79
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Tetragonal
Space group	*I4122*	*I4122*
a (Å)	27.600(4)	27.672(4)
b (Å)	27.600(4)	27.672(4)
c (Å)	26.700(5)	26.693(5)
Volume (Å ^{3})	20339(6)	20440(6)
Z	8	8
D $_{calc}$ (mg/m^{3})	2.004	1.999
Absorption coefficient (mm^{-1})	2.531	2.519
F (000)	12160	12128
Reflns collected	73861	64690
Unique reflns	8955	8514
R(int)	0.1410	0.1210
θ range (deg)	3.05≤θ≤25.00	3.05≤θ≤24.50
Limiting indices	-32≤*h*≤32, -32≤*k*≤32, -28≤*l*≤31	-31<=h<=30, -32<=k<=32, -30<=l<=31
Goodness-of-fit on F^{2}	1.041	0.926
Final *R* indices [*I*>2σ(*I*)]	R_1 =0.0748, wR_2 = 0.1861	R_1 =0.0620, wR_2 = 0.1471
R indices (all data)	R_1 =0.1116, wR_2=0.2084	R_1 =0.1204, wR_2=0.1721

Table S2. Selected Bond lengths (Å) and angles (°) for **1**.

$_{L}$-**1**			
V(1)-O(13)	1.581(10)	V(1)-O(1)	1.835(10)
V(1)-O(6)	1.893(10)	V(1)-O(14)#1	1.901(11)
V(1)-O(18)	1.996(9)	V(2)-O(3)	1.586(10)
V(2)-O(14)	1.928(8)	V(2)-O(18)#1	1.946(10)
V(2)-O(11)	1.920(10)	V(2)-O(12)	1.948(9)
V(3)-O(4)	1.596(9)	V(3)-O(12)	1.857(9)
V(3)-O(8)#1	1.875(10)	V(3)-O(15)	1.921(9)
V(3)-O(19)	1.924(10)	V(4)-O(5)	1.605(11)

V(4)-O(18)	1.861(18)	V(4)-O(8)	1.858(11)
V(4)-O(6)	1.902(10)	V(4)-O(7)	1.906(9)
V(5)-O(2)	1.578(9)	V(5)-O(15)	1.954(9)
V(5)-O(7)	1.967(10)	V(5)-O(6)	1.976(9)
V(5)-O(19)	2.002(9)	V(6)-O(10)	1.577(9)
V(6)-O(1)	1.836(10)	V(6)-O(19)	1.862(9)
V(6)-O(11)	1.929(9)	V(6)-O(12)	1.980(9)
V(7)-O(20)	1.607(17)	V(7)-O(17)	1.682(4)
V(7)-O(11)#1	1.838(10)	V(7)-O(14)	1.818(8)
V(7)-O(17')	1.884(10)	V(7)-O(1)#1	2.228(11)
V(8)-O(9)	1.586(9)	V(8)-O(16)	1.801(5)
V(8)-O(7)	1.888(9)	V(8)-O(15)#1	1.893(9)
V(8)-O(8)	2.082(11)	Cu(1)-N(1)	1.860(12)
Cu(1)-O4	2.688(3)	Cu(2)-N(3)	1.972(17)
Cu(2)-N(4)	2.023(16)	Cu(2)-N(5)	1.876(16)
Cu(3)-N(9)	1.967(17)	Cu(3)-N(10)	2.10(2)
Cu(3)-N(8)	1.915(19)		

Symmetry transformation used to generate equivalent atom: #1 -x+1,-y+2,z+0

D-**1**

V(1)-O(20)	1.577(7)	V(5)-O(9)	1.598(7)
V(1)-O(12)	1.804(4)	V(5)-O(3)#2	1.825(7)
V(1)-O(14)#2	1.872(7)	V(5)-O(1)#2	1.871(7)
V(1)-O(10)	1.884(6)	V(5)-O(8)	1.895(7)
V(1)-O(2)	2.046(7)	V(5)-O(15)	2.005(7)
V(2)-O(5)	1.628(8)	V(6)-O(6)	1.609(7)
V(2)-O(15)#2	1.852(7)	V(6)-O(14)	1.959(7)
V(2)-O(2)#2	1.880(9)	V(6)-O(10)	1.966(7)
V(2)-O(14)	1.931(7)	V(6)-O(1)	1.970(7)
V(2)-O(1)	1.934(8)	V(6)-O(16)	1.973(7)
V(3)-O(4)	1.565(7)	V(7)-O(13)	1.575(7)
V(3)-O(11)	1.938(7)	V(7)-O(3)	1.859(7)
V(3)-O(8)	1.938(7)	V(7)-O(16)	1.873(6)
V(3)-O(15)	1.946(7)	V(7)-O(17)	1.916(7)
V(3)-O(17)	1.957(7)	V(7)-O(11)	2.000(7)
V(4)-O(7)	1.589(7)	V(8)-O(18)	1.607(11)
V(4)-O(11)	1.852(7)	V(8)-O(19A)	1.674(4)
V(4)-O(2)	1.866(7)	V(8)-O(8)#2	1.819(8)
V(4)-O(10)	1.925(7)	V(8)-O(17)	1.890(7)
V(4)-O(16)	1.941(7)	V(8)-O(19)	1.867(7)
Cu(1)-N(1)	1.879(9)	Cu(1)-N(1)#1	1.879(9)
Cu(1)-O(7)	2.694 (3)	Cu(2)-N(5)	1.875(11)
Cu(2)-N(3)	2.028(11)	Cu(2)-N(4)	1.991(12)
Cu(3)-N(8)	1.923(15)	Cu(3)-N(9)	1.934(13)
Cu(3)-N(10)	2.055(12)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y,-z+7/4 #2 -x+1,-y+1,z+0

The details for the refinement:

In the refined structure of $_L$-1, N9, O20, C4, C8, C10, C11, C13, C14, C15, C22, C29, C31, C32, C35, C37 and C38 were treated as isotropic atoms. Besides, C5 in the butyl group is disordered and was modeled as isotropic.

In the refined structure of $_D$-1, N3, N9, C4, C7, C8, C10, C11, C13, C14, C28, C29, C30, C33, C34 and O1W were treated as isotropic atoms. Besides, C5 in the butyl group is disordered and was modeled as isotropic.

The confirmation of the molecular formula:

$[Cu_2(phen)_2(bbi)]_2[Cu(bbi)][V_{16}O_{38}Cl]\cdot 0.5H_2O$

The confirmation of the molecular formula is based upon the bond valence sum calculations ($\sum_S$) and the charge balance. For $_L$-**1**, the valence sums for all the V atoms are 4.73 (V1), 4.36 (V2), 4.62 (V3), 4.63 (V4), 4.16 (V5), 4.72 (V6), 4.44 (V7) and 4.68 (V8), respectively, and for the three Cu atoms are 1.12 (Cu1), 1.16 (Cu2) and 1.16(Cu3), respectively. For $_D$-**1**, the valence sums for all the V atoms are 4.71 (V1), 4.50 (V2), 4.38 (V3), 4.66 (V4), 4.69 (V5), 4.11 (V6), 4.64 (V7) and 4.52(V8), respectively, and for the three Cu atoms are 1.11 (Cu1), 1.14(Cu2) and 1.16(Cu3), respectively. The total sums of sixteen V are 72.68 for $_L$-**1** and 72.42 for $_D$-**1**. The average values for V atoms are 4.54 and 4.53 for $_L$-**1** and $_D$-**1**, respectively, very close to the expected value 4.5 for $V^{IV}_8V^{V}_8$. Thus the $\{V_{16}O_{38}Cl\}$ cluster, has a calculated charge of -4.32 and -4.58 for $_L$-**1** and $_D$-**1**, respectively, which is approximately balanced by five Cu(I) ions.

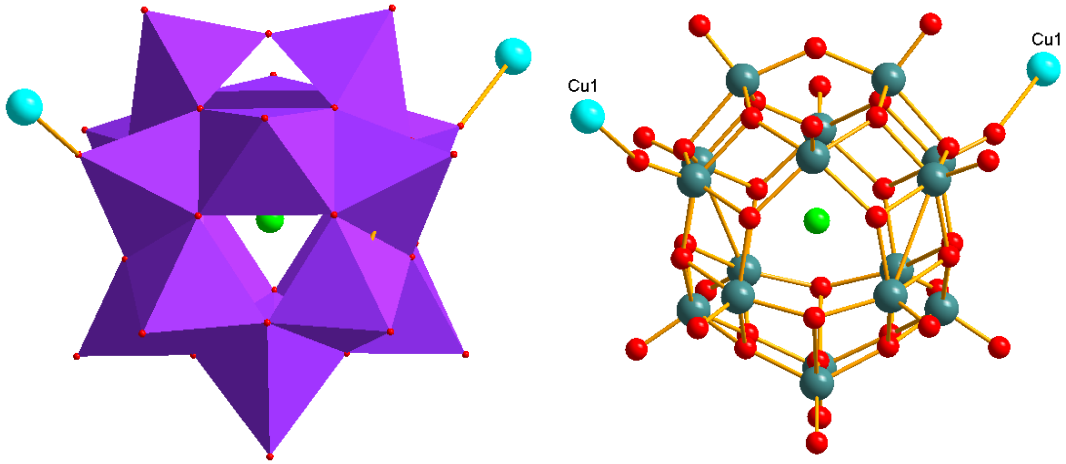

Figure S1. Ball-stick (left) and polyhedral (right) representations of $[V_{16}O_{38}Cl]^{5-}$ polyoxoanion as well as the connection mode with Cu^{I}(1).

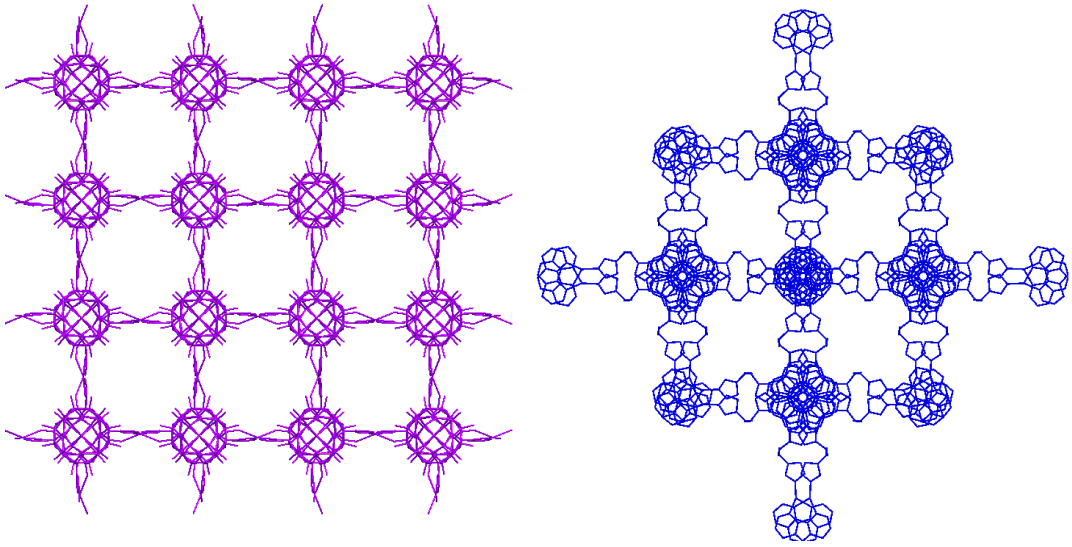

Figure S2. Representation of (a) the 3D homochiral $\{[Cu(bbi)][V_{16}O_{38}Cl]\}^{4-}$ anionic framework (left) and (b) a stacking cationic framework of $\{Cu_2(phen)_2(bbi)\}^{2+}$ (right).

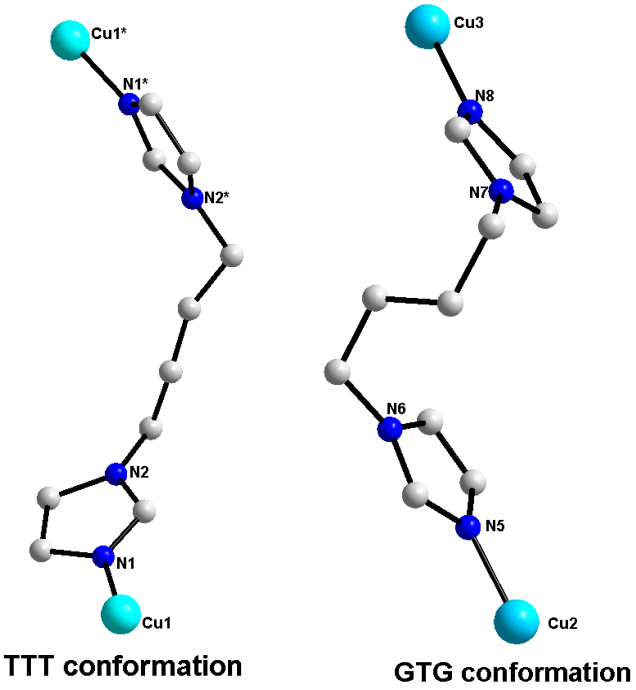

Figure S3. Illustration of the conformations of (a) bbi1 (TTT) and (b) bbi2 (GTG) in $_{L}$-**1**.

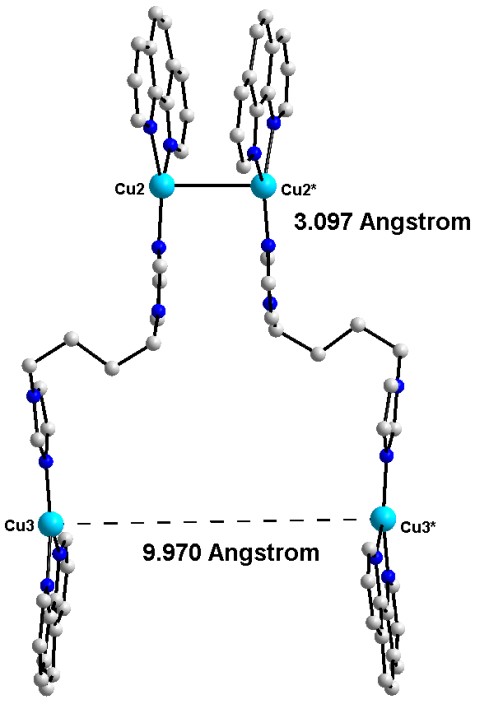

Figure S4. Illustration of the bottle-like $\{Cu_2(phen)_2(bbi)\}_2$ cationic dimer in $_{L}$-**1.**

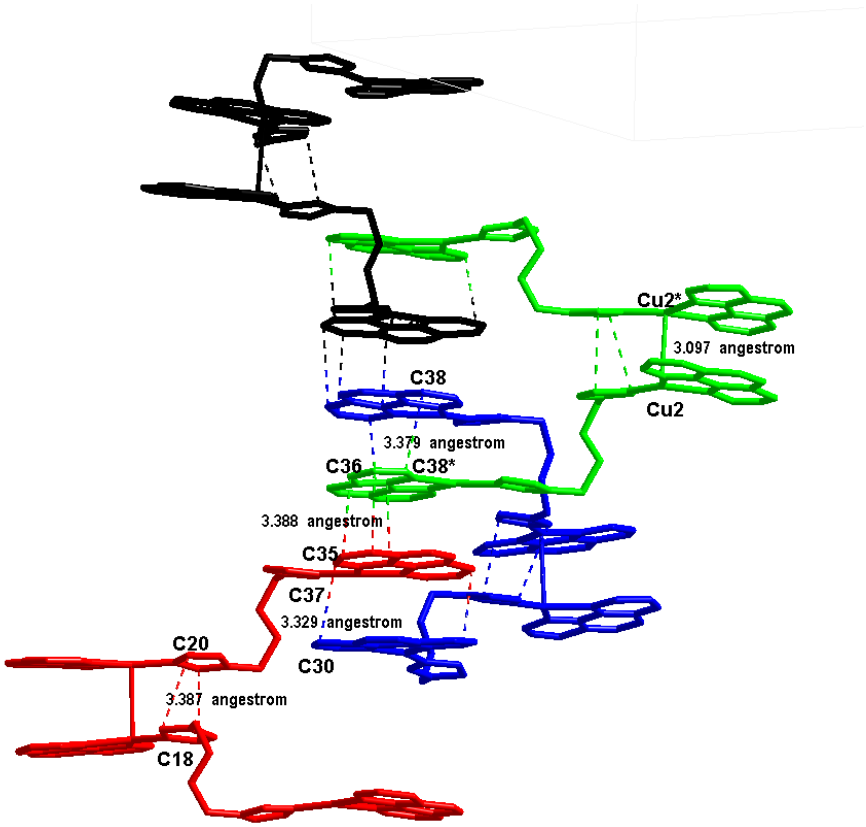

Figure S5. View of the short contact interactions between the adjacent $[Cu_2(phen)_2(bbi)]^{2+}$ cationic units.

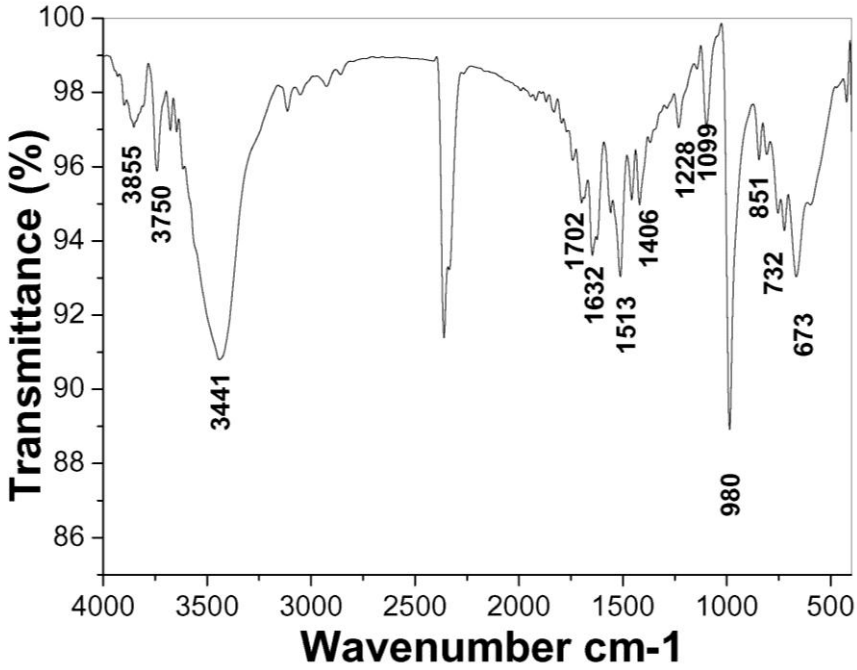

Figure S6. The IR spectrum of **1**.

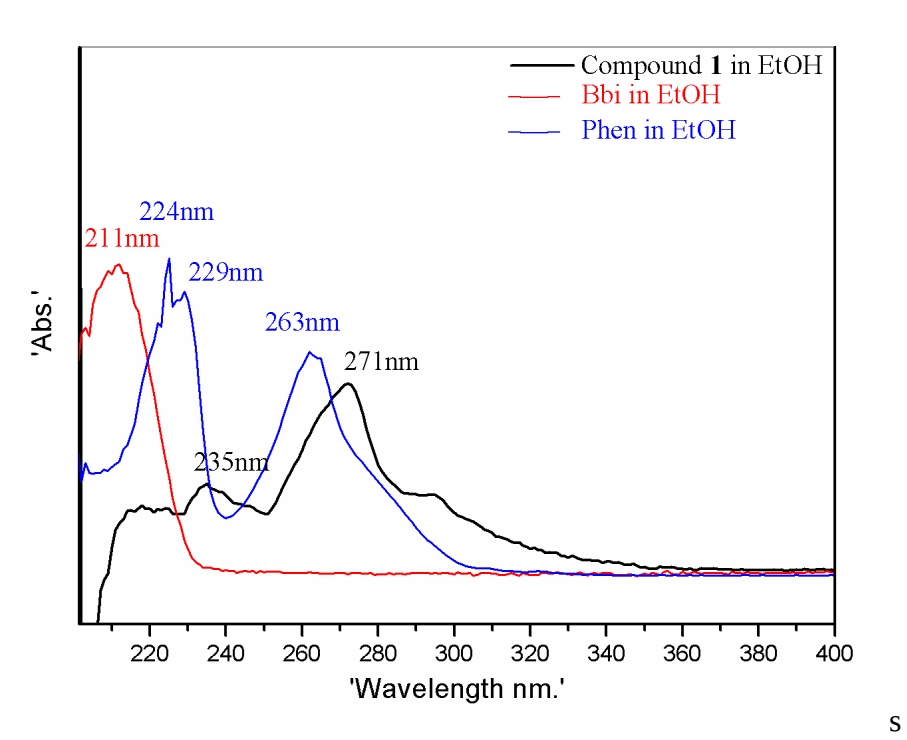

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Figure S7. UV spectra of ligands of bbi and phen molecules as well as compound **1** in EtOH.

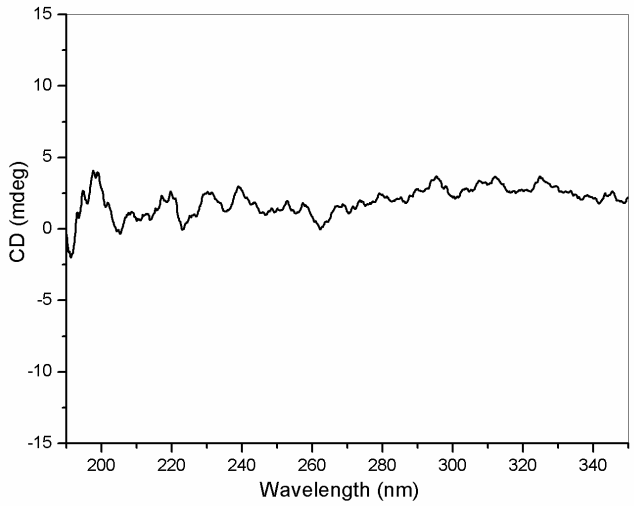

Figure S8. Solid-state CD spectrum of **1** (the mixture of $_{L}$-1 and $_{D}$-1).

The CD spectra of several samples of **1** were measured between 190 and 350 nm using a JASCO J-810 spectropolarimeter in solid state. However, it is too hard to differentiate the enantiomorphic crystals through the geometrical character in a racemic mixture under a microscope. The separated crystals, which are thought to be one kind of enantiomorphic crystal, did not show the expected dichroic signal, but some noise instead.