## (Supplementary information)

## Spontaneous resolution of 3D chiral

# hexadecavanadate-based frameworks incorporating achiral flexible and rigid ligands 

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Table S1 Crystal data and structure refinement for $\mathbf{1}$.

| Empirical formula | L-1 | D-1 |
| :---: | :---: | :---: |
|  | C78H75N20Cu5V16O38.5 | C78H75N20Cu5V16O38.5 |
|  | Cl | Cl |
| Formula weight | 3076.79 | 3076.79 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (A) | 0.71073 | 0.71073 |
| Crystal system | Tetragonal | Tetragonal |
| Space group | 14122 | 14122 |
| $a(\mathrm{~A})$ | 27.600(4) | 27.672(4) |
| $b$ ( $\AA$ ) | 27.600(4) | 27.672(4) |
| $c($ (̊) | 26.700(5) | 26.693(5) |
| Volume ( $\AA^{3}$ ) | 20339(6) | 20440(6) |
| Z | 8 | 8 |
| $\mathrm{D}_{\text {calc }}\left(\mathrm{mg} / \mathrm{m}^{3}\right)$ | 2.004 | 1.999 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 2.531 | 2.519 |
| $F(000)$ | 12160 | 12128 |
| Reflns collected | 73861 | 64690 |
| Unique reflns | 8955 | 8514 |
| R(int) | 0.1410 | 0.1210 |
| $\theta$ range (deg) | $3.05 \leq \theta \leq 25.00$ | $3.05 \leq \theta \leq 24.50$ |
| Limiting indices | $\begin{aligned} & -32 \leq h \leq 32, \quad-32 \leq k \leq 32, \\ & -28 \leq l \leq 31 \end{aligned}$ | $\begin{aligned} & -31<=\mathrm{h}<=30,-32<=\mathrm{k}<=32, \\ & -30<=1<=31 \end{aligned}$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.041 | 0.926 |
| Final $R$ indices [ $1>2 \sigma(I)]$ | $R_{1}=0.0748, w R_{2}=0.1861$ | $R_{1}=0.0620, w R_{2}=0.1471$ |
| $R$ indices (all data) | $R_{l}=0.1116, w R_{2}=0.2084$ | $R_{I}=0.1204, w R_{2}=0.1721$ |

Table S2. Selected Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{1}$.

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


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

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

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

# Symmetry transformations used to generate equivalent atoms: 

$\# 1-x+1 / 2, y,-z+7 / 4 \quad \# 2-x+1,-y+1, z+0$

## The details for the refinement:

In the refined structure of $\mathrm{L}_{\mathrm{L}}-1, \mathrm{~N} 9, \mathrm{O} 20, \mathrm{C} 4, \mathrm{C} 8, \mathrm{C} 10, \mathrm{C} 11, \mathrm{C} 13, \mathrm{C} 14, \mathrm{C} 15, \mathrm{C} 22$, 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 ${ }_{\mathrm{D}}-1, \mathrm{~N} 3, \mathrm{~N} 9, \mathrm{C} 4, \mathrm{C} 7, \mathrm{C} 8, \mathrm{C} 10, \mathrm{C} 11, \mathrm{C} 13, \mathrm{C} 14, \mathrm{C} 28, \mathrm{C} 29$, 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:
$\left[\mathrm{Cu}_{2}(\text { phen })_{2}(\mathrm{bbi})\right]_{2}[\mathrm{Cu}(\mathrm{bbi})]\left[\mathrm{V}_{16} \mathrm{O}_{38} \mathrm{Cl}\right] \cdot \mathbf{0 . 5} \mathrm{H}_{\mathbf{2}} \mathrm{O}$

The confirmation of the molecular formula is based upon the bond valence sum calculations $\left(\sum \mathrm{s}\right)$ and the charge balance. For $\mathrm{L}-\mathbf{1}$, 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 $4.68(\mathrm{~V} 8)$, respectively, and for the three Cu atoms are $1.12(\mathrm{Cu} 1), 1.16(\mathrm{Cu} 2)$ and $1.16(\mathrm{Cu} 3)$, respectively. For ${ }_{\mathrm{D}} \mathbf{- 1}$, the valence sums for all the V atoms are $4.71(\mathrm{~V} 1)$, 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 $1.11(\mathrm{Cu} 1), 1.14(\mathrm{Cu} 2)$ and $1.16(\mathrm{Cu} 3)$, respectively. The total sums of sixteen V are 72.68 for $_{\mathrm{L}} \mathbf{- 1}$ and 72.42 for ${ }_{\mathrm{D}} \mathbf{- 1}$. The average values for V atoms are 4.54 and 4.53 for $\mathrm{L}_{\mathrm{L}} \mathbf{- 1}$ and $\mathrm{D}_{\mathrm{D}} \mathbf{- 1}$, respectively, very close to the expected value 4.5 for $\mathrm{V}^{\mathrm{IV}}{ }_{8} \mathrm{~V}^{\mathrm{V}}{ }_{8}$. Thus the $\left\{\mathrm{V}_{16} \mathrm{O}_{38} \mathrm{Cl}\right\}$ cluster, has a calculated charge of -4.32 and -4.58 for ${ }_{L}-\mathbf{1}$ and ${ }_{D} \mathbf{- 1}$, respectively, which is approximately balanced by five $\mathrm{Cu}(\mathrm{I})$ ions.


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


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


TTT conformation
Bbil


Bbi2

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


Figure S4. Illustration of the bottle-like $\left\{\mathrm{Cu}_{2}(\mathrm{phen})_{2}(\mathrm{bbi})\right\}_{2}$ cationic dimer in $\mathrm{L}_{\mathrm{L}} \mathbf{- 1}$.


Figure S5. View of the short contact interactions between the adjacent $\left[\mathrm{Cu}_{2}(\text { phen })_{2}(\mathrm{bbi})\right]^{2+}$ cationic units.


Figure S6. The IR spectrum of $\mathbf{1}$.


Figure S7. UV spectra of ligands of bbi and phen molecules as well as compound $\mathbf{1}$ in EtOH .


Figure S 8 . Solid-state CD spectrum of $\mathbf{1}$ (the mixture of $\mathrm{L}_{\mathrm{L}}-1$ and $\mathrm{D}_{\mathrm{D}}-1$ ).

The CD spectra of several samples of $\mathbf{1}$ 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.

