Supplementary Material (ESI) for Chemical Communications

Supporting Information

Spontaneous resolution of 3D chiral polyoxometalate-based polythreaded framework consisting of achiral ligand

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The bond valence sum calculations for L-1 and D-1:

The bond valence sums (BVS)[1] are 4.415, 5.152, 5.135, 5.167, 5.256, 5.020, 5.090, 4.370, 5.138 and 5.100 for ten independent vanadium atoms (V1-V10), respectively, in L-**1**. While the correspongding values are 4.400, 5.161, 5.142, 5.156, 5.294, 5.129, 5.084, 4.396, 5.188 and 5.149 for ten independent vanadium atoms (V1-V10), respectively, in D-**1**. The calculated results reveal that, in the structure of the polyanion of **1**, two (V1 and V8) out of the ten vanadium centers are in the +4 oxidation state, and other vanadium centers (V2, V3, V4, V5, V6 , V7, V9 and V10) are +5 oxidation state. This result is similar to that in the reported complexes.[2-4] The values of BVS for Cu1, Cu2 and Cu3 centers are 1.557, 0.873 and 0.896 in L-**1** and 1.579, 0.893 and 0.922 in D-**1**, respectively, suggesting that the Cu1 atom in **1** exhibits an oxidation state of +2, and Cu2 and Cu3 atoms have an oxidation state of +1.

[1] The valence sum calculations are performed on a program of bond valence calculator, version 2.00 February 1993, written by C. Hormillosa with assistance from

S. Healy, distributed by I. D. Brown.

[2] A. Bino, S. Cohen and C. Heitner-Wirguin, *Inorg. Chem.,* 1982, **21**, 429.

[3] Y. Hayashi, N. Miyakoshi, T. Shinguchi and A. Uehara, *Chem. Lett.,* 2001, 170.

[4] Y. G. Li, Y. Lu, G. Y. Luan, E. B. Wang, Y. B. Duan, C. W. Hu, Ni. H. Hu and H. Q. Jia, *Polyhedron,* 2002, **21**, 2601.

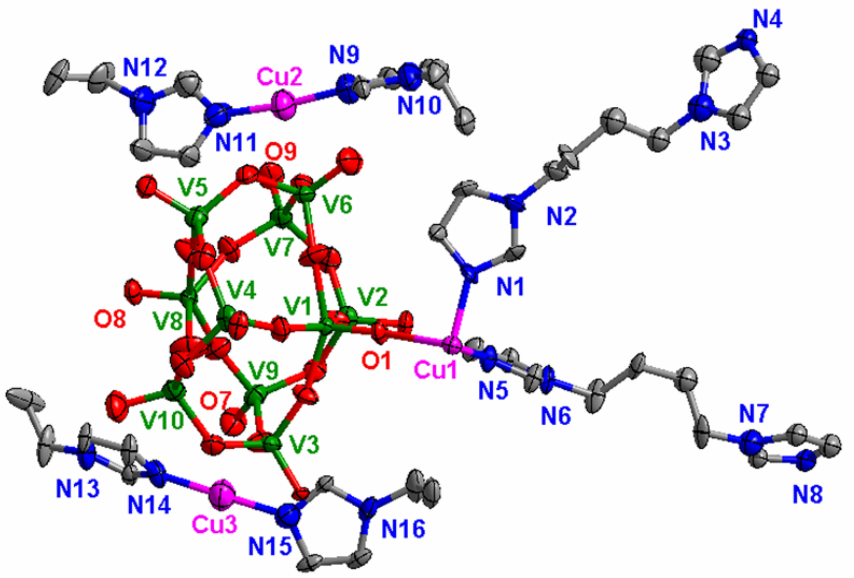


Figure S1. ORTEP diagram of the asymmetric unit of D-**1**with thermal ellipsoids at the 30% probability displacement, the hydrogen atoms and water molecules are omitted for clarity.

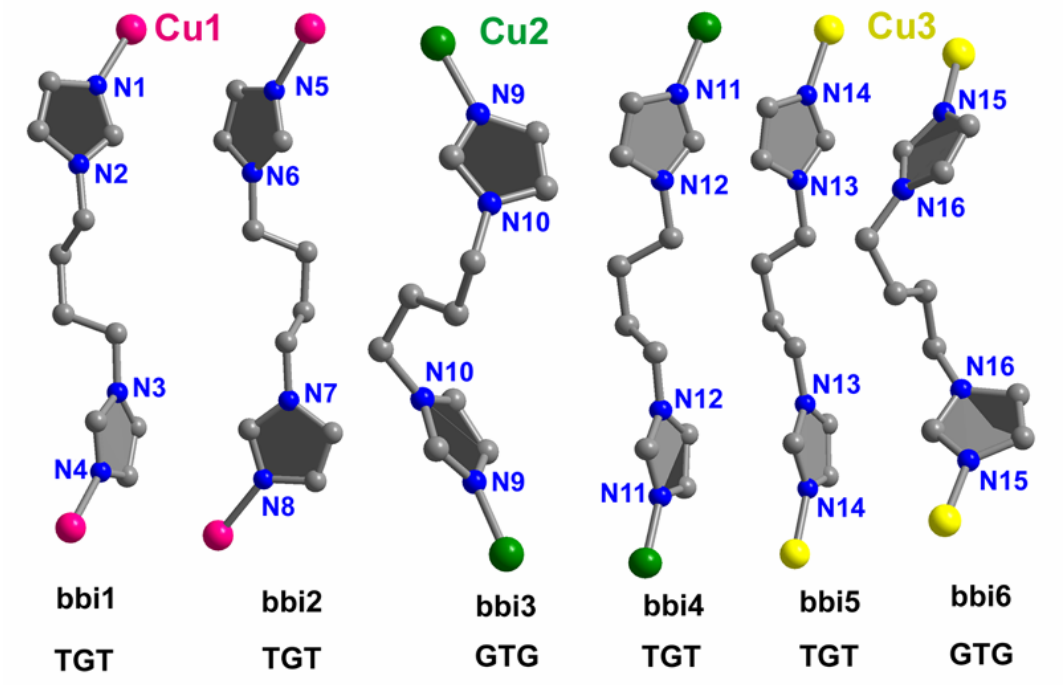
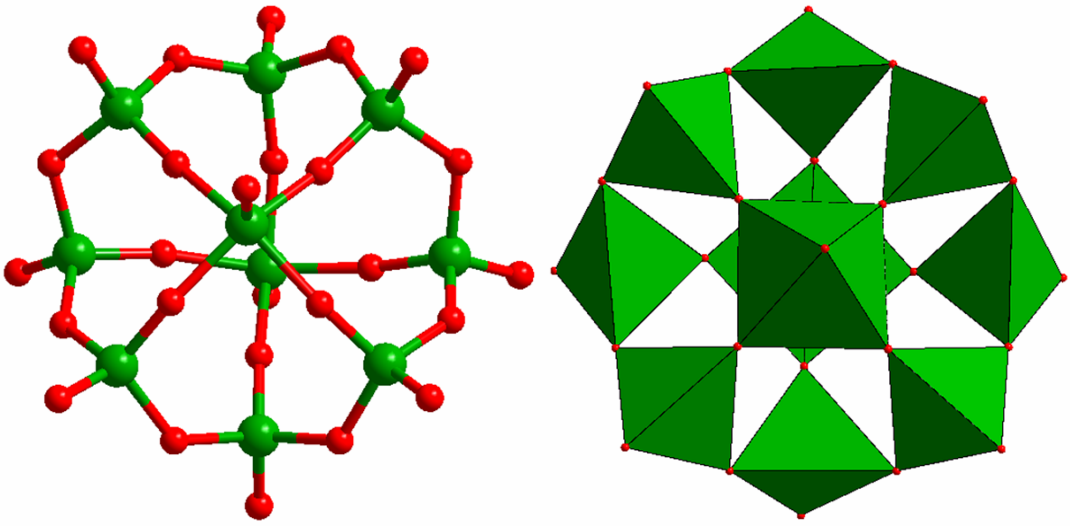


Figure S2. Ball-stick representation of the different conformations of six bbi ligands.

In compounds L-**1** and D-**1**, there are six kinds of bbi ligands. They all adopt a bis-monodentate coordination mode to bridge two metal centers. The bbi1 and bbi2 coordinate to Cu1 cations and adopt TGT (T = trans, G = gauche) conformations with the dihedral angles between two imidazol rings of 33.4º and 33.0º, respectively. While the bbi3 and bbi4 coordinate to Cu2 ions with GTG and TGT conformations with the corresponding dihedral angles of 38.5º and 24.7º, respectively. And the bbi5 and bbi6 coordinate to Cu3 ions with the different TGT and GTG conformations with the corresponding dihedral angles of 26.5º and 37.2º, respectively.



(a) **(b)**

Figure S3. Ball-stick (a) and polyhedral (b) representations of $[V_{10}O_{26}]^{4-}$ polyoxoanion.

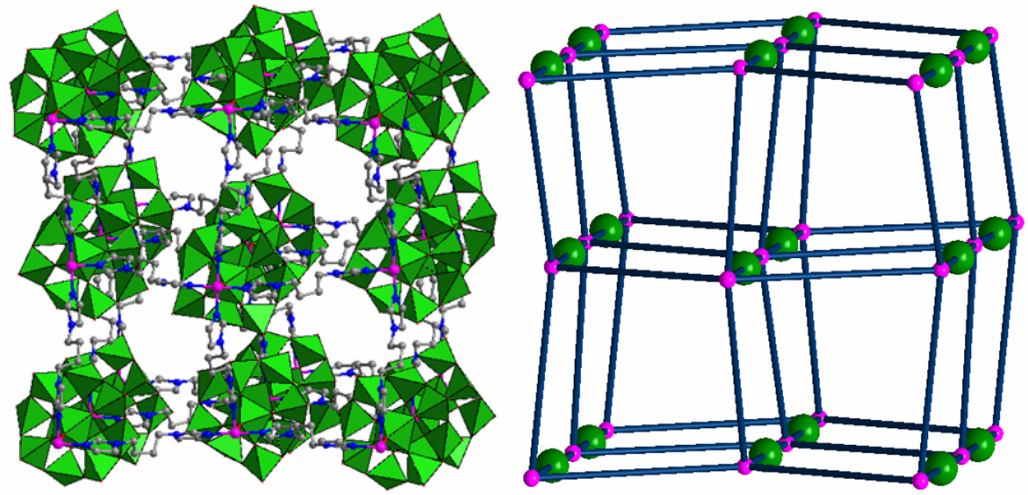
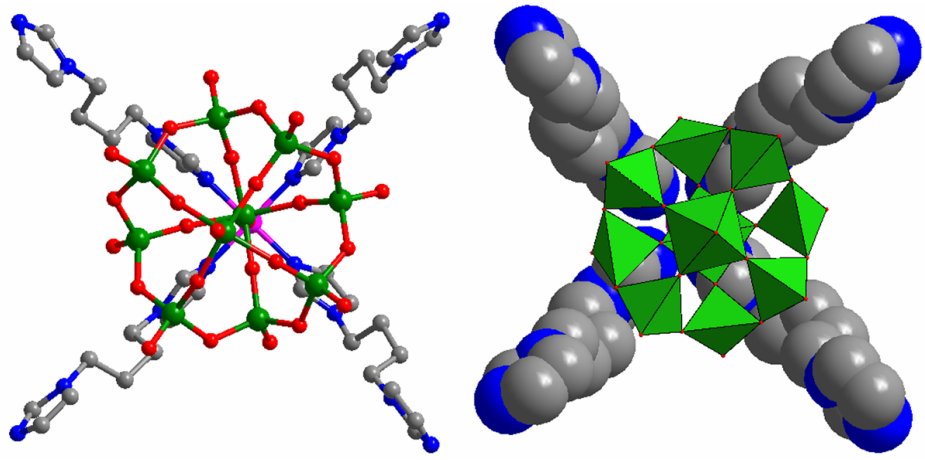
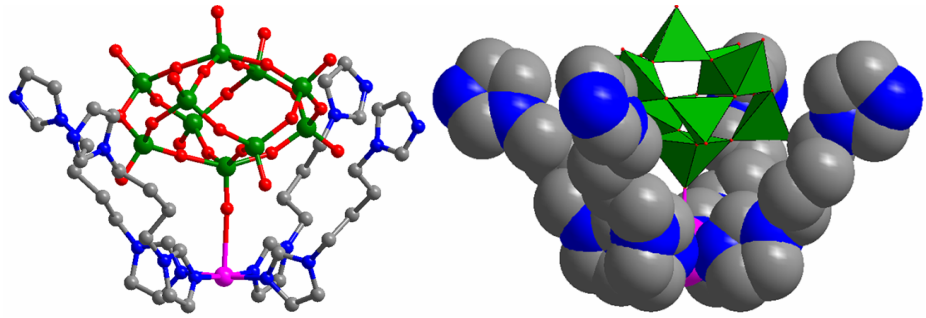


Figure S4. Schematic view of the twisted α-Po topology formed by Cu1, bbi1, bbi2 and $[V_{10}O_{26}]^{4-}$ polyoxoanion.



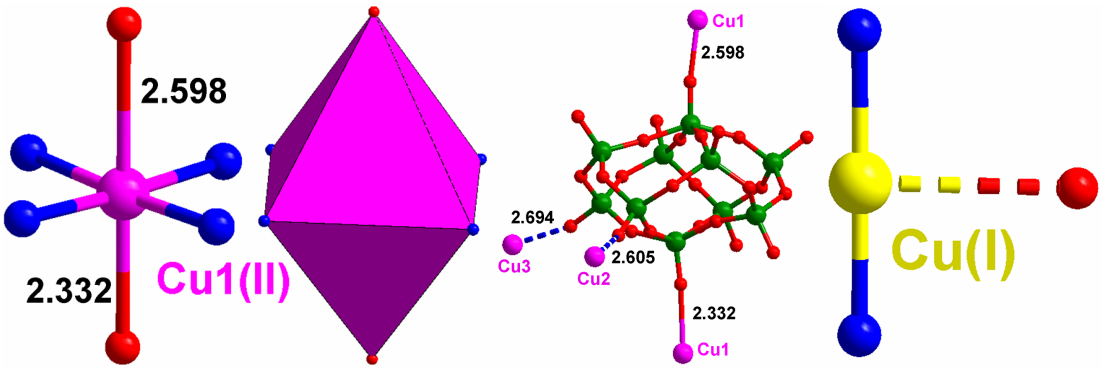
(a)



(b)

Figure S5. Ball-stick (left), and polyhedral and space-filling (right) representations of

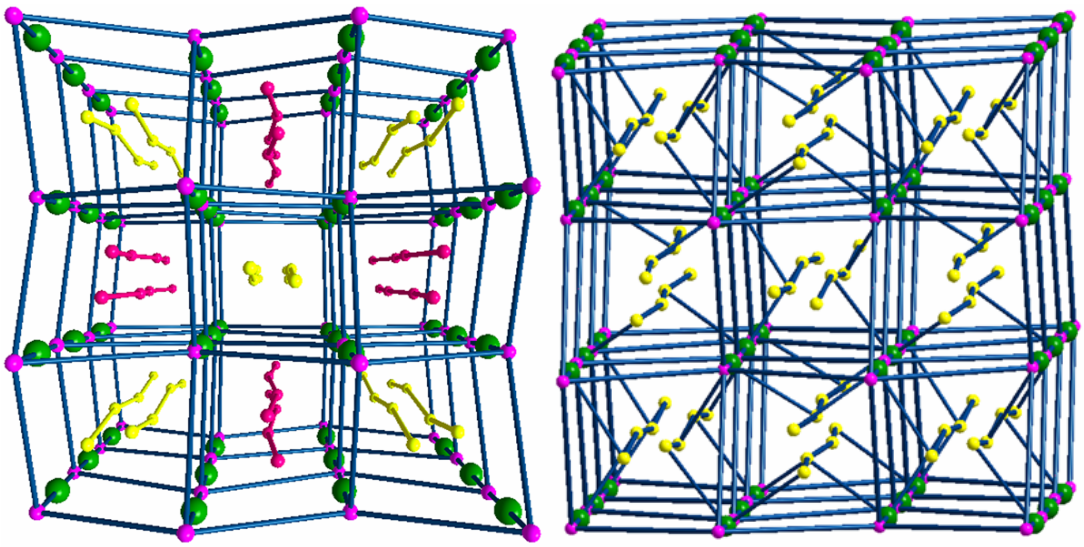
a floriated subunit in which two bbi1 and two bbi2 ligands act as petal and $[V_{10}O_{26}]^{4-}$ polyoxoanion acts as stamen along the different directions in (a) and (b).



(a) (b) (c)

Figure S6. (a) Ball-stick and polyhedral representations of a 6-connected node [Cu(II)]. (b) Ball-stick representation of a $[V_{10}O_{26}]^{4-}$ polyoxoanion as a 4-connected node coordinating to two Cu1 caions with covalent bonds and Cu2 and Cu3 cations with Cu-O interactions. (c) View of a Cu(I) cation as a 3-connected node.

The Cu-O distances are slightly different in L-**1** and D-**1**.(Cu1-O1 2.596 Å, Cu1-O8 2.331 Å, Cu2-O9 2.605 Å and Cu3-O7 2.694 Å in L-**1**, Cu1-O1 2.598 Å, Cu1-O8 2.332 Å, Cu2-O9 2.61Å and Cu3-O7 2.697 Å in D-**1**.)



(a) (b)

Figure S7. (a) Schematic representation of a polythreaded framework in compound **1**. (b) Schematic representation of the (3,4,6)-connected framework with

$(6.8^2)_2(6^5.8)(4^4.6^8.8^3)$ topology. (yellow, pink and green balls represent 3-, 4- and 6-connected nodes, respectively)

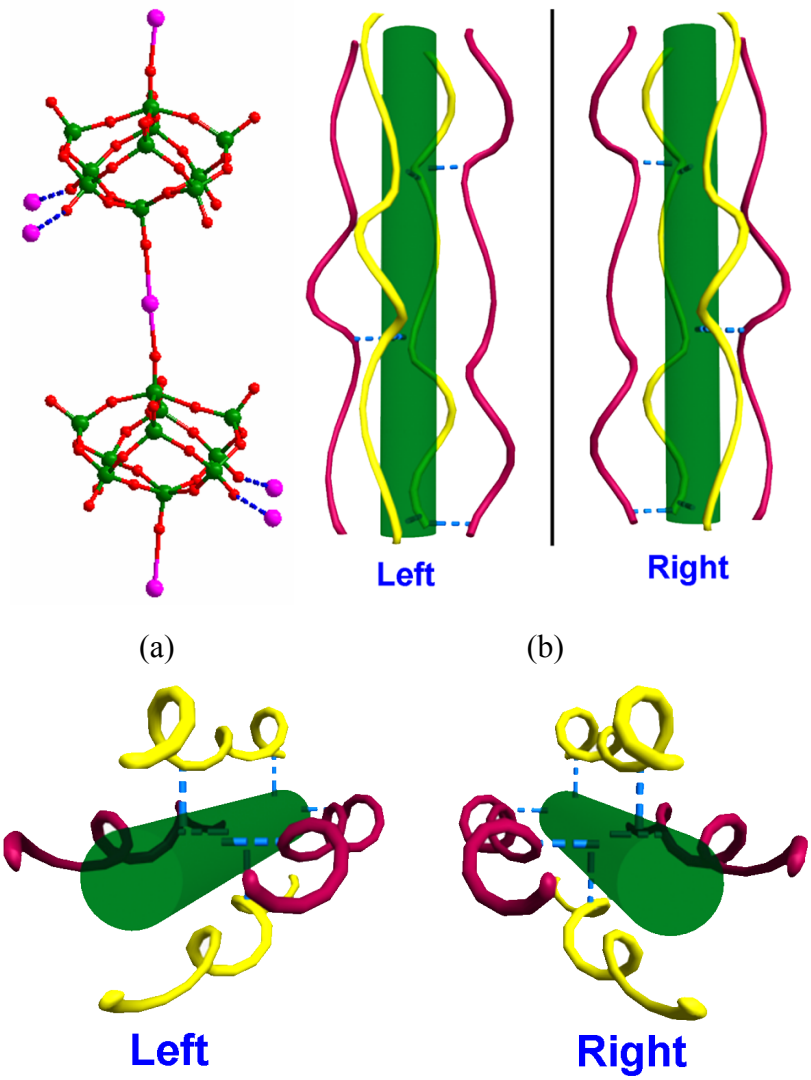
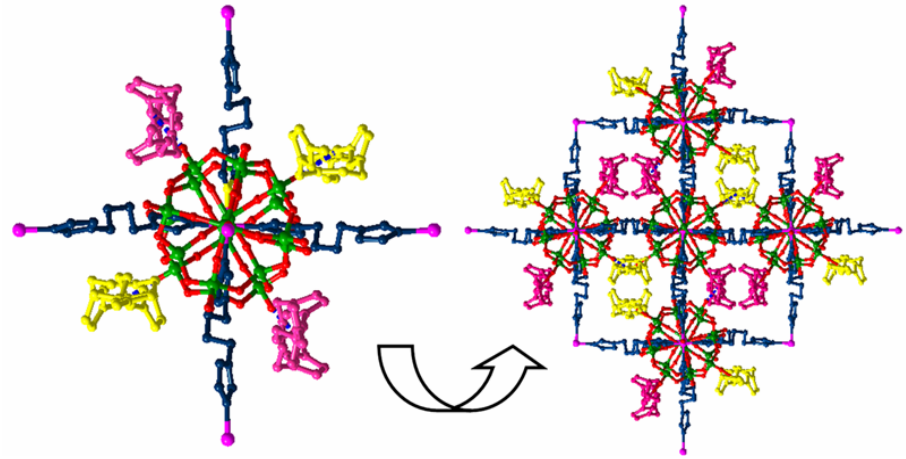


Figure S8. (a) Ball-stick representation of a $[Cu^{II}Cu^{I}_2V_{10}O_{26}]_\infty$ chain with a 2-fold screw axis. (b) and (c) Schematic view of the chiral subunit $[Cu^{II}Cu^{I}_2(bbi)_2V_{10}O_{26}]_\infty$ along the different directions (left in L-**1**, right in D-**1** and dashed lines represent Cu(I)-O interaction).



(a) (b)

Figure S9. (a) Ball-stick representation of a chiral subunit $[Cu^{II}Cu^{I}_{2}(bbi)_{2}V_{10}O_{26}]_{\infty}$ coordinating to four bbi ligands (two bbi1 and two bbi2) with similar conformations. (b) View of the whole 3D structure of D-**1**.

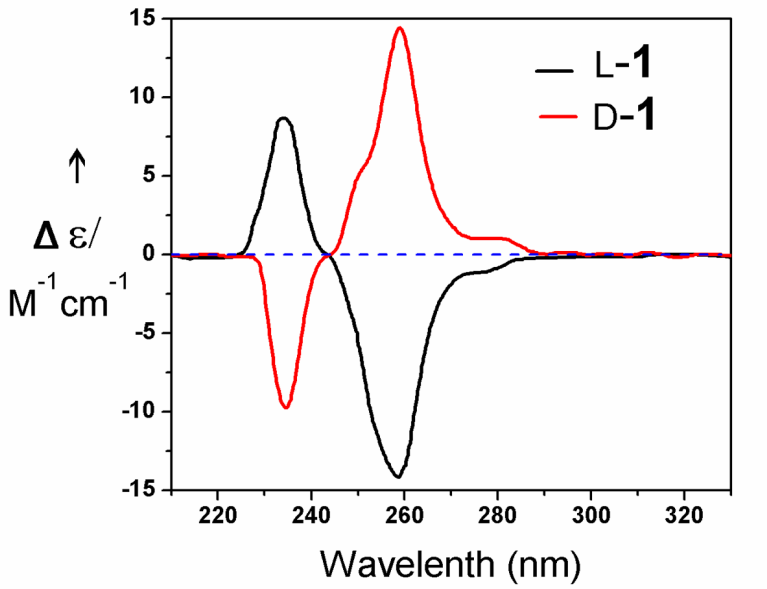


Figure S10. CD spectra of L-**1** and D-**1** in DMSO solution (L-**1** $c = 8.0 \times 10^{-4}$ M, D-**1** $c = 8.1 \times 10^{-4}$ M).

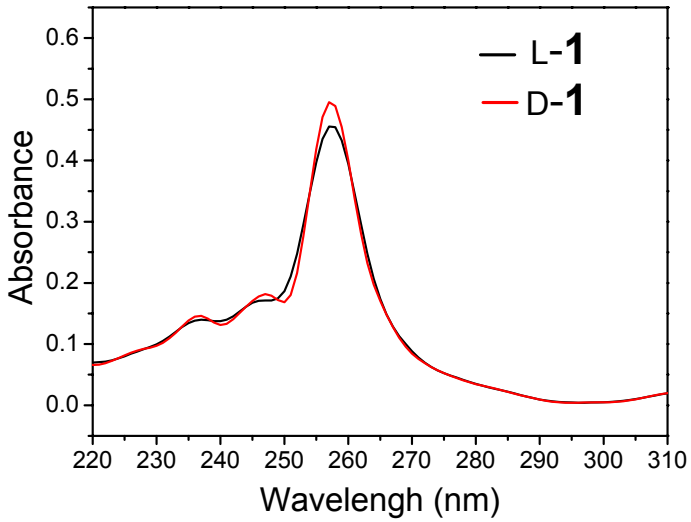


Figure S11. UV-Vis spectra of L-**1** and D-**1** in DMSO solution (L-**1** $c = 1.45 \times 10^{-5}$ M, D-**1** $c = 1.50 \times 10^{-5}$ M).

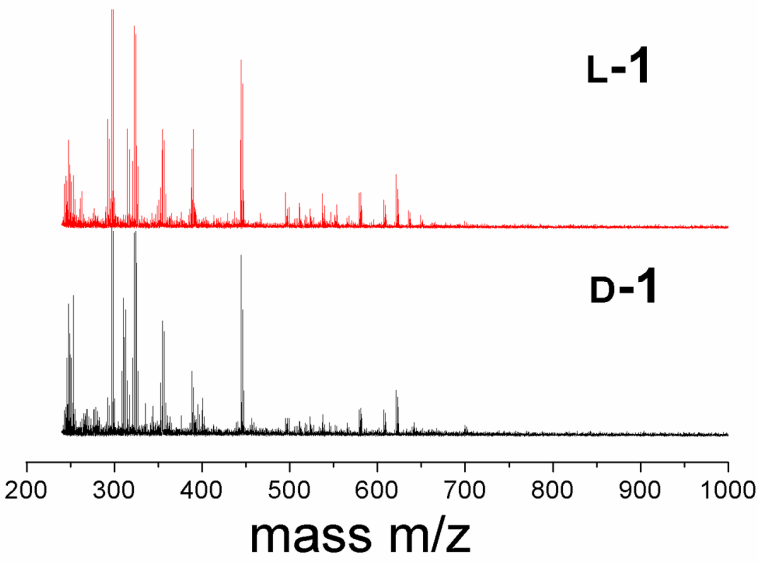


Figure S12. Electrospray ionization mass spectra of L-**1** and D-**1** in DMSO solution.

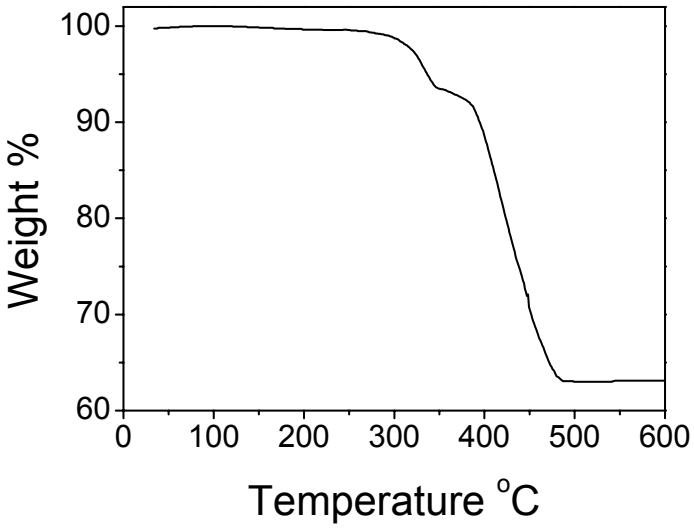


Figure S13. The TG curve of the mixture of L-**1** and D-**1**. The compound **1** was stable up to 253°C.