## Electronic Supplementary Information for MS:

# An unprecedented fivefold interpenetrated lvt network containing the exceptional racemic motifs originated from nine interwoven helices

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**The synthesis of compound 1:**

We learn from previous literature that it is benefit to complete deprotonation of carboxylic acids under basic solution would be essential in order to bind metal ions. Triethylamine ($Et_3N$) is a stronger base, and it can completely deprotonate carboxylic acids, but with poor affinity for binding to metal ions, thus ensuring the formation of 3D network (O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861). Furthermore, the paddle-wheel cluster motif is liable to form under basic conditions (see Refs: H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571; B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.* 2000, **122**, 11559; J. Kim, B. Chen, T. M. Reineke, H. L, M. Eddaoudi, D. B. Moler, M. O'Keeffe, and O. M. Yaghi, *J. Am. Chem. Soc.* 2001, **123**, 8239; M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.* 2001, **123**, 4368). Therefore, we chose $Et_3N$ as a deprotonated agent in the synthesis of complex **1**.

**[Cu(oba)($H_2O$)]$_2$·0.5$H_2O$** (**1**): A mixture of $CuCl_2·2H_2O$ (0.5 mmol, 0.085 g), $H_2$oba (0.5 mmol, 0.129 g), triethylamine (0.15 mL) and water (10 mL) was stirred for 15 min in air, then transferred and sealed in a 23ml Parr Teflon-lined stainless steel vessel, heated to 160℃ for 5 days and then cooled to room temperature at a rate of 10℃/h. The resulting blue block crystals were filtered, washed, and dried in air, yield 0.154 g, 45% based on Cu. Elemental analysis found: C, 49.28%; H, 3.26%. Calcd. for: C, 49.13%; H, 3.09%.

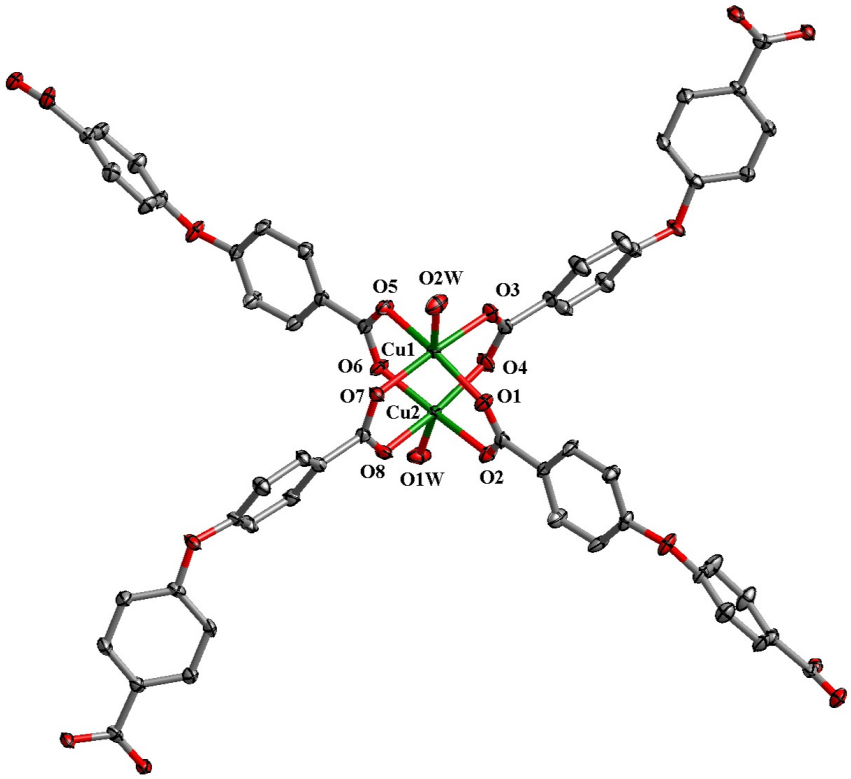


**Fig. S1** ORTEP representation showing the local coordination geometries of the two crystallographically distinct Cu atoms in **1** (50% probability ellipsoids).

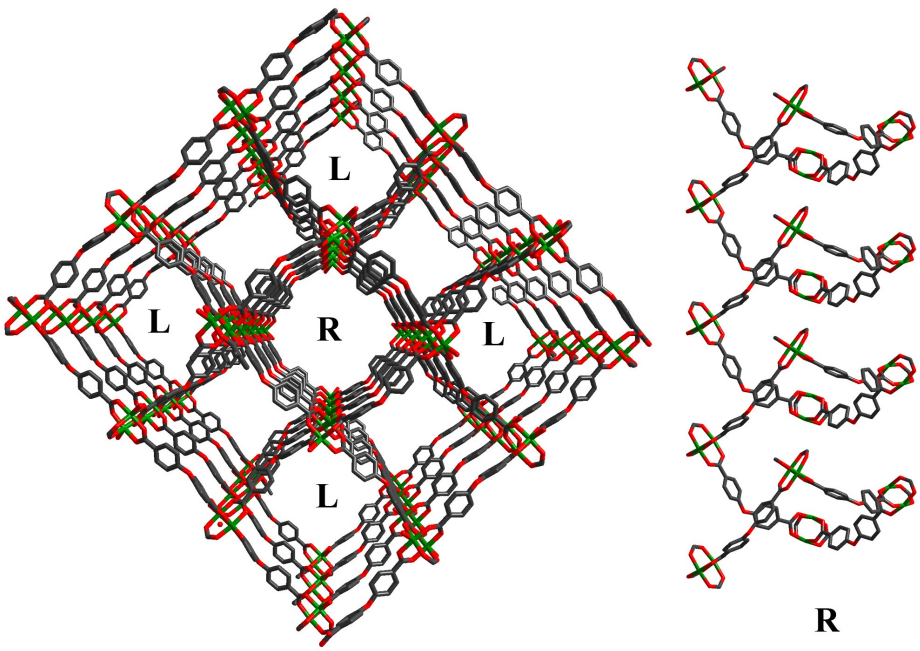


**Fig. S2** Perspective views of the 3D $4^2 8^4$ network (left) and a helical fragment (right). R and L represent right-handed and left-handed, respectively.

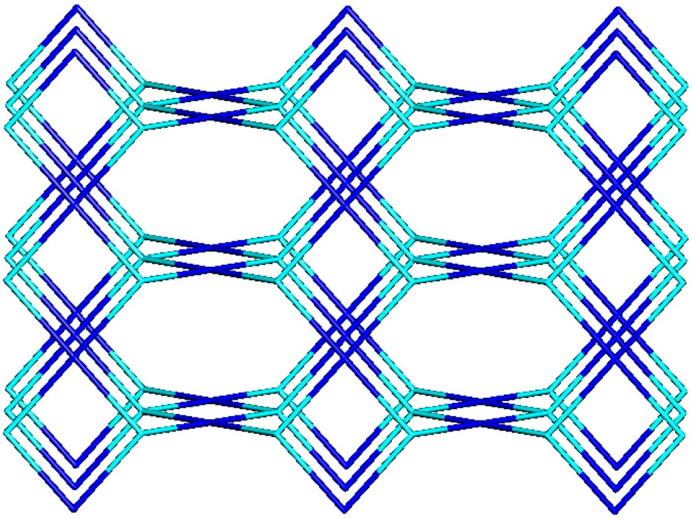

**Fig. S3** PtS topology

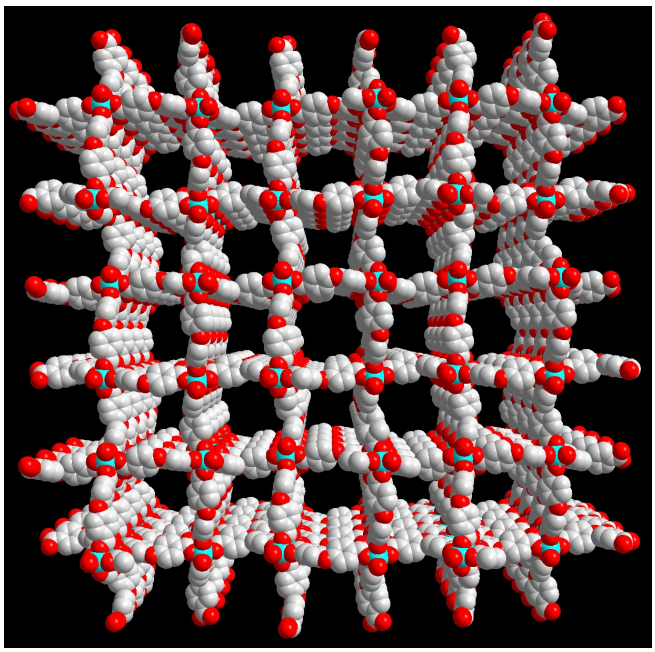

**Fig. S4** A space-filling view of a single net, showing the two types of channels.

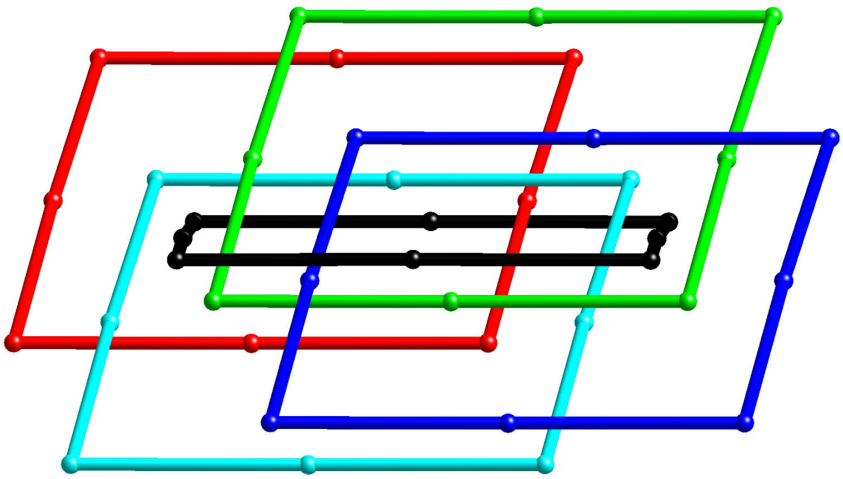

**Fig. S5** The detail of the interpenetration of any 8-membered ring (black) with four others from four independent nets.

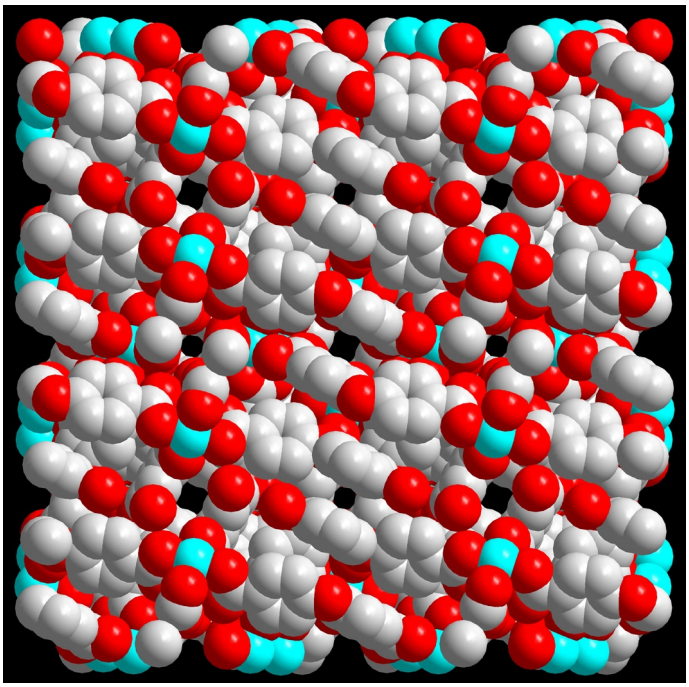

**Fig. S6** A space-filling diagram of the five-fold interpenetrated **lvt** network viewed down the *c* axis (guest water molecules have been omitted); gray C, red O, blue Cu.