Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

Progressive Decoration of Pentanuclear Cu(II) 12-Metallacrown-4 Nodes Towards Targeted 1- and 2D Extended Networks

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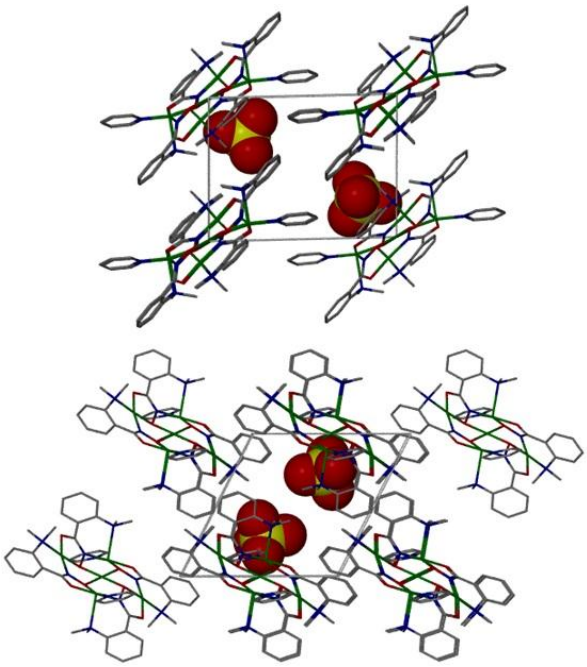

Fig. S1 Packing arrangement observed in **2** as viewed along the *b* (top) and *a* (bottom) cell directions. The pyridine solvent of crystallisation has been omitted for clarity. ClO_4^- counter anions are space-fill represented.

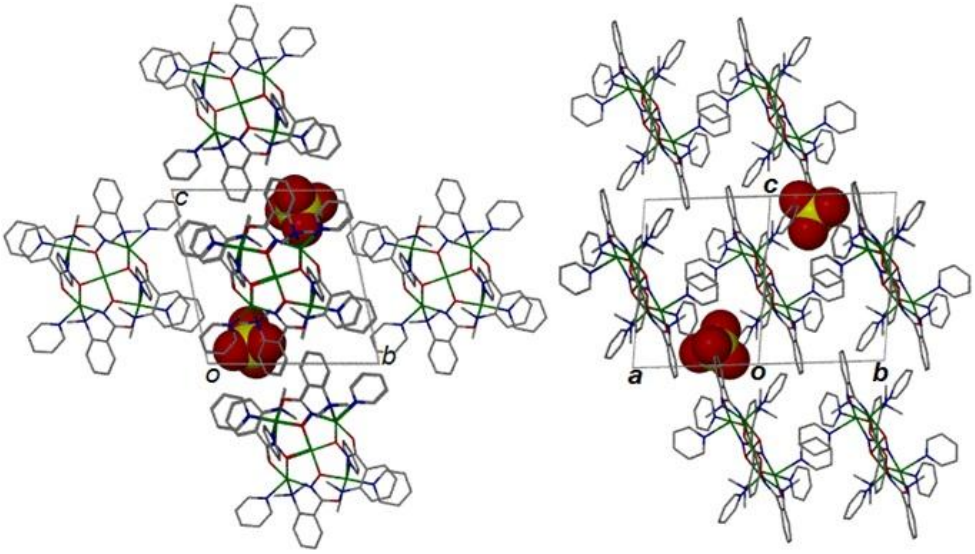

Figure S2 Packing observed in **3** as viewed along the *a* axis (left) and along the *ab* direction of the unit cell (right) . All Hydrogen atoms have been omitted for clarity. The ClO_4^- counter ions within the cell are represented as space-fill.

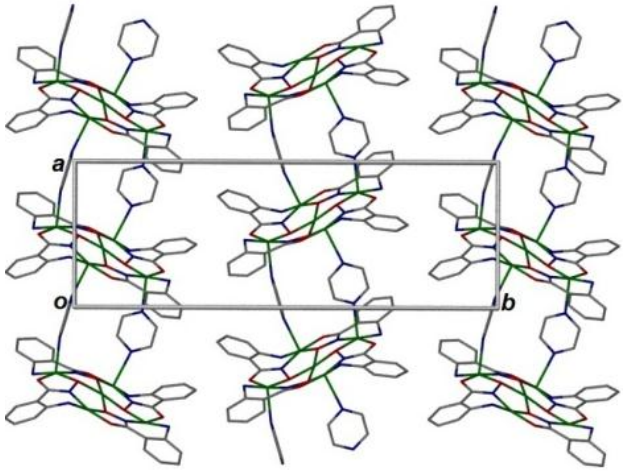

Figure S3 Three 1-D rows in **6** illustrating the alternating [Cu_5] tilt angles along the *b* direction of the unit cell.

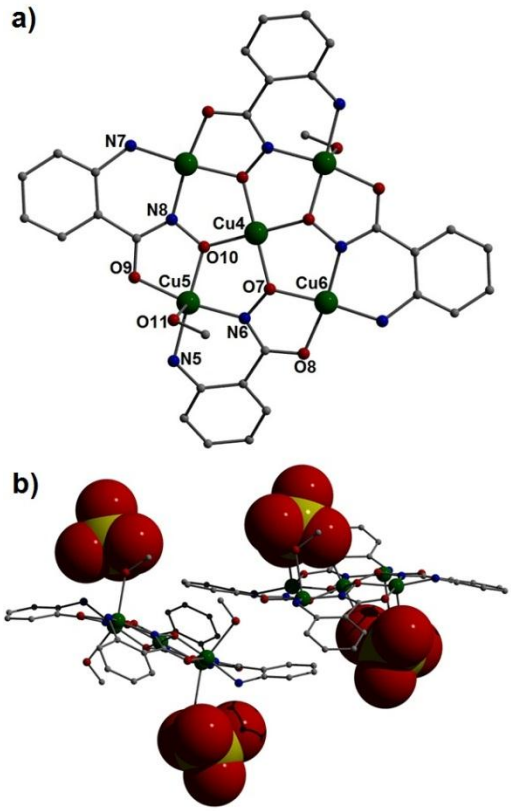

Figure S4 (a) Crystal structure of **7** showing only one of the two [Cu_5] moieties in the asymmetric unit. (b) The asymmetric units in **7** illustrating the close proximity of the two crystallographically unique [Cu_5] species. The ClO_4^- counter anions are represented as space-fill.

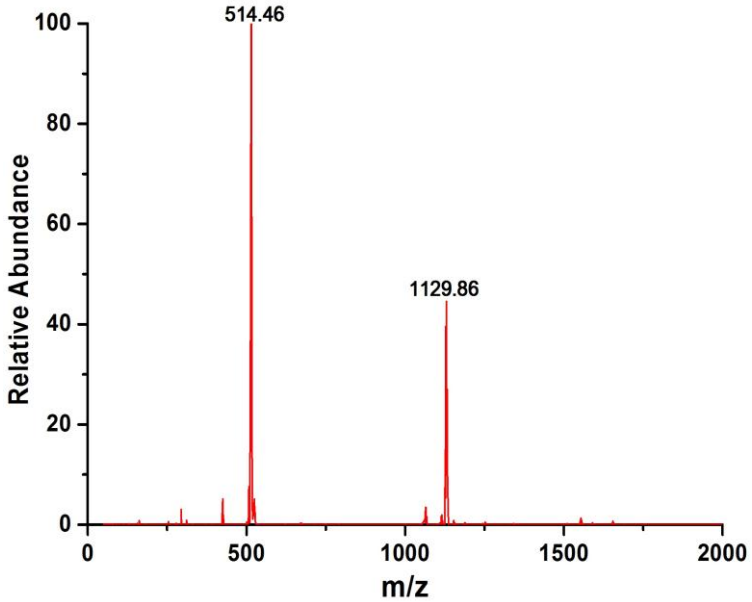

Fig. S5 Mass spectrum of **1** from a 50:50 MeCN/H_2O solvent matrix. TOF MS-ES (%) m/z: 514.46 (100, $[Cu(II)_5(L_1)_4]^{2+}$), 1129.86 (44, $[\{Cu(II)_5(L_1)_4\} + \{ClO_4\}]^+$).

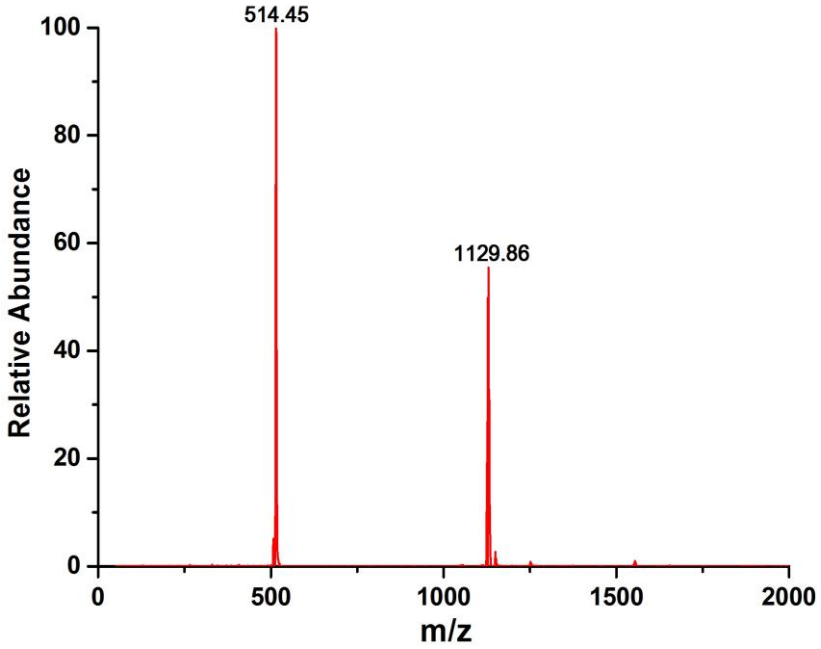

Fig. S6 Mass spectrum of **2** from a 50:50 MeCN/H_2O solvent matrix. TOF MS-ES (%) m/z: 514.45 (60, $[Cu(II)_5(L_1)_4]^{2+}$), 1129.86 (55, $[\{Cu(II)_5(L_1)_4\} + \{ClO_4\}]^+$).

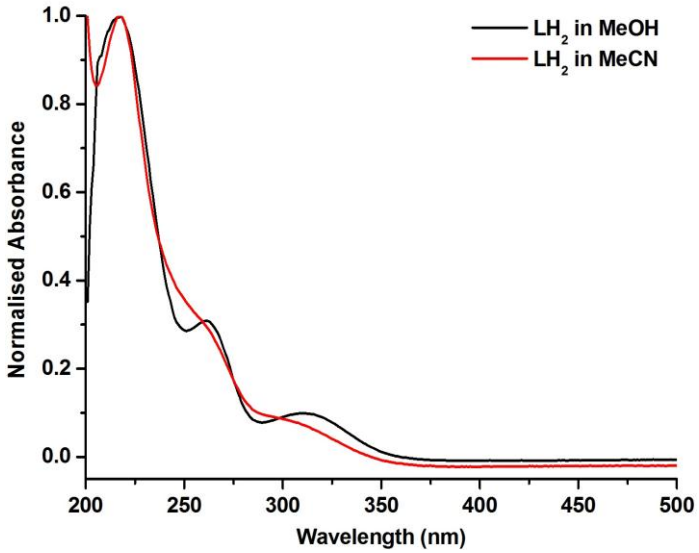

Fig. S7 Overlay UV-vis spectra of L_1H_2 obtained from MeOH (black line) and MeCN (red line) solutions.

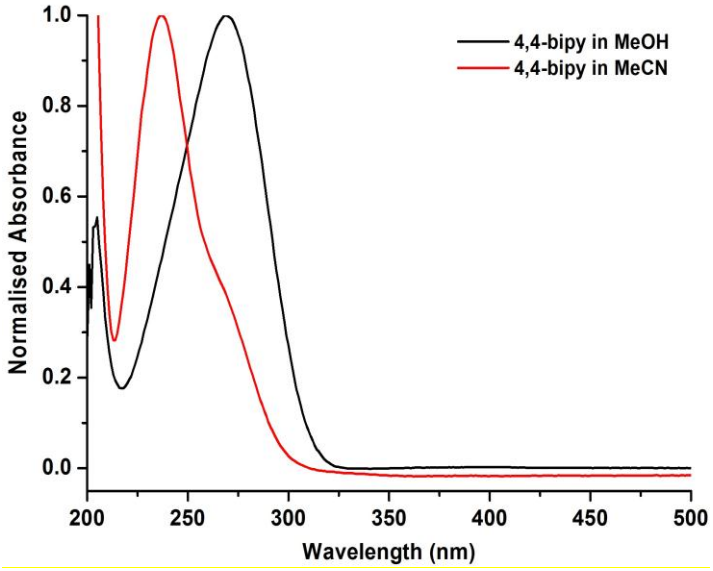

Fig. S8 Overlay UV-vis spectra of the 4,4'-bipyridine ligand obtained from MeOH (black line) and MeCN (red line) solutions.

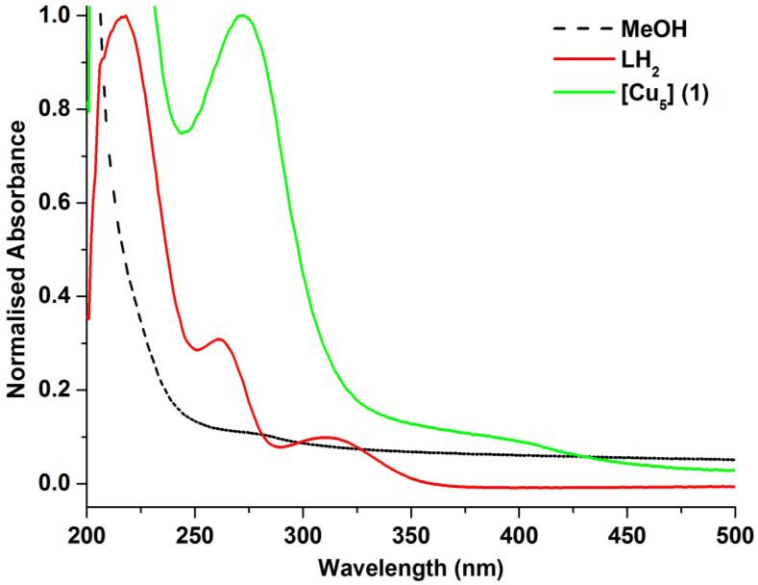

Fig. S9 Overlay UV-vis spectra of MeOH (dashed black line), L_1H_2 (red line) and $[Cu(II)_5(L_1)_4(MeOH)_2](ClO_4)_2$ (**1**) (green line).

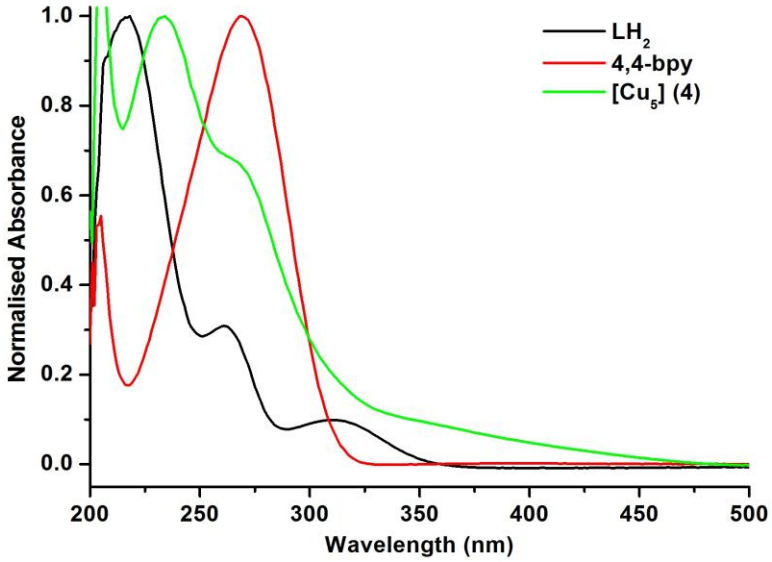

Fig. S10 Overlay UV-vis spectra in MeOH of L_1H_2 (black line), 4,4'-bipyridine (red line) and $\{[Cu_5(L_1)_4(4,4'\text{-bipy})_3](ClO_4)_2(H_2O)\}_n$ (**4**) (green line).

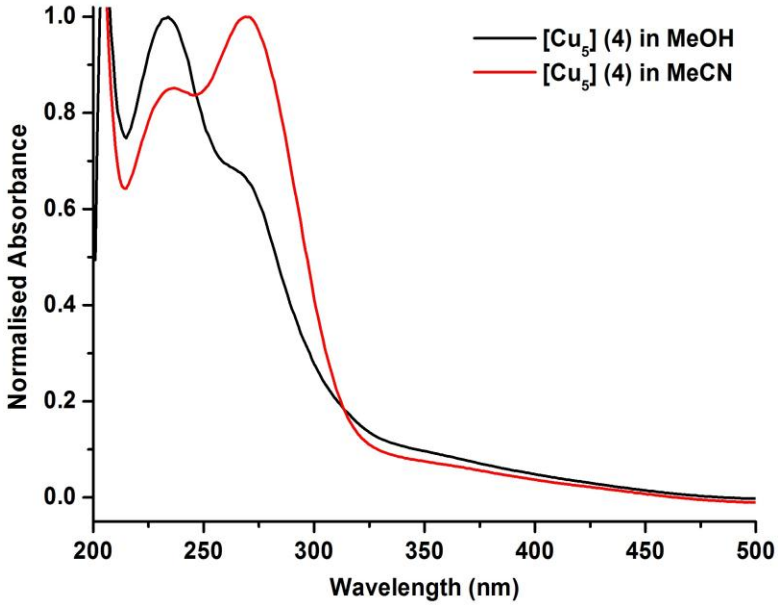

Fig. S11 Overlay UV-vis spectra of $\{[Cu_5(L_1)_4(4,4'\text{-bipy})_3](ClO_4)_2(H_2O)\}_n$ (**4**) obtained from MeOH (black line) and MeCN (red line) solutions.

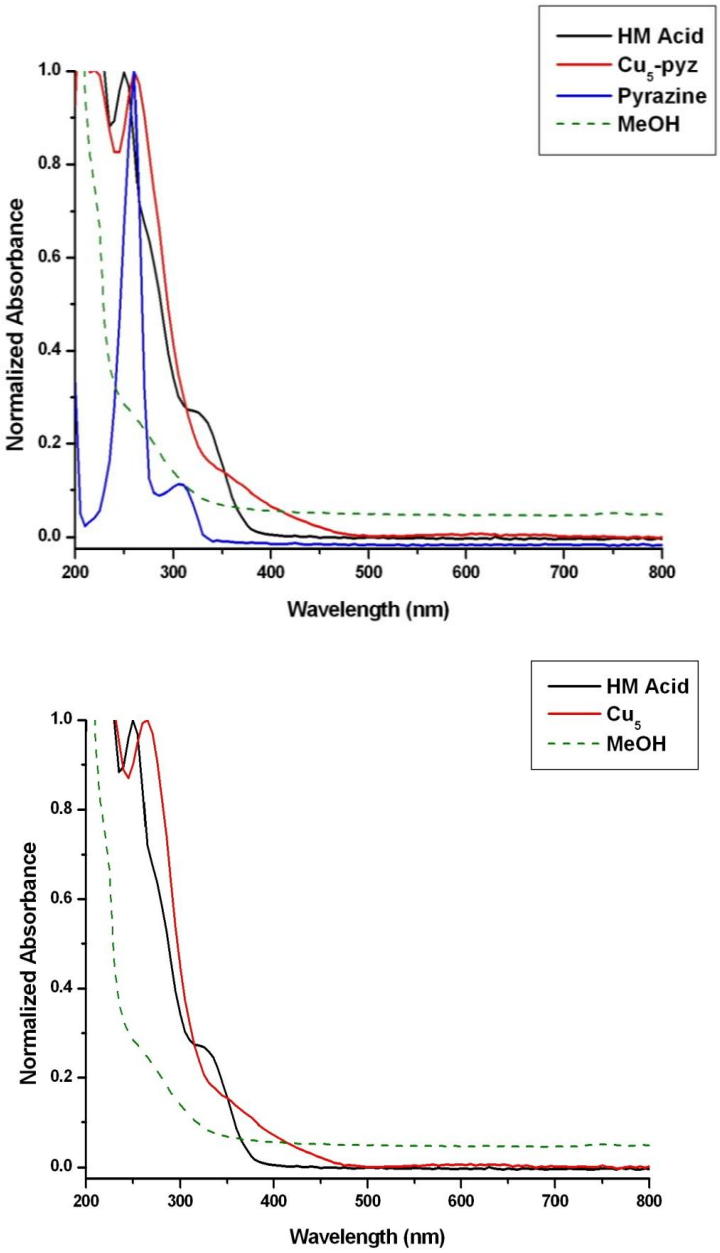

Fig. S12 (top) Overlay UV-vis spectra in MeOH (dashed line) of L_2H_2 (black line), pyrazine (blue line) and $\{[Cu_5(L_2)_4(pz)_2(MeOH)_3](ClO_4)_2.MeOH\}_n$ (**6**) (red line). (Bottom) Overlay UV-vis spectra in MeOH (dashed line) of L_2H_2 (black line) and $[Cu_5(L_2)_4(MeOH)_4](ClO_4)_2.H_2O$ (**7**) (red line).

Fig. S13 The UV-vis methanolic solutions of L_1H_2 (left), $[Cu(II)_5(L)_4(MeOH)_4(ClO_4)_2]$ (**1**) (middle) and the extended network (*dissociated in solution*) $\{[Cu(II)_5(L)_4(4,4\text{-bipy})_3](ClO_4)_2(H_2O)\}_n$ (**4**) (right) used in this work.