Electronic Supplementary Information

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

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\textbf{Fig. S1} Packing arrangement observed in 2 as viewed along the \textit{b} (top) and \textit{a} (bottom) cell directions. The pyridine solvent of crystallisation has been omitted for clarity. ClO$_4$\textsuperscript{−} 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$_3$] 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/H₂O solvent matrix. TOF MS-ES (％) m/z: 514.46 (100, [Cu(II)₅(L₁)₄]²⁺), 1129.86 (44, [[Cu(II)₅(L₁)₃] + {ClO₄}⁺]).

**Fig. S6** Mass spectrum of 2 from a 50:50 MeCN/H₂O solvent matrix. TOF MS-ES (％) m/z: 514.45 (60, [Cu(II)₅(L₁)₃]²⁺), 1129.86 (55, [[Cu(II)₅(L₁)₃] + {ClO₄}⁺]).
**Fig. S7** Overlay UV-vis spectra of $L_1H_2$ obtained from MeOH (black line) and MeCN (red line) solutions.

![Overlay UV-vis spectra of $L_1H_2$](image)

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

![Overlay UV-vis spectra of the 4,4'-bipyridine ligand](image)

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

![Overlay UV-vis spectra of MeOH, $L_1H_2$ and Cu complex](image)
Fig. S10 Overlay UV-vis spectra in MeOH of L1H2 (black line), 4,4'-bipyridine (red line) and [{Cu5(L1)4(4,4'-bipy)3(ClO4)2(H2O)}n (4) (green line).

Fig. S11 Overlay UV-vis spectra of [{Cu5(L1)4(4,4'-bipy)3(ClO4)2(H2O)}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$_2$H$_2$ (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$_2$H$_2$ (black line) and [Cu$_5$(L$_2$)$_4$(MeOH)$_4$](ClO$_4$)$_2$.H$_2$O (7) (red line).
Fig. S13 The UV-vis methanolic solutions of L₂H₂ (left), [Cu(II)₅(L)₄(MeOH)₄(ClO₄)₂] (1) (middle) and the extended network (dissociated in solution) {[Cu(II)₅(L)₄(4,4-bipy)₃](ClO₄)₂(H₂O)}ₙ (4) (right) used in this work.