# Self-assembly of a constitutional dynamic library of Cu(II) coordination polygons and reversible sorting by crystallization.

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## Electronic Supplementary Information

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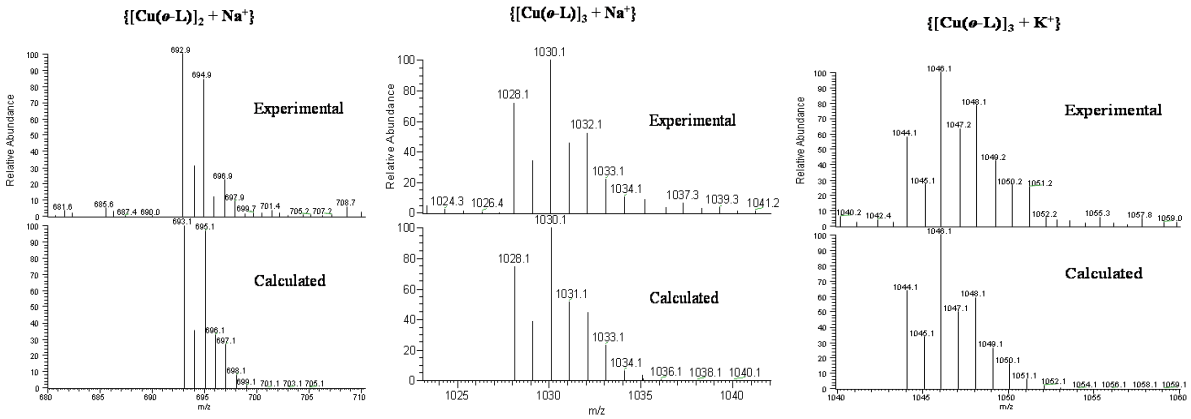


**Fig. S1.** Experimental and calculated isotopic patterns for {[Cu(*o*-L)]$_2$+Na$^+$}, {[Cu(*o*-L)]$_3$+Na$^+$} and {[Cu(*o*-L)]$_3$+K$^+$}.

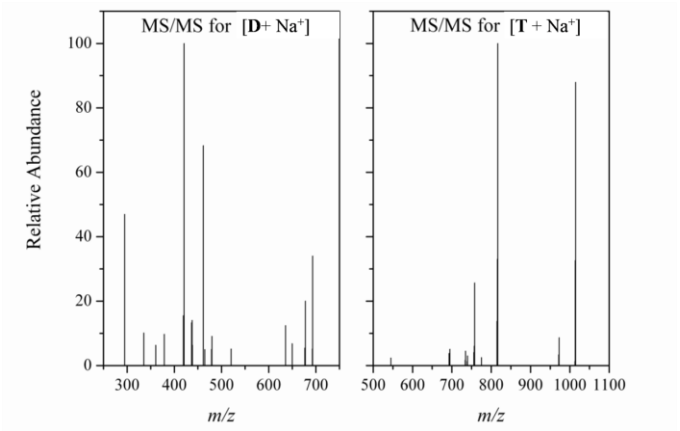


**Fig. S2.** MS/MS fragmentation for the ions [**D**+Na]$^+$ and [**T**+Na]$^+$.

**Table S1** MS/MS for [**D**+Na]$^+$, *m/z* 693

| | |
|---|---|
| 678 | -$CH_3^\bullet$ (-15 Da) |
| 650 | -$C_2H_3O^\bullet$ (-43 Da) |
| 636 | -$C_3H_5O^\bullet$ (- 57 Da) |
| 520 | -$C_{11}H_9O^\bullet$ (-173 Da) |
| 480 | -$C_{14}H_{13}O_2^\bullet$ (-213 Da) |
| 461 | -$C_{14}H_{16}O_3$ (-232 Da) |
| 421 | -$C_{16}H_{16}O_4$ (-272 Da) |

**Table S2** MS/MS for [**T**+Na]$^+$, *m/z* 1030

| | |
|---|---|
| 1015 | -$CH_3^\bullet$ (-15 Da) |
| 972 | -$C_3H_5O^\bullet$ (- 57 Da) |
| 817 | -$C_{14}H_{13}O_2^\bullet$ (-213 Da) |
| 758 | -$C_{16}H_{16}O_4$ (-272 Da) |

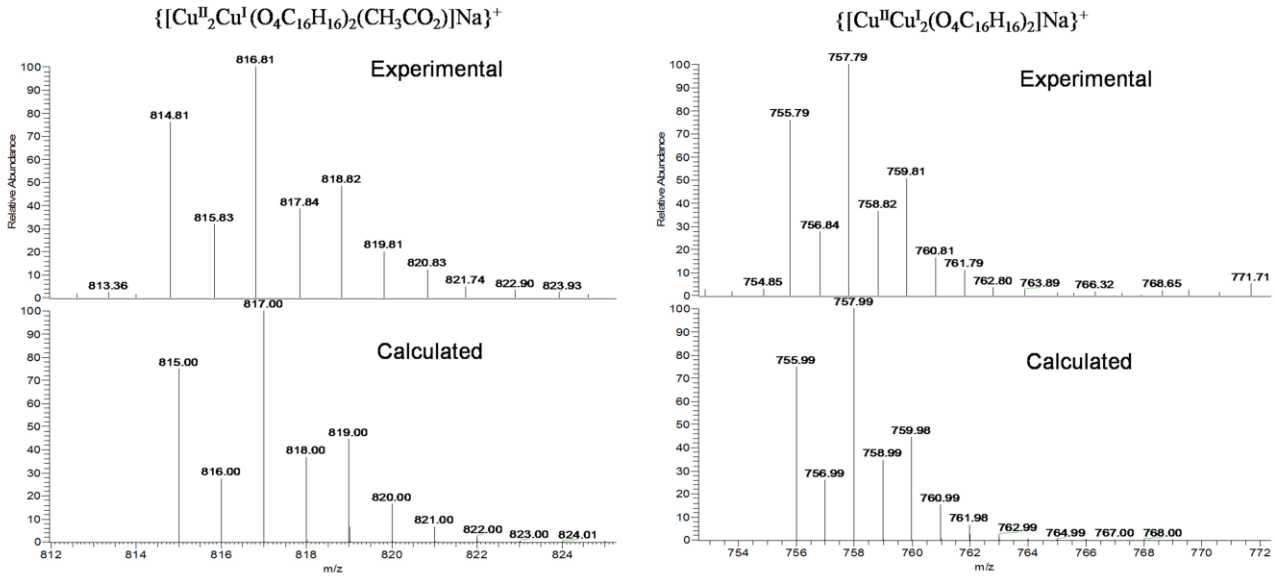


**Fig. S3**. Experimental and calculated isotopic patterns for $\{[Cu^{II}Cu^{I}_2(O_4C_{16}H_{16})_2]Na\}^+$ and for $\{[Cu^{II}_2Cu^{I}(O_4C_{16}H_{16})_2(CH_3CO_2)]Na\}^+$.

## Absorption spectra

Absorption spectra of $[Cu(o\text{-}L)]_n$ ($n$ = 2, 3) chloroform solutions at different total concentrations (Table S3, calculated considering the virtual monomer [Cu(*o*-L)] = **M**) have been recorded at different temperatures (293.15 – 323.15 K, every 5 K). Data have been collected using quartz suprasil cuvettes, filled with 3 mL of the solution. Spectra are shown in Figures S4-S10.

**Table S3**

| Concentration (mM) | Name |
|---|---|
| 2.034 | SolA |
| 1.695 | SolB |
| 1.356 | SolC |
| 0.678 | SolD |
| 0.339 | SolE |

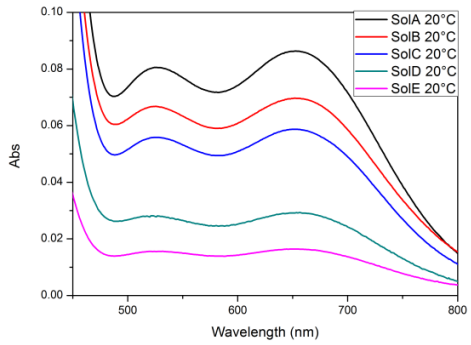


**Fig. S4** T = 293.15 K

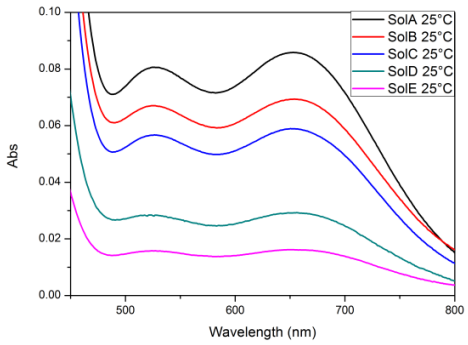


**Fig. S5** T = 298.15 K

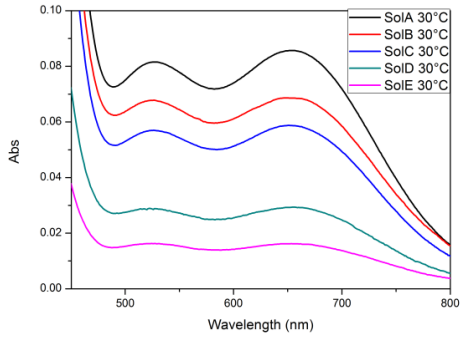


**Fig. S6** T = 303.15 K

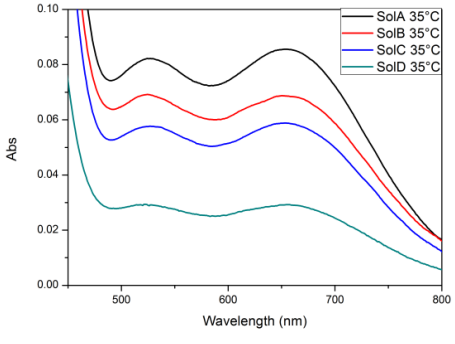


**Fig. S7** T = 308.15 K

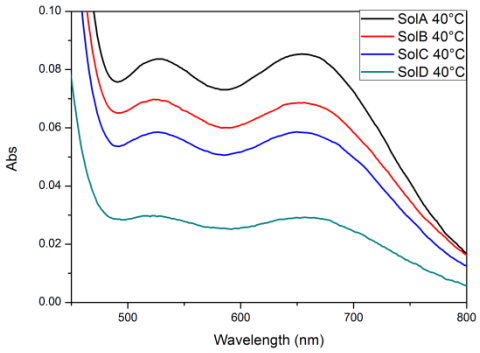


**Fig. S8** T = 313.15 K

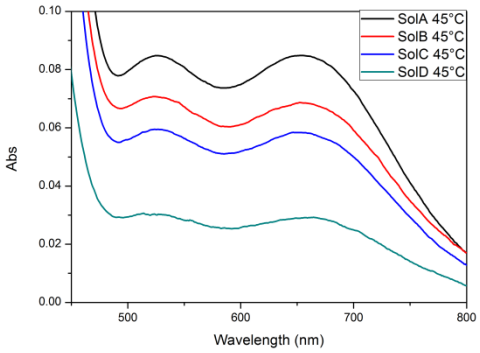


**Fig. S9** T = 318.15 K

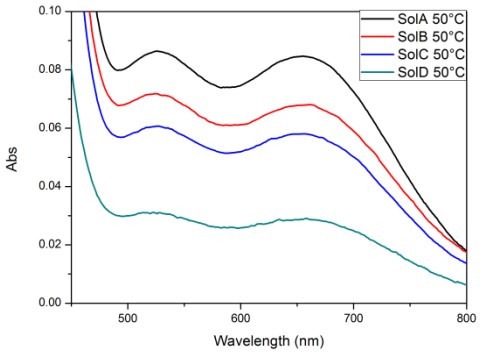


**Fig. S10** T = 323.15 K

Fig. S11 reports the almost linear trend of the CDL absorbance (at 298.15 K) as a function of the total concentration calculated on the basis of a virtual monomer [Cu(*o*-L)] = **M**. Fig. S12 shows simulated speciations for the equilibrium 3**D** ⇌ 2**T**, at increasing K values (4 < logK < 10). For logK > 5 the T/D ratio is practically constant for [**M**] > 1 mM.

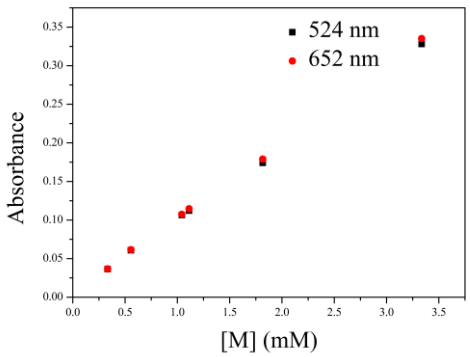


**Fig. S11**

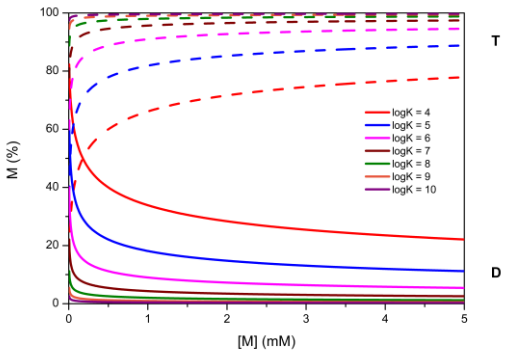


**Fig. S12**

Spectra at different concentrations have been recorded for a set of different temperatures. The temperature range is relatively small, from 293.15 K to 318.15 K. This choice is due to the solvent used ($CHCl_3$, bp 334.15 K) and to the experimental set up. As a matter of fact, a temperature decrease below room temperature (293.15 K) present a major drawback as moist can form on the cuvette walls.

Because of the large standard deviations, all the $logK_{DT}$ values reported in table S5, obtained at the different temperatures, can be considered practically identical and an average value of 4.8 has been chosen. Conversely, their difference is not sufficiently high to allow the vant'Hoff correlation $lnK_{DT}$ *vs* 1/T, preventing the quantification of enthalpic and entropic parameters. This is a consequence of the high $K_{DT}$ value and of the limited temperature range.

**Table S4** $logK_{DT}$ at different temperatures

| Temperature (K) | $logK_{DT}$ | σ |
|---|---|---|
| 293.15 | 4.9 | 0.4 |
| 298.15 | 4.8 | 0.4 |
| 303.15 | 4.9 | 0.5 |
| 313.15 | 4.8 | 0.7 |
| 318.15 | 4.8 | 0.7 |