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# ELECTRONIC SUPPLEMENTARY INFORMATION

## to the paper entitled

**Robust recognition of malonate and 2-amino-4-picolinium in conjunction with M(II) as a triad (M = Ni/Co/Mn): Role of this highly stable hydrogen-bonded motif in driving the supramolecular self-assembly**

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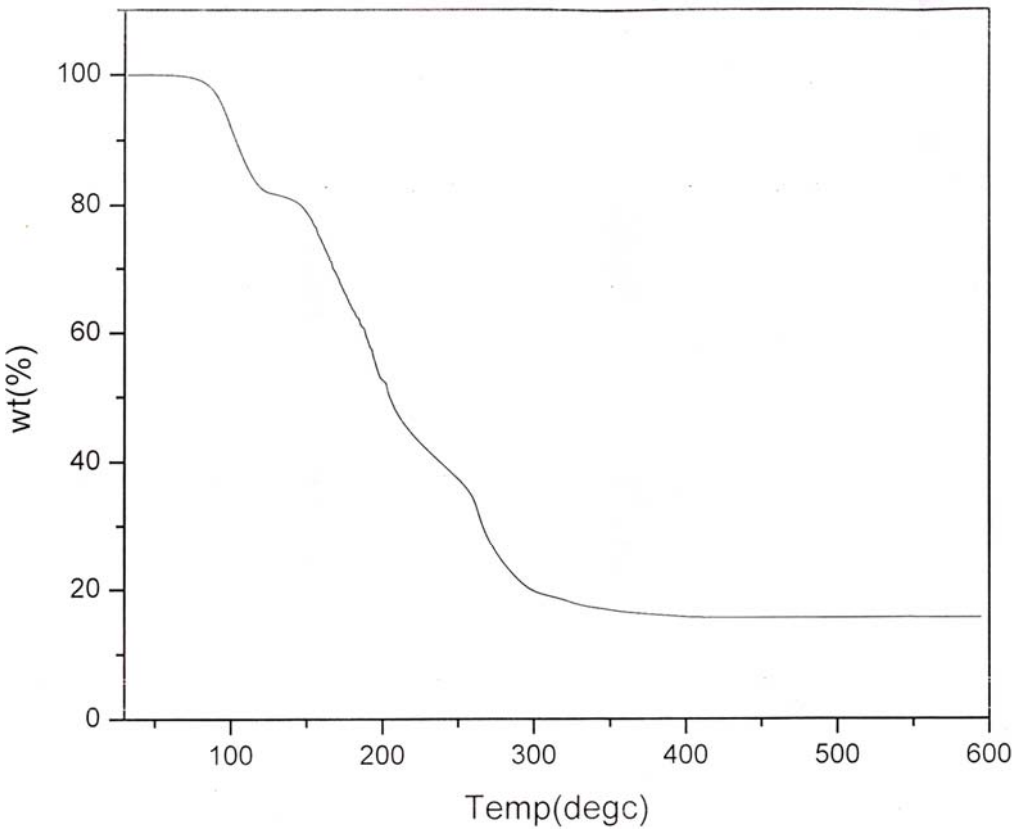


**Figure S1.** TG curve of **1**. Identical patterns have been found for compounds **2** and **3**. Heating rate: 10 °C per minute.

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**Table S1.** π-π interaction data for compounds **1-3**

| **π···π Interaction** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1** | | | | | | | |
| | Symmetry | Cg(i)-Cg(j) (Å) | Alpha (˚) | Beta (˚) | Cg(i)-perp (Å) | Cg(j)-perp (Å) | Slippage (˚) |
| Cg(3)->Cg(3) | –x, –y, 1–z | 4.0238(8) | 0.0 | 27.52 | 3.569 | 3.569 | 1.859 |
| **2** | | | | | | | |
| Cg(3)->Cg(3) | 2–x, 1-y, –z | 3.9985(9) | 0.0 | 26.66 | 3.574 | 3.574 | 1.794 |
| **3** | | | | | | | |
| Cg(3)->Cg(3) | –x, 1–y, 1–z | 4.0546(9) | 0.0 | 27.62 | 3.593 | 3.593 | 1.879 |
| Ring (3) N(2)-->C(5)-->C(6)-->C(7)-->C(8)-->C(9) | | | | | | | |

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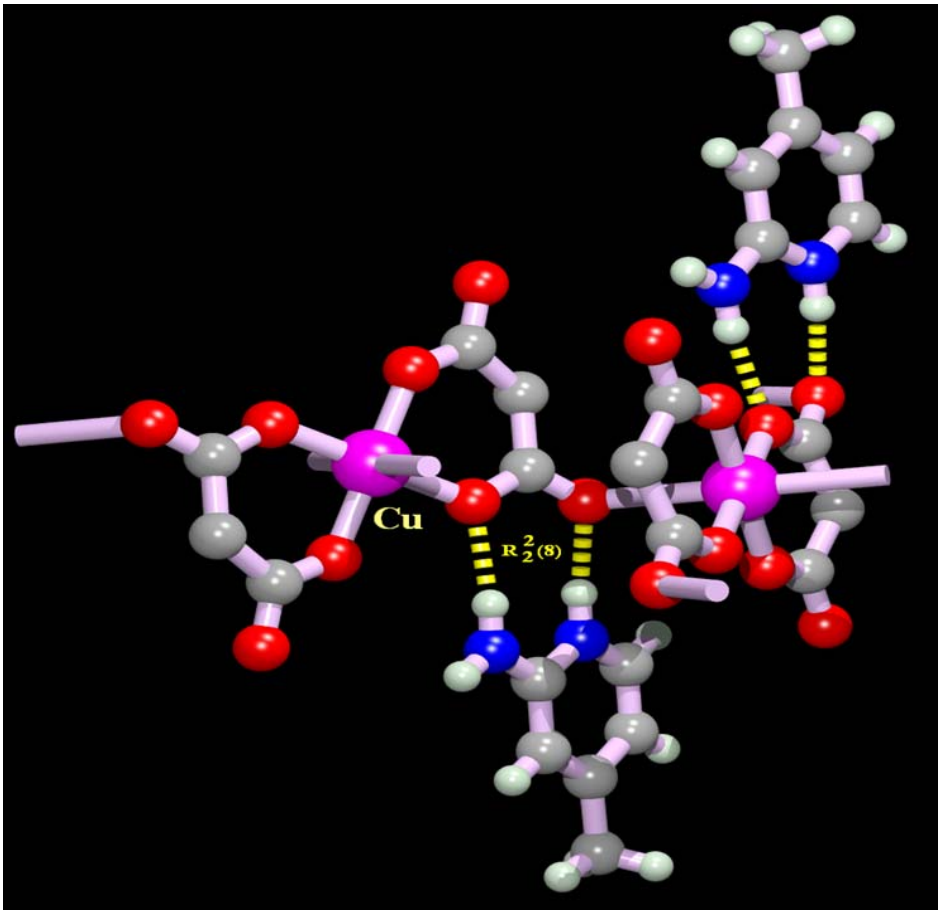


**Figure S2.** Recognition between protonated 2-amino-4-picoline molecules and malonate moieties in the copper compounds $\{[Cu(mal)_2](C_6H_8N_2H)_2.2H_2O\}n$ and $\{[Cu(mal)_2](C_6H_8N_2H)_2.5H_2O\}n$ (see references 34 and 35 of the main text). Here also the $R_2^2(8)$ hydrogen-bonded synthon is operative.

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**Table S2.** Formation energies (in kcal $mol^{-1}$) of **Motif 1** and **Motif 2** estimated on experimental and optimized structures.

| | B3LYP/6-31+G(d) | | BHandH/6-31+G(d) | |
|---|---|---|---|---|
| | Single-point | Optimization | Single-point | Optimization |
| **Motif 1** | +123 | Not a minimum | +105 | Not a minimum |
| **Motif 2** | -- | -- | –208.7 | –274.0 |

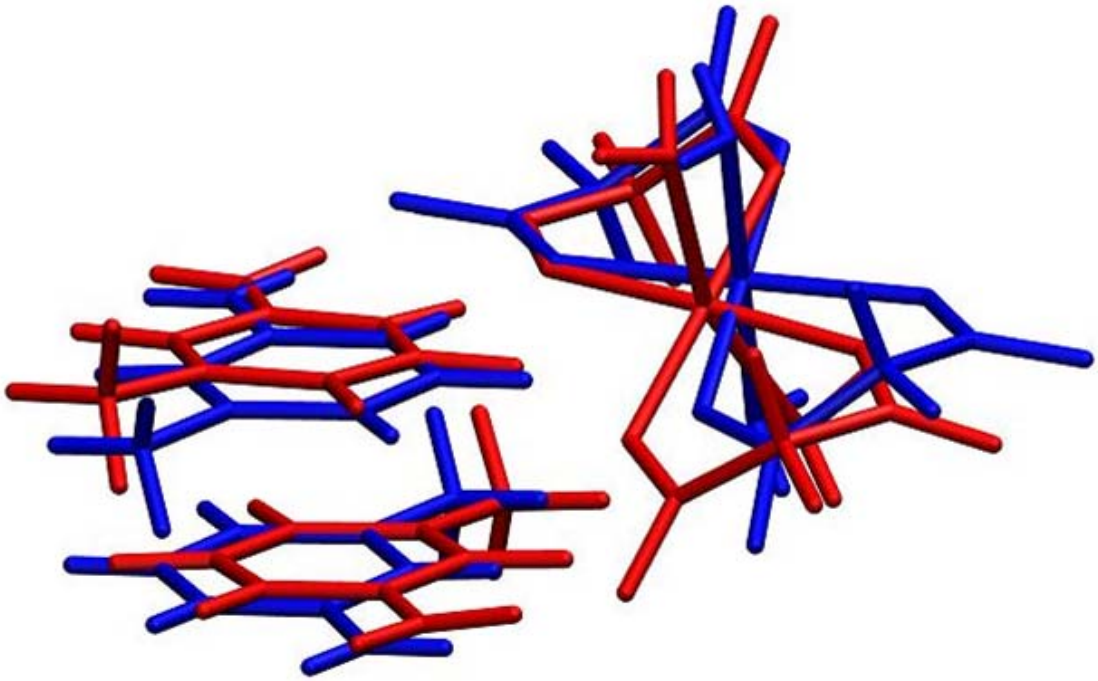

**Figure S3. Motif 2** (see Figure 5 of the main text): blue = experimental structure; red = optimized structure at BHandH/6-31+G(d).

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**Table S3.** Electron density analysis on the experimental and optimized structures of **Motif 2**. The outcome of the optimization is an increase of all interactions observed in the experimental structure.

| | $\rho_{tot}$ (Single-Point, au) | $\rho_{tot}$ (Optimization, au) |
|---|---|---|
| N···N | 0.01241 | 0.01602 |
| Lone pair···π | 0.00472 | 0.00891 |
| N–H···O | 0.0537 | 0.0952 |
| C–H···O | 0.00666 | 0.01245 |