

Supplementary Information

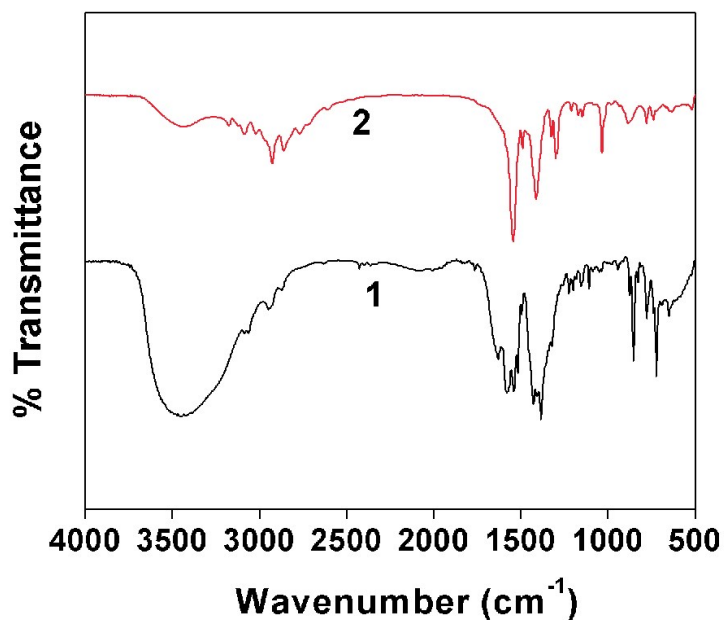


Fig. S1 FT-IR spectra of compounds 1 and 2

Table S1 Selected bond lengths (Å) and bond angles (°) of compounds 1 and 2

Bond	d(Å)	Bond	d(Å)
Compound 1			
Cu(1)-O(2)	1.938(6)	Cu(2)-N(4)	2.020(7)
Cu(1)-O(3)	1.987(5)	Cu(2)-N(3)	2.021(7)
Cu(1)-N(1)	1.995(7)	Cu(2)-O(4)	2.152(6)
Cu(1)-N(2)	2.001(6)	Cu(3)-O(8)	1.945(6)
Cu(1)-O(4)	2.424(6)	Cu(3)-O(6)	1.964(6)
Cu(2)-O(5)	1.940(6)	Cu(3)-N(6)	2.004(8)
Cu(2)-O(7)	1.960(6)	Cu(3)-N(5)	2.008(7)
Cu(3)-O(9)	2.195(7)		
Compound 2			
Co1-O6	2.034(7)	Co2-O3	2.051(7)
Co1-O7	2.097(7)	Co2-O1	2.065(7)
Co1-O5	2.166(6)	Co2-O5	2.222(6)
Co1-O5	2.174(6)	Co2-O3	2.051(7)
Angle	(°)	Angle	(°)
Compound 1			
O2-Cu1-O3	90.8(2)	O5-Cu2-O4	89.6(2)
O2-Cu1-N1	94.5(3)	O7-Cu2-O4	100.8(2)
O3-Cu1-N1	174.5(2)	N4-Cu2-O4	94.9(2)
O2-Cu1-N2	176.3(3)	N3-Cu2-O4	94.2(2)
O3-Cu1-N2	92.9(2)	O8-Cu3-O6	90.9(3)
N1-Cu1-N2	81.8(3)	O8-Cu3-N6	92.9(3)

O2-Cu1-O4	93.6(2)	O6-Cu3-N6	165.4(3)
O3-Cu1-O4	58.2(2)	O8-Cu3-N5	174.3(3)
N1-Cu1-O4	122.4(2)	O6-Cu3-N5	93.5(3)
N2-Cu1-O4	88.9(2)	N6-Cu3-N5	82.0(3)
O5-Cu2-O7	92.7(2)	O8-Cu3-O9	89.5(3)
O5-Cu2-N4	172.5(3)	O6-Cu3-O9	94.8(3)
O7-Cu2-N4	92.4(3)	N6-Cu3-O9	99.3(3)
O5-Cu2-N3	91.8(3)	N5-Cu3-O9	93.9(3)
O7-Cu2-N3	164.4(3)	N4-Cu2-N3	81.9(3)
Compound 2			
O6-Co1-O6	180.0(5)	O7-Co1-O5	93.0(3)
O6-Co1-O7	90.4(3)	O5-Co1-O5	180
O3-Co2-O3	180.0(6)	O7-Co1-O7	180
O3-Co2-O1	89.5(3)	O6-Co1-O5	94.6(3)
O1-Co2-O1	180	O3-Co2-O5	88.8(2)
O7-Co1-O5	93.0(3)	O1-Co2-O5	91.6(2)

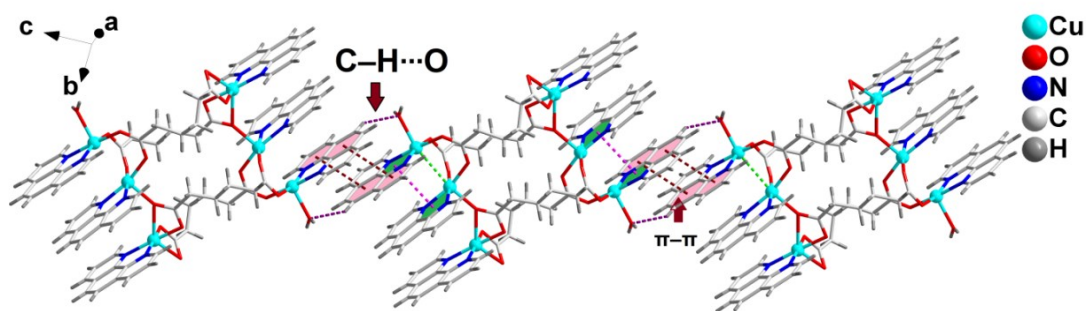


Fig. S2 Propagation of 1D chain of hexanuclear units of **1**

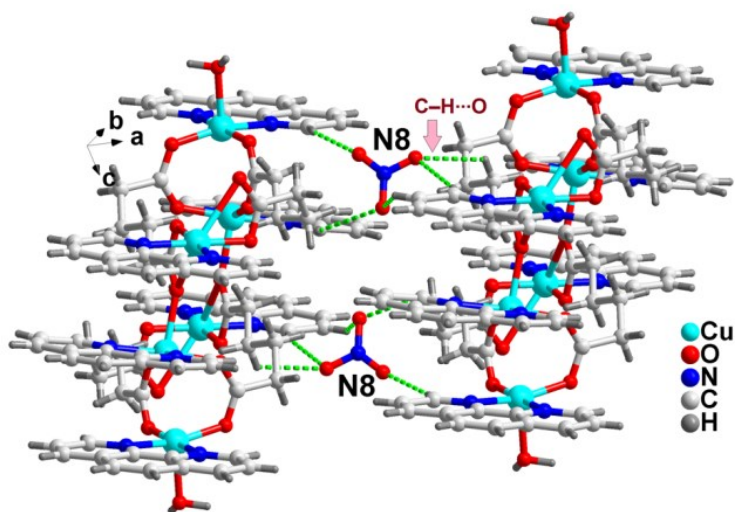


Fig. S3 Supramolecular association of neighboring complex hexanuclear units involving lattice NO_3^-

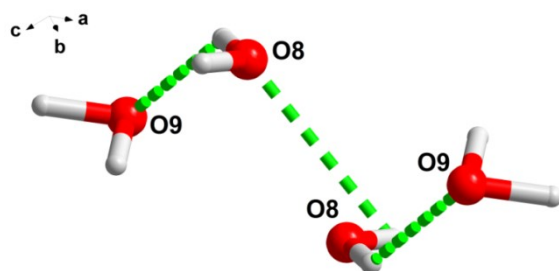


Fig. S4 Formation of linear $(\text{H}_2\text{O})_4$ core in compound **2** involving lattice aqua molecules

3.5 Electronic spectroscopy

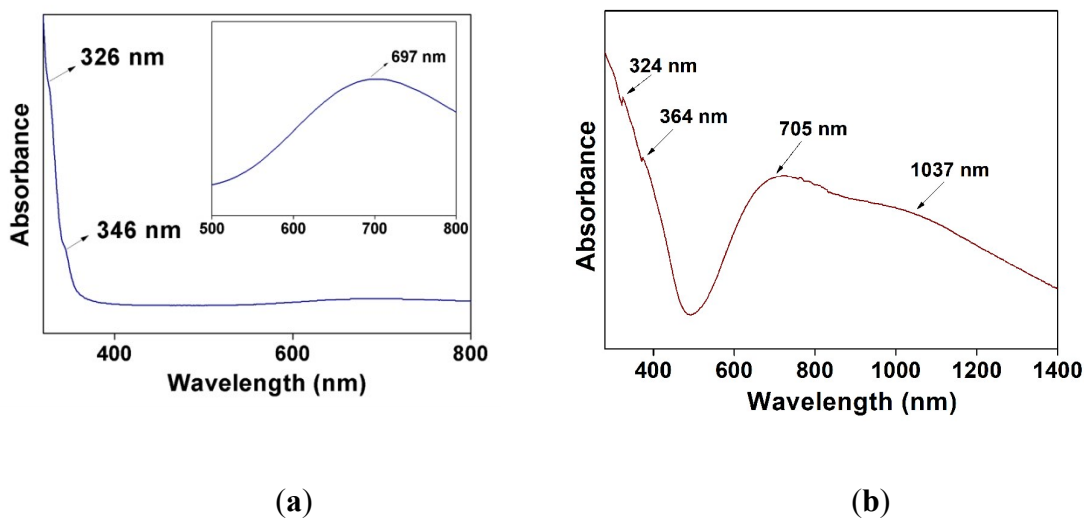


Fig. S5 Electronic spectra of **1** in (a) aqueous solution (10^{-3}M) and (b) solid state

We have recorded the UV-Vis spectra of the complexes **1** and **2** in solid as well as in solution phase. The spectra are shown in Fig. S5 and Fig. S6 respectively. The UV-Vis spectrum of **1** shows two sharp and intense absorption bands at 326 nm and 346 nm corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of the *phen* ligand, respectively.¹ The aqueous phase electronic spectrum of **1** shows a broad visible absorption band at 697 nm which may be attributed to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition for distorted octahedral complexes.² The UV-Vis-NIR spectrum of **1** indicates the distortion of Cu(II) coordination in the complex **1** from O_h symmetry [Fig. S5(b)]. The broad band at 705 nm due to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition, which gives rise to the characteristic

blue colour to octahedral copper(II) compounds, splits into 1037 nm, suggesting coordination environment of Cu(II) in the complex to be other than octahedral.³ The unusual spectra for **1** from usually observed for distorted octahedral structure may be attributed to the presence of copper centers with different coordination environments.⁴ The UV bands originating from the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the pyridine rings of *phen* are found in the expected positions.¹

Solid state UV-Vis-NIR spectrum of **2** exhibits band at 273 nm assigned to LMCT transitions. The spectrum is shown in [Fig. S6(a)]. We can expect three ligand field bands for high-spin octahedral Co(II) complex. The first band (ν_1) occurs at 1239 nm [${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$], the third band (ν_3) is seen at 470 nm [${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3)], and the ν_2 band due to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ appears at 510 nm with a shoulder at 629 nm because of a two-electron transition.⁵ The spectrum in water [Fig. S6(b)] shows similar splitting of band at 507 nm with a shoulder at 640 nm.⁶ The NIR band is not seen in the solution spectrum because of the limit in the wavelength window of the spectrophotometer used.

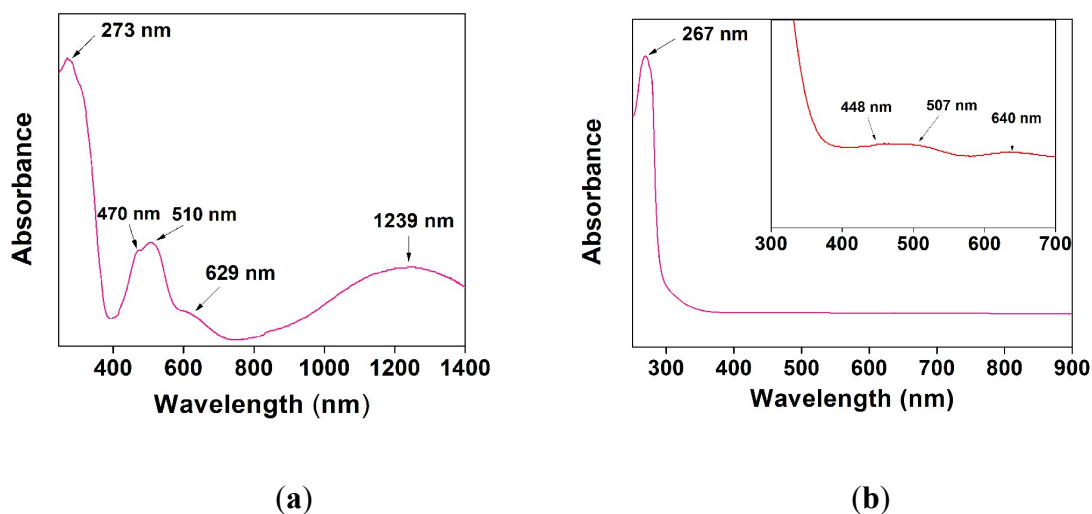
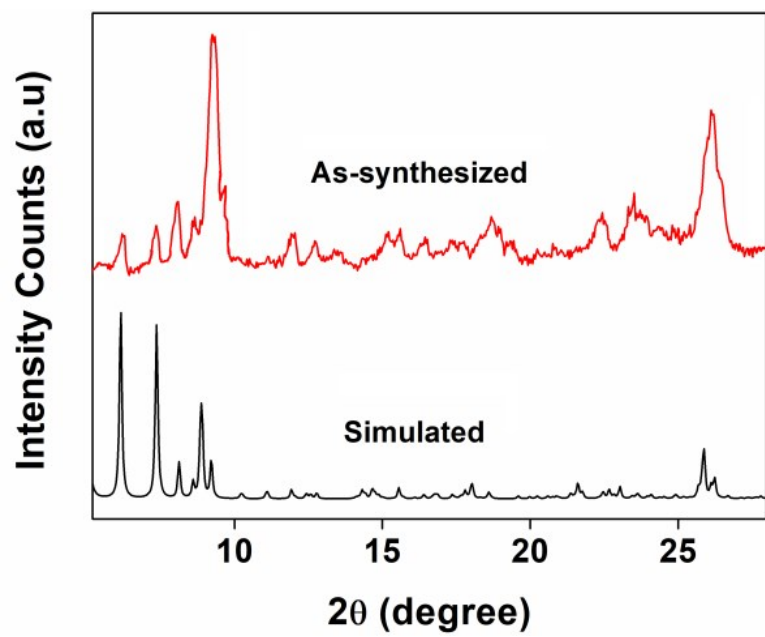
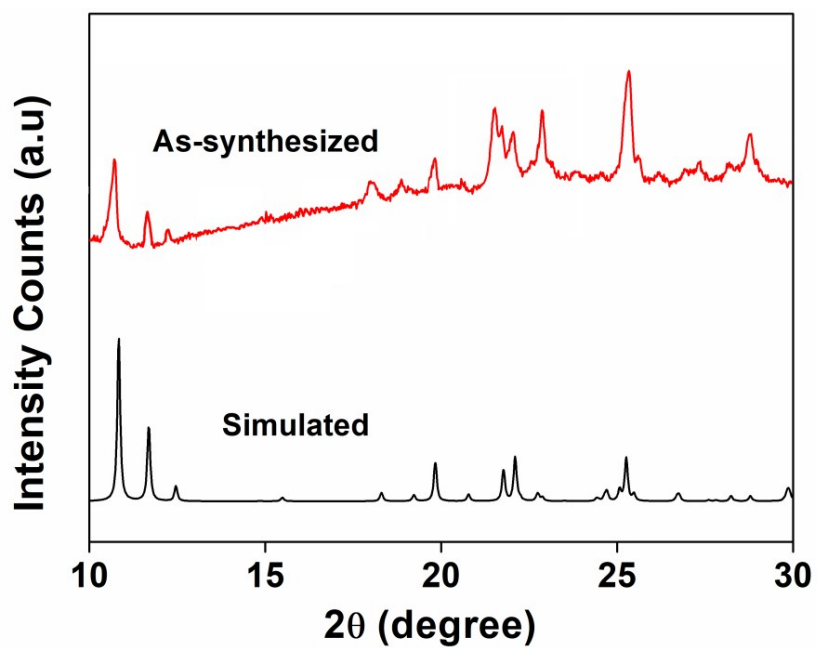


Fig. S6(a) Solid state UV-Vis-NIR spectrum of **2**; **(b)** UV-Vis spectrum of **2** in water

The electronic spectral studies reveal that the complexes **1** and **2** do not show marked differences in the position of the absorption peaks in the solid and in aqueous phases and therefore, it may be assumed that bonding modes as well as the geometries of the complexes does not change in the solution phase.⁷



(a)



(b)

Fig. 7 Powder X-ray diffraction patterns: as-synthesized (red) and simulated from MERCURY software (black) of compounds **1** (a) and **2** (b).

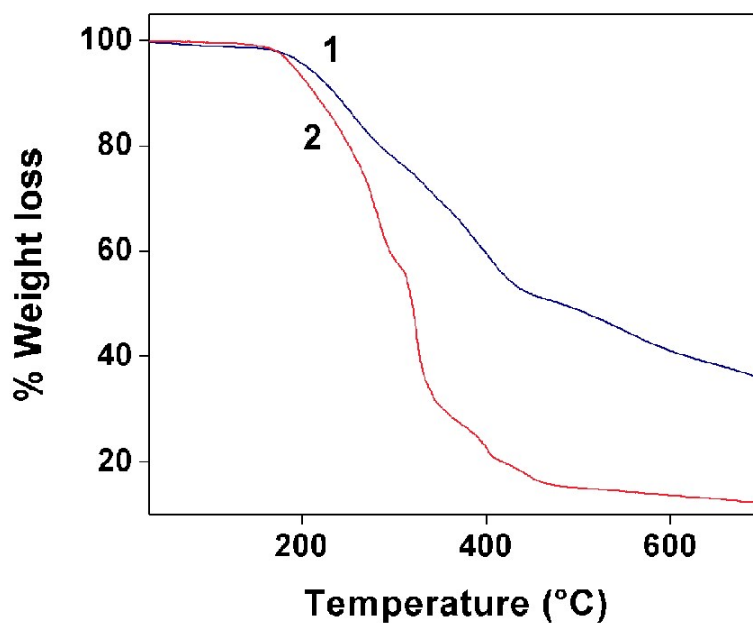


Fig. S8 Thermogravimetric analyses of **1** and **2**

Supplementary References

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7 M. Ghosh, A. Majee, M. Nethaji and T. Chattopadhyay, *Inorg. Chim. Acta*, 2009, **362** 2052-2055.