Supporting Information

Three New Cu-Azido Polymers and Their Systematic Inter Conversion: Role of the Amount of the Blocking Amine on the Structural Diversity and Magnetic Behavior

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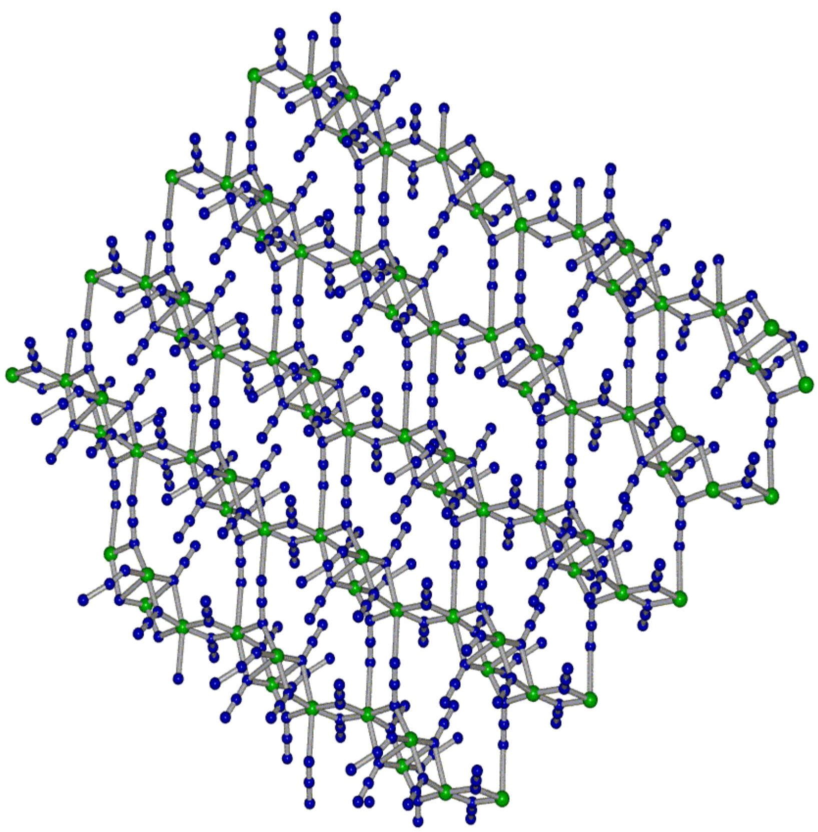


Fig. S1: View of the 2D sheet formed by the linking of the rail-road chain by 1,1,3 azido in complex-**1**.

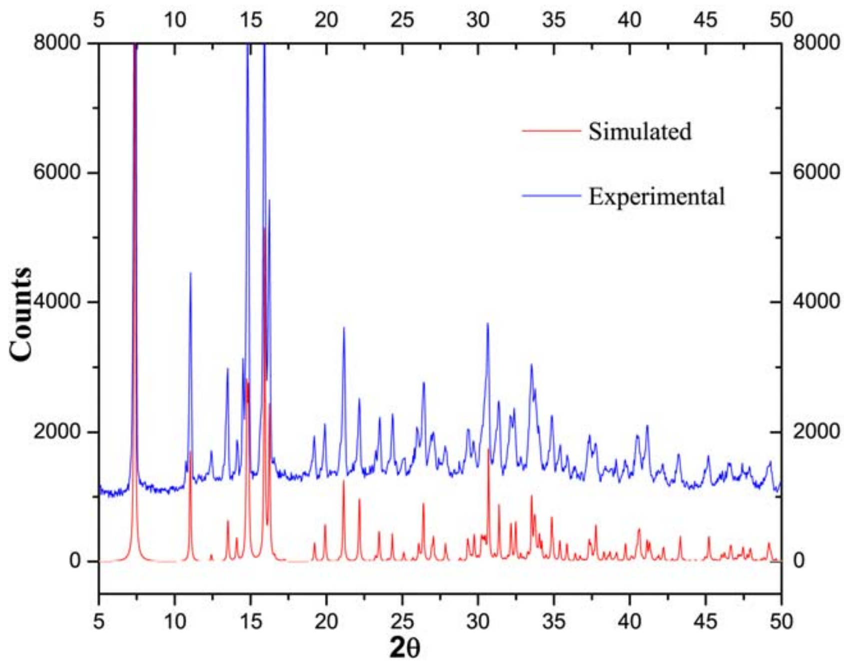


Fig. S2: Powder XRD pattern of the complex-**1**.

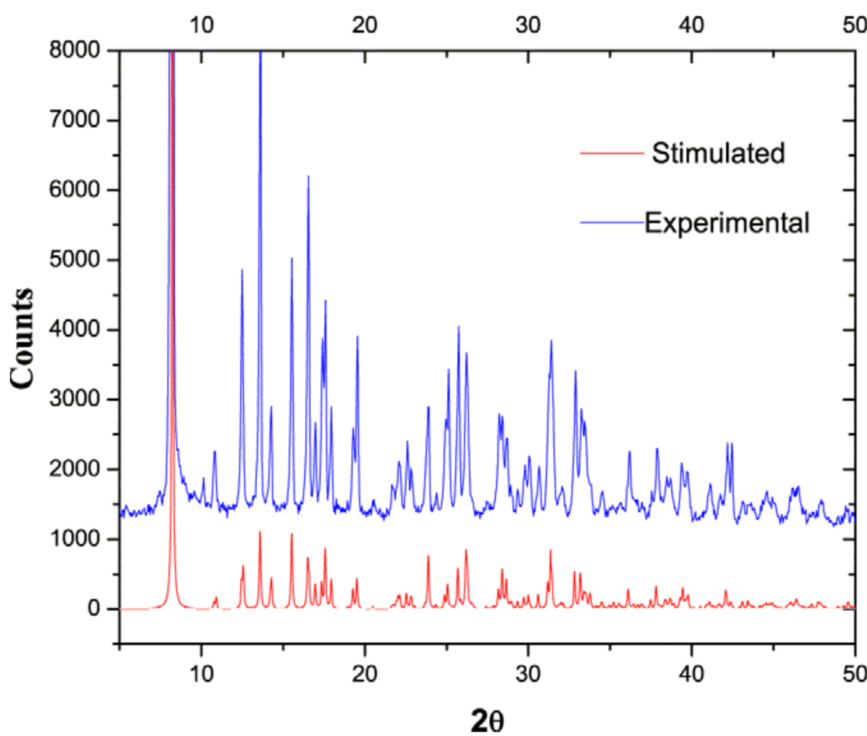


Fig. S3: Powder XRD pattern of the complex-**2**.

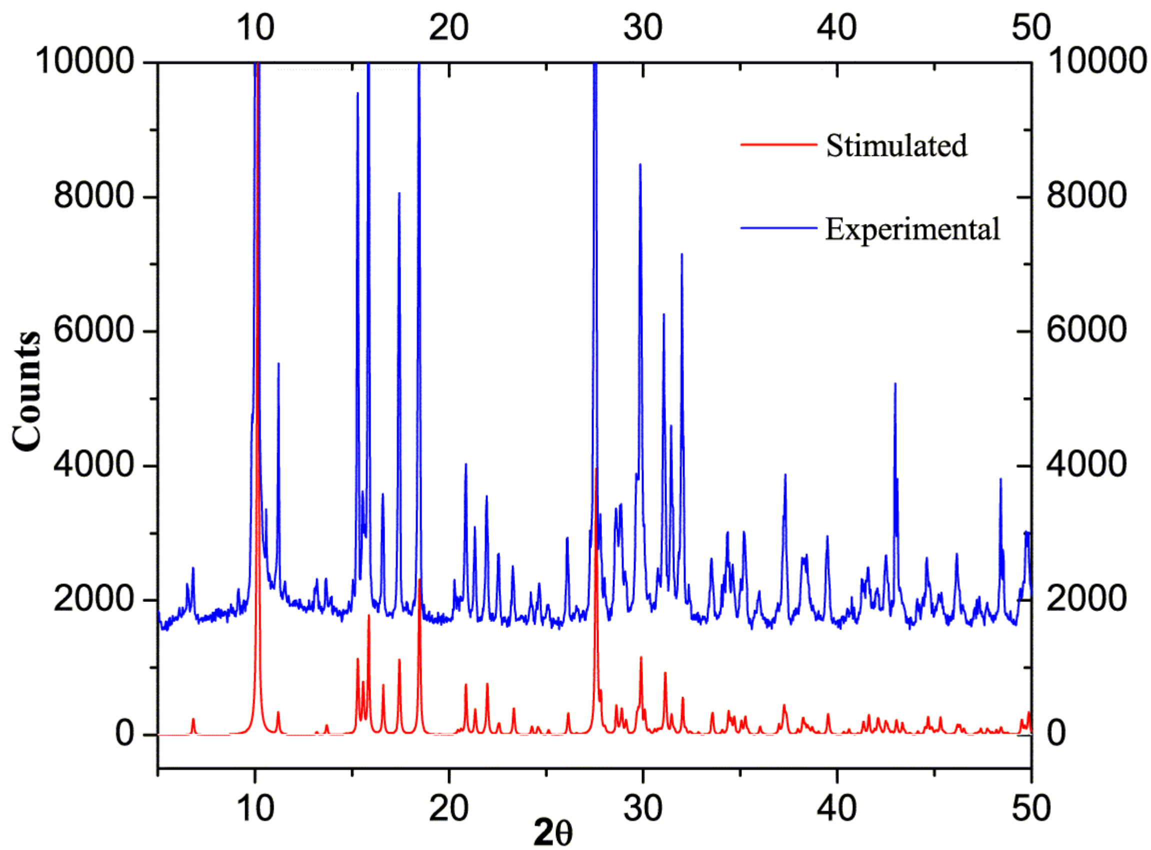


Fig. S4: Powder XRD pattern of the complex-**3**.

Magnetic analysis of **1**:

Since the main magnetic core (1D rail road core) of the complex **1** is nothing but a repetition of defect biscubane unit doubly connected by end-on azido group, thus Heisenberg spin Hamiltonian of the main magnetic unit can be written as

$$\mathbf{H} = -2J_1(\mathbf{S_1.S_2} + \mathbf{S_3.S_4} + \mathbf{S_1.S_3} + \mathbf{S_2.S_4}) - 2J_2\, \mathbf{S_2.S_3} - 2J_3\, (\mathbf{S_1.S_4})$$

The molar magnetic susceptibility per four Cu(II) ion can be written as equation –1[1-2] by applying Kambe's vector coupling method and the van Vleck equation. J_n are exchange coupling parameters (as shown in the following scheme).

$$\chi_M^{cluster} = \frac{N_A g^2 \mu_B^2}{2kT} \frac{A}{B} \text{............}(1)$$

Where A = [5exp(2J_1/kT)+ exp(-2J_2/kT)+ exp(-2J_3/kT)+ exp(-2J_1/kT)]

B = [5exp(2J_1/kT)+ 4exp(-2J_2/kT)+ 3exp(-2J_3/kT)+ exp{-2(J_1+J_3)/kT}

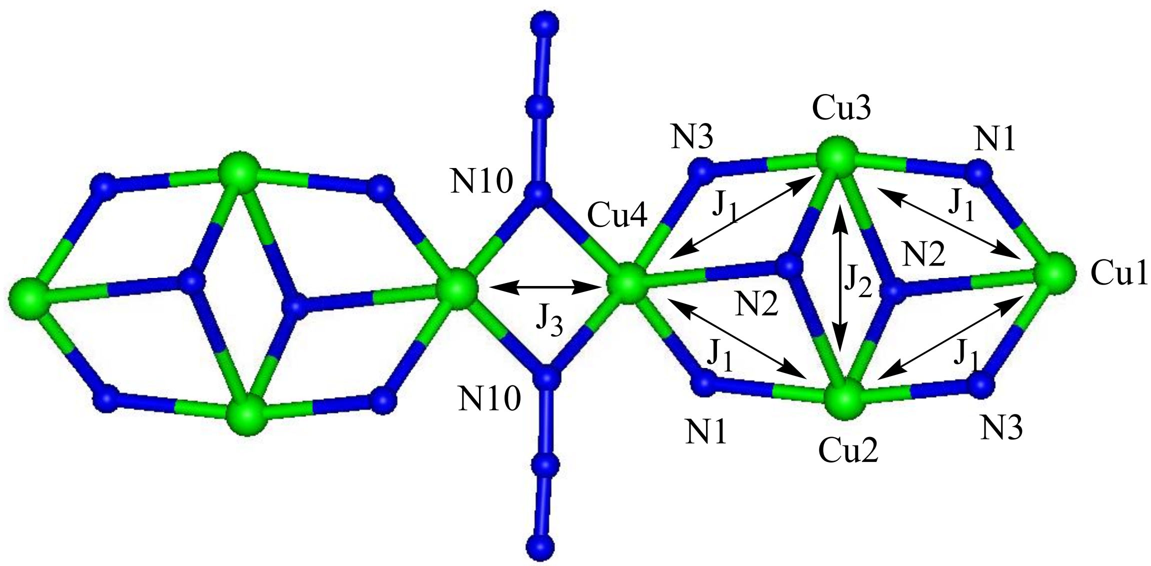
+ 3exp(-2J_1/kT)+ exp(-4J_1/kT)]

$$\chi_M^{inter-clust} = \frac{1}{\frac{1}{\chi_M^{cluster}} - \frac{2ZJ'}{N_A g^2 \mu_B^2}} \text{......}(Y)$$

Molecular field approximation was used to determine the inter-cluster interaction.

Interaction between Cu(1) & Cu(2), Cu(1) & Cu(2*), Cu(1*) & Cu(2), Cu(1*) & Cu(2) = J_1, Cu(2) & Cu(2*) = J_2, Cu(1) & Cu(1*) = J_3

Where Cu(1*) = Cu(4) & Cu(2*) = Cu(3) are assumed for magnetic model



Scheme-S1: Magnetic model for the basic unit of complex-**1**.

The experimental data (χ_M per four Cu(II) vs T) was fitted to equation (y)[1] to give J_1 = +22.828 cm^{-1}, J_2 = +23.111 cm^{-1}, J_3 = +22.914 cm^{-1} and ZJ' = 3.279 (g = 2.07) with the agreement factor R= $1*10^{-6}$ gave the best fit.

All the fittings considering the above models led to the conclusion that coupling between two adjacent Cu(2) centers through N(2) is ferromagnetic as bond angle [Cu(2)-N(2)-Cu(2*) = 92.2°] are close to 90°, Cu(2)- Cu(2*) and Cu-N bond distances are Cu(2)-Cu(2*) = 3.297Å , Cu(2)-N(2) = 1.989Å, & Cu(2*)-N(2) = 2.554Å respectively, the coupling between two adjacent Cu(1) and Cu(2) within the biscubane unit through N(1) and N(3) is also ferromagnetic as average coupling bond angles [Cu(1)-N(2)-Cu(2*) = 94.03°, Cu(1)-N(1)-Cu(2) = 111.87° & Cu(1)-N(2)-Cu(2) = 83.18°, Cu(1)-N(3)-Cu(2) = 113.22°] are less than 106° and bond distances are Cu(1)-N(1) = 1.976Å, Cu(2)-N(1) = 2.015Å, Cu(1)-N(3) = 2.007Å, Cu(2)-N(3) = 2.016Å, Cu(1)-Cu(2*) = 3.307Å & Cu(1)-Cu(2) = 3.358Å. Moreover inter biscubane coupling between Cu(1) and Cu(1*) through N(10) is ferromagnetic as Cu(1)-N(10)-Cu(1*) bond angle (101.91°) is less then 106° and Cu(1)-Cu(1*) distance is 3.087Å while interaction between adjacent 1D rail road chain through $\mu_{1,1,3}$-azido bridge is weakly antiferromagnetic as the inter chain separations are Cu(1)-Cu(1*) = 5.558Å & Cu(1)-Cu(2) = 6.6.318Å. Thus it can be concluded that ferromagnetically coupled 1D rail road chain antiferromagnetically couples with adjacent 1D rail road through $\mu_{1,1,3}$-azido bridge and this honey comb like 2D core couples antiferromagnetically to $\{Cu^{II}(3)(LL)_2\}^{2+}$ ions through cis- $\mu_{1,3}$-azido bridge [Cu(2)-Cu(3) = 6.275Å, Cu(2)-N(11) = 1.967Å, Cu(3)-N(15) = 2.228 Å] and that's why complex **1** shows dominant ferromagnetic coupling in the temperature range 300K to

7.93K while below which antiferromagnetic coupling becomes dominant because of antiferromagnetic coupling between 1D inter rail road chain.

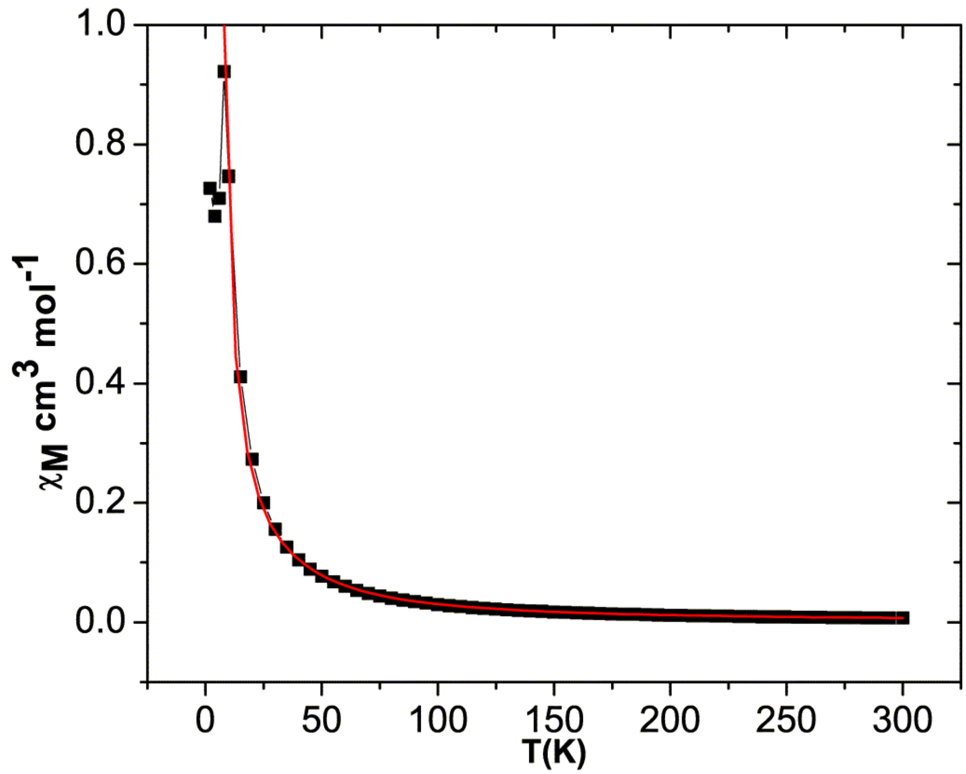


Fig. S5: Plots of χ_M vs. T (8-300K) and $\chi_M T$ vs. T (inset) of complex **1** in the temperature range 2-300K. The red line indicates the fitting.

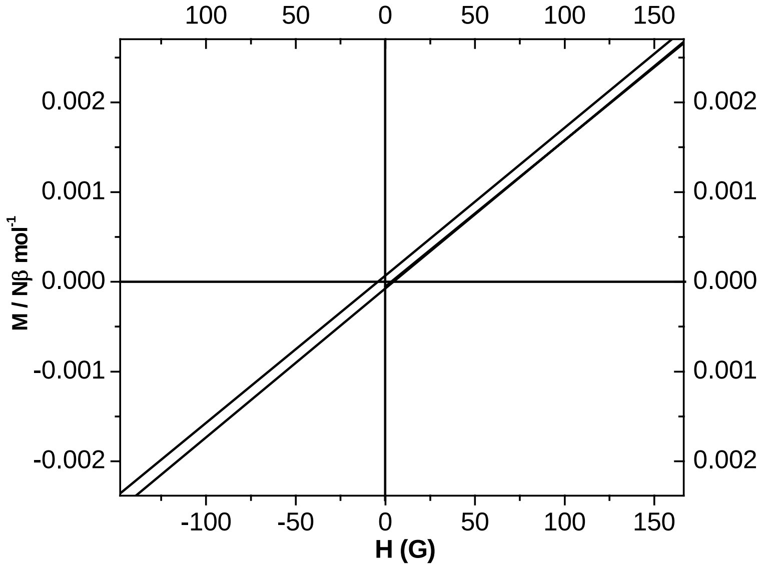


Fig. S6: M vs H plot at very low field range for **1** to show a very weak loop.

References:

1. (a) Lui, T.-F.; Sun, H.-L.; Gao, S.; Zhang, S.-W.; Lau, T.-C. *Inorg. Chem.* **2003,** *42*, 2003. (b) Li, D.-F. ; Zheng, L.-m.Wang, X.-Y.; Haung, J.; Gao, S.; Tang, W.-X. *Chem. Mater*. **2003,** *15*, 2094-2098.

2. (a) Colacio, E.; Domı´nguez-Vera, J. M.; Ghazi, M.; Kiveka¨s, R.; Lloret, F.; Moreno, J. M.; Stoeckli-Evans, H. *Chem. Commun.* **1999**, 987. (b) Herna´ndez, M.; Lloret, F.; Ruiz-Pe´rez, C.; Julve, M. *Inorg. Chem.* **1998**, *37*, 4131.