

Supporting Information

Zn/Cu Complexes Constructed through Selective in Situ Br–Cl Exchange: Synthesis, Structures, Properties, and DFT Insights into the Cu-Catalyzed Mechanism

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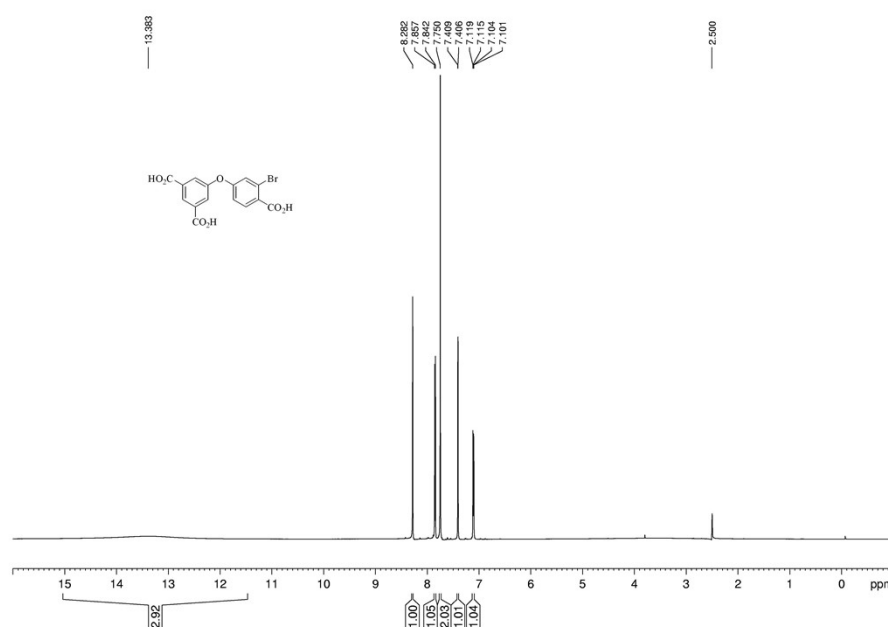


Figure S1. ¹H NMR spectrum of H₃L in DMSO-d₆ (r.t).

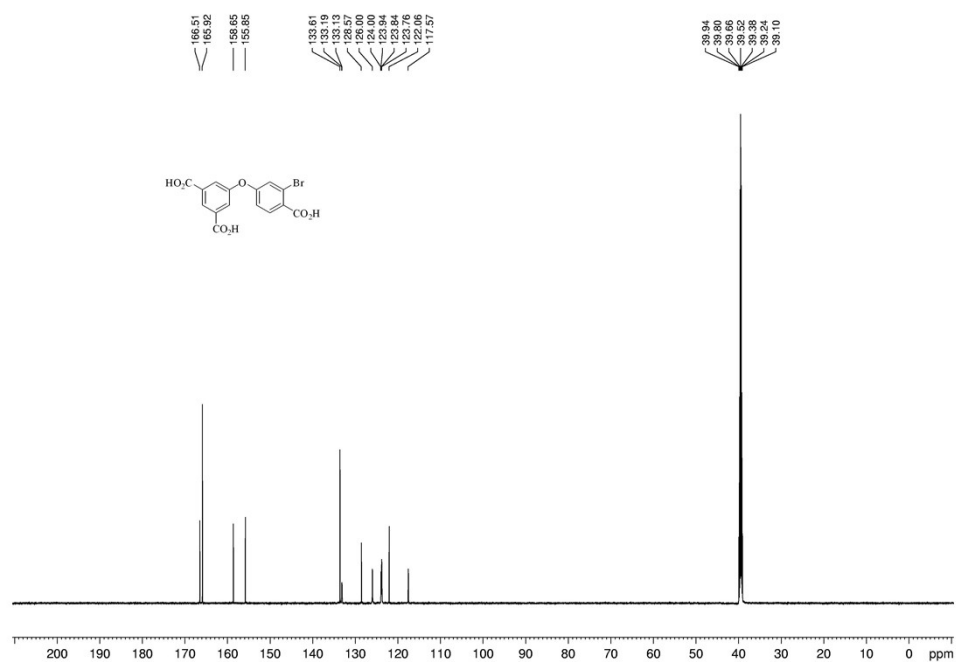


Figure S2. ¹³C NMR spectrum of H₃L in DMSO-d₆ (r.t).

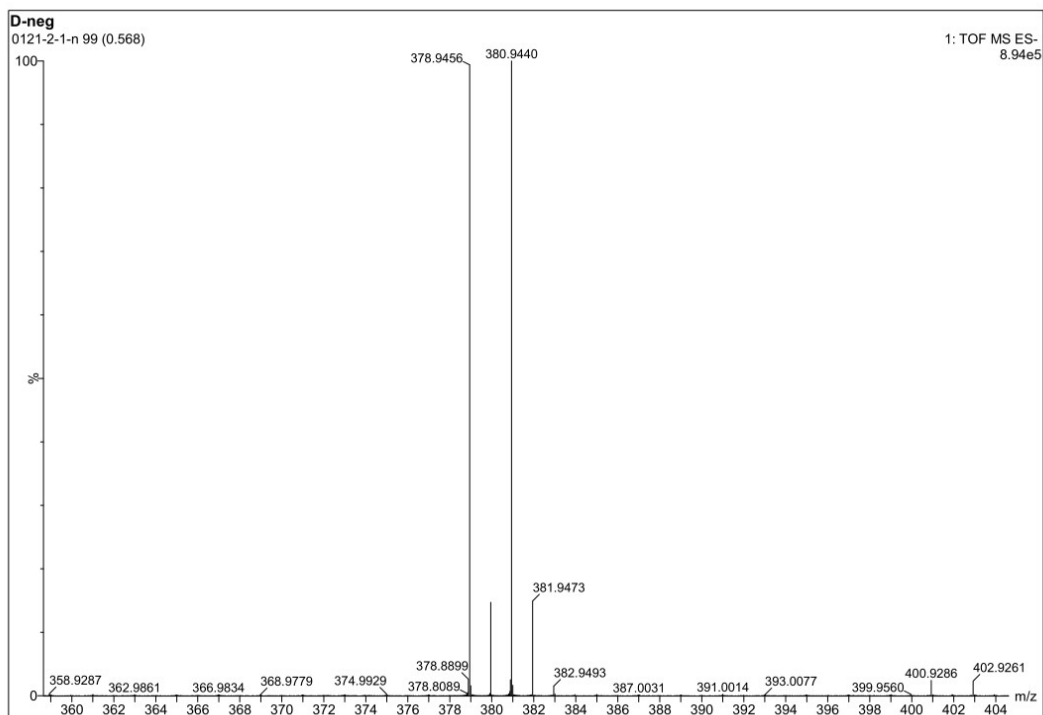


Figure S3. MS spectra of H₃L.

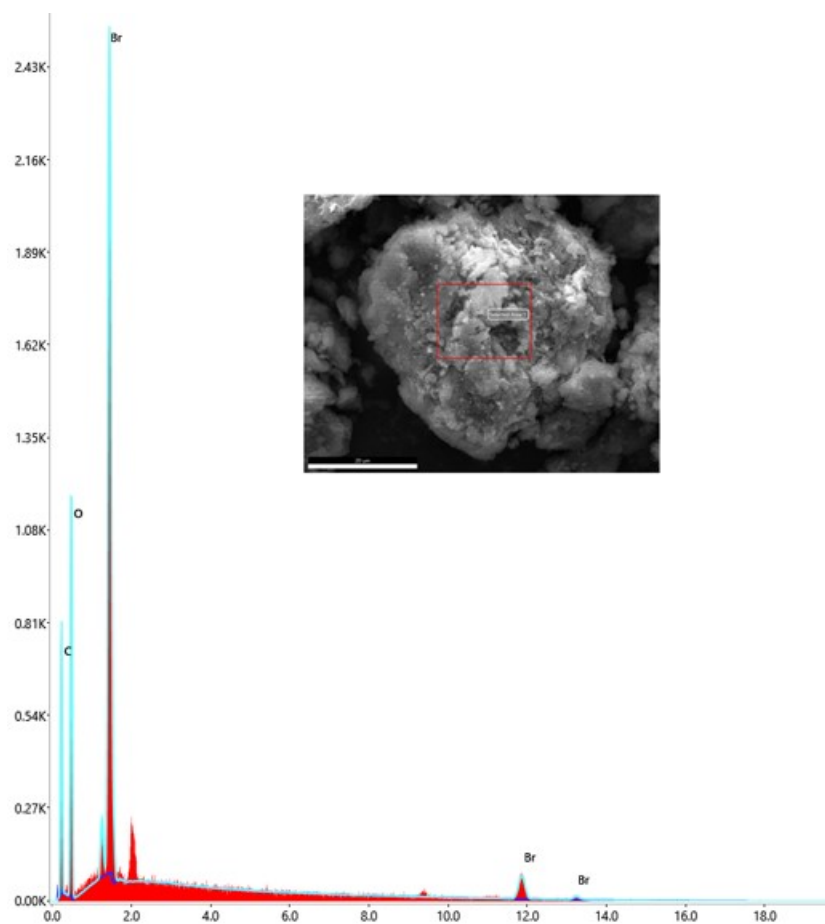


Figure S4. Elemental analysis of H₃L was performed by energy-dispersive X-ray spectroscopy (EDS) using SEM.

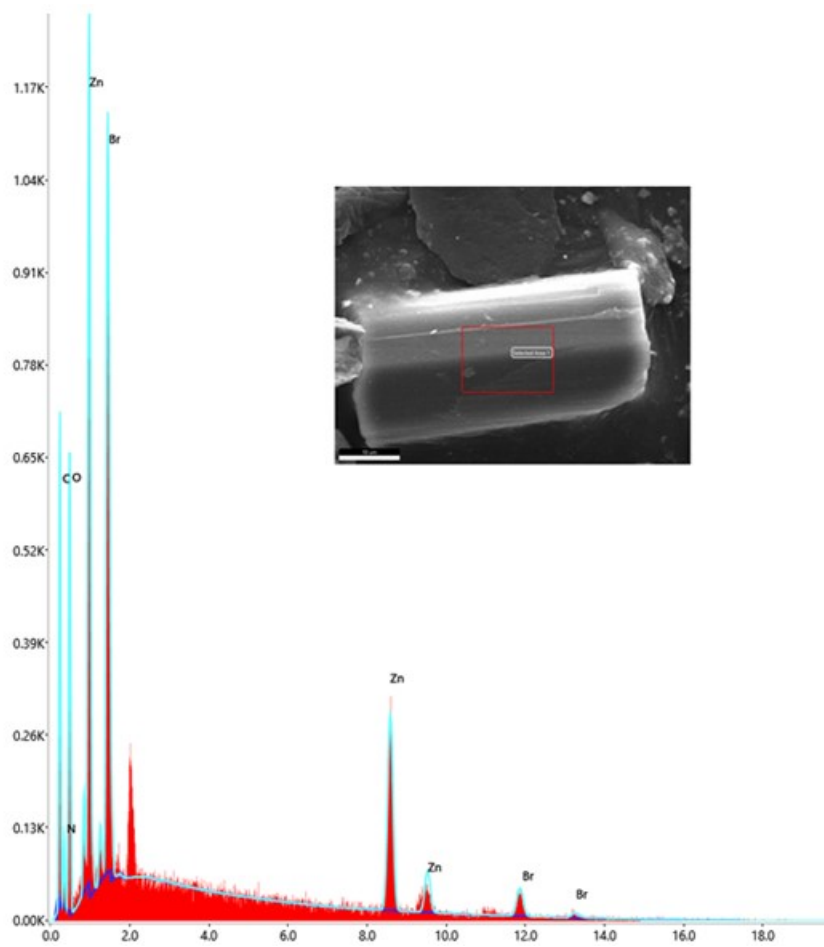


Figure S5. Elemental analysis of complex 2 was performed by energy-dispersive X-ray spectroscopy (EDS) using SEM.

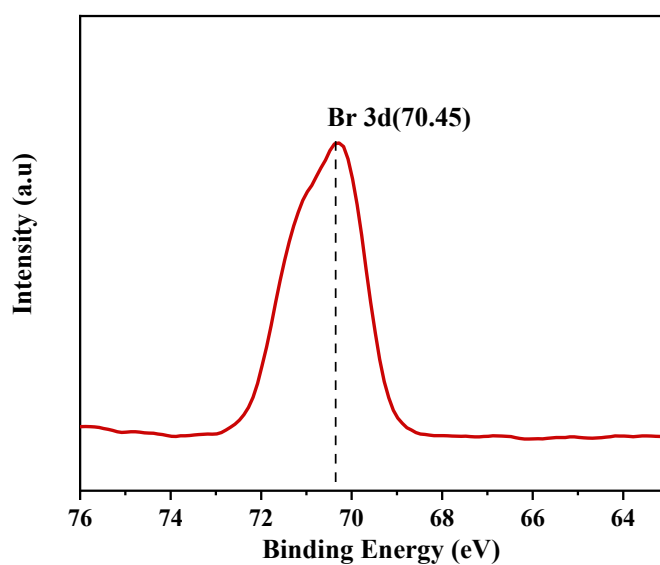
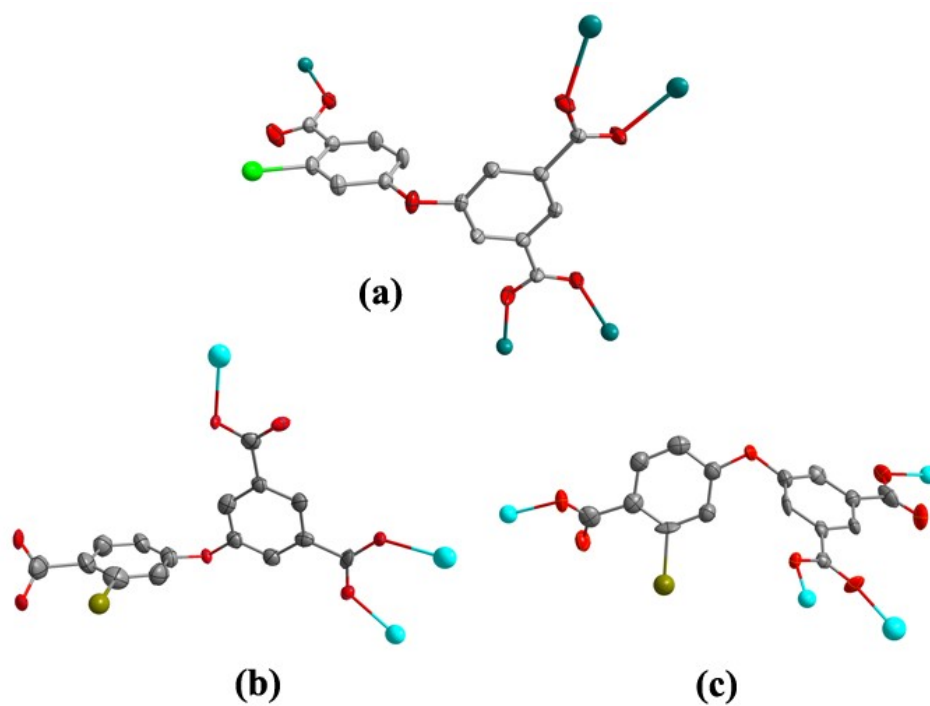


Figure S6. High-resolution XPS of Br 3d for H₃L.



Scheme S1. The different coordination modes of L in complexes 1-2.

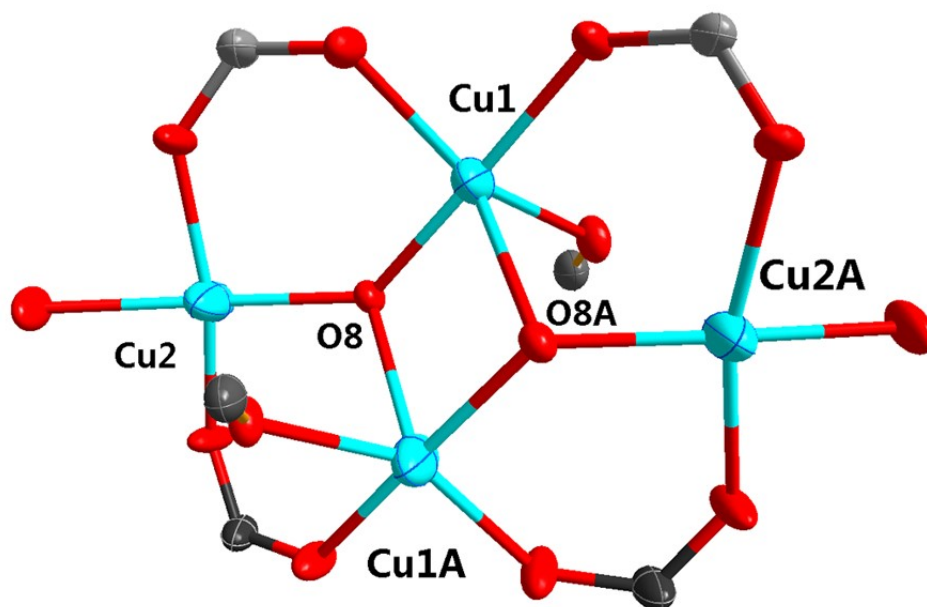


Figure S7. The coordination environment and the coordination number of Cu_4 cluster in complex 1.

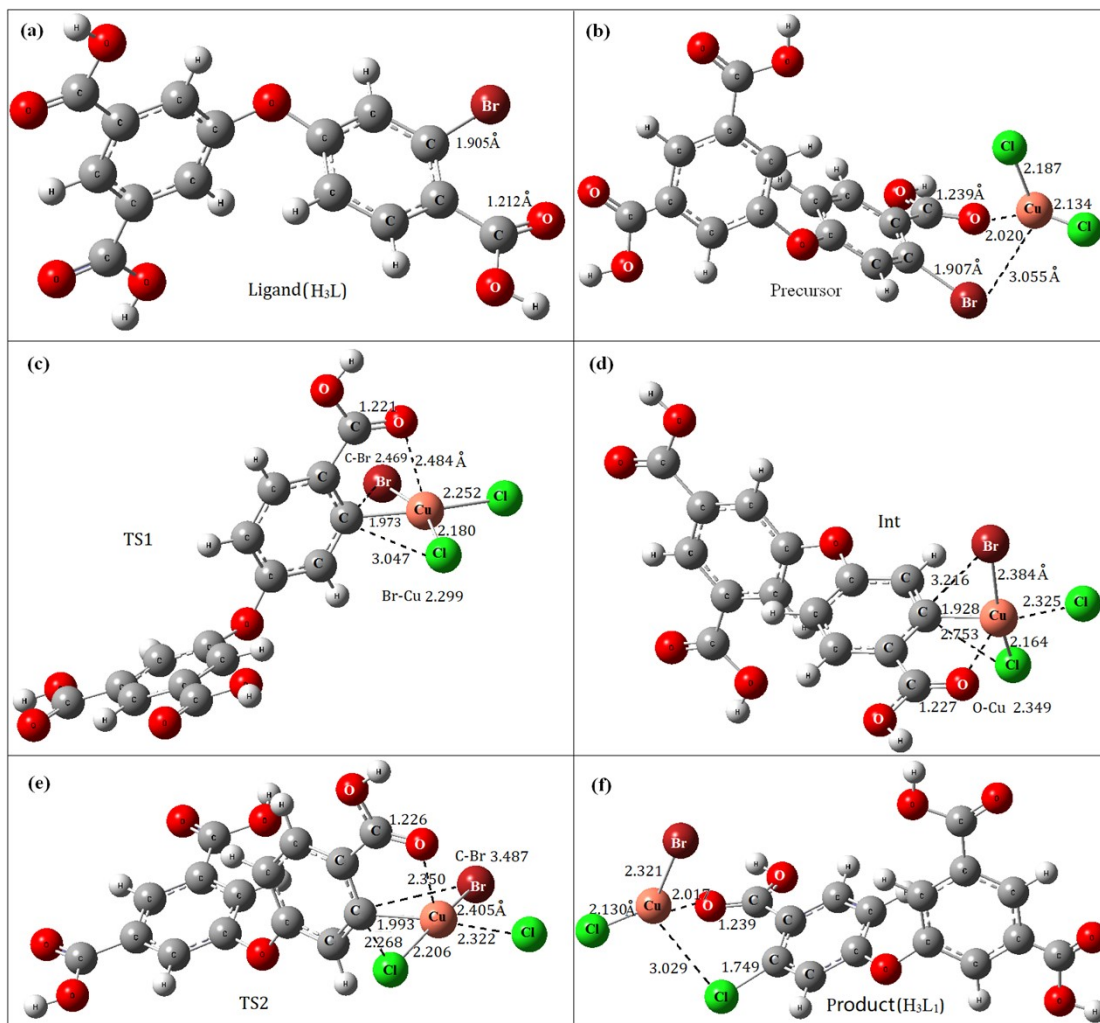
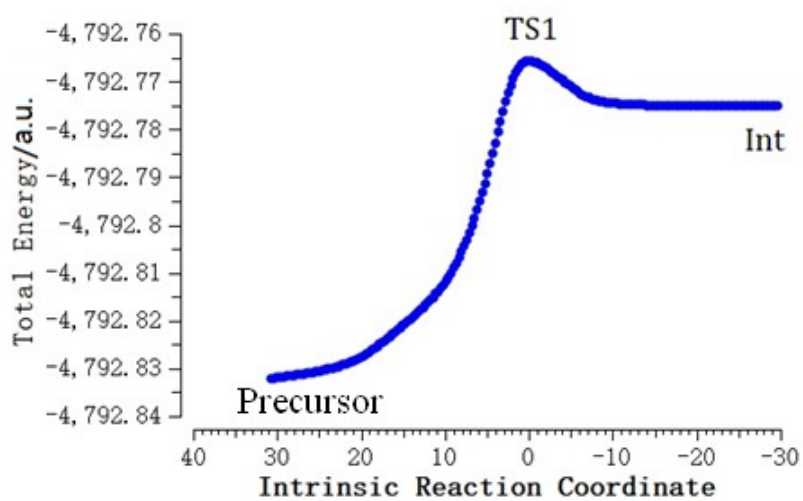
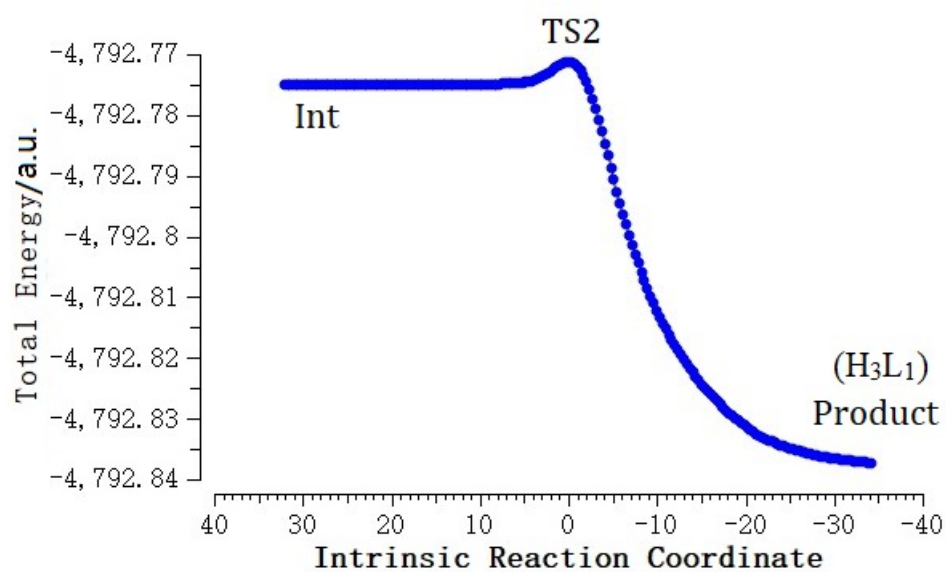


Figure S8. The geometric configurations and some key bond lengths of the species on the reaction path.



(a)



(b)

Figure S9. The corresponding intrinsic reaction coordinate (IRC) of TS1 and TS2.

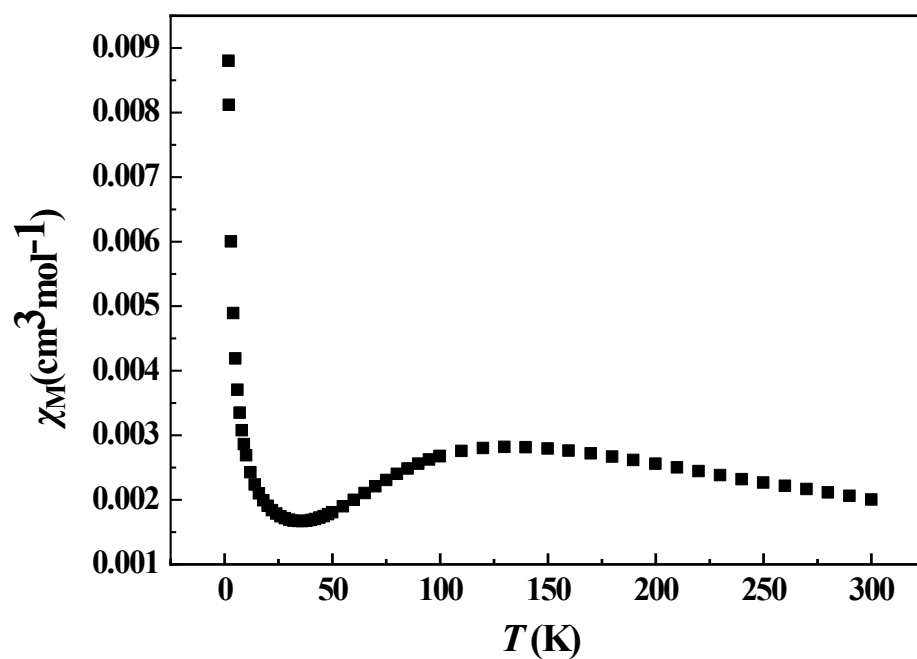


Figure S10. Temperature dependence of χ_M value at 1000 Oe for complex **1**

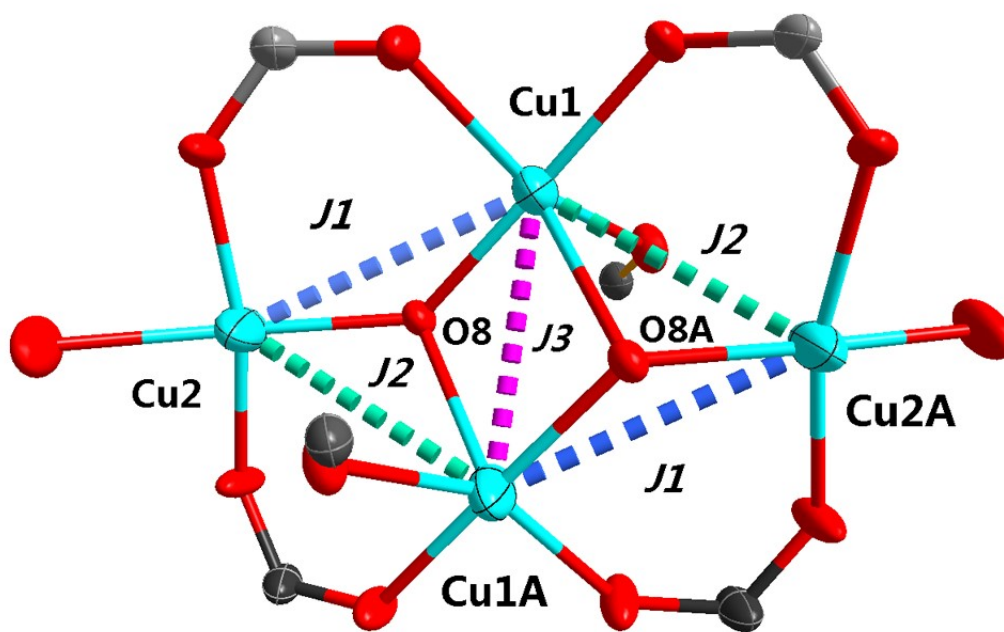


Figure S11. The magneto-structure of the Cu₄ unit in **1**.

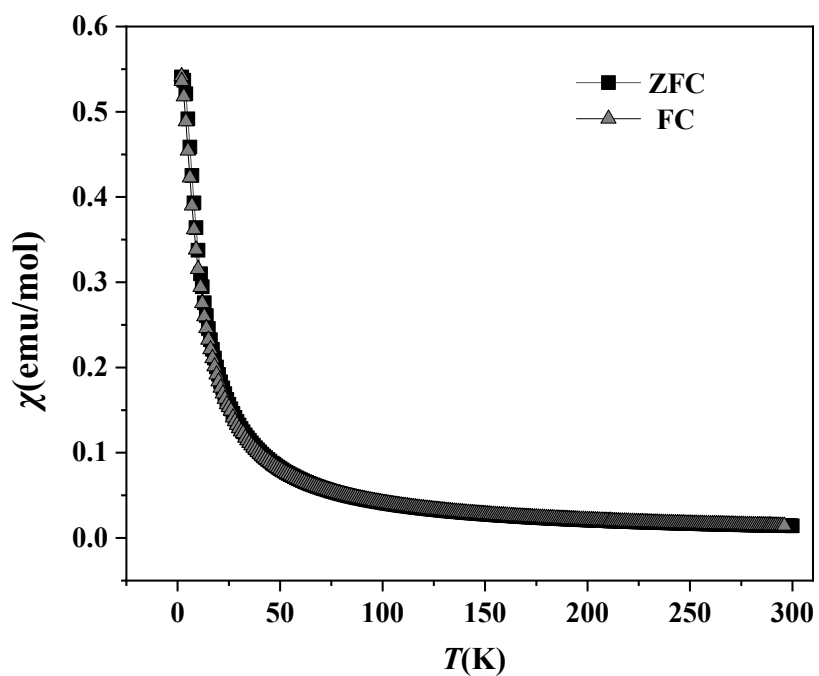


Figure S12. ZFC and FC susceptibility curves from 2 to 300 K measured under 1000 Oe.

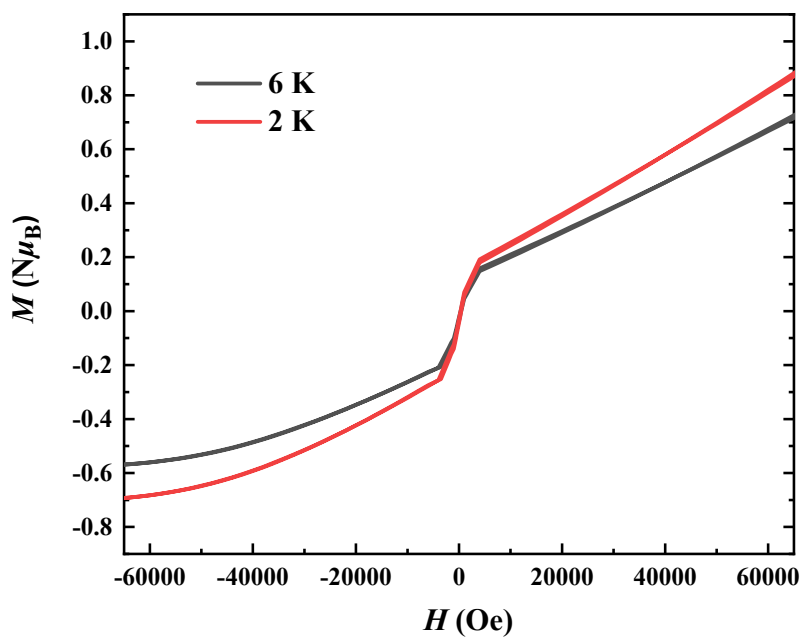


Figure S13. The isothermal field dependence of magnetization for 1.

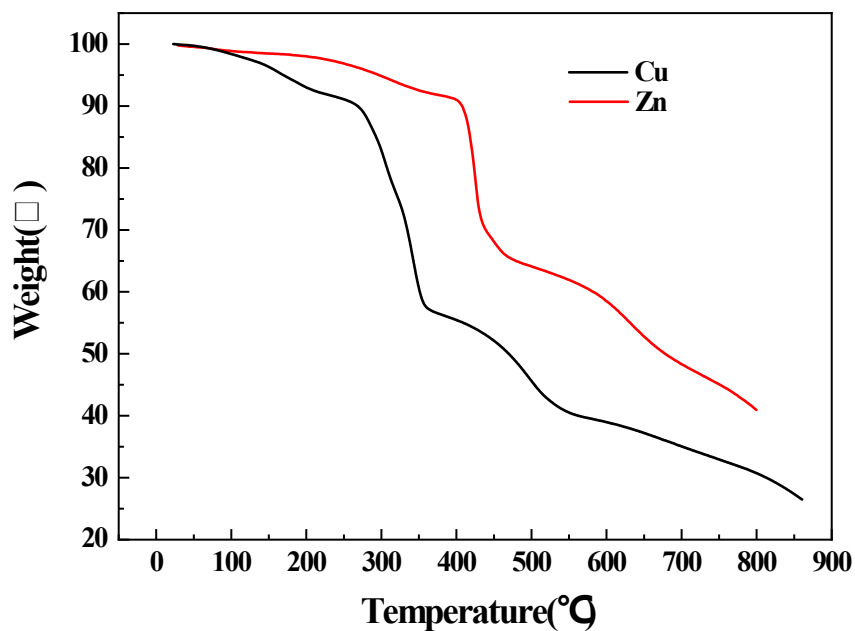


Figure S14. The TG curves of complexes 1-2.

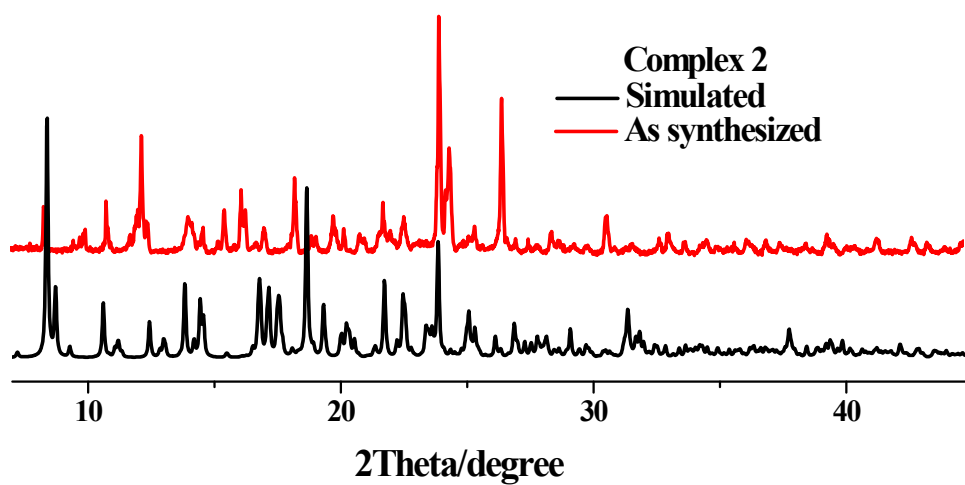
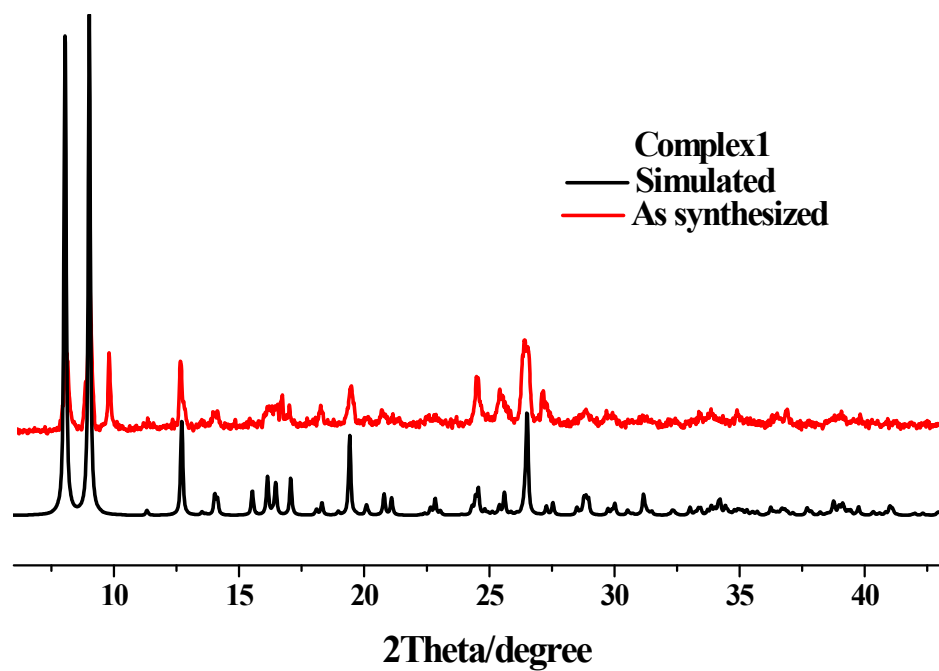


Figure S15. Simulated and observed PXRD patterns of complexes 1-2.

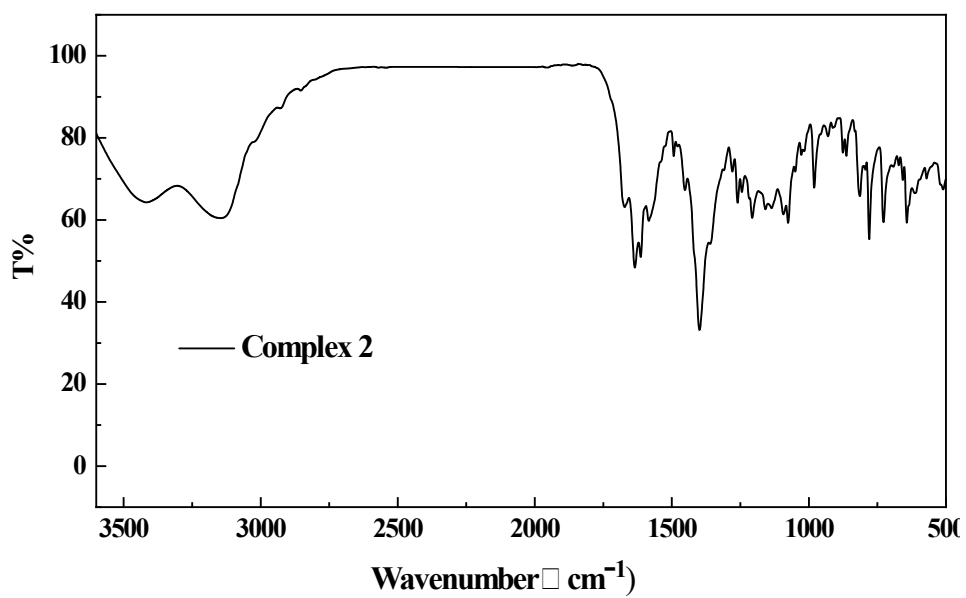
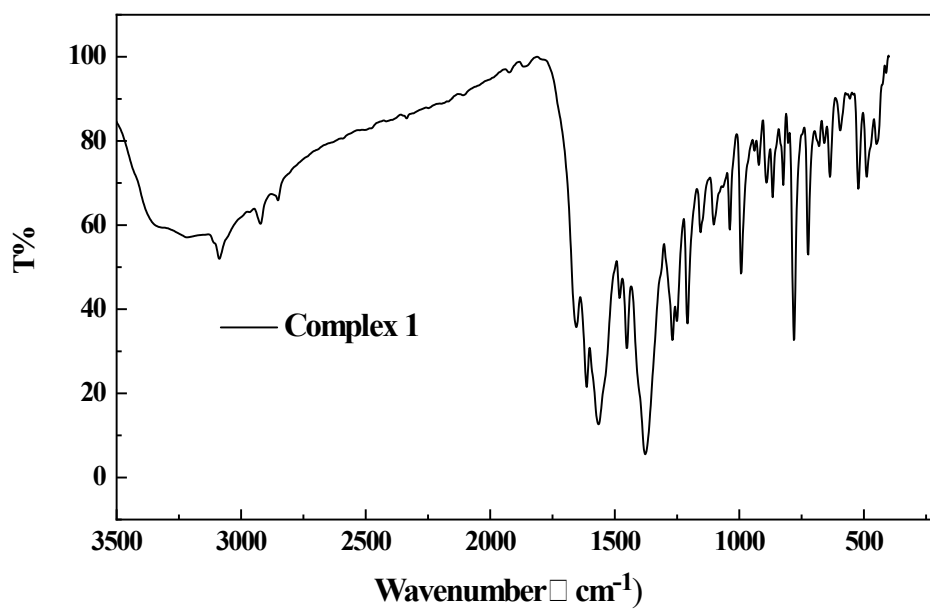


Figure S16. The IR spectra of complexes 1-2.

Theoretical Computational Method

The calculations were performed by using the B3LYP functional together with the 6-31G(d)~SDD basis set using Gaussian 16 program.^{1,2} The basis set 6-31G(d) is used for C, O, H, Br and Cl atoms and the relativistic pseudopotential basis set, SDD, is used for Cu and Zn atoms. The geometries of all the complexes and corresponding configurational isomers were fully optimized and characterized by harmonic vibrational frequency computations at the same level of theory to verify the stationary points or saddle points for transition state. Intrinsic reaction coordinate (IRC) analyses were employed to confirm all the transition states.³⁻⁵

References

- (1) A. D. Becke, Density-functional thermochemistry III. The role of exact exchange, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (2) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.

(3) K. Fukui, A Formulation of the Reaction Coordinate. *J. Phys. Chem.* **1970**, *74*, 4161–4163.

(4) C. Gonzalez, H. B. Schlegel, An Improved Algorithm for Reaction Path Following. *J. Chem. Phys.* **1989**, *90*, 2154–2161.

(5) C. Gonzalez, H. B. Schlegel, Reaction Path Following in Mass-Weighted Internal Coordinates. *J. Phys. Chem.* **1990**, *94*, 5523–5527.

Table S1. Selected Bond Lengths (Å) and angles (°) for complexes **1–2**.

Complex 1					
Cu(1)–O(2) #4	2.015(2)	Cu(1)–O(4) #1	1.959(5)	Cu(1)–O(8)	1.933(3)
Cu(1)–O(8)#2	2.249(0)	Cu(1)–O(6)	1.978(2)	Cu(2)–O(8)	1.902(1)
Cu(2)–O(5)	1.908(2)	Cu(2)–O(3) #3	1.939(2)	Cu(2)–O(9)	1.985(2)
O(8)–Cu(1)–O(4) #1		178.16(9)	O(8)–Cu(1)–O(6)		96.38(8)
O(4) #1–Cu(1)–O(6)		82.17(8)	O(8)–Cu(1)–O(2)#4		93.57(8)
O(4)–Cu(1)–O(2)		88.25(9)	O(4)–Cu(1)–O(2)#4		149.33(1)
O(8)–Cu(1)–O(8) #2		83.43(7)	O(4)#1–Cu(1)–O(8)#2		96.43(8)
O(4)–Cu(1)–O(8)		124.47(9)	O(2)–Cu(1)–O(8)		85.42(8)
O(8)–Cu(2)–O(5)		96.29(9)	O(8)–Cu(2)–O(3)#3		95.66(8)
O(5)–Cu(2)–O(3)#3		165.87(9)	O(8)–Cu(2)–O(9)		173.12(1)
O(5)–Cu(2)–O(9)		82.73(9)	O(3)#3–Cu(2)–O(9)		86.29(9)

Symmetry code for #1 -x, -y+1, -z; #2 -x, -y+2, -z; #3 x, y+1, z; #4 x-1, y+1, z-1

Complex 2					
Zn(1)–O(6)	1.986(5)	Zn(1)–O(8)	1.882(5)	Zn(1)–O(9)	1.983(4)
Zn(1)–O(10)	1.978(4)	Zn(2)–O(13)#4	2.033(4)	Zn(2)–O(16)	2.000(4)
Zn(2)–O(17)	1.936(5)	Zn(2)–N(3)	2.231(5)	Zn(2)–N(4)#3	2.258(5)
Zn(3)–O(8)	1.919(5)	Zn(3)–O(4)#4	2.004(4)	Zn(3)–O(7)	2.026(5)
Zn(3)–N(1)	2.220(5)	Zn(3)–N(2)#3	2.267(5)	Zn(4)–O(17)	1.974(4)

Zn(4)–O(18)	2.108(4)	Zn(4)–O(14)#4	2.118(5)	Zn(4)–O(19)	2.140(4)
Zn(4)–N(5)	2.226(5)	Zn(4)–N(6) #2	2.231(5)		
O(8)–Zn(1)–O(10)		111.6(2)	O(8)–Zn(1)–O(9)		120.46(1)
O(9)–Zn(1)–O(10)		107.04(1)	O(8)–Zn(1)–O(6)		104.3(2)
O(10)–Zn(1)–O(6)		111.40(1)	O(9)–Zn(1)–O(6)		101.43(1)
O(17)–Zn(2)–O(16)		129.32(1)	O(17)–Zn(2)–O(13)#4		119.44(1)
O(16)–Zn(2)–O(13)#4		111.23(1)	O(17)–Zn(2)–N(3)		91.72(1)
O(16)–Zn(2)–N(3)		91.89(1)	O(13)–Zn(2)–N(3)		86.86(1)
O(17)–Zn(2)–N(4)#3		95.02(19)	O(16)–Zn(2)–N(4)#3		86.25(1)
O(13)–Zn(2)–N(4)#3		87.11(18)	N(3)–Zn(2)–N(4)#3		172.6(2)
O(8)–Zn(3)–O(4)#4		138.95(19)	O(8)–Zn(3)–O(7)		105.93(19)
O(7)–Zn(3)–O(4)		105.93(19)	O(8)–Zn(3)–N(1)		92.4(2)
O(4)–Zn(3)–N(1)		87.31(18)	O(7)–Zn(3)–N(1)		89.03(18)
O(8)–Zn(3)–N(2)#3		92.2(2)	O(4)–Zn(3)–N(2)#3		90.49(19)
O(7)–Zn(3)–N(2)#3		87.81(19)	N(1)–Zn(3)–N(2)#3		175.0(2)
O(17)–Zn(4)–O(18)		96.17(18)	O(17)–Zn(4)–O(14)#4		89.18(18)
O(14)#4–Zn(4)–O(18)		174.58(18)	O(17)–Zn(4)–O(19)		170.86(18)
O(19)–Zn(4)–O(18)		92.61(17)	O(19)–Zn(4)–O(14)#4		82.09(17)
O(17)–Zn(4)–N(5)		93.51(18)	O(18)–Zn(4)–N(5)		89.79(18)
O(14)#4–Zn(4)–N(5)		90.78(18)	O(19)–Zn(4)–N(5)		83.97(17)
O(17)–Zn(4)–N(6)#2		97.27(18)	O(18)–Zn(4)–N(6)#2		88.42(18)
O(14)#4–Zn(4)–N(6)#2		90.03(18)	O(19)–Zn(4)–N(6)#2		85.47(17)
N(5)–Zn(3)–N(6)#2		169.2(2)			

Symmetry code for #1 $x-1, y, z$; #2 $x, y+1, z$; #3 $x, y-1, z$; #4 $x+1, y, z$

Table S2. Hydrogen bonding data for complexes 1–2.

Complex 1			
D-H···A	d(D···H) (Å)	d(H···A) (Å)	d(D···A) (Å)
C(6)–H(6)···Cl1	0.930	2.939	3.743
Complex 2			
D-H···A	d(D···H) (Å)	d(H···A) (Å)	d(D···A) (Å)
C(36)–H(36)···O	0.930	2.619	3.419
C(49)–H(49)···O	0.930	2.887	3.470