Supporting Information

Exploring the coordinative adaptation and molecular shapes of the trinuclear $Cu^{II}_2M^{II}$ (M = Zn/Cd) complexes derived from salen type Schiff bases: Structural and theoretical studies

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Table S1. Bond distances (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Cu(1)–O(10)	1.925(3)	1.936(4)
Cu(1)–O(30)	1.923(3)	1.963(4)
Cu(1)–N(18)	1.983(4)	2.022(5)
Cu(1)–N(22)	1.958(3)	1.995(5)
Cu(1)–N(2)	---	2.515(6)
Cu(2)–O(31)	1.925(3)	1.933(4)
Cu(2)–O(51)	1.924(3)	1.952(4)
Cu(2)–N(39)	1.976(4)	2.011(5)
Cu(2)–N(43)	1.961(3)	1.994(5)
Cu(2)–N(2)	---	2.525(6)
Zn(1)–O(10)	2.082(3)	2.020(4)
Zn(1)–O(30)	2.385(3)	2.121(4)
Zn(1)–O(31)	2.097(3)	2.020(4)
Zn(1)–O(51)	2.236(3)	2.105(3)
Zn(1)–N(1)	2.039(4)	1.930(6)
Zn(1)–N(2)	2.000(4)	---
O(10)–Cu(1)–O(30)	79.44(1)	78.64(2)
N(18)–Cu(1)–N(22)	97.56(1)	100.00(2)
N(22)–Cu(1)–O(30)	92.69(1)	89.00(2)
N(18)–Cu(1)–O(10)	91.07(1)	92.70(2)

N(18)–Cu(1)–O(30)	168.23(1)	155.50(2)
N(22)–Cu(1)–O(10)	169.30(1)	167.20(2)
N(2)–Cu(1)–O(30)	---	108.20(2)
N(2)–Cu(1)–N(22)	---	95.00(2)
N(2)–Cu(1)–O(10)	---	85.80(2)
N(2)–Cu(1)–N(18)	---	93.80(2)
O(31)–Cu(2)–O(51)	79.33(1)	78.65(2)
N(39)–Cu(2)–N(43)	97.78(1)	99.00(2)
N(43)–Cu(2)–O(51)	91.91(1)	89.42(2)
N(39)–Cu(2)–O(31)	90.98(1)	93.43(2)
N(39)–Cu(2)–O(51)	170.31(1)	156.03(2)
N(43)–Cu(2)–O(31)	171.16(1)	167.50(2)
N(2)–Cu(2)–O(51)	---	107.98(2)
N(2)–Cu(2)–N(43)	---	95.56(2)
N(2)–Cu(2)–O(31)	---	84.76(2)
N(2)–Cu(2)–N(39)	---	93.60(2)
O(10)–Zn(1)–O(30)	66.42(1)	73.19(2)
O(31)–Zn(1)–O(51)	68.99(1)	73.25(2)
O(30)–Zn(1)–O(31)	94.41(1)	91.51(2)
O(10)–Zn(1)–O(51)	91.43(1)	92.97(2)
O(10)–Zn(1)–O(31)	156.35(1)	118.98(2)
O(30)–Zn(1)–O(51)	73.47(1)	151.51(2)
N(1)–Zn(1)–N(2)	105.74(2)	---
N(1)–Zn(1)–O(10)	98.70(1)	122.80(2)
N(1)–Zn(1)–O(30)	88.99(1)	102.34(2)
N(1)–Zn(1)–O(31)	94.48(1)	118.16(2)
N(1)–Zn(1)–O(51)	154.31(1)	106.07(2)
N(2)–Zn(1)–O(10)	96.82(1)	---
N(2)–Zn(1)–O(30)	159.55(1)	---
N(2)–Zn(1)–O(31)	98.40(1)	---
N(2)–Zn(1)–O(51)	96.34(2)	---

Table S2. Bond distances (Å) and angles (°) for complexes **3/3′**and **4**

	3	**3′**	**4**
Cu(1)–O(10)	1.932(4)	1.920(3)	1.935(1)
Cu(1)–O(30)	1.921(3)	1.928(3)	1.934(1)
Cu(1)–N(18)	1.946(6)	1.952(4)	2.006(1)
Cu(1)–N(22)	1.978(5)	1.953(4)	2.014(1)
Cu(1)–N(1)	---	---	2.554(2)
Cu(2)–O(31)	1.925(4)	1.924(3)	1.932(1)
Cu(2)–O(51)	1.928(3)	1.929(3)	1.937(1)
Cu(2)–N(39)	1.983(6)	1.978(4)	2.000(1)
Cu(2)–N(43)	1.948(5)	1.962(4)	2.020(1)
Cu(2)–N(2)	---	---	2.674(2)
Cd(1)–O(10)	2.302(4)	2.271(3)	2.304(1)

Cd(1)–O(30)	2.362(4)	2.386(3)	2.244(1)
Cd(1)–O(31)	2.290(4)	2.338(3)	2.332(1)
Cd(1)–O(51)	2.401(4)	2.393(4)	2.263(1)
Cd(1)–N(1)/S(1)	2.235(6)	2.251(5)	2.779(5)
Cd(1)–N(2)/S(2)	2.219(5)	2.203(5)	2.688(5)
O(10)–Cu(1)–O(30)	81.91(1)	82.32(1)	83.20(4)
N(18)–Cu(1)–N(22)	95.70(2)	96.71(2)	94.60(5)
N(22)–Cu(1)–O(30)	90.90(2)	92.01(2)	93.70(5)
N(18)–Cu(1)–O(10)	92.80(2)	92.49(2)	93.00(5)
N(18)–Cu(1)–O(30)	169.10(2)	164.80(2)	169.60(5)
N(22)–Cu(1)–O(10)	168.55(2)	163.20(2)	148.80(5)
N(1)–Cu(1)–O(30)	---	---	88.40(4)
N(1)–Cu(1)–N(22)	---	---	109.30(5)
N(1)–Cu(1)–O(10)	---	---	101.70(5)
N(1)–Cu(1)–N(18)	---	---	82.90(5)
O(31)–Cu(2)–O(51)	79.54(2)	79.18(1)	83.70(4)
N(39)–Cu(2)–N(43)	97.90(2)	97.24(2)	93.60(5)
N(43)–Cu(2)–O(51)	91.96(2)	92.03(2)	93.50(5)
N(39)–Cu(2)–O(31)	90.78(2)	91.67(2)	93.60(5)
N(39)–Cu(2)–O(51)	169.83(2)	170.15(2)	168.90(5)
N(43)–Cu(2)–O(31)	170.80(2)	170.96(2)	153.80(4)
N(2)–Cu(2)–O(51)	---	---	85.40(4)
N(2)–Cu(2)–N(43)	---	---	110.80(5)
N(2)–Cu(2)–O(31)	---	---	95.00(5)
N(2)–Cu(2)–N(39)	---	---	84.0(5)
O(10)–Cd(1)–O(30)	65.56(1)	65.84(1)	68.7(4)
O(31)–Cd(1)–O(51)	63.33(1)	62.51(1)	68.3(4)
O(30)–Cd(1)–O(31)	84.94(1)	164.37(1)	96.3(4)
O(10)–Cd(1)–O(51)	88.94(1)	76.43(1)	95.6(4)
O(10)–Cd(1)–O(31)	144.04(1)	101.01()	88.9(3)
O(30)–Cd(1)–O(51)	76.39(1)	104.64(1)	158.8(4)
N(1)/S(1)–Cd(1)–N(2)/S(2)	97.50(2)	105.03(2)	95.21(1)
N(1)/S(1)–Cd(1)–O(10)	100.60(2)	95.24(1)	87.1(3)
N(1)/S(1)–Cd(1)–O(30)	96.98(2)	95.92(1)	88.2(3)
N(1)/S(1)–Cd(1)–O(31)	103.11(2)	93.63(1)	172.5(3)
N(1)/S(1)–Cd(1)–O(51)	165.06(2)	151.83(1)	105.8(3)
N(2)/S(2)–Cd(1)–O(10)	106.57(2)	151.46(1)	172.4(3)
N(2)/S(2)–Cd(1)–O(30)	164.66(2)	91.87(1)	104.0(3)
N(2)/S(2)–Cd(1)–O(31)	96.74(2)	97.57(1)	89.6(3)
N(2)/S(2)–Cd(1)–O(51)	90.69(2)	93.49(1)	90.8(3)

Table S3 Dihedral angles (in º) of Complexes **1**–**4**.

	1	**2**	**3**	**3′**	**4**
N(18)–Cu(1)–O(10) And N(22)–Cu(1)–O(30)	9.13(1)	22.72(2)	12.17(2)	19.80(1)	31.40(4)
N(39)–Cu(2)–O(31) And N(43)–Cu(2)–O(51)	1.24(1)	22.38(2)	4.27(2)	3.86(1)	27.09(4)

Table S4 The r.m.s deviations of the complexes **1**–**4**.

Metal Centers	R.M.S Deviations (Å)				
	1	**2**	**3**	**3′**	**4**
Cu(1)	0.111	0.201	0.148	0.239	0.330
Cu(2)	0.011	0.201	0.052	0.045	0.303

Table S5 The metal–metal separations (in Å)of the complexes **1**–**4**.

	1	2	3	3′	4
Cu(1)–Zn(1)/Cd(1)	3.158	2.992	3.355	3.335	3.294
Cu(2)–Zn(1)/Cd(1)	3.165	2.991	3.289	3.373	3.322
Cu(1)–Cu(2)	4.301	4.197	4.264	5.095	5.856

Table S6. Theoretical[a] and experimental stretching frequencies (cm^{-1}) for complexes 1, 2 and 4

Complexes	Theoretical ν	Experimental ν
1	CN: 2090 CS: 882	CN: 2091, 2063 CS: 856
2	CN: 2093, 2017 CS: 890, 762	CN: 2080, 2010 CS: 885, 786
4	CN: 2066, 2066 CS: 747	CN: 2078, 2063 CS:765[b]

[a]Scaled by a factor of 0.97

[b]The CS stretching band seems to be overlapped with other band at the same region

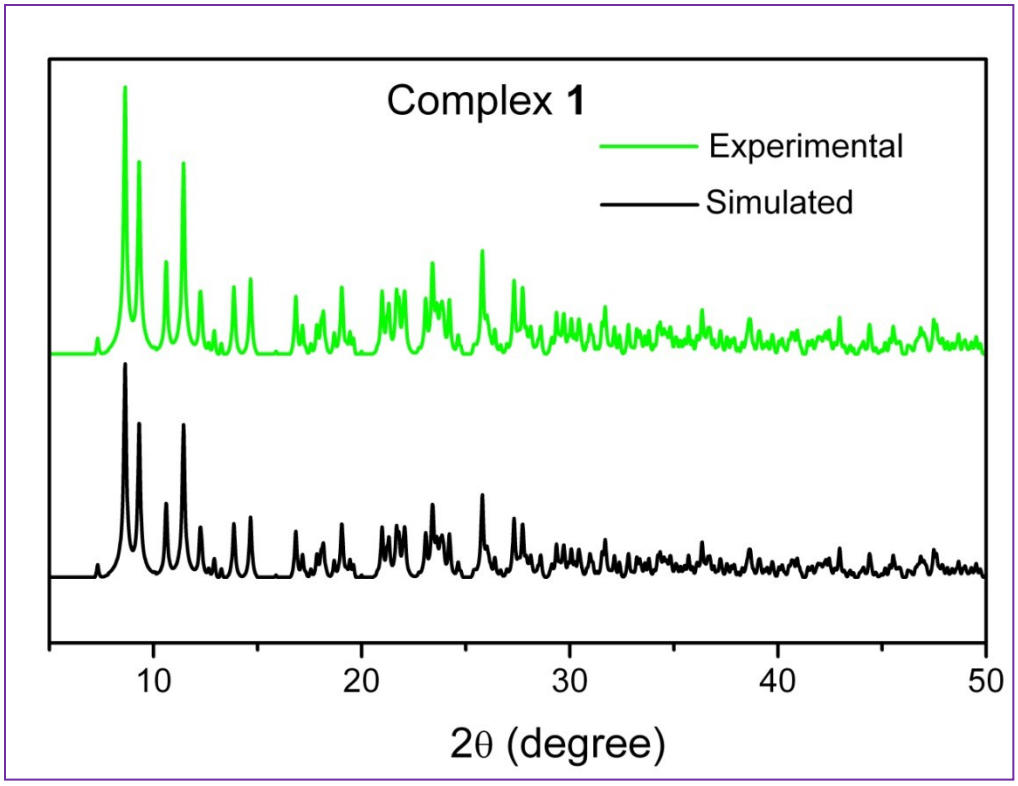

Fig. S1 Powder XRD diffraction pattern of complex **1**

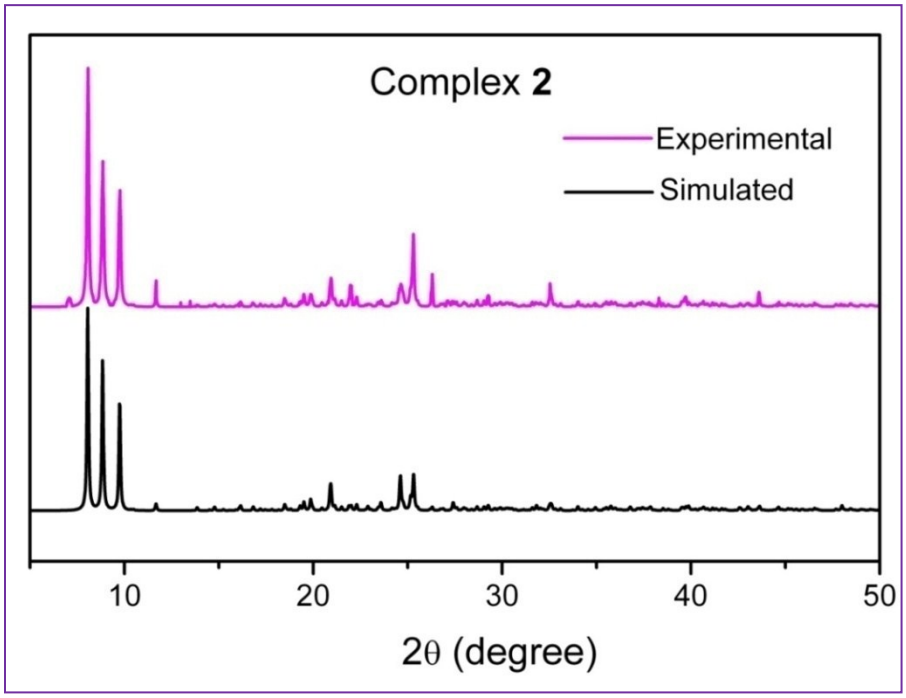

Fig. S2 Powder XRD diffraction pattern of complex **2**

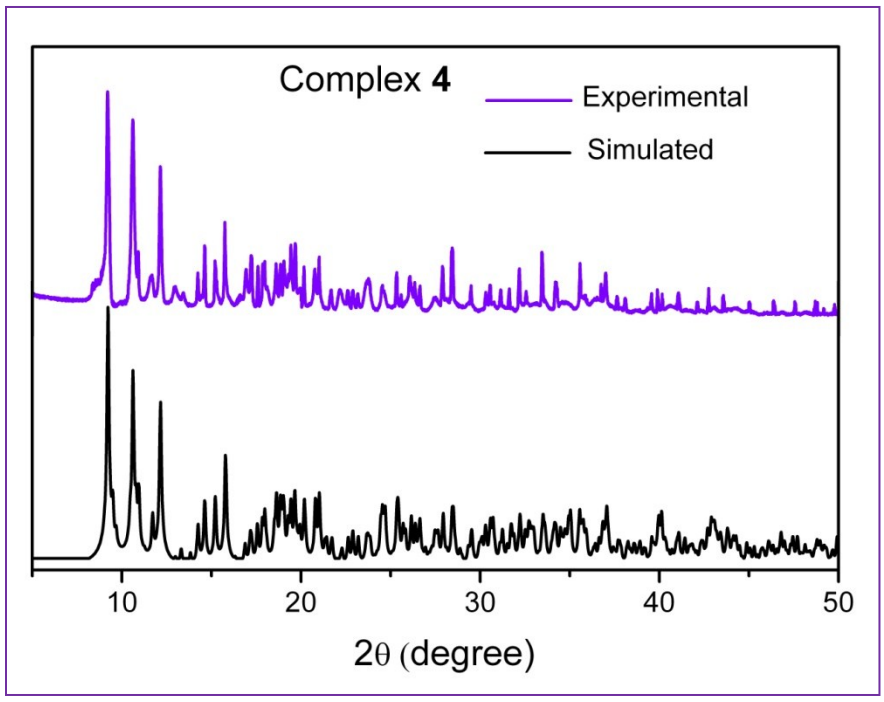

Fig. S3 Powder XRD diffraction pattern of complex **4**

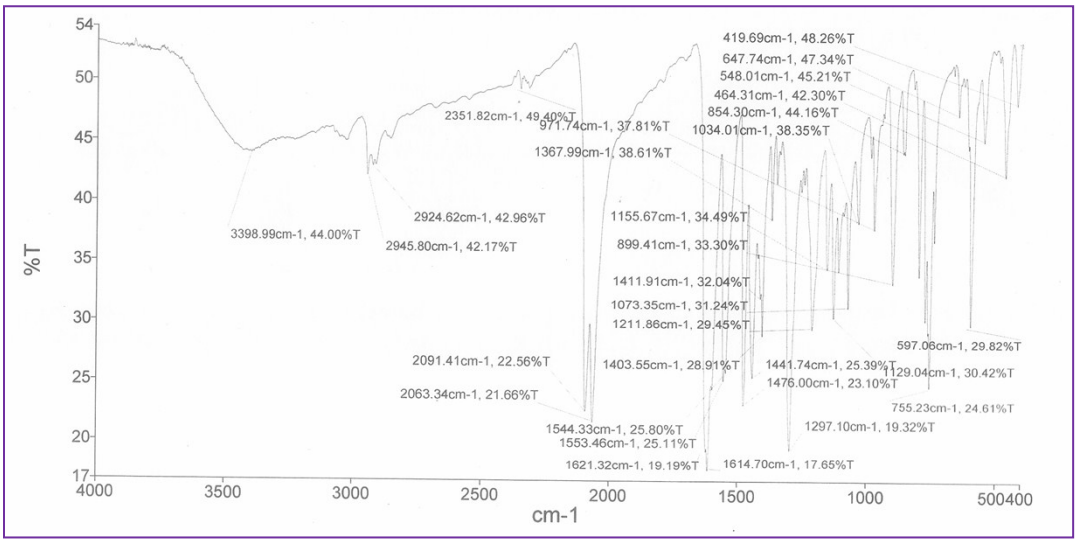

Fig. S4 IR Spectrum of complex **1**

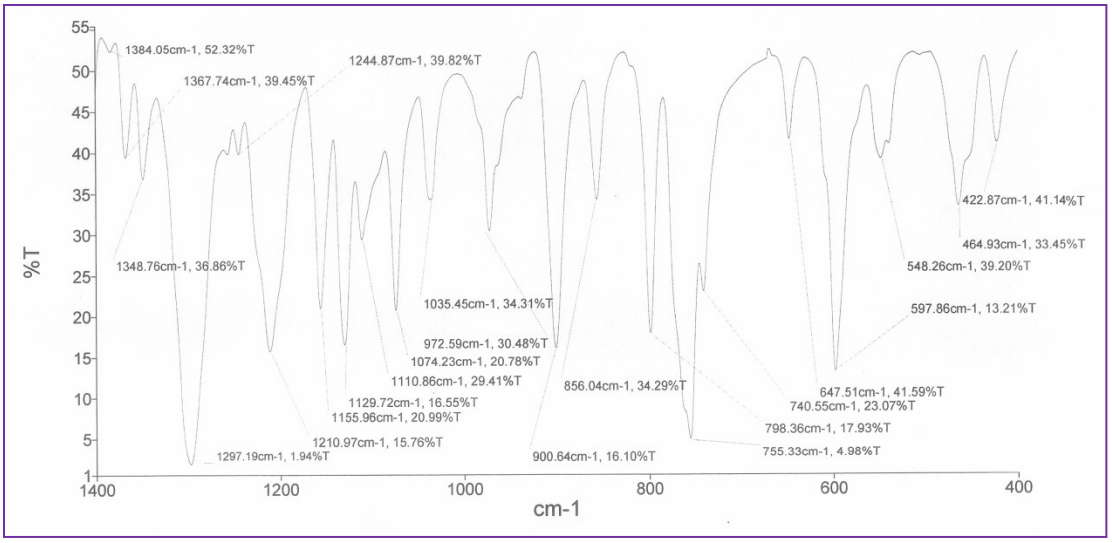

Fig. S4A IR Spectrum of complex **1** (from 400 to 1400 cm^{-1})

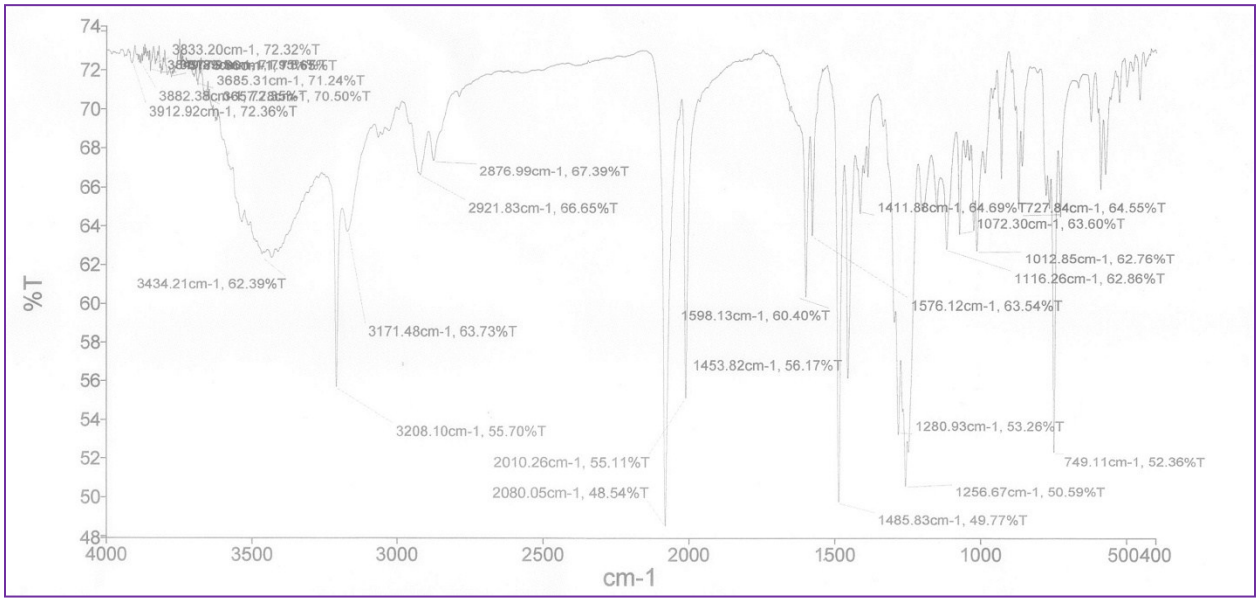

Fig. S5 IR Spectrum of complex **2**

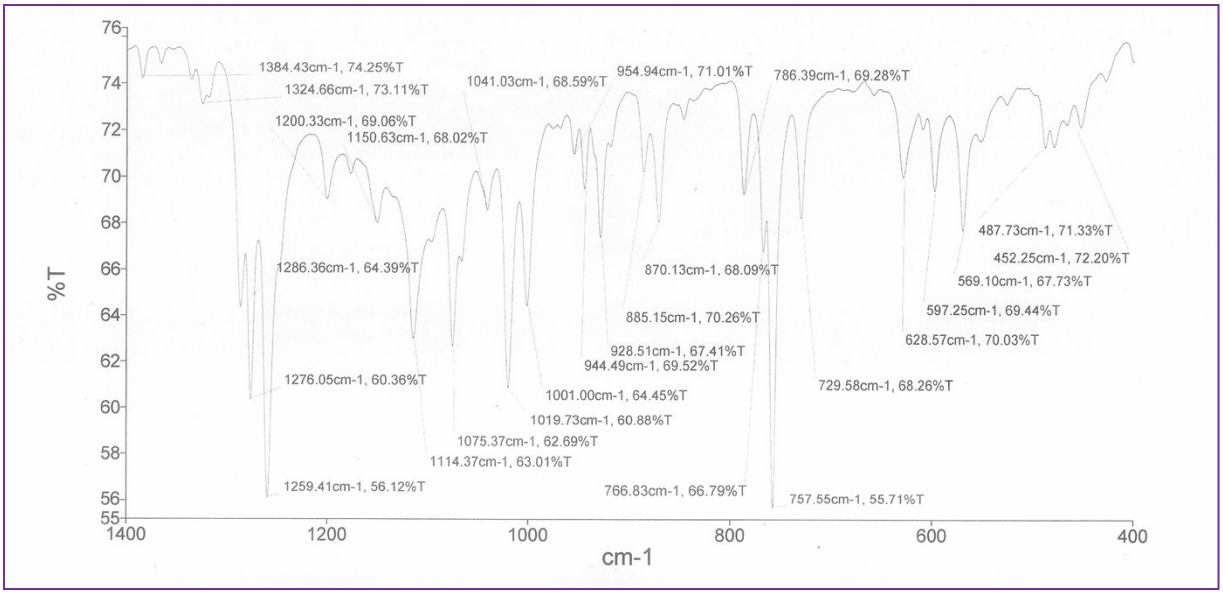

Fig. S5A IR Spectrum of complex **2** (from 400 to 1400 cm^{-1})

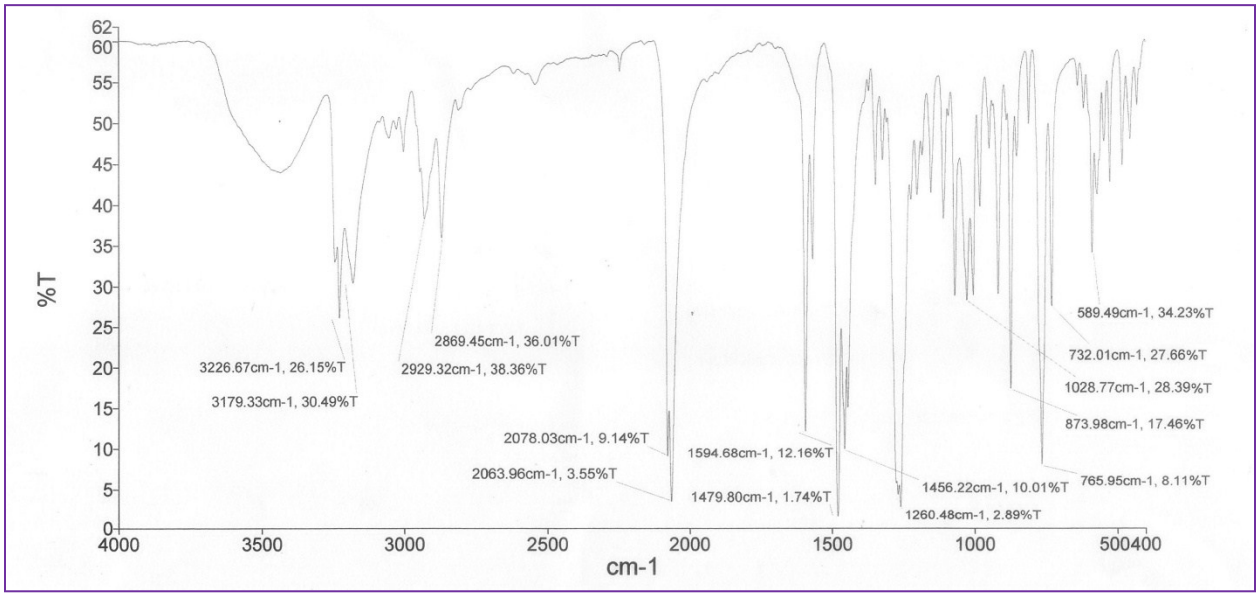

Fig. S6 IR Spectrum of complex **4**

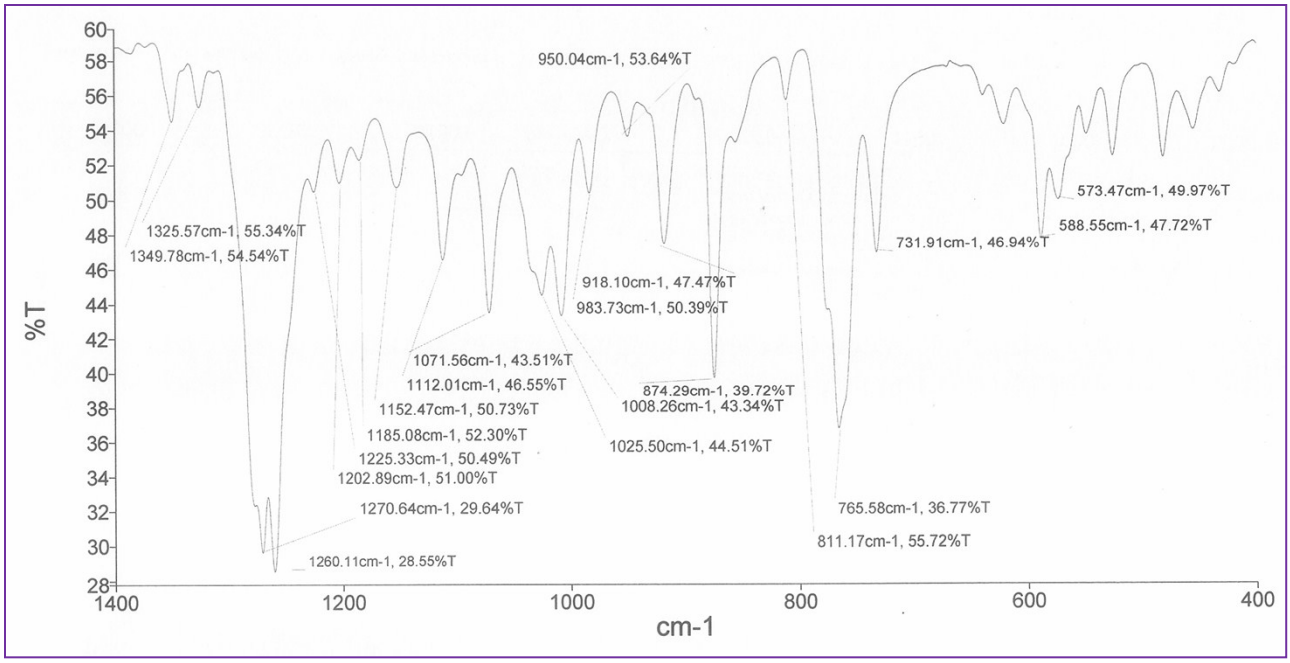

Fig. S6A IR Spectrum of complex **4** (from 400 to 1400 cm^{-1})

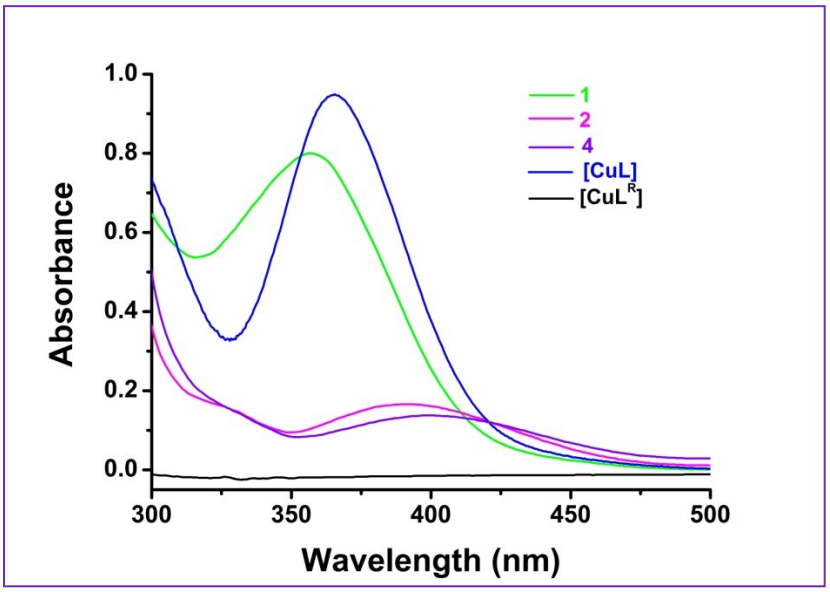

Fig. S7 UV-Vis spectra of trinuclear complexes (**1**-**4**) in acetonitrile solution (charge transfer band).

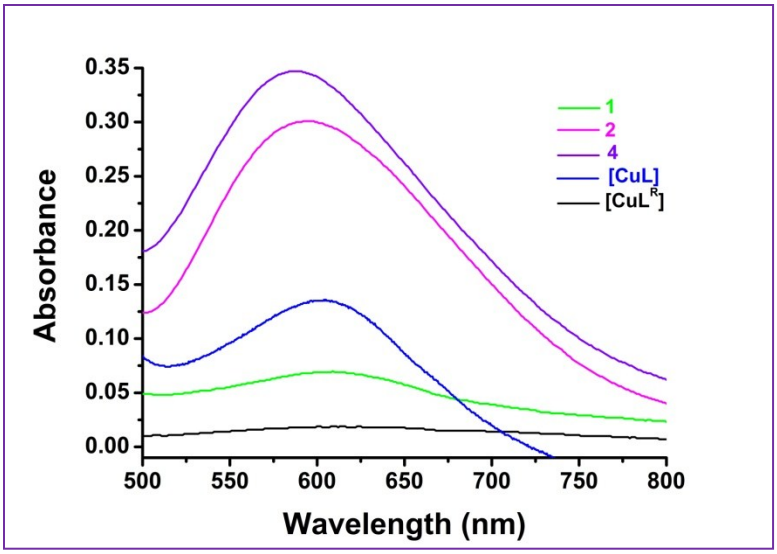

Fig. S8 UV-Vis spectra of trinuclear complexes (**1**-**4**) in acetonitrile solution (d-d transition band).

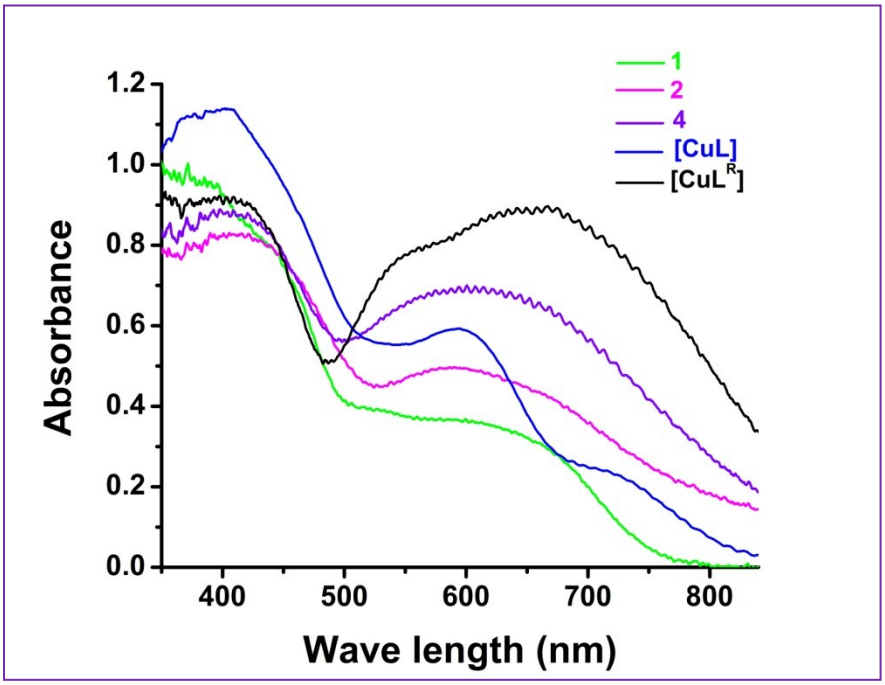

Fig. S9 UV-Vis spectra of trinuclear complexes (**1**-**4**) in solid state.

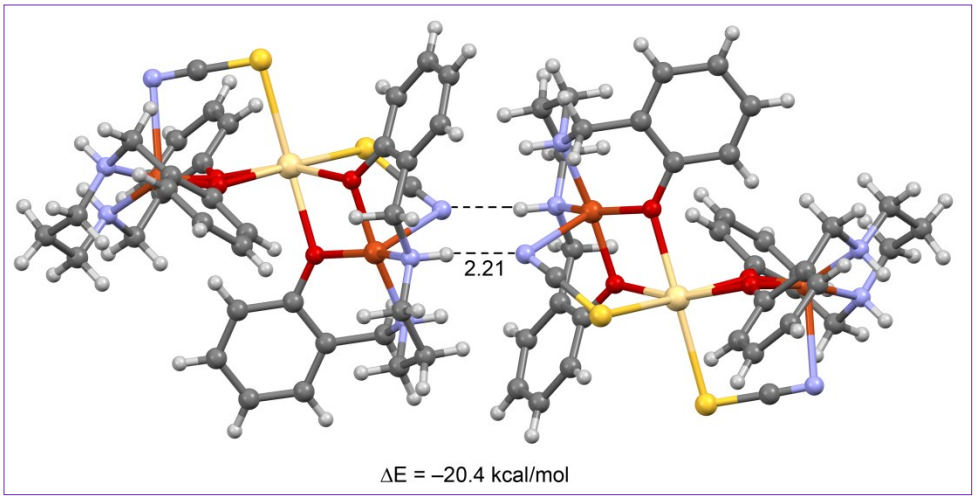

Fig. S10 Self-assembled dimer observed in the solid state of **4**. Distance in Å. Interaction energy computed at the BP86/def2-TZVP