Electronic Supplementary Information (ESI)

The copper(II) complexes with 2-ethylpyridine and related hydroxyl pyridine derivatives: the structural, spectroscopic, magnetic and anticancer *in vitro* studies.

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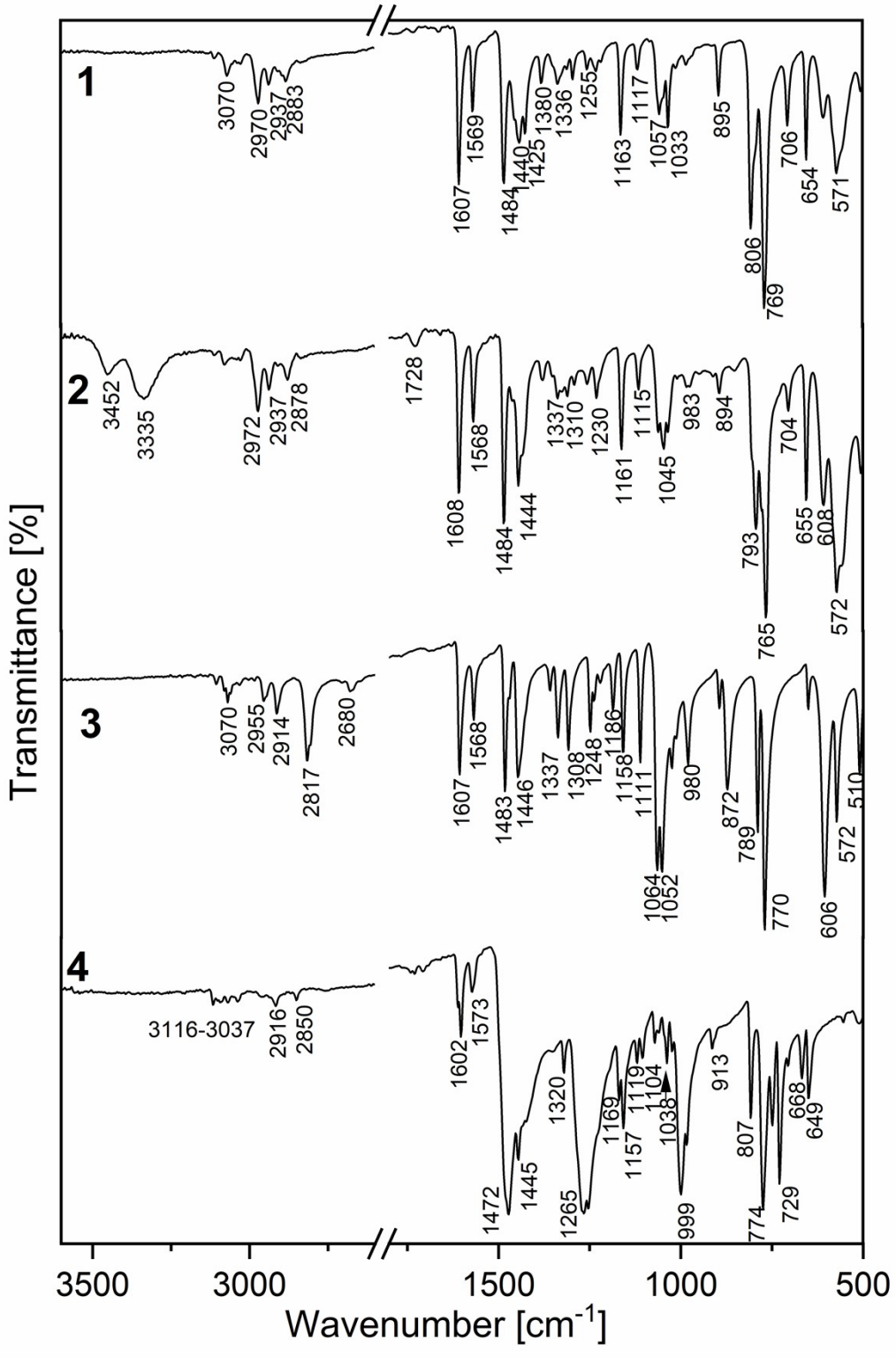


Fig. S1. The comparison of the FT-IR spectra of **1**-**4** in the 3600-500 cm^{-1} spectral range.

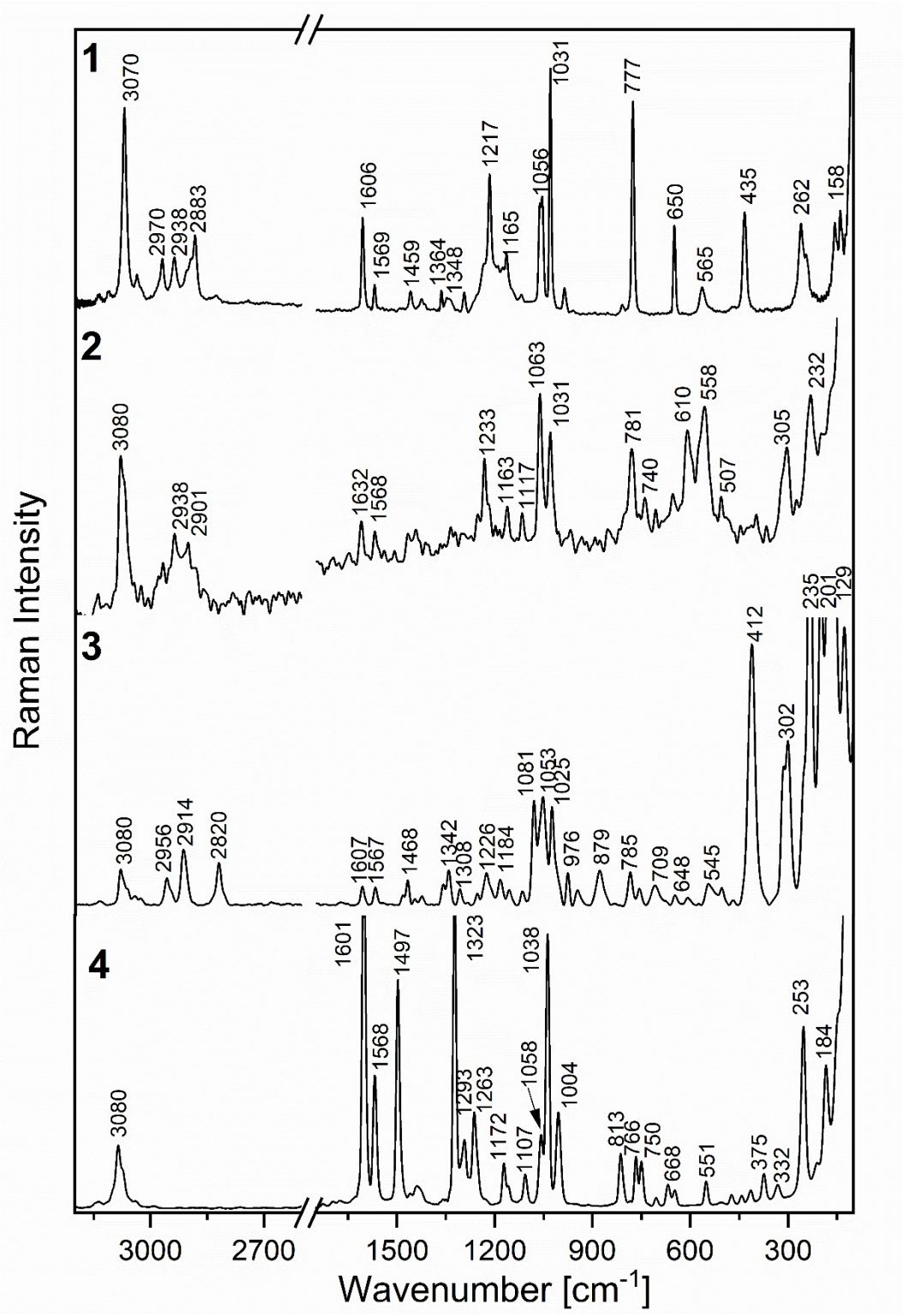


Fig. S2. The comparison of the Raman spectra of **1**-**4** in the 3200-100 cm^{-1} spectral range.

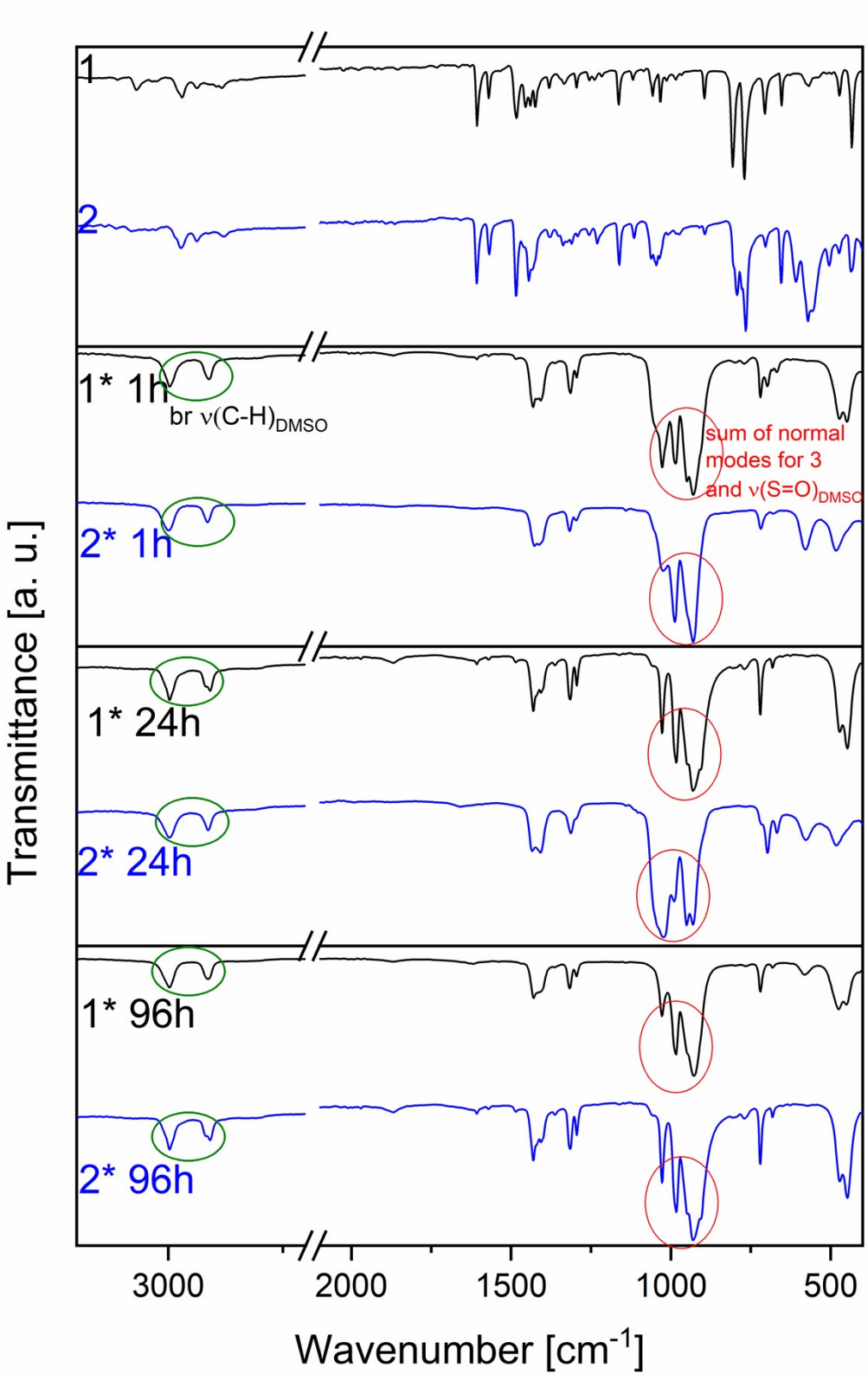


Fig. S3. The FT-IR spectra for complexes **1-2** in MIR spectral region; *-complex in DMSO solution.

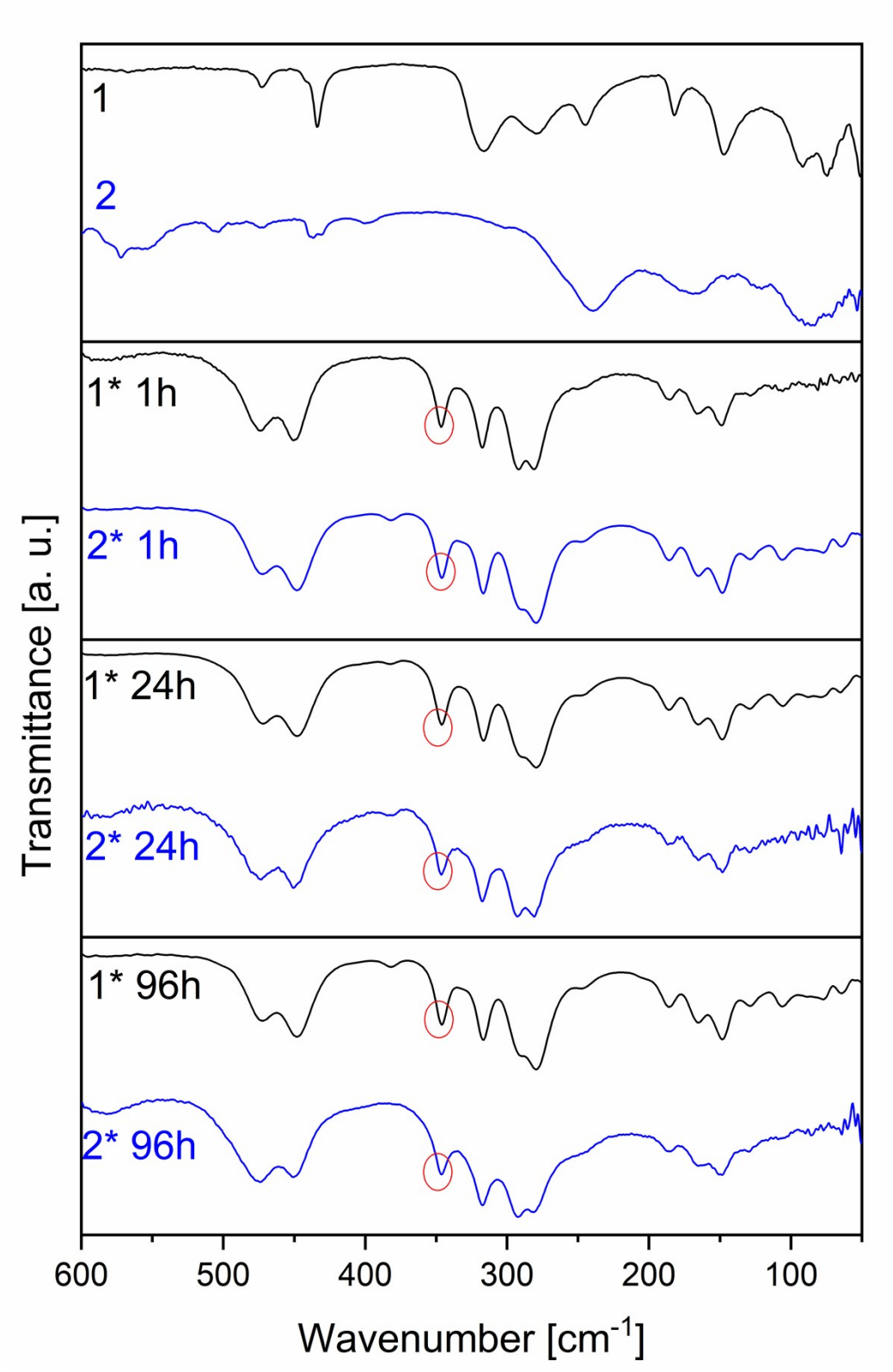


Fig. S4. The FT-IR spectra for complexes **1-2** in FIR spectral region; *-complex in DMSO solution.

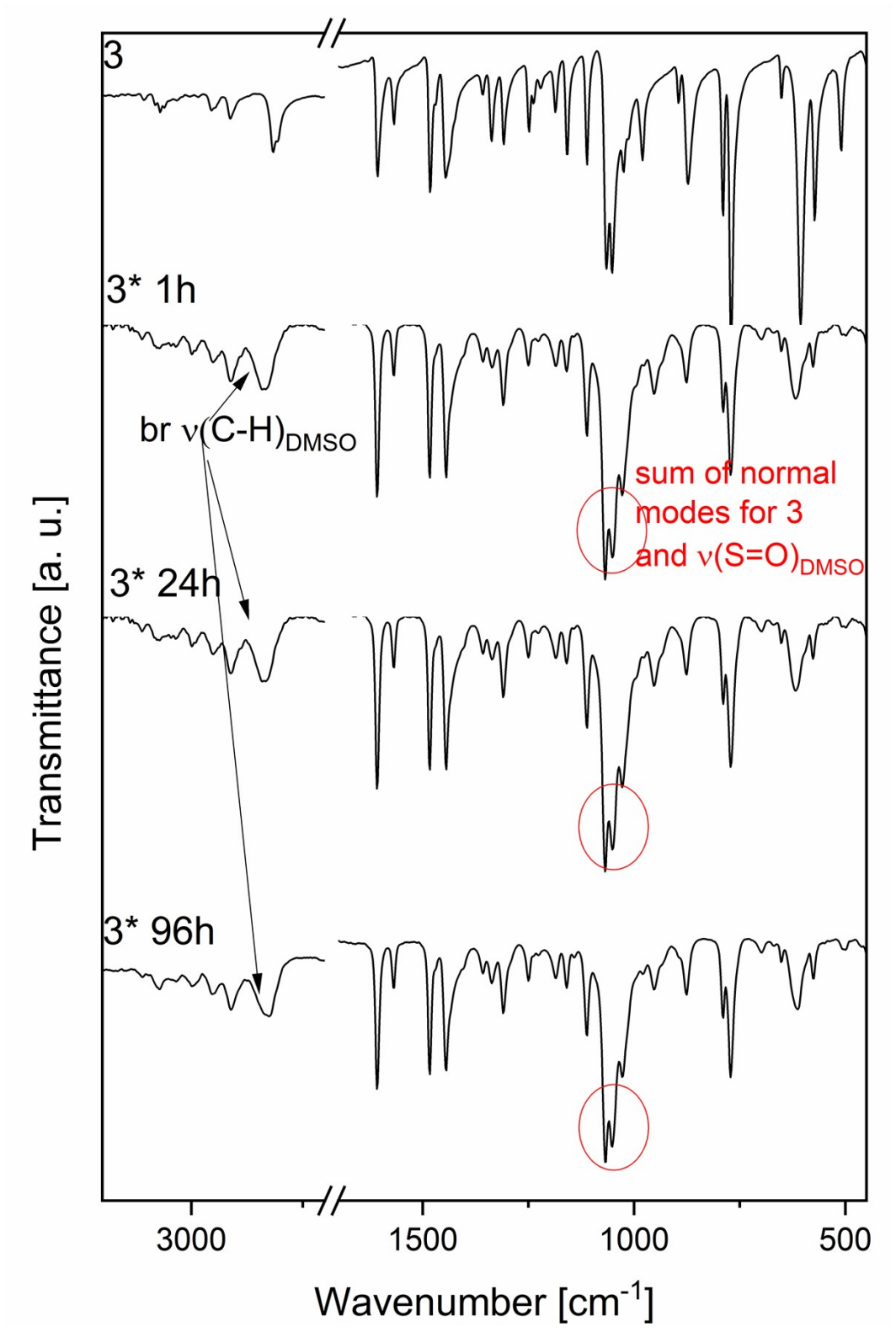


Fig. S5. The FT-IR spectra for complex **3** in MIR spectral region; *-complex in DMSO solution.

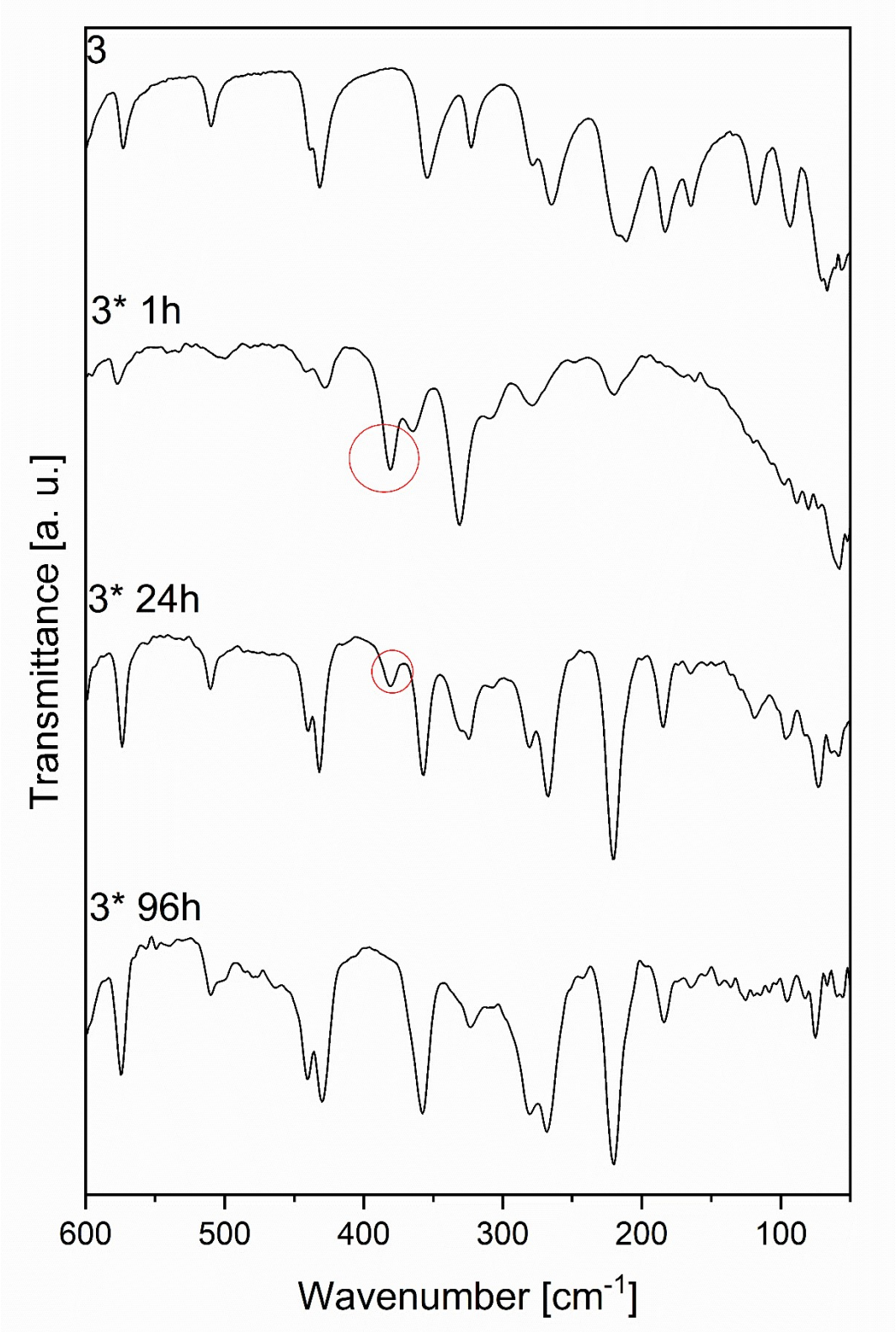


Fig. S6. The FT-IR spectra for complex **3** in FIR spectral region; *-complex in DMSO solution.

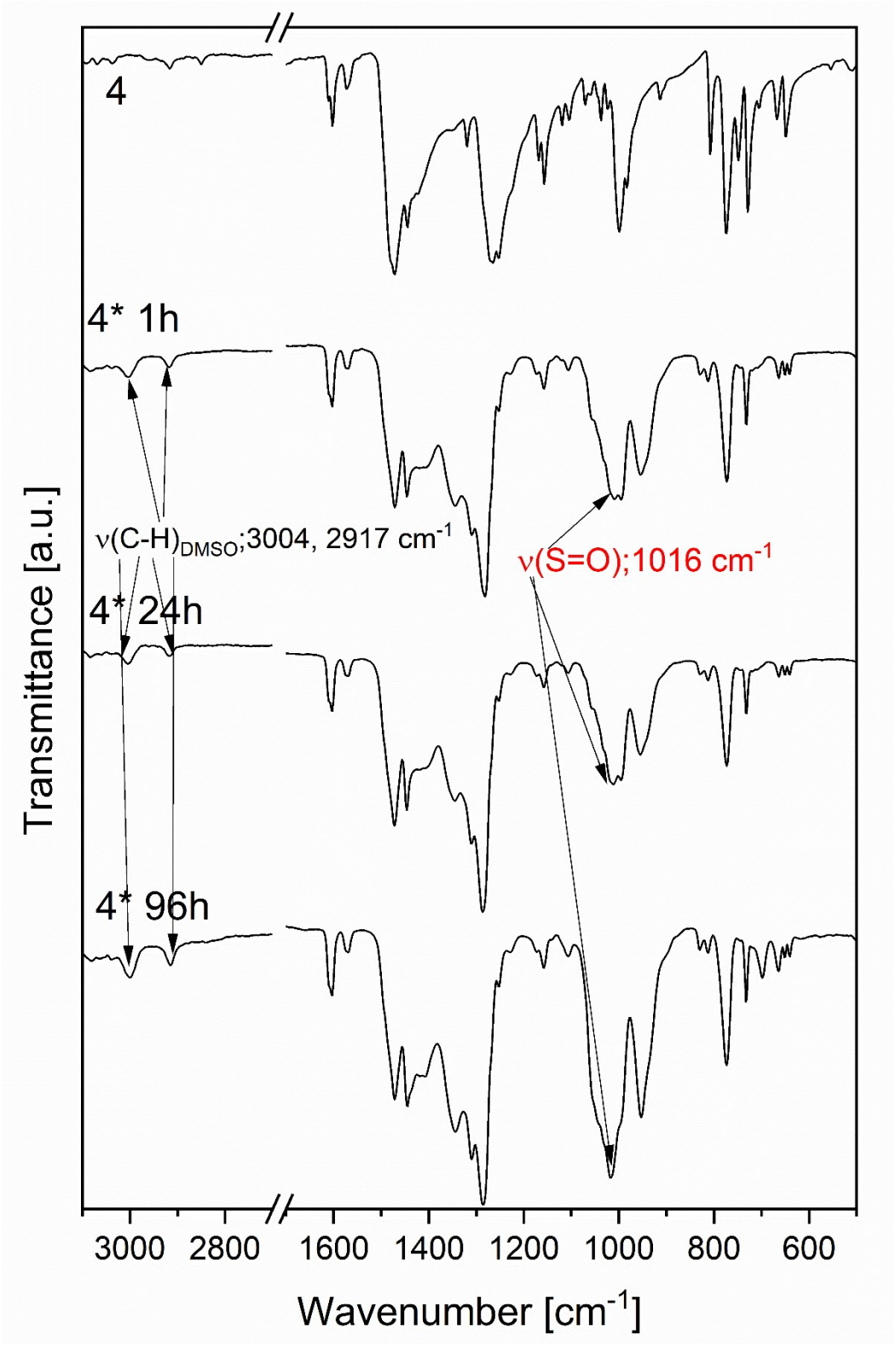


Fig. S7. The FT-IR spectra for complex **4** in MIR spectral region; *-complex in DMSO solution.

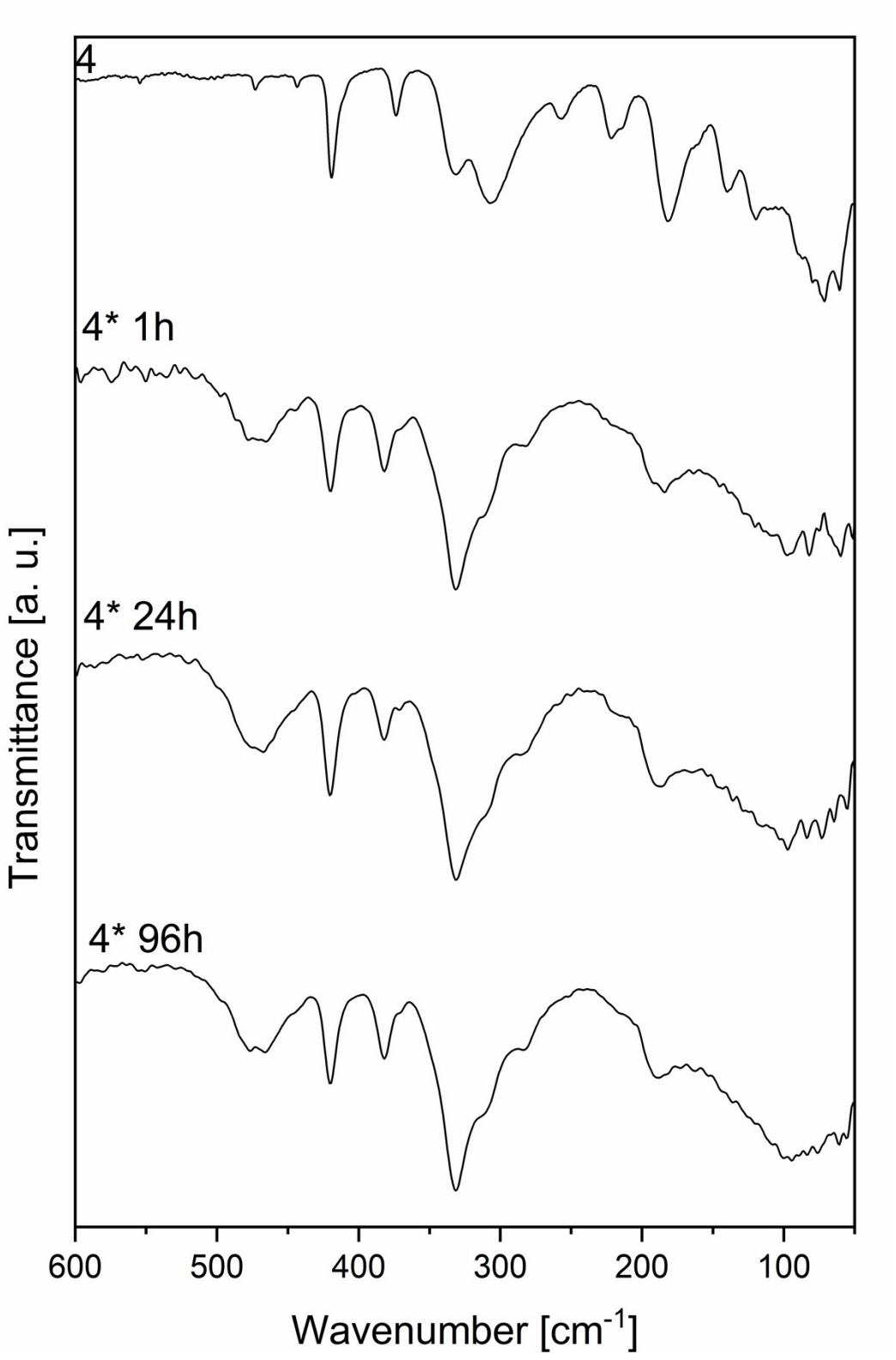


Fig. S8. The FT-IR spectra for complex **4** in FIR spectral region; *-complex in DMSO solution.

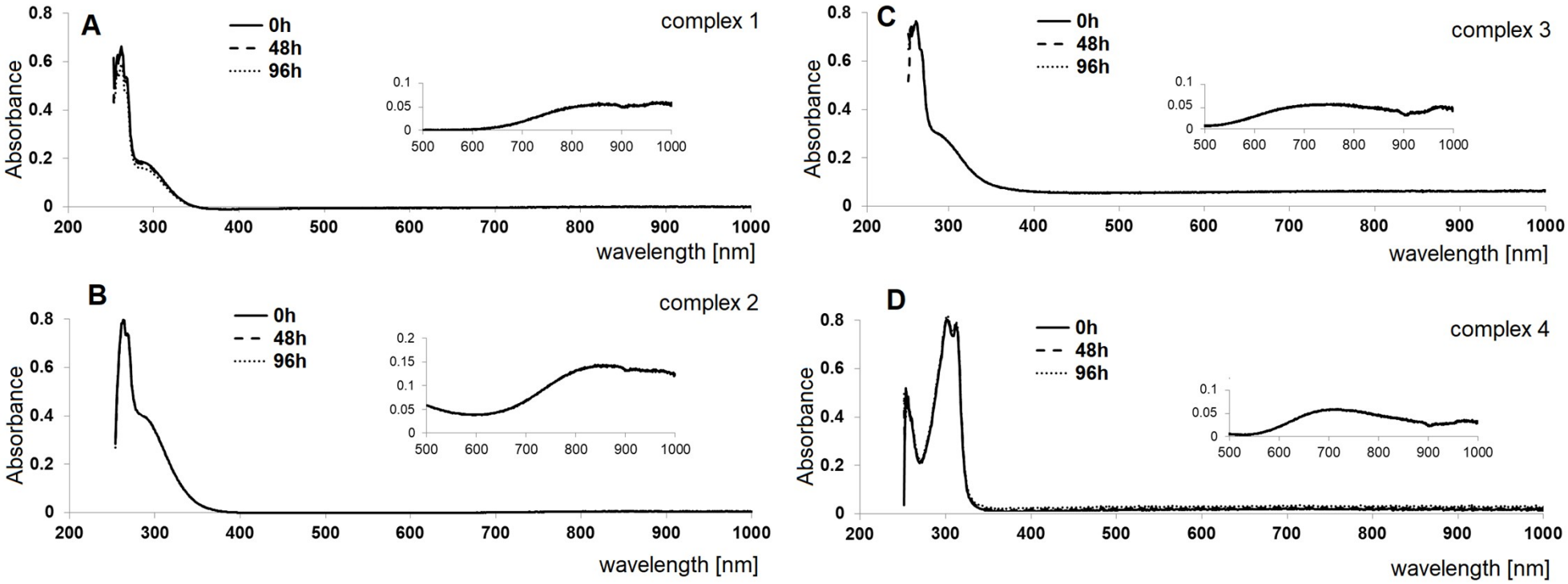
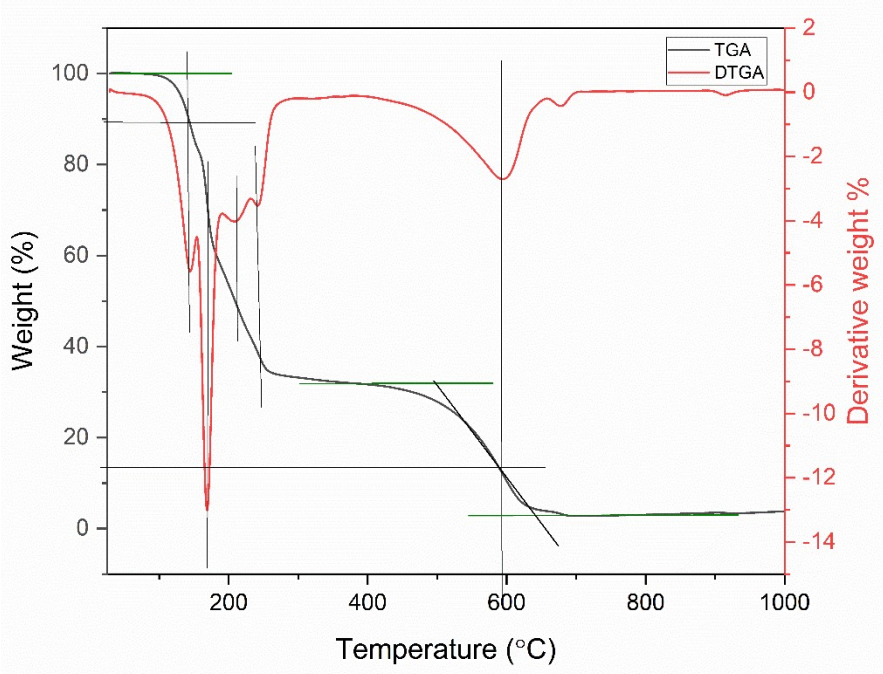
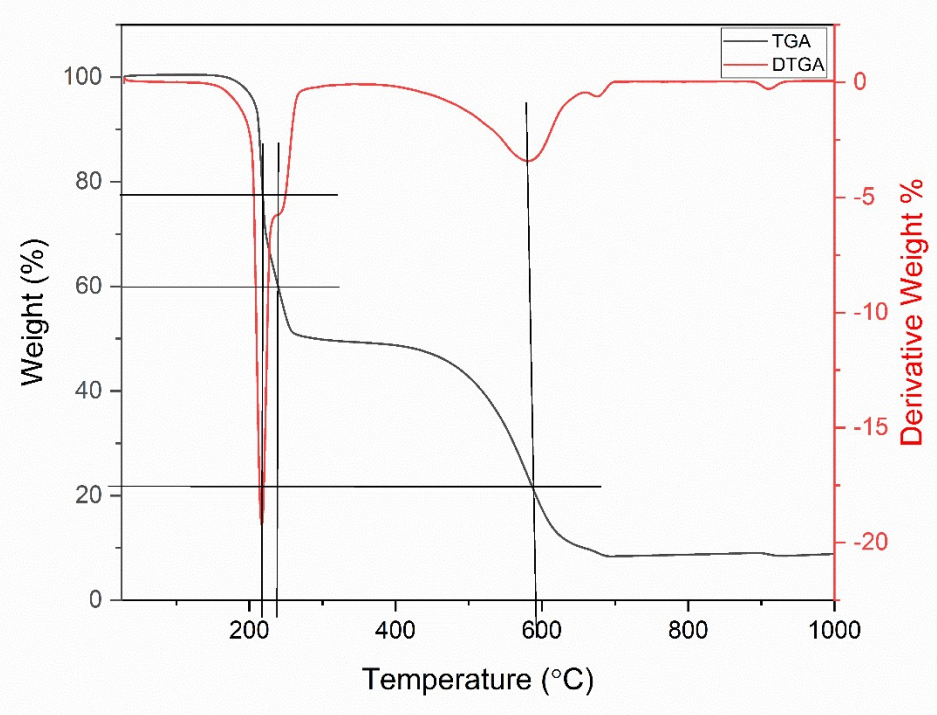


Fig. S9. UV-Vis spectra with inserted of d-d transition of **1-4** in DMSO/H_2O (9:1, v/v).

Complex 1



Complex 2



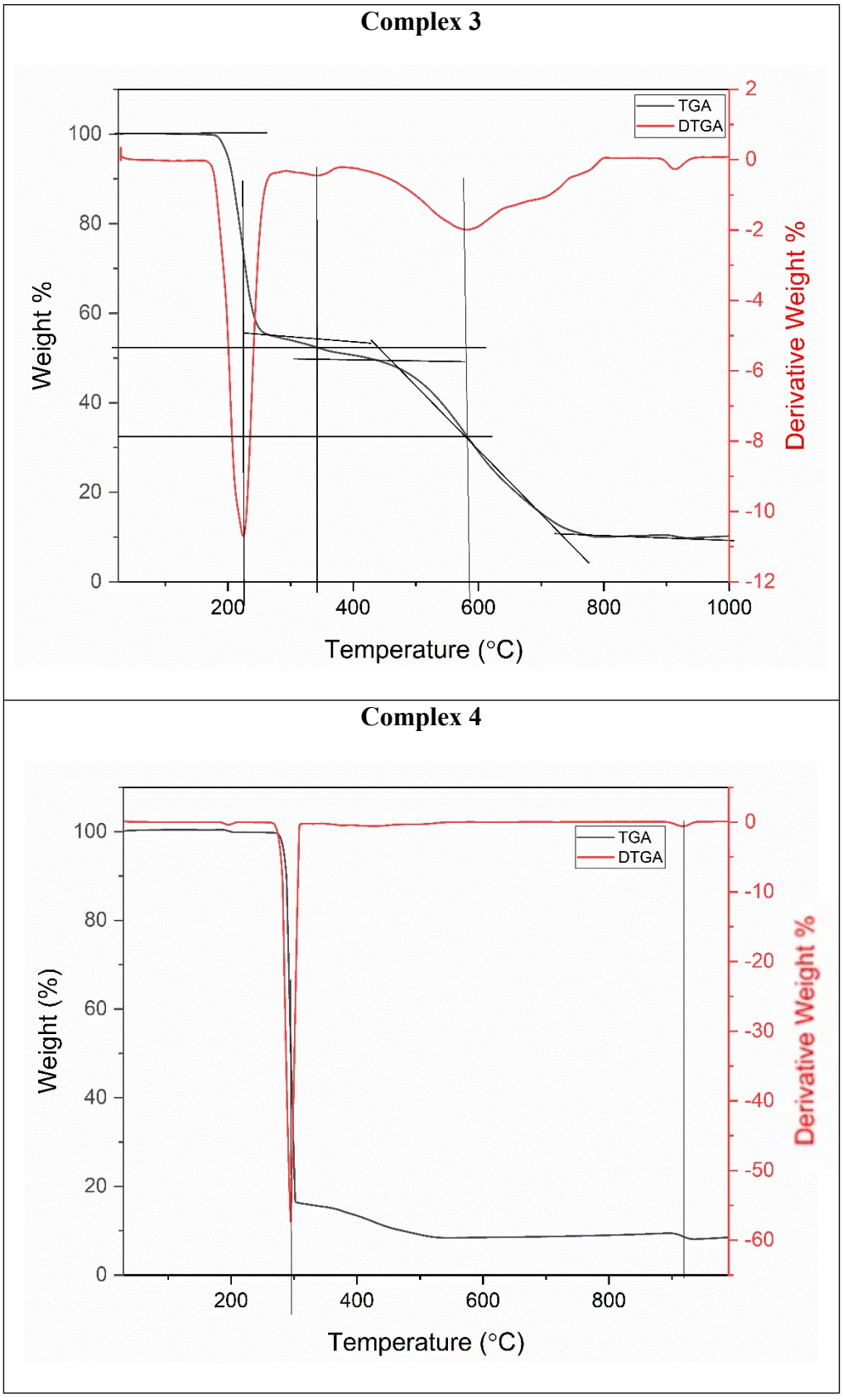


Fig. S10. Thermogravimetric, TG (black) and differential thermal analysis(DTG, red) curves of complexes **1-4**.

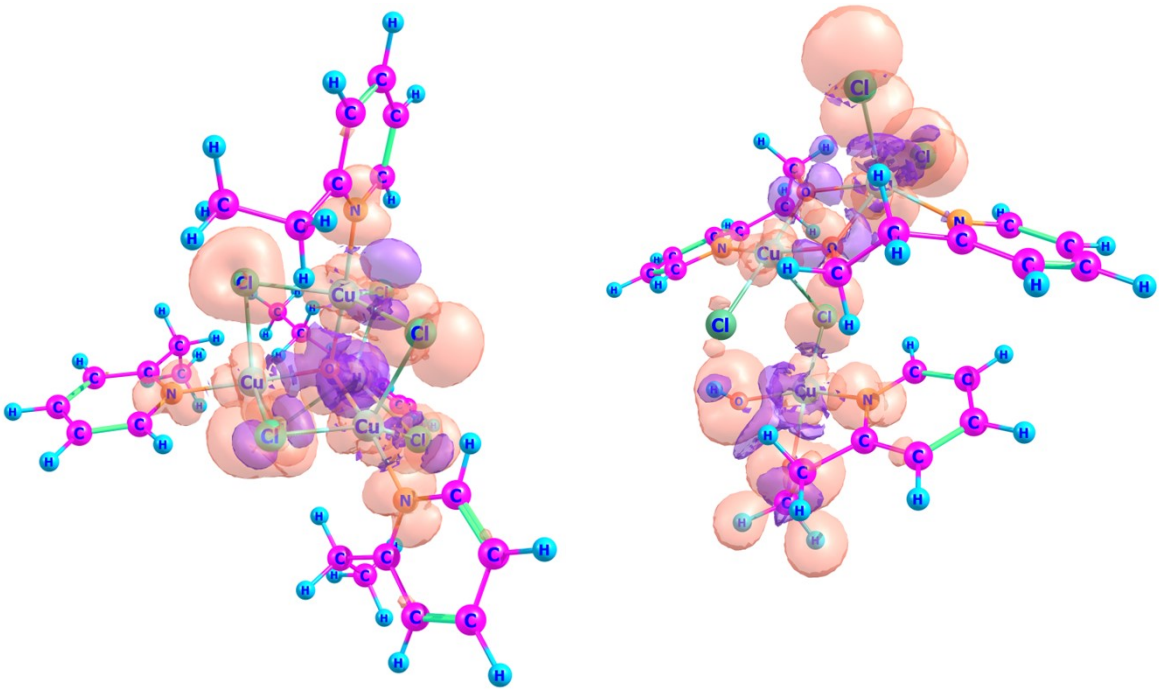


Fig. S11. Spin density isosurfaces (0.0075 a. u.) for high spin states of the 2–3 compounds, respectively (calculated with the hybrid B3LYP-D3 functional).

Table S1. Crystal data and structure refinement for **1-4.**

	1	**2**	**3**	**4**
Empirical formula	$C_{14}H_{18}Cl_2N_2Cu$	$C_{28}H_{36}Cl_6N_4OCu_4$	$C_{14}H_{16}Cl_2N_2O_2Cu_2$	$C_{12}H_{20}N_2O_6Cu$
Formula weight	348.74	911.47	442.27	351.84
Temperature [K]	293.0(2)	293.0(2)	293.0(2)	293.0(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$C2/m$
Unit cell dimensions [Å, °]	a = 7.4891(4)	a = 16.7450(7)	a = 6.1899(3)	a = 13.5721(14)
	b = 7.5179(5)	b = 11.9340(6)	b =8.0094(5)	b = 7.1790(5)
	c = 8.3461(4)	c = 18.8133(9)	c = 8.5356(4)	c = 8.2686(6)
	α = 97.096(5)		α = 89.741(5)	
	β = 113.966(5)	β = 103.620(4)	β = 79.214(4)	β = 110.398(7)
	γ = 108.729(5)		γ = 70.029(6)	
Volume [Å ^{3}]	388.75(4)	3653.8(3)	389.89(4)	755.12(11)
Z	1	4	1	2
Density (calculated) [Mg/m^3]	1.490	1.657	3.076	1.547
Absorption coefficient [mm^{-1}]	1.736	2.764	1.884	1.474
F(000)	179	1832		366
Crystal size [mm]	0.24 x 0.16 x 0.09	0.12 x 0.08 x 0.06	0.25 x 0.22 x 0.18	0.30 x 0.25 x 0.16
θ range for data collection [°]	3.44 to 25.05	3.39 to 25.05	3.53 to 25.05	3.36 to 25.05
Index ranges	$-8 \le h \le 8$	$-22 \le h \le 21$	$-8 \le h \le 7$	$-16 \le h \le 13$
	$-8 \le k \le 8$	$-16 \le k \le 13$	$-10 \le k \le 9$	$-8 \le k \le 8$
	$-9 \le l \le 9$	$-17 \le l \le 25$	$-11 \le l \le 10$	$-9 \le l \le 9$
Reflections collected	6599	25795	7390	3292
Independent reflections	3430 (R_{int} = 0.0397)	8883 (R_{int} = 0.0395)	1922 (R_{int} = 0.0403)	728 (R_{int} = 0.0253)
Completeness to 2θ [%]	99.6	99.6	99.9	99.6
Max. and min. transmission	1.00 and 0.796	1.00 and 0.649	1.00 and 0.360	1.00 and 0.078
Data / restraints / parameters	1373 / 0 / 89	8883 / 0 / 411	1922 / 0 / 100	728 / 0 / 66
Goodness-of-fit on F^2	1.074	1.011	1.033	1.113
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0274	R_1 = 0.0392	R_1 = 0.0309	R_1 = 0.0283
	wR_2 = 0.0635	wR_2 = 0.0857	wR_2 = 0.0641	wR_2 = 0.0723
R indices (all data)	R_1 = 0.0328	R_1 = 0.0793	R_1 = 0.0438	R_1 = 0.0291
	wR_2 = 0.0658	wR_2 = 0.0717	wR_2 = 0.0716	wR_2 = 0.0717
Largest diff. peak and hole [eÅ^{-3}]	0.388 and -0.408	0.589 and -0.394	0.328 and -0.578	0.381 and -0.275

Table S2. Selected bond lengths (Å) and angles (deg) for **2**.

Bond lengths [Å]		Bond angles [°]	
Cu(1)-N(1)	1.988(3)	N(1)–Cu(1)–Cl(1)	92.51(8)
Cu(1)-Cl(1)	2.3320(9)	N(1)–Cu(1)–Cl(3)	103.12(9)
Cu(1)-Cl(3)	2.4366(10)	N(1)–Cu(1)–Cl(6)	99.47(8)
Cu(1)-Cl(6)	2.5068(9)	N(1)–Cu(1)–O(1)	174.07(11)
Cu(1)-O(1)	1.9086(19)	Cl(1)–Cu(1)–Cl(3)	126.99(4)
Cu(2)-N(2)	1.972(2)	Cl(1)–Cu(1)–Cl(6)	127.84(4)
Cu(2)-Cl(1)	2.5136(9)	Cl(3)–Cu(1)–Cl(6)	99.36(4)
Cu(2)-Cl(2)	2.3199(9)	O(1)–Cu(1)–Cl(1)	84.33(6)
Cu(2)-Cl(5)	2.5672(10)	O(1)–Cu(1)–Cl(3)	82.77(6)
Cu(2)-O(1)	1.8853(18)	O(1)–Cu(1)–Cl(6)	78.70(6)
Cu(3)-N(3)	1.970(3)	N(2)–Cu(2)–Cl(1)	95.26(8)
Cu(3)-Cl(2)	2.6850(9)	N(2)–Cu(2)–Cl(2)	94.47(8)
Cu(3)-Cl(3)	2.3817(10)	N(2)–Cu(2)–Cl(5)	99.97(9)
Cu(3)-Cl(4)	2.3385(10)	N(2)–Cu(2)–O(1)	174.81(10)

Cu(3)-O(1)	1.8994(19)	Cl(1)–Cu(2)–Cl(2)	147.54(4)
Cu(4)-N(4)	1.973(3)	Cl(1)–Cu(2)–Cl(5)	91.93(3)
Cu(4)-Cl(4)	2.6099(9)	Cl(2)–Cu(2)–Cl(5)	116.69(4)
Cu(4)-Cl(5)	2.3400(8)	O(1)–Cu(2)–Cl(1)	79.85(6)
Cu(4)-Cl(6)	2.3848(9)	O(1)–Cu(2)–Cl(2)	88.85(6)
Cu(4)-O(1)	1.899(2)	O(1)–Cu(2)–Cl(5)	82.02(7)
		N(3)–Cu(3)–Cl(2)	103.90(8)
		N(3)–Cu(3)–Cl(3)	90.11(8)
		N(3)–Cu(3)–Cl(4)	95.93(8)
		N(3)–Cu(3)–O(1)	174.54(10)
		Cl(2)–Cu(3)–Cl(3)	106.16(4)
		Cl(2)–Cu(3)–Cl(4)	95.54(4)
		Cl(3)–Cu(3)–Cl(4)	155.37(4)
		O(1)–Cu(3)–Cl(2)	78.37(6)
		O(1)–Cu(3)–Cl(3)	84.48(6)
		O(1)–Cu(3)–Cl(4)	88.74(7)
		N(4)–Cu(4)–Cl(4)	100.54(9)
		N(4)–Cu(4)–Cl(5)	92.64(8)
		N(4)–Cu(4)–Cl(6)	96.24(8)
		N(4)–Cu(4)–O(1)	177.88(10)
		Cl(4)–Cu(4)–Cl(5)	106.69(3)
		Cl(4)–Cu(4)–Cl(6)	98.58(3)
		Cl(5)–Cu(4)–Cl(6)	151.16(4)
		O(1)–Cu(4)–Cl(4)	81.08(6)
		O(1)–Cu(4)–Cl(4)	81.08(6)
		O(1)–Cu(4)–Cl(5)	88.19(6)
		O(1)–Cu(4)–Cl(6)	82.12(6)
		Cu(1)–O(1)–Cu(2)	109.66(9)
		Cu(1)–O(1)–Cu(3)	108.01(9)
		Cu(1)–O(1)–Cu(4)	105.97(9)
		Cu(2)–O(1)–Cu(3)	113.99(10)
		Cu(2)–O(1)–Cu(4)	110.99(10)
		Cu(3)–O(1)–Cu(4)	107.86(9)
		Cu(1)–Cl(1)–Cu(2)	79.50(3)
		Cu(1)–Cl(3)–Cu(3)	79.49(3)
		Cu(1)–Cl(6)–Cu(4)	76.81(3)
		Cu(2)–Cl(2)–Cu(3)	78.34(3)
		Cu(2)–Cl(5)–Cu(4)	78.76(3)
		Cu(3)–Cl(4)–Cu(4)	76.48(3)

Table S3. The experimental and calculated vibrational frequencies of copper(II) complexes. B3LYP-D3/def2-TZVP level of theory was applied, the calculated frequencies are left unscaled; only selected bands are discussed.

No	Complex 1			Complex 2			Complex 3			Complex 4			Assignments
	expl		calcd	expl		calcd	expl		calcd	expl		calcd	
	IR	Raman		IR	Raman		IR	Raman		IR	Raman		
1				3452 m									H-bond intermolecular interaction
2				3335 m									
3	3070 m	3070 s	*3217-3180*	3079 w	3080 s	*3219-3176*	3070 m	3080 m	3220-3180	3116-3037 w	3085 m	3206–3171	ν(C-H)$_{arom}$
4	2970 m	2970 m	*3104*	2972 m		*3099*	2955 m	2956 m	3065			2880	ν_{as}(C-H)$_{alif}$
5	2937 m	2938 m	*3040*	2937 m	2938 m	*3068*	2914 m	2914 m	3096				ν_{as}(C-H)$_{alif}$ -CH$_2$-
6	2883 m	2883 m	*3034*	2878 m	2901 m	*3040*	2817	2820 m	3010	2916 m			ν_s(C-H)$_{alif}$
7	ov	ov	*3010*	ov	ov	*3041*	ov	ov	3046	2850		2885	ν_s(C-H)$_{alif}$ -CH$_2$-
							2680 w						overtone 1337
	1855 w			1864 w									overtone
	1732 w			1728 w									overtone
8	1607 s	1606 s	*1652*	1608 s	1632 w	*1654*	1607 s	1607 m	1652	1602 m	1601	1647	ν(C=C)
9	1569 m	1569 m	*1618*	1568 m	1568 w	*1614*	1568 m	1567 m	1614	1573	1568	1611	ν(C-C)
10	1484 s	1459 w	*1528*	1484 s	1467 w	*1532*	1483 s	1468 m	1526	1472	1497	1515	ν(C=N)
11	1440 m	1425 w	*1511*	1444 s	1443 w	*1515*	1446 m	1446 w	1506	1445 sh	vw	1478	δ(C-H) scissoring
	1425 m		*1506*			*1508*							
			1498			*1493*							
12	1380 m	1364 w	*1423*	1378 w		*1423*	-	-	-			–	δ_{sym}(C-CH$_3$) umbrella
13	1336 br, w	1348 w	*1396*	1337 w	1336 vw	*1382*	1337 m	1342 m	1383			1381	δC-H wagging
14	1295 m	1295 w	*1328*	1310 w		*1335*	1308 m	1308 m	1347	1320 w	1323 s	1315	δC-H twisting
15	1255 w	1217 s	*1298*	1230 w	1233 m	*1301*	1248 m	1226 m	1296	1265 s	1263 m	1299	δRpy
	1238 w						1237 sh						
16	1163 m	1165 m	*1195*	1161 m	1163 w	*1197*	1186 m	1184	1211				δC-H (in plane)
							1158 s	1157 m	1194	1157 m	1172 m	1186	
17	1117 w		*1146*	1115 m	1117 w	*1147*	1111 s	1116 w	1142	1104 w	1107 m		δC-H (in plane)
18	1057 m	1056 s	*1060*	1061sh	1063 s	*1071*	1064 s	1053 s	1059	-	-		ν (C-C)$_{in\ ethyl\ group}$+defR$_{py}$

19	-			-				1081 s	1099	ov	1058 m	1122	ν(C-O)
20	1033 m	1031 vs	*1049*	1045 m 1035 sh	1031 s	*1050*	1052 s	1025 s	1045	1038 m	1038 s	1044	Sym ring breathing (star of David)
21							980 m	976 m	992	999 vs	1004	998	γC-H (out of plane)
	895 m		*902*	894 w		*910*	872 s	879 m	888	913 w		899	
	806 vs		*794*	793 s	781 s	*783*	789 s	785 m	785	807 m	813 m		
	769 vs	777 vs	*775*	765 vs	740 m	*779*	770 vs	757 m	776			778	
	706 m		*728*	704 m	707 w	*725*		709 m					
22	654 s	650 s	*666*	655 s	655 w	*671*	651 m	648 w	667			675	δ R_{pyet}
23				608 s	610 s		606 vs	609 w	620				τR_{pyet}
24	571 m	565 m	*573*	572 s	558 s	*587*	572 s	545 m	573				Def R
25				505 m	507 w	*523*	510 m	505 w	516				τR_{pyet}
	472 m		*492*	474 w		*493*							τR_{pyet}
	434 s	435 s	*442*	437 m		*443*	432 s	412 vs	434	419 m		429	τR_{pyet}

Table S4. Mulliken populations computed at the B3LYP-D3 theory level of 2-3 (selected atoms).

Compound 2		Compound 3	
Cu:	0.5744	Cu	0.5668
Cu:	0.5833	Cl1	0.1199
Cu:	-0.5857	Cl1	0.0245
Cu:	0.5786	O	0.5705
Cl:	0.1577	Cu1	0.3237
Cl:	0.1261	Cl	0.1302
Cl:	-0.0414	O1	-0.0351
Cl:	-0.0972	Cu1	0.1820
Cl:	0.1353	Cl	0.4037
Cl:	0.1383	O1	-0.0538
O	0.2933		