Dalton Transactions

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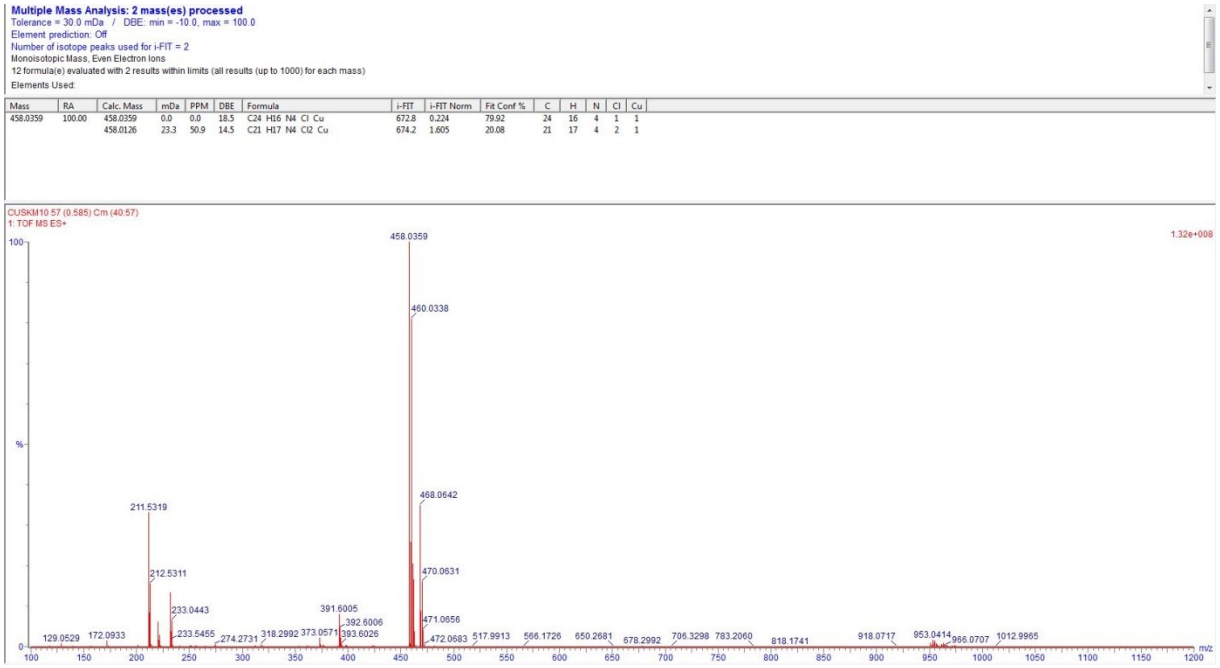
Copper(II) complexes with 2,2':6',2''-terpyridine, 2,6-di(thiazol-2-yl)pyridine and 2,6-di(pyrazin-2-yl)pyridine substituted with quinolines. Synthesis, structure, cytotoxicity, and catalytic activity in oxidation of alkanes with peroxides

Katarzyna Choroba,[a] Barbara Machura,*[a] Slawomir Kula,[a] Luis R. Raposo,[b] Alexandra R. Fernandes,*[b] Rafal Kruszynski,[c] Karol Erfurt,[d] Lidia S. Shul'pina,[a] Yuriy N. Kozlov [f,e] and Georgiy B. Shul'pin *[f,g,h]

Electronic Supplementary Information (ESI)



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Element prediction: Off
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Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:

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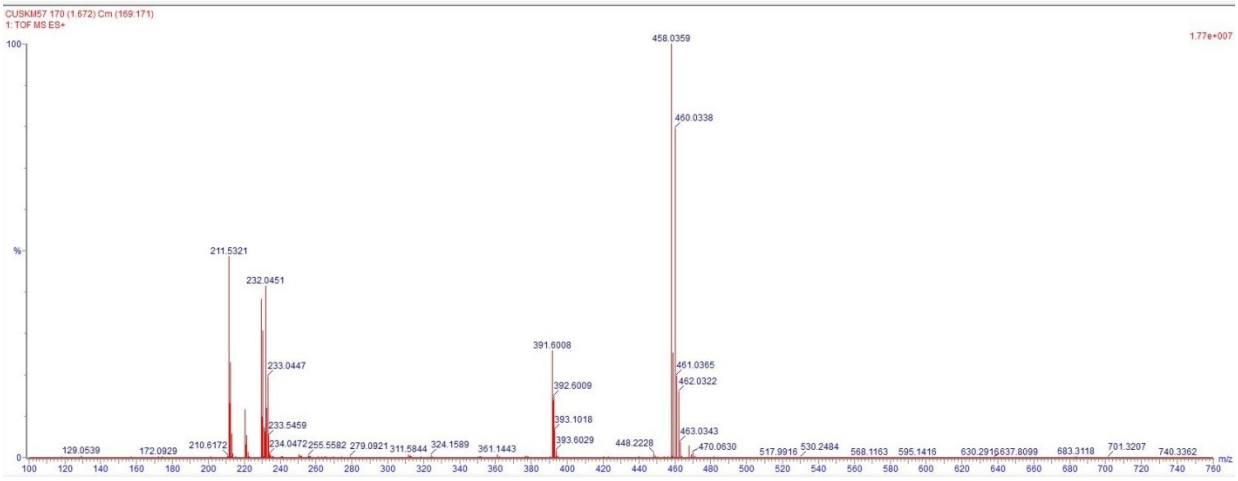
		458.0126	23.3	50.9	14.5	C21 H17 N4 Cl2 Cu	538.7	0.108	89.72	21	17	4	2	1
		458.1065	-70.6	-154.1	7.5	C20 H29 N4 Cl2 Cu	542.5	3.947	1.93	20	29	4	2	1
		457.9420	93.9	205.0	25.5	C25 H4 N4 Cl Cu	545.0	6.434	0.16	25	4	4	1	1
		458.1299	-94.0	-205.2	11.5	C23 H28 N4 Cl Cu	542.5	3.933	1.96	23	28	4	1	1



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Element prediction: Off
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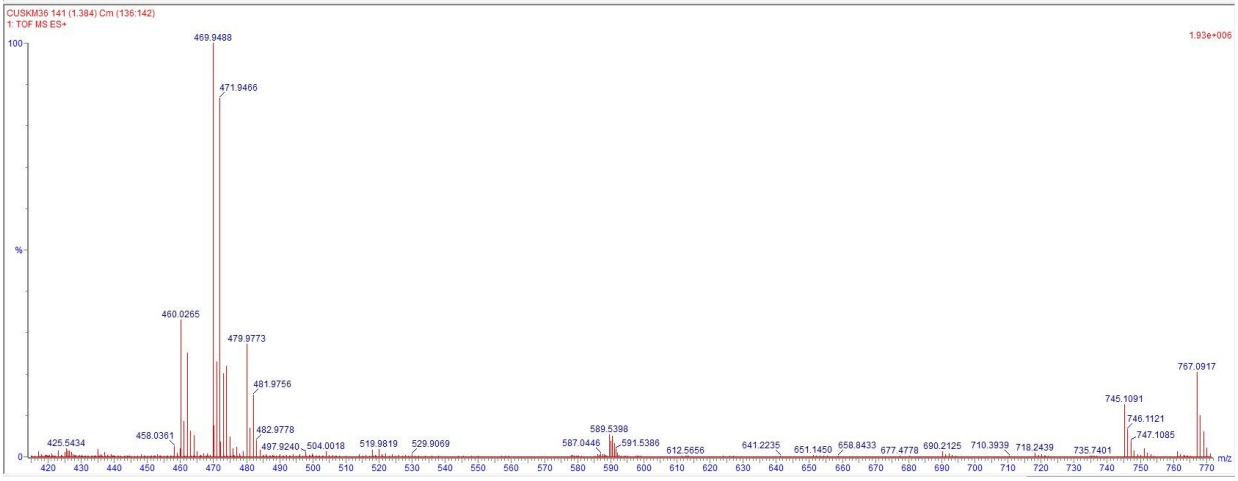
Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	S	Cl	Cu
469.9488	100.00	469.9488	0.0	0.0	16.5	C20 H12 N4 S2 Cl Cu	450.9	0.292	74.69	20	12	4	2	1	1
		469.9255	23.3	49.6	12.5	C17 H13 N4 S2 Cl2 Cu	452.0	1.374	25.31	17	13	4	2	2	1
471.9466	86.63	471.9411	5.5	11.7	11.5	C17 H15 N4 S2 Cl2 Cu	426.1	0.205	81.45	17	15	4	2	2	1
		471.9644	-17.8	-37.7	15.5	C20 H14 N4 S2 Cl Cu	427.6	1.685	18.55	20	14	4	2	1	1



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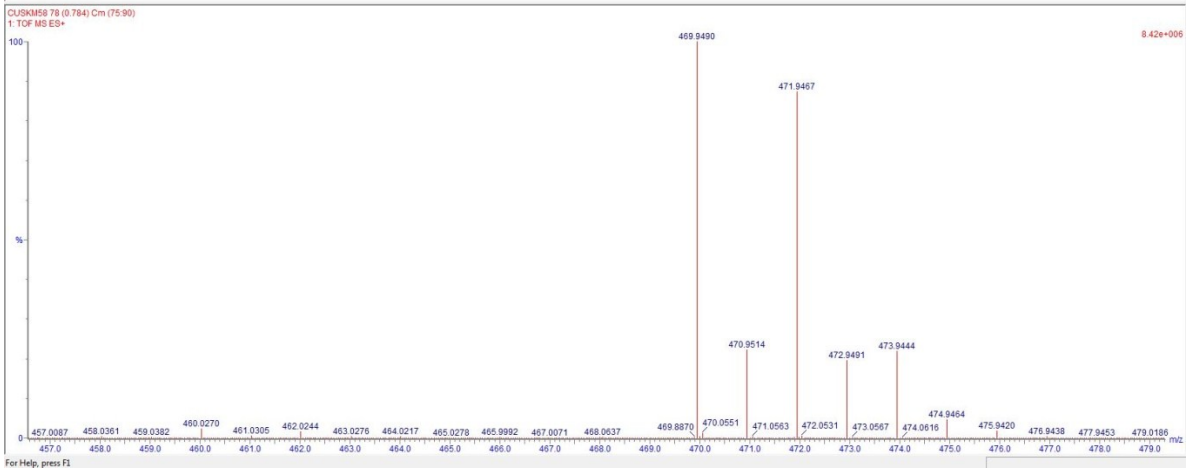
Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 30.0 mDa / DBE: min = -10.0, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2
Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	S	Cl	Cu
469.9490	100.00	469.9488	0.2	0.4	16.5	C20 H12 N4 S2 Cl Cu	529.5	1.977	13.85	20	12	4	2	1	1
		469.9255	23.5	50.0	12.5	C17 H13 N4 S2 Cl2 Cu	527.7	0.149	86.15	17	13	4	2	2	1
471.9467	87.28	471.9411	5.6	11.9	11.5	C17 H15 N4 S2 Cl2 Cu	522.3	0.010	99.04	17	15	4	2	2	1
		471.9644	-17.7	-37.5	15.5	C20 H14 N4 S2 Cl Cu	527.0	4.651	0.96	20	14	4	2	1	1



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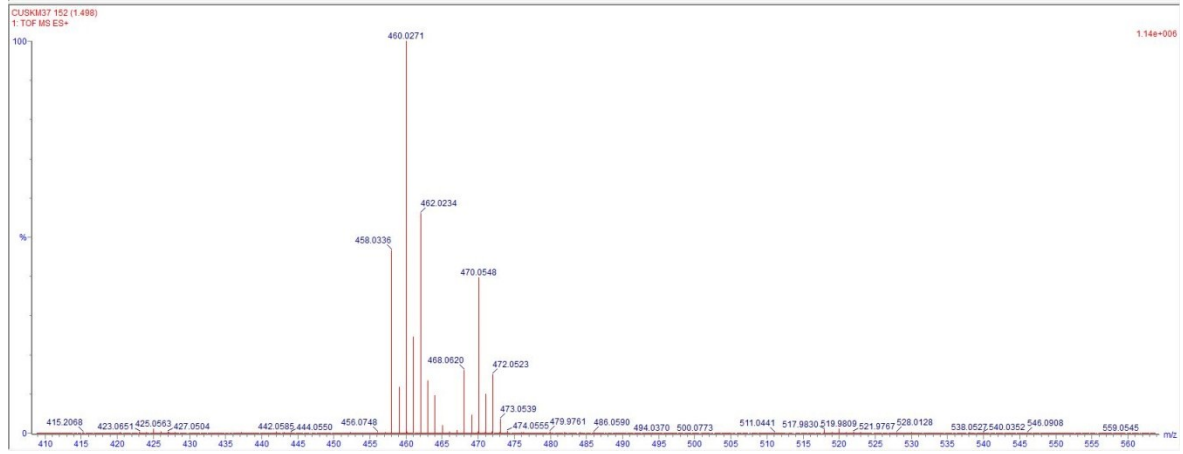
Element prediction: Off
Number of isotope peaks used for i-FIT = 2
Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	Cl	Cu
460.0271	100.00	460.0264	0.7	1.5	18.5	C22 H14 N6 Cl Cu	462.4	0.125	88.23	22	14	6	1	1
		460.0031	24.0	52.2	14.5	C19 H15 N6 Cl2 Cu	464.4	2.140	11.77	19	15	6	2	1



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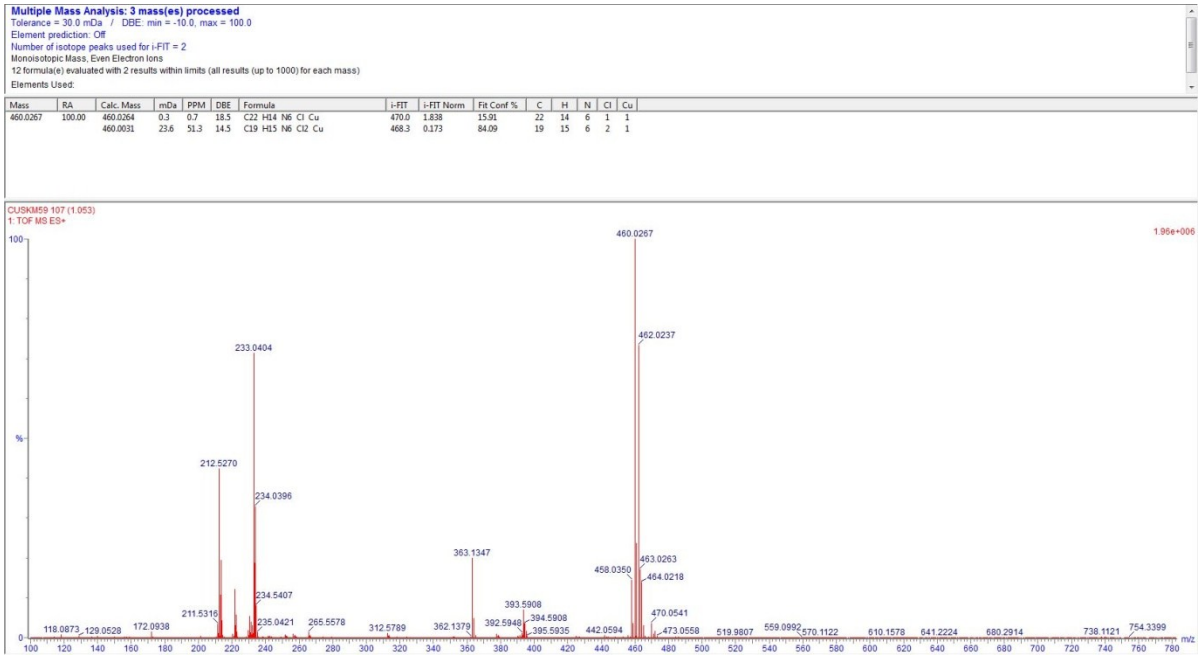
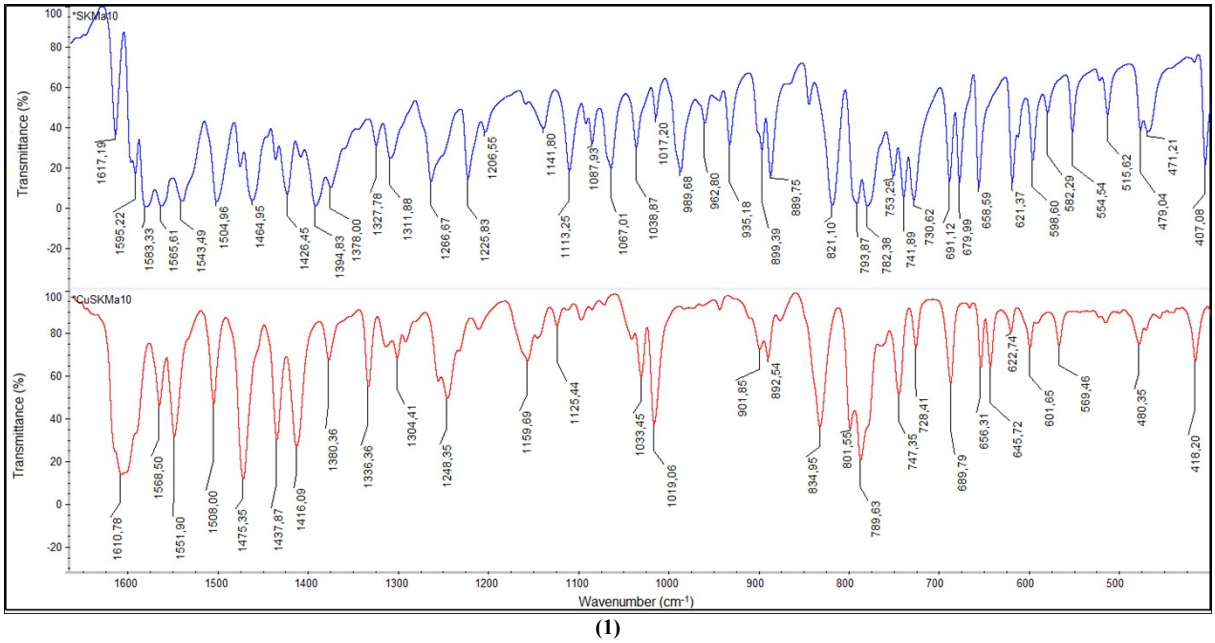
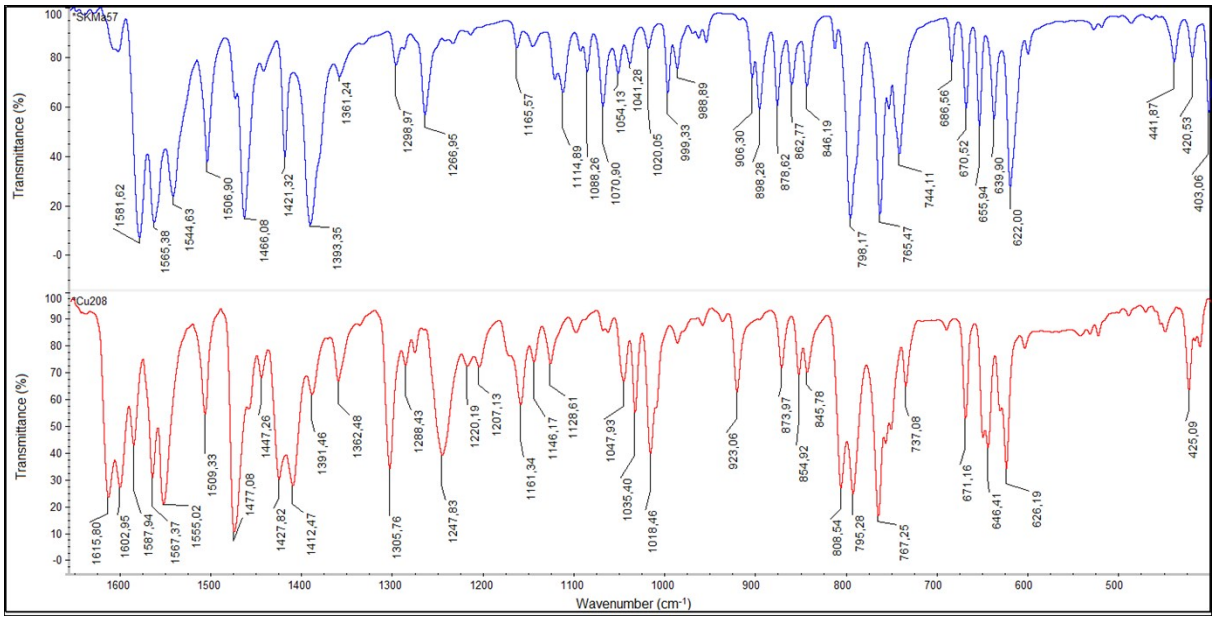


(6)

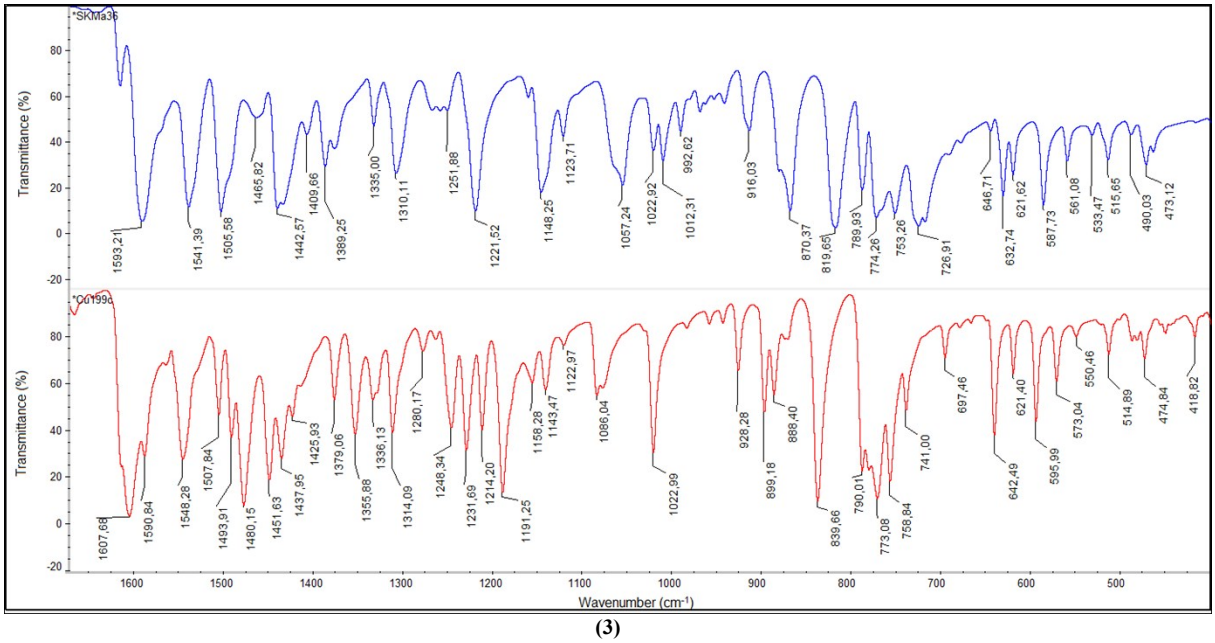
Figure S1. ESI-MS spectra of copper(II) complexes **1-6.**


*SKMa10
Transmittance (%)
1617,19
1595,22
1583,33
1565,61
1543,49
1504,96
1464,95
1426,45
1394,93
1378,00
1327,78
1311,88
1266,67
1225,83
1206,55
1141,80
1113,25
1087,93
1067,01
1038,87
1017,20
989,68
962,80
935,18
899,39
889,75
821,10
793,87
782,38
753,25
741,89
730,62
691,12
679,99
658,59
621,37
598,60
582,29
554,54
515,62
479,04
471,21
407,08
*CuSKMa10
Transmittance (%)
1610,78
1568,50
1551,90
1508,00
1475,35
1437,87
1416,09
1380,36
1338,36
1304,41
1248,35
1159,69
1125,44
1033,45
1019,06
901,85
892,54
834,95
801,55
789,63
747,35
728,41
689,79
656,31
645,72
622,74
601,65
569,46
480,35
418,20
Wavenumber (cm-1)

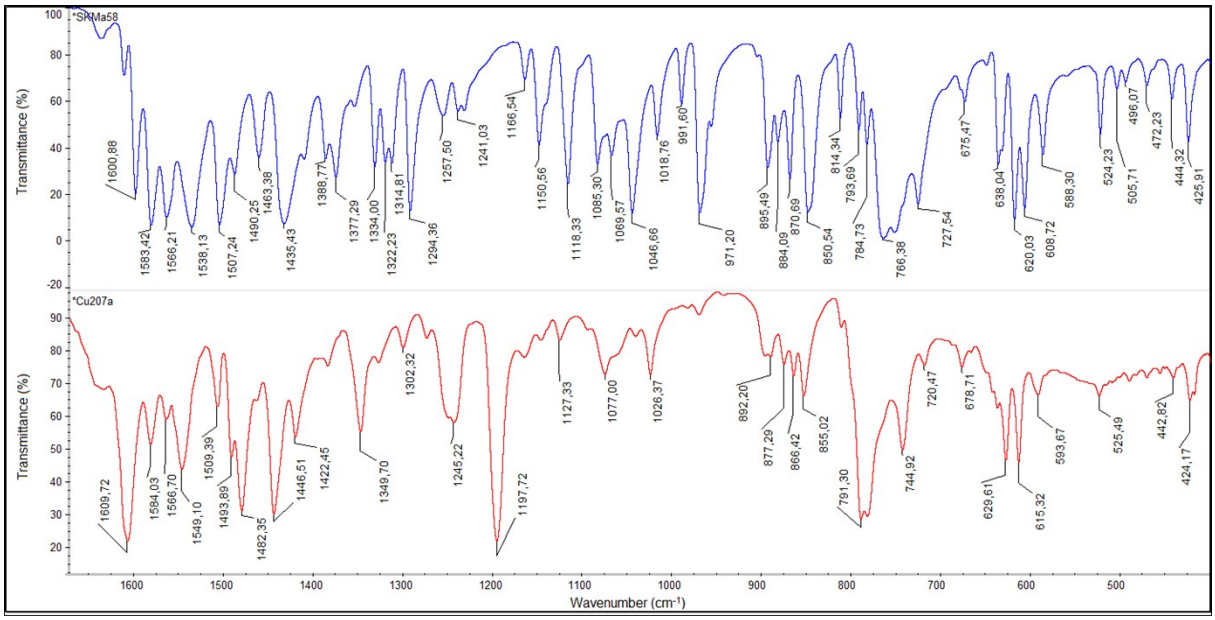
(1)


*SKMa57
Transmittance (%)
1581,62
1565,38
1544,63
1506,90
1466,08
1421,32
1393,35
1361,24
1298,97
1266,95
1165,57
1114,89
1088,26
1070,90
1054,13
1041,28
1020,05
999,33
988,89
906,30
898,28
878,62
862,77
846,19
798,17
765,47
744,11
686,56
670,52
655,94
639,90
622,00
441,87
420,53
403,06
*Cu208
Transmittance (%)
1615,80
1602,95
1587,94
1567,37
1555,02
1509,33
1477,08
1447,26
1427,82
1412,47
1391,46
1362,48
1305,76
1288,43
1247,83
1220,19
1207,13
1161,34
1146,17
1128,61
1047,93
1035,40
1018,46
923,06
873,97
854,92
845,78
808,54
795,28
767,25
737,08
671,16
646,41
626,19
425,09
Wavenumber (cm-1)

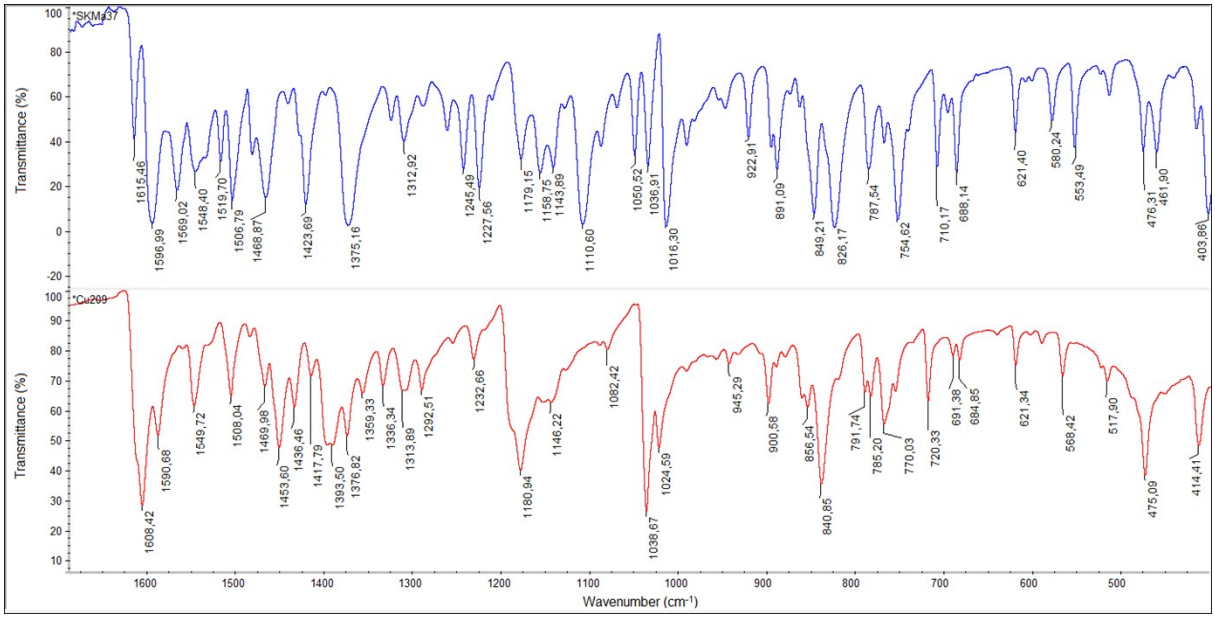
(2)


*SKMa36
Transmittance (%)
1593,21
1541,39
1505,58
1465,82
1442,57
1409,66
1389,25
1335,00
1310,11
1251,88
1221,52
1148,25
1123,71
1057,24
1022,92
1012,31
992,62
916,03
870,37
819,65
789,93
774,26
753,26
726,91
646,71
632,74
621,62
587,73
561,08
539,47
515,65
490,03
473,12
*Cu199c
Transmittance (%)
1607,68
1590,84
1548,28
1507,84
1493,91
1480,15
1451,63
1437,95
1425,93
1379,06
1355,88
1336,13
1314,09
1280,17
1248,34
1231,69
1214,20
1191,25
1158,28
1143,47
1122,97
1086,04
1022,99
928,28
899,18
888,40
839,66
790,01
773,08
758,84
741,00
697,46
642,49
621,40
595,99
573,04
550,46
514,89
474,84
418,82
Wavenumber (cm-1)

(3)


*SKMa58
Transmittance (%)
1600,88
1583,42
1566,21
1538,13
1507,24
1490,25
1463,38
1435,43
1388,77
1377,29
1334,00
1322,23
1314,81
1294,36
1257,50
1241,03
1166,54
1150,56
1118,33
1085,30
1069,57
1046,66
1018,76
991,60
971,20
895,49
884,09
870,69
850,54
814,34
793,69
784,73
766,38
727,54
675,47
638,04
620,03
608,72
588,30
524,23
505,71
496,07
472,23
444,32
425,91
*Cu207a
Transmittance (%)
1609,72
1584,03
1566,70
1549,10
1509,39
1493,89
1482,35
1446,51
1422,45
1349,70
1302,32
1245,22
1197,72
1127,33
1077,00
1028,37
892,20
877,29
866,42
855,02
791,30
744,92
720,47
678,71
629,61
615,32
593,67
525,49
442,82
424,17
Wavenumber (cm-1)

(4)



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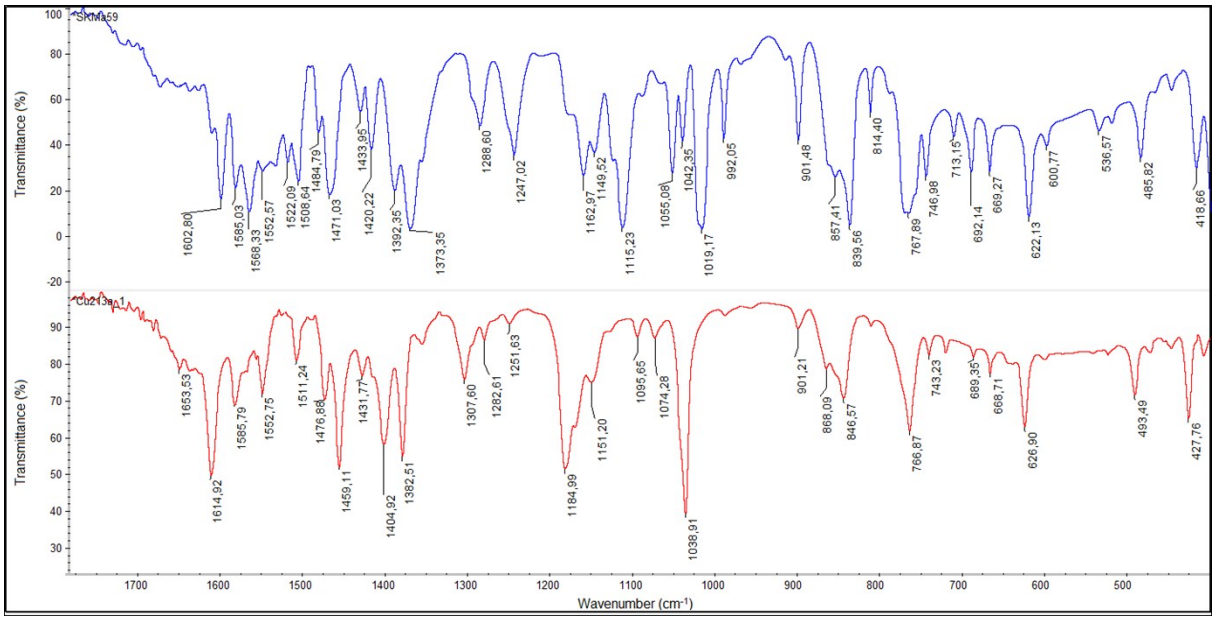
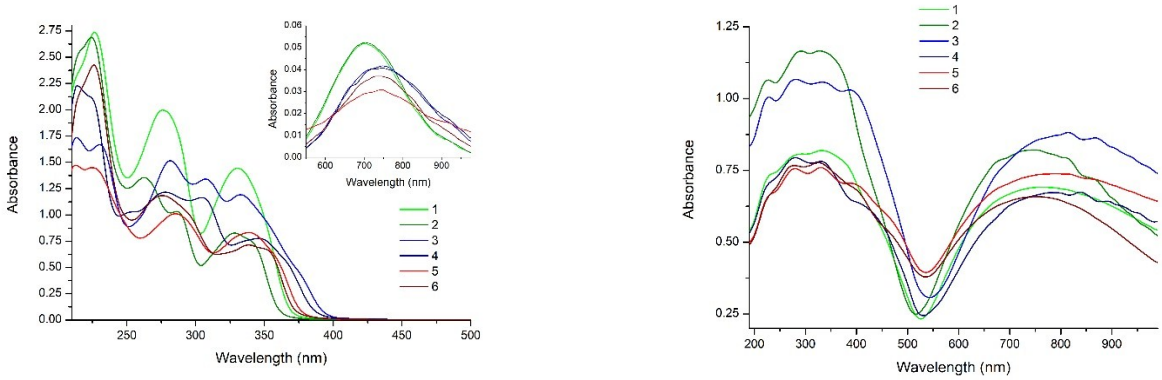


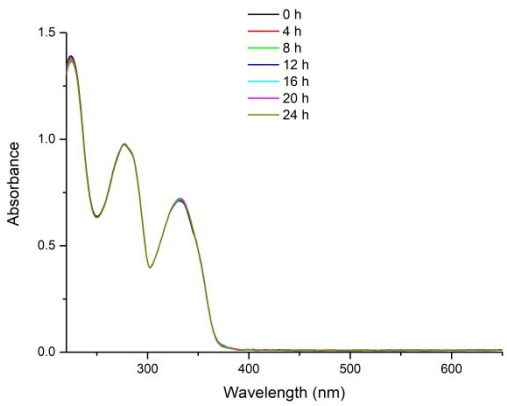
(6)

Figure S2. IR spectra of complexes **1-6** (red line) and appropriate free ligands (blue line).



(a) (b)

Figure S3. UV-Vis spectra of complexes **1-6** in methanol (a) ($5 \cdot 10^{-5}$ M, inset: $5 \cdot 10^{-4}$ M) and the reflectance spectra in powder samples (b).



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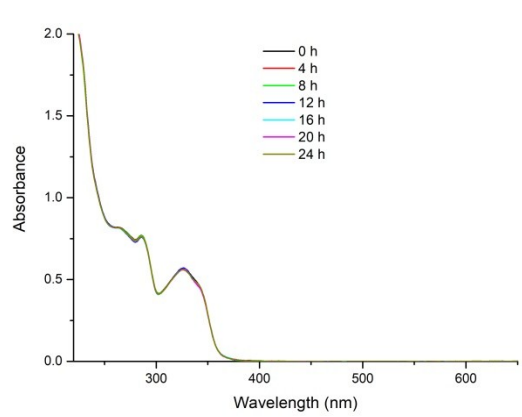

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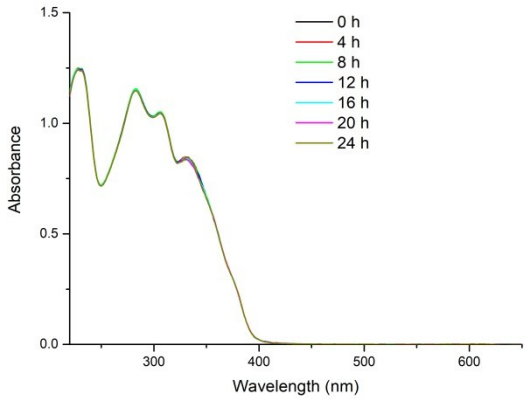

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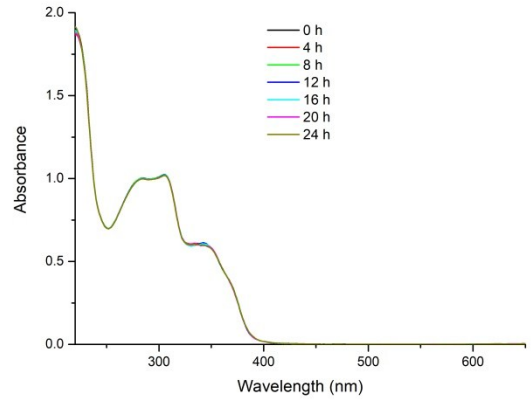

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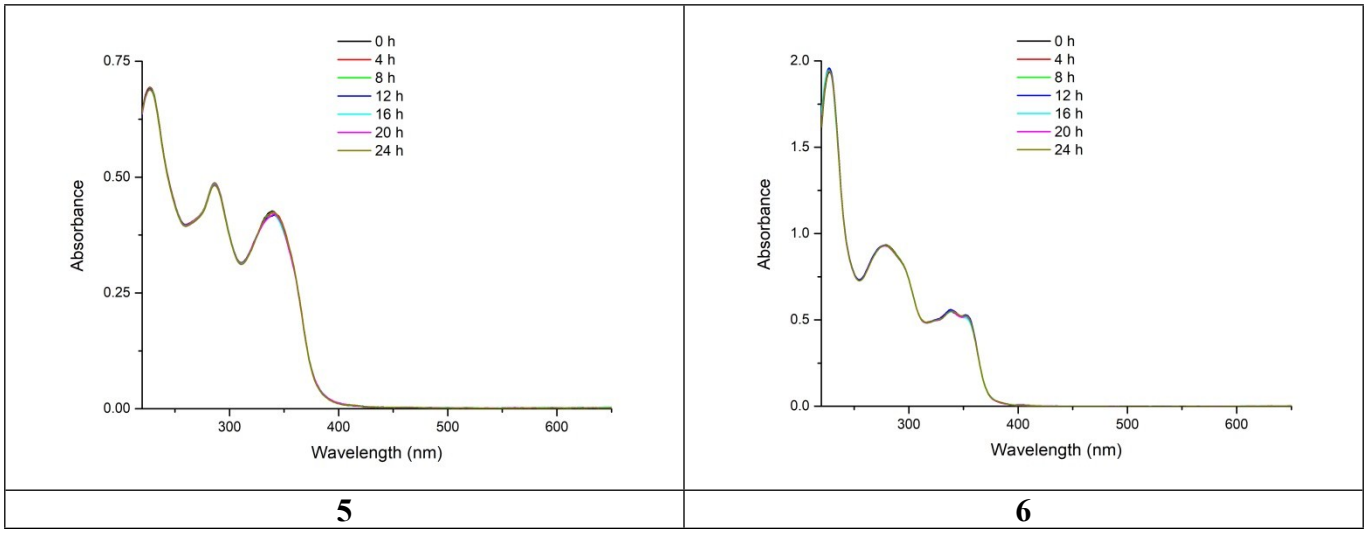


Figure S4. UV-Vis solutions stability of complexes **1-6** in methanol ($5 \cdot 10^{-5}$ M). Spectra were collected every 4 hours for 24 h.

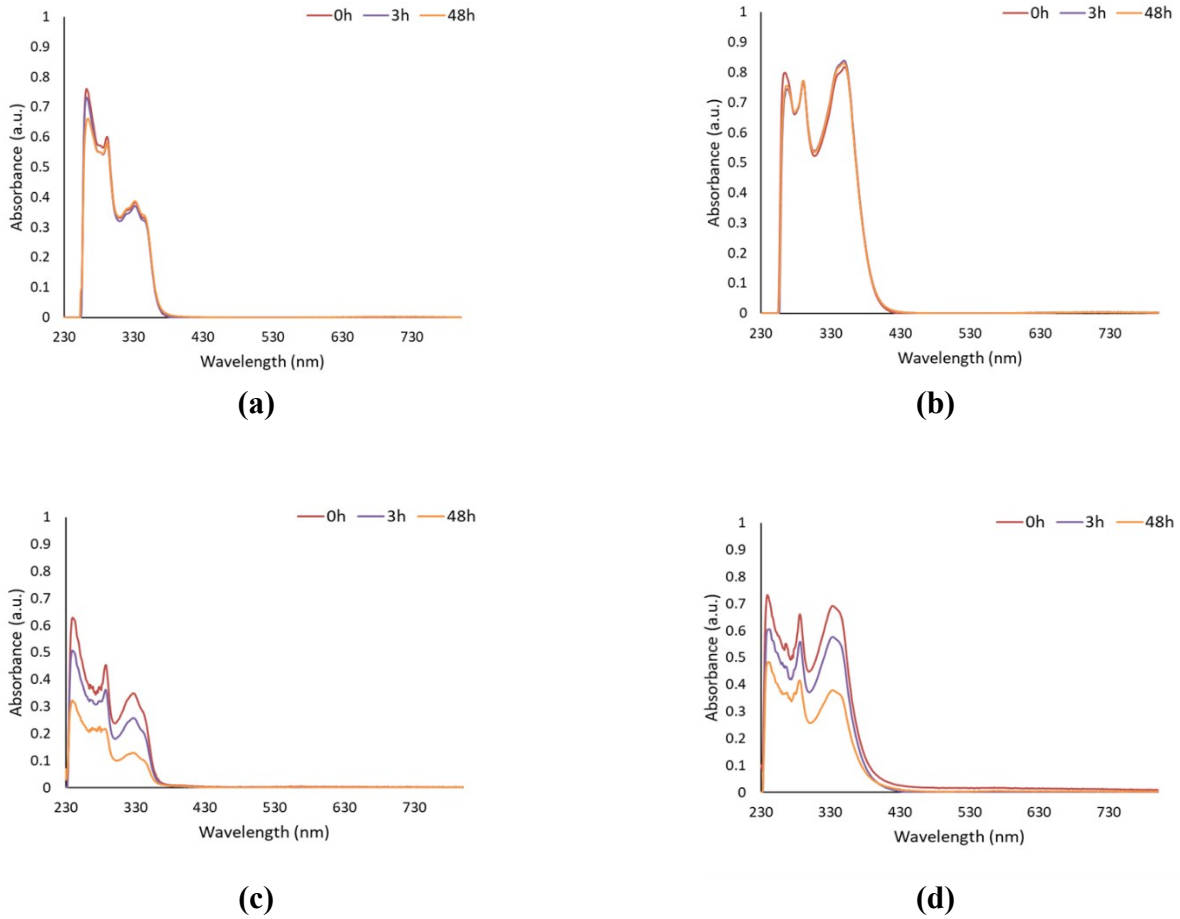
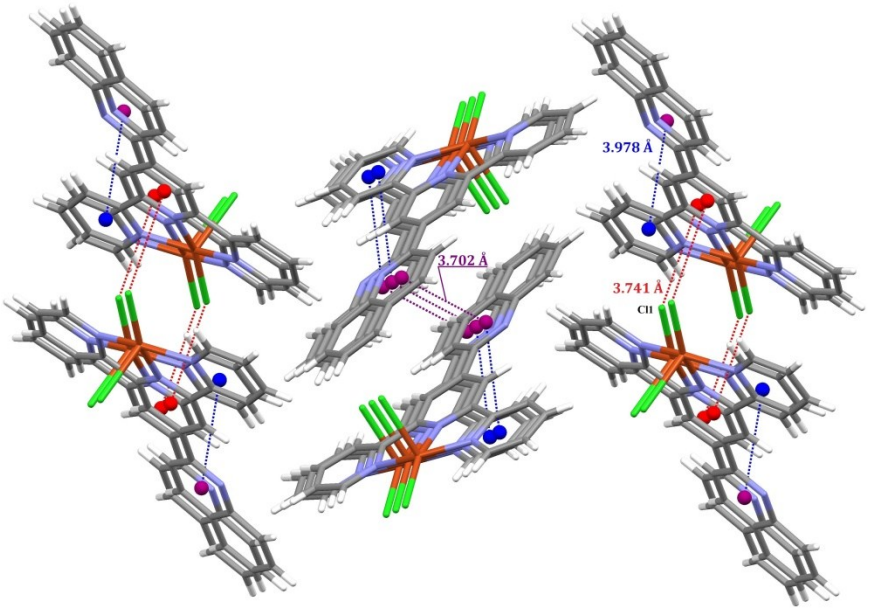
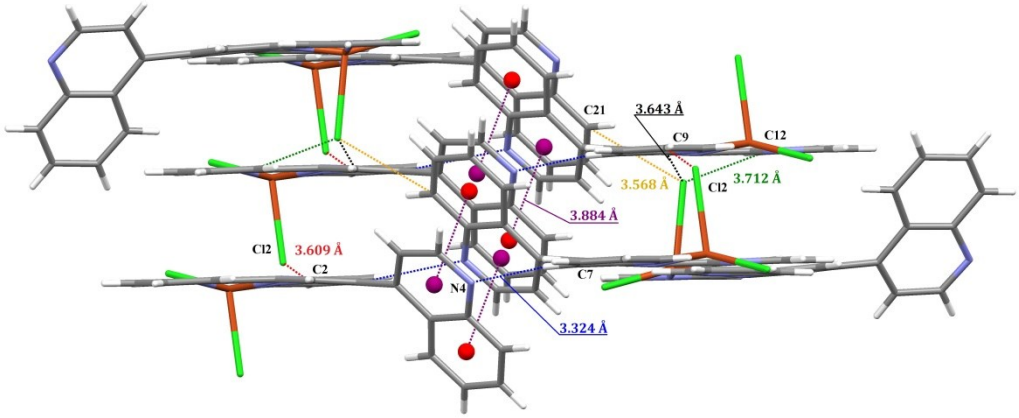


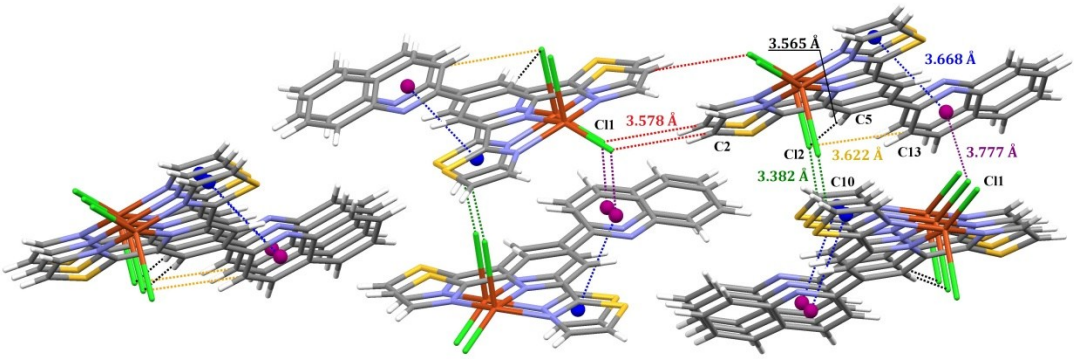
Figure S5. UV-Vis spectra of complexes **2** (a) and **5** (b) dissolved in DMSO and complexes **2** (c) and **5** (d) dissolved in DMEM incubated at 37 ºC for 0 h (control), 3 h and 48 h.


3.978 Å
3.702 Å
3.741 Å
Cl1

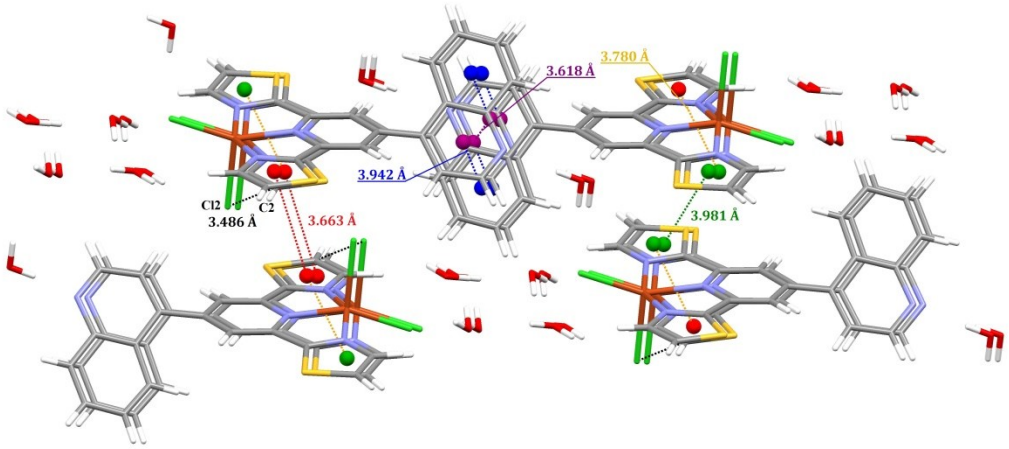
(1)


C21
3.643 Å
C9
C12
3.568 Å
Cl2
3.712 Å
3.884 Å
Cl2
3.609 Å
C2
N4
C7
3.324 Å

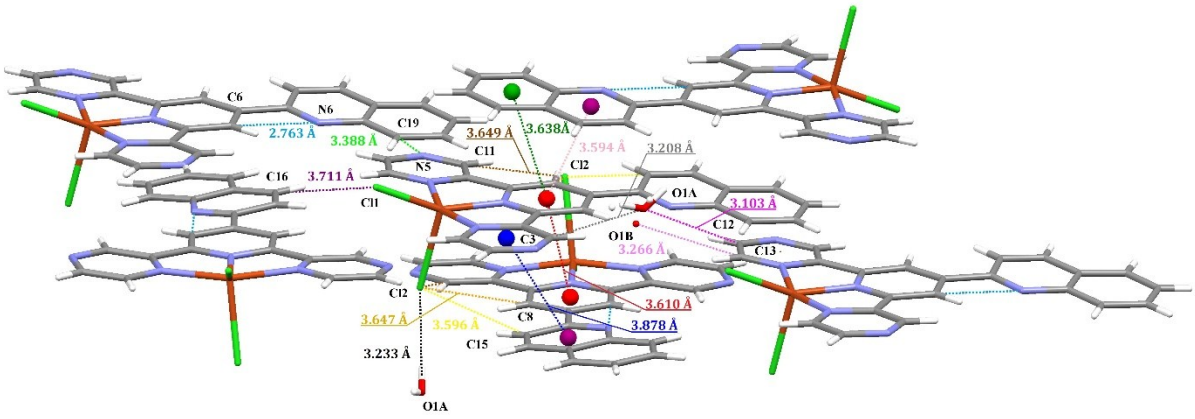
(2)


3.565 Å
3.668 Å
Cl1
3.578 Å
C5
C2
Cl2
3.622 Å
C13
3.777 Å
3.382 Å
C10
Cl1

(3)


3.780 Å
3.618 Å
3.942 Å
Cl2
C2
3.486 Å
3.663 Å
3.981 Å

(4)


C6
N6
2.763 Å
3.388 Å
C19
3.649 Å
3.638Å
C11
3.594 Å
3.208 Å
Cl2
C16
3.711 Å
N5
Cl1
O1A
3.103 Å
C12
C3
O1B
3.266 Å
C13
Cl2
3.610 Å
3.647 Å
3.596 Å
C8
3.878 Å
C15
3.233 Å
O1A

(5)

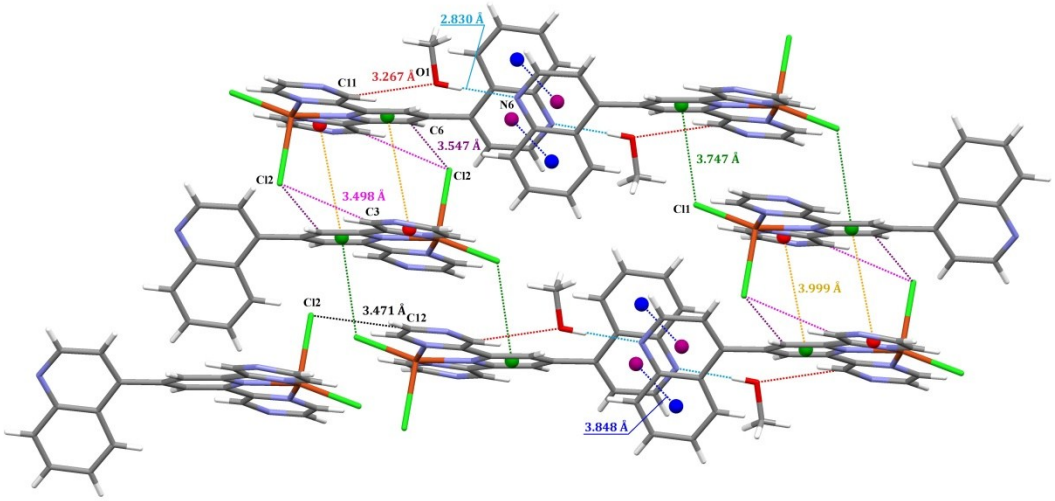


Figure S6. View of the supramolecular packing of complexes **1-6** arising from weak π•••π and D–H•••A and Cu–Cl•••A type interactions.[(6)]

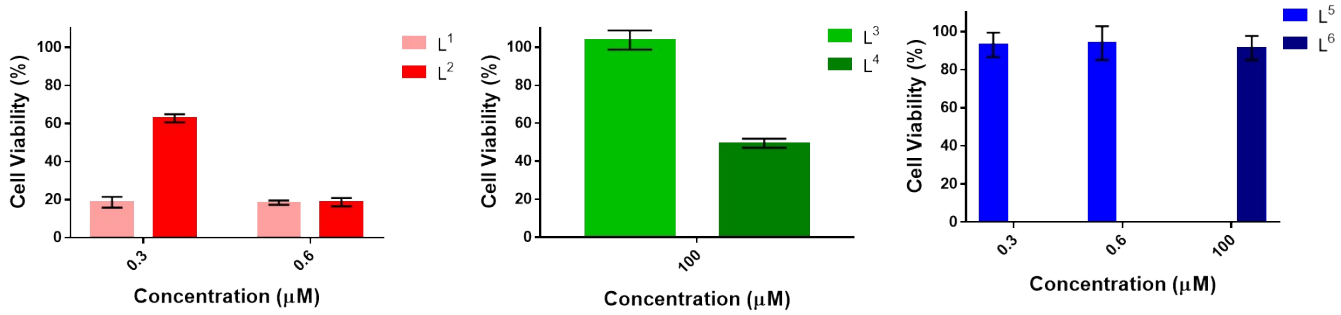
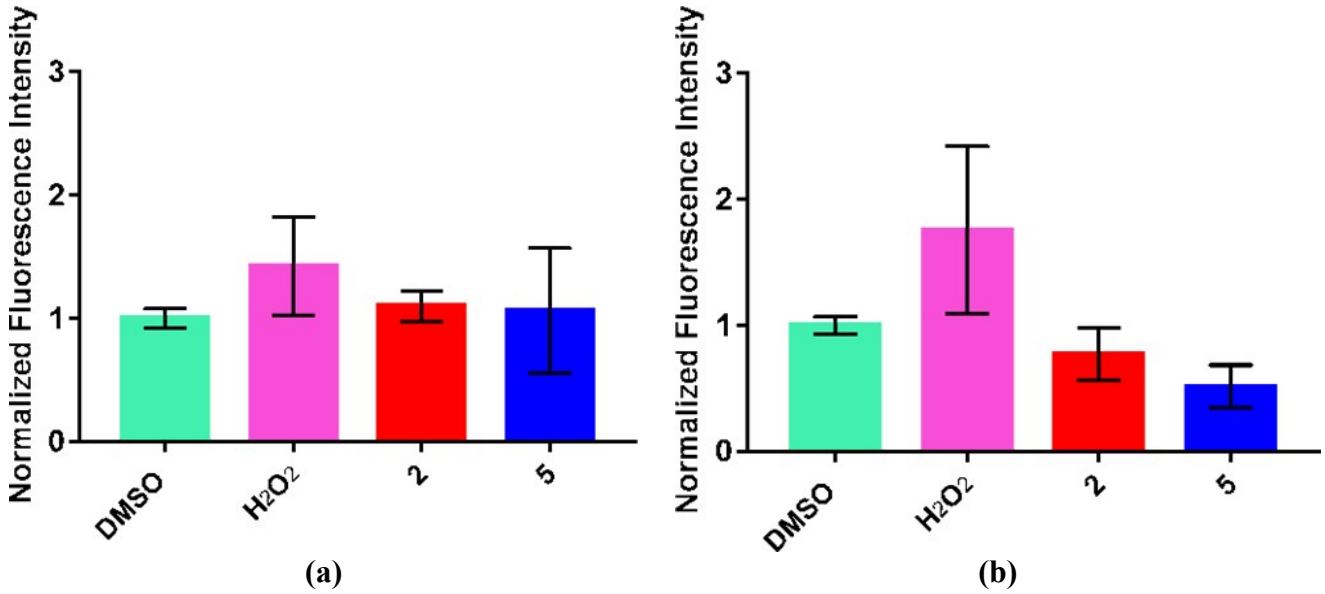


Figure S7. Cytotoxicity of ligands 2-quinolyl-terpy (L^1), 4-quinolyl-terpy (L^2), 2-quinolyl-dtpy (L^3) 4-quinolyl-dtpy (L^4), 2-quinolyl-dppy (L^5) and 4-quinolyl-dppy (L^6) employed in this research used to synthetize complexes **1-6** in HCT116 cell line evaluated 48 h after exposure to the IC_{50}, $2\times IC_{50}$ concentrations of the corresponding complexes, or at 100 μM when the complexes were not so effective against HCT116 cells. Cell viability was determined by the MTS method. DMSO 0.1% (v/v) was used as solvent control condition.



Fbigure S8. Production of reactive oxygen species (ROS) in HCT116 cells exposed for 3 h (a) and 6 h (b) to IC_{50} concentrations of complex **2** and **5**. DMSO 0.1% (v/v) was used as solvent control and 25 μM H_2O_2 was used as positive control.

Table S1. Selected bond lengths [Å] and angles [°] of complexes **1-6**

Bond lengths [Å]						
Name **used ligand**	**1** **4'-(2-quinoline)-terpy**	**2** **4'-(4-quinoline)-terpy**	**3** **4'-(2-quinoline)-dtpy**	**4** **4'-(4-quinoline)-dtpy**	**5** **4'-(2-quinoline)-dppy**	**6** **4'-(4-quinoline)-dppy**
Cu(1)–N(1)	2.049(2)	2.055(4)	2.068(4)	2.048(3)	2.047(2)	2.068(2)
Cu(1)–N(3)	2.059(2)	2.052(5)	2.067(4)	2.055(3)	2.047(3)	2.048(2)
Cu(1)–N(2)	1.9536(19)	1.947(4)	1.983(4)	1.973(4)	1.962(2)	1.9642(19)
Cu(1)–Cl(1)	2.2254(7)	2.2289(15)	2.2187(14)	2.2289(13)	2.2184(8)	2.2256(7)
Cu(1)–Cl(2)	2.5300(7)	2.5050(15)	2.4966(13)	2.4332(15)	2.5077(9)	2.4437(7)
Bond angles [°]						
N(1)–Cu(1)–N(2)	79.71(8)	78.89(18)	77.93(16)	78.92(14)	78.80(9)	78.44(8)
N(2)–Cu(1)–N(3)	78.39(8)	79.23(18)	78.41(16)	77.90(14)	78.77(10)	78.80(8)
N(1)–Cu(1)–N(3)	156.56(8)	156.33(17)	154.11(16)	154.91(17)	156.73(10)	153.97(8)
Cl(1)–Cu(1)–N(1)	98.69(6)	99.60(13)	101.01(11)	99.50(11)	99.46(7)	97.01(6)
Cl(1)–Cu(1)–N(2)	162.16(6)	159.71(13)	159.62(11)	154.73(12)	155.90(7)	159.36(6)
Cl(1)–Cu(1)–N(3)	99.56(6)	97.78(13)	97.50(11)	97.35(10)	98.46(8)	99.85(6)
Cl(2)–Cu(1)–N(1)	91.58(6)	92.11(12)	95.48(11)	96.35(11)	99.88(7)	100.09(6)
Cl(2)–Cu(1)–N(2)	93.18(6)	90.76(12)	95.35(11)	98.42(12)	101.70(7)	98.42(6)
Cl(2)–Cu(1)–N(3)	97.89(6)	97.10(13)	97.05(11)	96.42(11)	90.66(8)	95.57(6)
Cl(1)–Cu(1)–Cl(2)	104.64(3)	109.53(6)	105.00(5)	106.80(6)	102.27(3)	102.21(3)

Table S2. Short intra- and intermolecular hydrogen bonds detected in complexes **1-6**

D–H•••A	D–H [Å]	H•••A [Å]	D–A [Å]	D–H•••A [°]
1				
no hydrogen bonds detected				
2				
C(2)–H(2)•••Cl(2)[a]	0.93	2.72	3.609(6)	161.5
C(7)–H(7)•••N(4)[b]	0.93	2.43	3.324(7)	161.0
C(9)–H(9)•••Cl(2)[c]	0.93	2.75	3.643(6)	162.2
C(12)–H(12)•••Cl(2)[c]	0.93	2.81	3.712(6)	164.5
C(21)–H(21)•••Cl(2)[d]	0.93	2.83	3.568(6)	137.3
3				
C(2)–H(2)•••Cl(1)[e]	0.93	2.73	3.578(5)	151.9
C(5)–H(5)•••Cl(2)[e]	0.93	2.64	3.565(5)	173.5
C(10)–H(10)•••Cl(2)[f]	0.93	2.60	3.384(5)	141.8
C(13)–H(13)•••Cl(2)[e]	0.93	2.78	3.622(5)	150.9
4				
O(1)–H(1A)•••N(4)[g]	0.85	1.98	2.820(5)	172.9
O(1)–H(1B)•••Cl(1)[h]	0.85	2.47	3.298(4)	163.7
O(2)–H(2A)•••Cl(1)[i]	0.85	2.45	3.259(6)	158.7
O(2)–H(2B)•••O(3)	0.85	1.95	2.761(8)	158.3
O(3)–H(3B)•••O(2)[j]	0.85	2.07	2.824(11)	146.6
C(2)–H(2)•••Cl(2)[a]	0.93	2.62	3.486(4)	156.2
C(7)–H(7)•••O(1)[k]	0.93	2.35	3.265(5)	168.7
C(10)–H(10)•••O(1)	0.93	2.32	3.250(5)	177.6
C(14)–H(14)•••O(2)	0.93	2.60	3.503(7)	164.2
5				
O(1)–H(1AA)•••Cl(2)[l]	0.80	2.45	3.233(6)	164.4
C(3)–H(3)•••O(1A)	0.93	2.55	3.208(7)	127.8
C(6)–H(6)•••N(6)	0.93	2.45	2.763(4)	99.7
C(8)–H(8)•••Cl(2)[m]	0.93	2.77	3.647(3)	158.1
C(11)–H(11)•••Cl(2)[m]	0.93	2.74	3.649(4)	165.3
C(12)–H(12)•••O(1A)[n]	0.93	2.47	3.103(14)	125.5
C(13)–H(13)•••O(1B)[n]	0.93	2.54	3.266(8)	135.0
C(15)–H(15)•••Cl(2)[m]	0.93	2.76	3.596(3)	150.2
C(16)–H(16)•••Cl(1)[o]	0.93	2.80	3.711(3)	165.3
C(19)–H(19)•••N(5)[p]	0.93	2.61	3.388(5)	140.9
6				
O(1)–H(1A)•••N(6)[r]	0.82	2.02	2.830(3)	171.9
C(3)–H(3)•••Cl(2)[s]	0.93	2.61	3.498(3)	159.9
C(6)–H(6)•••Cl(2)[s]	0.93	2.71	3.545(2)	150.3
C(11)–H(11)•••O(1)	0.93	2.37	3.267(4)	160.9
C(12)–H(12)•••Cl(2)[t]	0.93	2.82	3.471(3)	128.3

Table S3. Short π•••π interactions for complexes **1-6**

Cg(I)•••Cg(J)	Cg(I)•••Cg(J) [Å]	α [°]	β [°]	γ [°]	Cg(I)-Perp [Å]	Cg(J)-Perp [Å]
1 Cg5 is the centroid of atoms N(3)/C(11)/C(12)/C(13)/C(14)/C(15); Cg6 is the centroid of atoms N(4)/C(16)/C(17)/C(18)/C(19)/C(20)						
Cg(5)•••Cg(6)[a]	3.9780	12.958	22.66	33.52	3.3165	-3.6710
Cg(6)•••Cg(6)[u]	3.7020	0	18.70	18.70	-3.5066	-3.5066
2 Cg6 is the centroid of atoms N(4)/C(16)/C(17)/C(22)/C(23)/C(24); Cg7 is the centroid of atoms C(17)/C(18)/C(19)/C(20)/C(21)/C(22)						
Cg(6)•••Cg(7)[v]	3.8835	2.216	15.24	16.93	-3.7151	-3.7470
3 Cg4 is the centroid of atoms S(2)/C(9)/N(3)/C(10)/C(11); Cg6 is the centroid of atoms N(4)/C(12)/C(13)/C(14)/C(15)/C(16)						
Cg(4)•••Cg(6)[w]	3.6682	8.682	26.24	20.66	-3.4324	3.2903
4 Cg3 is the centroid of atoms S(1)/C(3)/N(1)/C(1)/C(2); Cg4 is the centroid of atoms S(2)/C(9)/N(3)/C(10)/C(11); Cg6 is the centroid of atoms N(4)/C(12)/C(13)/C(14)/C(15)/C(16); Cg7 is the centroid of atoms C(15)/C(16)/C(17)/C(18)/C(19)/C(20)						
Cg(3)•••Cg(3)[x]	3.6633	0	21.50	21.50	3.4084	3.4084
Cg(3)•••Cg(4)[a]	3.7802	5.338	27.46	24.48	3.4403	-3.3545
Cg(4)•••Cg(4)[y]	3.981	0	27.94	27.94	-3.5197	-3.5197
Cg(6)•••Cg(6)[z]	3.6187	0	10.76	10.76	-3.5550	-3.5550
Cg(6)•••Cg(7)[b]	3.9429	4.146	26.14	29.14	3.4439	3.5395
5 Cg3 is the centroid of atoms N(1)/C(1)/C(2)/N(4)/C(3)/C(4); Cg4 is the centroid of atoms N(2)/C(5)/C(6)/C(7)/C(8)/C(9); Cg6 is the centroid of atoms N(6)/C(14)/C(15)/C(16)/C(17)/C(18); Cg7 is the centroid of atoms C(17)/C(18)/C(19)/C(20)/C(21)/C(22)						
Cg(3)•••Cg(6)[aa]	3.8775(16)	5.25(14)	32.4	28.8	3.3994(12)	3.2746(11)
Cg(4)•••Cg(4)[aa]	3.6104(15)	2.80(13)	21.2	21.2	3.3664(11)	3.3664(11)
Cg(4)•••Cg(6)[z]	3.5941(16)	4.86(13)	25.5	20.6	3.3643(11)	3.2450(11)
Cg(4)•••Cg(7)[z]	3.6376(18)	4.47(15)	19.8	22.5	3.3597(11)	3.4216(15)
6 Cg3 is the centroid of atoms N(1)/C(1)/C(2)/N(4)/C(3)/C(4); Cg4 is the centroid of atoms N(2)/C(5)/C(6)/C(7)/C(8)/C(9); Cg6 is the centroid of atoms N(6)/C(14)/C(15)/C(16)/C(17)/C(18); Cg7 is the centroid of atoms C(17)/C(18)/C(19)/C(20)/C(21)/C(22)						
Cg(3)•••Cg(4)[s]	3.9990	7.410	21.30	15.58	-3.8521	-3.7257
Cg(6)•••Cg(7)[r]	3.8485	3.982	25.88	24.73	-3.4955	-3.4624

α = dihedral angle between *Cg*(I) and *Cg*(J); *Cg*(I)-Perp = Perpendicular distance of *Cg*(I) on ring J; *Cg*(J)-Perp = perpendicular distance of *Cg*(J) on ring I; β = angle *Cg*(I)→*Cg*(J) vector and normal to ring I; γ = angle *Cg*(I) →*Cg*(J) vector and normal to plane J;

Table S4. X—Y•••Cg(J)(π-ring) interactions for complexes **1-6**

Y-X(I)•••Cg(J)	X(I)•••Cg(J) [Å]	X-Perp [Å]	γ [°]	Y-X(I)•••Cg(J) [°]
1 Cg4 is the centroid of atoms N(2)/C(6)/C(7)/C(8)/C(9)/C(10)				
Cu(1)-Cl(1)•••Cg(4)[ab]	3.7407	3.281	28.72	130.00
2				
no X—Y•••π interactions detected				
3 Cg6 is the centroid of atoms N(4)/C(12)/C(13)/C(14)/C(15)/C(16)				
Cu(1)-Cl(1)•••Cg(6)[f]	3.7777	3.502	22.02	79.00
4				
no X—Y•••π interactions detected				
5				
no X—Y•••π interactions detected				
6 Cg4 is the centroid of atoms N(2)/C(5)/C(6)/C(7)/C(8)/C(9)				
Cu(1)-Cl(1)•••Cg(4)[ab]	3.7473	3.255	29.71	114.00

γ = angle X(I)→Cg(J) vector and normal to plane J.

symmetry codes: (a) = -1+*x*,*y*,*z*; (b) = 1-*x*,1-*y*,1-*z*; (c) = 1/2+*x*,1/2-*y*,-1/2+*z*; (d) = 3/2-*x*,1/2+*y*,3/2-*z*; (e) = -*x*,1-*y*,-1/2+*z*; (f) = 1/2-*x*,-1/2+*y*,1/2+*z*; (g) = *x*,-1+*y*,1+*z*; (h) = 1+*x*,*y*,*z*; (i) = 1+*x*,1+*y*,-1+*z*; (j) = 2-*x*,2-*y*,-1-*z*; (k) = 3-*x*,-*y*,-*z*; (l) = -1/2+*x*,1-*y*,*z*; (m) = 1/2-*x*,*y*,1-*z*; (n) = *x*,1+*y*,*z*; (o) = *x*,3/2-*y*,1/2+*z*; (p) = *x*,-1+*y*,*z*; (r) = 1-*x*,2-*y*,1-*z*; (s) = -*x*,2-*y*,-*z*; (t) = -1-*x*,1-*y*,-*z*; (u) = 1-*x*,-*y*,-*z*; (v) = -*x*,-*y*,-*z*; (w) = *x*,*y*,1+*z*; (x) = -1-*x*,1-*y*,2-*z*; (y) = -*x*,-*y*,2-*z*; (z) = -*x*,1-*y*,1-*z*; (aa) = 1/2-*x*,*y*,1-*z*; (ab) = -*x*,1-*y*,-*z*