Supplementary file

Table S1 Crystal data and structure refinement parameters of the homoleptic and heteroleptic Cu(II) complexes.

Parameters	Complex 1	Complex 3	Complex 4
CCDC deposit No.	2060389	2060391	2060390
Empirical formula	$[Cu(C_{14}H_8O_2F_3)_2(C_2H_6S_1O_1)]$	$[Cu(C_{14}H_8O_2F_3)(C_9H_6N_1O_1)]_2$	$[Cu(C_{14}H_8O_2F_3)(C_9H_6N_1O_1)(C_2H_2O_4)]$
Formula weight	672.07	932.79	532.95
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Unit cell dimensions			
a (Å)	8.3115(12)	14.155(2)	11.762(4)
b (Å)	12.377(8)	10.244(6)	15.669(6)
c (Å)	14.844(2)	14.822(2)	12.864(5)
α (°)	68.362(5)	90.00	90.00
β (°)	86.264(6)	114.922(15)	107.927(8)
γ (°)	81.552(6)	90.00	90.00
Volume (Å^3)	1403.9(4)	1949(3)	2255.7(15)
Z	2	2	4
Density(calcd) (Mg m^{-3})	1.590	1.590	1.569
Absorption coefficient (mm^{-1})	0.932	1.174	1.031
F_{000}	682	942	1084
Crystal size (mm^3)	0.27×0.31×0.18	0.41×0.43×0.25	0.23×0.33×0.27
θ range for data collection	6.482 to 54.964	3.29º to 27.86º	3.09º to 27.48º
Index ranges	$-10 \le h \le 10$ $-15 \le k \le 16$ $-19 \le l \le 11$	$-10 \le h \le 18$ $-13 \le k \le 13$ $-19 \le l \le 18$	$-15 \le h \le 15$ $-20 \le k \le 18$ $-16 \le l \le 8$
Reflections collected	8154	11192	11866
Unique reflections	6274[R_{int}=0.0428]	4479[R_{int} = 0.1199]	5089[R_{int}=0.0435]
Absorption correction	multi-scan	multi-scan	multi-scan
Data/restraints/parameters	6274/0/390	4479 / 0 / 280	5089 / 0 / 318
Goodness-of-fit on F^2	1.004	1.033	1.020
Final [$I > 2\sigma(I)$]	$R1$ = 0.0618	$R1$ = 0.0891	$R1$ = 0.0508
R indices (all data)	$R1$ = 0.0928	$R1$ = 0.1580	$R1$ = 0.0844
Largest diff. peak and hole (eÅ^{-3})	0.91 and -1.09	0.639 and -0.793	0.618 and -0.328

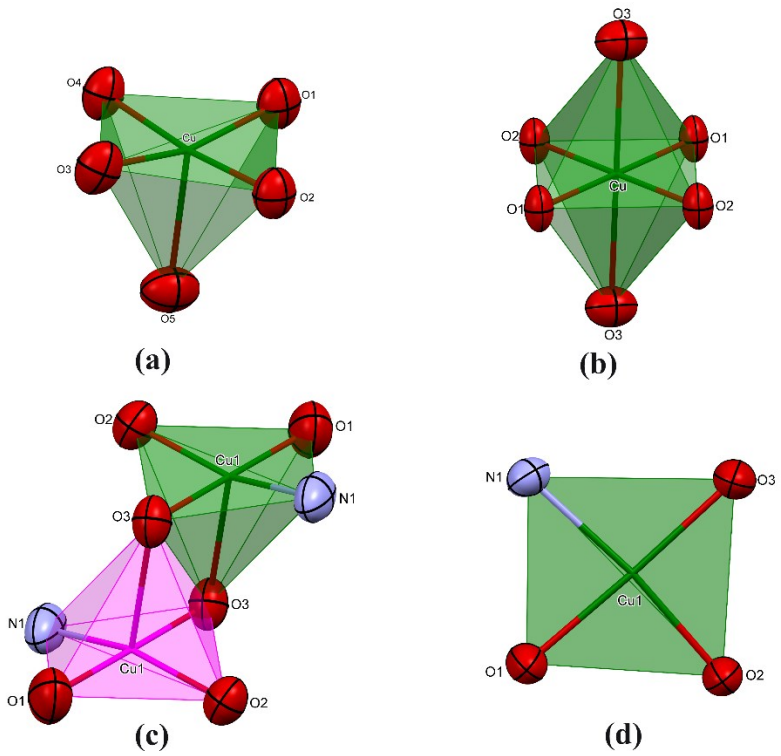

Fig. S1 Five and six coordinated square pyramidal (a), and octahedral geometry (b) in homoleptic complexes (1 and 2). Square pyramidal geometry by the doubly phenoxide bridged inversion dimer (c) and square planar geometry (d) in heteroleptic complex 3 and 4 respectively.

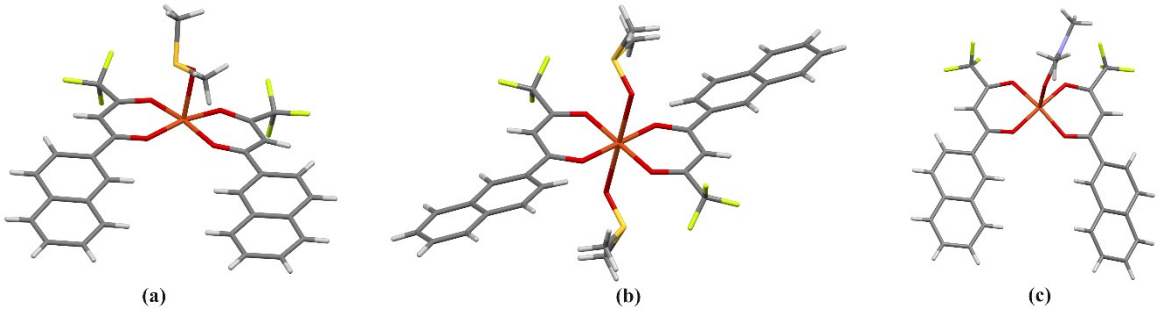

Fig. S2 The solvatomorphic forms of homoleptic β-diketone based Cu(II) complexes.

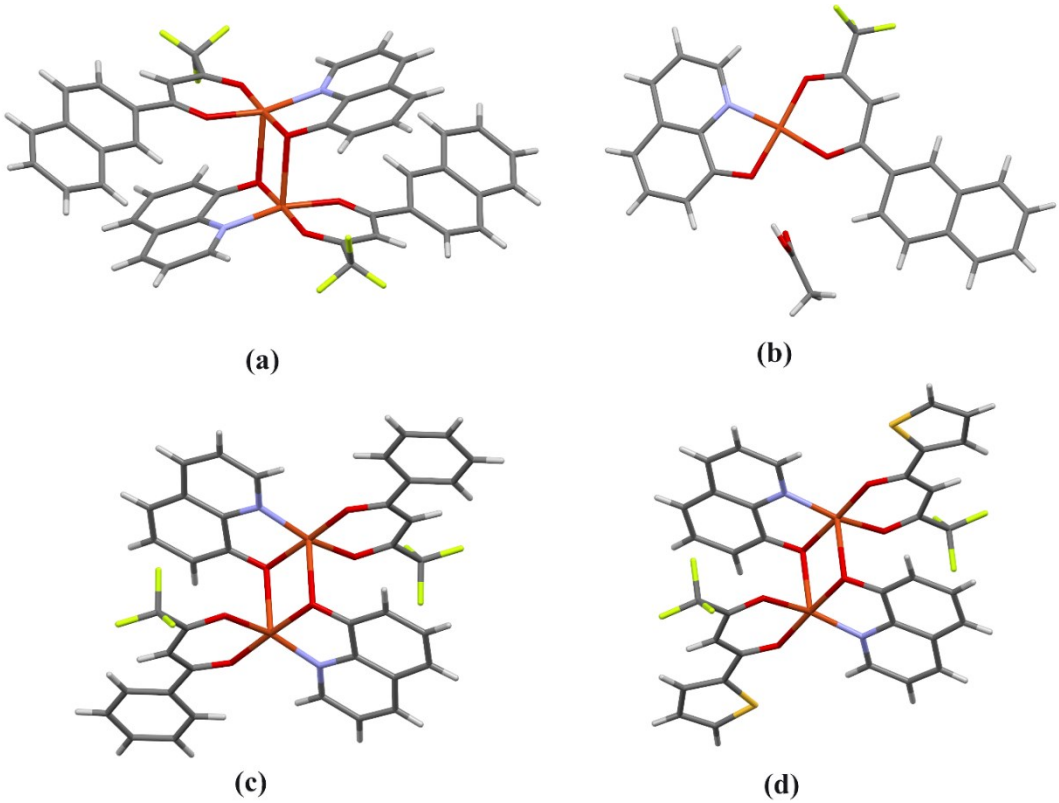

Fig. S3 The solvatomorphic forms (a and b) of heteroleptic β-diketone and 8HQ Cu(II) complexes; (c) and (d) similar phenoxide bridged dinuclear Cu(II) complexes from CSD.

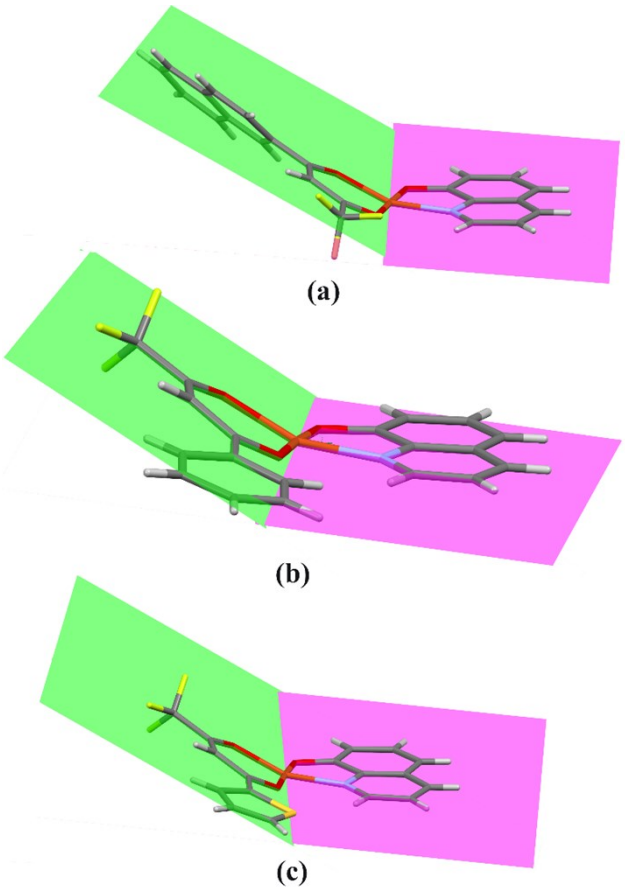

Fig. S4 Envelope conformation in the heteroleptic complex 3 (a), and similar conformation in the phenoxide bridged dinuclear complex 6 (b) and 7 (c).

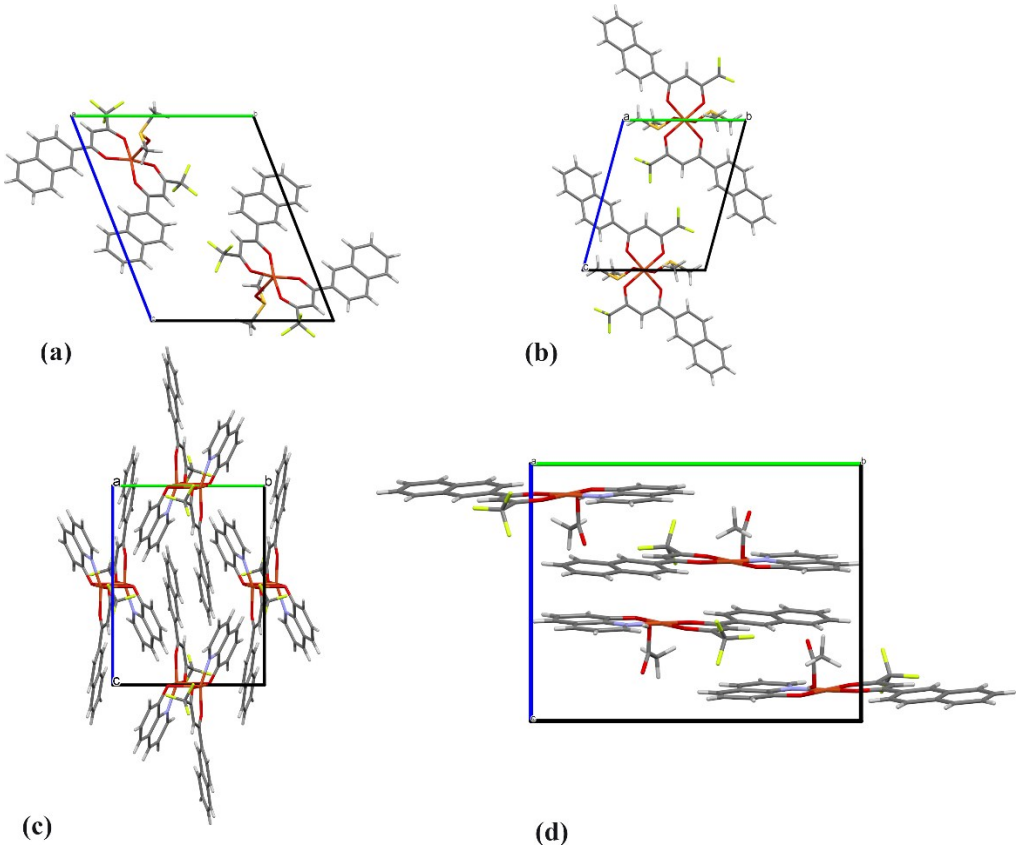

Fig. S5 The projection of crystal packing of homoleptic Cu(II) complexes [(a) and (b)]; heteroleptic dinuclear and mononuclear complex [(c) and (d)] view down along *a*-axis.

Table S2 Geometry of hydrogen bonds in homoleptic and heteroleptic Cu(II) complexes.

	D-H···A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symmetry
Complex 1	C3-H3···F1	0.93	2.35	2.727(5)	104	Intra
	C10-H10···O2	0.93	2.40	2.729(5)	100	Intra
	C17-H17···F6	0.93	2.38	2.741(5)	103	Intra
	C24-H24···O4	0.93	2.39	2.710(5)	100	intra
	C29-H29C···O5	0.96	2.60	3.347(4)	135	1-*x*,1-*y*,-*z*
	C20-H20···F6	0.93	2.64	3.263	171	1-*x*,1-*y*,-*z*
	C7-H7···S1	0.93	2.96	3.852	150	1-*x*,1-*y*,-*z*
Complex 3	C3-H3···F1	0.93	2.41	2.738(13)	101	Intra
	C15-H15···O1	0.93	2.58	3.040	110	Intra
	C20-H20…F1	0.93	2.69	3.512	148	1/2+*x*,-1/2-*y*,-1/2+*z*
Complex 4	C3-H3···F1	0.93	2.40	2.759(5)	103	Intra
	C14-H14···O3	0.93	2.42	2.733(4)	100	Intra
	C15-H15···O2	0.93	2.59	3.060(4)	112	Intra
	O4-H4···O1	0.82	1.81	2.620(4)	171	1/2-*x*,-1/2+*y*,1/2-*z*
	C6-H6···O5	0.93	2.42	2.733(4)	100	1/2-*x*,-1/2+*y*,1/2-*z*

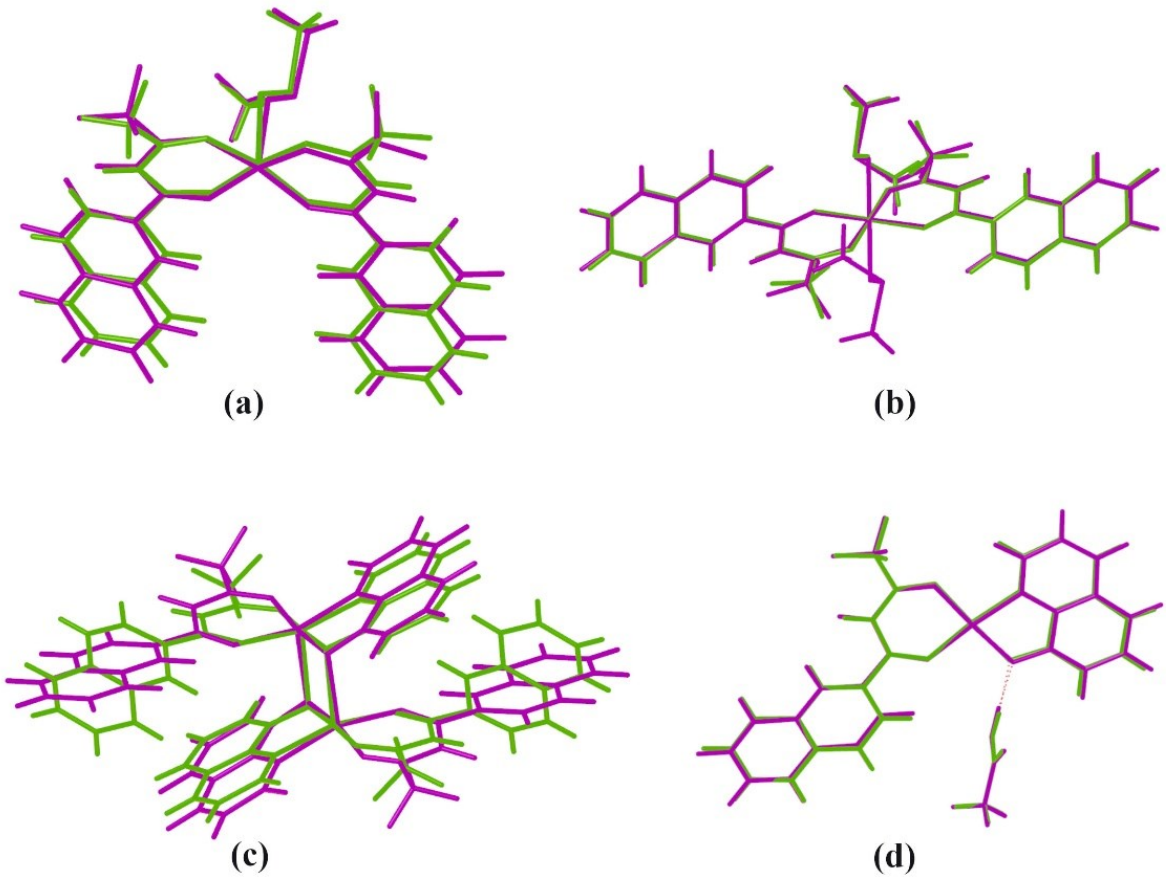

Fig. S6 Overlay of crystal structure (green) and optimized electronic structure (pink) of the homoleptic (a and b) and heteroleptic complexes (c and d).

Table S3 Comparison of experimental (XRD) and calculated (DFT) geometrical parameters of the complex 1.

Sl. No.	Bond lengths in (Å)				Bond angles in (º)				
	Atom1	Atom2	XRD	DFT	Atom1	Atom2	Atom3	XRD	DFT
1	Cu1	O3	1.942(3)	1.982	O3	Cu1	O2	169.0(1)	170.2
2	Cu1	O2	1.945(3)	1.985	O3	Cu1	O4	92.9(1)	90.7
3	Cu1	O4	1.939(3)	1.989	O3	Cu1	O1	88.8(1)	88.5
4	Cu1	O1	1.941(3)	1.986	O3	Cu1	O5	91.2(1)	93.4
5	Cu1	O5	2.235(2)	2.255	O2	Cu1	O4	84.0(1)	88.1
6	S1	O5	1.508(3)	1.548	O2	Cu1	O1	92.9(1)	90.6
7	S1	C30	1.772(4)	1.820	O2	Cu1	O5	99.4(1)	96.5
8	S1	C29	1.775(3)	1.818	O4	Cu1	O1	172.5(1)	167.7
9	F3	C1	1.336(4)	1.352	O4	Cu1	O5	91.8(1)	95.7
10	O3	C16	1.260(6)	1.268	O1	Cu1	O5	95.4(1)	96.6
11	F2	C1	1.341(5)	1.351	O5	S1	C30	106.0(2)	105.6
12	F5	C15	1.344(5)	1.351	O5	S1	C29	105.7(2)	104.8
13	F1	C1	1.332(6)	1.347	C30	S1	C29	99.0(2)	98.7
14	O2	C4	1.263(6)	1.268	Cu1	O3	C16	122.7(2)	124.2
15	F6	C15	1.323(6)	1.347	Cu1	O2	C4	127.9(2)	128.8
16	O4	C18	1.256(6)	1.267	Cu1	O4	C18	128.3(2)	128.6
17	O1	C2	1.277(6)	1.267	Cu1	O1	C2	122.5(2)	124.3
18	F4	C15	1.329(4)	1.352	Cu1	O5	S1	118.6(1)	125.6
19	C19	C20	1.413(7)	1.425	C20	C19	C18	123.4(3)	122.4
20	C19	C18	1.487(5)	1.491	C20	C19	C24	119.2(4)	119.1
21	C19	C24	1.379(6)	1.384	C18	C19	C24	117.5(3)	118.5
22	C16	C17	1.386(5)	1.383	O3	C16	C17	130.3(4)	129.8
23	C16	C15	1.535(7)	1.542	O3	C16	C15	112.7(3)	111.8
24	C20	C21	1.373(5)	1.372	C17	C16	C15	116.9(3)	118.4
25	C18	C17	1.426(6)	1.422	O3	Cu1	O2	169.0(1)	170.2
Correlation coefficient			**0.9978**		**Correlation coefficient**			**0.9938**	

Sl. No.	Torsion angles in (º)					
	Atom1	Atom2	Atom3	Atom4	XRD	DFT
1	O2	Cu1	O3	C16	-72.2(7)	-86.1
2	O4	Cu1	O3	C16	1.5(3)	-3.1
3	O1	Cu1	O3	C16	-171.3(3)	-170.8
4	O5	Cu1	O3	C16	93.4(3)	92.7
5	O3	Cu1	O2	C4	-98.1(6)	-87.1
6	O4	Cu1	O2	C4	-172.6(3)	-170.4
7	O1	Cu1	O2	C4	0.6(3)	-2.6
8	O5	Cu1	O2	C4	96.5(3)	94.1
9	O3	Cu1	O4	C18	-1.4(3)	3.8
10	O2	Cu1	O4	C18	168.0(3)	174.0
11	O1	Cu1	O4	C18	102.3(9)	89.8
12	O5	Cu1	O4	C18	-92.7(3)	-89.7
13	O3	Cu1	O1	C2	172.4(3)	172.2
14	O2	Cu1	O1	C2	3.2(3)	2.0
15	O4	Cu1	O1	C2	68.3(9)	85.9
16	O5	Cu1	O1	C2	-96.5(3)	-94.6
17	O3	Cu1	O5	S1	-170.1(2)	-162.3
18	O2	Cu1	O5	S1	7.1(2)	17.5
19	O4	Cu1	O5	S1	-77.1(2)	-71.3
20	O1	Cu1	O5	S1	100.9(2)	108.8
21	C30	S1	O5	Cu1	93.9(2)	94.2
22	C29	S1	O5	Cu1	-161.6(2)	-162.2
23	Cu1	O3	C16	C17	-1.5(6)	1.3
24	Cu1	O3	C16	C15	175.5(2)	-179.1
25	Cu1	O2	C4	C3	-4.7(5)	1.8
Correlation coefficient					**0.9955**	

Table S4 Comparison of experimental (XRD) and calculated (DFT) geometrical parameters of the heteroleptic dinuclear complex 3.

Sl. No.	Bond lengths in (Å)					Bond angles in (º)				
	Atom1	Atom2	XRD	DFT		Atom1	Atom2	Atom3	XRD	DFT
1	Cu1	O3	1.905(5)	2.030		O3	Cu1	O3	86.7(2)	83.2
2	Cu1	O2	1.941(4)	2.039		O3	Cu1	O2	89.8(2)	91.0
3	Cu1	O1	1.913(5)	1.987		O3	Cu1	O1	95.1(2)	103.0
4	Cu1	N1	1.979(5)	2.083		O3	Cu1	N1	108.7(2)	111.0
5	O3	C22	1.327(7)	1.310		O3	Cu1	O2	89.7(2)	95.1
6	O2	C4	1.23(1)	1.259		O3	Cu1	O1	177.2(2)	172.1
7	O1	C2	1.25(1)	1.267		O3	Cu1	N1	84.1(2)	80.5
8	N1	C23	1.34(1)	1.357		O2	Cu1	O1	92.4(2)	89.7
9	N1	C15	1.314(9)	1.320		O2	Cu1	N1	160.0(2)	156.7
10	C4	C5	1.479(9)	1.498		O1	Cu1	N1	93.3(2)	92.7
11	C4	C3	1.40(1)	1.425		Cu1	O3	Cu1	93.3(2)	96.7
12	C5	C14	1.40(1)	1.382		Cu1	O3	C22	111.1(4)	110.8
13	C5	C6	1.37(1)	1.423		Cu1	O3	C22	111.5(4)	112.4
14	C22	C23	1.403(9)	1.439		Cu1	O2	C4	127.1(4)	128.3
15	C22	C21	1.37(1)	1.396		Cu1	O1	C2	123.9(5)	125.0
16	C13	C14	1.393(9)	1.414		Cu1	N1	C23	110.4(4)	110.8
17	C13	C12	1.39(1)	1.421		Cu1	N1	C15	128.6(5)	129.0
18	C13	C8	1.41(2)	1.431		C23	N1	C15	120.6(6)	120.1
19	C23	C18	1.413(9)	1.419		O2	C4	C5	115.7(6)	116.5
20	F2	C1	1.26(1)	1.349		O2	C4	C3	124.5(7)	123.9
21	F3	C1	1.34(1)	1.346		C5	C4	C3	119.7(6)	119.6
22	C3	C2	1.36(1)	1.384		C4	C5	C14	117.3(6)	118.0
23	C12	C11	1.42(1)	1.373		C4	C5	C6	125.1(7)	123.0
24	C21	C20	1.36(1)	1.407		C14	C5	C6	117.5(7)	119.0
25	F1	C1	1.22(2)	1.349		O3	C22	C23	118.5(6)	118.4
Correlation coefficient			**0.9832**			**Correlation coefficient**			**0.9850**	

Sl. No.	Torsion angles in (º)					
	Atom1	Atom2	Atom3	Atom4	XRD	DFT
1	O3	Cu1	O3	Cu1	0.0(1)	0.0
2	O3	Cu1	O3	C22	114.2(4)	125.5
3	O2	Cu1	O3	Cu1	89.8(2)	90.4
4	O2	Cu1	O3	C22	-156.0(4)	-144.1
5	O1	Cu1	O3	Cu1	-133(4)	-142.8
6	O1	Cu1	O3	C22	-19(5)	-17.3
7	N1	Cu1	O3	Cu1	-109.2(2)	-112.7
8	N1	Cu1	O3	C22	5.0(4)	12.8
9	O3	Cu1	O2	C4	-101.5(5)	-108.4
10	O3	Cu1	O2	C4	171.8(5)	168.4
11	O1	Cu1	O2	C4	-6.4(6)	-5.3
12	N1	Cu1	O2	C4	100.2(8)	90.5
13	O3	Cu1	O1	C2	95.0(6)	94.1
14	O3	Cu1	O1	C2	-132(4)	-123.9
15	O2	Cu1	O1	C2	5.0(6)	3.2
16	N1	Cu1	O1	C2	-155.9(6)	-153.6
17	O3	Cu1	N1	C23	-90.0(5)	-87.7
18	O3	Cu1	N1	C15	97.1(7)	96.5
19	O3	Cu1	N1	C23	-5.4(5)	-8.8
20	O3	Cu1	N1	C15	-178.3(7)	175.4
21	O2	Cu1	N1	C23	67.1(8)	72.0
22	O2	Cu1	N1	C15	-105.8(8)	-103.8
23	O1	Cu1	N1	C23	173.4(5)	167.3
24	O1	Cu1	N1	C15	0.6(7)	-8.6
25	Cu1	O3	C22	C23	98.7(6)	97.2
Correlation coefficient					**0.9977**	

Table S5 Comparison of experimental (XRD) and calculated (DFT) geometrical parameters of the heteroleptic mononuclear complex 4.

Sl. No.	Bond lengths in (Å)				Bond angles in (º)				
	Atom1	Atom2	XRD	DFT	Atom1	Atom2	Atom3	XRD	DFT
1	Cu1	O2	1.919(2)	1.957	O2	Cu1	O3	93.23(9)	91.6
2	Cu1	O3	1.921(2)	1.959	O2	Cu1	O1	88.92(9)	91.7
3	Cu1	O1	1.925(2)	1.964	O2	Cu1	N1	173.5()	175.0
4	Cu1	N1	1.970(2)	2.008	O3	Cu1	O1	177.8()	176.8
5	O2	C4	1.263(3)	1.269	O3	Cu1	N1	93()	93.4
6	O3	C2	1.278(4)	1.274	O1	Cu1	N1	84.9()	83.3
7	O1	C22	1.330(4)	1.328	Cu1	O2	C4	128.7()	128.8
8	N1	C23	1.359(4)	1.365	Cu1	O3	C2	122.9()	123.9
9	N1	C15	1.325(5)	1.323	Cu1	O1	C22	112.3()	112.6
10	C22	C23	1.436(5)	1.429	Cu1	N1	C23	110.1()	110.6
11	C22	C21	1.377(5)	1.389	Cu1	N1	C15	130.1()	129.2
12	C5	C14	1.430(5)	1.426	C23	N1	C15	119.8(3)	120.2
13	C5	C6	1.368(4)	1.385	O1	C22	C23	116.7(3)	117.6
14	C5	C4	1.493(5)	1.487	O1	C22	C21	125.4(3)	124.9
15	F1	C1	1.307(4)	1.347	C23	C22	C21	118.0(3)	117.5
16	C14	C13	1.364(5)	1.370	C14	C5	C6	119.0(3)	119.2
17	C1	C2	1.536(5)	1.540	C14	C5	C4	118.4(3)	118.3
18	C1	F3	1.297(6)	1.350	C6	C5	C4	122.7(3)	122.5
19	C1	F2	1.317(4)	1.351	C5	C14	C13	120.7(3)	120.7
20	Cu1	O2	1.919(2)	1.957	F1	C1	C2	114.5(3)	113.7
21	C6	C7	1.415(5)	1.416	F1	C1	F3	107.9(3)	107.3
22	C12	C7	1.421(5)	1.431	F1	C1	F2	104.5(3)	107.3
23	C12	C13	1.413(4)	1.422	C2	C1	F3	110.9(3)	110.6
24	C12	C11	1.425(5)	1.418	C2	C1	F2	112.9(3)	110.6
25	C4	C3	1.428(5)	1.425	O2	Cu1	O3	93.23(9)	91.6
Correlation coefficient			**0.9970**		**Correlation coefficient**			**0.9979**	

Sl. No.	Torsion angles in (º)					
	Atom1	Atom2	Atom3	Atom4	XRD	DFT
1	O3	Cu1	O2	C4	1.7(3)	0.8
2	O1	Cu1	O2	C4	-177.9(3)	-179.4
3	N1	Cu1	O2	C4	165.6(8)	-173.3
4	O2	Cu1	O3	C2	1.7(3)	-1.7
5	O1	Cu1	O3	C2	172(2)	-178.9
6	N1	Cu1	O3	C2	-176.5(3)	177.7
7	O2	Cu1	O1	C22	-177.3(2)	179.0
8	O3	Cu1	O1	C22	13(3)	-3.9
9	N1	Cu1	O1	C22	0.8(2)	-0.5
10	O2	Cu1	N1	C23	16(1)	-5.7
11	O2	Cu1	N1	C15	-162.2(8)	174.1
12	O3	Cu1	N1	C23	179.5(2)	-179.8
13	O3	Cu1	N1	C15	1.8(3)	0.0
14	O1	Cu1	N1	C23	-1.0(2)	0.4
15	O1	Cu1	N1	C15	-178.7(3)	-179.9
16	Cu1	O2	C4	C5	177.2(2)	179.7
17	Cu1	O2	C4	C3	-2.6(5)	0.4
18	Cu1	O3	C2	C1	172.8(2)	-178.2
19	Cu1	O3	C2	C3	-4.7(5)	1.7
20	Cu1	O1	C22	C23	-0.5(4)	0.5
21	Cu1	O1	C22	C21	178.4(3)	-179.6
22	Cu1	N1	C23	C22	0.9(3)	-0.3
23	Cu1	N1	C23	C18	-178.4(3)	179.7
24	C15	N1	C23	C22	178.9(3)	180.0
25	C15	N1	C23	C18	-0.4(5)	-0.1
Correlation coefficient					**0.9989**	