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Supplementary Information for

A novel 1,3,5-triaminocyclohexane-based tripodal ligand forms a unique tetra(pyrazolate)-bridged tricopper(II) core: solution equilibrium, structure and catecholase activity

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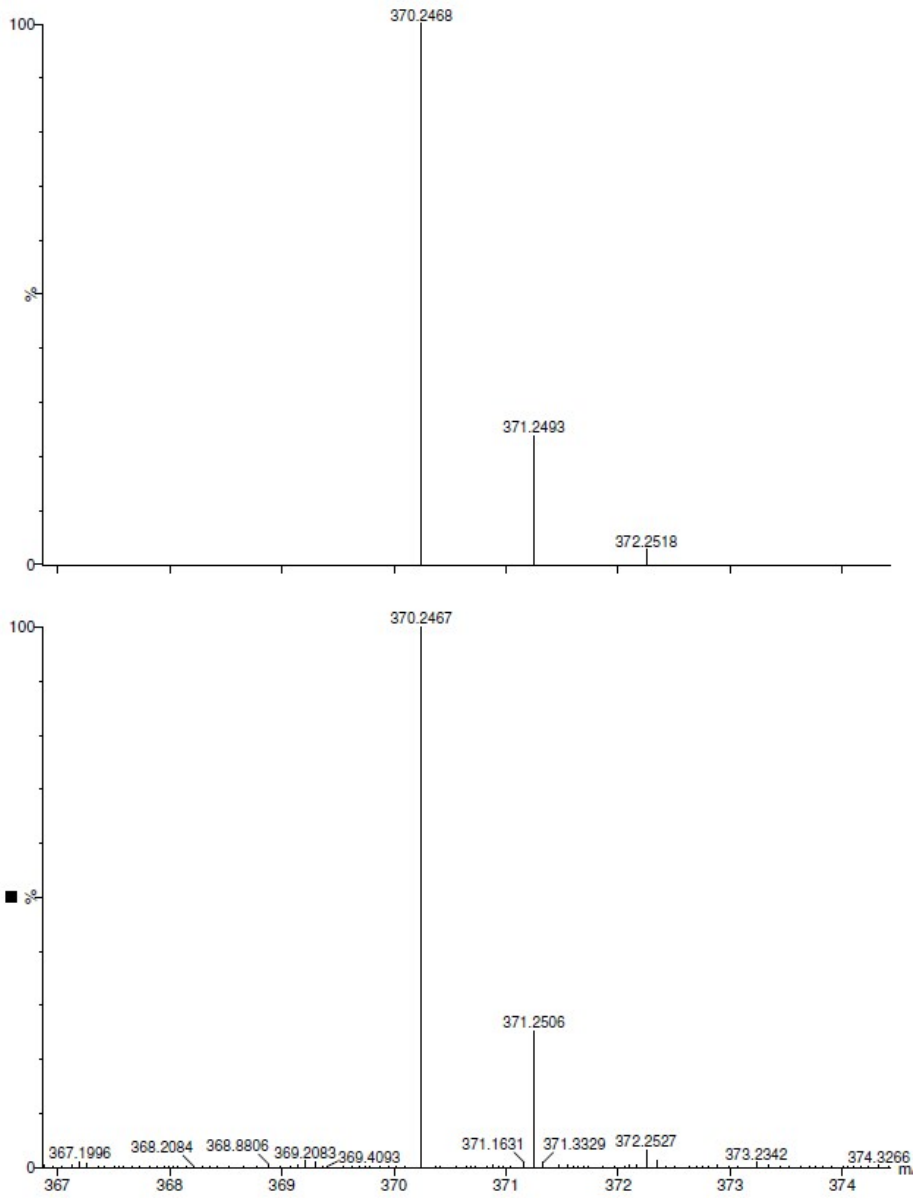

Figure S1: Calculated (top) and measured (bottom) (HR)ESI-MS spectra of tachpyz ($C_{18}H_{27}N_9$).

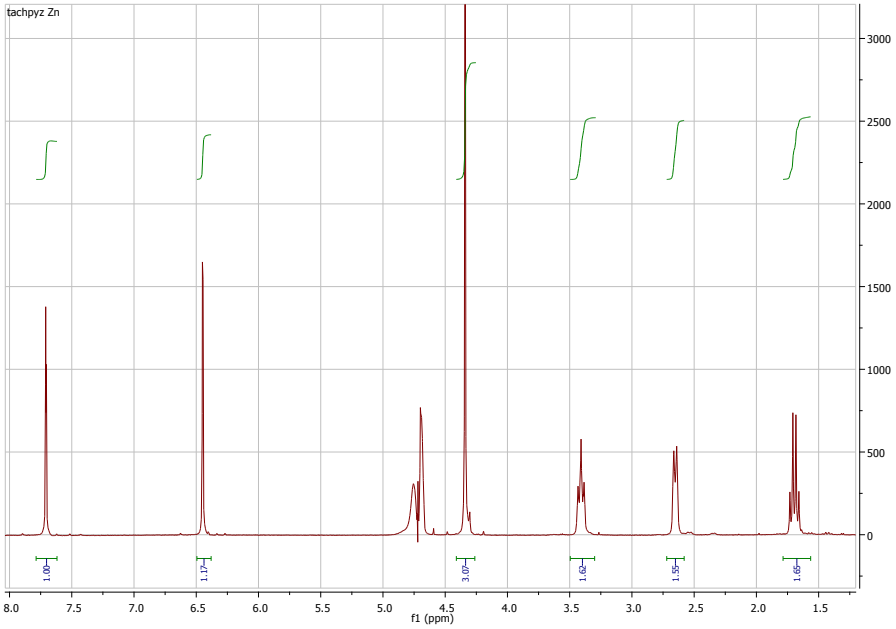

Figure S2: ^{1}H-NMR spectrum of tachpyz at pH = 3.5 in 10%-90% D_2O/H_2O ([tachpyz] = 0.0028 M).

Table S1 Crystallographic data of **1**.

Crystal data

$C_{36}H_{50}Cu_3N_{18}\cdot 2(ClO_4)\cdot 4(H_2O)\cdot O$	$F(000) = 2500$
$M_r = 1212.52$	$D_x = 1.673$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$a = 13.0393$ (2) Å	Cell parameters from 14467 reflections
$b = 28.5503$ (4) Å	$\theta = 3.7–73.4°$
$c = 13.3878$ (2) Å	$\mu = 3.26$ mm^{-1}
$\beta = 105.004$ (2)°	$T = 100$ K
$V = 4814.04$ (13) Å^3	Needle, brown
$Z = 4$	0.4 × 0.06 × 0.02 mm

Data collection

SuperNova, Dual, Cu at zero, Atlas diffractometer	9485 independent reflections
Radiation source: sealed X-ray tube, SuperNova (Cu) X-ray Source	8187 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.029$
Detector resolution: 10.5908 pixels mm^{-1}	$\theta_{max} = 73.5°$, $\theta_{min} = 3.1°$
ω scans	$h = -16\rightarrow16$
Absorption correction: multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -35\rightarrow35$
$T_{min} = 0.720$, $T_{max} = 1.000$	$l = -16\rightarrow16$
35344 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.074$	$w = 1/[\sigma^2(F_o^2) + (0.1399P)^2 + 13.6362P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.225$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rangle_{max} = 1.48$ e Å^{-3}
9485 reflections	$\Delta\rangle_{min} = -1.38$ e Å^{-3}
681 parameters	Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
123 restraints	Extinction coefficient: 0.00039 (8)

Table S2 Full list of bond length (Å) and bond angle (°) data for **1**.

C1—N1	1.489 (7)	C61—N62	1.318 (8)
C1—C6	1.529 (8)	C61—C65	1.364 (9)
C1—C2	1.530 (8)	N62—N63	1.363 (7)
C1—H1	1.0000	N63—C64	1.265 (10)
C2—C3	1.530 (8)	N63—H63	0.8800
C2—H2B	0.9900	C64—C65	1.364 (9)
C2—H2C	0.9900	C64—H64	0.9500
C3—N2	1.489 (6)	C65—H65	0.9500
C3—C4	1.523 (7)	C70—N52	1.493 (7)
C3—H3	1.0000	C70—C73	1.496 (7)
C4—C5	1.525 (8)	C70—H70A	0.9900
C4—H4A	0.9900	C70—H70B	0.9900
C4—H4B	0.9900	C73—N72	1.335 (6)
C5—N3	1.492 (7)	C73—C74	1.388 (7)
C5—C6	1.534 (9)	C74—C75	1.392 (7)
C5—H5	1.0000	C74—H74	0.9500
C6—H6A	0.9900	C75—N71	1.348 (6)
C6—H6B	0.9900	C75—H75	0.9500
C10—C11	1.463 (10)	C80—N53	1.481 (7)
C10—N1	1.470 (7)	C80—C83	1.495 (7)
C10—H10A	0.9900	C80—H80A	0.9900
C10—H10B	0.9900	C80—H80B	0.9900
C11—C15	1.252 (18)	C83—N82	1.343 (6)
C11—N12	1.39 (2)	C83—C84	1.387 (8)
N12—N13	1.358 (16)	C84—C85	1.380 (8)
N12—H92	0.8800	C84—H84	0.9500
N13—C14	1.39 (2)	C85—N81	1.336 (6)
C14—C15	1.265 (17)	C85—H85	0.9500
C14—H14	0.9500	Cl1—O14	1.243 (10)
C15—H15	0.9500	Cl1—O11	1.389 (8)
C20—C23	1.488 (7)	Cl1—O12	1.453 (9)
C20—N2	1.491 (6)	Cl1—O13	1.723 (17)
C20—H20A	0.9900	Cl2—O24A	1.25 (3)
C20—H20B	0.9900	Cl2—O24	1.354 (13)
C23—N22	1.350 (6)	Cl2—O21	1.383 (13)
C23—C24	1.385 (6)	Cl2—O21A	1.39 (3)
C24—C25	1.394 (7)	Cl2—O23A	1.433 (11)
C24—H24	0.9500	Cl2—O23	1.454 (9)

C25—N21	1.345 (6)	Cl2—O22	1.47 (2)
C25—H25	0.9500	Cl2—O22A	1.68 (3)
C30—N3	1.488 (7)	Cu1—N22	1.936 (3)
C30—C33	1.504 (7)	Cu1—N32	1.954 (4)
C30—H30A	0.9900	Cu1—N3	2.030 (4)
C30—H30B	0.9900	Cu1—N2	2.049 (4)
C33—N32	1.340 (6)	Cu1—N1	2.219 (5)
C33—C34	1.375 (7)	Cu2—N81	1.960 (4)
C34—C35	1.396 (7)	Cu2—N21	1.962 (4)
C34—H34	0.9500	Cu2—N31	1.971 (4)
C35—N31	1.343 (6)	Cu2—N71	1.973 (4)
C35—H35	0.9500	Cu3—N82	1.931 (4)
C51—N51	1.485 (6)	Cu3—N72	1.946 (4)
C51—C56	1.523 (8)	Cu3—N53	2.040 (4)
C51—C52	1.523 (8)	Cu3—N52	2.041 (4)
C51—H51	1.0000	Cu3—N51	2.262 (4)
C52—C53	1.520 (7)	N1—H1A	1.0000
C52—H52B	0.9900	N2—H2A	1.0000
C52—H52C	0.9900	N3—H3A	1.0000
C53—N52	1.507 (6)	N21—N22	1.350 (5)
C53—C54	1.537 (9)	N31—N32	1.352 (5)
C53—H53	1.0000	N51—H51A	1.0000
C54—C55	1.521 (8)	N52—H52A	1.0000
C54—H54A	0.9900	N53—H53A	1.0000
C54—H54B	0.9900	N71—N72	1.358 (5)
C55—N53	1.502 (6)	N81—N82	1.346 (5)
C55—C56	1.530 (7)	O1W—H81	0.8408
C55—H55	1.0000	O1W—H82	0.8420
C56—H56A	0.9900	O2W—H21	0.8426
C56—H56B	0.9900	O2W—H22	0.8426
C60—N51	1.461 (7)	O3W—H31	0.8417
C60—C61	1.510 (7)	O3W—H32	0.8405
C60—H60A	0.9900	O4W—H41	0.8412
C60—H60B	0.9900	O4W—H42	0.8432
N1—C1—C6	111.3 (4)	C61—C65—H65	127.1
N1—C1—C2	108.4 (4)	N52—C70—C73	108.8 (4)
C6—C1—C2	112.7 (5)	N52—C70—H70A	109.9
N1—C1—H1	108.1	C73—C70—H70A	109.9
C6—C1—H1	108.1	N52—C70—H70B	109.9

C2—C1—H1	108.1	C73—C70—H70B	109.9
C1—C2—C3	115.2 (5)	H70A—C70—H70B	108.3
C1—C2—H2B	108.5	N72—C73—C74	109.1 (4)
C3—C2—H2B	108.5	N72—C73—C70	116.7 (4)
C1—C2—H2C	108.5	C74—C73—C70	134.2 (4)
C3—C2—H2C	108.5	C73—C74—C75	104.3 (4)
H2B—C2—H2C	107.5	C73—C74—H74	127.8
N2—C3—C4	108.7 (4)	C75—C74—H74	127.8
N2—C3—C2	113.5 (4)	N71—C75—C74	110.1 (4)
C4—C3—C2	111.1 (5)	N71—C75—H75	124.9
N2—C3—H3	107.8	C74—C75—H75	124.9
C4—C3—H3	107.8	N53—C80—C83	108.8 (4)
C2—C3—H3	107.8	N53—C80—H80A	109.9
C3—C4—C5	114.2 (5)	C83—C80—H80A	109.9
C3—C4—H4A	108.7	N53—C80—H80B	109.9
C5—C4—H4A	108.7	C83—C80—H80B	109.9
C3—C4—H4B	108.7	H80A—C80—H80B	108.3
C5—C4—H4B	108.7	N82—C83—C84	108.7 (4)
H4A—C4—H4B	107.6	N82—C83—C80	116.7 (4)
N3—C5—C4	109.3 (4)	C84—C83—C80	134.5 (5)
N3—C5—C6	112.9 (5)	C85—C84—C83	104.5 (4)
C4—C5—C6	110.6 (5)	C85—C84—H84	127.7
N3—C5—H5	108.0	C83—C84—H84	127.7
C4—C5—H5	108.0	N81—C85—C84	110.1 (5)
C6—C5—H5	108.0	N81—C85—H85	124.9
C1—C6—C5	114.7 (4)	C84—C85—H85	124.9
C1—C6—H6A	108.6	O14—Cl1—O11	113.9 (5)
C5—C6—H6A	108.6	O14—Cl1—O12	110.8 (7)
C1—C6—H6B	108.6	O11—Cl1—O12	108.9 (5)
C5—C6—H6B	108.6	O14—Cl1—O13	114.6 (6)
H6A—C6—H6B	107.6	O11—Cl1—O13	98.8 (6)
C11—C10—N1	116.4 (6)	O12—Cl1—O13	109.1 (5)
C11—C10—H10A	108.2	O24—Cl2—O21	107.3 (11)
N1—C10—H10A	108.2	O24A—Cl2—O21A	118 (2)
C11—C10—H10B	108.2	O24A—Cl2—O23A	121.4 (18)
N1—C10—H10B	108.2	O21A—Cl2—O23A	118.1 (14)
H10A—C10—H10B	107.3	O24—Cl2—O23	118.0 (11)
C15—C11—N12	101.7 (9)	O21—Cl2—O23	107.2 (9)
C15—C11—C10	138.7 (16)	O24—Cl2—O22	111.3 (10)
N12—C11—C10	119.1 (13)	O21—Cl2—O22	110.7 (11)

N13—N12—C11	108.6 (12)	O23—Cl2—O22	102.2 (9)
N13—N12—H92	125.7	O24A—Cl2—O22A	97.7 (19)
C11—N12—H92	125.7	O21A—Cl2—O22A	98 (2)
N12—N13—C14	105.9 (12)	O23A—Cl2—O22A	89.9 (11)
C15—C14—N13	103.4 (11)	N22—Cu1—N32	98.23 (15)
C15—C14—H14	128.3	N22—Cu1—N3	164.03 (18)
N13—C14—H14	128.3	N32—Cu1—N3	82.76 (17)
C11—C15—C14	120.3 (15)	N22—Cu1—N2	82.78 (16)
C11—C15—H15	119.8	N32—Cu1—N2	158.42 (17)
C14—C15—H15	119.8	N3—Cu1—N2	90.51 (17)
C23—C20—N2	108.3 (4)	N22—Cu1—N1	101.20 (17)
C23—C20—H20A	110.0	N32—Cu1—N1	106.91 (16)
N2—C20—H20A	110.0	N3—Cu1—N1	93.69 (17)
C23—C20—H20B	110.0	N2—Cu1—N1	93.92 (17)
N2—C20—H20B	110.0	N81—Cu2—N21	136.45 (15)
H20A—C20—H20B	108.4	N81—Cu2—N31	95.71 (16)
N22—C23—C24	109.1 (4)	N21—Cu2—N31	100.51 (15)
N22—C23—C20	115.9 (4)	N81—Cu2—N71	102.63 (16)
C24—C23—C20	135.0 (4)	N21—Cu2—N71	96.67 (15)
C23—C24—C25	104.1 (4)	N31—Cu2—N71	130.86 (15)
C23—C24—H24	128.0	N82—Cu3—N72	98.22 (15)
C25—C24—H24	128.0	N82—Cu3—N53	82.20 (16)
N21—C25—C24	110.4 (4)	N72—Cu3—N53	162.11 (16)
N21—C25—H25	124.8	N82—Cu3—N52	166.36 (15)
C24—C25—H25	124.8	N72—Cu3—N52	82.00 (17)
N3—C30—C33	108.5 (4)	N53—Cu3—N52	93.42 (17)
N3—C30—H30A	110.0	N82—Cu3—N51	102.76 (15)
C33—C30—H30A	110.0	N72—Cu3—N51	103.76 (15)
N3—C30—H30B	110.0	N53—Cu3—N51	93.51 (16)
C33—C30—H30B	110.0	N52—Cu3—N51	90.37 (15)
H30A—C30—H30B	108.4	C10—N1—C1	114.8 (5)
N32—C33—C34	109.6 (4)	C10—N1—Cu1	112.2 (3)
N32—C33—C30	115.8 (4)	C1—N1—Cu1	110.3 (3)
C34—C33—C30	134.6 (4)	C10—N1—H1A	106.3
C33—C34—C35	104.3 (4)	C1—N1—H1A	106.3
C33—C34—H34	127.8	Cu1—N1—H1A	106.3
C35—C34—H34	127.8	C3—N2—C20	115.3 (4)
N31—C35—C34	109.7 (4)	C3—N2—Cu1	113.5 (3)
N31—C35—H35	125.1	C20—N2—Cu1	110.4 (3)
C34—C35—H35	125.1	C3—N2—H2A	105.6

N51—C51—C56	111.9 (4)	C20—N2—H2A	105.6
N51—C51—C52	110.0 (4)	Cu1—N2—H2A	105.6
C56—C51—C52	111.7 (5)	C30—N3—C5	115.6 (4)
N51—C51—H51	107.7	C30—N3—Cu1	110.0 (3)
C56—C51—H51	107.7	C5—N3—Cu1	114.7 (3)
C52—C51—H51	107.7	C30—N3—H3A	105.1
C53—C52—C51	114.7 (4)	C5—N3—H3A	105.1
C53—C52—H52B	108.6	Cu1—N3—H3A	105.1
C51—C52—H52B	108.6	C25—N21—N22	107.0 (4)
C53—C52—H52C	108.6	C25—N21—Cu2	128.3 (3)
C51—C52—H52C	108.6	N22—N21—Cu2	124.5 (3)
H52B—C52—H52C	107.6	C23—N22—N21	109.4 (3)
N52—C53—C52	113.1 (4)	C23—N22—Cu1	115.9 (3)
N52—C53—C54	109.4 (4)	N21—N22—Cu1	131.5 (3)
C52—C53—C54	110.6 (5)	C35—N31—N32	107.4 (4)
N52—C53—H53	107.9	C35—N31—Cu2	130.8 (3)
C52—C53—H53	107.9	N32—N31—Cu2	120.5 (3)
C54—C53—H53	107.9	C33—N32—N31	108.9 (4)
C55—C54—C53	114.5 (4)	C33—N32—Cu1	116.1 (3)
C55—C54—H54A	108.6	N31—N32—Cu1	133.6 (3)
C53—C54—H54A	108.6	C60—N51—C51	114.8 (4)
C55—C54—H54B	108.6	C60—N51—Cu3	113.4 (3)
C53—C54—H54B	108.6	C51—N51—Cu3	109.8 (3)
H54A—C54—H54B	107.6	C60—N51—H51A	106.0
N53—C55—C54	109.0 (4)	C51—N51—H51A	106.0
N53—C55—C56	112.4 (4)	Cu3—N51—H51A	106.0
C54—C55—C56	111.1 (5)	C70—N52—C53	115.2 (4)
N53—C55—H55	108.1	C70—N52—Cu3	110.2 (3)
C54—C55—H55	108.1	C53—N52—Cu3	114.2 (3)
C56—C55—H55	108.1	C70—N52—H52A	105.4
C51—C56—C55	115.3 (4)	C53—N52—H52A	105.4
C51—C56—H56A	108.5	Cu3—N52—H52A	105.4
C55—C56—H56A	108.5	C80—N53—C55	114.2 (4)
C51—C56—H56B	108.5	C80—N53—Cu3	111.4 (3)
C55—C56—H56B	108.5	C55—N53—Cu3	114.2 (3)
H56A—C56—H56B	107.5	C80—N53—H53A	105.3
N51—C60—C61	113.7 (4)	C55—N53—H53A	105.3
N51—C60—H60A	108.8	Cu3—N53—H53A	105.3
C61—C60—H60A	108.8	C75—N71—N72	106.8 (4)
N51—C60—H60B	108.8	C75—N71—Cu2	127.9 (3)

C61—C60—H60B	108.8	N72—N71—Cu2	124.2 (3)
H60A—C60—H60B	107.7	C73—N72—N71	109.7 (4)
N62—C61—C65	110.1 (5)	C73—N72—Cu3	116.9 (3)
N62—C61—C60	121.1 (5)	N71—N72—Cu3	133.4 (3)
C65—C61—C60	128.8 (5)	C85—N81—N82	107.7 (4)
C61—N62—N63	104.2 (6)	C85—N81—Cu2	126.4 (3)
C64—N63—N62	112.6 (5)	N82—N81—Cu2	125.6 (3)
C64—N63—H63	123.7	C83—N82—N81	109.0 (4)
N62—N63—H63	123.7	C83—N82—Cu3	117.3 (3)
N63—C64—C65	107.4 (6)	N81—N82—Cu3	133.7 (3)
N63—C64—H64	126.3	H81—O1W—H82	109.4
C65—C64—H64	126.3	H21—O2W—H22	109.4
C64—C65—C61	105.7 (6)	H31—O3W—H32	109.4
C64—C65—H65	127.1	H41—O4W—H42	109.4

Table S3 Hydrogen-bond geometry (Å, º) for **1.**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O22^{i}	1.00	2.55	3.454 (18)	150
C6—H6*B*···O22*A*^{i}	0.99	2.44	3.34 (3)	151
C20—H20*B*···O3*W*	0.99	2.52	3.261 (7)	131
C30—H30*B*···Cl1^{ii}	0.99	2.96	3.773 (6)	140
C30—H30*B*···O11^{ii}	0.99	2.58	3.441 (9)	146
C54—H54*B*···O11^{iii}	0.99	2.63	3.531 (10)	151
C55—H55···O13^{iv}	1.00	2.45	3.379 (10)	154
N63—H63···O2*W*^{iii}	0.88	2.04	2.904 (9)	165.5
C70—H70*B*···O24*A*^{v}	0.99	2.55	3.47 (3)	155
C80—H80*A*···O12^{iv}	0.99	2.65	3.305 (9)	124
N2—H2*A*···Cl2	1.00	2.93	3.791 (5)	145
N2—H2*A*···O21	1.00	2.22	3.183 (18)	162
N2—H2*A*···O21*A*	1.00	2.15	3.06 (3)	150
N3—H3*A*···O13^{ii}	1.00	2.03	2.987 (12)	159
N52—H52*A*···Cl1^{iii}	1.00	2.67	3.644 (5)	165
N52—H52*A*···O11^{iii}	1.00	2.36	3.312 (8)	158
N52—H52*A*···O14^{iii}	1.00	2.16	3.015 (8)	142
N53—H53*A*···O1*W*^{iii}	1.00	1.92	2.907 (7)	169
N53—H53*A*···O12^{iv}	1.00	2.30	3.072 (9)	133
O1*W*—H81···Cl1^{vi}	0.84	2.45	3.108 (11)	135

O1*W*—H81···O11^{vi}	0.84	2.50	3.298 (12)	159
O2*W*—H21···O12^{iii}	0.84	2.57	3.292 (12)	145
O2*W*—H21···O14^{iii}	0.84	2.48	3.279 (11)	159
O4*W*—H42···N62	0.84	2.41	3.025 (13)	130
C5—H5···O22^{i}	1.00	2.55	3.454 (18)	150
C6—H6*B*···O22*A*^{i}	0.99	2.44	3.34 (3)	151
C20—H20*B*···O3*W*	0.99	2.52	3.261 (7)	131
C30—H30*B*···Cl1^{ii}	0.99	2.96	3.773 (6)	140
C30—H30*B*···O11^{ii}	0.99	2.58	3.441 (9)	146
C54—H54*B*···O11^{iii}	0.99	2.63	3.531 (10)	151
C55—H55···O13^{iv}	1.00	2.45	3.379 (10)	154
N63—H63···O2*W*^{iii}	0.88	2.04	2.904 (9)	165.5
C70—H70*B*···O24*A*^{v}	0.99	2.55	3.47 (3)	155
C80—H80*A*···O12^{iv}	0.99	2.65	3.305 (9)	124
N2—H2*A*···Cl2	1.00	2.93	3.791 (5)	145
N2—H2*A*···O21	1.00	2.22	3.183 (18)	162
N2—H2*A*···O21*A*	1.00	2.15	3.06 (3)	150
N3—H3*A*···O13^{ii}	1.00	2.03	2.987 (12)	159
N52—H52*A*···Cl1^{iii}	1.00	2.67	3.644 (5)	165
N52—H52*A*···O11^{iii}	1.00	2.36	3.312 (8)	158
N52—H52*A*···O14^{iii}	1.00	2.16	3.015 (8)	142
N53—H53*A*···O1*W*^{iii}	1.00	1.92	2.907 (7)	169
N53—H53*A*···O12^{iv}	1.00	2.30	3.072 (9)	133
O1*W*—H81···Cl1^{vi}	0.84	2.45	3.108 (11)	135
O1*W*—H81···O11^{vi}	0.84	2.50	3.298 (12)	159
O2*W*—H21···O12^{iii}	0.84	2.57	3.292 (12)	145
O2*W*—H21···O14^{iii}	0.84	2.48	3.279 (11)	159
O4*W*—H42···N62	0.84	2.41	3.025 (13)	130

Symmetry codes: (i) -*x*+2, -*y*+1, -*z*+1; (ii) -*x*+1, *y*-1/2, -*z*+3/2; (iii) -*x*+1, -*y*+2, -*z*+1; (iv) *x*, *y*, *z*-1; (v) -*x*+2, *y*+1/2, -*z*+1/2; (vi) -*x*+1, -*y*+2, -*z*+2.

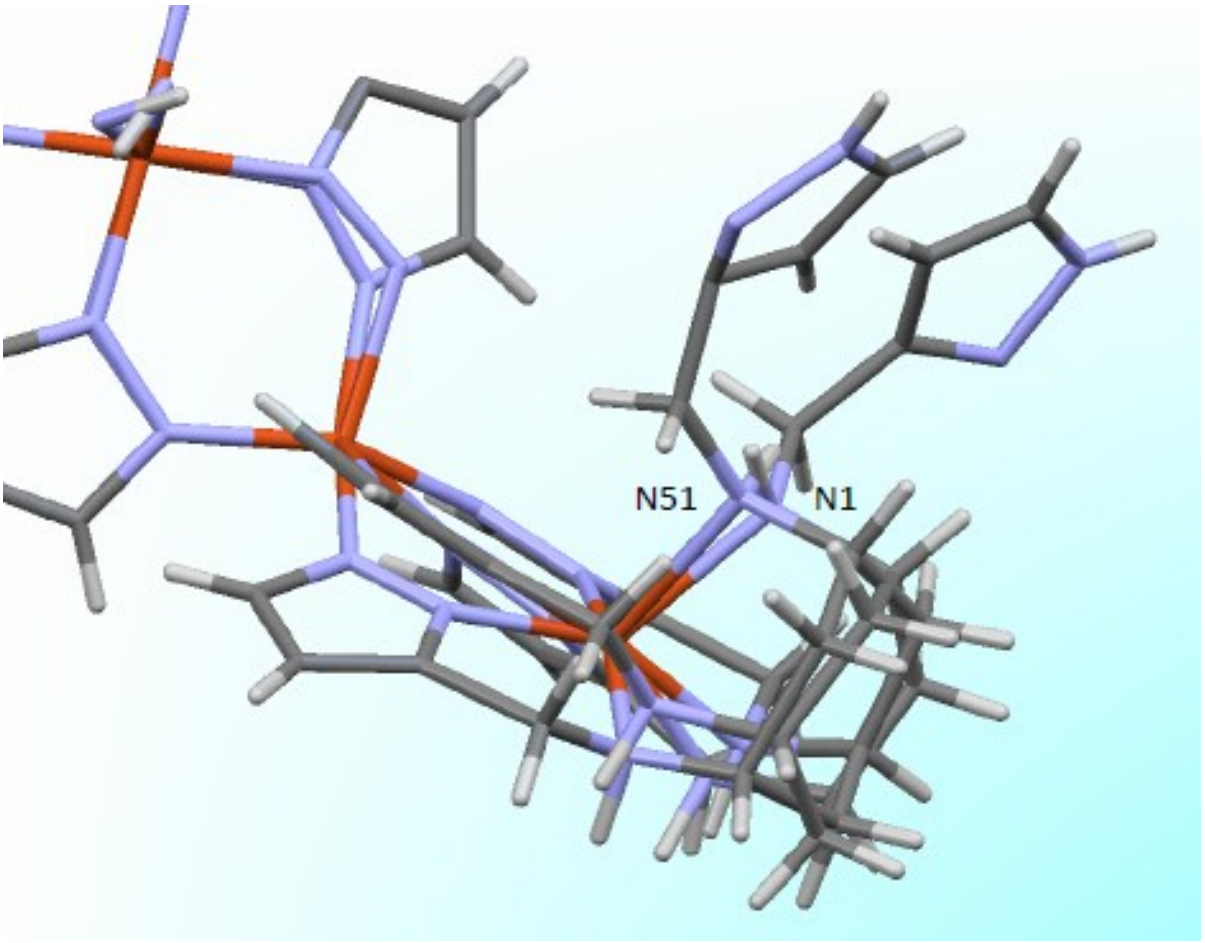

Figure S3. Overlay of Cu1 and Cu3 coordination in **1** showing the opposite configuration of N1 and N52.

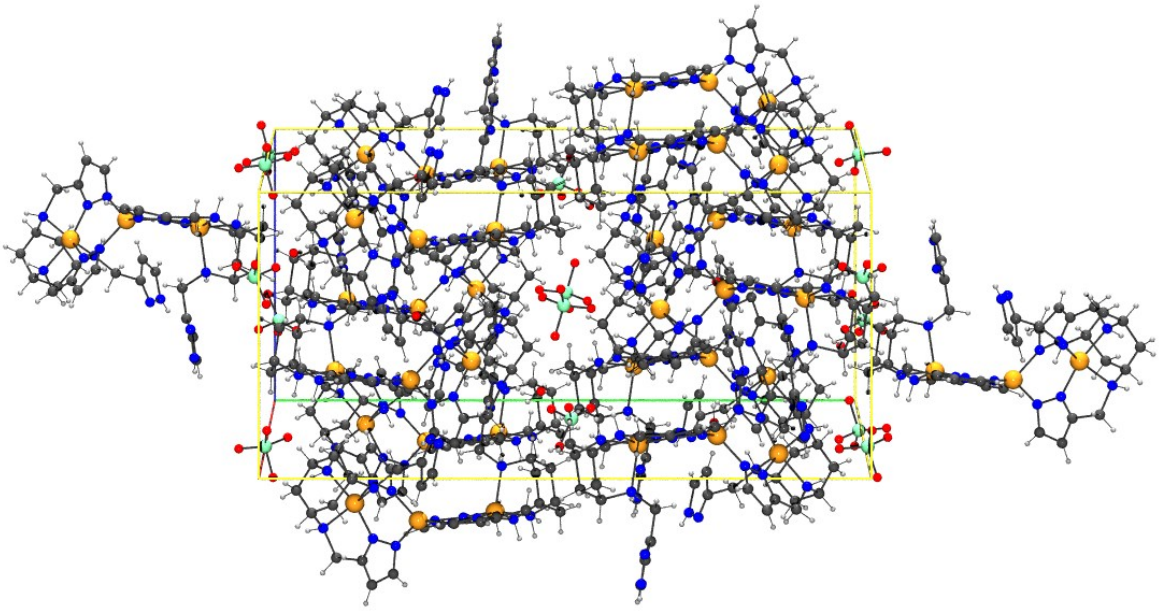

Figure S4. Unit cell packing diagram of **1**, view normal to (100) showing the perchlorate counter ions in the channel

Table S4 XYZ coordinates of the calculated structure shown in Figure 2A

B38HFP86/def2TZVP Ms=1/2 E= -6859.56299058 Hartree <S2> = 1.7513

Cu	-3.842661	-0.178519	-0.198362	C	1.809258	3.410167	1.096530
C	-2.359297	2.769419	-2.512761	C	2.895602	2.582523	0.864307
C	-1.162010	2.236406	-2.063918	N	2.472340	1.442917	0.325988
N	-1.392983	1.230623	-1.216841	N	1.147024	1.485899	0.178932
N	-2.714681	1.103035	-1.099096	C	0.731842	2.666260	0.645693
C	-3.318071	2.008347	-1.864196	C	2.359317	-2.770031	-2.512090
C	-1.809249	-3.409906	1.097333	C	3.318084	-2.008791	-1.863713
C	-0.731837	-2.666138	0.646256	N	2.714687	-1.103283	-1.098851
N	-1.147010	-1.485869	0.179255	N	1.392990	-1.230890	-1.216590
N	-2.472320	-1.442828	0.326338	C	1.162025	-2.236864	-2.063442
C	-2.895587	-2.582305	0.864929	H	1.796840	4.399621	1.515996
H	-2.500372	3.579436	-3.204901	H	-0.311068	2.927911	0.619894
H	-0.155290	2.527307	-2.310324	H	2.500399	-3.580236	-3.204009
H	-1.796836	-4.399254	1.517048	H	0.155308	-2.527806	-2.309810
H	0.311066	-2.927819	0.620476	N	5.077617	1.781117	0.221239
N	-4.555518	0.948739	1.628826	C	6.450306	1.415521	0.629654
H	-4.337853	1.907398	1.389280	H	5.154468	2.241206	-0.679001
N	-5.077597	-1.781065	0.221665	N	4.555465	-0.948334	1.629083
H	-5.154409	-2.241383	-0.678461	N	5.315601	-0.743789	-1.348464
C	-6.450302	-1.415386	0.629948	H	5.375475	-0.134582	-2.156284
N	-5.315587	0.743457	-1.348672	C	6.658122	-0.760753	-0.729308
H	-5.375431	0.134044	-2.156337	C	4.810375	-2.041938	-1.840112
C	-6.658122	0.760556	-0.729551	H	5.156101	-2.826294	-1.168478
C	-4.361727	-2.720337	1.107429	H	5.219107	-2.274762	-2.824248
H	-4.697776	-3.745968	0.947847	C	4.361746	2.720636	1.106742
H	-4.598049	-2.470885	2.140483	H	4.598087	2.471495	2.139865
C	-4.810363	2.041485	-1.840635	H	4.697783	3.746223	0.946853
H	-5.219075	2.274057	-2.824840	H	7.011016	2.337098	0.813358
H	-5.156110	2.826011	-1.169210	C	6.492961	0.584195	1.905383
H	-7.011005	-2.336925	0.813863	H	7.352123	-1.244719	-1.423219
C	-7.138054	-0.671922	-0.511976	C	6.701691	-1.532405	0.583723
C	-6.493001	-0.583749	1.905472	C	7.138076	0.671768	-0.512069
H	-7.352115	1.244342	-1.423595	H	8.203860	0.632374	-0.286659
C	-6.701733	1.532525	0.583291	H	7.057455	1.243690	-1.441391
H	-8.203845	-0.632494	-0.286605	H	7.536564	0.550619	2.221982
H	-7.057395	-1.244067	-1.441156	H	6.317188	-2.546001	0.460929
H	-7.536613	-0.550106	2.222033	H	7.754855	-1.657565	0.838609
C	-6.014783	0.855298	1.761248	C	6.014728	-0.854882	1.761502
H	-5.969042	-1.081373	2.719501	H	6.321414	-1.386654	2.670202
H	-6.317242	2.546096	0.460256	H	5.968985	1.082026	2.719274
H	-7.754905	1.657731	0.838125	C	3.834068	-0.638482	2.859449
C	-3.834132	0.639156	2.859266	H	4.337789	-1.907041	1.389739
H	-3.892000	-0.423005	3.082862	H	2.783432	-0.884917	2.729874
H	-4.224438	1.193437	3.717346	H	3.892014	0.423711	3.082870
H	-2.783512	0.885651	2.729680	H	4.224307	-1.192646	3.717635
H	-6.321486	1.387287	2.669815	Cu	3.842667	0.178486	-0.198422
Cu	0.000008	-0.000057	-0.486429				

Table S5 XYZ coordinates of the calculated structure shown in Figure 2B

B3LYP/def2TZVP Ms=1/2 E= -6859.51849445 Hartree <S2> = 1.7394

Cu	-3.865819	-0.189685	-0.198666	C	1.799125	3.437788	1.095425
C	-2.427192	2.745094	-2.605083	C	2.895422	2.607140	0.881732
C	-1.211540	2.218368	-2.178501	N	2.476717	1.461914	0.323769
N	-1.418845	1.226906	-1.292965	N	1.142975	1.509118	0.151584
N	-2.752203	1.110517	-1.127665	C	0.721080	2.699722	0.618076
C	-3.377425	2.005889	-1.907339	C	2.423776	-2.731875	-2.615069
C	-1.798243	-3.442599	1.083339	C	3.376375	-1.995757	-1.917001
C	-0.718946	-2.701652	0.613425	N	2.752122	-1.104297	-1.131779
N	-1.137385	-1.508179	0.152406	N	1.422099	-1.219277	-1.293021
N	-2.475472	-1.461469	0.322998	C	1.209560	-2.206494	-2.182575
C	-2.893852	-2.610557	0.872498	H	1.781021	4.426272	1.521357
H	-2.585183	3.537870	-3.315932	H	-0.320823	2.966954	0.576029
H	-0.212082	2.502317	-2.464371	H	2.579474	-3.522220	-3.329162
H	-1.781016	-4.433213	1.504284	H	0.208740	-2.487242	-2.466503
H	0.322645	-2.970563	0.572287	N	5.109802	1.811135	0.269647
N	-4.606959	0.976051	1.683534	C	6.494441	1.436961	0.687705
H	-4.405195	1.934494	1.415492	H	5.192967	2.284421	-0.627455
N	-5.108028	-1.812845	0.261557	N	4.602276	-0.983429	1.678842
H	-5.189093	-2.282280	-0.637783	N	5.383159	-0.733650	-1.345705
C	-6.493778	-1.443013	0.679178	H	5.446132	-0.113811	-2.149945
N	-5.382722	0.738708	-1.342290	C	6.731880	-0.741237	-0.702608
H	-5.443162	0.123149	-2.150005	C	4.874780	-2.040132	-1.859906
C	-6.732509	0.740990	-0.701606	H	5.205050	-2.829731	-1.184540
C	-4.360516	-2.747021	1.153843	H	5.304517	-2.265978	-2.838794
H	-4.701041	-3.776121	1.014124	C	4.361951	2.741512	1.164790
H	-4.575410	-2.480639	2.188397	H	4.575933	2.471582	2.198624
C	-4.875746	2.048889	-1.848745	H	4.702363	3.771156	1.028861
H	-5.307131	2.280591	-2.825552	H	7.049792	2.360972	0.883684
H	-5.205755	2.833982	-1.168024	C	6.534979	0.587777	1.965332
H	-7.047919	-2.368819	0.870235	H	7.437554	-1.211040	-1.396737
C	-7.195700	-0.707785	-0.474881	C	6.772714	-1.531902	0.612153
C	-6.537482	-0.599605	1.960560	C	7.196838	0.705840	-0.468654
H	-7.437662	1.212879	-1.394900	H	8.264126	0.676730	-0.241466
C	-6.777002	1.525656	0.616666	H	7.111347	1.286274	-1.393878
H	-8.263361	-0.681270	-0.249128	H	7.577093	0.567447	2.293393
H	-7.107999	-1.283935	-1.402565	H	6.391739	-2.546334	0.474673
H	-7.580059	-0.582416	2.287339	H	7.827100	-1.656800	0.868908
C	-6.079469	0.857863	1.809080	C	6.074809	-0.868266	1.806682
H	-5.996874	-1.088114	2.770766	H	6.394410	-1.405063	2.709785
H	-6.397972	2.541520	0.484513	H	5.994112	1.073499	2.777052
H	-7.832036	1.647165	0.872399	C	3.871166	-0.734557	2.933350
C	-3.876895	0.722673	2.937699	H	4.399360	-1.940411	1.406448
H	-3.924818	-0.330942	3.206321	H	2.822231	-0.988001	2.789169
H	-4.273343	1.308980	3.774060	H	3.919796	0.317889	3.206376
H	-2.828034	0.977546	2.795520	H	4.266275	-1.324663	3.767652
H	-6.401083	1.390061	2.714201	Cu	3.865896	0.191241	-0.199028
Cu	0.003196	0.002554	-0.536409				

Scheme S1 Labelling scheme used for summarizing the computational results

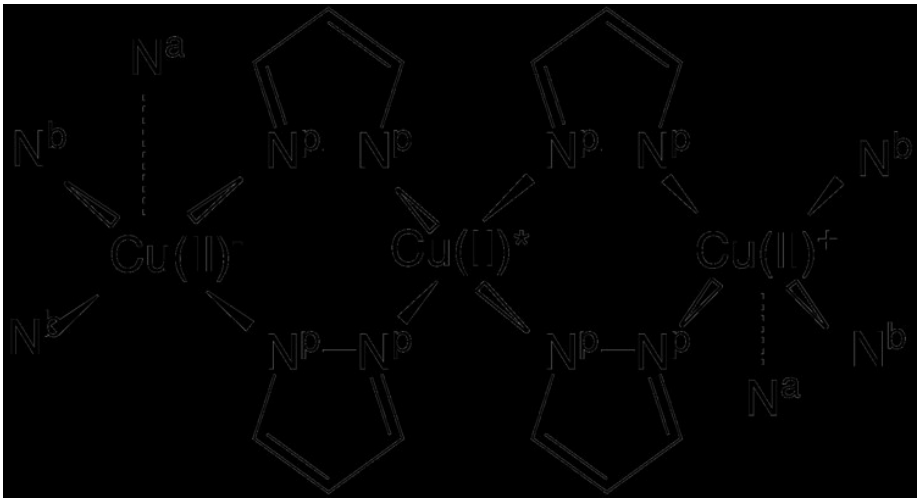

Table S6 Comparison of experimental and calculated Cu-based bond lengths and intramolecular distances for S_t=3/2 state employing various functionals and using def2TZVP basis set

			Cu^c environment				Cu^{p-} environment					Cu^{p+} environment				
	Cu^{p-}…Cu^c	Cu^c…Cu^{p+}	N^{p-}		N^{p+}		N^a	N^b		N^p		N^a	N^b		N^p	
Experimental	3.83	3.77	1.94	2.01	1.93	1.91	2.22	2.02	2.01	1.97	1.93	2.22	2.03	2.06	1.90	1.97
HF	3.89	3.89	2.07	2.08	2.08	2.07	2.31	2.12	2.14	1.98	1.98	2.31	2.12	2.14	1.98	1.98
HFP86	3.83	3.83	2.00	2.00	2.00	2.00	2.19	2.05	2.07	1.93	1.93	2.19	2.05	2.07	1.93	1.93
B75HFP86	3.84	3.84	2.00	2.00	2.00	2.00	2.21	2.06	2.07	1.93	1.93	2.21	2.06	2.07	1.93	1.93
B38HFP86	3.86	3.86	1.99	2.00	2.00	1.99	2.26	2.07	2.08	1.94	1.93	2.26	2.07	2.08	1.93	1.94
B3LYP	3.89	3.89	2.01	2.02	2.02	2.01	2.33	2.09	2.11	1.95	1.95	2.33	2.09	2.11	1.95	1.95
B18HFP86	3.87	3.87	1.99	2.00	2.00	1.99	2.29	2.08	2.10	1.94	1.94	2.29	2.08	2.10	1.94	1.94
BP86	3.88	3.88	2.00	2.01	2.01	2.00	2.31	2.10	2.12	1.95	1.95	2.31	2.10	2.12	1.95	1.95
min	3.83	3.83	1.99	2.00	2.00	1.99	2.19	2.05	2.07	1.93	1.93	2.19	2.05	2.07	1.93	1.93
max	3.89	3.89	2.07	2.08	2.08	2.07	2.33	2.12	2.14	1.98	1.98	2.33	2.12	2.14	1.98	1.98
			Cu^c environment				Cu^{p-} environment					Cu^{p+} environment				
xp. deviations	Cu^{p-}…Cu^c	Cu^c…Cu^{p+}	N^{p-}		N^{p+}		N^a	N^b		N^p		N^a	N^b		N^p	
HF	0.06	0.13	0.12	0.06	0.15	0.16	0.09	0.11	0.13	0.01	0.05	0.09	0.10	0.09	0.07	0.01
HFP86	0.00	0.06	0.05	-0.01	0.07	0.09	-0.03	0.03	0.05	-0.04	0.00	-0.03	0.02	0.01	0.02	-0.04
B75HFP86	0.01	0.07	0.05	-0.01	0.07	0.09	0.00	0.04	0.06	-0.04	0.00	0.00	0.03	0.02	0.02	-0.04
B38HFP86	0.03	0.09	0.05	-0.01	0.07	0.09	0.04	0.05	0.07	-0.04	0.00	0.04	0.04	0.03	0.03	-0.04
B3LYP	0.06	0.12	0.07	0.01	0.10	0.11	0.12	0.08	0.10	-0.02	0.02	0.12	0.07	0.06	0.04	-0.02
B18HFP86	0.04	0.11	0.05	-0.01	0.07	0.09	0.07	0.06	0.08	-0.03	0.01	0.07	0.05	0.04	0.03	-0.03
BP86	0.05	0.11	0.05	-0.01	0.08	0.09	0.09	0.08	0.10	-0.02	0.02	0.09	0.07	0.06	0.04	-0.02

Table S7 Comparison of experimental and calculated Cu-based bond lengths and intramolecular distances for M_s=1/2 broken symmetry state employing various functionals and using def2TZVP basis set

				Cu^c environment				Cu^{p-} environment					Cu^{p+} environment				
		Cu^{p-}…Cu^c	Cu^c…Cu^{p+}	N^{p-}		N^{p+}		N^a	N^b		N^p		N^a	N^b		N^p	
Experimental	coupling	3.83	3.77	1.94	2.01	1.93	1.91	2.22	2.02	2.01	1.97	1.93	2.22	2.03	2.06	1.90	1.97
HF	aab	3.90	3.89	2.08	2.07	2.07	2.08	2.31	2.12	2.14	1.98	1.98	2.31	2.12	2.14	1.98	1.98
	aba	3.89	3.89	2.08	2.07	2.07	2.08	2.31	2.12	2.14	1.98	1.98	2.31	2.12	2.14	1.98	1.98
	baa	3.89	3.90	2.08	2.07	2.07	2.08	2.31	2.12	2.14	1.98	1.98	2.31	2.12	2.14	1.98	1.98
HFP86	aab	3.90	3.89	2.08	2.07	2.07	2.08	2.31	2.12	2.14	1.98	1.98	2.31	2.12	2.14	1.98	1.98
	aba	3.83	3.83	2.00	1.99	1.99	2.00	2.19	2.05	2.07	1.93	1.93	2.19	2.05	2.07	1.93	1.93
	baa	3.83	3.83	2.00	1.99	1.99	2.00	2.19	2.05	2.07	1.93	1.93	2.19	2.05	2.07	1.93	1.93
B75HFP86	aab	3.84	3.84	2.00	2.00	2.00	2.00	2.22	2.06	2.07	1.93	1.93	2.22	2.06	2.07	1.93	1.93
	aba	3.84	3.84	2.00	2.00	2.00	2.00	2.22	2.06	2.07	1.93	1.93	2.22	2.06	2.07	1.93	1.93
	baa	3.84	3.84	2.00	2.00	2.00	2.00	2.22	2.06	2.07	1.93	1.93	2.22	2.06	2.07	1.93	1.93
B38HFP86	aab	3.86	3.86	2.00	1.99	1.99	2.00	2.26	2.07	2.08	1.93	1.94	2.26	2.07	2.08	1.94	1.93
	aba	3.86	3.86	2.00	1.99	1.99	2.00	2.26	2.07	2.08	1.93	1.94	2.26	2.07	2.08	1.94	1.93
	baa	3.86	3.86	2.00	1.99	1.99	2.00	2.26	2.07	2.08	1.93	1.94	2.26	2.07	2.08	1.94	1.93
B3LYP	aab	3.89	3.88	2.02	2.01	2.01	2.02	2.33	2.10	2.11	1.95	1.96	2.33	2.10	2.11	1.95	1.95
	aba	3.88	3.88	2.02	2.01	2.01	2.02	2.33	2.10	2.12	1.95	1.95	2.33	2.10	2.12	1.95	1.95
	baa	3.88	3.89	2.02	2.01	2.01	2.02	2.33	2.10	2.11	1.95	1.95	2.33	2.10	2.11	1.96	1.95
B18HFP86	aab	3.94	3.94	2.03	2.03	2.02	2.03	2.33	2.12	2.13	1.97	1.98	2.33	2.12	2.13	1.98	1.97
	aba	3.94	3.94	2.03	2.02	2.02	2.03	2.33	2.12	2.14	1.97	1.98	2.33	2.12	2.14	1.98	1.97
	baa	3.94	3.94	2.03	2.02	2.03	2.03	2.33	2.12	2.13	1.97	1.98	2.33	2.12	2.13	1.98	1.97
BP86	aab	3.88	3.87	2.01	2.00	2.00	2.01	2.31	2.10	2.12	1.95	1.95	2.31	2.10	2.11	1.95	1.94
	aba	3.87	3.87	2.01	2.00	2.00	2.01	2.31	2.10	2.12	1.94	1.95	2.31	2.10	2.12	1.95	1.94
	baa	3.87	3.88	2.01	2.00	2.00	2.01	2.31	2.10	2.11	1.94	1.95	2.31	2.10	2.12	1.95	1.95
	min	3.83	3.83	2.00	1.99	1.99	2.00	2.19	2.05	2.07	1.93	1.93	2.19	2.05	2.07	1.93	1.93
	max	3.94	3.94	2.08	2.07	2.07	2.08	2.33	2.12	2.14	1.98	1.98	2.33	2.12	2.14	1.98	1.98
				Cu^c environment				Cu^{p-} environment					Cu^{p+} environment				
xp. deviations		Cu^{p-}…Cu^c	Cu^c…Cu^{p+}	N^{p-}		N^{p+}		N^a	N^b		N^p		N^a	N^b		N^p	
HF	aab	0.07	0.13	0.13	0.05	0.14	0.17	0.09	0.10	0.13	0.00	0.05	0.09	0.09	0.09	0.08	0.01
	aba	0.06	0.13	0.13	0.05	0.14	0.17	0.09	0.10	0.13	0.00	0.05	0.09	0.09	0.09	0.08	0.01
	baa	0.06	0.13	0.13	0.05	0.14	0.17	0.09	0.10	0.13	0.00	0.05	0.09	0.09	0.09	0.08	0.01
HFP86	aab	0.07	0.13	0.13	0.05	0.14	0.17	0.09	0.10	0.13	0.00	0.05	0.09	0.09	0.09	0.08	0.01
	aba	0.00	0.06	0.05	-0.02	0.07	0.09	-0.03	0.03	0.05	-0.05	0.00	-0.03	0.02	0.01	0.03	-0.05
	baa	-0.01	0.06	0.05	-0.02	0.07	0.09	-0.03	0.03	0.05	-0.05	0.00	-0.03	0.02	0.01	0.03	-0.05
B75HFP86	aab	0.01	0.07	0.05	-0.02	0.07	0.09	0.00	0.04	0.06	-0.04	0.00	0.00	0.03	0.02	0.03	-0.04
	aba	0.01	0.07	0.05	-0.02	0.07	0.09	0.00	0.04	0.06	-0.05	0.00	0.00	0.03	0.02	0.03	-0.04
	baa	0.01	0.07	0.05	-0.02	0.07	0.09	0.00	0.04	0.06	-0.05	0.00	0.00	0.03	0.02	0.03	-0.04
B38HFP86	aab	0.03	0.09	0.05	-0.02	0.07	0.09	0.04	0.05	0.07	-0.04	0.01	0.04	0.04	0.03	0.03	-0.04
	aba	0.03	0.09	0.05	-0.02	0.07	0.09	0.04	0.05	0.07	-0.04	0.01	0.04	0.04	0.03	0.03	-0.04
	baa	0.03	0.09	0.05	-0.02	0.07	0.09	0.04	0.05	0.07	-0.04	0.01	0.04	0.04	0.03	0.03	-0.04
B3LYP	aab	0.06	0.12	0.08	0.00	0.09	0.11	0.12	0.08	0.10	-0.03	0.03	0.12	0.07	0.06	0.05	-0.03
	aba	0.05	0.12	0.08	0.00	0.09	0.11	0.12	0.08	0.10	-0.03	0.02	0.12	0.07	0.06	0.05	-0.03
	baa	0.05	0.12	0.08	0.00	0.09	0.12	0.12	0.08	0.10	-0.03	0.02	0.12	0.07	0.06	0.05	-0.02
B18HFP86	aab	0.11	0.17	0.09	0.01	0.10	0.12	0.11	0.10	0.12	0.00	0.05	0.11	0.09	0.08	0.07	0.00
	aba	0.11	0.17	0.09	0.01	0.10	0.13	0.11	0.10	0.12	0.00	0.05	0.11	0.09	0.08	0.07	0.00
	baa	0.11	0.18	0.09	0.01	0.10	0.13	0.11	0.10	0.12	0.00	0.05	0.11	0.09	0.08	0.07	0.00
BP86	aab	0.05	0.10	0.07	-0.01	0.07	0.10	0.09	0.08	0.11	-0.03	0.02	0.09	0.07	0.06	0.04	-0.03
	aba	0.04	0.10	0.07	-0.01	0.08	0.11	0.09	0.08	0.10	-0.03	0.02	0.09	0.07	0.06	0.04	-0.03
	baa	0.04	0.11	0.06	-0.02	0.08	0.11	0.09	0.08	0.10	-0.04	0.02	0.09	0.07	0.06	0.05	-0.03

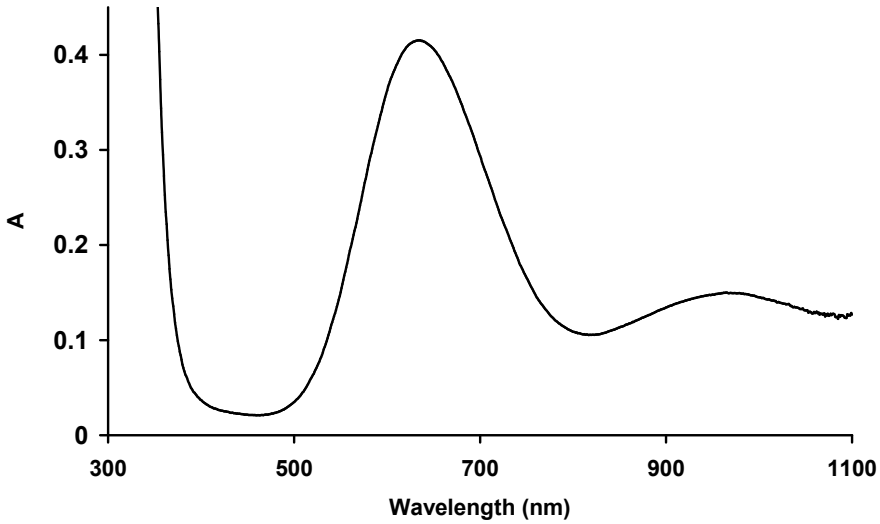

Figure S5. The UV-VIS/near IR spectrum of Cu**L** ([Cu] = [**L**] = 3.7 mM) at pH 5

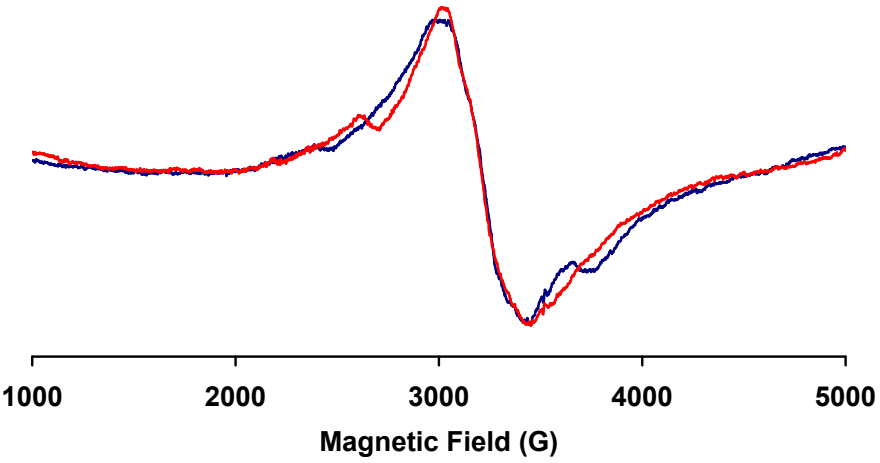

Figure S6. Single-crystal EPR spectra of $[Cu_3H_{-4}\mathbf{L}_2](ClO_4)_2\times 5H_2O$ (**1**) (the needles crystal was positioned parallel (red) and perpendicular (blue) to the applied magnetic field).

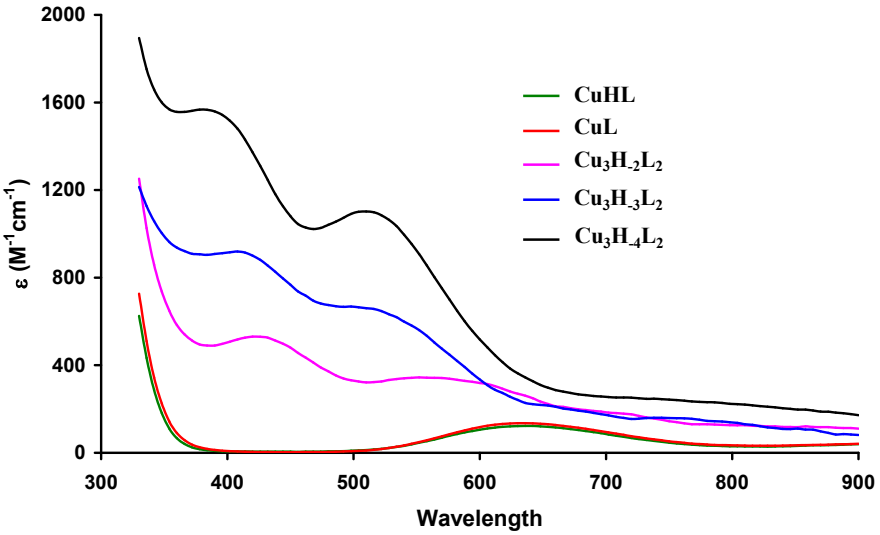

Figure S7. The individual spectra of the complexes formed in the copper(II)-tachpyz (L) system

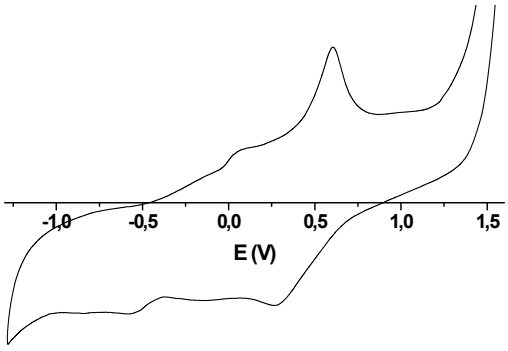

Figure S8. Cyclic voltammogram of the copper(II)-tachpyz 3:2 system in 50 w% ethanol-water at pH 5.3 (T = 298 K, I = 0.1 M NaCl, $[Cu^{2+}]$ = 0.002 M, 100 mVs^{-1}).

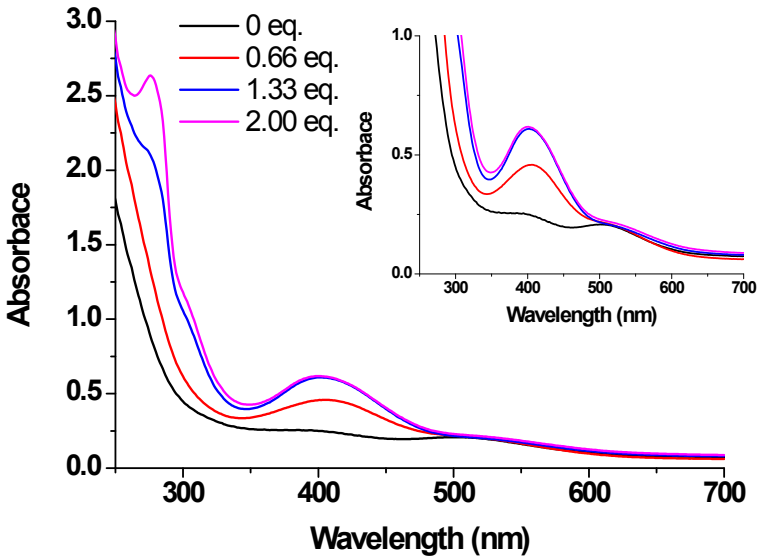

Figure S9. Changes in the UV-Vis spectrum upon addition of H_2dtbc to the copper(II)-tachpyz 3:2 system in anaerobic conditions (50 w% ethanol-water, pH 5.7, $[Cu^{2+}]/3$ = 0.129 mM, $[H_2dtbc]$ = 0, 0.172, 0.344 and 0.516 mM).

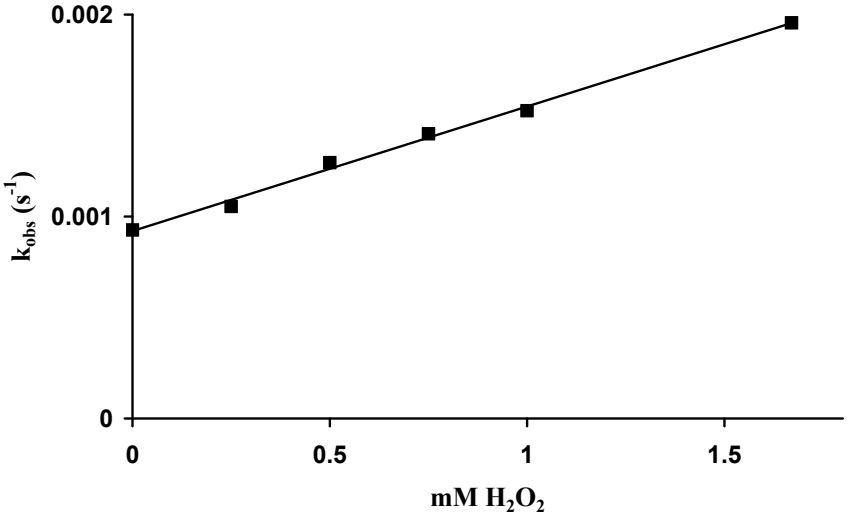

Figure S10. The dependence of the rate constant of H_2dtbc oxidation catalyzed by the Cu(II)/tachpyz 3/2 system on the hydrogen peroxide concentration ($[Cu^{2+}]/3$ = 0.025 mM, pH = 5.7, $[H_2dtbc]_0$ = 1.0 mM).