Supporting Information

Control of structure, stability and catechol oxidase activity of copper(II) complexes by the denticity of tripodal platforms

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Table S1. Geometric parameters (Å, º) for trenpyz×3HCl×2H$_2$O

C2—N1	1.472 (9)	C14—H14	0.93
C2—C3	1.504 (12)	C15—N11	1.343 (15)
C2—H2C	0.97	C15—H11	0.93
C2—H2D	0.97	N1—C2^{i}	1.472 (9)
C3—N4	1.462 (10)	N1—C2^{ii}	1.472 (9)
C3—H3A	0.97	N4—H4A	0.89
C3—H3B	0.97	N4—H4B	0.89
C5—C13	1.463 (12)	N11—N12	1.327 (12)
C5—N4	1.512 (10)	N11—H11A	0.86
C5—H5A	0.97	O1W—H1A	0.86 (2)
C5—H5B	0.97	O1W—H1B	0.86 (2)
C13—N12	1.336 (13)	O2W—H2A	1.0 (2)
C13—C14	1.401 (14)	O2W—H2B	0.96 (17)
C14—C15	1.329 (15)		
N1—C2—C3	114.0 (7)	C15—C14—C13	106.9 (10)
N1—C2—H2C	108.8	C15—C14—H14	126.6
C3—C2—H2C	108.8	C13—C14—H14	126.6
N1—C2—H2D	108.8	C14—C15—N11	105.9 (9)
C3—C2—H2D	108.8	C14—C15—H11	127.1
H2C—C2—H2D	107.7	N11—C15—H11	127
N4—C3—C2	112.2 (6)	C2^{i}—N1—C2^{ii}	109.9 (5)
N4—C3—H3A	109.2	C2^{i}—N1—C2	109.9 (5)
C2—C3—H3A	109.2	C2^{ii}—N1—C2	109.9 (5)
N4—C3—H3B	109.2	C3—N4—C5	113.8 (6)
C2—C3—H3B	109.2	C3—N4—H4A	108.8
H3A—C3—H3B	107.9	C5—N4—H4A	108.8
C13—C5—N4	113.1 (7)	C3—N4—H4B	108.8
C13—C5—H5A	109	C5—N4—H4B	108.8
N4—C5—H5A	109	H4A—N4—H4B	107.7
C13—C5—H5B	108.9	N12—N11—C15	113.3 (9)
N4—C5—H5B	108.9	N12—N11—H11A	123.4
H5A—C5—H5B	107.8	C15—N11—H11A	123.4
N12—C13—C14	109.3 (7)	N11—N12—C13	104.5 (8)
N12—C13—C5	121.6 (9)	H1A—O1W—H1B	136 (6)
C14—C13—C5	129.1 (10)	H2A—O2W—H2B	121 (10)
N1—C2—C3—N4	70.7 (9)	C3—C2—N1—C2^{ii}	79.6 (11)

N4—C5—C13—N12	88.4 (10)	C2—C3—N4—C5	-178.8 (8)
N4—C5—C13—C14	-90.3 (11)	C13—C5—N4—C3	-166.5 (8)
N12—C13—C14—C15	-0.6 (10)	C14—C15—N11—N12	-3.8 (11)
C5—C13—C14—C15	178.3 (8)	C15—N11—N12—C13	3.4 (10)
C13—C14—C15—N11	2.5 (10)	C14—C13—N12—N11	-1.6 (9)
C3—C2—N1—C2^{i}	-159.2 (8)	C5—C13—N12—N11	179.4 (7)

Symmetry codes: (i) *y*, *z*, *x*; (ii) *z*, *x*, *y*.

Hydrogen-bond geometries (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*D*···CL2	0.97	2.91	3.699 (9)	140
C5—H5*A*···CL2_$1^{iii}	0.97	2.84	3.755 (9)	157
N4—H4*A*···CL2	0.89	2.21	3.091 (7)	168
N4—H4*B*···CL1	0.89	2.34	3.216 (7)	170
N11—H11*A*···CL2_$2^{iv}	0.86	2.33	3.173 (9)	168
O1*W*—H1*B*···N12	0.86 (2)	2.34 (13)	2.859 (9)	119 (11)
O1*W*—H1*B*···O2*W*	0.86 (2)	1.84 (8)	2.37 (3)	118 (8)

Symmetry codes: (iii) -*y*+1/2, -*z*+1/2, *x*+1/2; (iv) *x*, -*y*+1, -*z*+1.

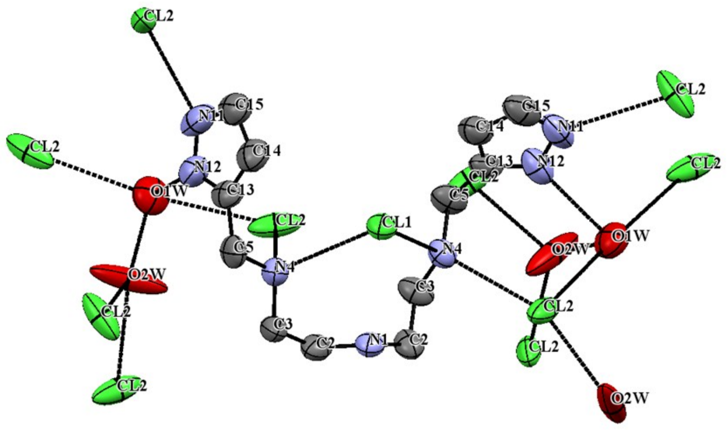

Figure S1. H-bonding network in the immediate surrounding of the ligand in trenpyz×3HCl×2H_2O (H atoms and the third leg of the ligand are omitted for clarity).

Table S2. Selected hydrogen bond distances and angles in the crystal structure **1**

D*—H···*A	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
N2—H2N···N9	1.00	2.07	2.926(4)	143
N4—H4N···N6	0.88	2.07	2.808(5)	140
N5—H5N…O5	1.00	2.08	2.996(5)	151
N7—H7N…O2^{i}	0.88	2.49	3.084(4)	126
N7—H7N—O4^{i}	0.88	2.11	2.945(4)	159
N8— H8N…O2^{ii}	1.00	2.58	3.215(5)	121
N10—H10N…O6^{iii}	0.88	2.25	3.028(6)	148
C2—H2A…O7^{iv}	0.99	2.54	3.096(5)	115
C13—H13A…O3	0.99	2.59	3.232(5)	123
C13—H13B…O1	0.99	2.59	3.338(5)	132
C14—H14B…O2^{ii}	0.99	2.45	3.151(5)	127
C17—H17…O1^{v}	0.95	2.49	3.311(5)	145
C18—H18…O1^{vi}	0.95	2.59	3.295(4)	131

Symmetry codes: ^{i} x,1/2-y,-1/2+z; ^{ii} -x,-1/2+y,1/2-z; ^{iii} 1-x,1/2+y,1/2-z; ^{iv} 1-x,1-y,1-z; ^{v}x,3/2-y,-1/2+z; ^{vi} -x,1-y,-z

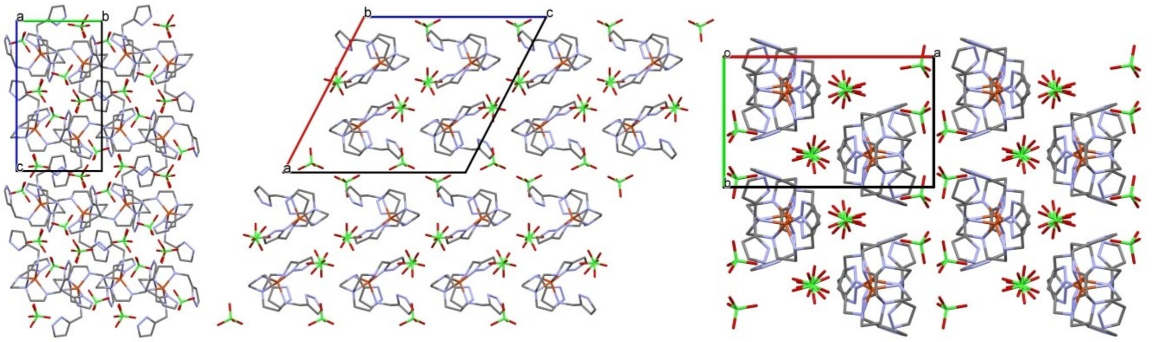

Figure S2. Packing arrangement of **1** viewing from the crystallographic directions a, b and c

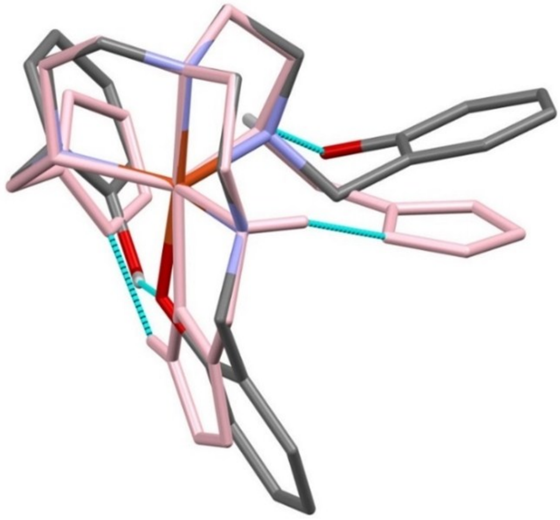

Figure S3. Conformational comparison of the metal complex cation [Cu(trenpyz)]$^{2+}$ in crystal structure **1** (pink), with [Cu(H$_2$L)]$^+$ in OREGAU [OREGAU] (coloured by element). Selected bond lengths (Å) and angles (°) for OREGAU: Cu1-N2 2.028(2), Cu1-N1 2.042(3), Cu1-N3 2.058(2), Cu1-N4 2.205(2), N2-Cu1-N1 85.62(9), N2-Cu1-N4 84.52(9), N2-Cu1-N3 85.60(9), N1-Cu1-N3 134.9(1), N3-Cu1-N4 116.15(9), N1-Cu1-N4 106.9(1), O1-Cu1-N2 175.13(8).

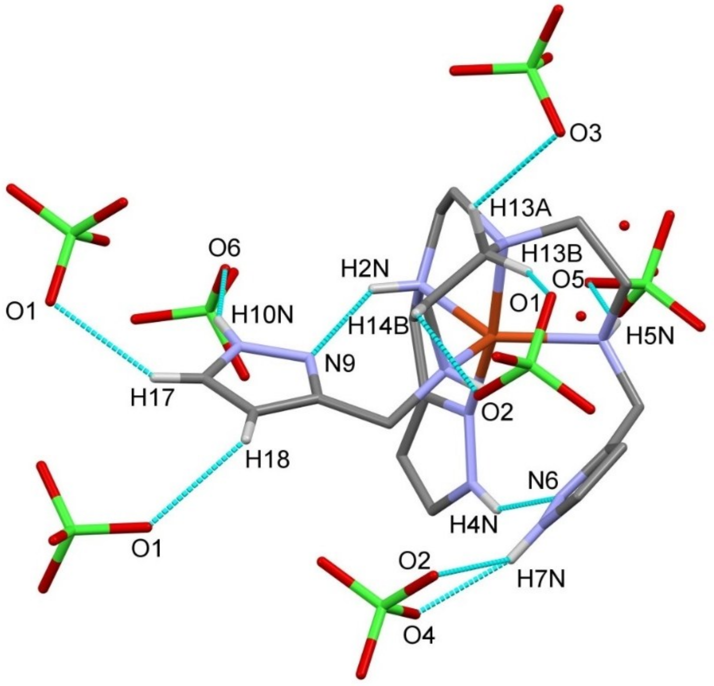

Figure S4. Hydrogen bond connections between the [Cu(trenpyz)]$^{2+}$ complex cation and perchlorate

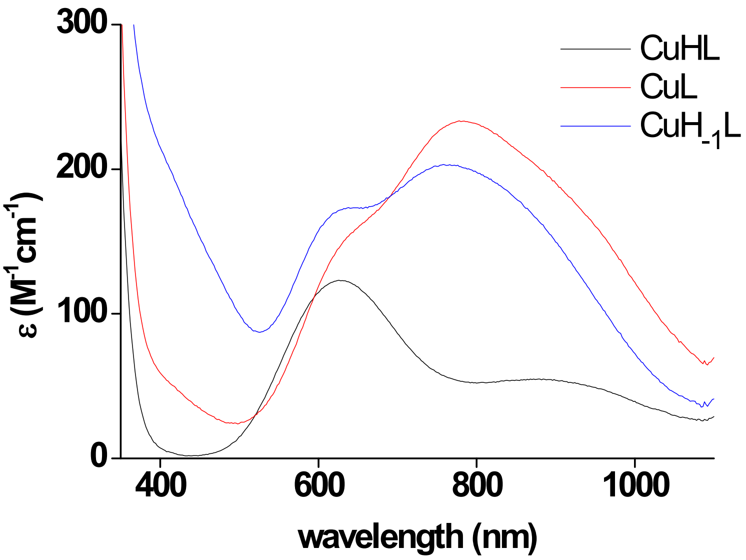

Figure S5 Individual molar Vis/NIR spectra of the mononuclear copper(II)-trenpyz complexes

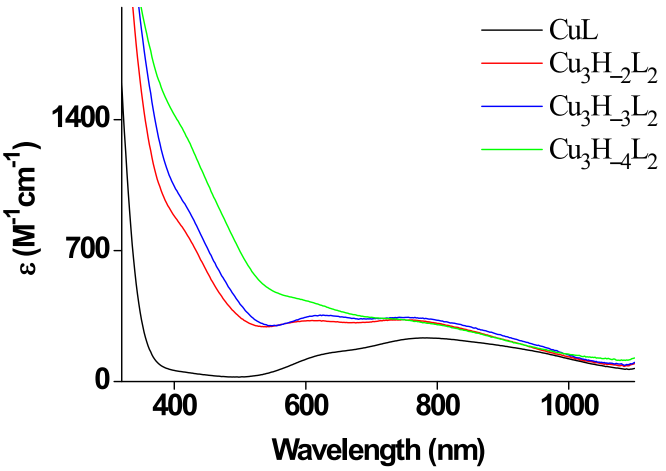

Figure S6 Individual molar Vis/NIR spectra of the trinuclear copper(II)-trenpyz complexes

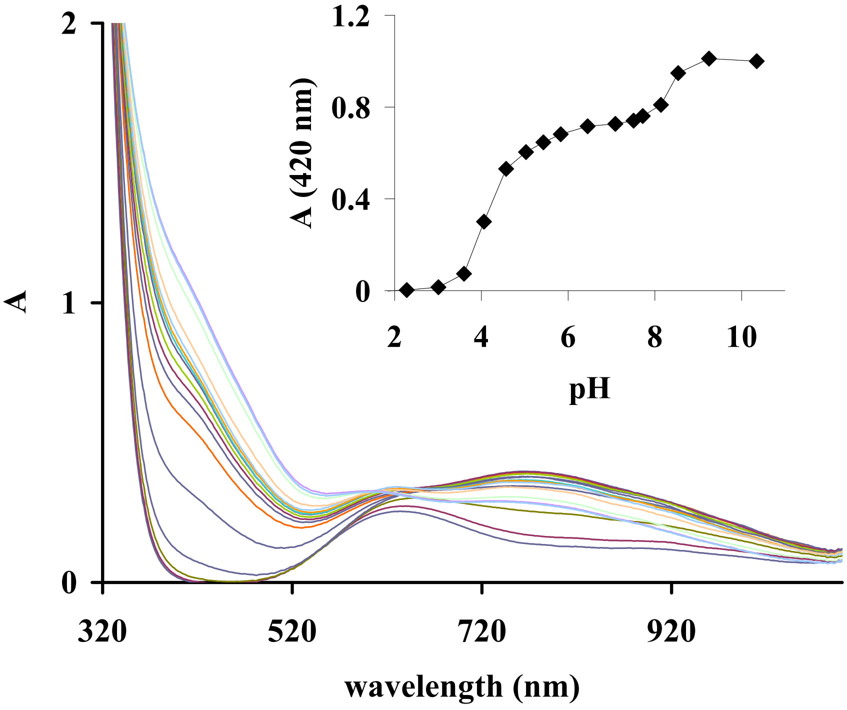

Figure S7 Effect of pH on the Vis/NIR spectra of the copper(II)-trenpyz 3:2 systems in 50% EtOH-H_2O, insert shows the change of absorbances at 420 nm (T = 298 K, *I* = 0.1 M NaCl, $[Cu^{2+}]_{tot}$ = 2.881 mM, [trenpyz] = 1.938 mM, pH = 2.0–11.3)

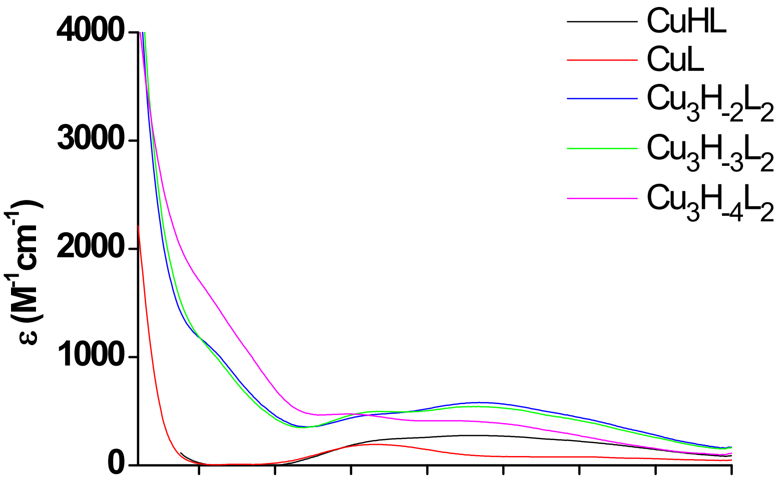

Figure S8 Individual molar Vis/NIR spectra of the trinuclear copper(II)-trenpyz complexes in 50% EtOH-H_2O

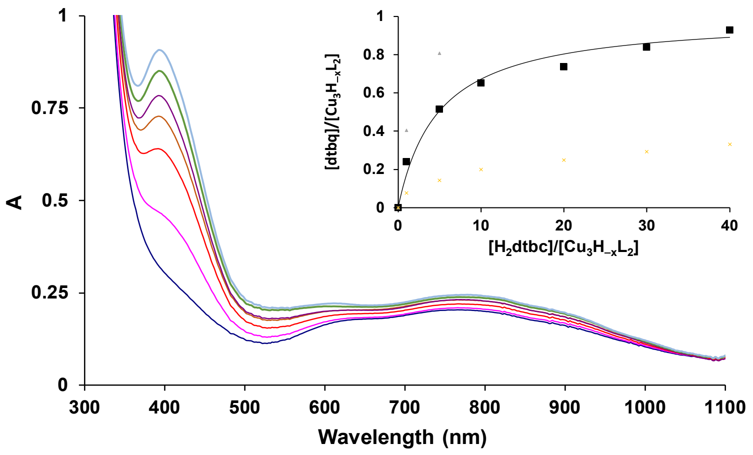

Figure S9. UV-Vis spectra of Cu(II)-**L** 3/2 system as a function of H_2dtbc concentration under anaerobic conditions in 50% EtOH-H_2O at pH = 7.2 ($c_{Cu_3H_{-x}\mathbf{L}_2}$ = 3.358×10^{-4} M). Insert shows the formation of dtbq (measured at 400 nm) as a function of H_2dtbc concentration.

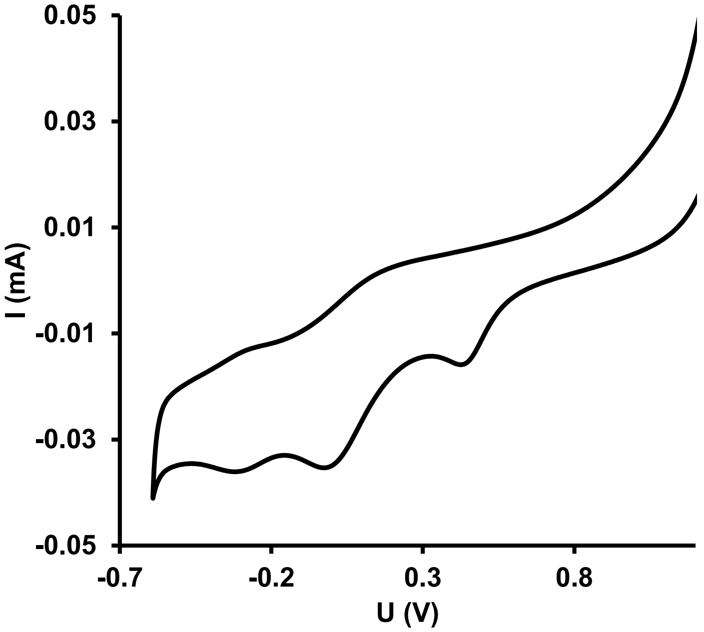

Figure S10. Cyclic voltammogram of the copper(II)-trenpyz 3/2 system in 50 % EtOH-H_2O at pH = 7.2 ([L] = 1.24 mM, [Cu^{2+}] = 1.86 mM)

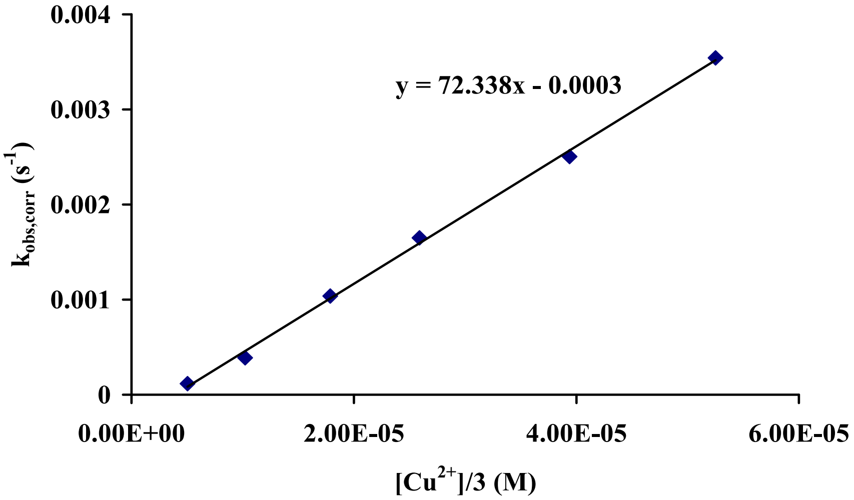

Figure S11. Rate constants of H_2dtbc oxidation promoted by the copper(II)-trenpyz 3/2 system in 50% EtOH-H_2O as a function of the concentration of trinuclear complexes (T = 298 K, [H_2dtbc]$_0$ = 2 mM)

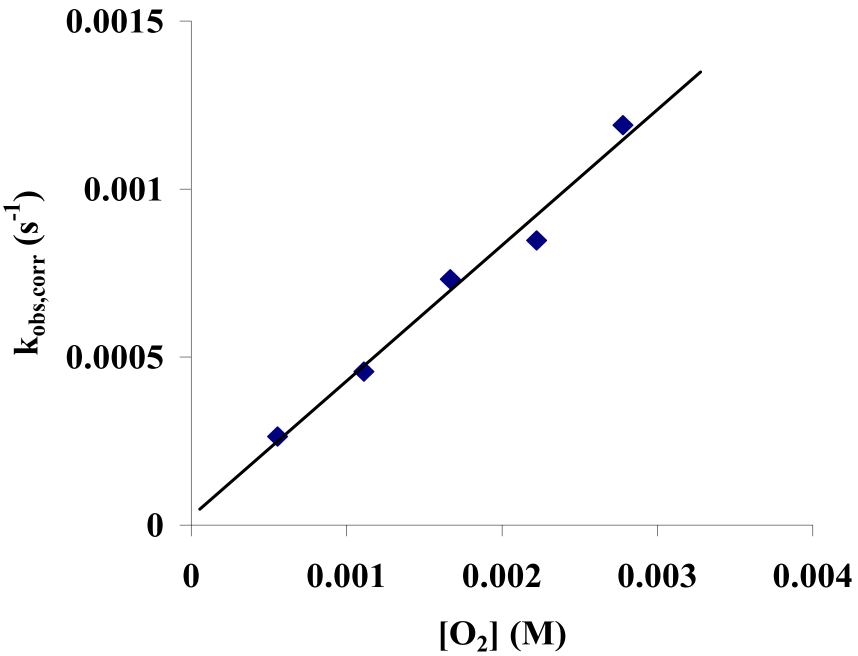

Figure S12. Rate constants of H_2dtbc oxidation promoted by the copper(II)-trenpyz 3/2 system in 50% EtOH-H_2O as a function of the concentration of dissolved dioxygen (T = 298 K, [Cu^{2+}]$_{tot}$ = 75 μM, [**L**] = 50 μM, [H_2dtbc]$_0$ = 2 mM)

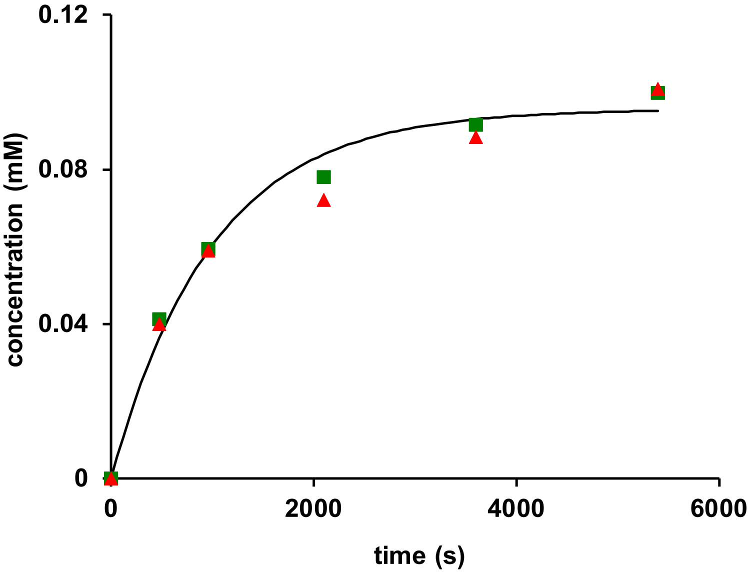

Figure S13. H_2O_2 (green square) and dtbq (red triangle) formation during H_2dtbc oxidation promoted by the copper(II)-trenpyz 3/2 system in aqueous solution at pH = 8.1 (T = 298 K, I = 0.1 M, $[\mathbf{L}]_{tot} = 6.84\times10^{-5}$ M, $[Cu^{2+}]_{tot} = 1.02\times10^{-4}$ M, $c_{H_2dtbc,0}$ = 0.1 mM).

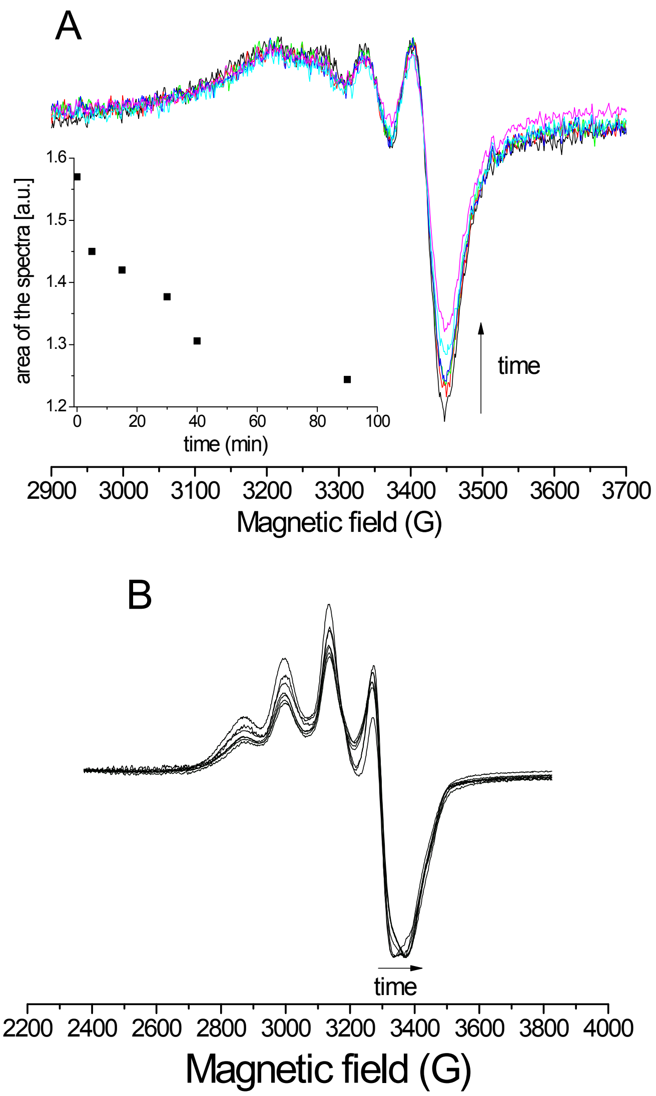

Figure S14. Time dependence of EPR spectra detected at room temperature (A) and at 77 K (B) of the Cu(II)-trenpyz 3/2 system during the oxidation of H_2dtbc under aerobic conditions (pH = 7.2, [Cu(II)] = 1.5 mM, C_{H_2dtbc} = 5 mM). The insert in figure A shows the timed dependence of calculated EPR intensity. Note, that the spectra were recorded in a capillary, therefore the dissolution of oxygen into the solution was rather limited.