Structure, EPR/ENDOR and DFT characterisation of a $[Cu^{II}(en)_2](OTf)_2$ complex.

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Electronic Supplementary Information

Contents

Table S1. X-ray data for $[Cu(en)_2](OTf)_2$ **1**

	1
Empirical formula	$C_6H_{16}CuF_6N_4O_6S_2$
Formula weight	481.89
Crystal size/mm	0.18 × 0.10 × 0.02
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	16.7332(6)
b/Å	10.3150(4)
c/Å	20.3164(14)
α/°	90
β/°	101.664(7)
γ/°	90
V/Å^3	3434.3(3)

Z	8
D_c/Mg m^{-3}	1.864
μ/mm^{-1}	1.609
T/K	100(2)
F(000)	1944
Refl. collected	23245
Refl. indep. (R_{int})	7846 (0.0242)
Data/rest./par.	7846/16/515
Goodness of fit on F^2	1.097
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0251$, $wR_2 = 0.0683$
R indices (all data)	$R_1 = 0.0301$, $wR_2 = 0.0703$
Largest residual peak and hole/e Å^{-3}	0.497 and -0.362

2. Computational data

All calculations were performed using the Gaussian 09 program. The structure of $[Cu(en)_2(OTf)_2]$ **1** was optimised without geometry restraints using the unrestricted B3LYP hybrid functional, employing the 6-31+G(d,p) basis set on all atoms. The geometry optimisation was followed by a frequency calculation to ascertain the nature of the stationary point (minimum *vs.* saddle point). TD-DFT calculations were performed on the optimised geometry.

Cartesian coordinates of $[Cu(en)_2](OTf)_2$ **1**.

Cu	-0.00106	0.0005	-0.00075
H	0.60215	1.61567	1.85931
H	-1.06016	1.55655	1.80837
H	1.37653	1.05136	-1.84765
H	-0.22125	1.48595	-2.0889
S	3.27949	-0.58813	-0.13393
S	-3.28021	0.58815	0.13715
H	1.06163	-1.55383	-1.80728
H	-0.60063	-1.61515	-1.86255
H	0.22527	-1.4851	2.08588
H	-1.37362	-1.05119	1.84936
F	4.74655	1.63167	-0.02573
F	5.29814	0.12629	1.45138
F	5.85612	-0.14266	-0.6382
F	-4.74341	-1.63373	0.01825
F	-5.29676	-0.12269	-1.45232
F	-5.85632	0.13589	0.63814
O	2.3321	0.06072	0.83046
O	3.55364	-2.00834	0.13748
O	2.95992	-0.25663	-1.55368

O	-2.33142	-0.05516	-0.8297
O	-3.55655	2.00897	-0.12861
O	-2.96077	0.25128	1.55556
N	-0.2117	1.63365	1.24504
N	0.52441	1.40115	-1.39957
N	0.21171	-1.6325	-1.24633
N	-0.52253	-1.40035	1.39882
C	-0.22766	2.86715	0.41522
H	0.00907	3.75772	1.00867
H	-1.24196	2.97949	0.02198
C	0.78181	2.69545	-0.71721
H	0.7257	3.5393	-1.4137
H	1.79866	2.65086	-0.31826
C	0.22714	-2.86623	-0.41685
H	1.24154	-2.97953	-0.02406
H	-0.0105	-3.75646	-1.01043
C	-0.78133	-2.69435	0.71648
H	-1.79866	-2.64905	0.31889
H	-0.72486	-3.53842	1.4127
C	4.89898	0.30764	0.18329
C	-4.89796	-0.30902	-0.18489

TD-DFT calculated excited state:

Multiplicity and symmetry: 2.001-A

Energy: 2.3134 eV, 535.95 nm

Oscillator strength: f=0.0000

S^2: 0.751

Principal Orbital contributions:

107B ->122B 38.7%

110B ->122B 50.7%

112B ->122B 1.5%

119B ->122B 3.1%

121B ->122B 3.6%

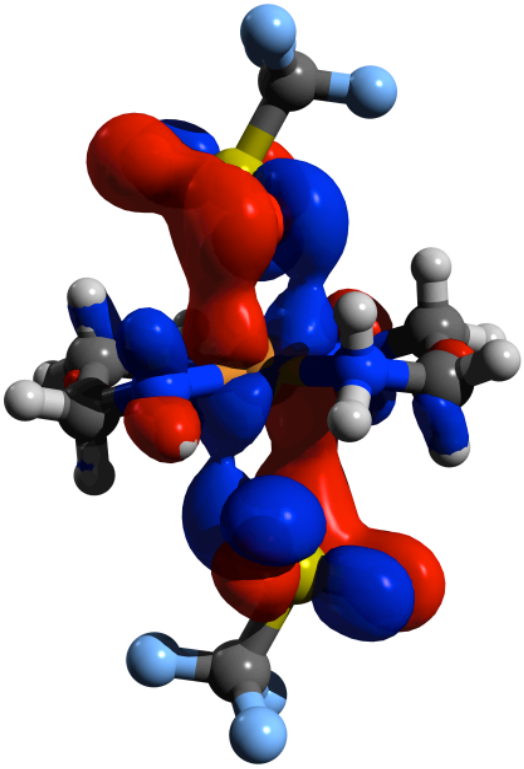

Fig S1a; Molecular orbital 107B of $[Cu(en)_2](OTf)_2$

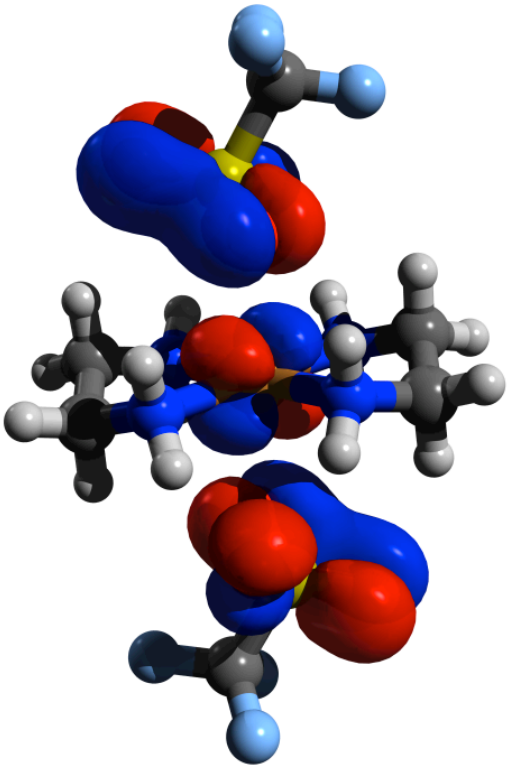

Fig S1b; Molecular orbital 110B of $[Cu(en)_2](OTf)_2$

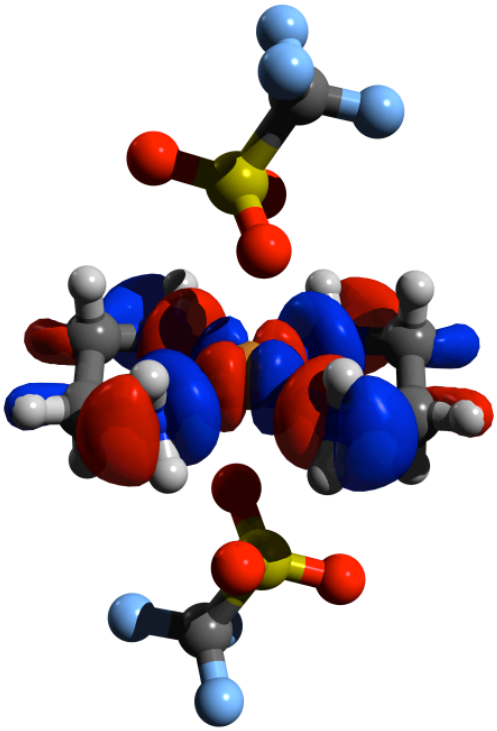

Fig S1c; Molecular orbital 122B of $[Cu(en)_2](OTf)_2$

3. Additional X-band CW and pulsed EPR and ENDOR data.

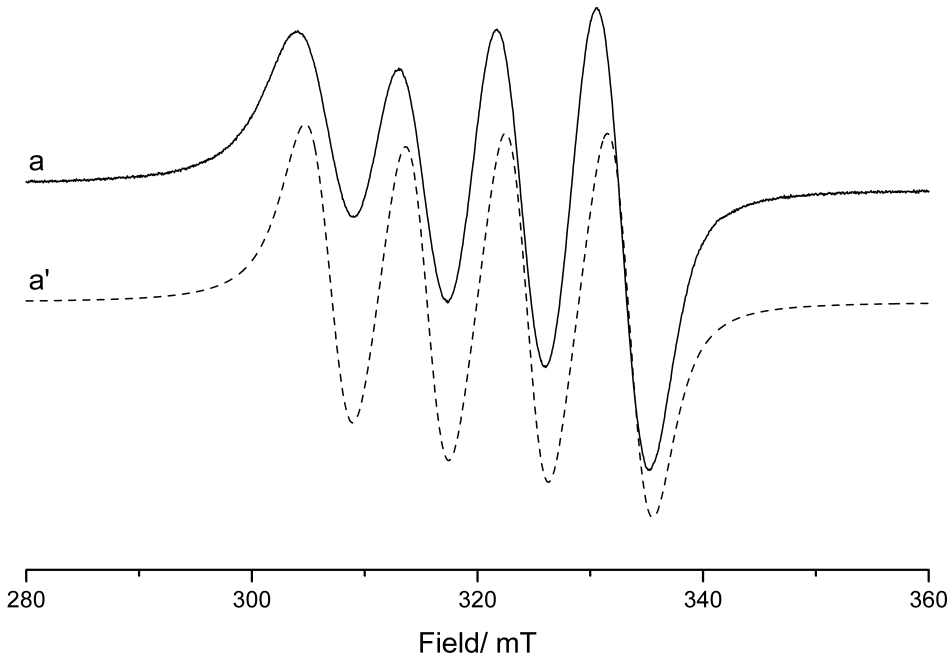

Fig S2; CW EPR spectrum (298 K) of $[Cu(en)_2](OTf)_2$ dissolved in acetonitrile:tetrahydrofuran (1:1). a) experimental and a′) simulation.

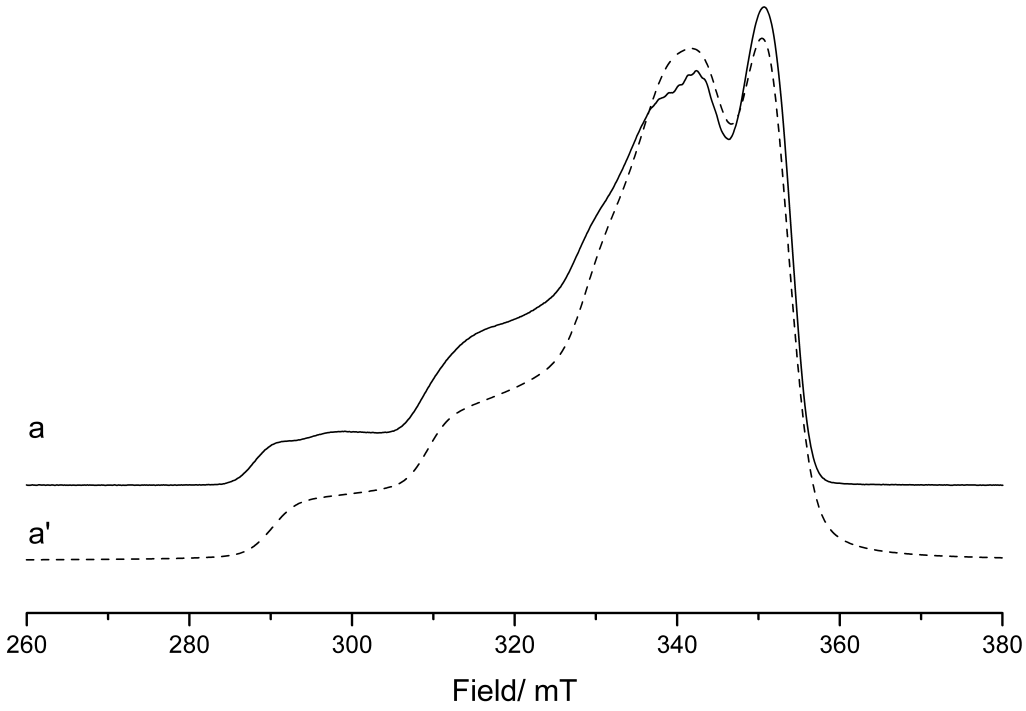

Fig S3; Field Sweep Echo Detected EPR spectrum (10 K) of $[Cu(en)_2](OTf)_2$ a) experimental and a′) simulation.

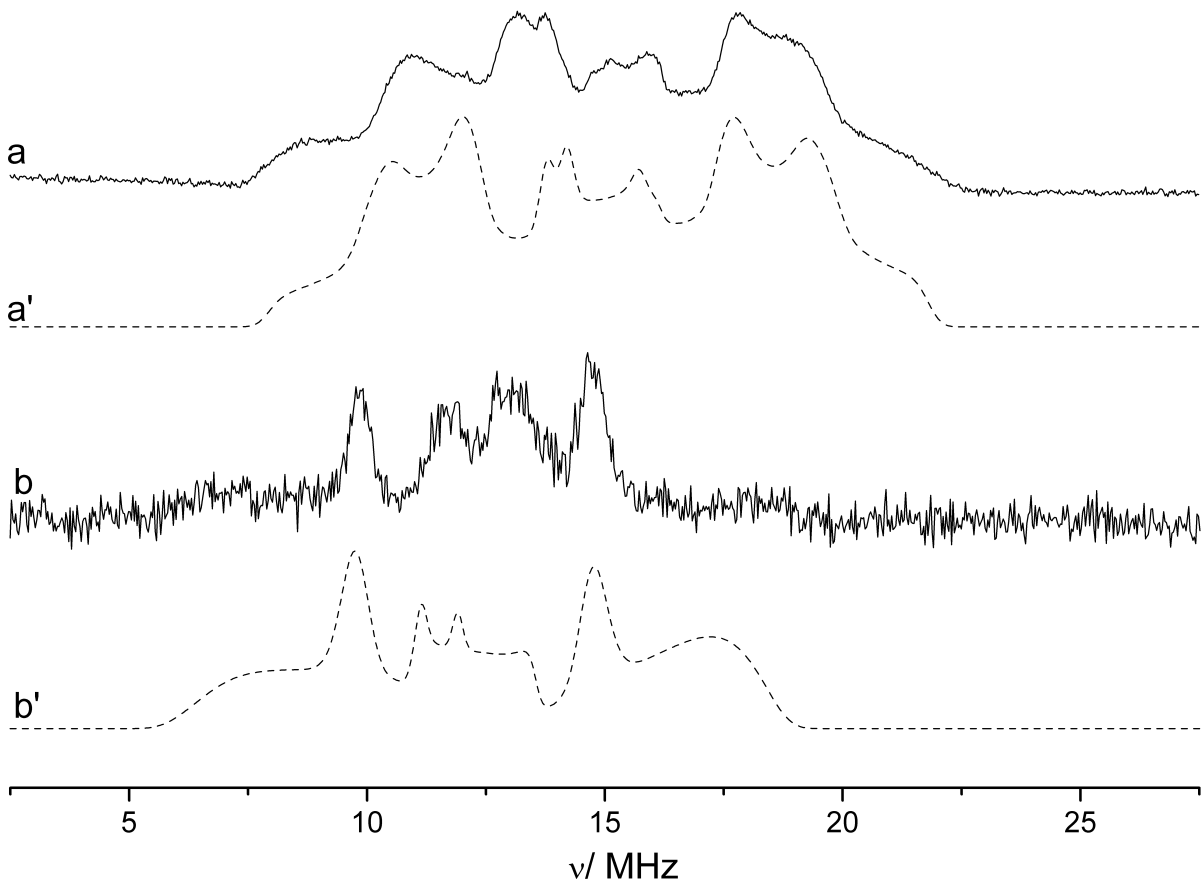

Fig S4 Pulsed Davies ENDOR spectra of $[Cu(en)_2](OTf)_2$ **1** recorded at a) 350 mT and b) 288 mT. Corresponding simulations are shown in a′,b′. The spectra were taken at 10 K, with a repetition rate of 333 kHz. The pulse sequence π-T-π/2-τ-π-τ-echo using mw pulse lengths of t_π = 256 ns, $t_{\pi/2}$ = 128 ns, and an interpulse time τ of 820 ns was used. An rf π pulse of variable frequency and a length of 8 μs was applied during time T of 10 μs.

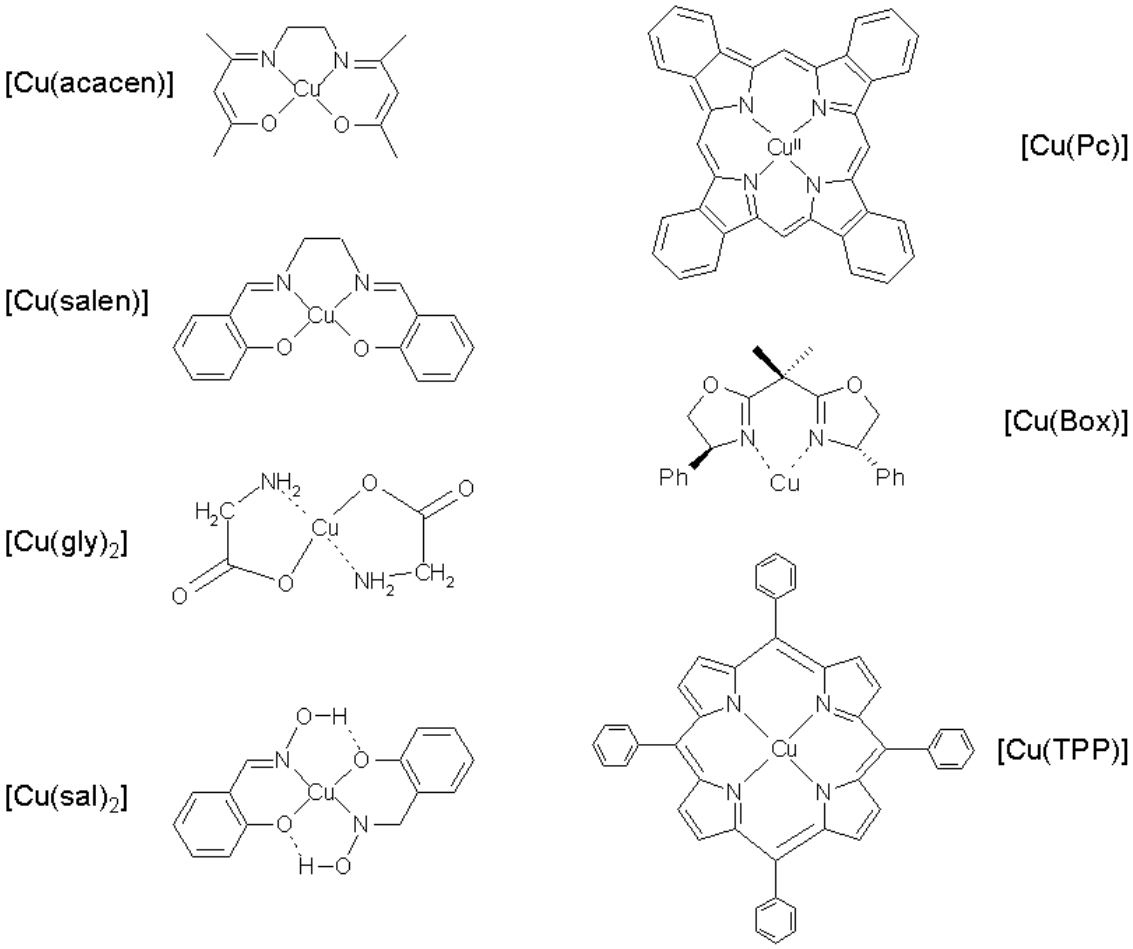

Fig S5; Schematic illustration of the Cu(II) complexes referenced in Table 3 (main text).