Electronic Supplementary Information

Understanding the coordination modes of [Cu(acac)$_2$(Imidazole)$_{n=1,2}$] adducts by EPR, ENDOR, HYSCORE and DFT analysis.

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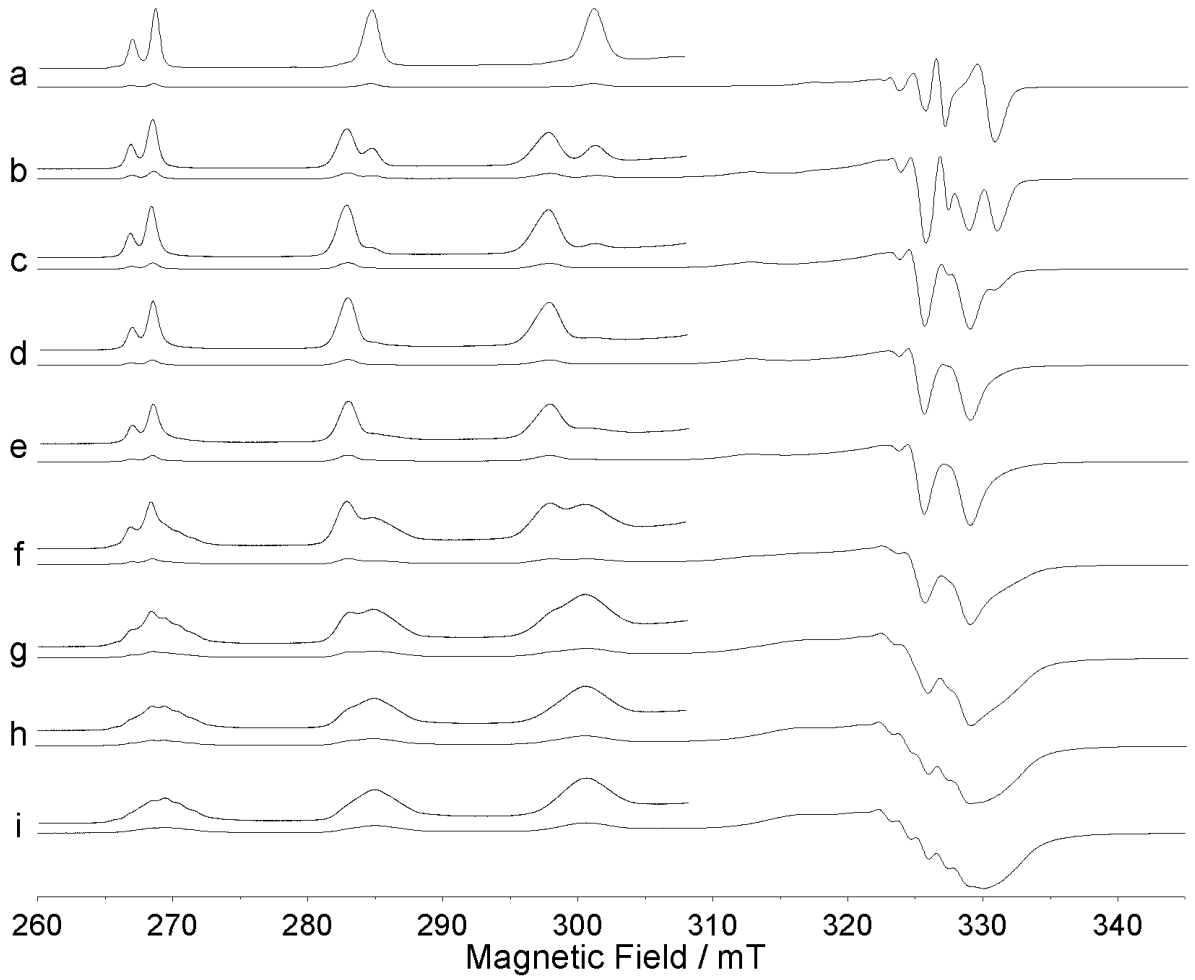

Figure S1: X-band CW EPR spectra (140 K) of [$Cu(acac)_2$] in the presence of increasing ratios of imidazole; a) 1:0, b) 1:1, c) 1:2, d) 1:5, e) 1:10, f) 1:20, g) 1:30, h) 1:40 and i) 1:50.

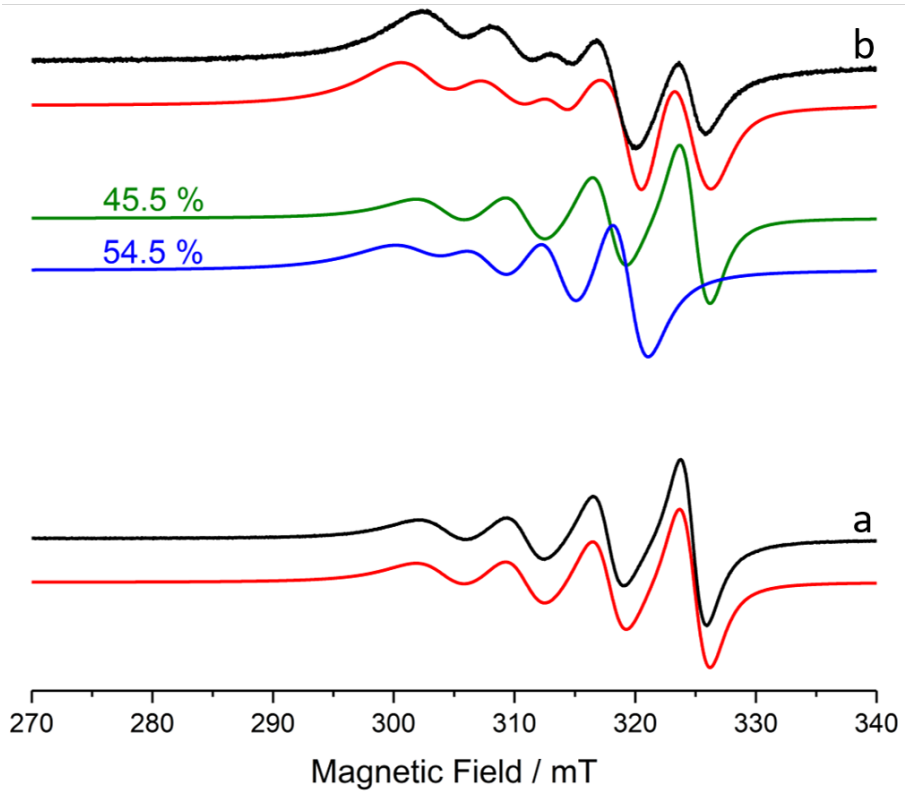

Figure S2: Experimental (black) and simulated (red) X-band CW EPR spectra (298 K) of $[Cu(acac)_2]$ recorded with a Cu:Im ratios of a) 1:0 and b) 1.10. The deconvoluted simulation of b), shown in the green and blue traces, is due to 45.5% $[Cu(acac)_2]$ (green) and 54.5% $[Cu(acac)_2Im]$ (blue). The spectra were recorded in a $CHCl_3$:DMF (1:1) solvent. The simulation parameters are listed in Table 2 (main paper).

Comment on the DFT energies & basis sets used:

Despite the excellent agreement between experimental data and theoretical prediction for the *trans*-equatorial coordination complex, the latter is predicted to lie ca. 23 kJ mol^{-1} higher in energy than the *trans*-axial coordination complex. We ascribe this discrepancy to the fact that functional (PBE0) and especially basis set used (EPRII for the light weight p-block elements and core-property CP for Cu) are designed to predict EPR-related properties (g-tensor and hyperfine coupling) rather than relative energies.

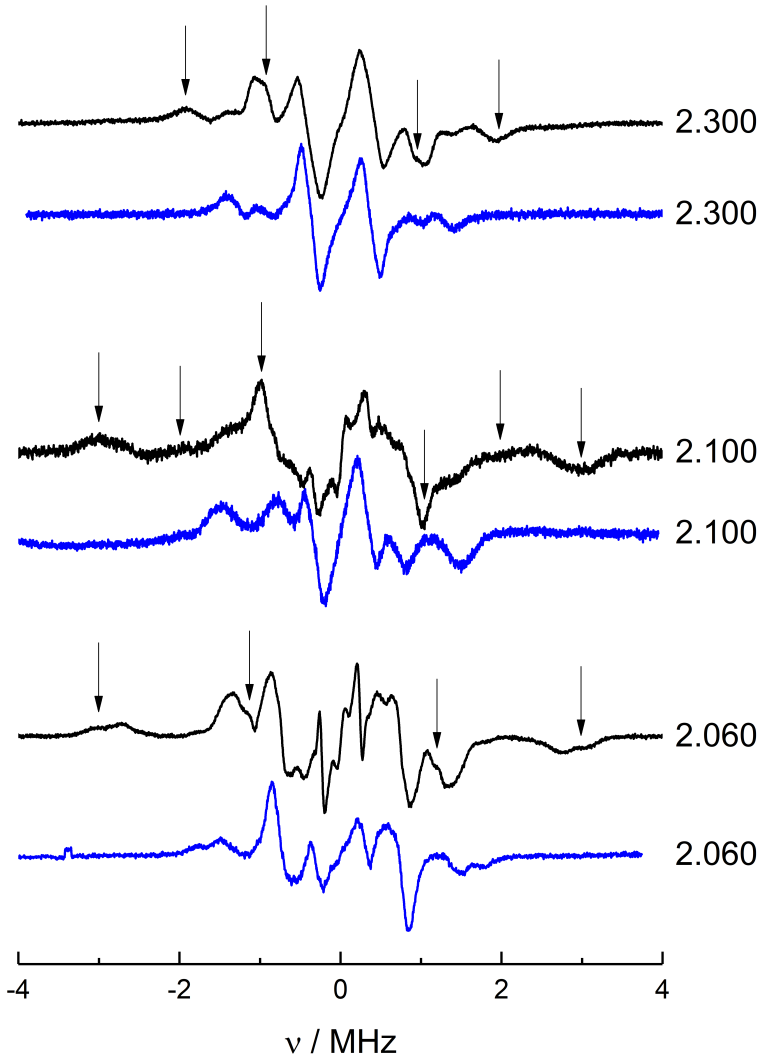

Figure S3: Q-band CW ^{1}H ENDOR spectra (10 K) of protic [Cu(acac)$_2$Im$_2$] (black) and deuterated [Cu(acac)$_2$(Im-*d*$_4$)$_2$] (blue) in CDCl$_3$:DMF-*d7* (1:1) recorded at the field positions corresponding to g = 2.300, 2.100, 2.060, indicated besides each spectrum. The imidazole derived ^{1}H ENDOR resonances are highlighted with the arrows.

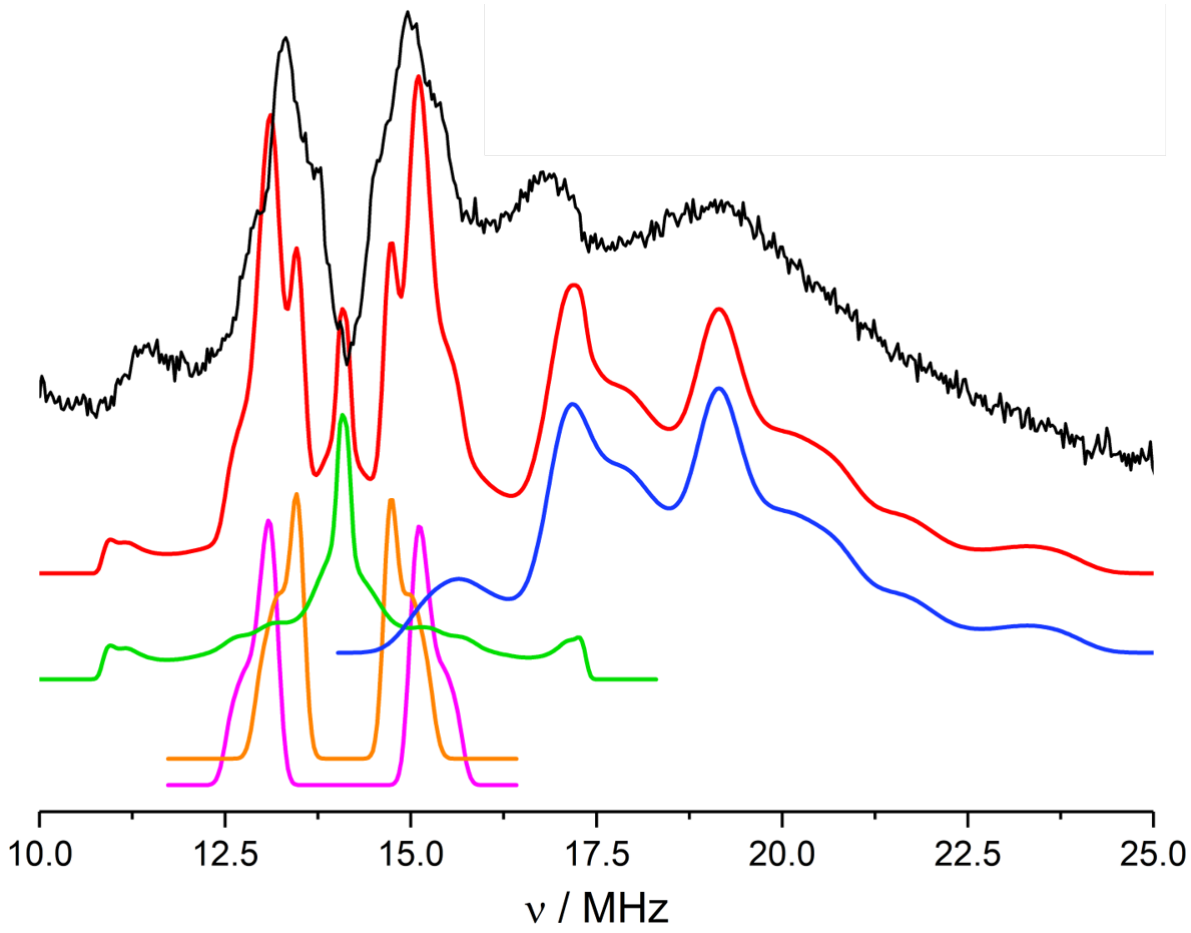

Figure S4: Experimental (black) and simulated (red) X-band Davies ^{1}H and ^{14}N ENDOR spectra (10 K) of the $[Cu(acac)_2Im_2]$ adduct dissolved in dry $CDCl_3$:DMF-d_7 (1:1), recorded at g = 2.111. The deconvoluted simulated contributions are as follow: imino N^3 (blue), $H^{2,4}$ (green), H^5 (orange), H^1 (magenta).

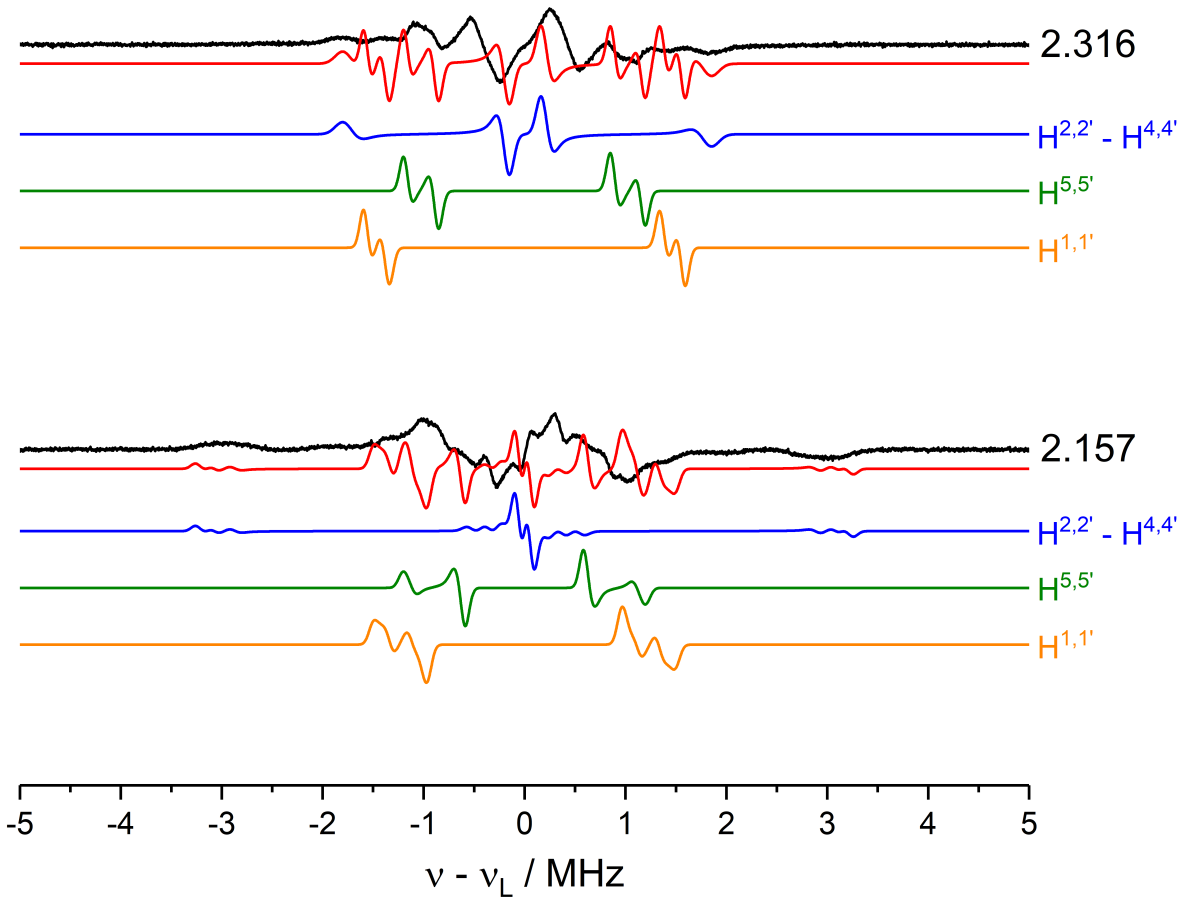

Figure S5: Experimental (black) and simulated (red) X-band ^{1}H ENDOR spectra (10 K) of the [Cu(acac)$_2$Im$_2$] bis-adduct dissolved in dry CDCl$_3$:DMF-d_7 (1:1), recorded at the two field position corresponding to g = 2.316 and 2.157 (see Figure 5, main paper). The deconvoluted simulated contributions are as follow: $H^{2,2'}$ - $H^{4,4'}$ (blue), $H^{5,5'}$ (green), $H^{1,1'}$ (orange).

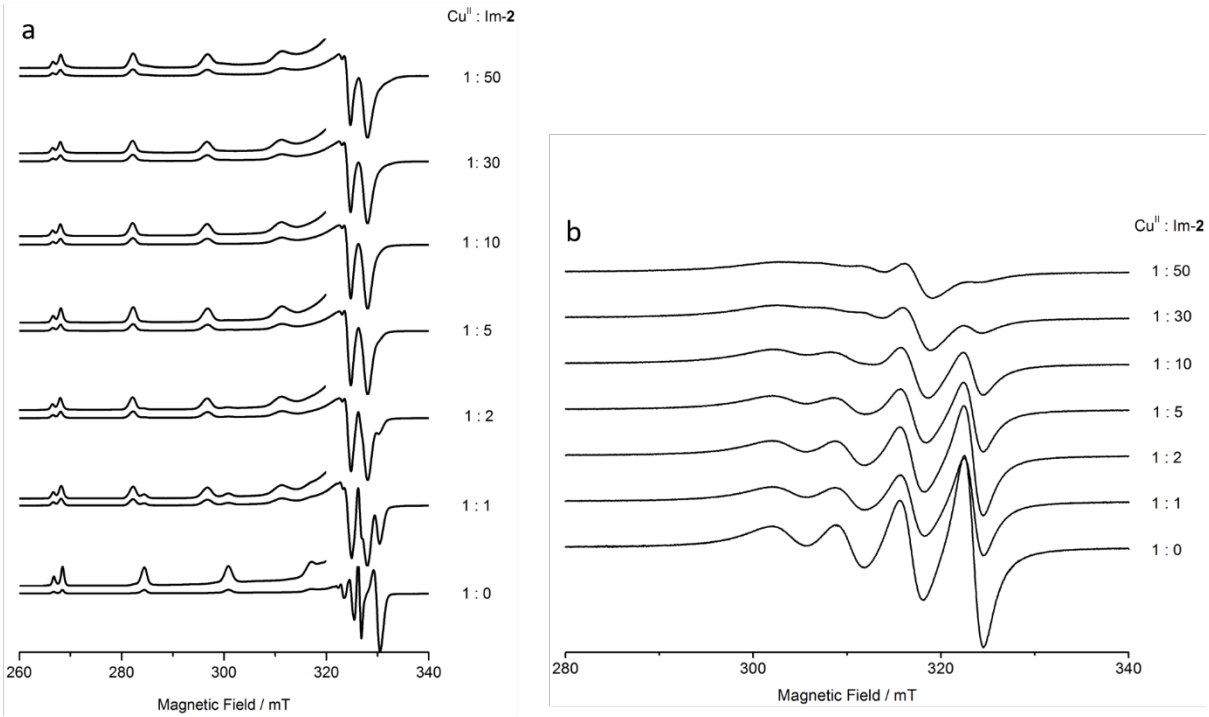

Figure S6: X-band CW EPR recorded a) 140 K and b) 298 K of [Cu(acac)$_2$] in the presence of increasing molar ratios of 2-methyl-imidazole (Im-**2**).

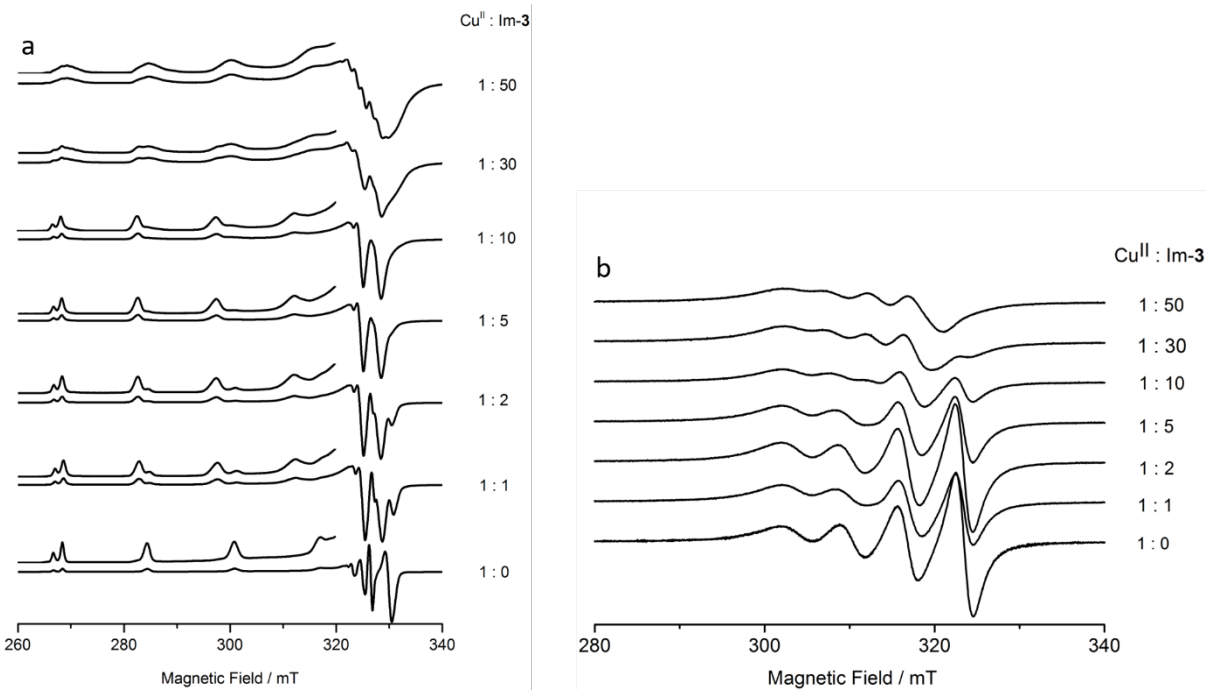

Figure S7: X-band CW EPR recorded at a) 140 K and b) 298 K of [Cu(acac)$_2$] in the presence of increasing molar ratios of 4(5)-methyl-imidazole (Im-**3**).

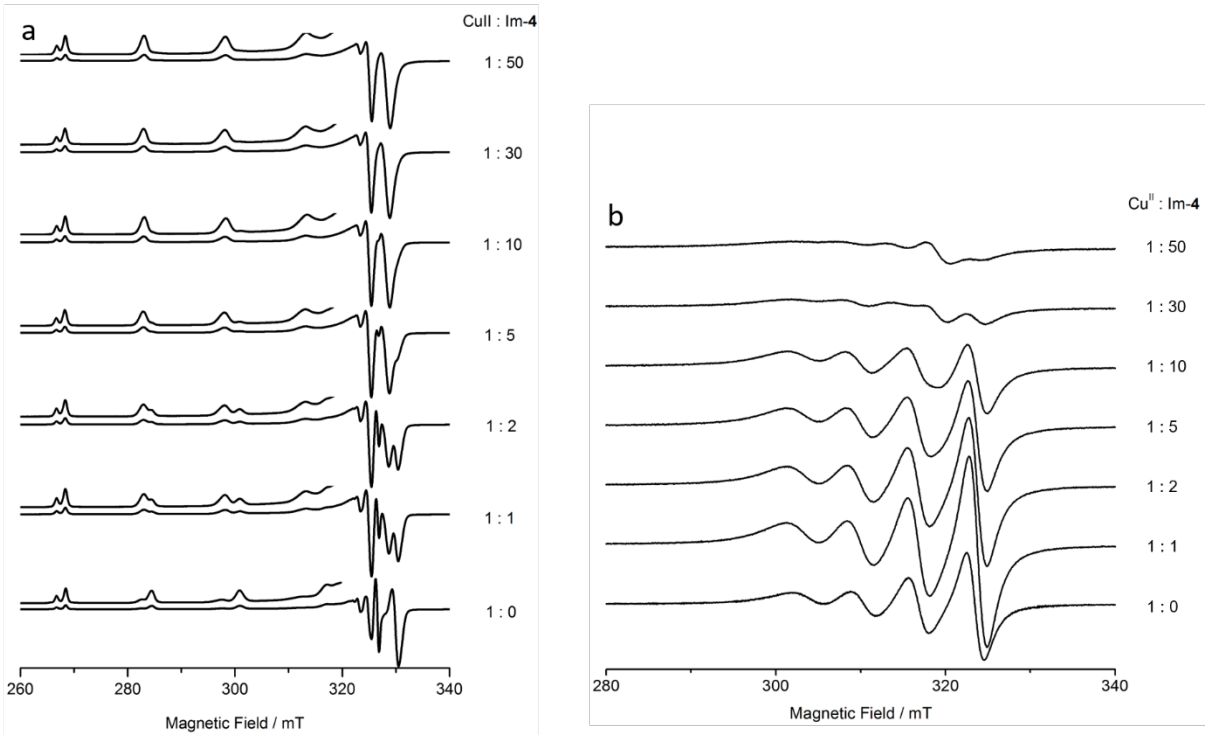

Figure S8: X-band CW EPR recorded at a) 140 K and b) 298 K of [Cu(acac)$_2$] in the presence of increasing molar ratios of benzimidazole (Im-**4**).

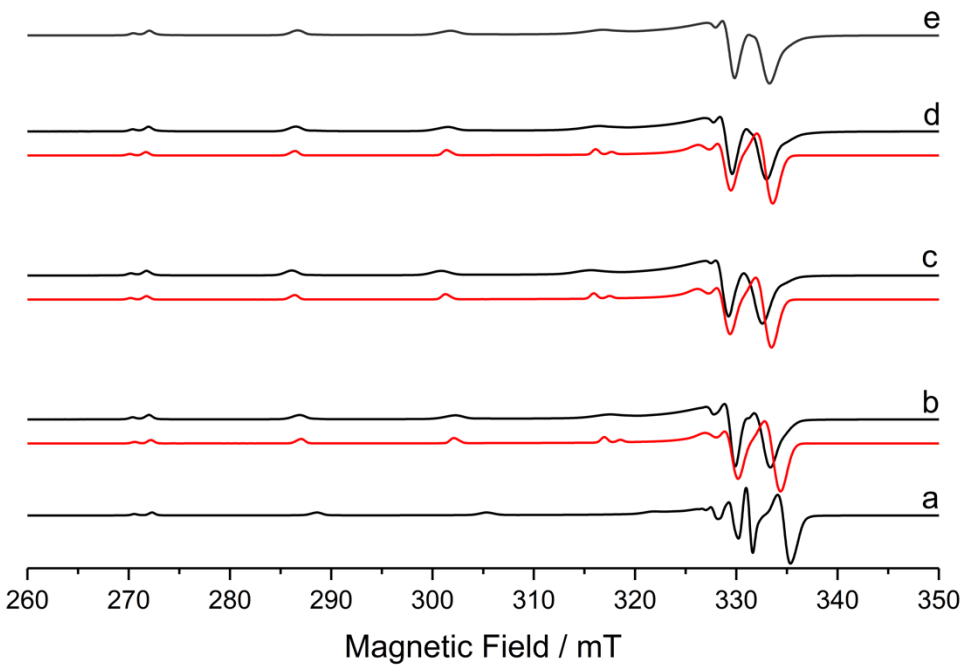

Figure S9: Experimental (black) and simulated (red) X-band CW EPR spectra of a) [Cu(acac)$_2$], b) [Cu(acac)$_2$(Im-**4**)], c) [Cu(acac)$_2$(Im-**2**)], d) [Cu(acac)$_2$(Im-**3**)], and e) [Cu(acac)$_2$Im]. The spectra were recorded at 140 K in a $CHCl_3$:DMF (1:1) solvent with a Cu:Im-**1**,**2**,**3**,**4** ratio of 1:5. The simulated spectra and parameters for a) and e) are shown in Figure 1 and Table 1 (main paper).

Cartesian coordinates of the geometry optimized complexes used for the DFT calculation of g, A and nuclear quadrupole values

$Cu(acac)_2Im$

CARTESIAN COORDINATES (ANGSTROEM)

Cu	-0.036249	0.032810	-0.722325
O	-1.454303	1.392681	-0.508375
O	1.263384	1.399991	-1.288098
O	1.331577	-1.332404	-1.088392
O	-1.460440	-1.335745	-0.646979
C	-1.303791	2.648559	-0.608756
C	1.083245	2.650951	-1.289826
C	-2.543254	3.464890	-0.321116
H	-3.346446	3.131944	-0.984081
H	-2.867052	3.270560	0.706123
H	-2.379752	4.535503	-0.450944
C	2.283859	3.472889	-1.697265
H	3.104330	3.263296	-1.005135
H	2.607373	3.153984	-2.691837
H	2.076391	4.543757	-1.704746
C	-0.116751	3.309872	-0.957178
H	-0.132904	4.390864	-1.007063
C	-1.276170	-2.586592	-0.588435
C	1.176416	-2.583554	-0.970631
C	-0.036295	-3.241053	-0.698875
H	-0.023566	-4.320999	-0.628644
C	-2.528008	-3.411305	-0.395588
H	-3.221068	-3.193045	-1.212806
H	-2.324188	-4.482467	-0.364535
H	-3.014581	-3.103785	0.534439
C	2.428934	-3.405604	-1.169457
H	3.202551	-3.047023	-0.484890
H	2.260305	-4.471263	-1.008796
H	2.795645	-3.244276	-2.187293
N	0.286512	0.013340	1.525871
C	1.316414	-0.384777	2.340236
C	-0.728520	0.289189	2.311717
C	0.912824	-0.343079	3.647590
H	2.273853	-0.671665	1.931822
H	-1.699767	0.622964	1.972409
H	1.418811	-0.571518	4.571626
N	-0.394610	0.088514	3.611019
H	-0.998856	0.228448	4.405757

***Cis*-mixed plane $Cu(acac)_2Im_2$**

CARTESIAN COORDINATES (ANGSTROEM)

Cu	0.024584	0.123722	0.191301
N	0.365892	-0.651101	-2.000113
C	0.662054	-1.944169	-2.351524
C	0.054226	-0.025818	-3.109196
C	0.531774	-2.097144	-3.706144
H	0.937889	-2.664592	-1.595442
H	-0.241003	1.011508	-3.182204
H	0.670804	-2.943052	-4.359961
N	1.905853	1.001511	0.279943
C	2.266345	2.288446	-0.031500
C	2.986798	0.386712	0.701758
C	3.603041	2.451277	0.207183
H	1.530303	2.989721	-0.392897
H	3.022859	-0.643746	1.023570
H	4.260776	3.297821	0.096511
N	0.142667	-0.861883	-4.176923
H	-0.049284	-0.622188	-5.136772
N	4.044711	1.231084	0.672295
H	4.985811	1.003853	0.952630
O	-0.647614	1.832645	-0.577713
O	-1.800598	-0.713314	0.076298
O	-0.319138	0.552065	2.339210
O	0.822027	-1.613076	0.783811
C	-1.843438	2.059773	-0.942757
C	-2.827952	-0.168005	-0.396676
C	-2.907651	1.150471	-0.910539
H	-3.871080	1.491396	-1.268139
C	-4.078614	-1.020419	-0.395724
H	-3.875693	-1.941033	-0.950021
H	-4.306477	-1.304531	0.635479
H	-4.938835	-0.511048	-0.832623
C	-2.094308	3.460625	-1.458037
H	-3.107979	3.594078	-1.838821
H	-1.918578	4.169008	-0.642738
H	-1.372459	3.688512	-2.248466
C	-0.458274	-0.358992	3.179015
C	0.503063	-2.250669	1.844537
C	-0.093010	-1.726264	2.989975
H	-0.289398	-2.411816	3.805322
C	0.838492	-3.727184	1.808003
H	0.648062	-4.228755	2.758256
H	0.237013	-4.200621	1.025012
H	1.890332	-3.852507	1.533186
C	-1.066078	0.032817	4.514855
H	-2.083815	0.394559	4.340498
H	-1.093572	-0.790908	5.230562
H	-0.491901	0.864210	4.932723

***Trans*-axial $Cu(acac)_2Im_2$**

CARTESIAN COORDINATES (ANGSTROEM)

Cu	-0.022628	0.029356	0.009025
O	0.011297	-1.365641	1.434212
O	0.391957	-1.304716	-1.420036
O	0.050631	1.442668	-1.402128
O	-0.521122	1.357976	1.419319
C	0.268762	-2.587806	1.248631
C	0.599604	-2.535130	-1.225420
C	0.256015	-3.444292	2.497299
H	0.475614	-4.493014	2.291864
H	0.991477	-3.048678	3.203778
H	-0.726616	-3.362083	2.970634
C	0.915863	-3.338728	-2.469142
H	0.076544	-3.255414	-3.165825
H	1.790091	-2.900422	-2.959082
H	1.107014	-4.391171	-2.254275
C	0.559279	-3.201075	0.014466
H	0.762087	-4.264512	0.018973
C	-0.657950	2.599600	1.233201
C	-0.167119	2.672522	-1.213170
C	-0.503212	3.281309	0.010864
H	-0.657277	4.352881	0.011852
C	-1.028801	3.397946	2.465245
H	-0.261864	3.243201	3.229278
H	-1.132552	4.464736	2.261535
H	-1.970878	3.012062	2.866503
C	-0.045419	3.543109	-2.445836
H	0.961664	3.433308	-2.859299
H	-0.748440	3.181386	-3.201462
H	-0.240015	4.596601	-2.239912
N	-2.314856	-0.332181	-0.279586
C	-3.092524	-0.746351	-1.330408
C	-3.109295	-0.241254	0.759627
C	-4.387842	-0.905994	-0.914727
H	-2.667353	-0.899588	-2.311239
H	-2.798678	0.057984	1.751421
H	-5.284654	-1.210538	-1.429711
N	-4.381598	-0.579991	0.423749
H	-5.175831	-0.592002	1.043992
N	2.284212	0.365538	0.284724
C	3.176050	0.187858	1.310936
C	2.995588	0.619256	-0.787481
C	4.455351	0.342745	0.847270
H	2.837816	-0.039964	2.310904
H	2.585488	0.797755	-1.772392
H	5.416961	0.282406	1.330997
N	4.322813	0.617125	-0.496311
H	5.073398	0.785732	-1.147363

***Trans*-equatorial Cu(acac)$_2$Im$_2$**

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CARTESIAN COORDINATES (ANGSTROEM)
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  Cu    -0.000744   -0.001280    0.004396
  O     -1.399157    1.531154    0.646834
  O      1.513256    1.303701    0.446305
  O      1.399250   -1.530899   -0.642224
  O     -1.513748   -1.304143   -0.438613
  C     -1.098235    2.735007    0.911312
  C      1.409128    2.529838    0.774146
  C     -2.243665    3.703788    1.175686
  H     -2.166542    4.591700    0.530353
  H     -3.202588    3.202086    0.994672
  H     -2.215193    4.057090    2.217787
  C      2.721141    3.283402    0.929659
  H      3.563343    2.598019    0.777555
  H      2.781000    4.100380    0.194967
  H      2.789737    3.736358    1.929649
  C      0.216920    3.250945    0.995077
  H      0.323875    4.308323    1.247029
  C     -1.411485   -2.527495   -0.777421
  C      1.095182   -2.729579   -0.926001
  C     -0.219837   -3.245417   -1.010688
  H     -0.327069   -4.298859   -1.278320
  C     -2.724196   -3.278332   -0.940023
  H     -3.564571   -2.606285   -0.730642
  H     -2.816045   -3.671080   -1.963430
  H     -2.761843   -4.138140   -0.254737
  C      2.239728   -3.697411   -1.198015
  H      3.197726   -3.165763   -1.137885
  H      2.235447   -4.518597   -0.464555
  H      2.136827   -4.153761   -2.193970
  N      0.052799   -0.701388    1.873148
  C      1.027063   -1.480392    2.462836
  C     -0.880104   -0.492358    2.792692
  C      0.674471   -1.747310    3.762190
  H      1.905713   -1.779131    1.905173
  H     -1.779292    0.092594    2.635869
  H      1.161772   -2.312487    4.546013
  N     -0.540869   -1.111753    3.951612
  H     -1.092180   -1.100936    4.801967
  N     -0.051180    0.699033   -1.866235
  C     -1.044495    1.440628   -2.471708
  C      0.902918    0.523689   -2.770711
  C     -0.682225    1.718942   -3.766024
  H     -1.941618    1.708707   -1.927082
  H      1.820965   -0.027556   -2.602425
  H     -1.178035    2.264582   -4.558336
  N      0.558565    1.128783   -3.935931
  H      1.124217    1.136113   -4.776839
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