Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A combined continuous wave electron paramagnetic resonance and DFT calculations of copper-doped $^{3}_{\infty}[Cd_{0.98}Cu_{0.02}(prz - trz - ia)]$ metal–organic framework

Anastasia Kultaeva,[1] Timur Biktagirov,[2] Jens Bergmann,[3] Linda Hensel,[1] Harald Krautscheid[3] and Andreas Pöppl*[1]

[1] *University Leipzig, Faculty of Physics and Earth Science, Linnestrasse 5, D-04103 Leipzig, Germany*

[2] *University Paderborn, Physics Department, 33098 Paderborn, Germany*

[3] *University Leipzig, Faculty of Chemistry and Mineralogy, Johannisallee 29, D-04103 Leipzig, Germany*

E-mail: poeppl@physik.uni-leipzig.de Phone: +49 (0)341 9732608. Fax: +49 (0)3419732649

Supporting Information

1. DFT calculations for pure $^{3}_{\infty}[Cu(prz-trz-ia)]$ and $^{3}_{\infty}[Cd(prz-trz-ia)]$ MOFs

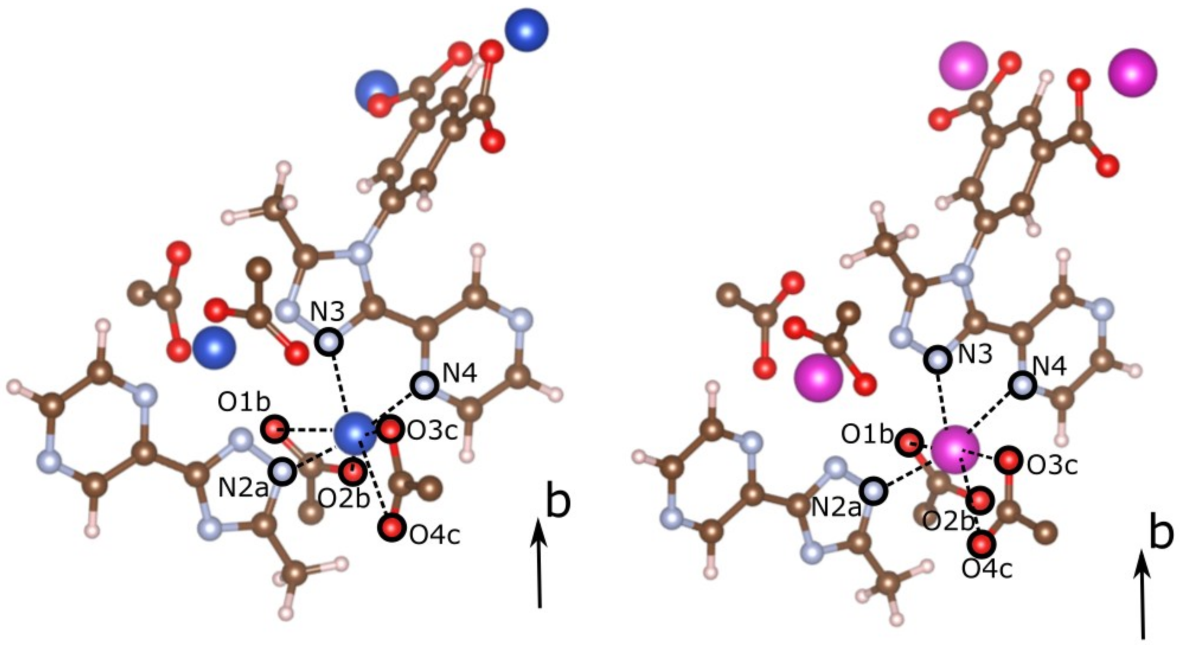


Figure S1. Coordination of the metal ions in $^{3}_{\infty}[Cu(prz-trz-ia)]$ (*left*) and $^{3}_{\infty}[Cd(prz-trz-ia)]$ (*right*). Arrows show the direction of the crystallographic *b* axis. The coordinating atoms are denoted in accordance with those from ref. [S1]. For DFT calculations have been used $^{3}_{\infty}[Cd(prz-trz-ia)]$.

Table S1. Comparison of DFT calculated structural parameters of $^{3}_{\infty}[Cu(prz-trz-ia)]$ and $^{3}_{\infty}[Cd(prz-trz-ia)]$ obtained with various computational methods (see Materials and Methods section of the main text), and the experimental data from ref. [S1].

	$^{3}_{\infty}[Cu(prz-trz-ia)]$						$^{3}_{\infty}[Cd(prz-trz-ia)]$		
Method	PBE	PBE-D2	PBE U_{Cu}=4.0eV	PBE-D2+*U* U_{Cu}=4.0eV	PBE-D2+*U* U_{Cu}=10.5eV U_N=8.6eV	Expt.	PBE	PBE-D2	Expt.
Lattice parameters									
a, Å	10.111	10.106	10.122	10.118	10.030	10.080	10.031	9.916	9.9977
b, Å	17.142	17.166	17.120	17.130	17.196	17.451	18.583	18.669	18.289
c, Å	11.981	11.238	11.804	11.239	11.254	11.519	12.370	11.852	12.008
α, deg	90.10	89.93	90.10	89.93	90.11	90.00	90.00	90.00	90.00
β, deg	98.17	102.35	98.65	102.28	100.49	99.78	95.87	97.60	100.58
γ, deg	89.99	90.05	89.99	90.09	89.95	90.00	90.00	90.00	90.00
V, $Å^3$	2055.4	1904.5	2031.1	1903.3	1907.1	1996.8	2293.7	2174.7	2158.3
Bond lengths, Å *									

M-O1b	3.352	3.212	3.366	3.208	2.989	3.101	2.614	2.521	2.685
M-O2b	1.959	1.957	1.953	1.958	2.006	1.948	2.294	2.316	2.227
M-O3c	2.026	2.022	2.021	2.018	2.112	2.073	2.322	2.267	2.279
M-O4c	2.775	2.838	2.734	2.834	3.039	2.797	2.614	2.763	2.612
M-N2a	2.008	1.985	2.026	1.998	2.014	1.989	2.399	2.333	2.295
M-N3	2.289	2.240	2.305	2.263	2.137	2.214	2.414	2.376	2.338
M-N4	2.034	2.041	2.066	2.069	2.111	2.045	2.511	2.463	2.395
MAD_{length}	0.062	0.035	0.076	0.042	0.088		0.068	0.080	
Bond angles, deg *									
O1b-M-O2b	41.27	44.43	40.83	44.51	49.24	45.5	53.96	55.17	52.44
O1b-M-O3c	158.23	168.43	158.23	166.77	176.05	172.3	165.99	170.73	169.42
O2b-M-N2a	89.10	92.85	88.97	93.20	93.78	92.3	101.45	101.22	95.92
O2b-M-N4	92.27	87.82	92.24	87.91	87.13	87.7	84.92	83.10	85.30
N2a-M-N3	96.62	96.56	96.95	96.68	98.27	97.6	96.81	99.50	99.28
N2a-M-N4	172.77	173.06	172.31	172.33	175.44	173.4	158.61	162.06	162.39
N3-M-N4	76.63	77.49	75.91	76.58	78.42	77.5	67.65	68.68	69.79
MAD_{angle}	4.08	1.00	4.28	1.51	1.88		2.75	1.89	

*For calculated bond lengths and bond angles, the values of mean average difference (MAD) are also presented: $MAD = \sum_{i}^{N} \frac{abs(x_i - x_i^{expt})}{N}$, where x is either a bond length or a bond angle.

2.EPR spectroscopy of $^{3}_{\infty}[Cd_{0.98}Cu_{0.02}(prz-trz-ia)]$

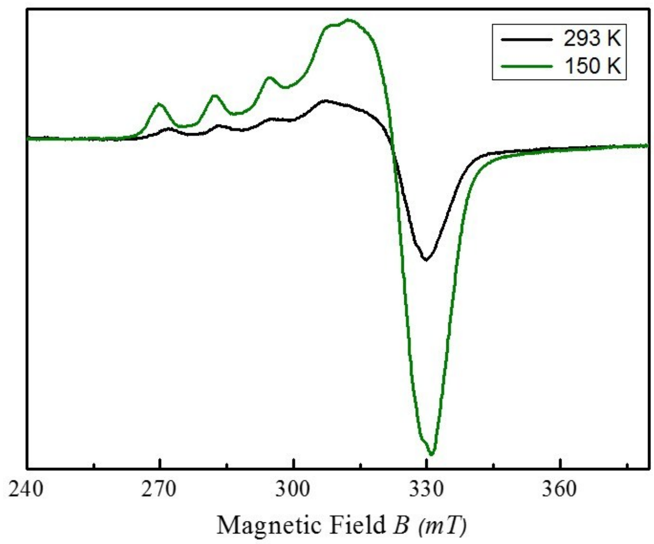


Figure S2. Experimental X-band CW EPR spectra of **asCu$_{0.02}$Cd** recorded at 150 K and 293 K.

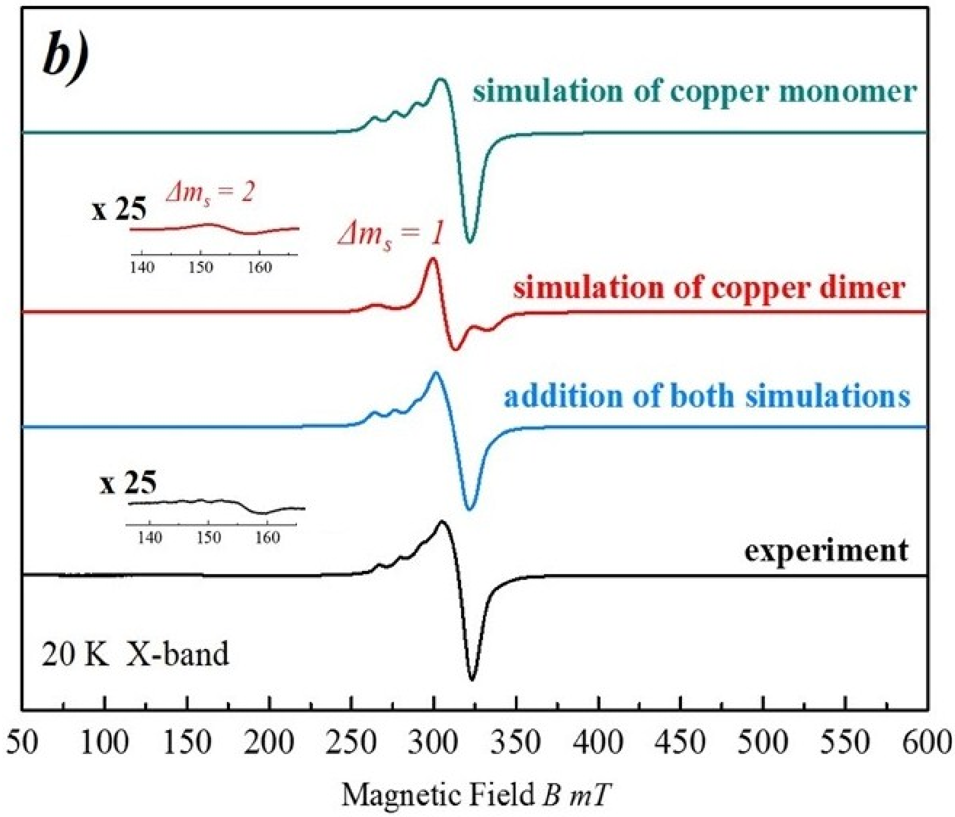
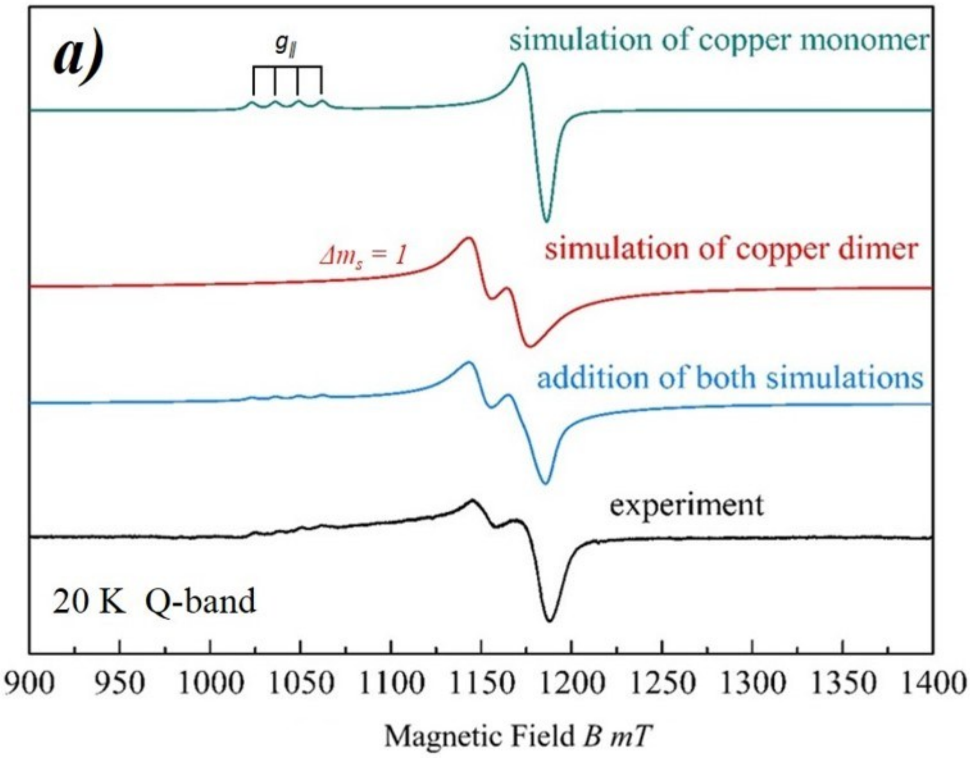


Figure S3: Experimental and simulated Q-band (a) and X-band (b) CW EPR spectra of **as$Cu_{0.02}$Cd** recorded at 20K. The simulation of copper dimer with S = 1 was performed by using EasySpin program with the following spin Hamiltonian parameters $g_{zz} = 2.33(1)$, $g_{xx.yy}= 2.09(1)$, |D| = 600 MHz.


a)
g∥
simulation of copper monomer
Δm_s = 1
simulation of copper dimer
addition of both simulations
experiment
20 K Q-band
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
Magnetic Field B mT

.

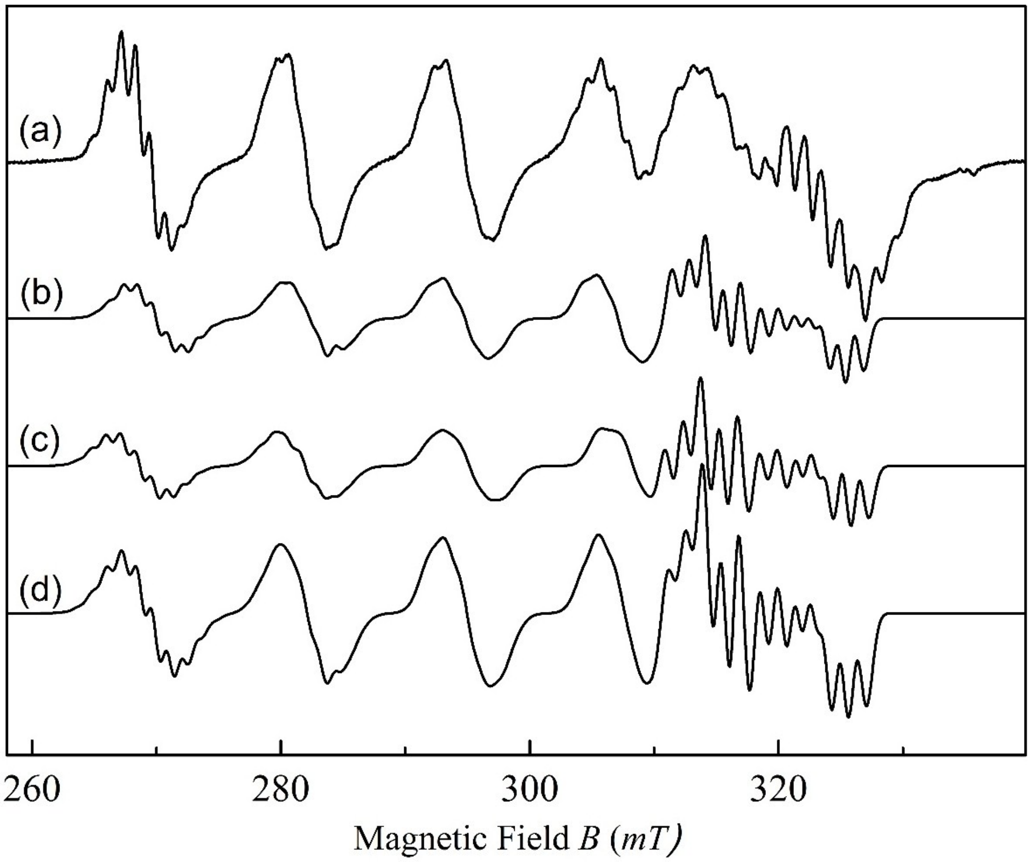


Figure S4: X-band EPR spectrum of an *asCu$_{0.02}$Cd* crystal at 20K for B_0 within the bc* plane and $\angle(B_0, b) = 45°$: (a) experimental spectrum, (d) sum of simulated spectra of (b) the ^{63}Cu, and (c) ^{65}Cu isotopes. The ^{14}N shf splitting into more than five lines results from the inequivalence of the two ^{14}N nuclei and depends crucial on the difference in their isotropic shf interaction constants $A_{iso,1}^{N}$ and $A_{iso,2}^{N}$. Both Cu^{2+} species A and B have been included in the simulation. For corresponding simulation parameters see Table I.

3. DFT calculations for a single substitutional Cu atom in MOF

For all the methods applied for structural optimization, initial geometries were built from the relaxed $^{3}_{\infty}[Cd(prz-trz-ia)]$ supercell with one cadmium ion being further substituted with copper ion. For all the obtained geometries, the EPR parameters were calculated within the same computational framework in Orca package (for details, see Materials and Methods section of the main text).

Table S2. DFT calculated EPR parameters, spin density localization and structural information for a single substitutional Cu atom in MOF supercell (containing 272 atoms) with the geometry optimized by the various computational schemes considered in this work.

	PBE	PBE-D2	PBE+U U_{Cu} = 4.0 eV	PBE-D2+U U_{Cu} = 4.0 eV	PBE-D2+U U_{Cu} = 10.5 eV U_N = 8.6 eV
EPR parameters					

$(g_{XX}\ g_{XX}\ g_{ZZ})$	2.0540 2.0948 2.2356	2.0659 2.0694 2.2168	2.0459 2.1090 2.2400	2.0600 2.0828 2.2239	2.0726 2.0802 2.2329
$(\alpha\ \beta\ \gamma)_g$, deg *	-88.59 154.14 71.60	-84.05 60.40 125.50	-87.88 152.41 73.82	-83.35 60.85 94.13	-80.74 59.87 103.59
Cu: $(A_{XX}\ A_{XX}\ A_{ZZ})$, MHz	23.25 125.52 -474.02	94.82 59.10 -491.70	14.40 171.20 -439.83	84.51 115.00 -463.82	112.20 81.93 -455.32
$(\alpha\ \beta\ \gamma)_A$, deg **	-22.9 2.7 -68.6	22.3 1.6 98.6	-16.6 3.0 -74.2	23.1 1.8 75.1	15.6 1.8 82.8
N2a: $(A_{XX}\ A_{XX}\ A_{ZZ})$, MHz	0.10 -0.73 -0.77	44.46 45.69 53.99	0.07 0.11 1.05	42.66 43.84 51.89	40.25 41.28 49.77
N3: $(A_{XX}\ A_{XX}\ A_{ZZ})$, MHz	28.74 29.67 35.35	-0.20 -1.21 -1.35	26.99 27.85 33.17	-0.56 -1.50 -1.62	-0.30 -1.29 -1.38
N4: $(A_{XX}\ A_{XX}\ A_{ZZ})$, MHz	-0.70 -1.32 -1.43	31.01 32.19 40.75	-0.59 -1.24 -1.32	28.50 29.58 37.60	25.26 26.19 35.11
Spin densities at the nuclei of ligand atoms, a.u./Å^3					
O1b	-0.004	-0.009	-0.004	-0.008	-0.009
O2b	0.338	0.313	0.324	0.309	0.282
O3c	0.306	0.347	0.307	0.336	0.294
O4c	0.351	0.007	0.329	0.012	0.006
N2a	-0.010	1.004	0.009	0.964	0.914
N3	0.653	-0.019	0.613	-0.026	-0.021
N4	-0.024	0.724	-0.022	0.666	0.603
Bond lengths, Å					
M-O1b	3.070	3.076	3.058	3.061	3.165
M-O2b	1.980	2.011	1.981	2.007	2.037
M-O3c	2.160	2.055	2.138	2.057	2.111
M-O4c	2.067	2.671	2.093	2.624	2.607
M-N2a	2.445	2.046	2.464	2.071	2.072
M-N3	2.043	2.264	2.091	2.285	2.208
M-N4	2.552	2.138	2.521	2.181	2.211

Bond angles, deg					
O1b-M-O2b	47.64	47.61	47.89	47.91	45.76
O1b-M-O3c	125.41	116.21	125.19	117.23	117.82
O2b-M-N2a	99.62	97.34	99.06	97.47	97.25
O2b-M-N4	92.36	88.60	92.20	88.59	88.97
N2a-M-N3	105.31	99.32	103.20	99.08	101.22
N2a-M-N4	167.88	172.10	168.05	171.25	173.18
N3-M-N4	72.49	75.25	72.37	74.42	75.51

*Orientations of the g-tensor are determined with respect to an *a-b-c** coordinate frame. Euler angles specify *z-y-z* rotation. The orientations are provided for a chosen Cu^{2+} site, while the principle axes directions for symmetry inequivalent sites are implied by the symmetry operations of $P2_{1/n}$ space group.

**Orientation of Cu hyperfine coupling tensor is defined with respect to the g-tensor. The principle axes A_X, A_Y, A_Z are assigned such that the Euler rotation is minimal.

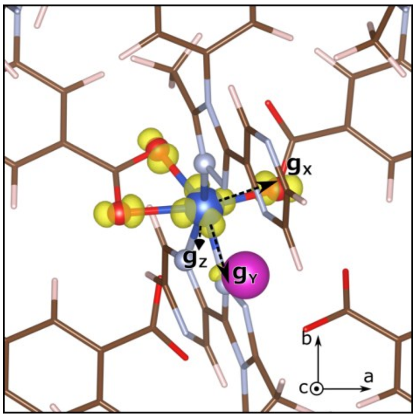
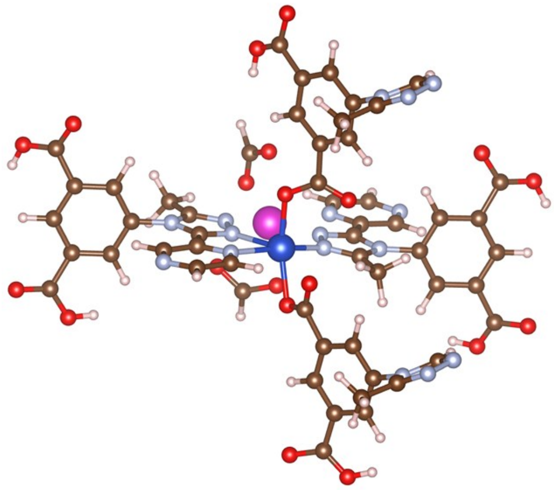


Figure S5. Cu^{2+} center in **as$Cu_{0.02}$Cd** as optimized using DFT-PBE+*U* method (without dispersion correction) viewed along the crystallographic *c* axis. The principal axes frame of the calculated tensor ***g*** is indicated by dashed arrows. Isosurfaces (isovalue of 0.05 electron/Å^3) illustrate the spin density distribution.

Table S3. An example of a hydrogen-terminated molecular cluster cut from the structure optimised with Quantum Espresso (PBE-D2+U with U_{Cu} = 4 eV) and used for calculating the EPR parameters in ORCA. The coordinates are in angstroms.

0 2			
Cu	3.71543	10.18480	4.09106
Cd	4.32261	8.38832	8.07501
C	2.72307	1.80243	2.83195
C	5.33417	16.83230	9.11827
C	1.56408	11.30265	3.03482
C	11.02482	10.86071	3.58549
C	6.79057	7.53204	8.91351
C	7.74843	2.49302	2.59820
C	0.30939	16.14936	9.37879
C	6.00859	11.84746	3.89164
C	-3.55228	11.50897	3.36604
C	1.90080	7.07146	8.40568
C	5.23074	2.16542	2.74713
C	2.82230	16.48950	9.18501
C	8.52455	11.31623	3.64124
C	-1.01192	11.40219	3.25128
H	5.34398	1.15454	2.34653
H	2.72230	17.47032	9.65741
H	8.39552	10.32212	4.07945
H	-1.05516	10.38189	3.64307
C	3.95403	2.63229	3.08395
C	4.09255	16.04167	8.79873
C	0.21638	11.97371	2.89025
C	9.81950	11.73339	3.29195
C	6.35411	2.98269	2.90893
C	1.69335	15.68489	8.99592
C	7.43089	12.17338	3.47473
C	-2.20432	12.12645	3.09602
C	3.80853	3.91609	3.61930
C	4.22473	14.79357	8.18289
C	0.23606	13.26859	2.36028
C	10.01070	13.00136	2.73119
H	2.81655	4.26400	3.92066
H	5.21176	14.44978	7.86154
H	1.18839	13.69753	2.03700
H	11.01739	13.31566	2.44266
C	6.20188	4.28613	3.39622
C	1.83405	14.41192	8.43196
C	7.63310	13.45447	2.94420
C	-2.17207	13.44026	2.61230
H	7.08578	4.92097	3.50371
H	0.95250	13.77456	8.32349
H	6.77781	14.12746	2.84237
H	-3.10907	13.99352	2.50819
C	4.93278	4.72764	3.75544
C	3.09522	13.99343	8.02568
C	8.91285	13.84485	2.57380
C	-0.94750	13.98776	2.24827
C	5.35728	5.17025	6.67247
C	2.62708	13.40294	5.14561
C	8.50369	14.41760	-0.32798
C	-1.40338	14.52690	-0.64514
H	6.33975	4.76154	6.38019
H	1.52720	13.47082	5.21152
H	7.52785	13.99199	-0.03814
H	-2.33577	14.02870	-0.33080
H	4.63271	4.33776	6.66102
H	3.04176	14.39566	5.38113
H	9.23885	13.59642	-0.35969
H	-0.60652	13.76606	-0.70774
H	5.39063	5.58794	7.68872
H	2.93623	13.11978	4.13264
H	8.45857	14.87506	-1.32553



H	-1.50573	14.98246	-1.63920
C	4.93192	6.21672	5.72254
C	3.13314	12.41428	6.11534
C	8.92728	15.42236	0.66305
C	-1.01446	15.55492	0.33740
C	4.34588	7.21751	3.86524
C	3.74198	11.54566	8.03736
C	9.48368	16.32817	2.58129
C	-0.44859	16.47911	2.24623
C	4.04399	7.59629	2.49301
C	4.02591	11.32111	9.45746
C	4.01580	6.71570	1.40006
C	3.92441	12.28424	10.47920
H	4.24202	5.65280	1.53637
H	3.59887	13.30630	10.27389
C	3.44488	8.42891	0.00600
C	4.62860	10.75694	12.03473
H	3.21837	8.76884	-1.01284
H	4.85309	10.52747	13.08409
C	3.47779	9.32517	1.08233
C	4.72548	9.78307	11.03390
H	3.25836	10.39199	0.97816
H	5.04659	8.75223	11.22890
N	4.77221	6.01427	4.37658
N	3.26898	12.69155	7.44597
N	9.10176	15.14726	1.99366
N	-0.87074	15.30291	1.67725
N	4.62145	7.47782	5.99593
N	3.51791	11.15439	5.91070
N	9.19443	16.70665	0.45899
N	-0.70834	16.82707	0.11469
N	4.25182	8.09769	4.85076
N	3.89102	10.61545	7.10068
N	9.54460	17.26561	1.64367
N	-0.35393	17.39710	1.29376
N	3.76298	8.91126	2.32048
N	4.42229	10.07018	9.76800
N	3.70708	7.12472	0.16473
N	4.22724	12.00296	11.75269
O	2.79920	0.79445	2.08372
O	5.25536	17.81925	9.89600
O	1.67432	10.33794	3.88097
O	10.87845	9.78204	4.19092
O	6.86832	8.52319	8.14281
O	1.62506	2.23075	3.34991
O	6.43926	16.39227	8.62997
O	2.52340	11.77745	2.37958
O	12.16279	11.36240	3.21484
O	5.69687	7.11621	9.44639
O	7.92137	1.21769	2.71610
O	0.12167	17.42512	9.30362
O	5.65374	10.60416	3.78083
O	-3.64160	10.23714	3.32180
O	2.03859	8.34672	8.46258
O	8.62382	3.32360	2.28516
O	-0.54822	15.30403	9.70533
O	5.30482	12.79453	4.27375
O	-4.53953	12.27723	3.56032
O	2.83407	6.26536	8.16309
H	7.20202	0.66762	2.95680
H	1.63126	2.98877	3.90068
H	-4.41353	13.20544	3.58282
H	10.01972	9.48834	4.42393
H	4.42056	18.09455	10.22047
H	-0.32310	14.39490	9.73316
H	-0.24010	16.62431	3.24647
H	9.68885	16.46394	3.58354
H	7.75948	6.98418	9.69935
H	0.95427	6.65191	9.15663

4. Correlated g and A strain effects

For the simulations of the single crystal spectra with nitrogen **shfs** (see Figure 6 in main manuscript) we have assumed a Gaussian distribution of the $g_{zz}(i)$ values. The **hf coupling** parameters $_{zz}(i)$ are in first approximation assumed to be correlated with the Gaussian distributed values $g_{zz}(i)$ by

$$A_{zz}(i) = -m \cdot g_{zz}(i) + k$$

where m and k are fitted to the respective EPR spectra.

The following values for the spectral simulations with correlated g and A strain effects have been taken: $\Delta g_{\parallel} = 0.009$, m = 900 MHz, k = 1674 MHz.

References

S1. Bergmann J, Stein K, Kobalz M, Handke M, Lange M, Möllmer J, Heinke F, Oeckler O, Gläser R, Staudt R, Krautscheid H. A series of isomorphous Metal-Organic Frameworks with rtl topology–Metal distribution and tunable sorption capacity via substitution of metal ions. *Microporous and Mesoporous Materials* 2015, **216**, 56-63.