# A folded [2×2] metallosupramolecular grid from a bis-tridentate (1,2,3-triazol-4-yl)-picolinamide (tzpa) ligand

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### Additional UV-Visible and Fluorescence Spectra and fitting



**Figure S1.** (a) Speciation distribution diagram obtained from UV-visible absorption titration data fit and (b) fit of experimental binding isotherms using the nonlinear regression analysis program ReactLab Equilibria.



**Figure S2.** (a) The overall changes in the fluorescence emission spectra upon titrating 1 (1 x  $10^{-5}$  M) against Zn(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0 $\rightarrow$ 5equiv.) in CH<sub>3</sub>CN at RT and (b) corresponding experimental binding isotherm at  $\lambda = 350$  nm.

## NMR Titration and VT-NMR Figures



**Figure S3.** <sup>1</sup>H NMR titration of **1** (1 x  $10^{-3}$  M) with Zn<sup>II</sup> from 0 - 5 equiv. in CD<sub>3</sub>CN.



**Figure S4.** <sup>1</sup>H NMR spectrum of  $[Zn_4(1)_4]^{8+}$  (assembled *in situ* in CD<sub>3</sub>CN) at 25 °C, 20 °C, 0 °C, -10 °C and -20 °C.

## T<sub>1</sub> Data Table and DOSY Spectra

**Table S1.** <sup>1</sup>H NMR assignment for **1** and re-dissolved  $[Zn_4(1)_4]^{8+}$  in CD<sub>3</sub>CN and associated  $T_1$  relaxation times. Uncertainties presented at 95% confidence level.



	Liga	nd 1	[Zn <sub>4</sub> (1) <sub>4</sub> ] complex				
Proton label	ppm	<i>T</i> <sub>1</sub> (s)	ppm	<i>T</i> <sub>1</sub> (s)			
а	3.83	0.56(1)	3.86	1.4(2)			
b	7.97	2.55(4)	7.94	2.83(9)			
С	7.41	2.24(3)	7.30	2.26(7)			
d	5.65	1.1(2)	5.61	0.64(3)			
е	8.40	1.79(4)	8.72	2.07(13)			
f	8.13	2.24(4)	8.29	1.60(7)			
g	7.86	2.01(3)	8.54	1.33(5)			
h	7.86	2.01(3)	8.24	0.96(4)			
i	8.74	0.59(3)	9.22	0.49(2)			
j	4.56	0.57(1)	4.59	0.37(4)			
k	7.27	1.30(5)	7.60	1.83(10)			
I.	7.27	1.30(5)	7.30	2.26(8)			
m	7.20	1.68(2)	7.21	1.68(4)			



Figure S5 Comparison of DOSY NMR spectra for ligand 1 (left) and  $[Zn_4(1)_4]^{8+}$  (right)

## **Mass Spectrometry**



Figure S6 Electrospray mass spectrum (positive ionisation mode) for  $[Zn_4(1)_4]^{8+}$ 



**Figure S7** Enlarged regions corresponding to the identified complex fragments listed in Figure S9, comparing measured data (black) to simulated isotopic distribution (red, or red/blue in the case of two overlapping fragments for  $[M+L+ClO_4]^+/[2M+2L+2ClO_4]^{2+}$ ).<sup>S1</sup>

### **Computational Data and Figures**

Geometry optimized structures of  $[Zn_4(1)_4]^{8+}$  were calculated from the crystal structure with the semiempirical method PM3 using Gaussian Software.<sup>S2</sup> The optimization in acetonitrile was carried out with polarizable continuum model (PCM).



**Figure S8** Comparison of the X-ray crystal structure (left), energy-minimized structure in MeCN (middle) and energy-minimized structure in vacuum (right). All structures are presented without pendant benzyl groups for clarity and/or to simply geometry optimization calculation.

Atom	x	У	z	Atom	x	у	z	Atom	x	у	z
С	15.238	-3.099	2.679	С	1.327	-13.554	3.299	н	-3.200	15.419	3.761
С	-15.238	3.099	2.679	С	-15.225	-3.167	-2.678	Н	3.199	-15.419	3.760
с	3.099	15.238	-2.679	с	15.225	3.167	-2.678	N	14.151	-2.141	2.392
с	-3.099	-15.238	-2.679	с	-3.167	15.224	2.678	N	-14.151	2.141	2.392
с	13.559	-1.266	3.299	с	3.167	-15.224	2.678	N	2.141	14.151	-2.392
с	-13.559	1.266	3.299	н	-3.769	8.175	-1.832	N	-2.141	-14.151	-2.392
с	1.266	13.559	-3.299	н	3.769	-8.175	-1.832	N	13.602	-1.987	1.161
с	-1.266	-13.559	-3.299	н	8.175	3.769	1.832	N	-13.602	1.987	1.161
с	12.614	-0.567	2.544	н	-8.175	-3.769	1.832	N	1.987	13.602	-1.161
с	-12.614	0.567	2.544	н	-8.192	3.732	-1.832	N	-1.987	-13.602	-1.161
с	0.567	12.614	-2.544	н	8.192	-3.732	-1.832	N	12.694	-1.065	1.229
с	-0.567	-12.614	-2.544	н	3.732	8.192	1.832	N	-12.694	1.065	1.229
с	11.668	0.494	2.866	н	-3.732	-8.192	1.832	N	1.065	12.694	-1.229
с	-11.668	-0.494	2.866	н	13.823	-1.182	4.361	N	-1.065	-12.694	-1.229
с	-0.494	11.668	-2.866	н	-13.823	1.182	4.361	N	-0.940	10.899	-1.816
с	0.494	-11.668	-2.866	н	1.182	13.823	-4.361	N	0.940	-10.899	-1.816
с	11.535	1.051	4.145	н	-1.182	-13.823	-4.361	N	10.899	0.940	1.816
с	-11.535	-1.051	4.145	н	12.158	0.686	4.975	N	-10.899	-0.940	1.816
с	-1.051	11.535	-4.145	н	-12.158	-0.686	4.975	N	-3.272	8.170	-0.963

**Table S2:** Coordinates for  $[Zn_4(1)_4]^{8+}$  in vacuum; PM3

с	1.051	-11.535	-4.145	н	-0.686	12.158	-4.975	N	3.272	-8.170	-0.963
С	-2.076	10.612	-4.342	н	0.686	-12.158	-4.975	N	8.170	3.272	0.963
С	2.076	-10.612	-4.342	н	-2.531	10.499	-5.336	N	-8.170	-3.272	0.963
С	10.612	2.076	4.342	н	2.531	-10.499	-5.336	N	-8.185	3.234	-0.963
С	-10.612	-2.076	4.342	н	10.499	2.531	5.336	N	8.185	-3.234	-0.963
С	-2.527	9.839	-3.272	н	-10.499	-2.531	5.336	N	3.234	8.185	0.963
С	2.527	-9.839	-3.272	н	-3.342	9.112	-3.414	N	-3.234	-8.185	0.963
С	9.839	2.527	3.272	н	3.342	-9.112	-3.414	N	-10.903	0.891	-1.816
С	-9.839	-2.527	3.272	н	9.112	3.342	3.414	N	10.903	-0.891	-1.816
С	-1.943	9.995	-2.009	н	-9.112	-3.342	3.414	N	0.891	10.903	1.816
С	1.943	-9.995	-2.009	н	-2.500	5.520	-1.083	Ν	-0.891	-10.903	1.816
С	9.995	1.943	2.009	н	2.500	-5.520	-1.083	N	-12.690	-1.122	-1.228
С	-9.995	-1.943	2.009	н	5.520	2.500	1.083	Ν	12.690	1.122	-1.228
С	-2.361	9.216	-0.789	н	-5.520	-2.500	1.083	Ν	-1.122	12.690	1.228
С	2.361	-9.216	-0.789	н	-3.245	3.231	-1.658	N	1.122	-12.690	1.228
С	9.216	2.361	0.789	н	3.245	-3.231	-1.658	N	-13.593	-2.049	-1.161
С	-9.216	-2.361	0.789	н	3.231	3.245	1.657	N	13.593	2.049	-1.161
С	-3.946	7.472	0.163	н	-3.231	-3.245	1.658	N	-2.049	13.593	1.161
С	3.946	-7.472	0.163	н	-5.531	2.475	-1.083	N	2.049	-13.593	1.161
С	7.472	3.946	-0.163	н	5.531	-2.475	-1.083	N	-14.141	-2.205	-2.392
с	-7.472	-3.946	-0.163	н	2.475	5.531	1.083	N	14.141	2.205	-2.392
С	-4.412	6.104	-0.248	н	-2.475	-5.531	1.083	N	-2.205	14.141	2.392
С	4.412	-6.104	-0.248	н	-6.414	6.385	0.527	Ν	2.205	-14.141	2.392
С	6.104	4.412	0.248	н	6.414	-6.385	0.527	0	-1.858	9.454	0.317
С	-6.104	-4.412	0.248	н	6.385	6.414	-0.527	0	1.858	-9.454	0.317
С	-3.528	5.213	-0.859	н	-6.385	-6.414	-0.527	0	9.454	1.858	-0.317
С	3.528	-5.213	-0.858	н	-9.126	3.300	-3.413	0	-9.454	-1.858	-0.317
С	5.213	3.528	0.858	Н	9.126	-3.300	-3.413	0	-9.463	1.815	0.317
С	-5.213	-3.528	0.858	н	3.300	9.126	3.413	0	9.463	-1.815	0.317
С	-3.941	3.924	-1.172	Н	-3.300	-9.126	3.413	0	1.815	9.463	-0.317
с	3.941	-3.924	-1.172	н	-10.510	2.484	-5.336	0	-1.815	-9.463	-0.317
с	3.924	3.941	1.172	н	10.510	-2.484	-5.336	Zn	11.376	0.026	0.000
с	-3.924	-3.941	1.172	н	-2.484	-10.510	5.336	Zn	-11.376	-0.026	0.000
С	-5.229	3.504	-0.858	н	2.484	10.510	5.336	Zn	-0.026	11.376	0.000
с	5.229	-3.504	-0.858	н	-12.161	0.631	-4.975	Zn	0.026	-11.376	0.000
с	3.504	5.229	0.858	н	12.161	-0.631	-4.975	н	-8.108	4.758	0.532
С	-3.504	-5.229	0.858	н	0.631	12.161	4.975	Н	8.108	-4.758	0.532
с	-6.124	4.384	-0.248	н	-0.631	-12.161	4.975	н	4.758	8.108	-0.532
С	6.124	-4.384	-0.248	Н	-13.818	-1.244	-4.360	Н	-4.758	-8.108	-0.532
С	4.385	6.124	0.248	Н	13.818	1.244	-4.360	Н	-14.953	-4.179	-2.339
С	-4.385	-6.124	0.248	Н	-1.244	13.818	4.360	Н	14.952	4.179	-2.340
С	-5.715	5.689	0.045	Н	1.244	-13.818	4.360	Н	-4.178	14.953	2.338
С	5.715	-5.689	0.045	Н	16.163	-2.808	2.155	Н	4.179	-14.953	2.339
С	5.689	5.715	-0.045	н	-16.163	2.808	2.156	Н	-16.154	-2.872	-2.165

С	-5.689	-5.715	-0.045	н	2.809	16.163	-2.155	н	16.154	2.873	-2.164
С	-7.489	3.912	0.163	н	-2.808	-16.163	-2.155	н	-2.872	16.154	2.166
с	7.489	-3.912	0.163	н	14.965	-4.114	2.351	н	2.873	-16.154	2.165
С	3.912	7.489	-0.163	Н	-14.965	4.114	2.350	Н	-15.419	-3.199	-3.761
с	-3.912	-7.489	-0.163	н	4.114	14.964	-2.352	н	15.420	3.198	-3.760
С	-9.226	2.319	-0.788	н	-4.114	-14.964	-2.352	С	11.540	-0.999	-4.145
с	9.226	-2.319	-0.788	н	15.441	-3.121	3.760	С	0.999	11.540	4.145
с	2.319	9.226	0.788	н	-15.441	3.121	3.760	С	-0.999	-11.540	4.145
с	-2.319	-9.226	0.788	н	3.120	15.442	-3.760	С	-11.670	0.441	-2.866
с	-10.003	1.898	-2.009	н	-3.121	-15.441	-3.760	С	11.670	-0.441	-2.866
с	10.003	-1.898	-2.009	н	-4.795	8.087	0.532	С	0.441	11.670	2.866
с	1.898	10.003	2.009	н	4.795	-8.087	0.532	С	-0.441	-11.670	2.866
с	-1.898	-10.003	2.009	н	8.087	4.795	-0.532	С	-12.612	-0.624	-2.544
С	-9.850	2.482	-3.272	н	-8.087	-4.795	-0.532	С	12.612	0.624	-2.544
с	9.850	-2.482	-3.272	н	-3.233	7.375	1.007	С	-0.624	12.612	2.544
с	2.482	9.850	3.272	н	3.233	-7.375	1.007	С	0.624	-12.612	2.544
с	-2.482	-9.850	3.272	н	7.375	3.233	-1.007	С	-13.554	-1.327	-3.299
с	-10.621	2.028	-4.342	н	-7.375	-3.233	-1.007	С	13.554	1.327	-3.299
с	10.621	-2.028	-4.342	н	-7.389	3.199	1.007	С	-1.327	13.554	3.299
С	2.028	10.621	4.342	н	7.389	-3.199	1.008	Н	-3.199	-7.389	-1.008
с	-2.028	-10.621	4.342	Н	3.199	7.389	-1.008	С	-11.540	0.999	-4.145

**Table S3:** Coordinates for  $[Zn_4(1)_4]^{8+}$  in acetonitrile; PM3/PCM

Atom	x	у	z	Atom	x	У	z	Atom	x	у	z
С	-2.643	9.348	6.744	С	11.553	-0.921	-2.471	н	-14.005	-3.145	-1.346
С	3.030	-0.685	10.695	С	4.002	-8.787	7.441	н	13.759	0.581	-2.262
с	-7.642	-6.551	-7.575	с	-2.852	12.122	-1.451	N	-2.724	8.617	5.468
С	8.555	-0.677	-9.799	С	-13.228	-3.912	-1.473	N	3.036	-1.215	9.321
С	-3.666	7.655	5.122	С	12.952	1.212	-2.660	N	-7.442	-5.943	-6.249
С	3.835	-0.779	8.270	н	-5.393	-3.252	1.456	N	8.098	-0.295	-8.452
с	-6.675	-6.457	-5.211	н	4.661	2.484	-1.303	N	-1.839	8.805	4.453
С	7.238	0.750	-8.135	н	-3.933	3.784	-1.316	N	2.235	-2.237	8.920
С	-3.306	7.266	3.831	Н	3.871	-3.444	1.255	N	-8.014	-4.765	-5.883
с	3.474	-1.598	7.197	н	-3.035	-2.205	5.331	N	8.484	-0.955	-7.328
С	-6.809	-5.520	-4.183	н	2.969	5.063	2.243	N	-2.168	8.017	3.479
с	7.119	0.691	-6.745	н	-5.565	1.175	-5.049	N	2.479	-2.475	7.670
с	-3.865	6.298	2.895	н	5.296	-4.971	-3.252	N	-7.652	-4.501	-4.667
С	3.917	-1.665	5.810	н	-4.491	7.317	5.760	N	7.916	-0.386	-6.312
с	-6.248	-5.439	-2.840	н	4.570	0.032	8.326	N	-6.597	-4.321	-2.122
С	6.363	1.479	-5.780	н	-6.108	-7.394	-5.243	N	6.496	1.086	-4.471
С	-4.985	5.503	3.167	Н	6.782	1.437	-8.856	N	-3.206	6.199	1.694

С	4.902	-0.833	5.265	н	-5.506	5.594	4.129	N	3.290	-2.615	5.039
С	-5.398	-6.409	-2.294	н	5.401	-0.084	5.895	N	-6.109	-2.632	1.128
С	5.538	2.557	-6.126	н	-5.134	-7.301	-2.878	N	5.358	1.814	-1.041
С	-4.901	-6.218	-1.007	н	5.445	2.865	-7.175	N	-3.228	4.454	-1.552
С	4.843	3.222	-5.117	н	-4.235	-6.967	-0.559	Ν	3.228	-4.097	1.661
С	-5.420	4.600	2.198	н	4.193	4.071	-5.366	Ν	-2.190	-1.669	5.408
С	5.231	-0.973	3.918	н	-6.297	3.969	2.391	N	2.082	4.922	2.691
С	-5.245	-5.074	-0.289	н	5.996	-0.327	3.468	Ν	-5.277	0.215	-5.050
С	4.967	2.805	-3.793	н	-4.848	-4.905	0.725	Ν	5.053	-4.219	-3.869
С	-4.740	4.496	0.986	н	4.411	3.313	-2.989	Ν	0.003	-4.546	6.096
С	4.584	-1.930	3.139	н	-5.068	3.779	0.217	Ν	0.385	7.723	0.990
С	-6.101	-4.129	-0.867	н	4.827	-2.041	2.070	Ν	-8.380	-1.118	-3.580
с	5.805	1.726	-3.486	н	-4.431	-0.227	-0.115	Ν	8.176	-2.327	-3.321
С	-3.626	5.311	0.750	н	2.974	-0.270	-0.423	Ν	2.457	-5.696	6.597
С	3.611	-2.751	3.722	н	-0.829	2.305	-1.341	Ν	-1.836	9.223	0.343
С	-6.514	-2.850	-0.192	н	0.787	-2.578	0.255	Ν	-9.923	-3.149	-2.544
С	5.993	1.173	-2.102	н	-2.126	0.619	0.237	Ν	9.740	-0.067	-3.501
С	-2.806	5.275	-0.510	н	0.662	0.011	0.419	Ν	3.498	-6.423	6.859
С	2.839	-3.798	2.969	н	-0.695	-0.147	-1.722	Ν	-2.740	10.054	-0.074
С	-6.109	-1.286	1.754	н	0.603	-1.270	-1.842	Ν	-10.816	-3.965	-2.079
С	5.177	1.172	0.287	н	-1.114	0.597	2.502	Ν	10.626	0.879	-3.476
с	-2.357	4.105	-2.704	н	0.141	1.737	2.118	Ν	3.077	-7.691	7.106
с	2.325	-4.784	0.700	н	-2.106	-1.219	-3.458	Ν	-2.124	11.007	-0.822
с	-4.716	-0.774	1.961	н	1.925	-1.927	-3.845	Ν	-11.988	-3.285	-1.961
с	3.773	1.354	0.776	н	-4.739	-1.170	4.083	N	11.740	0.400	-2.861
с	-2.299	2.621	-2.903	н	4.287	2.988	2.094	0	-7.254	-2.039	-0.765
с	2.205	-3.996	-0.569	н	-3.718	2.646	-4.532	0	6.744	0.207	-1.893
С	-3.987	-0.260	0.886	н	3.553	-5.283	-1.660	0	-1.816	6.010	-0.650
С	2.756	0.518	0.311	н	-3.315	-4.033	5.618	0	1.924	-4.432	3.513
С	-1.450	1.840	-2.117	н	3.544	6.502	1.186	0	0.092	-1.902	5.370
С	1.369	-2.880	-0.625	н	-7.268	1.892	-4.677	0	-0.133	5.483	2.479
С	-2.699	0.220	1.088	н	6.982	-5.407	-2.550	0	-5.776	-1.804	-4.081
С	1.460	0.670	0.788	н	-3.361	-6.471	6.186	0	5.664	-2.067	-4.380
с	-1.382	0.468	-2.325	н	3.977	8.520	-0.231	Zn	-1.606	7.509	1.523
с	1.270	-2.147	-1.802	н	9.281	-5.608	-1.578	Zn	1.909	-3.738	6.104
С	-2.132	0.196	2.357	н	-9.636	2.504	-4.145	Zn	-7.917	-3.091	-3.148
с	1.169	1.651	1.730	н	-1.216	-7.670	6.689	Zn	7.818	-0.492	-4.219
С	-2.167	-0.134	-3.304	н	2.072	10.018	-0.877	Н	-3.526	0.414	-6.161
С	2.006	-2.516	-2.923	н	-11.197	0.763	-3.236	Н	3.221	-5.016	-4.470
С	-2.853	-0.315	3.436	Н	10.861	-3.664	-1.710	Н	4.724	-8.949	6.628
С	2.178	2.497	2.190	Н	1.101	-8.686	7.148	Н	-3.708	11.752	-2.035
С		0.644	4 000	l <sup>_</sup>	0.020	11 200	1 4 2 4	н	-13 062	-1 107	-0 505
	-3.016	0.641	-4.093	н	-0.029	11.590	-1.424		10.002	4.407	0.303
С	-3.016 2.838	-3.636	-4.093 -2.875	H H	-0.029	-1.208	-1.424	н	12.758	2.026	-1.946

С	3.482	2.341	1.717	Н	-2.561	10.431	6.571	н	-3.228	12.819	-0.687
С	-3.074	2.023	-3.896	н	3.544	-1.379	11.377	н	-13.591	-4.662	-2.191
С	2.924	-4.383	-1.700	Н	-8.693	-6.846	-7.712	Н	13.289	1.654	-3.609
С	-2.251	-0.316	4.810	Н	9.651	-0.616	-9.870	н	3.435	-9.716	7.595
с	1.871	3.551	3.212	н	-1.767	9.020	7.322	н	-2.180	12.671	-2.125
с	-3.821	-0.009	-5.179	н	2.002	-0.541	11.056	с	9.853	-3.600	-2.141
с	3.602	-4.042	-4.101	н	-7.372	-5.845	-8.374	с	-0.013	-5.887	6.401
с	-1.023	-2.430	5.487	н	8.249	-1.707	-10.037	С	0.613	8.825	0.200
с	1.046	5.712	2.179	н	-3.548	9.155	7.338	с	-9.680	-0.789	-3.280
с	-6.131	-0.651	-4.364	н	3.550	0.282	10.722	с	9.432	-2.422	-2.772
с	5.953	-3.147	-3.849	н	-7.012	-7.446	-7.670	С	1.291	-6.482	6.665
с	-1.160	-3.891	5.821	н	8.117	0.000	-10.546	С	-0.569	9.613	-0.129
с	1.416	6.902	1.337	н	-6.643	-1.391	2.721	с	-10.491	-1.879	-2.752
с	-7.529	-0.176	-4.075	н	5.907	1.639	0.981	С	10.253	-1.224	-2.885
с	7.310	-3.377	-3.243	н	-2.784	4.611	-3.595	С	1.694	-7.778	6.996
с	-2.383	-4.572	5.846	н	2.760	-5.787	0.511	С	-0.756	10.772	-0.885
с	2.719	7.175	0.902	н	-6.695	-0.568	1.145	С	-11.832	-1.967	-2.373
с	-7.966	1.138	-4.283	н	5.428	0.090	0.249	н	3.455	-3.311	-4.923
с	7.693	-4.568	-2.613	н	-1.334	4.513	-2.569	н	-2.879	0.298	5.489
с	-2.406	-5.930	6.160	н	1.322	-4.952	1.144	н	2.550	3.440	4.083
С	2.958	8.297	0.111	Н	-1.243	0.147	4.805	С	-1.217	-6.601	6.441
С	-9.285	1.477	-3.983	Н	0.838	3.445	3.601	С	1.903	9.132	-0.250
с	8.971	-4.676	-2.068	н	-3.617	-1.098	-5.229	С	-10.155	0.514	-3.479





Figure S10. <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN) spectrum of 1.

[mqq]



Figure S11. HSQC (400 MHz, CD<sub>3</sub>CN) spectrum of 1.



Figure S12. HMBC (600 MHz, CD<sub>3</sub>CN) spectrum of 1.



Figure S13. NHCOSY (600 MHz, CD<sub>3</sub>CN) spectrum of 1.



Figure S14. <sup>19</sup>F NMR spectrum of  $[Zn_4.1_4]^{8+}$  assembled *in situ* from 1 and  $Zn(BF_4)_2.xH_2O$ .



Figure S15. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) spectrum of isolated  $[Zn_4(1)_4]^{8+}$  complex.



Figure S16. <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN) spectrum of isolated  $[Zn_4(1)_4]^{8+}$  complex.



Figure S17. HSQC (600 MHz, CD<sub>3</sub>CN) spectrum of isolated  $[Zn_4(1)_4]^{8+}$  complex.



Figure S18. HMBC (600 MHz, CD<sub>3</sub>CN) spectrum of isolated  $[Zn_4(1)_4]^{8+}$  complex.



Figure S19. NHCOSY (600 MHz, CD<sub>3</sub>CN) spectrum of isolated  $[Zn_4(1)_4]^{8+}$  complex.

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