Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A PN(Pz)P Ligand Protected Au_2Cu_2 Complex for Photoluminescent Ultra-low Humidity Detection with Reversible Single-crystal-to-single-crystal Transformations

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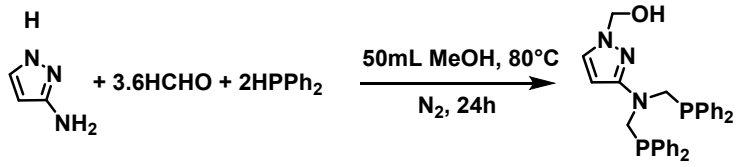
Contents

Scheme S1. Synthesis of 3-dppmapz-1-ol.



Computational methodology

Theoretical calculations were performed by DFT and TD-DFT methods using the CP2K program[s1] (2023.1) and analyzed by the Multiwfn 3.8dev program. The input file for CP2K was also generate with Multiwfn[s2].

1. Optimization of ground state structure

Using the cif crystal structure data as the initial structure, the input file of CP2K was generated using the Multiwfn program. PBE0-D3(BJ) functional, DZVP-MOLOPT-SR-GTH base set, periodic and ADMM mode acceleration were used for structural optimization.

2. Triplet state structure optimization

The ground state structure obtained by the above optimization was taken as the initial structure and set as the triplet state in Multiwfn. The UKS mode was used to optimize the structure with the same functional and base group, and the triplet state was thereby obtained.

3. TDDFT calculation

The above optimization results were used to calculate the excited states of S0-S50 and T1-T50 respectively using the TD-DFT method. PBE0-D3(BJ) functional and TZVP-MOLOPT-GTH base set were then employed. The wavefunction file *.molden was output for the Multiwfn wavefunction analysis.

4. Orbit wavefunctions graphic

The grid file output from the Multiwfn program was imported into VESTA to calculate the HOMO, LUMO graphic.

References

[s1] T. D. Kuhne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schutt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borstnik, M. Taillefumier, A. S. Jakobovits, A. Lazzaro, H. Pabst, T. Muller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G. K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Gloss, M. Lass, I. Bethune, C. J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack and J. Hutter, CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations, J. Chem. Phys., 2020, **152**, 194103.

[s2] T. Lu and F. Chen, Multiwfn: a multifunctional wavefunction analyzer, *J. Comput. Chem.*, 2012, **33**, 580-592.

Cartesian Coordinates

1

CELL

1.1121489155579125E+01 0.0000000000000000E+00 0.0000000000000000E+00

3.9989687658713948E+00 1.1466017897776954E+01 0.0000000000000000E+00

4.1555353987692243E+00 5.4507843387310047E+00 1.1547750256204958E+01

Au	17.629152	16.797687	15.564295	C	15.378990	19.857146	9.874112	C	11.399274	17.034727	17.445932
Cu	20.140246	17.367571	10.978242	C	12.077271	17.671275	12.067857	C	11.291008	18.147421	19.843499
N	18.698936	22.376076	9.926965	H	11.080870	15.876981	12.161297	H	12.409358	19.812130	20.238536
N	17.921517	19.962238	10.182448	H	10.712467	19.168663	11.659721	C	30.761443	17.136516	21.704219
N	14.016027	17.493881	10.030197	C	12.683448	17.045510	7.590464	H	22.811989	7.715213	1.720206
P	13.560239	18.357028	15.144884	H	11.384403	18.601326	7.192136	C	29.332324	14.982696	21.215031
P	14.912502	16.732063	4.935075	H	11.604464	15.305562	7.757489	H	20.275988	3.918633	0.859570
P	25.562539	22.054445	11.397344	C	13.451195	21.734343	15.529760	C	8.463783	13.836551	18.858334
F	24.195984	20.379218	9.198360	C	11.122084	22.965178	15.756714	H	7.410547	12.129183	18.460301
F	23.268919	21.350272	13.321777	H	30.402978	21.893822	15.836199	C	9.992576	14.851485	16.972649
F	26.984252	23.563487	13.643998	C	32.053673	25.586549	15.829859	H	10.095541	13.890352	15.178284
F	27.930396	22.576813	9.498023	H	30.254982	26.541397	15.987579	C	15.353738	19.808228	3.530278
F	24.177619	24.557651	10.497648	C	13.266649	26.978037	15.677958	C	17.573468	21.126400	4.060857
F	27.056569	19.456421	12.328204	H	13.197201	29.019653	15.726332	H	18.999453	20.301697	5.273386
C	16.635118	23.756521	9.468955	C	15.583456	25.763440	15.437019	C	10.378637	1.875920	3.098112
H	16.805362	25.770834	9.228849	H	17.301055	26.851633	15.226783	H	12.076581	2.890179	3.611552
C	14.453578	22.252455	9.410977	C	15.680449	23.138088	15.367851	C	8.565265	2.957146	1.541815
H	12.522350	22.837074	9.152261	H	17.474179	22.192767	15.086317	H	8.850497	4.826126	0.758102

C	6.358849	1.635588	0.969512	F	9.369844	12.511853	9.493888	C	7.093936	16.985432	0.607038
H	4.958224	2.474762	-0.255679	C	19.791262	8.211626	12.353234	H	16.150227	28.049511	20.962469
C	13.518605	20.914121	1.975299	H	19.621027	6.197304	12.593331	C	27.962551	18.131544	2.963751
H	11.816800	19.884737	1.512671	C	21.972819	9.715687	12.411144	H	29.015842	19.838865	3.361800
C	13.235073	14.837122	2.635296	H	23.904047	9.131011	12.669898	C	26.433834	17.116585	4.849481
C	13.821697	15.153723	0.075561	C	21.047342	12.110986	11.948035	H	26.330922	18.077677	6.643864
H	15.121652	16.621694	-0.488207	C	24.349049	14.296838	9.754257	C	21.072590	12.159976	18.291888
C	20.611634	23.884247	20.081112	H	25.345472	16.091120	9.660793	C	18.852892	10.841727	17.761287
H	21.102042	24.130859	18.110294	H	25.713838	12.799454	10.162376	H	17.426915	11.666523	16.548847
C	18.964678	21.970009	20.808672	C	23.742900	14.922619	14.231646	C	26.047657	30.092203	18.723993
H	18.163970	20.718943	19.400339	H	25.041932	13.366828	14.630053	H	24.349714	29.077938	18.210545
C	10.514653	11.351890	1.522666	H	24.821923	16.662537	14.064640	C	27.861026	29.011034	20.280339
H	9.237517	9.864535	2.104470	C	22.975135	10.233765	6.292381	H	27.575843	27.141978	21.063908
C	11.560668	12.922068	3.348061	C	25.304230	9.002922	6.065356	C	30.067508	30.332528	20.852547
H	11.084105	12.596546	5.299445	H	6.023351	10.074240	5.985879	H	31.468030	29.493409	22.077916
Au	18.797283	15.170556	6.257823	C	4.372628	6.381556	5.992237	C	22.907720	11.054047	19.846849
Cu	16.286031	14.600546	10.843864	H	6.171305	5.426701	5.834483	H	24.609571	12.083343	20.309492
N	17.727429	9.592061	11.895220	C	23.159664	4.990072	6.144159	C	23.191273	17.131069	19.186848
N	18.504813	12.005909	11.639723	H	23.229122	2.948455	6.095774	C	22.604641	16.814485	21.746588
N	22.410313	14.474225	11.791931	C	20.842869	6.204682	6.385083	H	21.304699	15.346501	22.310365
P	22.866110	13.611074	6.677257	H	19.125297	5.116469	6.595343	C	15.814707	8.083969	1.741025
P	21.513906	15.236129	16.887056	C	20.745878	8.830033	6.454265	H	15.324312	7.837358	3.711849
P	10.863786	9.913708	10.424649	H	18.952153	9.775355	6.735780	C	17.461630	9.998222	1.013430
F	12.230401	11.588762	12.623630	C	25.027089	14.933370	4.376213	H	18.262383	11.249266	2.421751
F	13.157471	10.617898	8.500252	C	25.135244	13.820718	1.978618	C	25.911638	20.616325	20.299430
F	9.442142	8.404624	8.178035	H	24.016878	12.155999	1.583577	H	27.188797	22.103632	19.717599
F	8.495973	9.391481	12.324121	C	5.664784	14.831623	0.117864	C	24.865649	19.046126	18.474051
F	12.248616	7.410403	11.324231	H	13.614200	24.252928	20.101866	H	25.342193	19.371642	16.522664

1·2H_2O

CELL

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Au	6.113532	4.205605	6.432235	C	-1.677500	5.966129	5.057921	C	9.406040	8.950213	10.118984
Cu	8.582731	3.659224	11.096892	H	-1.712751	6.826909	6.900541	C	12.713108	6.825430	12.349814
P	2.061763	2.595329	6.822657	C	3.691164	1.186903	18.579662	H	13.772412	5.070455	12.429373
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P	14.413895	-0.789097	11.148947	H	7.323229	0.556777	16.853254	C	12.170197	6.149900	7.873121
F	12.564793	0.823303	12.995038	C	6.223064	-2.565516	19.188894	H	13.473197	7.707734	7.494406
F	12.390567	-0.414922	8.862214	H	7.888069	-3.652968	18.714174	H	13.263076	4.420628	8.072528
F	16.268188	-2.306495	9.272103	C	4.394416	-3.536603	20.801488	C	11.344254	10.806891	15.900086
F	16.446200	-1.065731	13.414391	H	4.660964	-5.366211	21.679482	C	-7.467877	11.999574	16.140180
F	13.056355	-3.361685	11.961443	C	2.203824	-2.162620	21.305049	H	-5.751965	10.894374	16.171126
F	15.786308	1.866983	10.302633	H	0.786781	-2.921508	22.564780	C	0.166093	-6.872605	16.305135
N	7.208915	-1.426803	12.117324	C	1.840390	0.180029	20.183668	H	1.979949	-5.944671	16.469700
N	6.430775	0.996170	11.867471	H	0.156218	1.255527	20.600495	C	19.107936	-5.452732	16.263811
N	2.497239	3.438689	11.966097	C	1.574410	6.172335	19.339681	H	-1.952289	-3.416270	16.398352
C	5.136228	-2.810856	12.536327	C	2.090353	5.888768	21.918590	C	16.768432	-6.630396	16.041437
H	5.288087	-4.824388	12.780827	H	3.390002	4.449287	22.556909	H	15.041899	-5.538530	15.966904
C	2.955335	-1.312330	12.574163	C	1.288670	18.892569	1.422588	C	9.129363	12.237771	15.849834
H	1.024939	-1.906484	12.823521	H	1.693506	18.598470	3.403145	H	7.318335	11.318752	15.594503
C	3.884537	1.087852	12.142382	C	-0.360037	20.777808	0.631931	C	13.399655	6.125259	17.734322
C	0.577025	3.212559	9.912036	H	6.269078	0.516884	2.014404	C	13.368735	7.129252	20.185114
H	-0.481813	4.967709	9.832156	C	-1.225177	9.637820	20.339870	H	12.137627	8.699739	20.631511
H	-0.739855	1.673661	10.308983	H	5.011355	-10.381397	19.705430	C	-6.232504	6.130029	22.041299
C	1.120457	3.887736	14.388660	C	-0.101077	8.064073	18.564569	H	-5.886628	18.370174	1.655341
H	-0.182856	2.330112	14.766858	H	-0.525413	8.362696	16.597912	C	-4.659492	4.090603	21.500460
H	0.028154	5.617254	14.189824	O	10.067944	-5.971904	15.600678	H	-3.093671	14.784867	0.702139
C	1.944776	-0.769461	6.362256	H	10.083016	-4.553625	14.451225	C	16.497351	3.058246	19.089802
C	20.756533	-1.961879	6.124277	H	9.775286	-7.404420	14.515520	H	17.669642	1.445104	18.640258
H	19.040747	-0.856330	6.094266	Au	7.176668	5.831285	15.829416	C	14.968738	4.073562	17.205094
C	13.122279	16.910232	5.960104	Cu	4.707553	6.378960	11.164399	H	15.005700	3.213355	15.362245
H	11.308123	15.982663	5.796720	P	11.228128	7.442283	15.439258	C	9.598771	8.849838	3.682404
C	-5.819648	15.490112	6.000537	P	9.999690	5.801369	5.162796	C	7.400526	10.228825	4.156363
H	15.240264	13.453652	5.866787	P	-1.124806	10.826419	11.117459	H	5.965769	9.478731	5.407221
C	-3.479836	16.667497	6.221013	F	0.724496	9.215740	9.271617	C	7.066147	12.601655	3.072460
H	-1.753395	15.575417	6.295053	F	0.899399	10.452558	13.404503	H	5.400519	13.688583	3.545959
C	4.159569	-2.200587	6.411335	F	-2.977975	12.344344	12.993578	C	8.895435	13.573679	1.461189
H	5.970837	-1.281563	6.664940	F	-3.157501	11.100660	8.851161	H	8.628888	15.403422	0.583434
C	-0.109997	3.913339	4.528134	F	0.231899	13.399831	10.304913	C	11.086790	12.200525	0.958670
C	-0.080855	2.909235	2.077358	F	-2.497989	8.170177	11.964401	H	12.504495	12.960370	-0.299794
H	1.149434	1.338269	1.630303	N	6.081682	11.464556	10.143793	C	11.450138	9.857664	2.079677
C	19.519737	3.909002	0.221974	N	6.859738	9.041565	10.393073	H	13.134979	8.782814	1.663904
H	19.172198	-8.331491	20.608089	N	10.793045	6.599520	10.295422	C	11.716409	3.864353	2.922639
C	17.947912	5.949081	0.763567	C	8.154442	12.848884	9.725822	C	11.202127	4.148271	0.343469
H	16.381254	-4.745125	21.562700	H	8.002101	14.862634	9.482234	H	9.903547	5.588381	-0.295646
C	-3.206878	6.981756	3.174057	C	10.335550	11.350511	9.688309	C	12.004132	-8.856170	20.840268
H	-4.378122	8.595370	3.624383	H	12.265978	11.945512	9.439963	H	11.600093	-8.562350	18.859578

C	13.651970	-10.741740	21.631822	H	8.278564	20.417110	2.559235	O	3.221497	16.006981	6.664004
H	7.023143	9.518848	20.249871	C	13.390762	1.971984	3.698765	H	3.211004	14.586732	7.811121
C	14.515707	0.398109	1.924115	H	13.813331	1.673101	5.665783	H	3.512261	17.438011	7.751563

1·4MeOH

CELL

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-1.1989028423230075E+00	-6.0755859522528031E+00	1.2070545967347677E+01

Au	5.188841	4.866797	6.774853	C	-1.406161	-7.129919	15.844293	H	-2.198222	1.582209	18.539491
Cu	3.351864	7.269750	11.128558	H	0.345353	-6.074170	15.830825	C	-0.095709	-1.607677	19.861855
P	9.072980	6.611983	5.832480	C	11.551021	13.682538	16.015429	H	-1.763639	-2.710821	20.280738
P	9.387678	8.908913	15.957939	H	-7.490179	12.725517	16.137532	C	2.296777	-2.634855	20.266304
P	-2.797878	11.414090	9.810331	C	11.244105	7.942835	18.654263	H	2.472879	-4.544899	20.977159
F	-0.636737	9.955434	8.228169	C	10.491782	8.896394	21.010219	C	4.444720	-1.224616	19.732925
F	-1.116676	11.144433	12.351857	H	8.978780	10.269778	21.125219	H	6.312534	-2.015296	19.983481
F	-5.014773	12.828991	11.415245	C	13.938626	19.561184	0.395566	C	4.212925	1.221799	18.796845
F	-4.529314	11.628266	7.286409	H	13.348987	20.298101	2.207535	H	5.886266	2.307022	18.339895
F	-1.509801	14.111579	9.198698	C	-4.972883	17.777990	0.265963	C	-0.266549	7.289361	19.120547
F	-4.162879	8.719282	10.455990	H	-4.034457	17.149562	1.970817	C	-0.262817	6.735999	21.706032
N	4.704921	12.294992	9.937882	C	-6.485288	5.362854	20.744811	H	0.641107	5.039543	22.398193
N	5.517108	9.933838	10.462524	H	-4.969392	4.003342	20.639070	C	0.819722	19.843123	0.586948
N	9.488515	7.597965	10.933001	C	13.197202	6.176168	18.533528	H	0.805656	19.371169	2.571638
C	6.776575	13.708042	9.607866	H	13.816443	5.396802	16.755171	C	-2.626271	10.544268	22.534849
H	6.607495	15.682102	9.137194	C	7.356184	-7.075676	15.512449	H	6.706437	-0.136475	1.057741
C	8.987640	12.286036	9.917406	H	7.736215	-5.656252	16.951630	C	-2.631750	11.108553	19.969012
H	10.920780	12.905417	9.784145	H	7.835796	-6.284840	13.666155	H	-3.502668	12.820007	19.263955
C	8.081916	9.897725	10.452741	H	0.586253	14.698869	15.845304	C	-1.447032	9.495779	18.264373
C	11.060512	6.968217	8.670166	O	4.744348	-7.696582	15.691398	H	-1.431909	9.995200	16.285132
H	12.052188	5.200616	9.028143	H	-3.655515	14.756676	14.219511	C	1.321471	-0.352423	6.786895
H	12.459648	8.447894	8.334802	C	-0.936203	12.541419	2.500610	C	3.642256	-1.599830	6.881408
C	11.203344	8.009569	13.136225	H	-0.041544	10.750923	3.003568	H	5.380143	-0.518179	6.909381
H	12.579262	9.487963	12.714643	H	-0.527833	12.931725	0.523900	C	-4.256442	19.207813	7.031854
H	12.206957	6.258173	13.498223	H	-2.977815	12.344252	2.740813	H	-2.465053	18.233405	7.129937
C	8.793040	9.698149	4.438499	O	0.037068	14.592382	3.925708	C	-6.499333	17.839704	7.100863
C	10.953619	11.127600	3.902249	H	-0.027159	14.134043	5.688649	H	-6.434900	15.803335	7.259576
H	12.814882	10.366966	4.270519	Au	5.427881	7.082304	16.035203	C	12.022837	19.079036	6.965715
C	10.712320	13.556808	2.948143	Cu	7.264867	4.679358	11.681395	H	10.271327	18.023280	6.979247
H	12.380235	14.659973	2.529261	P	1.543707	5.337126	16.977492	C	-0.934329	-1.733415	6.794608
C	8.319819	14.583949	2.543693	P	1.229033	3.040220	6.852044	H	18.106872	-0.776382	6.672519
H	8.143692	16.493993	1.832850	P	13.413748	0.534830	13.000415	C	-0.627407	4.006253	4.155713
C	6.171898	13.173686	3.077083	F	11.252748	1.993643	14.582184	C	0.124881	3.052667	1.799755
H	4.304064	13.964318	2.826518	F	11.732993	0.804611	10.458546	H	1.637844	1.679244	1.684764
C	6.403727	10.727268	4.013145	F	15.630956	-0.879626	11.395737	C	-3.321967	-7.612116	22.414409
H	4.730394	9.642022	4.470102	F	15.145187	0.320713	15.524277	H	-2.732365	-8.349074	20.602448
C	10.883232	4.659715	3.689450	F	12.125767	-2.162954	13.611782	C	15.589594	-5.828870	22.544010
C	10.879593	5.213068	1.103959	F	14.779093	3.229669	12.354582	H	14.651147	-5.200464	20.839154
H	9.975727	6.909525	0.411738	N	5.911769	-0.345835	12.872043	C	17.102036	6.586299	2.065157
C	9.797099	-7.894060	22.223068	N	5.099598	2.015302	12.347392	H	15.586177	7.945849	2.170889
H	9.811240	-7.422107	20.238371	N	1.128187	4.351165	11.876967	C	-2.580461	5.772971	4.276438
C	13.243051	1.404796	0.275222	C	3.840148	-1.758897	13.202082	H	-3.199651	6.552372	6.054797
H	3.910382	12.085552	21.752338	H	4.009263	-3.732952	13.672767	C	3.260548	19.024811	7.297571
C	13.248395	0.840501	2.841064	C	1.629055	-0.336906	12.892558	H	2.880552	17.605290	5.858467
H	14.119250	-0.870963	3.546164	H	-0.304050	-0.956336	13.025858	H	2.780959	18.234079	9.143913
C	12.063632	2.453274	4.545678	C	2.534798	2.051414	12.357207	H	10.030436	-2.749801	6.964558
H	12.048409	1.953838	6.524922	C	-0.443802	4.980926	14.139789	O	5.872383	19.645780	7.118641
C	9.295232	12.301540	16.023105	H	-1.435501	6.748519	13.781809	H	14.272240	-2.807517	8.590556
C	6.974440	13.548915	15.928495	H	-1.842982	3.501281	14.475140	C	11.552795	-0.592345	20.309487
H	5.236577	12.467223	15.900490	C	-0.586648	3.939570	9.673758	H	10.658119	1.198129	19.806519
C	14.873109	-7.258731	15.778028	H	-1.962531	2.461132	10.095334	H	11.144297	-0.982757	22.286145
H	13.081706	-6.284352	15.679927	H	-1.590277	5.690974	9.311798	H	13.594413	-0.395099	20.069416
C	17.115998	-5.890615	15.709069	C	1.823631	2.250950	18.371471	O	10.579658	-2.643247	18.884231
H	17.051540	-3.854246	15.550362	C	-0.336971	0.821531	18.907728	H	10.644132	-2.184885	17.121312

Triplet for 1

CELL

10.97544182	0.00000000	0.00000000
3.61735786	11.40140194	0.00000000
3.84669792	5.35682306	11.62018304

Au	16.802553	16.601325	15.579899	F	26.790632	22.362626	9.555165	C	11.903828	16.893747	7.573504
Cu	19.217254	17.249093	10.890760	F	22.985353	24.207232	10.471003	H	10.645622	18.460139	7.107017
N	17.623260	22.453925	10.213825	F	26.042541	19.281188	12.407553	H	10.787030	15.181817	7.731729
N	16.956349	20.008384	10.408892	C	15.518543	23.733031	9.653948	C	12.565370	21.518529	15.576337
N	13.151932	17.357386	10.048486	H	15.593982	25.753089	9.436347	C	10.204167	22.696704	15.770081
P	12.713438	18.146872	15.166447	C	13.423991	22.123144	9.464715	H	29.232145	21.585762	15.792616
P	14.211929	16.509593	4.947590	H	11.481808	22.617199	9.112955	C	30.799923	25.312082	15.899184
P	24.443702	21.787303	11.438823	C	14.442255	19.769751	9.953163	H	28.978463	26.225630	16.043478
F	23.132096	19.985130	9.255675	C	11.215495	17.465803	12.082772	C	12.262214	26.753416	15.829683
F	22.135432	20.951841	13.312489	H	10.233696	15.664842	12.158505	H	12.142474	28.791515	15.917685
F	25.724058	23.374583	13.709559	H	9.836929	18.958824	11.716357	C	14.608627	25.591194	15.630573

H	16.311089	26.714589	15.500317	H	10.279543	12.450132	5.333033	C	20.070284	8.732202	6.434768
C	14.765526	22.969634	15.511011	Au	18.070111	15.084849	6.418656	H	18.264903	9.663164	6.688593
H	16.585289	22.067594	15.271383	Cu	15.674820	14.411296	10.805216	C	24.341406	14.868051	4.408656
C	10.602825	16.809936	17.505283	N	17.108741	9.328146	12.156837	C	24.416112	13.803888	1.985776
C	10.499860	17.941916	19.895398	N	17.829073	11.748977	11.867724	H	23.299733	12.140559	1.578097
H	11.570556	19.644152	20.261317	N	21.717055	14.289148	11.842899	C	5.166803	14.867348	0.113466
C	29.750146	16.905533	21.788437	P	22.137213	13.545758	6.664525	H	12.510071	24.139924	20.220161
H	22.382308	7.679470	1.659468	P	20.705720	15.073507	16.913236	C	6.559159	17.046293	0.603946
C	28.382617	14.703532	21.342838	P	10.389932	9.866080	10.520632	H	14.969446	27.989423	21.077664
H	19.963903	3.791433	0.879663	F	11.697444	11.616152	12.721865	C	27.193238	18.140538	2.986642
C	7.784002	13.543312	18.992178	F	12.709903	10.712899	8.650154	H	28.227037	19.857684	3.391343
H	6.777583	11.802142	18.624958	F	9.114733	8.290532	8.242700	C	25.741165	17.053178	4.892313
C	9.242386	14.590321	17.071605	F	8.027123	9.298762	12.396791	H	25.678782	17.963815	6.713123
H	9.331507	13.629258	15.278391	F	11.845266	7.438417	11.478470	C	20.289010	12.011269	18.351194
C	14.612524	19.616055	3.578259	F	8.807914	12.385094	9.553706	C	18.078799	10.653179	17.891847
C	16.761608	21.012904	4.201623	C	19.219535	7.983516	12.491736	H	16.619279	11.427715	16.688970
H	18.176832	20.223251	5.449907	H	19.101912	5.967633	12.732291	C	24.600305	29.804320	18.927437
C	10.231041	1.908899	3.283406	C	21.374850	9.524472	12.428536	H	22.900004	28.763002	18.482556
H	11.873327	2.980715	3.859849	H	23.327471	8.969757	12.578075	C	26.450644	28.782221	20.481494
C	8.424974	2.951981	1.687706	C	20.386257	11.905520	12.020910	H	26.196966	26.939039	21.335658
H	8.658443	4.848182	0.954759	C	23.638090	14.134252	9.793450	C	28.649515	30.146237	20.980070
C	6.296031	1.554672	1.019747	H	24.675070	15.905126	9.751375	H	30.080685	29.361190	22.206884
H	4.901383	2.357492	-0.237490	H	24.972299	12.603346	10.155549	C	22.160606	10.966685	19.906422
C	12.796566	20.678738	1.974757	C	22.993574	14.762641	14.295677	H	23.848049	12.035803	20.322162
H	11.154758	19.591566	1.438603	H	24.279241	13.212578	14.751159	C	22.313065	17.007193	19.227815
C	12.490611	14.623609	2.666523	H	24.076043	16.498082	14.150991	C	21.672841	16.700013	21.776438
C	13.117836	14.878545	0.107973	C	22.283239	10.162132	6.300645	H	20.378399	15.219183	22.321796
H	14.451965	16.314553	-0.458075	C	24.625212	8.955026	6.090023	C	15.412960	8.169435	1.642791
C	19.334998	23.414316	20.264900	H	5.607608	10.049047	6.029225	H	14.883832	7.928272	3.603511
H	19.852050	23.630254	18.298088	C	4.001019	6.334343	5.995931	C	17.060613	10.093326	0.941449
C	17.661053	21.524633	21.001445	H	5.810125	5.398852	5.837492	H	17.813356	11.369798	2.355623
H	16.863892	20.261484	19.602721	C	22.526190	4.918596	6.120640	C	24.980034	20.523038	20.375497
C	9.766109	11.127253	1.575511	H	22.618509	2.878390	6.055669	H	26.257690	22.018360	19.815368
H	8.467805	9.661338	2.164674	C	20.194721	6.109286	6.351926	C	23.986617	18.931937	18.539944
C	10.794762	12.728580	3.385033	H	18.485172	5.003514	6.531941	H	24.507027	19.238472	16.598040

Triplet for 1·2H_2O

CELL

1.1036705208502834E+01 0.0000000000000000E+00 0.0000000000000000E+00
-3.3623672291754594E+00 1.1368278169639343E+01 0.0000000000000000E+00
-4.5830841964142544E-01 -6.0444900166508022E+00 1.1792851243773342E+01

Au	6.246027	4.139285	6.598537	C	19.318285	4.021150	0.214728	F	1.578291	10.351511	13.423791
Cu	8.554873	3.618166	11.108586	H	18.376323	-8.235163	20.640021	F	-2.211999	12.445191	12.983287
P	2.166660	2.601808	6.789073	C	17.931166	6.200800	0.719027	F	-2.418036	11.000875	8.854163
P	3.471970	4.349891	17.059748	H	15.922730	-4.391002	21.525699	F	0.995313	13.229768	10.213710
P	14.107192	-0.713977	11.131103	C	-2.816608	7.277381	3.109188	F	-1.960045	8.232525	12.085721
F	12.280135	1.106520	12.898302	H	-3.838381	8.997160	3.531393	N	6.573262	11.718056	10.266867
F	12.062771	-0.296098	8.864534	C	-1.376374	6.164810	5.008126	N	7.220995	9.258166	10.497926
F	15.852696	-2.387979	9.295850	H	-1.330116	7.054460	6.835672	N	11.055886	6.614574	10.276573
F	16.124895	-0.939123	13.416993	C	3.847057	1.303120	18.545666	C	8.701303	12.980527	9.747247
F	12.657703	-3.165888	12.075698	C	6.065672	-0.073305	18.191773	H	8.653496	14.995607	9.492315
F	15.599997	1.828906	10.196229	H	7.581504	0.694100	17.055217	C	10.785790	11.361600	9.621662
N	7.110009	-1.572605	12.446015	C	6.314697	-2.468525	19.247894	H	12.732286	11.850100	9.284480
N	6.434812	0.870157	12.125674	H	8.008072	-3.549760	18.879823	C	9.745468	9.016215	10.108761
N	2.547565	3.429694	11.972128	C	4.377907	-3.470364	20.707601	C	12.976434	6.817244	12.319079
C	4.969102	-2.886139	12.729019	H	4.575877	-5.322680	21.556288	H	14.040262	5.067999	12.409055
H	5.042377	-4.898763	13.004770	C	2.173330	-2.084809	21.113151	H	14.289465	8.362730	11.941820
C	2.844831	-1.319062	12.603034	H	0.680261	-2.856404	22.275430	C	12.339996	6.079817	7.828234
H	0.885060	-1.853210	12.730968	C	1.901725	0.285767	20.027444	H	13.621020	7.622546	7.341511
C	3.877442	1.047651	12.212497	H	0.215061	1.379626	20.374327	H	13.443690	4.364923	8.048642
C	0.647729	3.192046	9.909794	C	1.811607	6.302372	19.323052	C	11.701706	10.819044	15.869643
H	-0.448543	4.922514	9.836455	C	2.410824	6.008081	21.882981	C	-6.759596	11.920100	16.094098
H	-0.638359	1.627316	10.288404	H	3.709393	4.544748	22.463298	H	-5.084212	10.753513	16.088339
C	1.239475	3.971285	14.399100	C	2.209058	19.000905	1.407579	C	-0.181303	-6.957694	16.292715
H	-0.064683	2.442732	14.877218	H	2.689917	18.710295	3.371703	H	1.667822	-6.101259	16.453892
H	0.165952	5.706749	14.191016	C	0.557590	20.909193	0.675577	C	18.513439	-5.453935	16.284150
C	1.915733	-0.766373	6.361566	H	6.112948	0.681227	2.084230	H	-2.160537	-3.425142	16.443107
C	20.385183	-1.880316	6.137781	C	-0.907245	9.797390	20.422245	C	16.129900	-6.538741	16.065021
H	18.706356	-0.718524	6.130016	H	4.168486	-10.199753	19.839253	H	14.441489	-5.388300	16.014297
C	13.815763	16.993586	5.954712	C	0.129374	8.209663	18.605161	C	9.545445	12.333728	15.852743
H	11.970531	16.129534	5.789839	H	-0.362656	8.503455	16.653658	H	7.698679	11.487544	15.612685
C	-4.874763	15.497626	5.984854	O	9.637075	-6.027001	15.382862	C	13.551936	6.075365	17.743604
H	15.810358	13.466852	5.836869	H	9.416072	-4.471036	14.444264	C	13.628591	7.157176	20.158796
C	-2.495866	16.594347	6.211405	H	9.807888	-7.291207	14.084370	H	12.546458	8.843987	20.557910
H	-0.804430	15.449919	6.280715	Au	7.370076	5.923655	15.772110	C	-5.742658	6.089467	22.037842
C	4.076490	-2.276299	6.402035	Cu	5.012591	6.429689	10.969602	H	-4.795726	18.367692	1.602964
H	5.920233	-1.418231	6.632744	P	11.469441	7.461380	15.408229	C	-4.358380	3.904515	21.556028
C	0.016307	3.981229	4.513077	P	10.092139	5.629699	5.161549	H	-2.344124	14.516041	0.755864
C	-0.052626	2.937001	2.080232	P	-0.447294	10.776756	11.163606	C	16.377166	2.791894	19.181856
H	1.052279	1.270366	1.658608	F	1.377445	8.943242	9.389942	H	17.391346	1.063237	18.778643

C	14.929616	3.876719	17.275201	C	11.408521	12.126608	1.188395	C	13.148535	-10.874322	21.582935
H	14.872619	2.961005	15.461575	H	12.892575	12.900872	0.016334	H	7.628090	9.370443	20.181971
C	9.739023	8.706601	3.718123	C	11.664548	9.726777	2.216772	C	14.606236	0.253405	1.838754
C	7.553793	10.114674	4.156844	H	13.329662	8.617944	1.816677	H	9.550619	20.272142	2.431458
H	6.053402	9.344796	5.315659	C	11.844224	3.725461	2.918025	C	13.548946	1.841654	3.645859
C	7.315284	12.532338	3.152991	C	11.245610	3.989698	0.353464	H	14.047377	1.567164	5.599236
H	5.653132	13.638931	3.582977	H	9.916373	5.421957	-0.233968	O	4.001417	16.118924	6.860576
C	9.237485	13.535952	1.671988	C	11.473300	-8.990827	20.836456	H	4.139195	14.648622	7.937195
H	9.053337	15.415099	0.882000	H	10.991187	-8.711111	18.870430	H	4.115088	17.517194	8.018180

Triplet for 1·4MeOH

CELL

12.01637485 0.00000000 0.00000000

-4.69961786 13.17957400 0.00000000

-1.50006367 -6.10678794 12.92039636

Au	5.410555	5.564826	7.521619	C	-2.184812	-7.907076	17.055796	H	-2.319346	2.367834	19.469278
Cu	3.683162	8.121436	12.094347	H	-0.404588	-6.897135	17.101151	C	-0.224370	-0.786291	20.896657
P	9.390312	7.296964	6.706591	C	11.648668	14.372493	17.140174	H	-1.901353	-1.867686	21.343251
P	9.391671	9.618363	16.975668	H	-9.275585	13.378306	17.282217	C	2.163664	-1.803705	21.355620
P	-3.398293	12.378979	10.364071	C	11.386378	8.767551	19.640504	H	2.333485	-3.683904	22.142136
F	-1.268281	10.814559	8.762198	C	10.629782	9.740089	21.989337	C	4.321976	-0.416000	20.794683
F	-1.705965	12.043382	12.913988	H	8.995849	10.967284	22.100920	H	6.184620	-1.203524	21.106484
F	-5.529995	13.908883	11.994980	C	14.786533	20.677473	-0.243049	C	4.094464	1.998373	19.775811
F	-5.096772	12.679477	7.834300	H	14.189336	21.444321	1.557421	H	5.770420	3.086218	19.330116
F	-1.968532	14.993775	9.751062	C	-5.826183	19.082554	-0.371449	C	-0.469371	8.032141	19.831579
F	-4.833738	9.736042	10.994289	H	-4.779969	18.619836	1.324920	C	-0.645434	7.467073	22.412152
N	5.078165	13.107644	10.185757	C	-7.910390	6.565966	21.726670	H	0.213696	5.767270	23.152273
N	5.814589	10.761849	10.833072	H	-6.274769	5.346436	21.611930	C	0.920735	20.632012	-0.375429
N	9.660294	8.382396	11.825366	C	13.478948	7.164399	19.525754	H	0.782042	20.145619	1.607296
C	7.176632	14.515738	10.124245	H	14.108809	6.354457	17.761497	C	-3.004441	11.300897	23.114244
H	7.073137	16.489131	9.619651	C	7.270537	-7.054369	16.565146	H	7.726468	-0.802026	-0.030583
C	9.327491	13.099118	10.752339	H	7.455234	-5.785293	18.178317	C	-2.825980	11.885033	20.556015
H	11.259961	13.729323	10.855954	H	7.920524	-6.058805	14.874037	H	-3.656116	13.603288	19.813372
C	8.355362	10.720121	11.196935	H	-0.391595	16.208692	16.868663	C	-1.559953	10.262650	18.917043
C	11.288783	7.628859	9.636415	O	4.678740	-7.755941	16.391609	H	-1.418999	10.770568	16.942455
H	12.200722	5.826811	10.061605	H	-4.415417	16.142208	14.887964	C	1.502857	0.303295	7.507361
H	12.763358	9.043785	9.319977	C	-0.898059	13.788242	2.693817	C	3.798923	-0.992884	7.574459
C	11.270031	8.718846	14.129533	H	-0.106434	11.907306	3.021936	H	5.559725	0.042093	7.697736
H	12.714241	10.157362	13.789544	H	-0.562387	14.302487	0.725972	C	-5.062936	21.281071	7.547026
H	12.214853	6.923366	14.490887	H	-2.937804	13.703728	3.021935	H	-3.284239	20.274976	7.626350
C	9.238629	10.345856	5.203695	O	0.289746	15.660092	4.209792	C	-7.327105	19.947220	7.467275
C	11.458517	11.683500	4.653338	H	0.063738	15.197016	5.958743	H	-7.296705	17.900866	7.493845
H	13.290490	10.917984	5.148777	Au	5.367912	7.885213	16.776072	C	13.081596	21.236886	7.381881
C	11.312796	14.017834	3.466490	Cu	7.278879	5.501673	12.569530	H	11.307262	20.217720	7.323854
H	13.026315	15.046647	3.034951	P	1.503534	6.097146	17.819240	C	-0.773874	-1.043701	7.386889
C	8.964165	15.037870	2.835692	P	1.419494	3.711571	7.586619	H	20.139610	-0.062734	7.304364
H	8.863273	16.862885	1.917840	P	14.358552	1.023306	13.904587	C	-0.398060	4.579076	4.815063
C	6.760239	13.725049	3.391444	F	12.132625	2.357773	15.560984	C	0.456773	3.569798	2.517591
H	4.925755	14.521950	2.962352	F	12.623113	1.264791	11.385265	H	2.074933	2.317304	2.490081
C	6.896558	11.374114	4.565979	F	16.600219	-0.246839	12.207568	C	-3.606147	-7.389199	24.688433
H	5.177657	10.361568	5.018909	F	16.115379	0.785091	16.395122	H	-2.938856	-8.181071	22.923910
C	11.249917	5.300167	4.638174	F	13.180672	-1.738465	14.453000	C	17.002234	-5.797596	24.713998
C	11.497733	5.939431	2.082290	F	15.556887	3.799343	13.322842	H	16.023895	-5.363912	22.969751
H	10.714504	7.689260	1.376805	N	6.051684	0.362362	13.478835	C	18.990480	6.752066	2.569632
C	9.921038	-7.215823	24.848027	N	5.175428	2.699579	12.980860	H	17.355156	7.976680	2.598845
H	10.115676	-6.679519	22.882473	N	1.167324	4.990329	12.650974	C	-2.488333	6.186979	4.829393
C	13.766478	2.063640	1.318550	C	4.022265	-1.072833	13.932145	H	-3.176434	7.022268	6.559447
H	3.029125	14.175802	24.448516	H	4.242894	-3.045363	14.395976	C	3.741655	20.378405	7.839605
C	13.513167	1.407996	3.854504	C	1.776521	0.314863	13.729311	H	3.566815	19.157812	6.188595
H	14.291072	-0.347482	4.566037	H	-0.135169	-0.335457	13.976490	H	3.214704	19.290181	9.515849
C	12.245262	3.010253	5.510199	C	2.608606	2.711225	13.123285	H	11.304062	-2.946649	7.643603
H	12.042215	2.448391	7.464441	C	-0.426708	5.616975	14.895697	O	6.296644	21.221214	7.942291
C	9.367122	13.036948	17.026853	H	-1.457320	7.360491	14.498123	H	15.380907	-2.677729	9.447981
C	7.084141	14.351385	16.889876	H	-1.809198	4.118732	15.232532	C	11.961313	-0.421079	21.660500
H	5.319214	13.317770	16.790807	C	-0.465945	4.661969	10.379330	H	11.128570	1.428815	21.265597
C	15.962774	-7.924479	16.829363	H	-1.914258	3.223116	10.713551	H	11.558496	-0.912356	23.621653
H	14.192925	-6.908638	16.698027	H	-1.401631	6.456467	9.985852	H	14.009275	-0.280636	21.415053
C	18.236827	-6.603773	16.890585	C	1.712513	3.015912	19.281281	O	10.898438	-2.356146	20.129735
H	18.221735	-4.559703	16.788178	C	-0.456666	1.610501	19.850595	H	11.188771	-1.915049	18.384910

Table S1. Selected crystallographic data and refinement parameter for **1**, **1**·2H_2O and **1**·4MeOH

Compound	**1**	**1**·2H_2O	**1**·4MeOH
Formula	$C_{58}H_{52}Au_2Cu_2F_{12}N_6P_6$	$C_{58}H_{56}Au_2Cu_2F_{12}N_6O_2P_6$	$C_{62}H_{68}Au_2Cu_2F_{12}N_6O_4P_6$
Formula weight	1767.89	1803.92	1896.05
Crystal system	triclinic	triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.8076(7)	10.9155(4)	10.6061(5)
b/Å	11.6775(8)	11.8013(5)	12.9767(6)
c/Å	13.5011(10)	13.5470 (6)	13.741 (7)
α/°	64.779 (2)	115.465(2)	112.947(2)
β/°	74.739(3)	91.221(2)	95.182(2)
γ/°	74.868(3)	106.447(2)	106.205(2)
V/Å^3	1465.33(18)	1490.32(11)	1629.29(14)
Z	1	1	1
ρ_{calc}/ *g.cm*^{3}	2.003	2.010	1.932
F(000)	856	876	928
μ/ *mm*$^{-1}$	11.694	11.524	10.574
R^a	0.0237	0.0453	0.0288
wR^b	0.0606	0.1189	0.0739
GOF^c	1.069	1.112	1.072

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. ^{c}GOF = $\{\Sigma w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflection and p = total number of parameters refined.

Table S2. Selected bond lengths (Å) of **1**, **1**·2H_2O and **1**·4MeOH.

	1	**1**·2H_2O	**1**·4MeOH
Cu1-Cu1A	2.6842(8)	2.6575(15)	2.6723(10)
Au1-Cu1	2.8135(4)	2.8420(8)	2.8227(5)
Au1-Cu1A	2.8843(5)	2.8894(8)	2.8726(5)
Cu1-F1	2.3209(19)	2.390(4)	2.402(2)
Cu1-N2	1.936(2)	1.936(4)	1.919(3)
Cu1-N3	2.060(2)	2.051(4)	2.031(3)
Au1-P1	2.3113(7)	2.3149(12)	2.3052(8)
Au1-P2	2.3161(7)	2.3153(12)	2.3093(8)

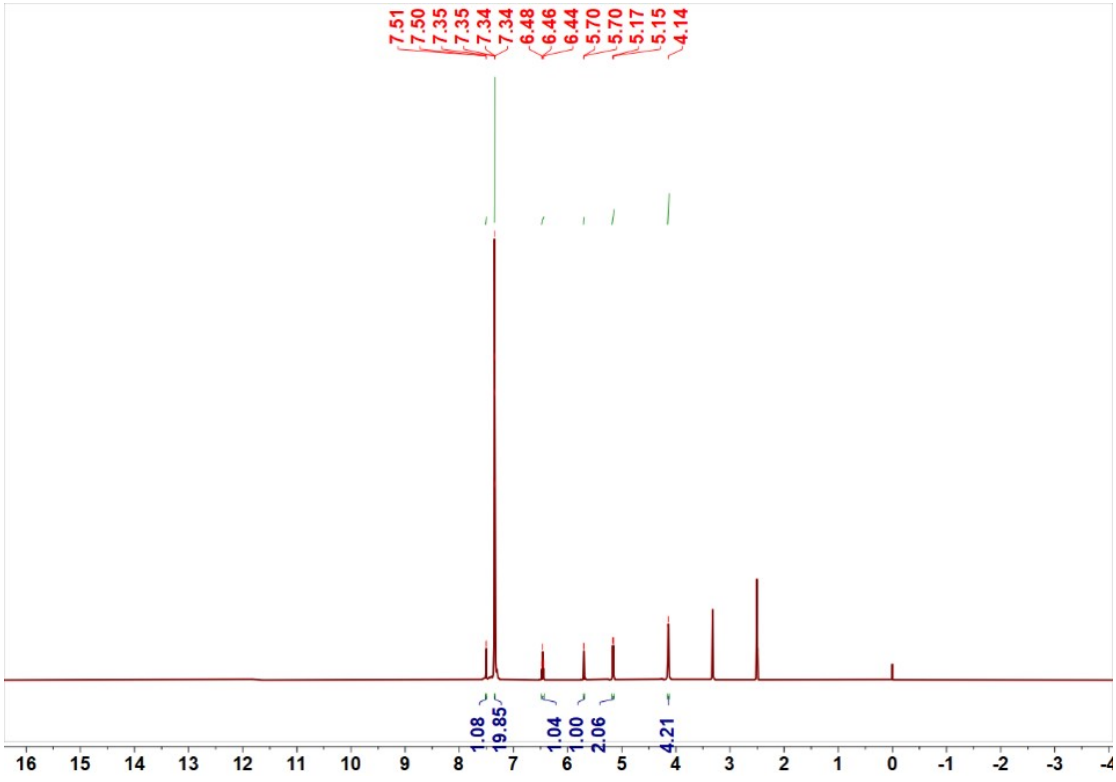

Fig. S1. ^{1}H NMR spectra of 3-dppmapz-1-ol in DMSO-d_6.

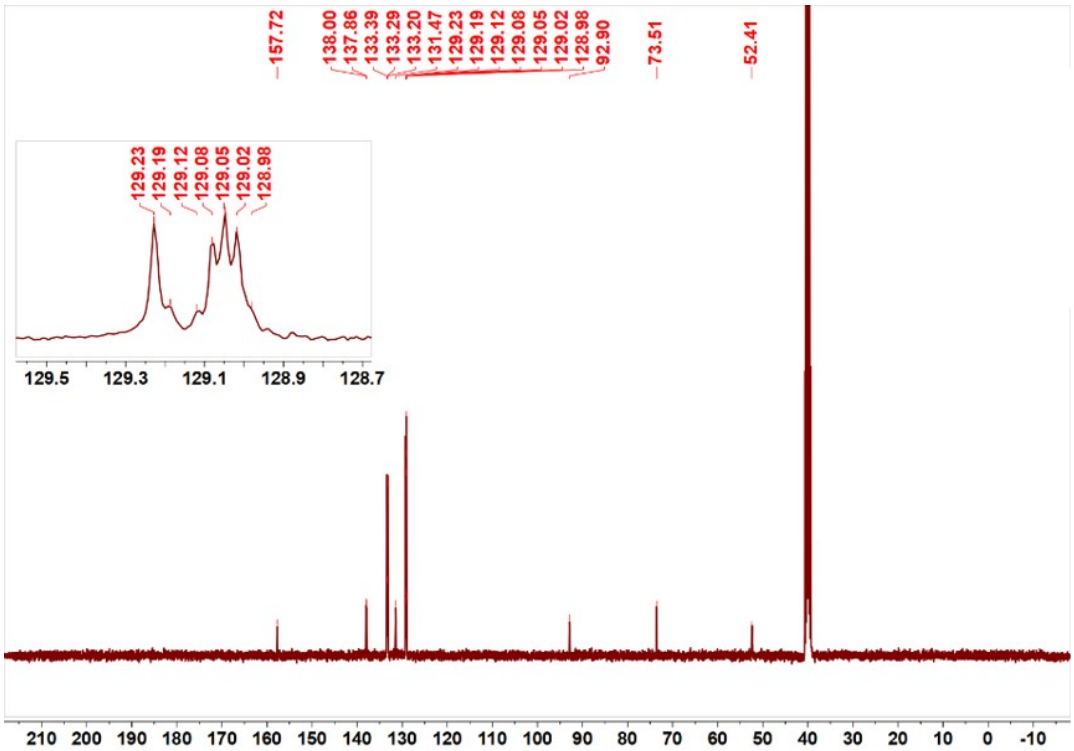

Fig. S2. ^{13}C NMR spectra of 3-dppmapz-1-ol in DMSO-d_6.

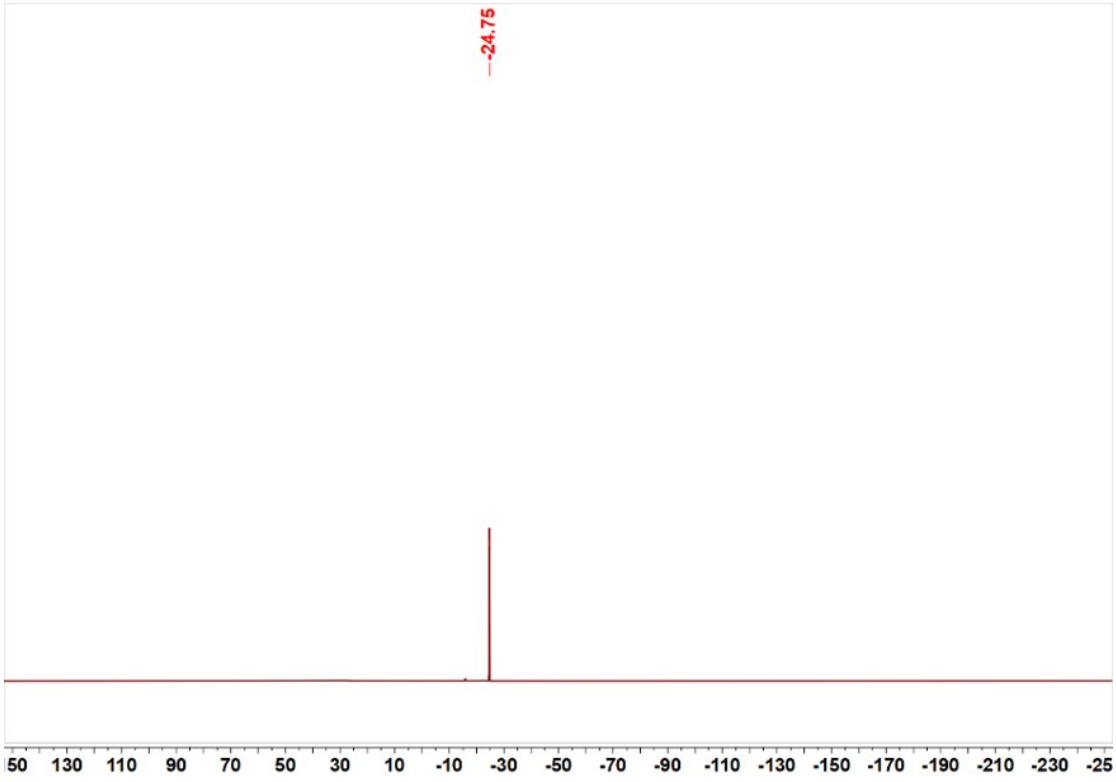

Fig. S3. ^{31}P NMR spectra of 3-dppmapz-1-ol in DMSO-d_6.

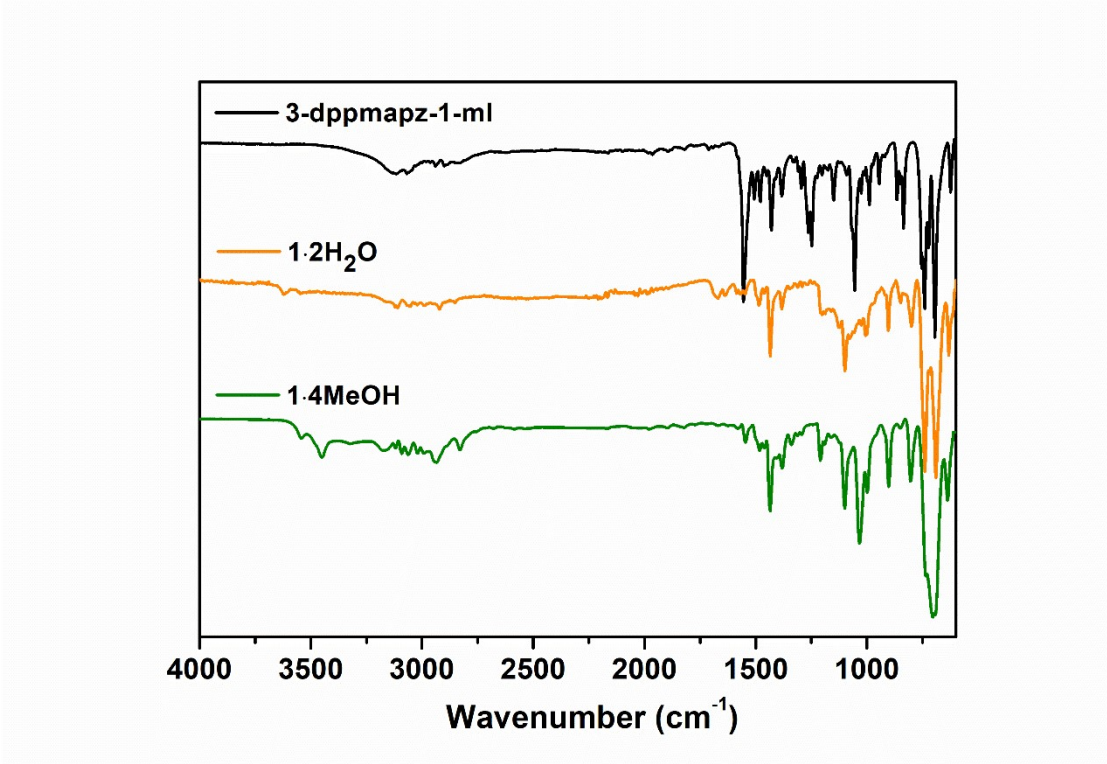

Fig. S4. IR spectra of 3-dppmapz-1-ol (black), **1**·2H_2O (orange) and **1**·4MeOH (green).

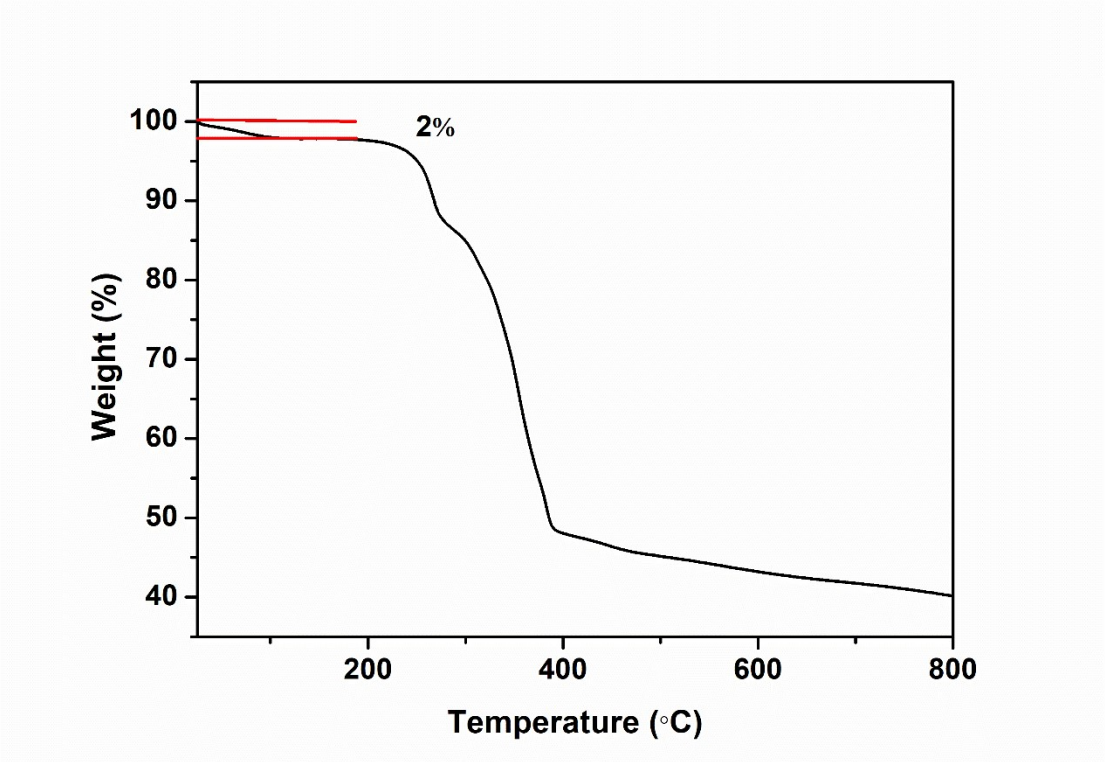

Fig. S5. TGA curve of **1**·2H_2O from room temperature to 800°C.

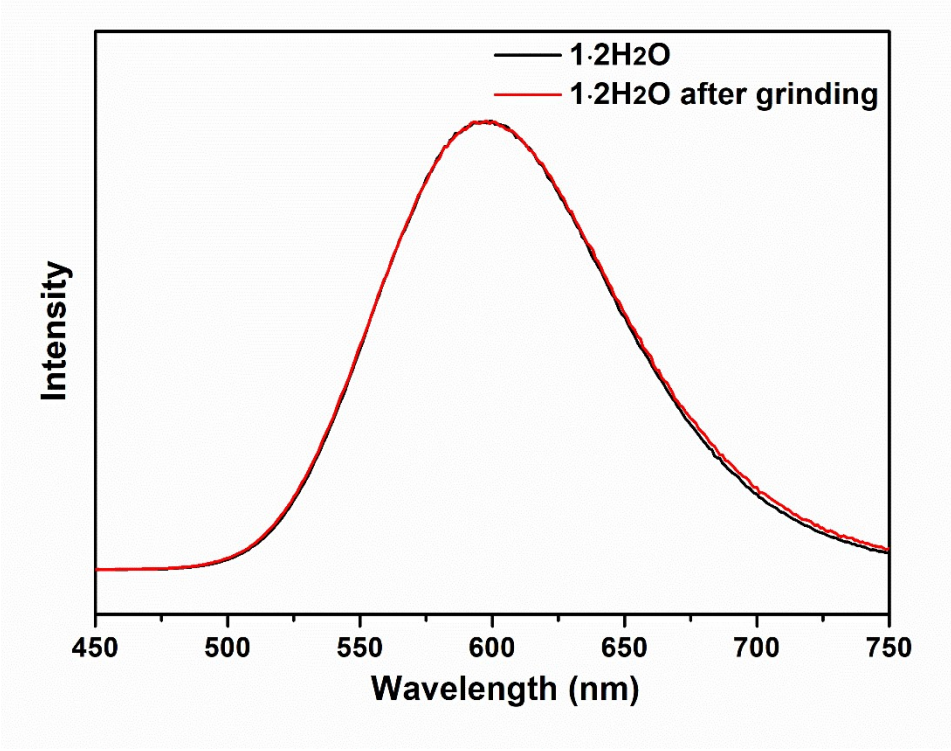

Fig. S6. Solid-state emission spectra of **1** 2H_2O before and after grinding in air for 5 min.

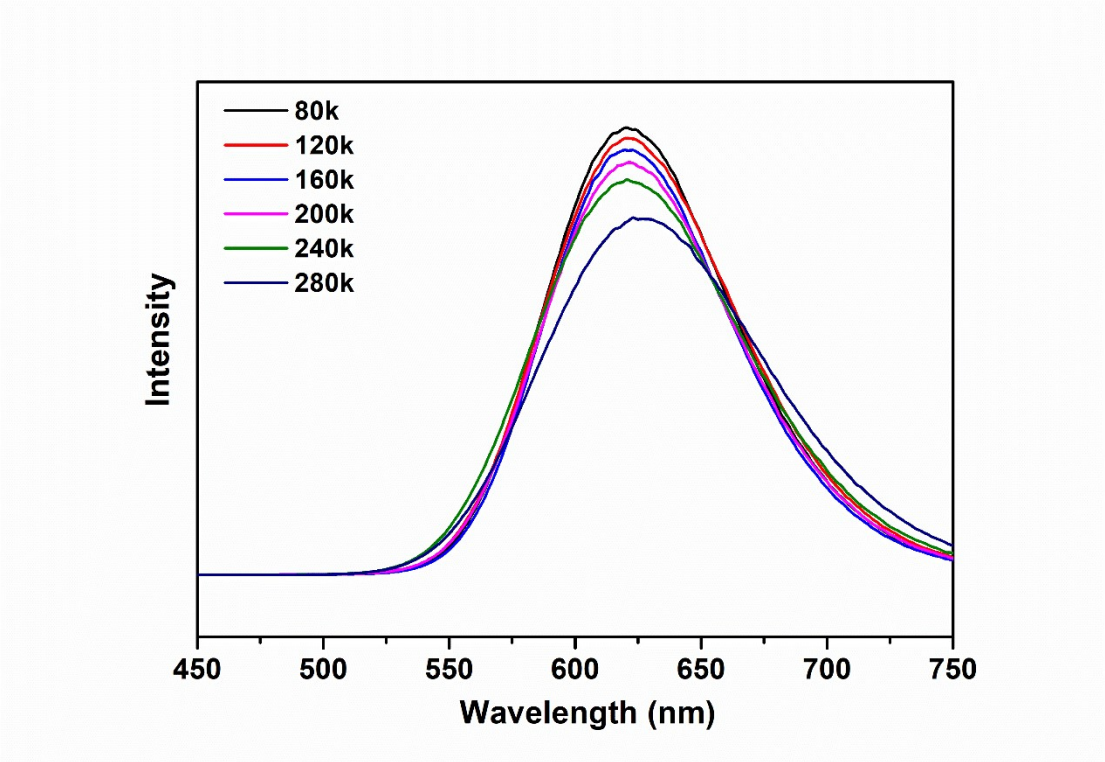

Fig. S7. Solid-state emission spectra of **1** at 80–280 K under 365 nm excitation.

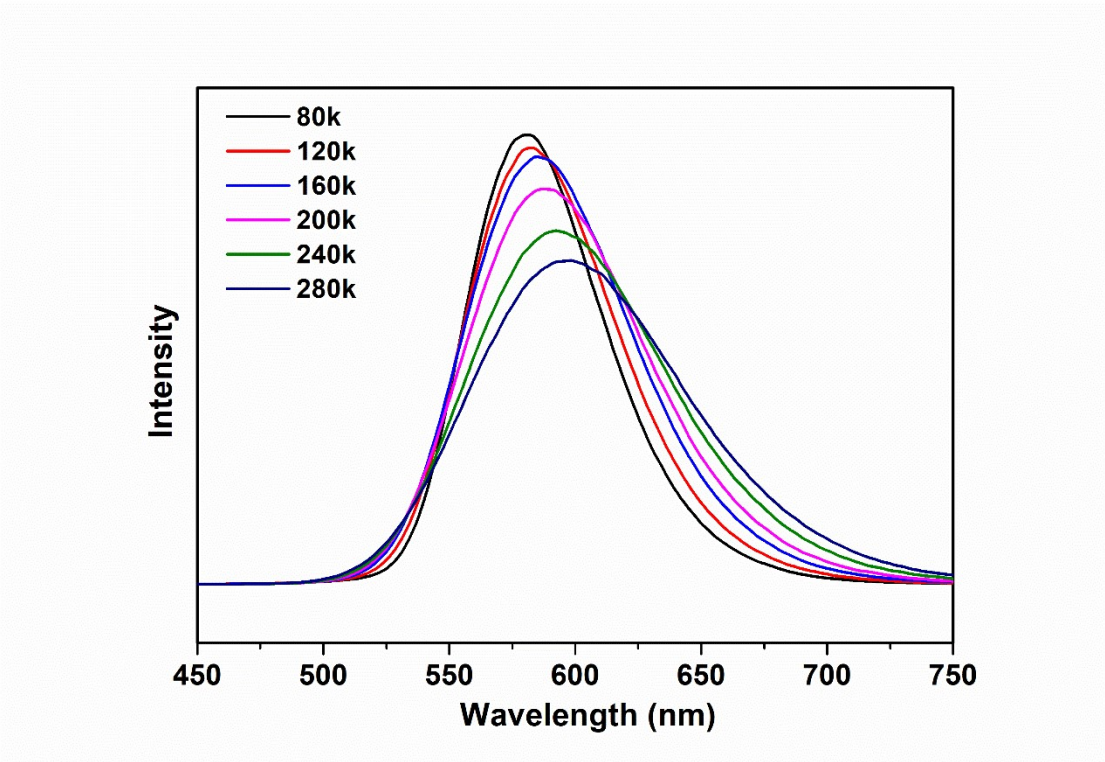

Fig. S8. Solid-state emission spectra of **1**·2H_2O at 80–280 K under 365 nm excitation.

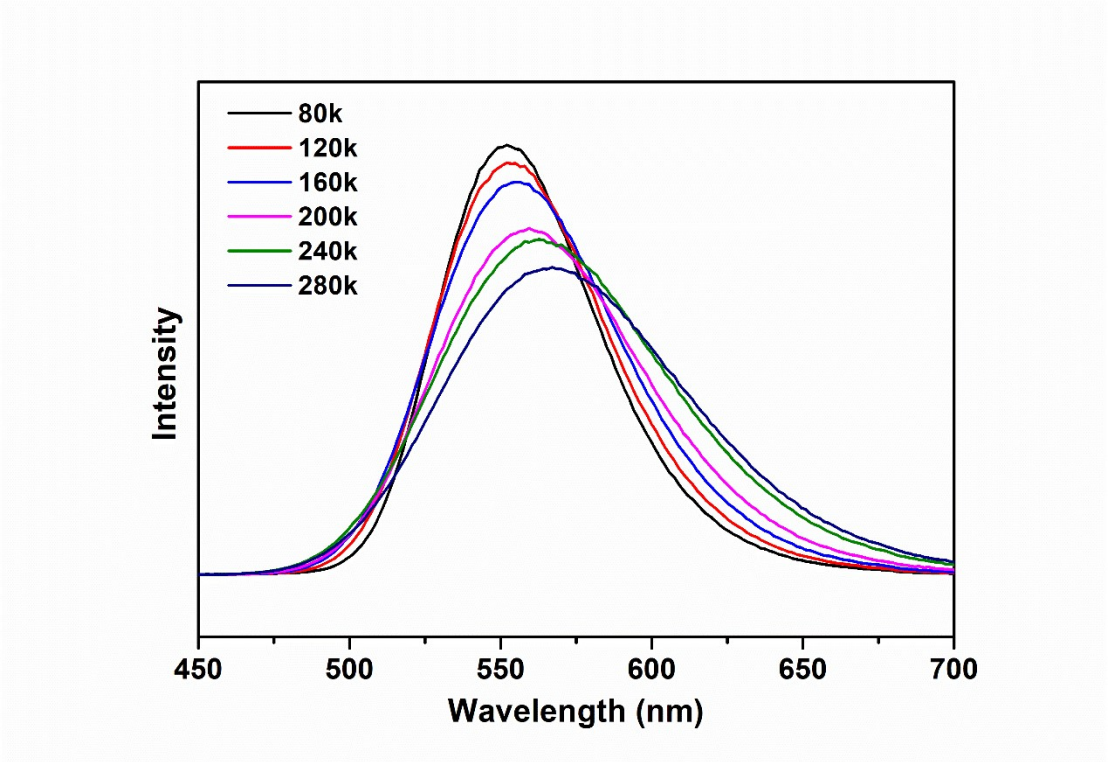

Fig. S9. Solid-state emission spectra of **1**·4MeOH at 80–280 K under 365 nm excitation.

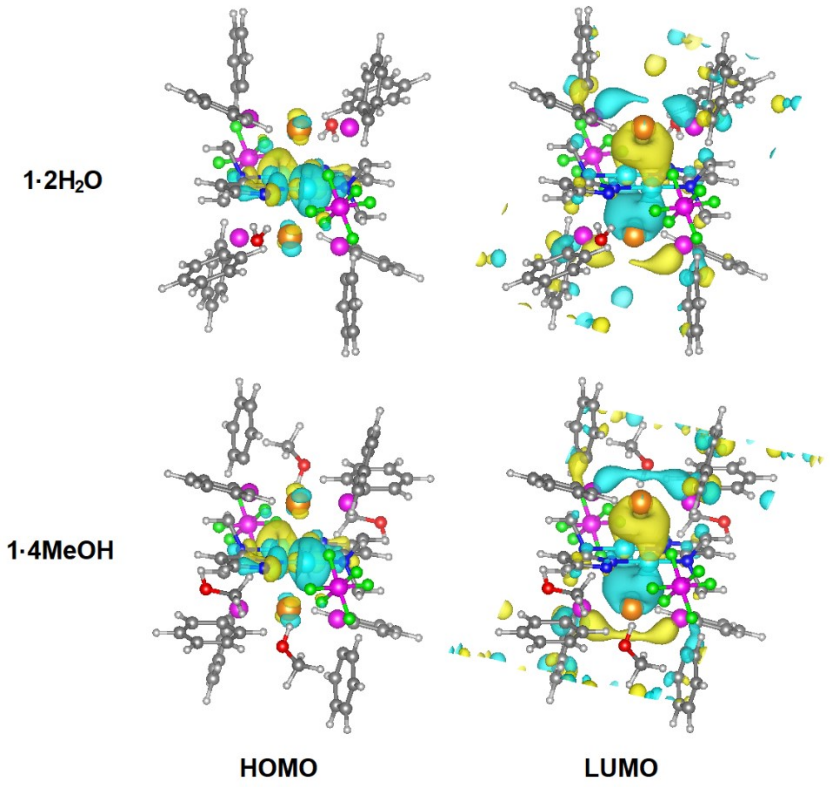

Fig. S10. The distribution of HOMOs and LUMOs for **1**·2H_2O and **1**·4MeOH.

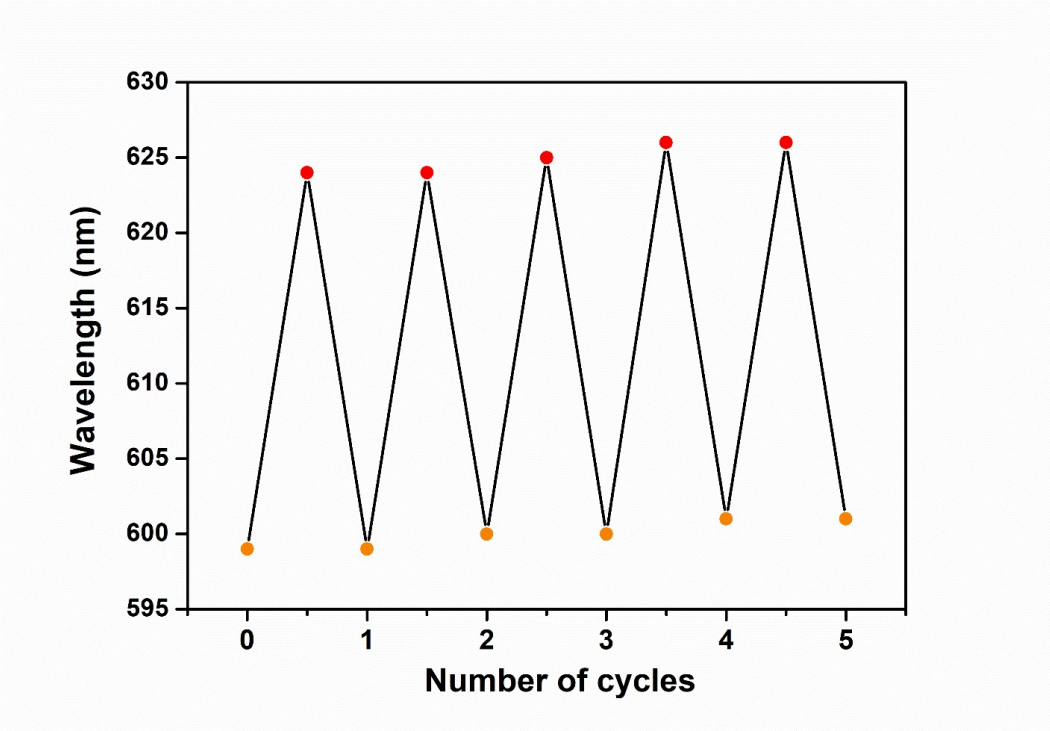

Fig. S11. Emission λ_{max} of **1**·2H_2O when treated with vacuum and air, alternatively.

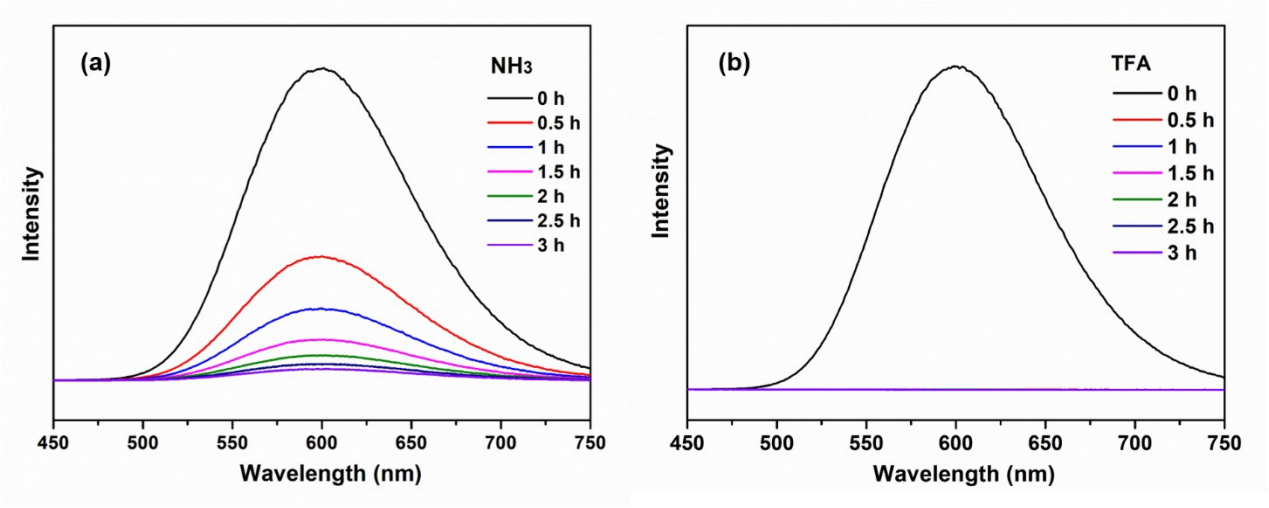

Fig. S12. Solid-state emission spectra of **1** 2H_2O in (a) NH_3 and (b) TFA vapour at 30min time intervals.

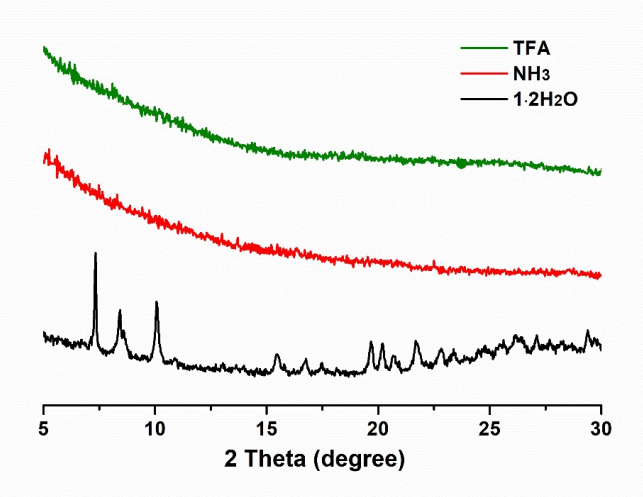

Fig. S13. PXRD patterns of **1** $2H_2O$ and **1** $2H_2O$ after exposure to NH_3 and TFA vapour.

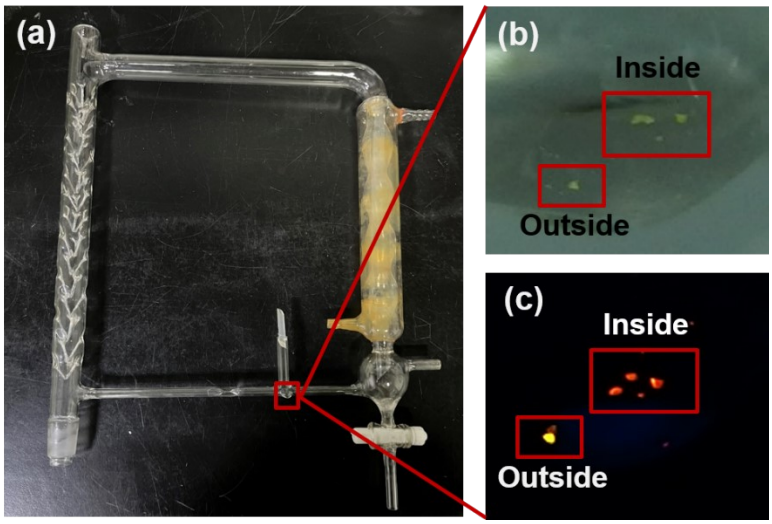

Fig. S14. Photo of the (a) reflux equipment and partial magnification of the return line containing several crystals of **1**·$2H_2O$ under (b) natural light and (c) 365 nm LED excitation.