Electronic Supplementary Information (ESI) for

"Characterization and photocatalytic behavior of 2,9-di(aryl)-1,10-phenanthroline copper(I) complexes"

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^{1}H NMR and ^{13}C NMR Spectra

Fig. S1 ^{1}H NMR spectrum of $[Cu\cdot(\mathbf{1})_2]PF_6$

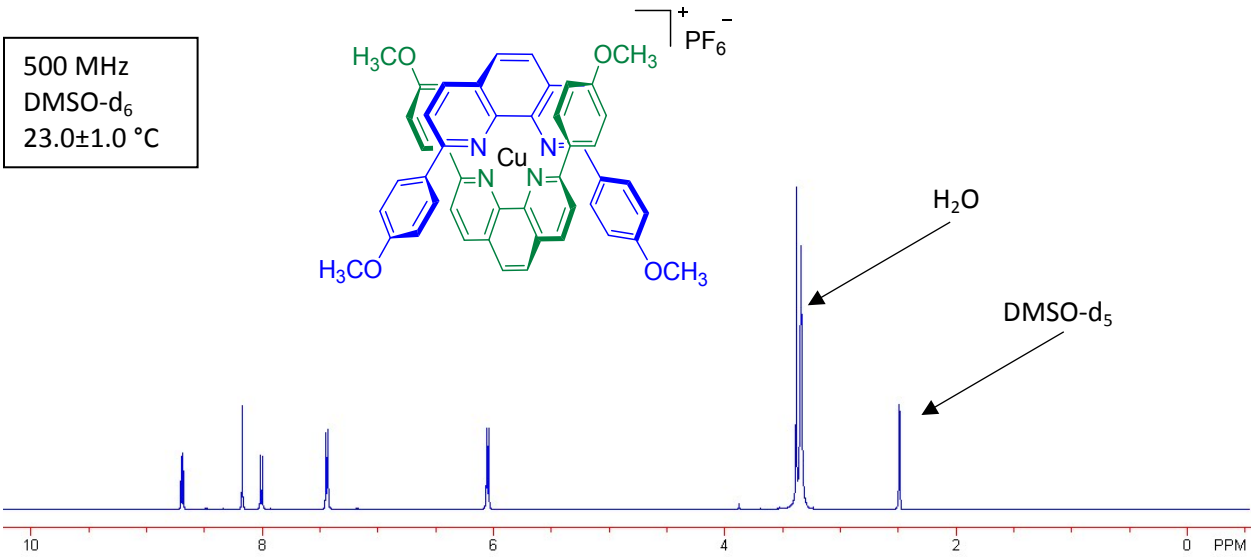

Fig. S2 ^{13}C NMR spectrum of $[Cu\cdot(\mathbf{1})_2]PF_6$

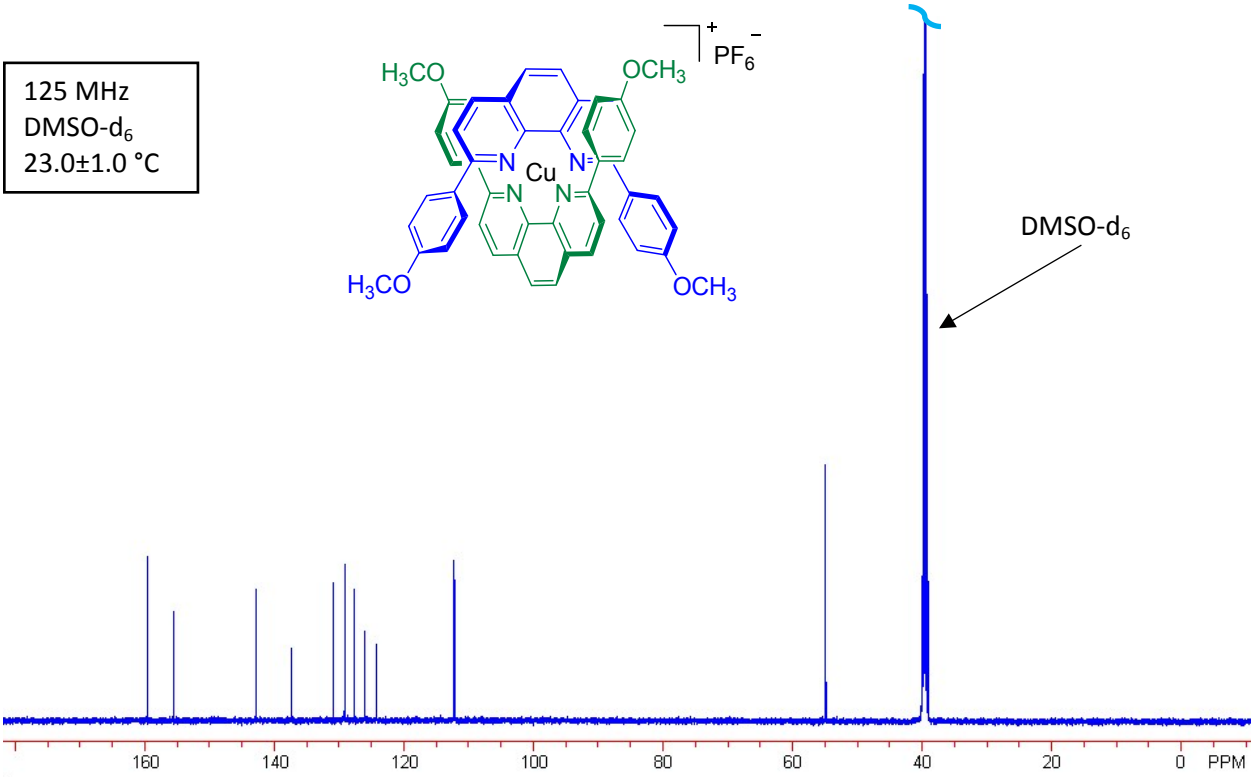

Fig. S3 ^{1}H NMR spectrum of [Cu·(**2**)$_2$]PF$_6$

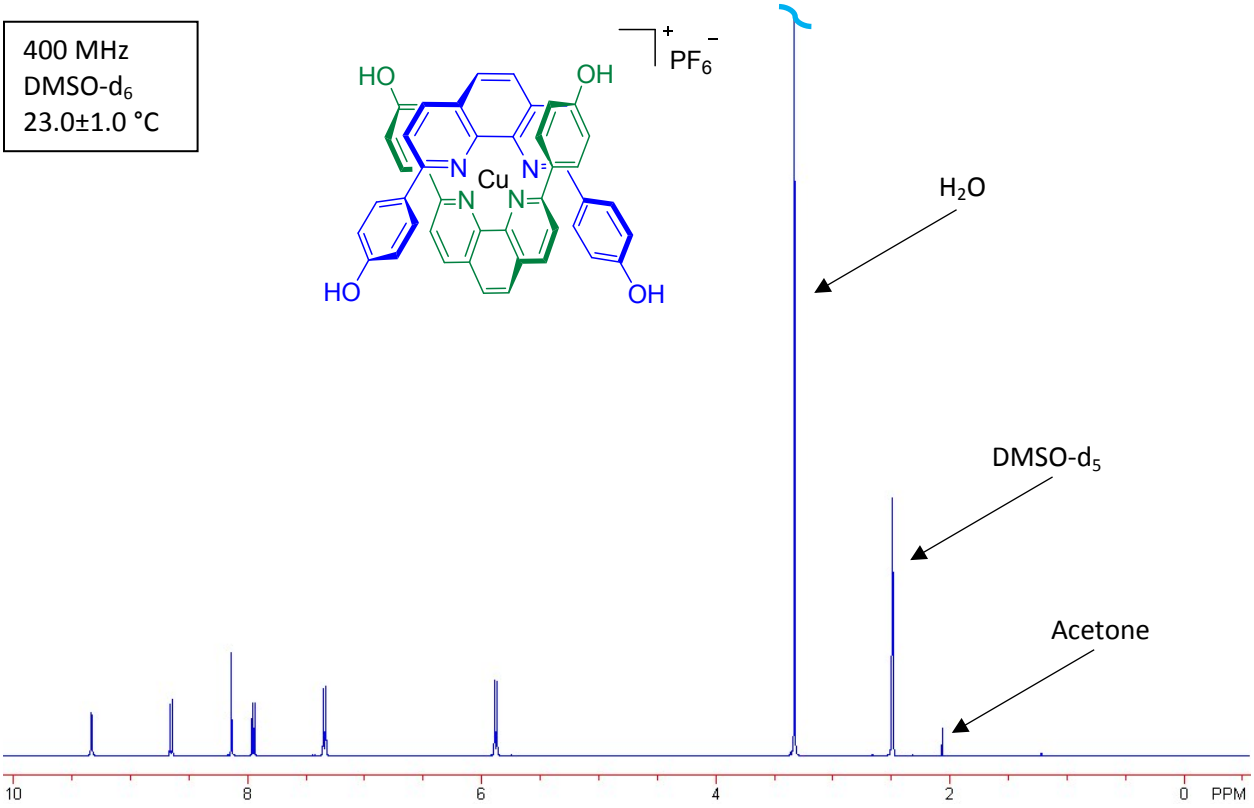

Fig. S4 ^{13}C NMR spectrum of [Cu·(**2**)$_2$]PF$_6$

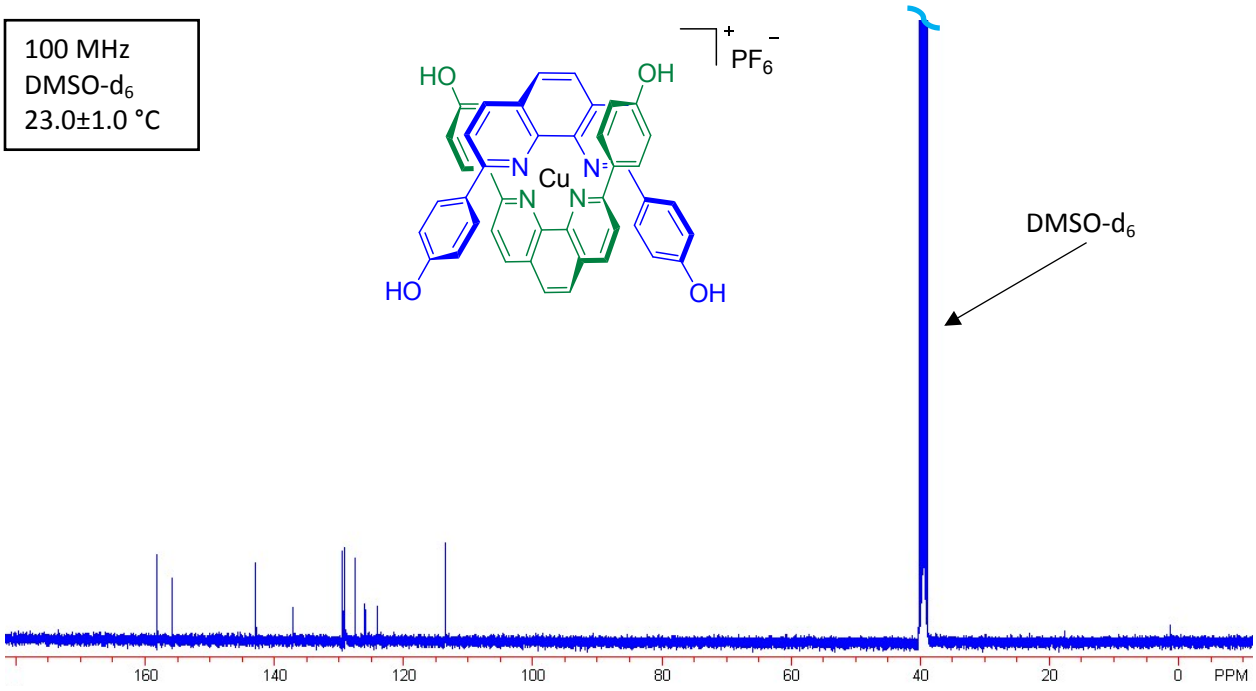

Fig. S5 ^{1}H NMR spectrum of [Cu·(**3**)$_2$]PF$_6$

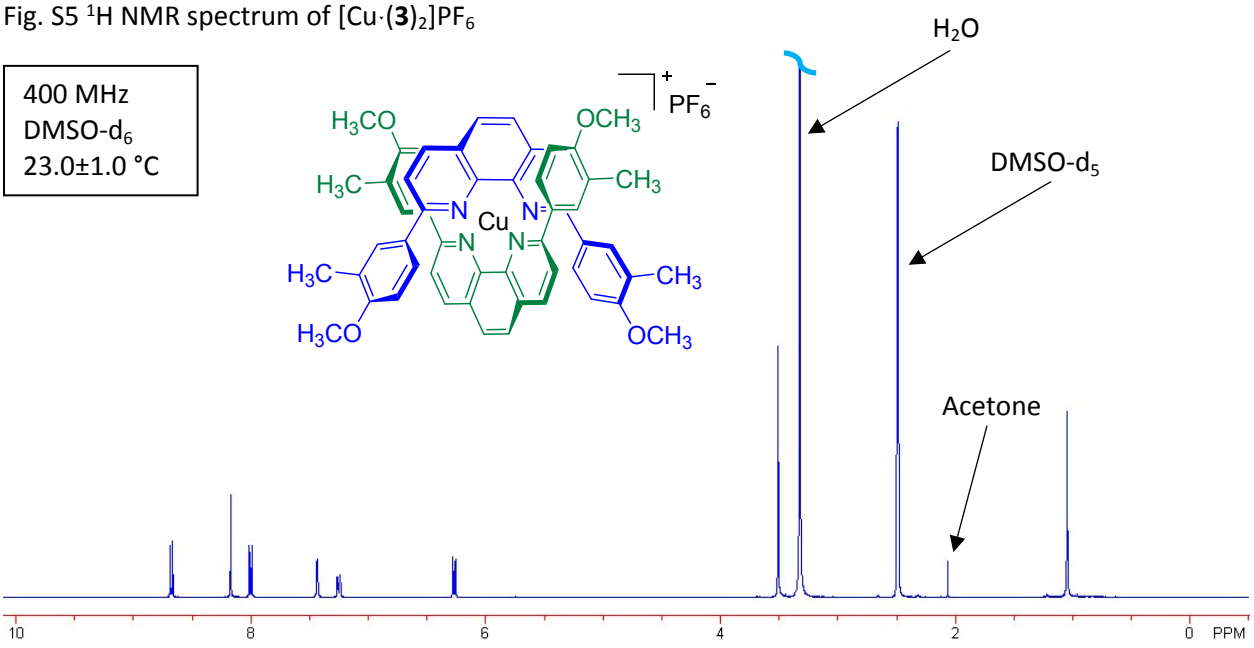

Fig. S6 ^{13}C NMR spectrum of [Cu·(**3**)$_2$]PF$_6$

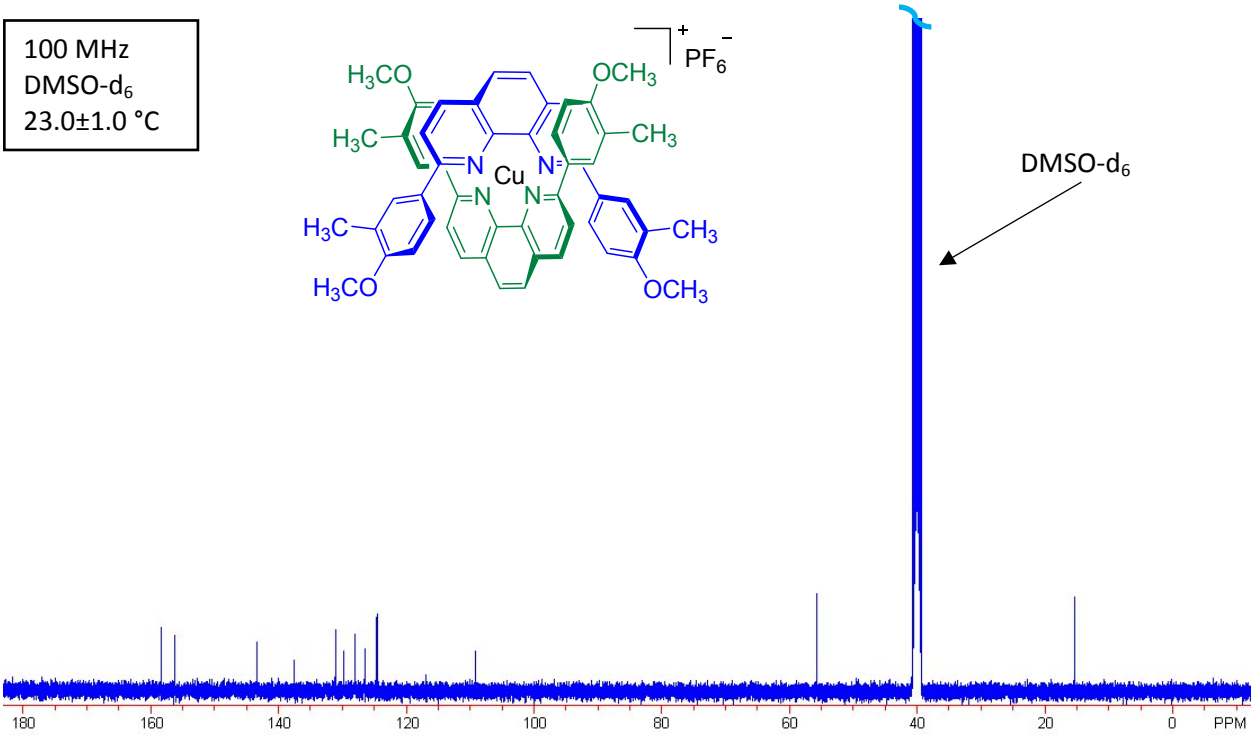

Fig. S7 ^{1}H NMR spectrum of [Cu·(**4**)$_2$]PF$_6$

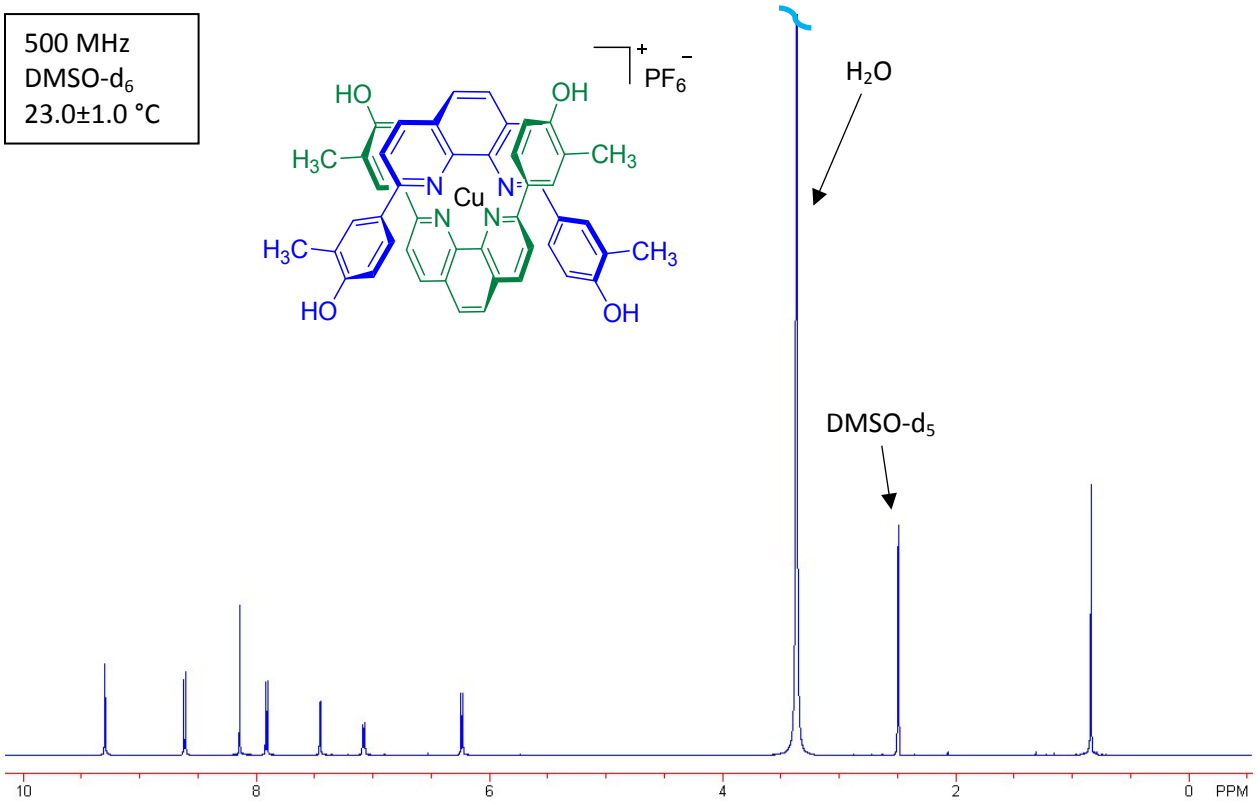

Fig. S8 ^{13}C NMR spectrum of [Cu·(**4**)$_2$]PF$_6$

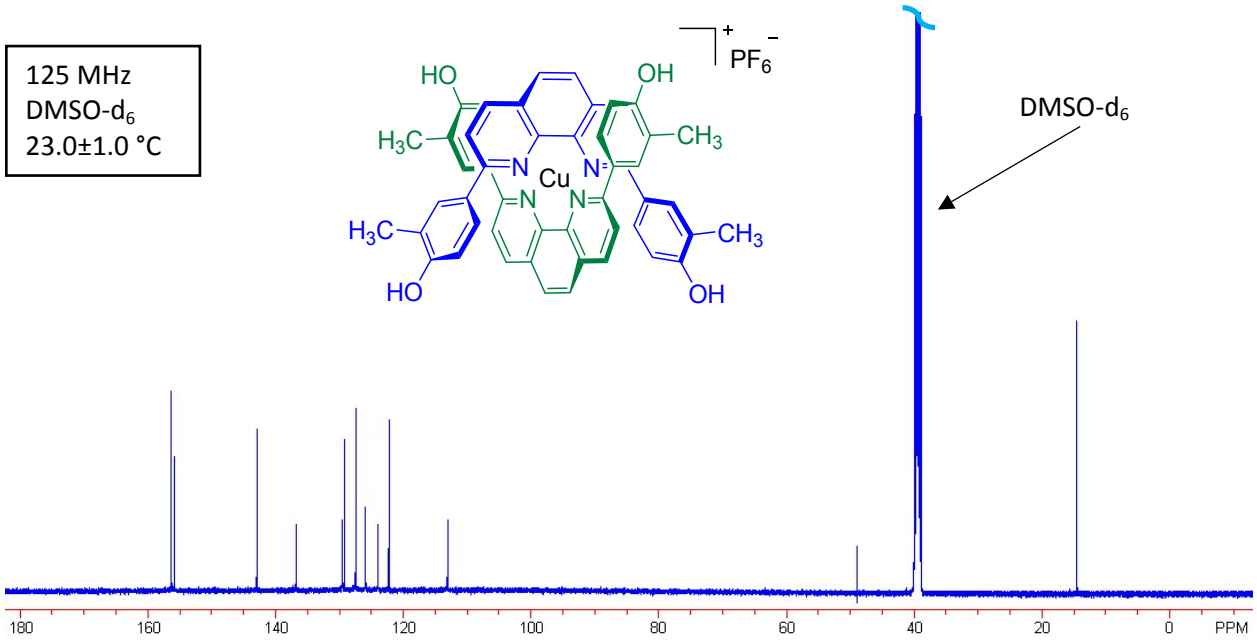

Fig. S9 Assigned protons on the ligands and respective complexes.

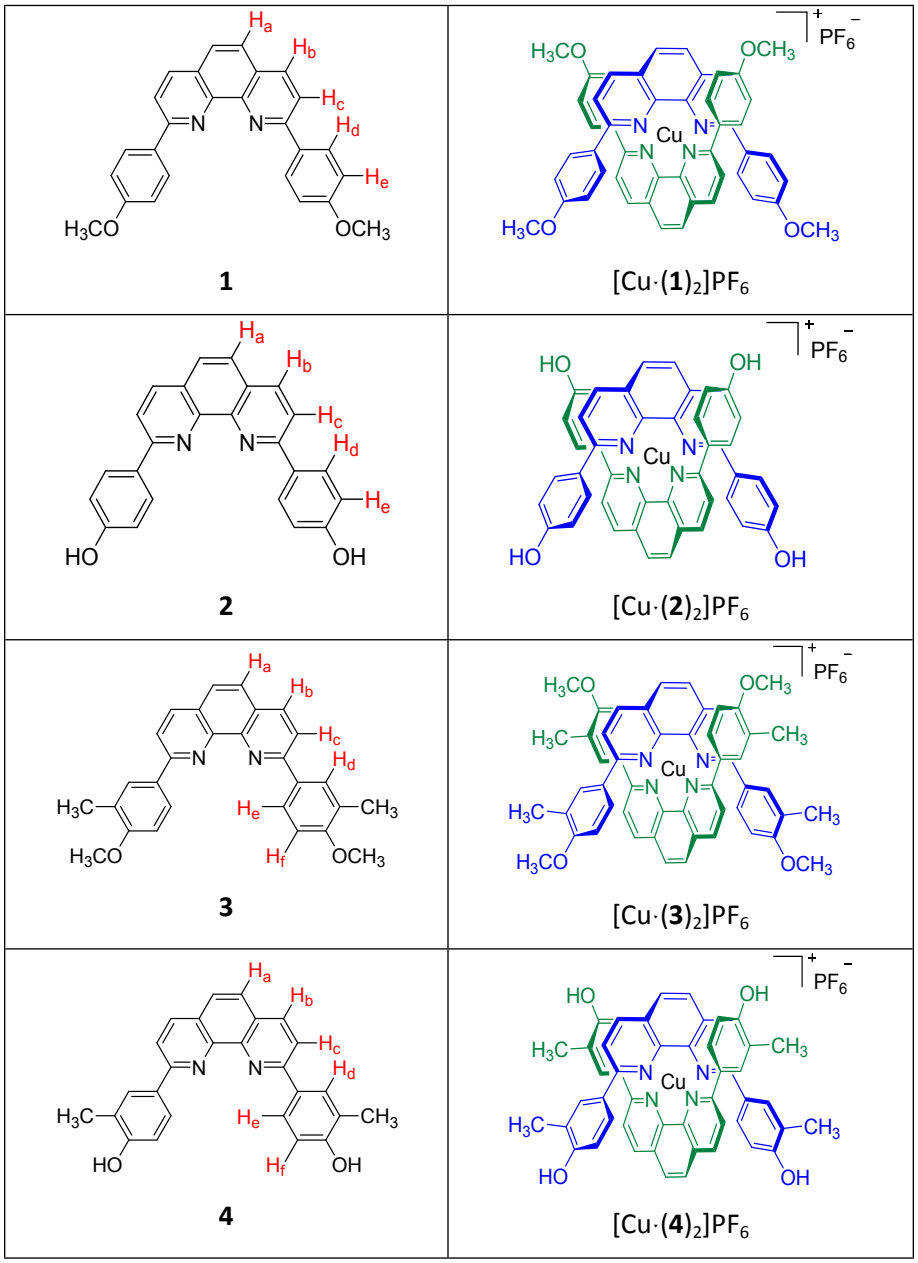

Table S1 Chemical shifts and Δδ of **1** and $[Cu\cdot(\mathbf{1})_2]PF_6$.

Protons	**H_a**	**H_b**	**H_c**	**H_d**	**H_e**	**OCH_3**
δ of **1** (ppm)	7.93	8.50	8.33	8.48	7.18	3.88
δ of $[Cu\cdot(\mathbf{1})_2]PF_6$ (ppm)	8.17	8.69	8.01	7.44	6.05	3.38
Δδ of $[Cu\cdot(\mathbf{1})_2]PF_6$ and **1** (ppm)	0.24	0.19	-0.32	-1.04	-1.13	-0.50

Table S2 Chemical shifts and Δδ of **2** and $[Cu\cdot(\mathbf{2})_2]PF_6$.

Protons	**H_a**	**H_b**	**H_c**	**H_d**	**H_e**	**OH**
δ of **2** (ppm)	7.89	8.45	8.26	8.36	6.99	9.87
δ of $[Cu\cdot(\mathbf{2})_2]PF_6$ (ppm)	8.14	8.65	7.95	7.34	5.88	9.33
Δδ of $[Cu\cdot(\mathbf{2})_2]PF_6$ and **2** (ppm)	0.25	0.20	-0.31	-1.02	-1.11	-0.54

Table S3 Chemical shifts and Δδ of **3** and $[Cu\cdot(\mathbf{3})_2]PF_6$.

Protons	**H_a**	**H_b**	**H_c**	**H_d**	**H_e**	**H_f**	**OCH_3**	**CH_3**
δ of **3** (ppm)	7.91	8.49	8.33	8.46	8.34	7.15	3.91	2.35
δ of $[Cu\cdot(\mathbf{3})_2]PF_6$ (ppm)	8.17	8.67	8.00	7.43	7.25	6.27	3.51	1.05
Δδ of $[Cu\cdot(\mathbf{3})_2]PF_6$ and **3** (ppm)	0.26	0.18	-0.33	-1.03	-1.09	-0.88	-0.40	-1.30

Table S4 Chemical shifts and Δδ of **4** and $[Cu\cdot(\mathbf{4})_2]PF_6$.

Protons	**H_a**	**H_b**	**H_c**	**H_d**	**H_e**	**H_f**	**OH**	**CH_3**
δ of **4** (ppm)	7.87	8.45	8.26	8.43	8.15	6.98	9.78	2.31
δ of $[Cu\cdot(\mathbf{4})_2]PF_6$ (ppm)	8.14	8.61	7.91	7.45	7.08	6.23	9.30	0.84
Δδ of $[Cu\cdot(\mathbf{4})_2]PF_6$ and **4** (ppm)	0.27	0.16	-0.35	-0.98	-1.07	-0.75	-0.48	-1.47

Notes:

1- Δδ values have been calculated with ($\boldsymbol{\delta_{complex} - \delta_{ligand}}$).
2- Negative Δδ values indicate upfield shifts.
3- Positive Δδ values indicate downfield shifts.

DFT Optimized Coordinates

Table S5 DFT optimized coordinates of **1**.

Atom	x	y	z
O	-3.53773	-4.06614	2.647037
O	1.320967	4.762322	4.127254
N	-0.15681	-0.94766	-1.72573
N	1.133494	1.459898	-1.31926
C	-0.79766	-2.10671	-1.90372
C	-0.80636	-2.76208	-3.16529
C	-0.11806	-2.20524	-4.21874
C	0.575911	-0.98653	-4.04686
C	1.306012	-0.36112	-5.10306
C	1.957582	0.822245	-4.89724
C	1.921698	1.464644	-3.62222
C	2.587747	2.683808	-3.36447
C	2.519547	3.25714	-2.11544
C	1.760845	2.618921	-1.09633
C	1.201434	0.882731	-2.53388
C	0.511991	-0.38661	-2.75141
C	-1.51424	-2.65674	-0.73137
C	-1.79888	-1.82285	0.365884
C	-2.47482	-2.30987	1.47427
C	-2.87668	-3.64909	1.519974
C	-2.59981	-4.51835	0.446728
C	-1.92489	-3.99774	-0.65968
C	1.644397	3.187123	0.265334
C	1.976633	4.521949	0.560771
C	1.869806	5.061215	1.842495
C	1.413489	4.216019	2.871384
C	1.071553	2.885663	2.604222
C	1.181708	2.377902	1.316314
H	-1.36725	-3.68449	-3.30879
H	-0.11355	-2.68956	-5.19751
H	1.333245	-0.84774	-6.08015
H	2.517368	1.296109	-5.70624
H	3.166366	3.15592	-4.16131
H	3.058574	4.181023	-1.9115
H	-1.47521	-0.78399	0.323335
H	-2.70676	-1.66543	2.322215
C	-3.01523	-5.96454	0.509805
H	-1.69147	-4.68325	-1.47612
H	2.309797	5.189173	-0.23567

C	2.216539	6.491993	2.141236
H	0.717549	2.242522	3.41517
H	0.911971	1.345745	1.098043
H	-2.54972	-6.49684	1.355654
H	-2.7183	-6.4962	-0.40143
H	-4.10739	-6.08259	0.605098
H	3.019698	6.561781	2.88864
H	1.35672	7.033958	2.55981
H	2.544153	7.013511	1.233962
H	0.987545	4.084191	4.743809
H	-3.77161	-5.00846	2.554135

Table S6 DFT optimized coordinates of **2**.

Atom	**x**	**y**	**z**
O	-3.60897	-3.865	2.740447
O	1.704884	4.701373	4.136194
N	-0.25663	-0.84679	-1.73092
N	1.155947	1.494849	-1.34695
C	-0.95374	-1.97429	-1.89803
C	-1.04001	-2.6124	-3.16527
C	-0.36909	-2.07195	-4.23825
C	0.383543	-0.88682	-4.07931
C	1.098255	-0.27938	-5.15636
C	1.808129	0.871966	-4.96287
C	1.850534	1.497906	-3.67986
C	2.579371	2.683297	-3.43494
C	2.586607	3.241655	-2.17729
C	1.842084	2.622173	-1.13661
C	1.149566	0.932394	-2.57052
C	0.396264	-0.30185	-2.77565
C	-1.65013	-2.50889	-0.70653
C	-1.86313	-1.67633	0.409846
C	-2.5163	-2.13775	1.543014
C	-2.97168	-3.46149	1.596987
C	-2.76055	-4.31033	0.504169
C	-2.1105	-3.83352	-0.63141
C	1.807261	3.17638	0.235123
C	2.195627	4.495952	0.532284
C	2.153747	4.991377	1.830037
C	1.721232	4.167638	2.875067
C	1.32434	2.851801	2.600465
C	1.364566	2.369407	1.298387

H	-1.6458	-3.5078	-3.29711
H	-0.42346	-2.54301	-5.22194
H	1.06594	-0.7537	-6.13932
H	2.355753	1.332134	-5.78786
H	3.14574	3.140712	-4.2489
H	3.173603	4.13816	-1.98358
H	-1.49901	-0.65101	0.361369
H	-2.68765	-1.48636	2.399823
H	-1.93875	-4.52559	-1.45593
H	2.514931	5.168328	-0.26394
H	0.984319	2.202112	3.411774
H	1.051262	1.350326	1.07537
H	1.377907	4.029212	4.762872
H	-3.87438	-4.7989	2.647235
H	-3.10019	-5.34882	0.541441
H	2.446589	6.017264	2.051628

Table S7 DFT optimized coordinates of **3**.

Atom	**x**	**y**	**z**
O	-3.7373	-4.44665	2.403346
O	1.403934	4.439914	4.14839
N	-0.14199	-1.22437	-1.77334
N	1.198979	1.14859	-1.31837
C	-0.80572	-2.36699	-1.97503
C	-0.80022	-3.01288	-3.24148
C	-0.07653	-2.46374	-4.27502
C	0.639821	-1.26202	-4.07836
C	1.404849	-0.64473	-5.11438
C	2.07758	0.522395	-4.88595
C	2.030071	1.155101	-3.60643
C	2.717568	2.357142	-3.32635
C	2.63881	2.921531	-2.07387
C	1.848152	2.291371	-1.0744
C	1.276601	0.580086	-2.53675
C	0.561601	-0.67086	-2.77948
C	-1.56482	-2.90887	-0.82593
C	-1.85131	-2.08258	0.269958
C	-2.57471	-2.55988	1.359417
C	-3.02117	-3.88743	1.378119
C	-2.73903	-4.75228	0.297321
C	-2.02065	-4.24035	-0.77975
C	1.72403	2.851041	0.290118

C	2.064551	4.182718	0.596135
C	1.953592	4.711565	1.879128
C	1.484637	3.864523	2.907853
C	1.134549	2.537153	2.62923
C	1.250455	2.04251	1.333145
C	-4.04837	-3.62524	3.525829
C	0.929409	3.637299	5.226462
H	-1.37685	-3.92218	-3.40389
H	-0.06068	-2.94097	-5.25717
H	1.441428	-1.12454	-6.09454
H	2.663608	0.99049	-5.6796
H	3.321271	2.822476	-4.10846
H	3.194428	3.831177	-1.85117
H	-1.49531	-1.05345	0.250941
H	-2.78814	-1.88778	2.188939
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H	-2.89988	-6.71516	-0.57158
H	-4.29938	-6.24266	0.421862
H	3.108355	6.201026	2.936992
H	1.451852	6.687283	2.598682
H	2.647121	6.659227	1.279805

Table S8 DFT optimized coordinates of **4**.

Atom	**x**	**y**	**z**
O	-3.53773	-4.06614	2.647037
O	1.320967	4.762322	4.127254
N	-0.15681	-0.94766	-1.72573
N	1.133494	1.459898	-1.31926
C	-0.79766	-2.10671	-1.90372
C	-0.80636	-2.76208	-3.16529

C	-0.11806	-2.20524	-4.21874
C	0.575911	-0.98653	-4.04686
C	1.306012	-0.36112	-5.10306
C	1.957582	0.822245	-4.89724
C	1.921698	1.464644	-3.62222
C	2.587747	2.683808	-3.36447
C	2.519547	3.25714	-2.11544
C	1.760845	2.618921	-1.09633
C	1.201434	0.882731	-2.53388
C	0.511991	-0.38661	-2.75141
C	-1.51424	-2.65674	-0.73137
C	-1.79888	-1.82285	0.365884
C	-2.47482	-2.30987	1.47427
C	-2.87668	-3.64909	1.519974
C	-2.59981	-4.51835	0.446728
C	-1.92489	-3.99774	-0.65968
C	1.644397	3.187123	0.265334
C	1.976633	4.521949	0.560771
C	1.869806	5.061215	1.842495
C	1.413489	4.216019	2.871384
C	1.071553	2.885663	2.604222
C	1.181708	2.377902	1.316314
H	-1.36725	-3.68449	-3.30879
H	-0.11355	-2.68956	-5.19751
H	1.333245	-0.84774	-6.08015
H	2.517368	1.296109	-5.70624
H	3.166366	3.15592	-4.16131
H	3.058574	4.181023	-1.9115
H	-1.47521	-0.78399	0.323335
H	-2.70676	-1.66543	2.322215
C	-3.01523	-5.96454	0.509805
H	-1.69147	-4.68325	-1.47612
H	2.309797	5.189173	-0.23567
C	2.216539	6.491993	2.141236
H	0.717549	2.242522	3.41517
H	0.911971	1.345745	1.098043
H	-2.54972	-6.49684	1.355654
H	-2.7183	-6.4962	-0.40143
H	-4.10739	-6.08259	0.605098
H	3.019698	6.561781	2.88864
H	1.35672	7.033958	2.55981
H	2.544153	7.013511	1.233962
H	0.987545	4.084191	4.743809

H	-3.77161	-5.00846	2.554135

Table S9 DFT optimized coordinates of $[Cu\cdot(\mathbf{1})_2]^+$.

Atom	**x**	**y**	**z**
Cu	-0.00073	0.186569	-0.00018
O	-4.17528	-4.18719	2.294942
O	2.158483	4.708394	4.175678
N	-0.32842	-0.91095	-1.70215
N	1.199457	1.301218	-1.23482
C	-1.01074	-2.06242	-1.88411
C	-0.99408	-2.72367	-3.13875
C	-0.29787	-2.19428	-4.20038
C	0.422276	-0.99174	-4.03176
C	1.141545	-0.36336	-5.09356
C	1.811168	0.809416	-4.88665
C	1.834361	1.419882	-3.59569
C	2.520378	2.624936	-3.32929
C	2.520815	3.138645	-2.0533
C	1.860603	2.455249	-1.00073
C	1.163878	0.801222	-2.50604
C	0.39213	-0.39378	-2.74278
C	-1.81124	-2.62658	-0.78196
C	-2.55672	-1.81114	0.091265
C	-3.33317	-2.35746	1.099013
C	-3.38636	-3.75106	1.278347
C	-2.64701	-4.58225	0.422513
C	-1.88226	-4.01663	-0.59589
C	1.9253	3.001339	0.366618
C	1.838145	4.392716	0.582005
C	1.909328	4.928238	1.857126
C	2.094942	4.087447	2.968791
C	2.203816	2.701942	2.772573
C	2.110557	2.177783	1.485209
C	-4.30632	-5.59842	2.490918
C	2.36358	3.903374	5.339769
H	-1.58522	-3.62867	-3.26492
H	-0.31099	-2.68351	-5.17532
H	1.140837	-0.83723	-6.076
H	2.349452	1.293748	-5.70246
H	3.057577	3.129785	-4.1334
H	3.073276	4.048353	-1.82592
H	-2.54256	-0.73015	-0.03755

H	-3.92888	-1.72496	1.756858
H	-2.66135	-5.66416	0.538269
H	-1.29819	-4.67863	-1.23643
H	1.674913	5.062865	-0.26263
H	1.825239	6.001774	2.023621
H	2.373545	2.027629	3.609624
H	2.206284	1.101305	1.349973
H	-4.72915	-6.08953	1.602163
H	-3.34096	-6.06177	2.744158
H	-4.99519	-5.71731	3.331315
H	1.542413	3.184292	5.48192
H	3.321244	3.364272	5.292394
H	2.383506	4.60091	6.181258
N	0.326834	-0.91068	1.701991
N	-1.20088	1.301515	1.234236
C	1.009474	-2.06191	1.884262
C	-0.39421	-0.39366	2.742353
C	-1.86159	2.455782	1.000066
C	-1.16584	0.801379	2.505415
C	0.992546	-2.72313	3.138913
C	1.81075	-2.62572	0.7825
C	-0.42467	-0.9916	4.031343
C	-2.52207	3.139175	2.052468
C	-1.9254	3.002269	-0.36717
C	-1.8366	1.420062	3.594907
C	0.295718	-2.19396	4.200245
H	1.583971	-3.6279	3.265365
C	2.556571	-1.80997	-0.09014
C	1.882243	-4.01573	0.596288
C	-1.14442	-0.36334	5.092886
C	-2.52227	2.625286	3.32839
H	-3.07414	4.0491	1.825022
C	-1.83814	4.393715	-0.58207
C	-2.10973	2.179048	-1.48616
C	-1.81389	0.8095	4.885826
H	0.308639	-2.68315	5.175218
C	3.333767	-2.35595	-1.09749
H	2.542107	-0.72899	0.038869
C	2.64775	-4.581	-0.42174
H	1.297956	-4.67798	1.236373
H	-1.144	-0.83721	6.075315
H	-3.05961	3.130188	4.13237
C	-1.90848	4.929629	-1.85707

H	-1.67555	5.063612	0.262891
C	-2.20211	2.703595	-2.77343
H	-2.2054	1.102524	-1.35134
H	-2.35239	1.293831	5.701497
C	3.387393	-3.74951	-1.27702
H	3.929733	-1.7232	-1.75487
H	2.662442	-5.66289	-0.53763
C	-2.09323	4.089177	-2.96914
H	-1.82436	6.003223	-2.02317
H	-2.37115	2.029521	-3.61081
O	4.177034	-4.1853	-2.2932
O	-2.15596	4.710494	-4.17588
C	4.308499	-5.59646	-2.48933
C	-2.36005	3.905815	-5.34038
H	4.730905	-6.08762	-1.6004
H	3.343389	-6.05998	-2.74321
H	4.997894	-5.71507	-3.32934
H	-1.53868	3.18689	-5.48213
H	-3.31768	3.36657	-5.29391
H	-2.37942	4.603614	-6.18166

Table S10 DFT optimized coordinates of $[Cu\cdot(\mathbf{2})_2]^+$.

Atom	**x**	**y**	**z**
Cu	0.004318	0.321841	0.006109
O	-4.13422	-4.03846	2.39132
O	2.167126	4.918409	4.09884
N	-0.33601	-0.79505	-1.67944
N	1.185734	1.430597	-1.25466
C	-1.01263	-1.95334	-1.83913
C	-0.99316	-2.63933	-3.08002
C	-0.3015	-2.1266	-4.15272
C	0.411417	-0.91656	-4.0082
C	1.124597	-0.30393	-5.08343
C	1.787866	0.876451	-4.89993
C	1.811037	1.510665	-3.62029
C	2.492113	2.723631	-3.37813
C	2.495812	3.259184	-2.11117
C	1.842254	2.591819	-1.04406
C	1.14711	0.908508	-2.51727
C	0.380241	-0.2941	-2.73079
C	-1.80887	-2.49961	-0.72486
C	-2.55843	-1.67076	0.129396

C	-3.32981	-2.19679	1.155189
C	-3.36559	-3.58268	1.363272
C	-2.62506	-4.42754	0.524529
C	-1.86792	-3.88824	-0.50983
C	1.909782	3.164361	0.312744
C	1.829303	4.5589	0.499343
C	1.906191	5.125451	1.763251
C	2.090413	4.30527	2.885184
C	2.188119	2.916554	2.719059
C	2.090871	2.360057	1.448654
H	-1.57746	-3.55103	-3.18801
H	-0.31258	-2.63548	-5.1175
H	1.12154	-0.79432	-6.05775
H	2.317953	1.350808	-5.7269
H	3.022821	3.217548	-4.19325
H	3.04546	4.174982	-1.90258
H	-2.55367	-0.59337	-0.02723
H	-3.92872	-1.55218	1.797814
H	-1.28231	-4.5609	-1.13723
H	1.667272	5.211413	-0.35899
H	2.352545	2.270615	3.584888
H	2.175282	1.279973	1.337301
N	0.349394	-0.77867	1.697995
N	-1.18862	1.431108	1.258163
C	1.032339	-1.93173	1.863072
C	-0.37425	-0.27937	2.744984
C	-1.85575	2.584343	1.039563
C	-1.15001	0.915564	2.523375
C	1.011972	-2.61558	3.104766
C	1.83381	-2.47646	0.751332
C	-0.40642	-0.89845	4.023773
C	-2.51906	3.251011	2.100848
C	-1.92475	3.148036	-0.32113
C	-1.82433	1.515764	3.620802
C	0.313433	-2.10362	4.173887
H	1.600679	-3.52428	3.215659
C	2.602933	-1.64936	-0.08201
C	1.876092	-3.86564	0.5204
C	-1.13028	-0.28843	5.093278
C	-2.51564	2.721151	3.370316
H	-3.07677	4.160397	1.885531
C	-1.84734	4.541194	-0.51677
C	-2.10583	2.335429	-1.4511

C	-1.80185	0.88585	4.902603
H	0.323183	-2.61	5.139998
C	3.381723	-2.17933	-1.10475
H	2.610082	-0.57321	0.083279
C	2.634581	-4.40591	-0.50823
H	1.275963	-4.53448	1.138271
H	-1.13158	-0.77739	6.068182
H	-3.05554	3.212937	4.180614
C	-1.92648	5.099315	-1.78454
H	-1.68708	5.199448	0.337559
C	-2.20547	2.883384	-2.72509
H	-2.19072	1.256224	-1.33181
H	-2.34294	1.356429	5.724465
C	3.397781	-3.56337	-1.32825
H	3.990304	-1.51608	-1.72447
C	-2.11039	4.271194	-2.90048
H	-2.37081	2.231758	-3.58651
O	4.129447	-4.15124	-2.31559
O	-2.18982	4.875935	-4.11857
H	-2.35487	4.208891	-4.81141
H	2.328019	4.256508	4.797575
H	-4.11958	-5.01402	2.412233
H	4.646147	-3.476	-2.79449
H	-2.64199	-5.50885	0.679626
H	2.65427	-5.47952	-0.69172
H	1.82902	6.202877	1.90455
H	-1.85255	6.176	-1.93302

Table S11 DFT optimized coordinates of $[Cu\cdot(\mathbf{3})_2]^+$.

Atom	**x**	**y**	**z**
Cu	0.000673	-0.04003	-0.00172
O	-4.19863	-4.5652	2.09801
O	1.957363	4.562123	4.197802
N	-0.2482	-1.15135	-1.70787
N	1.248749	1.068488	-1.19477
C	-0.91442	-2.30979	-1.90366
C	-0.8254	-2.99627	-3.14162
C	-0.08042	-2.47999	-4.17642
C	0.621224	-1.26821	-3.99348
C	1.389199	-0.65113	-5.02759
C	2.040382	0.529874	-4.80575
C	1.99676	1.15973	-3.5245

C	2.662465	2.372519	-3.24154
C	2.598423	2.902504	-1.97377
C	1.892847	2.228904	-0.94404
C	1.276788	0.552827	-2.46005
C	0.522157	-0.64862	-2.71824
C	-1.77018	-2.85431	-0.83463
C	-2.57785	-2.02922	-0.04328
C	-3.40794	-2.56533	0.938043
C	-3.43071	-3.94915	1.157334
C	-2.62461	-4.81286	0.376744
C	-1.82383	-4.24479	-0.6077
C	1.892951	2.791844	0.417946
C	1.792084	4.18527	0.607103
C	1.80298	4.773393	1.866739
C	1.945533	3.927294	2.99319
C	2.065212	2.540791	2.829358
C	2.029652	1.984265	1.553073
C	-5.05856	-3.759	2.906997
C	2.117935	3.773401	5.379245
H	-1.40007	-3.91033	-3.27834
H	-0.03998	-2.98727	-5.14139
H	1.437442	-1.13774	-6.00273
H	2.612608	1.007327	-5.60247
H	3.235213	2.87022	-4.02545
H	3.134914	3.818002	-1.73185
H	-2.57964	-0.95261	-0.20663
H	-4.04123	-1.89813	1.519765
C	-2.65033	-6.29307	0.626405
H	-1.18731	-4.90786	-1.1968
H	1.661729	4.834471	-0.26068
C	1.667033	6.256702	2.054305
H	2.197265	1.887246	3.689469
H	2.133875	0.905733	1.443997
H	-4.48554	-3.0372	3.5086
H	-5.79885	-3.2221	2.295495
H	-5.57663	-4.45489	3.572424
H	1.293712	3.05377	5.498117
H	3.077655	3.235879	5.376629
H	2.103258	4.481698	6.212038
N	0.249819	-1.15431	1.702506
N	-1.24704	1.066599	1.193267
C	0.916081	-2.31304	1.896366
C	-0.52016	-0.65299	2.713883

C	-1.89129	2.227354	0.944559
C	-1.27484	0.548847	2.457736
C	0.827544	-3.00131	3.133349
C	1.771285	-2.85599	0.826091
C	-0.61874	-1.27444	3.988263
C	-2.59693	2.899142	1.975439
C	-1.89136	2.79272	-0.41646
C	-1.99462	1.154035	3.523282
C	0.082988	-2.48648	4.169177
H	1.402185	-3.91561	3.268519
C	2.57883	-2.02978	0.035838
C	1.824417	-4.24609	0.596693
C	-1.38639	-0.65894	5.023551
C	-2.66064	2.367131	3.242364
H	-3.13361	3.81491	1.734981
C	-1.79052	4.186483	-0.60309
C	-2.02797	1.987148	-1.55302
C	-2.03779	0.522301	4.803635
H	0.042929	-2.99511	5.133449
C	3.408107	-2.5644	-0.94701
H	2.581105	-0.95346	0.201051
C	2.624342	-4.81263	-0.38933
H	1.188199	-4.91	1.185161
H	-1.43423	-1.14699	5.997987
H	-3.23333	2.863451	4.027198
C	-1.80133	4.776857	-1.86168
H	-1.66023	4.834091	0.265887
C	-2.06345	2.545968	-2.82831
H	-2.13218	0.908429	-1.44589
H	-2.60985	0.998528	5.601203
C	3.430169	-3.94782	-1.16896
H	4.041366	-1.89626	-1.52769
C	2.649275	-6.29239	-0.64178
C	-1.94377	3.932758	-2.98964
C	-1.66542	6.260498	-2.0466
H	-2.19542	1.893982	-3.68961
O	4.197056	-4.56237	-2.11153
O	-1.9555	4.569748	-4.19312
C	5.057151	-3.75481	-2.91907
C	-2.11595	3.783146	-5.37599
H	4.484631	-3.03104	-3.51877
H	5.797931	-3.22003	-2.30631
H	5.574396	-4.44941	-3.58648

H	-1.29168	3.063767	-5.4961
H	-3.07564	3.245574	-5.37443
H	-2.10124	4.492943	-6.20751
H	-2.35778	-6.53089	1.658832
H	-1.97276	-6.81892	-0.05647
H	-3.66122	-6.7024	0.493163
H	-2.54271	6.680557	-2.55775
H	-0.79808	6.509095	-2.6743
H	-1.55297	6.768438	-1.08157
H	2.544358	6.675902	2.566098
H	0.799737	6.504149	2.682525
H	1.554436	6.766337	1.090181
H	2.352613	-6.52832	-1.67349
H	1.974058	-6.81936	0.042593
H	3.660576	-6.70203	-0.51306

Table S12 DFT optimized coordinates of $[Cu\cdot(\mathbf{4})_2]^+$.

Atom	**x**	**y**	**z**
Cu	0.006346	0.253236	0.006003
O	-4.20565	-4.11821	2.228924
O	1.994735	4.859332	4.164417
N	-0.27263	-0.86741	-1.69342
N	1.231068	1.357171	-1.20975
C	-0.94427	-2.02473	-1.87878
C	-0.8806	-2.70826	-3.11996
C	-0.15033	-2.19423	-4.16612
C	0.55824	-0.98517	-3.99381
C	1.309867	-0.37061	-5.04125
C	1.966012	0.809546	-4.83164
C	1.942663	1.441575	-3.55097
C	2.613244	2.654776	-3.28207
C	2.568848	3.188714	-2.01516
C	1.87743	2.519396	-0.97335
C	1.239754	0.83704	-2.47376
C	0.481185	-0.36524	-2.71705
C	-1.78057	-2.57049	-0.79445
C	-2.55601	-1.74068	0.032494
C	-3.3607	-2.2777	1.026126
C	-3.40208	-3.66259	1.224875
C	-2.63627	-4.52904	0.416152
C	-1.84917	-3.95951	-0.58476
C	1.892226	3.091209	0.385368

C	1.790309	4.484592	0.564965
C	1.812579	5.085484	1.820954
C	1.967334	4.246285	2.944505
C	2.086861	2.860243	2.791685
C	2.041209	2.288737	1.525221
H	-1.46305	-3.6182	-3.25062
H	-0.12813	-2.70045	-5.13218
H	1.341849	-0.85886	-6.01616
H	2.525446	1.285565	-5.63813
H	3.173644	3.150022	-4.07631
H	3.109073	4.104864	-1.78448
H	-2.54468	-0.66261	-0.11828
H	-3.98311	-1.64104	1.654414
C	-2.67287	-6.01636	0.644073
H	-1.23685	-4.62439	-1.19698
H	1.650727	5.126504	-0.30667
C	1.677858	6.569352	2.003402
H	2.226177	2.225855	3.670717
H	2.143381	1.209555	1.423442
N	0.2898	-0.85346	1.709671
N	-1.2304	1.355812	1.214522
C	0.967862	-2.00556	1.898862
C	-0.47051	-0.35429	2.729947
C	-1.88774	2.510021	0.971673
C	-1.23836	0.840309	2.480308
C	0.905193	-2.68808	3.140181
C	1.807394	-2.54935	0.815178
C	-0.54732	-0.97242	4.007345
C	-2.58902	3.176542	2.008504
C	-1.90393	3.075437	-0.38993
C	-1.95133	1.440902	3.55273
C	0.168855	-2.1763	4.183709
H	1.491988	-3.59519	3.272113
C	2.599585	-1.72111	0.007931
C	1.858335	-3.93855	0.588951
C	-1.3092	-0.36231	5.049924
C	-2.63292	2.646375	3.277114
H	-3.1379	4.086138	1.772274
C	-1.80415	4.467939	-0.57592
C	-2.05304	2.267268	-1.52563
C	-1.97437	0.811493	4.83472
H	0.146032	-2.68124	5.150409
C	3.407736	-2.2633	-0.98491

H	2.602063	-0.64434	0.168037
C	2.642387	-4.51071	-0.40994
H	1.23491	-4.60084	1.192749
H	-1.3448	-0.85054	6.024578
H	-3.20241	3.137837	4.06716
C	-1.82788	5.063004	-1.83478
H	-1.6662	5.113779	0.293108
C	-2.10034	2.833015	-2.7948
H	-2.15661	1.188673	-1.41877
H	-2.54462	1.282184	5.636629
C	3.427421	-3.6459	-1.20096
H	4.037664	-1.60784	-1.59194
C	2.670921	-5.9908	-0.6594
C	-1.98243	4.218425	-2.95414
C	-1.69599	6.546322	-2.02402
H	-2.2407	2.194199	-3.67049
O	4.193665	-4.23132	-2.16831
O	-2.01155	4.825709	-4.1773
H	-2.33577	-6.29106	1.656611
H	-2.01939	-6.53848	-0.06378
H	-3.68369	-6.4338	0.508113
H	-2.57921	6.962963	-2.5277
H	-0.83509	6.794629	-2.66067
H	-1.57524	7.057475	-1.06178
H	2.561802	6.990676	2.501955
H	0.818634	6.818575	2.641862
H	1.552661	7.07562	1.039147
H	2.358355	-6.23063	-1.68552
H	2.011279	-6.52083	0.037716
H	3.686792	-6.39383	-0.5467
H	-2.15591	4.158067	-4.87392
H	2.133808	4.195095	4.86537
H	-4.20203	-5.09405	2.242774
H	4.718556	-3.55107	-2.63054

Crystallographic Data

Table S13 Crystallographic data for compounds $[Cu\cdot(\mathbf{1})_2]PF_6$, **1**, **2**, and $[Cu\cdot(\mathbf{3})_2]PF_6$

	$[Cu\cdot(\mathbf{1})_2]PF_6$	$[Cu\cdot(\mathbf{3})_2]PF_6 \cdot CH_3CN$	$\mathbf{1}\cdot 2H_2O$	$\mathbf{2}\cdot 2H_2O$
Empirical formula	$\mathbf{C_{52}H_{40}CuF_6N_4O_4P}$	$\mathbf{C_{58}H_{51}CuF_6N_5O_4P}$	$\mathbf{C_{26}H_{24}N_2O_4}$	$\mathbf{C_{24}H_{20}N_2O_4}$
M (g mol^{-1})	993.39	1090.55	428.47	400.42
T (K)	100	100	173	298
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Hexagonal, $P6_1$	Monoclinic, $C2/c$
a (Å)	13.724(4)	8.3698(2)	17.652 (2)	13.077(3)
b (Å)	14.159(4)	32.873(6)	17.652 (2)	10.396(2)
c (Å)	14.164(4)	18.214(3)	12.122(1)	15.667(3)
α (°)	63.147(4)			
β (°)	61.260(3)	93.458(3)		109.261(2)
γ (°)	73.411(4)			
Volume (Å^3)	2145 (1)	5002(2)	3271.3(8)	2010.7(8)
Z	2	4	6	4
Calculated density (g cm^1)	1.538	1.448	1.305	1.323
μ (mm^1)	0.627	0.546	0.089	0.091
F(0 0 0)	1020	2256	1356	840
Crystal size (mm), color	0.18×0.15×0.06, red	0.18×0.07×0.02, red	0.27×0.13×0. 11, colorless	0.30×0.10×0. 10, yellow
Reflections collected	25825	30457	34388	11772
Independent reflections (R_{int})	10029 (0.0625)	5955 (0.1083)	5011 (0.1313)	2395 (0.0241)
Maximum and minimum transmission	0.7456, 0.6260	0.9892, 0.9081	0.9903, 0.9765	0.9910, 0.9732
Data/restraints/parameters	10029 / 0 / 619	5955 / 0 / 354	5011 / 1 / 271	2395 / 3 / 148
Goodness-of-fit on F^2	1.075	1.007	1.047	1.046
R_1, wR_2 [$I > 2\sigma(I)$]	0.0713, 0.2050	0.0544, 0.0927	0.0809, 0.1659	0.0423, 0.1062
R_1, wR_2 (all data)	0.0999, 0.2248	0.1174, 0.1103	0.1375, 0.1941	0.0619, 0.1183
Largest difference peak and hole (e$^-$ Å^{-3})	1.548 and -0.817	0.360 and -0.498	0.608 and -0.210	0.263 and -0.195

Table S14 Bond lengths [Å] and angles [°] for $[Cu\cdot(\mathbf{1})_2]PF_6$

Cu(1)-N(2)	2.026(4)
Cu(1)-N(3)	2.028(4)
Cu(1)-N(4)	2.042(4)
Cu(1)-N(1)	2.050(4)
P(1)-F(2)	1.571(4)
P(1)-F(1)	1.577(4)
P(1)-F(3)	1.586(4)
P(1)-F(5)	1.586(3)
P(1)-F(6)	1.595(4)
P(1)-F(4)	1.596(4)
O(1)-C(16)	1.366(6)
O(1)-C(19)	1.417(6)
O(2)-C(23)	1.357(6)
O(2)-C(26)	1.431(6)
O(3)-C(42)	1.362(5)
O(3)-C(45)	1.428(6)
O(4)-C(49)	1.369(5)
O(4)-C(52)	1.432(6)
N(1)-C(1)	1.328(6)
N(1)-C(12)	1.361(6)
N(2)-C(10)	1.343(6)
N(2)-C(11)	1.362(6)
N(3)-C(27)	1.337(6)
N(3)-C(38)	1.367(6)
N(4)-C(36)	1.336(6)
N(4)-C(37)	1.365(5)
C(1)-C(2)	1.410(6)
C(1)-C(13)	1.479(6)
C(2)-C(3)	1.366(7)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.401(7)
C(3)-H(3A)	0.9500
C(4)-C(12)	1.409(6)
C(4)-C(5)	1.441(7)

C(5)-C(6)	1.336(8)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.432(7)
C(6)-H(6A)	0.9500
C(7)-C(11)	1.405(6)
C(7)-C(8)	1.407(7)
C(8)-C(9)	1.358(7)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.411(6)
C(9)-H(9A)	0.9500
C(10)-C(20)	1.477(6)
C(11)-C(12)	1.439(7)
C(13)-C(14)	1.395(6)
C(13)-C(18)	1.404(6)
C(14)-C(15)	1.379(7)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.404(7)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.392(7)
C(17)-C(18)	1.375(6)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.387(6)
C(20)-C(25)	1.403(6)
C(21)-C(22)	1.395(7)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.392(7)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.397(7)
C(24)-C(25)	1.376(7)
C(24)-H(24A)	0.9500
C(25)-H(25A)	0.9500
C(26)-H(26A)	0.9800

C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-C(28)	1.407(6)
C(27)-C(39)	1.475(6)
C(28)-C(29)	1.356(7)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.408(7)
C(29)-H(29A)	0.9500
C(30)-C(38)	1.405(6)
C(30)-C(31)	1.429(6)
C(31)-C(32)	1.348(7)
C(31)-H(31A)	0.9500
C(32)-C(33)	1.429(6)
C(32)-H(32A)	0.9500
C(33)-C(37)	1.397(6)
C(33)-C(34)	1.412(7)
C(34)-C(35)	1.375(7)
C(34)-H(34A)	0.9500
C(35)-C(36)	1.416(6)
C(35)-H(35A)	0.9500
C(36)-C(46)	1.471(6)
C(37)-C(38)	1.442(6)
C(39)-C(44)	1.395(6)
C(39)-C(40)	1.405(6)
C(40)-C(41)	1.388(7)
C(40)-H(40A)	0.9500
C(41)-C(42)	1.384(7)
C(41)-H(41A)	0.9500
C(42)-C(43)	1.388(7)
C(43)-C(44)	1.369(6)
C(43)-H(43A)	0.9500
C(44)-H(44A)	0.9500
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-C(47)	1.388(6)

C(46)-C(51)	1.397(6)
C(47)-C(48)	1.378(7)
C(47)-H(47A)	0.9500
C(48)-C(49)	1.392(7)
C(48)-H(48A)	0.9500
C(49)-C(50)	1.390(7)
C(50)-C(51)	1.395(6)
C(50)-H(50A)	0.9500
C(51)-H(51A)	0.9500
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800

N(2)-Cu(1)-N(3)	127.54(15)
N(2)-Cu(1)-N(4)	134.19(15)
N(3)-Cu(1)-N(4)	83.37(15)
N(2)-Cu(1)-N(1)	83.08(15)
N(3)-Cu(1)-N(1)	129.77(15)
N(4)-Cu(1)-N(1)	102.73(15)
F(2)-P(1)-F(1)	91.0(3)
F(2)-P(1)-F(3)	89.5(2)
F(1)-P(1)-F(3)	178.8(3)
F(2)-P(1)-F(5)	90.4(2)
F(1)-P(1)-F(5)	91.2(3)
F(3)-P(1)-F(5)	89.9(2)
F(2)-P(1)-F(6)	91.4(2)
F(1)-P(1)-F(6)	90.2(2)
F(3)-P(1)-F(6)	88.6(2)
F(5)-P(1)-F(6)	177.7(2)
F(2)-P(1)-F(4)	178.7(2)
F(1)-P(1)-F(4)	89.2(2)
F(3)-P(1)-F(4)	90.4(2)
F(5)-P(1)-F(4)	88.35(19)
F(6)-P(1)-F(4)	89.9(2)
C(16)-O(1)-C(19)	118.2(4)
C(23)-O(2)-C(26)	117.3(4)

C(42)-O(3)-C(45)	117.1(4)
C(49)-O(4)-C(52)	117.1(4)
C(1)-N(1)-C(12)	119.0(4)
C(1)-N(1)-Cu(1)	128.9(3)
C(12)-N(1)-Cu(1)	110.2(3)
C(10)-N(2)-C(11)	118.7(4)
C(10)-N(2)-Cu(1)	130.3(3)
C(11)-N(2)-Cu(1)	110.9(3)
C(27)-N(3)-C(38)	118.6(4)
C(27)-N(3)-Cu(1)	130.7(3)
C(38)-N(3)-Cu(1)	110.5(3)
C(36)-N(4)-C(37)	119.1(4)
C(36)-N(4)-Cu(1)	128.9(3)
C(37)-N(4)-Cu(1)	110.0(3)
N(1)-C(1)-C(2)	121.6(4)
N(1)-C(1)-C(13)	117.2(4)
C(2)-C(1)-C(13)	121.2(4)
C(3)-C(2)-C(1)	119.5(5)
C(3)-C(2)-H(2A)	120.3
C(1)-C(2)-H(2A)	120.3
C(2)-C(3)-C(4)	120.1(4)
C(2)-C(3)-H(3A)	120.0
C(4)-C(3)-H(3A)	120.0
C(3)-C(4)-C(12)	117.1(4)
C(3)-C(4)-C(5)	124.8(4)
C(12)-C(4)-C(5)	118.1(5)
C(6)-C(5)-C(4)	121.6(5)
C(6)-C(5)-H(5A)	119.2
C(4)-C(5)-H(5A)	119.2
C(5)-C(6)-C(7)	121.1(4)
C(5)-C(6)-H(6A)	119.4
C(7)-C(6)-H(6A)	119.4
C(11)-C(7)-C(8)	116.7(4)
C(11)-C(7)-C(6)	119.5(5)
C(8)-C(7)-C(6)	123.7(4)
C(9)-C(8)-C(7)	119.9(4)

C(9)-C(8)-H(8A)	120.1
C(7)-C(8)-H(8A)	120.1
C(8)-C(9)-C(10)	120.7(5)
C(8)-C(9)-H(9A)	119.6
C(10)-C(9)-H(9A)	119.6
N(2)-C(10)-C(9)	120.6(4)
N(2)-C(10)-C(20)	118.6(4)
C(9)-C(10)-C(20)	120.8(4)
N(2)-C(11)-C(7)	123.3(4)
N(2)-C(11)-C(12)	117.8(4)
C(7)-C(11)-C(12)	118.9(4)
N(1)-C(12)-C(4)	122.4(4)
N(1)-C(12)-C(11)	117.3(4)
C(4)-C(12)-C(11)	120.3(4)
C(14)-C(13)-C(18)	118.4(4)
C(14)-C(13)-C(1)	121.6(4)
C(18)-C(13)-C(1)	120.0(4)
C(15)-C(14)-C(13)	121.1(4)
C(15)-C(14)-H(14A)	119.5
C(13)-C(14)-H(14A)	119.5
C(14)-C(15)-C(16)	119.9(4)
C(14)-C(15)-H(15A)	120.1
C(16)-C(15)-H(15A)	120.1
O(1)-C(16)-C(17)	115.8(4)
O(1)-C(16)-C(15)	124.8(4)
C(17)-C(16)-C(15)	119.4(4)
C(18)-C(17)-C(16)	120.3(4)
C(18)-C(17)-H(17A)	119.8
C(16)-C(17)-H(17A)	119.8
C(17)-C(18)-C(13)	120.9(4)
C(17)-C(18)-H(18A)	119.6
C(13)-C(18)-H(18A)	119.6
O(1)-C(19)-H(19A)	109.5
O(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(1)-C(19)-H(19C)	109.5

H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-C(25)	117.7(4)
C(21)-C(20)-C(10)	121.0(4)
C(25)-C(20)-C(10)	121.3(4)
C(20)-C(21)-C(22)	122.2(4)
C(20)-C(21)-H(21A)	118.9
C(22)-C(21)-H(21A)	118.9
C(23)-C(22)-C(21)	118.8(4)
C(23)-C(22)-H(22A)	120.6
C(21)-C(22)-H(22A)	120.6
O(2)-C(23)-C(22)	124.9(4)
O(2)-C(23)-C(24)	115.1(4)
C(22)-C(23)-C(24)	120.0(4)
C(25)-C(24)-C(23)	120.1(4)
C(25)-C(24)-H(24A)	119.9
C(23)-C(24)-H(24A)	119.9
C(24)-C(25)-C(20)	121.2(4)
C(24)-C(25)-H(25A)	119.4
C(20)-C(25)-H(25A)	119.4
O(2)-C(26)-H(26A)	109.5
O(2)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
O(2)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
N(3)-C(27)-C(28)	120.8(4)
N(3)-C(27)-C(39)	118.0(4)
C(28)-C(27)-C(39)	121.2(4)
C(29)-C(28)-C(27)	121.0(4)
C(29)-C(28)-H(28A)	119.5
C(27)-C(28)-H(28A)	119.5
C(28)-C(29)-C(30)	119.5(4)
C(28)-C(29)-H(29A)	120.2
C(30)-C(29)-H(29A)	120.2
C(38)-C(30)-C(29)	116.9(4)

C(38)-C(30)-C(31)	119.5(4)
C(29)-C(30)-C(31)	123.6(4)
C(32)-C(31)-C(30)	121.4(4)
C(32)-C(31)-H(31A)	119.3
C(30)-C(31)-H(31A)	119.3
C(31)-C(32)-C(33)	120.1(4)
C(31)-C(32)-H(32A)	119.9
C(33)-C(32)-H(32A)	119.9
C(37)-C(33)-C(34)	116.5(4)
C(37)-C(33)-C(32)	120.5(4)
C(34)-C(33)-C(32)	122.9(4)
C(35)-C(34)-C(33)	120.6(4)
C(35)-C(34)-H(34A)	119.7
C(33)-C(34)-H(34A)	119.7
C(34)-C(35)-C(36)	119.2(4)
C(34)-C(35)-H(35A)	120.4
C(36)-C(35)-H(35A)	120.4
N(4)-C(36)-C(35)	121.2(4)
N(4)-C(36)-C(46)	117.1(4)
C(35)-C(36)-C(46)	121.6(4)
N(4)-C(37)-C(33)	123.4(4)
N(4)-C(37)-C(38)	117.5(4)
C(33)-C(37)-C(38)	119.1(4)
N(3)-C(38)-C(30)	123.1(4)
N(3)-C(38)-C(37)	117.6(4)
C(30)-C(38)-C(37)	119.3(4)
C(44)-C(39)-C(40)	117.7(4)
C(44)-C(39)-C(27)	122.0(4)
C(40)-C(39)-C(27)	120.3(4)
C(41)-C(40)-C(39)	120.9(4)
C(41)-C(40)-H(40A)	119.5
C(39)-C(40)-H(40A)	119.5
C(42)-C(41)-C(40)	119.9(4)
C(42)-C(41)-H(41A)	120.1
C(40)-C(41)-H(41A)	120.1
O(3)-C(42)-C(41)	125.0(4)

O(3)-C(42)-C(43)	115.5(4)
C(41)-C(42)-C(43)	119.5(4)
C(44)-C(43)-C(42)	120.6(4)
C(44)-C(43)-H(43A)	119.7
C(42)-C(43)-H(43A)	119.7
C(43)-C(44)-C(39)	121.3(4)
C(43)-C(44)-H(44A)	119.4
C(39)-C(44)-H(44A)	119.4
O(3)-C(45)-H(45A)	109.5
O(3)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
O(3)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(47)-C(46)-C(51)	118.1(4)
C(47)-C(46)-C(36)	119.8(4)
C(51)-C(46)-C(36)	122.0(4)
C(48)-C(47)-C(46)	121.6(4)
C(48)-C(47)-H(47A)	119.2
C(46)-C(47)-H(47A)	119.2
C(47)-C(48)-C(49)	119.8(4)
C(47)-C(48)-H(48A)	120.1
C(49)-C(48)-H(48A)	120.1
O(4)-C(49)-C(50)	124.3(4)
O(4)-C(49)-C(48)	115.8(4)
C(50)-C(49)-C(48)	119.9(4)
C(49)-C(50)-C(51)	119.5(4)
C(49)-C(50)-H(50A)	120.2
C(51)-C(50)-H(50A)	120.2
C(50)-C(51)-C(46)	121.0(4)
C(50)-C(51)-H(51A)	119.5
C(46)-C(51)-H(51A)	119.5
O(4)-C(52)-H(52A)	109.5
O(4)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
O(4)-C(52)-H(52C)	109.5

H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.

Table S15 Bond lengths [Å] and angles [°] for [Cu·(**3**)$_2$]PF_6

Cu(1)-N(1)	2.049(2)
Cu(1)-N(1)#1	2.049(2)
Cu(1)-N(2)	2.050(2)
Cu(1)-N(2)#1	2.050(2)
P(1)-F(2)#1	1.589(2)
P(1)-F(2)	1.589(2)
P(1)-F(1)#1	1.592(2)
P(1)-F(1)	1.592(2)
P(1)-F(3)	1.6018(18)
P(1)-F(3)#1	1.6018(18)
O(1)-C(16)	1.370(3)
O(1)-C(19)	1.429(3)
O(2)-C(24)	1.371(3)
O(2)-C(27)	1.435(3)
N(1)-C(1)	1.345(3)
N(1)-C(12)	1.367(3)
N(2)-C(10)	1.343(3)
N(2)-C(11)	1.371(3)
N(31)-C(31)	1.134(10)
C(1)-C(2)	1.409(4)
C(1)-C(13)	1.475(4)
C(2)-C(3)	1.360(4)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.402(4)
C(3)-H(3A)	0.9500
C(4)-C(12)	1.405(4)
C(4)-C(5)	1.427(4)
C(5)-C(6)	1.346(4)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.427(4)
C(6)-H(6A)	0.9500

C(7)-C(8)	1.408(4)
C(7)-C(11)	1.410(4)
C(8)-C(9)	1.348(4)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.422(4)
C(9)-H(9A)	0.9500
C(10)-C(21)	1.465(4)
C(11)-C(12)	1.441(4)
C(13)-C(14)	1.389(4)
C(13)-C(18)	1.399(4)
C(14)-C(15)	1.382(4)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.389(4)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.407(4)
C(17)-C(18)	1.376(4)
C(17)-C(20)	1.511(4)
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.392(4)
C(21)-C(26)	1.404(4)
C(22)-C(23)	1.377(4)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.378(4)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.409(4)
C(25)-C(26)	1.381(4)
C(25)-C(28)	1.493(4)
C(26)-H(26A)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800

C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(31)-C(32)	1.643(9)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800

N(1)-Cu(1)-N(1)#1	114.35(12)
N(1)-Cu(1)-N(2)	83.00(9)
N(1)#1-Cu(1)-N(2)	134.13(9)
N(1)-Cu(1)-N(2)#1	134.13(9)
N(1)#1-Cu(1)-N(2)#1	83.00(9)
N(2)-Cu(1)-N(2)#1	116.02(13)
F(2)#1-P(1)-F(2)	90.43(17)
F(2)#1-P(1)-F(1)#1	89.69(12)
F(2)-P(1)-F(1)#1	179.71(13)
F(2)#1-P(1)-F(1)	179.71(13)
F(2)-P(1)-F(1)	89.69(12)
F(1)#1-P(1)-F(1)	90.18(18)
F(2)#1-P(1)-F(3)	90.12(10)
F(2)-P(1)-F(3)	89.81(10)
F(1)#1-P(1)-F(3)	90.45(10)
F(1)-P(1)-F(3)	89.62(10)
F(2)#1-P(1)-F(3)#1	89.80(10)
F(2)-P(1)-F(3)#1	90.11(10)
F(1)#1-P(1)-F(3)#1	89.63(10)
F(1)-P(1)-F(3)#1	90.46(10)
F(3)-P(1)-F(3)#1	179.89(15)
C(16)-O(1)-C(19)	117.0(2)
C(24)-O(2)-C(27)	116.8(3)
C(1)-N(1)-C(12)	118.4(2)
C(1)-N(1)-Cu(1)	130.69(18)
C(12)-N(1)-Cu(1)	110.81(18)
C(10)-N(2)-C(11)	118.3(2)

C(10)-N(2)-Cu(1)	130.92(19)
C(11)-N(2)-Cu(1)	110.53(18)
N(1)-C(1)-C(2)	121.1(3)
N(1)-C(1)-C(13)	119.1(2)
C(2)-C(1)-C(13)	119.8(2)
C(3)-C(2)-C(1)	120.3(3)
C(3)-C(2)-H(2A)	119.8
C(1)-C(2)-H(2A)	119.8
C(2)-C(3)-C(4)	120.0(3)
C(2)-C(3)-H(3A)	120.0
C(4)-C(3)-H(3A)	120.0
C(3)-C(4)-C(12)	117.1(3)
C(3)-C(4)-C(5)	122.9(3)
C(12)-C(4)-C(5)	119.9(3)
C(6)-C(5)-C(4)	120.8(3)
C(6)-C(5)-H(5A)	119.6
C(4)-C(5)-H(5A)	119.6
C(5)-C(6)-C(7)	121.0(3)
C(5)-C(6)-H(6A)	119.5
C(7)-C(6)-H(6A)	119.5
C(8)-C(7)-C(11)	116.9(3)
C(8)-C(7)-C(6)	123.2(3)
C(11)-C(7)-C(6)	119.9(3)
C(9)-C(8)-C(7)	119.9(3)
C(9)-C(8)-H(8A)	120.1
C(7)-C(8)-H(8A)	120.1
C(8)-C(9)-C(10)	121.0(3)
C(8)-C(9)-H(9A)	119.5
C(10)-C(9)-H(9A)	119.5
N(2)-C(10)-C(9)	120.7(3)
N(2)-C(10)-C(21)	119.8(3)
C(9)-C(10)-C(21)	119.5(3)
N(2)-C(11)-C(7)	123.3(3)
N(2)-C(11)-C(12)	117.8(2)
C(7)-C(11)-C(12)	118.9(3)
N(1)-C(12)-C(4)	123.0(3)

N(1)-C(12)-C(11)	117.7(2)
C(4)-C(12)-C(11)	119.3(3)
C(14)-C(13)-C(18)	117.9(3)
C(14)-C(13)-C(1)	120.3(2)
C(18)-C(13)-C(1)	121.8(2)
C(15)-C(14)-C(13)	121.1(3)
C(15)-C(14)-H(14A)	119.4
C(13)-C(14)-H(14A)	119.4
C(14)-C(15)-C(16)	119.9(3)
C(14)-C(15)-H(15A)	120.0
C(16)-C(15)-H(15A)	120.0
O(1)-C(16)-C(15)	124.2(3)
O(1)-C(16)-C(17)	115.6(2)
C(15)-C(16)-C(17)	120.2(3)
C(18)-C(17)-C(16)	118.2(2)
C(18)-C(17)-C(20)	121.0(3)
C(16)-C(17)-C(20)	120.8(2)
C(17)-C(18)-C(13)	122.5(3)
C(17)-C(18)-H(18A)	118.7
C(13)-C(18)-H(18A)	118.7
O(1)-C(19)-H(19A)	109.5
O(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(26)	117.3(3)
C(22)-C(21)-C(10)	120.5(3)
C(26)-C(21)-C(10)	122.1(3)
C(23)-C(22)-C(21)	121.4(3)

C(23)-C(22)-H(22A)	119.3
C(21)-C(22)-H(22A)	119.3
C(22)-C(23)-C(24)	119.9(3)
C(22)-C(23)-H(23A)	120.0
C(24)-C(23)-H(23A)	120.0
O(2)-C(24)-C(23)	124.6(3)
O(2)-C(24)-C(25)	114.2(3)
C(23)-C(24)-C(25)	121.1(3)
C(26)-C(25)-C(24)	117.3(3)
C(26)-C(25)-C(28)	121.8(3)
C(24)-C(25)-C(28)	120.8(3)
C(25)-C(26)-C(21)	122.9(3)
C(25)-C(26)-H(26A)	118.6
C(21)-C(26)-H(26A)	118.6
O(2)-C(27)-H(27A)	109.5
O(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
O(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
N(31)-C(31)-C(32)	176.6(9)
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+0.5

Table S16 Bond lengths [Å] and angles [°] for **1**

O(1)-C(16)	1.375(7)
O(1)-C(19)	1.437(9)
O(2)-C(23)	1.363(7)
O(2)-C(26)	1.440(8)
N(1)-C(1)	1.348(7)
N(1)-C(12)	1.368(8)
N(2)-C(10)	1.338(7)
N(2)-C(11)	1.378(7)
C(1)-C(2)	1.409(8)
C(1)-C(13)	1.498(8)
C(2)-C(3)	1.364(9)
C(2)-H(2B)	0.9500
C(3)-C(4)	1.413(9)
C(3)-H(3A)	0.9500
C(4)-C(12)	1.414(8)
C(4)-C(5)	1.430(9)
C(5)-C(6)	1.356(9)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.414(8)
C(6)-H(6A)	0.9500
C(7)-C(11)	1.407(8)
C(7)-C(8)	1.413(9)
C(8)-C(9)	1.370(9)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.425(8)
C(9)-H(9A)	0.9500
C(10)-C(20)	1.497(8)
C(11)-C(12)	1.465(8)
C(13)-C(14)	1.381(8)
C(13)-C(18)	1.417(8)
C(14)-C(15)	1.387(10)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.380(9)
C(15)-H(15A)	0.9500

C(16)-C(17)	1.394(9)
C(17)-C(18)	1.368(8)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(25)	1.375(8)
C(20)-C(21)	1.397(8)
C(21)-C(22)	1.376(8)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.405(8)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.393(8)
C(24)-C(25)	1.417(8)
C(24)-H(24A)	0.9500
C(25)-H(25A)	0.9500
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800

C(16)-O(1)-C(19)	117.0(6)
C(23)-O(2)-C(26)	116.5(5)
C(1)-N(1)-C(12)	118.8(5)
C(10)-N(2)-C(11)	118.3(5)
N(1)-C(1)-C(2)	121.5(6)
N(1)-C(1)-C(13)	115.8(5)
C(2)-C(1)-C(13)	122.6(6)
C(3)-C(2)-C(1)	119.8(6)
C(3)-C(2)-H(2B)	120.1
C(1)-C(2)-H(2B)	120.1
C(2)-C(3)-C(4)	120.3(6)
C(2)-C(3)-H(3A)	119.8
C(4)-C(3)-H(3A)	119.8
C(3)-C(4)-C(12)	116.9(6)
C(3)-C(4)-C(5)	123.0(6)

C(12)-C(4)-C(5)	120.0(6)
C(6)-C(5)-C(4)	120.4(6)
C(6)-C(5)-H(5A)	119.8
C(4)-C(5)-H(5A)	119.8
C(5)-C(6)-C(7)	122.2(6)
C(5)-C(6)-H(6A)	118.9
C(7)-C(6)-H(6A)	118.9
C(11)-C(7)-C(8)	117.4(5)
C(11)-C(7)-C(6)	119.3(6)
C(8)-C(7)-C(6)	123.3(6)
C(9)-C(8)-C(7)	119.6(6)
C(9)-C(8)-H(8A)	120.2
C(7)-C(8)-H(8A)	120.2
C(8)-C(9)-C(10)	120.0(6)
C(8)-C(9)-H(9A)	120.0
C(10)-C(9)-H(9A)	120.0
N(2)-C(10)-C(9)	121.6(5)
N(2)-C(10)-C(20)	117.1(5)
C(9)-C(10)-C(20)	121.3(5)
N(2)-C(11)-C(7)	123.1(5)
N(2)-C(11)-C(12)	117.2(5)
C(7)-C(11)-C(12)	119.6(5)
N(1)-C(12)-C(4)	122.5(5)
N(1)-C(12)-C(11)	119.1(5)
C(4)-C(12)-C(11)	118.4(5)
C(14)-C(13)-C(18)	117.4(6)
C(14)-C(13)-C(1)	122.6(5)
C(18)-C(13)-C(1)	119.9(5)
C(13)-C(14)-C(15)	122.3(6)
C(13)-C(14)-H(14A)	118.9
C(15)-C(14)-H(14A)	118.9
C(16)-C(15)-C(14)	119.5(6)
C(16)-C(15)-H(15A)	120.2
C(14)-C(15)-H(15A)	120.2
O(1)-C(16)-C(15)	125.2(6)
O(1)-C(16)-C(17)	115.4(6)

C(15)-C(16)-C(17)	119.3(6)
C(18)-C(17)-C(16)	121.0(6)
C(18)-C(17)-H(17A)	119.5
C(16)-C(17)-H(17A)	119.5
C(17)-C(18)-C(13)	120.5(6)
C(17)-C(18)-H(18A)	119.8
C(13)-C(18)-H(18A)	119.8
O(1)-C(19)-H(19A)	109.5
O(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(25)-C(20)-C(21)	118.8(5)
C(25)-C(20)-C(10)	120.5(5)
C(21)-C(20)-C(10)	120.8(5)
C(22)-C(21)-C(20)	121.5(6)
C(22)-C(21)-H(21A)	119.2
C(20)-C(21)-H(21A)	119.2
C(21)-C(22)-C(23)	119.7(6)
C(21)-C(22)-H(22A)	120.1
C(23)-C(22)-H(22A)	120.1
O(2)-C(23)-C(24)	124.1(5)
O(2)-C(23)-C(22)	116.0(5)
C(24)-C(23)-C(22)	119.8(5)
C(23)-C(24)-C(25)	119.0(5)
C(23)-C(24)-H(24A)	120.5
C(25)-C(24)-H(24A)	120.5
C(20)-C(25)-C(24)	121.2(6)
C(20)-C(25)-H(25A)	119.4
C(24)-C(25)-H(25A)	119.4
O(2)-C(26)-H(26A)	109.5
O(2)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
O(2)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C)	109.5

Table S17 Bond lengths [Å] and angles [°] for **2**

O(1)-C(10)	1.3656(17)
O(1)-H(1A)	0.986(16)
O(2)-H(2C)	0.907(15)
O(2)-H(2B)	0.919(15)
N(1)-C(1)	1.3376(16)
N(1)-C(6)	1.3555(16)
C(1)-C(2)	1.4095(19)
C(1)-C(7)	1.4786(19)
C(2)-C(3)	1.354(2)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.408(2)
C(3)-H(3A)	0.9300
C(4)-C(6)	1.4100(19)
C(4)-C(5)	1.427(2)
C(5)-C(5)#1	1.339(3)
C(5)-H(5A)	0.9300
C(6)-C(6)#1	1.457(3)
C(7)-C(12)	1.3918(19)
C(7)-C(8)	1.3962(19)
C(8)-C(9)	1.381(2)
C(8)-H(8A)	0.9300
C(9)-C(10)	1.380(2)
C(9)-H(9A)	0.9300
C(10)-C(11)	1.383(2)
C(11)-C(12)	1.376(2)
C(11)-H(11A)	0.9300
C(12)-H(12A)	0.9300

C(10)-O(1)-H(1A)	109.6(13)
H(2C)-O(2)-H(2B)	101.4(17)
C(1)-N(1)-C(6)	118.98(11)
N(1)-C(1)-C(2)	121.35(13)

N(1)-C(1)-C(7)	116.50(12)
C(2)-C(1)-C(7)	122.15(12)
C(3)-C(2)-C(1)	119.91(14)
C(3)-C(2)-H(2A)	120.0
C(1)-C(2)-H(2A)	120.0
C(2)-C(3)-C(4)	120.18(13)
C(2)-C(3)-H(3A)	119.9
C(4)-C(3)-H(3A)	119.9
C(3)-C(4)-C(6)	116.89(13)
C(3)-C(4)-C(5)	122.96(13)
C(6)-C(4)-C(5)	120.14(14)
C(5)#1-C(5)-C(4)	121.10(9)
C(5)#1-C(5)-H(5A)	119.5
C(4)-C(5)-H(5A)	119.5
N(1)-C(6)-C(4)	122.67(12)
N(1)-C(6)-C(6)#1	118.57(7)
C(4)-C(6)-C(6)#1	118.76(8)
C(12)-C(7)-C(8)	117.56(13)
C(12)-C(7)-C(1)	120.38(12)
C(8)-C(7)-C(1)	122.05(13)
C(9)-C(8)-C(7)	121.07(14)
C(9)-C(8)-H(8A)	119.5
C(7)-C(8)-H(8A)	119.5
C(10)-C(9)-C(8)	120.27(13)
C(10)-C(9)-H(9A)	119.9
C(8)-C(9)-H(9A)	119.9
O(1)-C(10)-C(9)	122.98(13)
O(1)-C(10)-C(11)	117.61(13)
C(9)-C(10)-C(11)	119.41(13)
C(12)-C(11)-C(10)	120.22(14)
C(12)-C(11)-H(11A)	119.9
C(10)-C(11)-H(11A)	119.9
C(11)-C(12)-C(7)	121.39(13)
C(11)-C(12)-H(12A)	119.3
C(7)-C(12)-H(12A)	119.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1.5

Fig. S10 Representative structure of stereoisomers

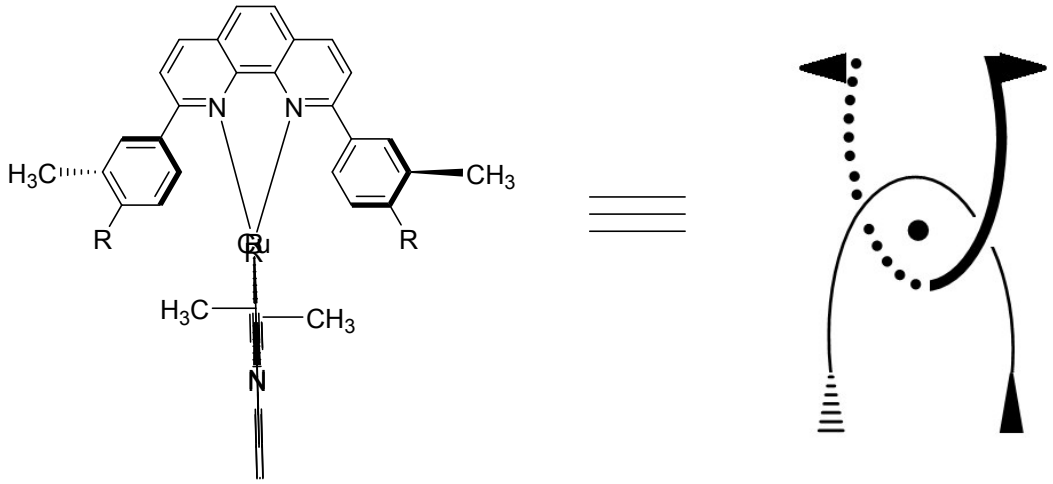
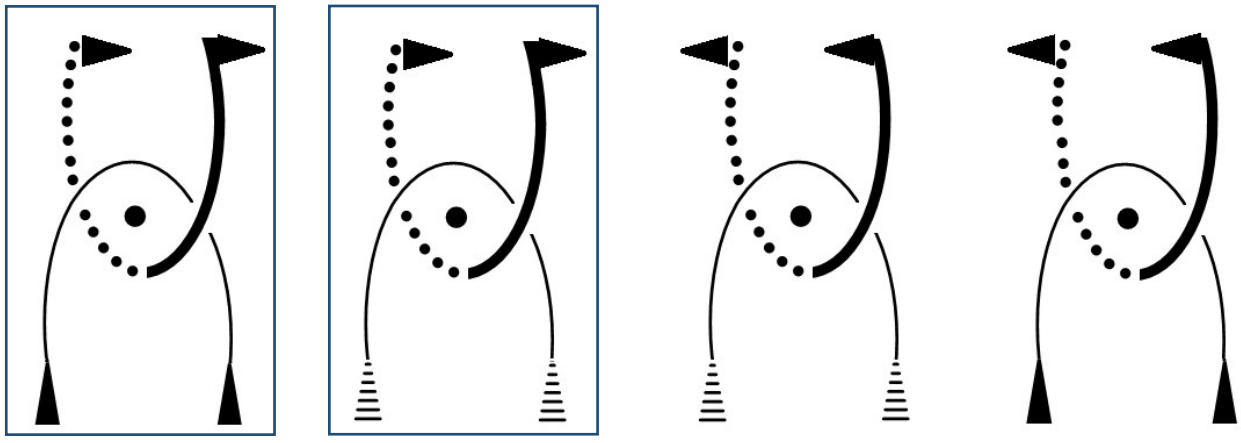


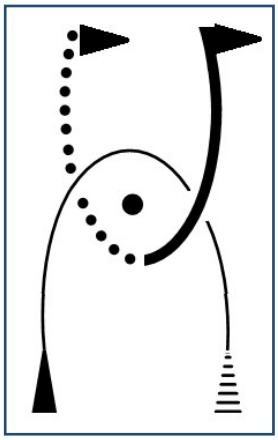
Fig. S11 Representation of stereoisomers

cis, cis isomers:



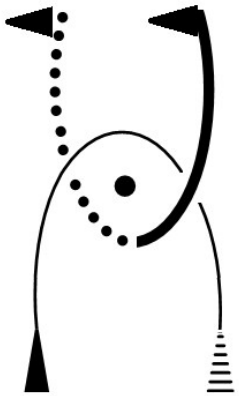
A (chiral)	**B (chiral)**	**C**	**D**
enantiomer of B	**enantiomer of A**	**same as A**	**same as B**

cis, trans isomers:



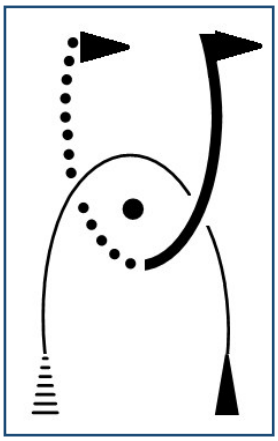
E (chiral)

enantiomer of G



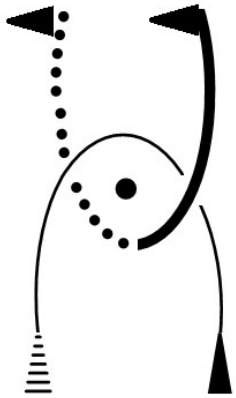
F

same as E



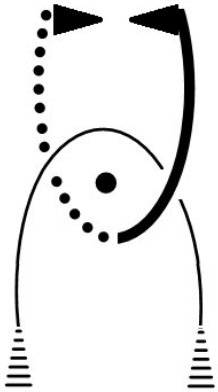
G (chiral)

enantiomer of E



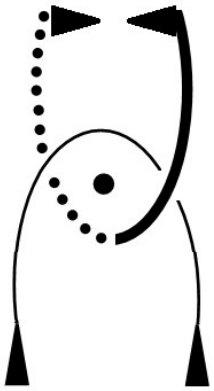
H

same as G



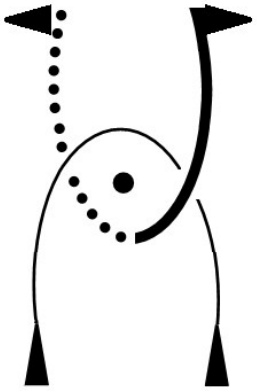
I

same as E



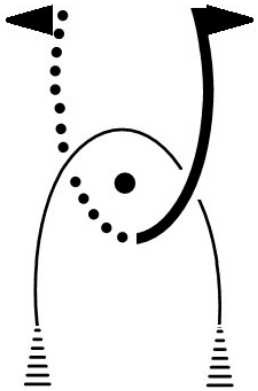
J

same as E



K

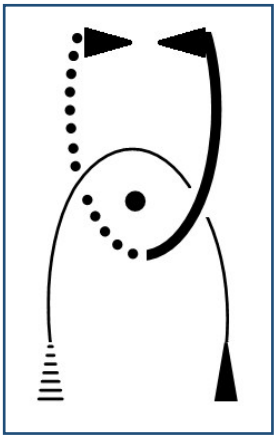
same as G



L

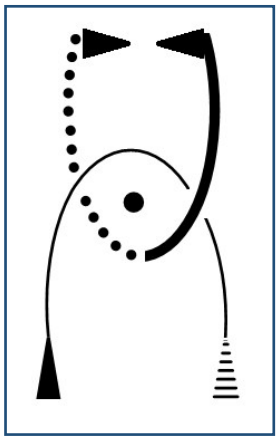
same as G

trans, trans:



M (achiral)

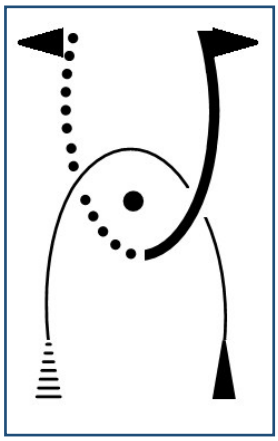
diastereomer of N and O



N (chiral)

enantiomer of O

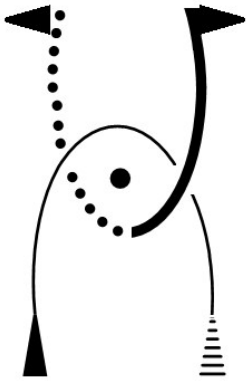
diastereomer of M



O (chiral)

enantiomer of N

diastereomer of M



P

same as M

Photocatalytic Experimental Setup

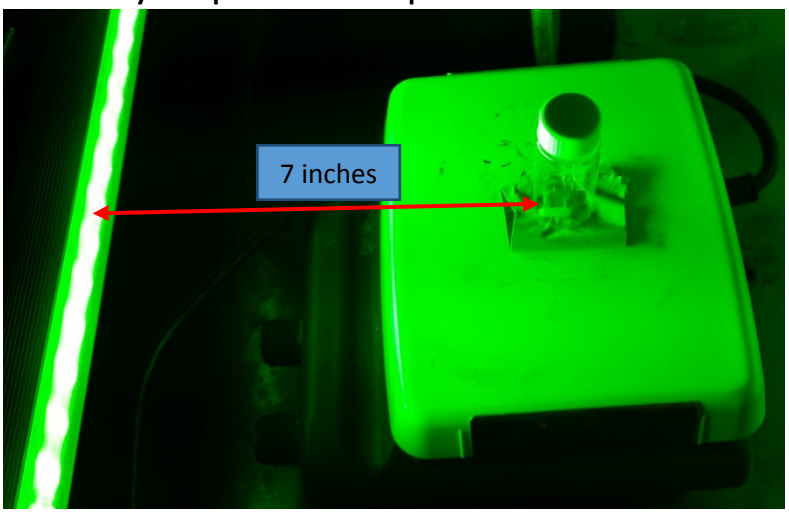


Fig. S12 Green LED light experimental setup

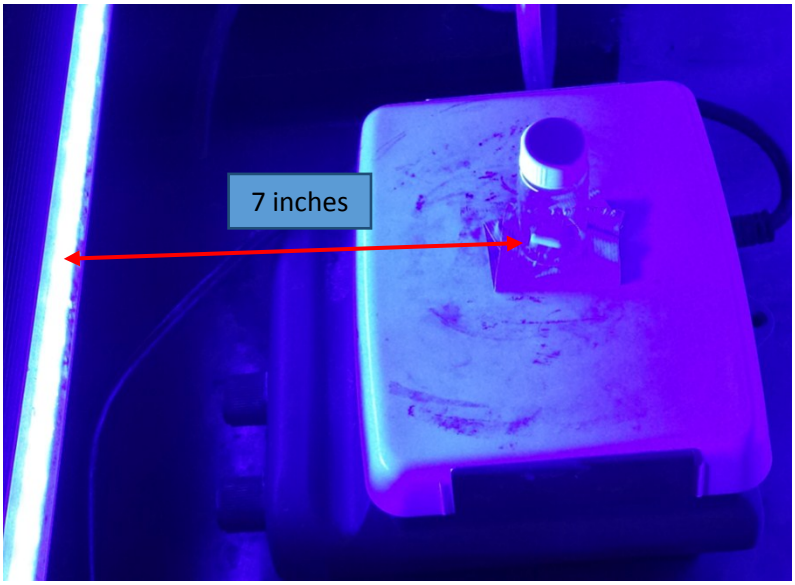


Fig. S13 Blue LED light experimental setup

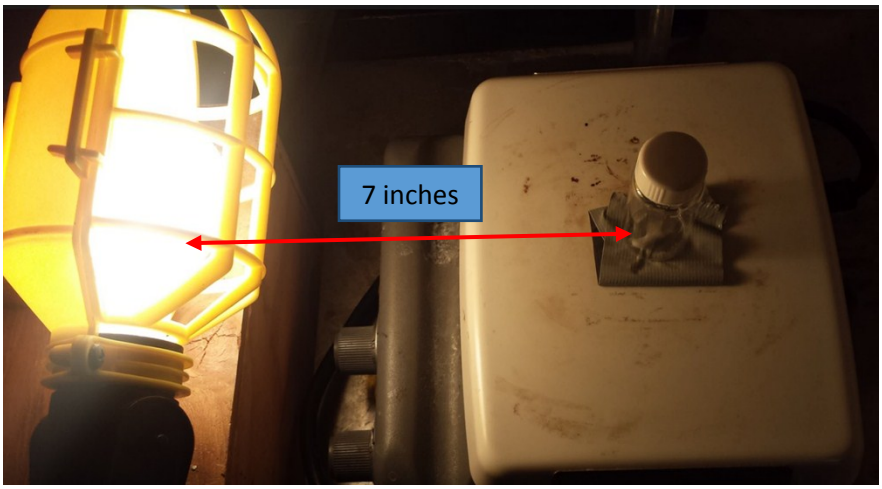


Fig. S14 White light experimental setup

Features of LED lights (used in photoredox)

Company where LED lights were purchased:

http://www.bmlhorticulture.com/led-light-bar-525nm-green/

http://www.bmlhorticulture.com/led-light-bar-450nm-royal-blue/

Blue LED light (PS1230S201LLLLLLLLLLLLLL)

LED Light Bar – 450 nm Royal Blue

Fixture Length : 12"

Beam Angle : 30°

Green LED light (PS1230S201PPPPPPPPPPPPPP)

LED Light Bar – 525 nm Green

Fixture Length : 12"

Beam Angle : 30°

Possible Transitions after Different LED Light Irradiation

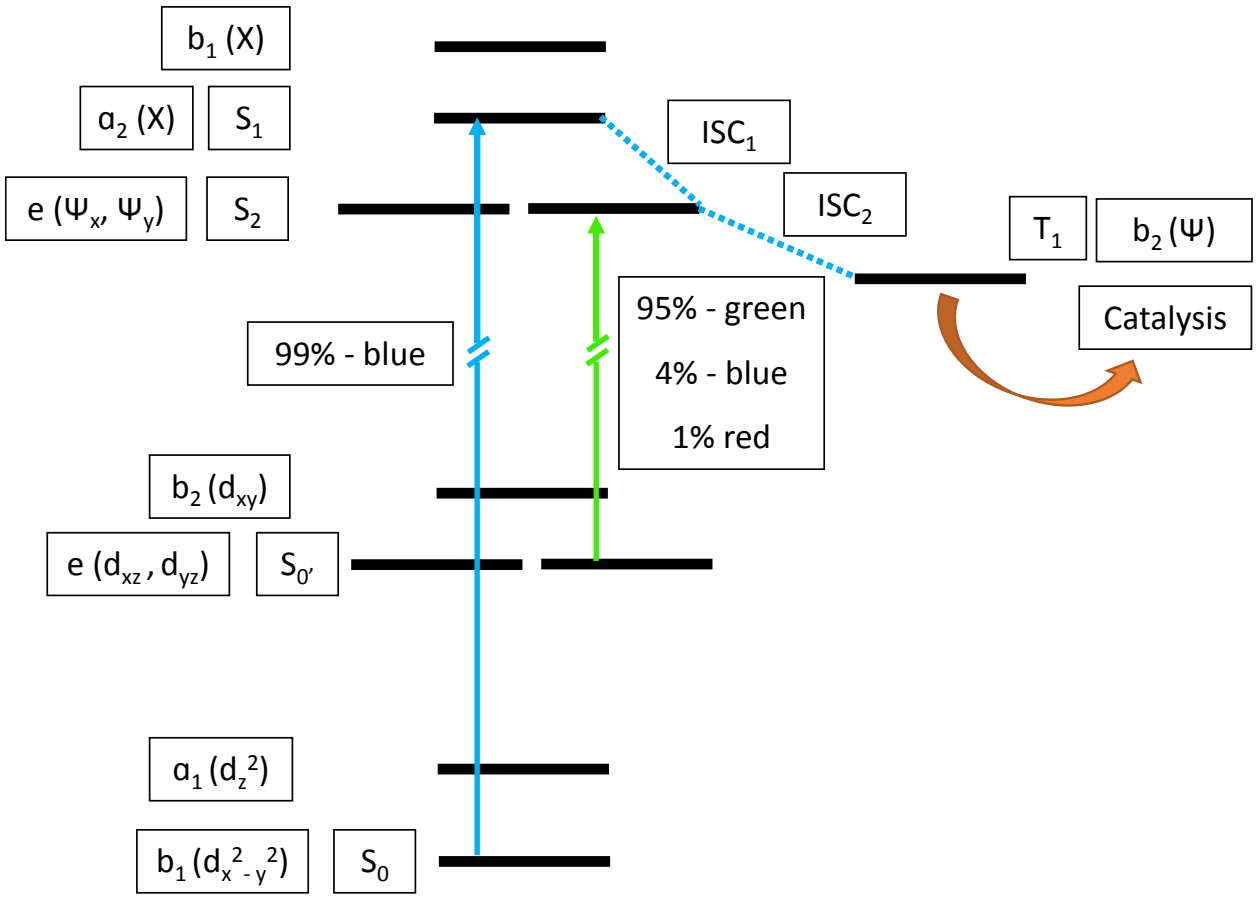


Fig. S15 Possible transitions with irradiation

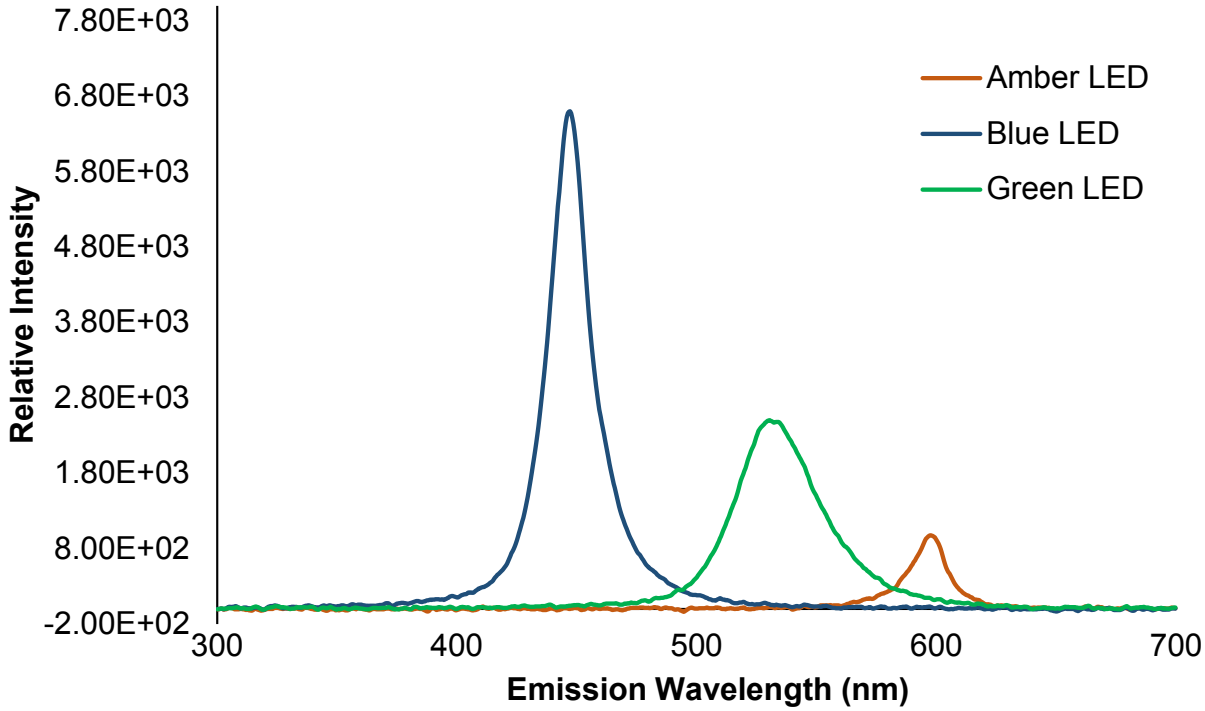
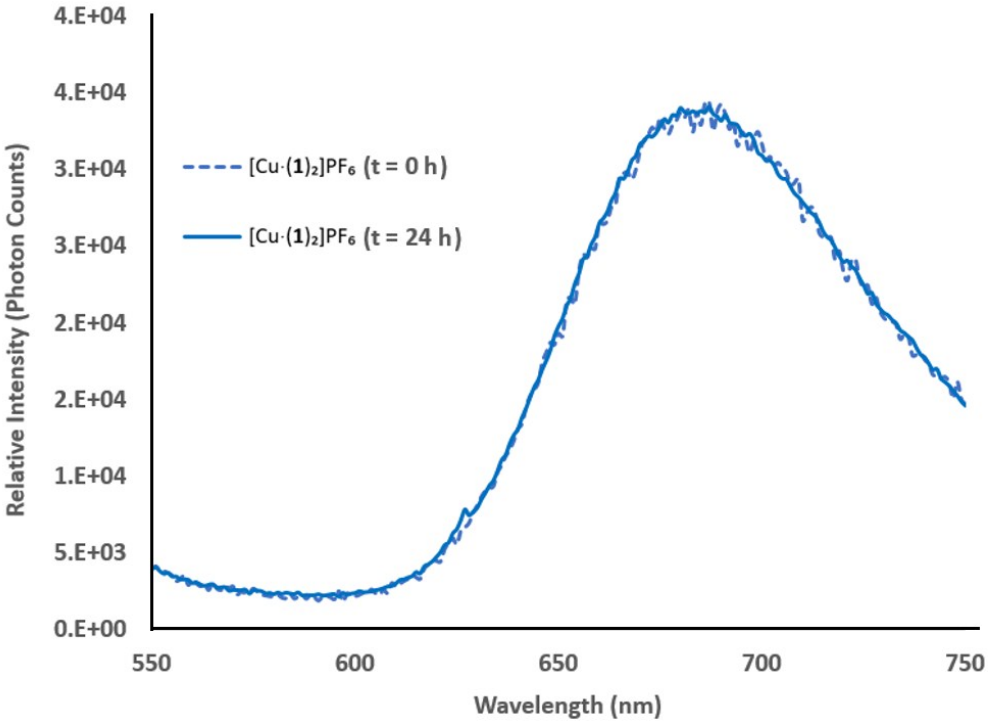
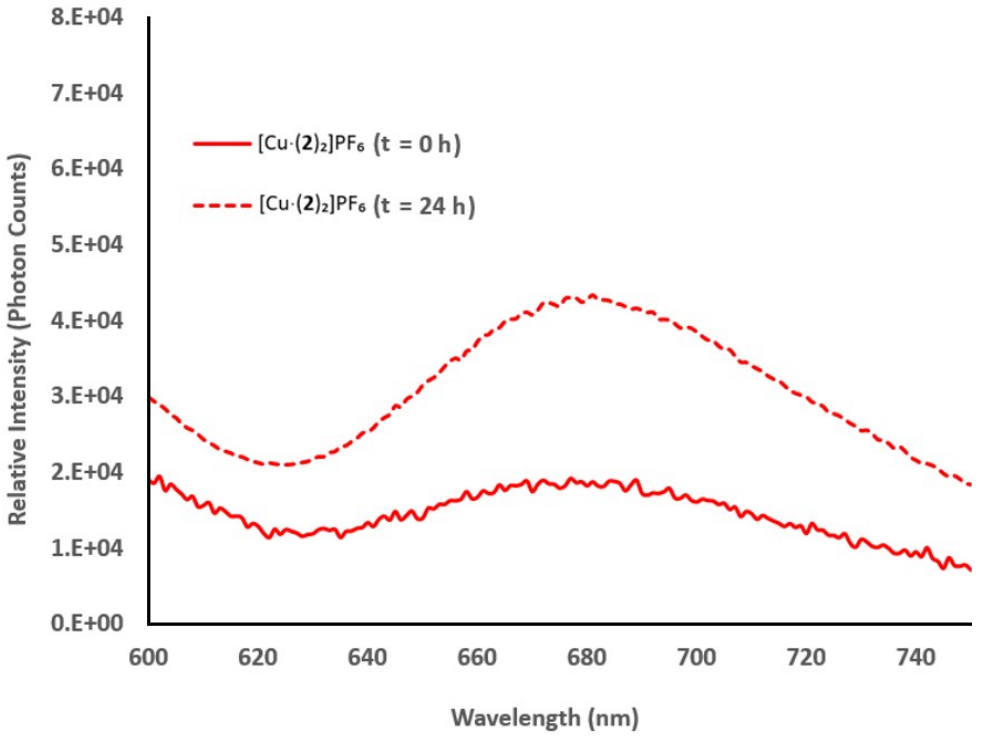


Fig. S16 Relative emission profiles of LEDs (blue LED in blue, green LED in green and orange LED in orange)



(a)



(b)

Fig. S17 Changes in emission intensity after initial dissolution of (a) $[Cu\cdot(\mathbf{1})_2]PF_6$ and (b) $[Cu\cdot(\mathbf{2})_2]PF_6$ in degassed DCM

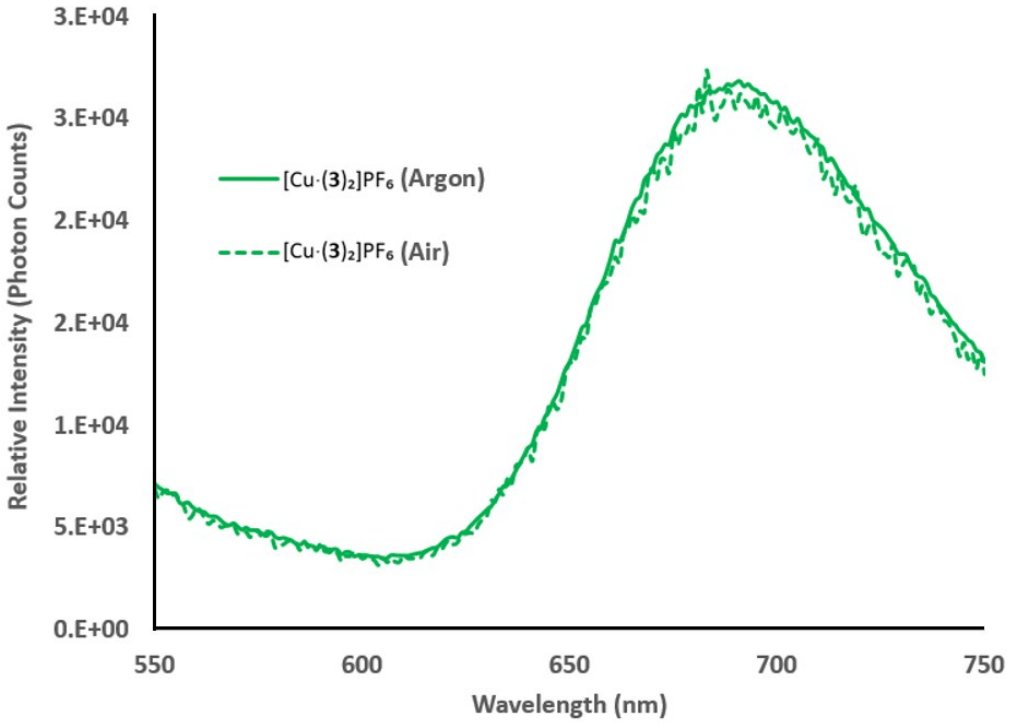


Fig. S18 Emission spectra of $[Cu\cdot(\mathbf{3})_2]PF_6$ before and after exposure to air