Supporting Information for

Donor-driven conformational flexibility in a real-life catalytic di-copper(II) peroxo complex

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Table S1: Geometric Key Parameters with TPSSh/6-31g(d) for the pzpz conformer without PCM model. with PCM model and with GD3BJ

	S2	Cu-Cu	O-O	Cu-Npz	Cu-Npy	Energy in H	relative E in kcal/mol
Singlet Oxo		2.890	2.137	1.962/1.991/1.999	2.516/2.527	-5535.00489041	9.29
Singlet Peroxo		3.559	1.453	1.990/1.994/2.004	2.197/2.210	-5535.01436777	3.34
Peroxo BS	0.54	3.577	1.473	1.995/2.000//1.998/2.013	2.185/2.202	-5535.01969604	0.00
Singlet Oxo DCM	0	2.874	2.155	1.956/1.989//1.957/1.989	2.538//2.504	-5535.16046361	8.74
Singlet Peroxo DCM		3.554	1.453	1.982/1.991//1.994/2.007	2.201//2.177	-5535.16879833	3.51
Peroxo BS DCM	0.58	3.563	1.472	1.997/1.992//2.019/1.997	2.196//2.168	-5535.17438927	0.00
Singlet Oxo with GD3BJ		2.852	2.169	1.939/1.968//1.941/1.970	2.481//2.462	-5535.23019510	4.30
Peroxo Singlet with GD3BJ		3.516	1.463	1.960/1.972//1.962/1.977	2.186//2.175	-5535.23222714	3.02
Peroxo BS with GD3BJ	0.52	3.537	1.481	1.965/1.976//1.966/1.985	2.175//2.164	-5535.23704209	0.00

Table S2: Geometric Key Parameters with TPSSh/6-31g(d) for the pypz conformer without PCM model. with PCM model and with GD3BJ

	S2	Cu-Cu	O-O	Cu-Npz	Cu-Npy	Energy in H	relative E in kcal/mol
Singlet Oxo		2.839	2.180	1.974/2.781//1.978/2.660	1.928//1.928	-5535.01770212	1.73
Singlet Peroxo		3.534	1.463	2.258/1.994//2.273/1.995	1.987/1.973	-5535.01508482	3.37
Peroxo BS	0.54	3.562	1.483	2.002/2.253//1.998/2.250	1.978/1.991	-5535.02045700	0.00
Singlet Oxo DCM		2.817	2.196	1.954/2.790//1.977/2.693	1.914//1.933	-5535.17631098	-0.10
Singlet Peroxo DCM		3.526	1.466	1.991/2.283//1.993/2.284	1.975//1.967	-5535.17085847	3.33
Peroxo BS DCM	0.53	3.553	1.485	1.999/2.266//1.996/2.270	1.969//1.978	-5535.17615812	0.00
Singlet Oxo GD3BJ		2.800	2.198	1.960/2.531//2.009/2.308	1.924/1.942	-5535.24637358	-5.62
Peroxo Singlet GD3BJ		3.491	1.47	1.961/2.223//1.978/2.164	1.962//1.991	-5535.23168565	3.59
Peroxo BS GD3BJ	0.62	3.488	1.484	1.973/2.197//1.979/2.162	1.975//1.992	-5535.23741430	0.00

Table S3: Geometric Key Parameters with TPSSh/6-31g(d) for the pypz-cis conformer without PCM model. with PCM model and with GD3BJ

	S2	Cu-Cu	O-O	Cu-Npz	Cu-Npy	Energy in H	relative E in kcal/mol
Singlet Oxo		2.760	2.247	1.916/3.071//1.916/3.071	1.912/1.912	-5535.01482937	0.93
Singlet Peroxo		3.544	1.456	1.985/2.263//2.018/2.236	1.983/1.990	-5535.01126086	3.17
Peroxo BS	0.55	3.564	1.475	2.251/1.997//2.024/2.221	1.986/1.998	-5535.01630540	0.00
Singlet Oxo BS DCM		2.749	2.259	1.908/3.118//1.911/3.154	1.906//1.906	-5535.17519504	-1.58
Singlet Peroxo DCM		3.536	1.458	1.978/2.286//2.018/2.251	1.974//1.980	-5535.16801440	2.93
Peroxo BS DCM	0.54	3.56	1.476	2.017/2.242//1.988/2.271	1.987/1.979	-5535.17268228	0.00
Singulett Oxo GD3BJ		2.889	2.135	1.977/2.503//1.977/2.504	1.963//1.963	-5535.23119818	0.67
Peroxo Singlet GD3BJ		3.48	1.469	1.960/2.180//2.001/2.140	1.989//2.001	-5535.23673134	-2.80
Peroxo BS GD3BJ	0.58	3.521	1.477	2.000/2.160//1.975/2.189	1.996//1.981	-5535.23227042	0.00

Table S4: Geometric Key Parameters with TPSSh/6-31g(d) for the pzpz-pypz conformer without PCM model. with PCM model and with GD3BJ

	S2	Cu-Cu	O-O	Cu-Npz	Cu-Npy	Energy in H	relative E in kcal/mol
Singlet Oxo		2.825	2.167	1.954/1.953//1.984/2.650	2.577/1.959	-5535.00928993	7.44
Singlet Peroxo		3.535	1.456	1.991/2.162//1.978/1.979	2.042/2.243	-5535.01550273	3.54
Peroxo BS	0.62	3.521	1.475	1.992/1.986//1.987/2.128	2.223/2.066	-5535.02114732	0.00
Singlet Oxo DCM		2.806	2.183	1.950/1.952//1.973/2.721	2.557//1.946	-5535.16817550	5.28
Singlet Peroxo DCM		3.524	1.458	1.987/2.193//1.976/1.977	2.017//2.228	-5535.17132626	3.30
Peroxo BS DCM	0.68	3.51	1.522	1.991/1.983//1.992/2.193	2.207/2.008	-5535.17658338	0.00
Singlet Oxo GD3BJ		2.756	2.193	1.995/2.325//1.925/1.941	1.975//2.510	-5535.23436646	-1.56
Peroxo Singlet GD3BJ		3.503	1.46	1.970/2.133//1.972/1.951	2.021//2.207	-5535.22716696	2.96
Peroxo BS GD3BJ	0.55	3.499	1.477	1.969/2.136//1.957/1.979	2.025//2.189	-5535.23187835	0.00

Table S5: Geometric Key Parameters with TPSSh/def2-TZVP

	Cu…Cu	O…O	Cu-Npz	Cu-Npy	Energy in H	relative E in kcal/mol	S2
Oxo pzpz	2.952	2.123	1.998/2.038//1.998/2.024	2.514//2.455	-5536.26555175	21.7	
Peroxo pzpz	3.650	1.422	2.026/2.041//2.025/2.040	2.252//2.253	-5536.29702216		
Peroxo BS pzpz	3.656	1.443	2.026/2.042//2.026/2.039	2.247//2.247	-5536.30010788	0	0.43
Oxo pypz	2.888	2.170	2.000/2.831//1.997/2.756	1.958//1.955	-5536.27744123	14.2	
Peroxo pypz	3.630	1.427	2.013/2.364//2.017/2.344	2.022//2.013	-5536.29489114		
Peroxo BS pypz	3.641	1.447	2.018/2.339//2.016/2.347	2.012//2.022	-5536.29811337	1.3	0.44
Oxo pypz-cis	2.804	2.247	1.944/3.149//1.944/3.148	1.941//1.941	-5536.27529794	15.6	
Peroxo pypz-cis	3.636	1.422	2.008/2.352//2.039/2.320	2.019//2.034	-5536.29228750		
Peroxo BS pypz-cis	3.641	1.440	2.043/2.318//2.013/2.344	2.033//2.024	-5536.29527764	3.0	0.47
Oxo pzpz-pypz	2.922	2.114	1.998/1.992//2.002/2.791	2.510//1.983	-5536.26969688	19.1	
Peroxo pzpz-pypz	3.624	1.423	2.014/2.015//2.016/2.260	2.294//2.068	-5536.29565716		
Peroxo BS pzpz-pypz	3.582	1.439	2.017/2.253//2.019/2.029	2.061//2.273	-5536.29998385	0.1	0.64

Table S6: Geometric Key Parameters with TPSSh/def2-TZVP and PCM DCM

	Cu…Cu	O…O	Cu-Npz	Cu-Npy	Energy in H	relative E in kcal/mol	S2
Oxo pzpz	2.961	2.101	1.998/2.016//1.999/2.008	2.463//2.490	-5536.42176741	22.5	
Peroxo pzpz	3.643	1.422	2.021/2.041//2.021/2.041	2.233/2.233	-5536.45125959		
Peroxo BS pzpz	3.647	1.443	2.020/2.048//2.020/2.038	2.226//2.223	-5536.45475572	1.8	0.45
Oxo pypz	2.865	2.192	1.992/2.782//1.987/2.952	1.949//1.945	-5536.43745468	12.7	
Peroxo pypz	3.615	1.430	2.012/2.386//2.011/2.374	2.010//2.000	-5536.45145830		
Peroxo BS pypz	3.626	1.450	2.014/2.362//2.013/2.385	2.002//2.009	-5536.45455710	1.9	0.45
Oxo pypz-cis	2.790	2.262	1.938/3.184//1.938/3.184	1.935//1.935	-5536.43648794	13.3	
Peroxo pypz-cis	3.623	1.424	2.002/2.373//2.032/2.349	2.008//2.018	-5536.44962871		
Peroxo BS pypz-cis	3.631	1.443	2.007/2.358//2.034/2.349	2.012//2.018	-5536.45245840	3.2	0.43
Oxo pzpz-pypz	2.887	2.151	1.984/1.990//1.994/2.816	2.512//1.971	-5536.42898403	18.0	
Peroxo pzpz-pypz	3.606	1.425	2.011/2.017//2.010/2.307	2.281//2.041	-5536.45225764		
Peroxo BS pzpz-pypz	3.535	1.436	2.031/2.025//2.014/2.274	2.270//2.043	-5536.45762374	0	0.72

Table S7: Geometric Key Parameters with TPSSh/def2-TZVP and GD3BJ

	Cu…Cu	O…O	Cu-Npz	Cu-Npy	Energy in H	S2	relative E in kcal/mol
Oxo pzpz	2.927	2.129	1.975/1.992//1.975/1.993	2.462//2.462	-5536.48803989		16.73
Peroxo pzpz	3.605	1.430	1.996/2.012//1.996/2.012	2.228/2.228	-5536.51019402		
Peroxo BS pzpz	3.612	1.450	1.993/2.015//1.994/2.013	2.218//2.216	-5536.51349922	0.44	
Oxo pypz	2.836	2.201	1.998/2.535//1.967/2.607	1.959//1.940	-5536.49544032		12.09
Peroxo pypz	3.586	1.434	1.985/2.284//1.995/2.264	1.999/2.017	-5536.50721699		
Peroxo BS pypz	3.573	1.450	2.003/2.248//1.992/2.275	2.013//2.007	-5536.51122729	0.56	2.18
Oxo pypz-cis	2.760	2.283	1.930/2.911//1.930/2.911	1.929//1.929	-5536.48793370		16.80
Peroxo pypz-cis	3.597	1.428	2.017/2.230//1.984/2.274	2.026/2.006	-5536.50433854		
Peroxo BS pypz-cis	3.602	1.445	2.011/2.257//2.019/2.237	2.011//2.024	-5536.50750143	0.48	4.52
Oxo pzpz-pypz	2.831	2.169	1.961/1.974//1.993/2.486	2.499//1.986	-5536.48954867		15.78
Peroxo pzpz-pypz	3.571	1.431	1.976/1.995//2.002/2.189	2.281//2.035	-5536.50975584		
Peroxo BS pzpz-pypz	3.475	1.443	1.992/1.995//1.987/2.155	2.262//2.071	-5536.51469962	0.71	0

Table S8: Geometric Key Parameters with TPSSh/def2-TZVP and PCM DCM and GD3BJ

	Cu…Cu	O…O	Cu-Npz	Cu-Npy	Energy in H	S2	relative E in kcal/mol
Oxo pzpz	2.897	2.162	1.966/1.983//1.968/1.984	2.471//2.464	-5536.64485154		17.82
Peroxo pzpz	3.596	1.431	1.985/2.013//1.985/2.013	2.209/2.209	-5536.66520187		
Peroxo BS pzpz	3.606	1.451	1.987/2.015//1.989/2.010	2.200//2.203	-5536.66872505	0.45	2.84
Peroxo triplett pzpz	3.510	1.412	2.000/2.058//2.008/2.045	2.175//2.223	-5536.66125087	2.00	7.53
Oxo pypz	2.814	2.217	1.994/2.547//1.956/2.655	1.954//1.932	-5536.65568405		11.02
Peroxo pypz	3.568	1.439	1.994/2.271//1.977/2.327	2.003//1.983	-5536.66428708		
Peroxo BS pypz	3.518	1.451	1.988/2.315//2.000/2.251	1.995//2.003	-5536.66838862	0.65	3.05
Peroxo triplett pypz	3.373	1.424	2.019/2.262//2.011/2.289	2.018//2.011	-5536.66244037	2.00	6.78
Oxo pypz-cis	2.752	2.289	1.928/3.300//1.928/3.300	1.923//1.923	-5536.65382724		12.19
Peroxo pypz-cis	3.585	1.430	1.974/2.292//2.006/2.235	1.994//2.016	-5536.66197332		
Peroxo BS pypz-cis	3.596	1.448	1.986/2.274//2.013/2.251	2.001//2.014	-5536.66501325	0.47	5.17
Peroxo triplett pypz-cis	3.473	1.417	2.025/2.245//1.987/2.242	2.028//2.065	-5536.65905840	2.00	8.91
Oxo pzpz-pypz	2.790	2.193	1.953/1.966//1.989/2.472	2.495//1.977	-5536.64990958		14.65
Peroxo pzpz-pypz	3.552	1.432	1.974/1.994//1.997/2.191	2.258//2.023	-5536.66695401		
Peroxo BS pzpz-pypz	3.393	1.443	1.994/1.994//1.982/2.160	2.244//2.059	-5536.67324993	0.80	0
Peroxo triplett pzpz-pypz	3.228	1.419	2.012/2.032//1.988/2.204	2.250//2.039	-5536.66727961	2.00	3.75

Table S9: Geometric Key Parameters with M06L/def2-TZVP

	Cu…Cu	O…O	Cu-Npz	Cu-Npy	Energie in H	relative E in kcal/mol	S2
Oxo pzpz	2.949	2.148	1.998/2.006//1.998/2.006	2.461//2.462	-5535.90238350	15.45	
Peroxo pzpz	3.630	1.423	2.007/2.041//2.009/2.054	2.247//2.231	-5535.92260253	2.76	
Peroxo BS pzpz	3.633	1.431	2.004/2.038//2.005/2.059	2.238//2.234	-5535.92316134	2.41	0.19
Peroxo Triplett pzpz	3.535	1.388	2.028/2.091//2.032/2.066	2.197//2.253	-5535.91917420	4.91	2.01
Oxo pypz	2.901	2.191	2.018/2.657//2.019/2.592	1.969//1.970	-5535.91402860	8.14	
Peroxo pypz	3.606	1.435	2.014/2.355//2.005/2.361	2.020//2.010	-5535.92370515	2.07	
Peroxo BS pypz	3.592	1.441	2.018/2.281//1.996/2.362	2.032//2.012	-5535.92464520	1.48	0.26
Peroxo Triplett pypz	3.434	1.395	2.074/2.240//2.038/2.341	2.045//2.040	-5535.92011999	4.32	2.01
Oxo pypz-cis	2.786	2.297	1.952/2.919//1.952/2.918	1.945//1.945	-5535.90386710	14.52	
Peroxo pypz-cis	3.607	1.428	2.037/2.253//1.994/2.349	2.043//2.010	-5535.92322078	2.37	
Peroxo BS pypz-cis	3.610	1.433	2.037/2.253//1.997/2.346	2.043//2.012	-5535.92353189	2.18	0.18
Peroxo Triplett pypz-cis	3.516	1.391	2.091/2.228//2.014/2.180	2.046//2.139	-5535.91877474	5.16	2.00
Oxo pzpz-pypz	2.851	2.194	1.986/1.998//2.014/2.517	2.509//1.992	-5535.90704080	12.52	
Peroxo pzpz-pypz	3.594	1.429	1.998/2.024//2.023/2.253	2.279//2.033	-5535.92633666	0.42	
Peroxo BS pzpz-pypz	3.586	1.437	2.001/2.025//2.022/2.255	2.274//2.032	-5535.92699842	0.00	0.29
Peroxo Triplett pzpz-pypz	3.326	1.396	2.036/2.255//2.052/2.057	2.046//2.240	-5535.92290680	2.57	2.01

Table S10: Geometric Key Parameters with B3LYP/def2-TZVP

	Cu…Cu	O…O	Cu-Npz	Cu-Npy	Energie in H		S2
Oxo pzpz	3.025	2.037	2.028/2.046//2.032/2.027	2.501//2.522	-5536.33164946	31.49	
Peroxo pzpz	3.693	1.397	2.036//2.066//2.042/2.083	2.273//2.259	-5536.36772900	8.85	
Peroxo BS pzpz	3.661	1.435	2.065/2.044//2.076/2.050	2.257//2.270	-5536.37792816	2.45	0.71
Peroxo Triplett pzpz	3.628	1.392	2.070/2.108//2.076/2.078	2.214//2.293	-5536.37302213	5.53	2.00
Oxo pypz	2.864	2.201	1.999/2.967//2.006/2.947	1.960//1.962	-5536.34837040	21.00	
Peroxo pypz	3.659	1.407	2.027/2.482//2.028//2.453	2.022//2.017	-5536.36878522	8.19	
Peroxo BS pypz	3.653	1.449	2.029/2.470//2.033/2.457	2.022//2.016	-5536.37843179	2.13	0.65
Peroxo Triplett pypz	trans-μ Peroxo after geometry optimisation						
Oxo pypz-cis	2.803	2.260	1.957/3.192//1.957/3.213	1.953//1.953	-5536.34715478	21.76	
Peroxo pypz-cis	3.672	1.401	2.018/2.467//2.054/2.402	2.022//2.043	-5536.36696258	9.33	
Peroxo BS pypz-cis	3.665	1.446	2.021//2.429//2.022/2.455	2.036//2.032	-5536.37943841	1.50	0.63
Peroxo Triplett pypz-cis	trans-μ Peroxo after geometry optimisation						
Oxo pzpz-pypz	2.886	2.165	2.003/2.003//2.000/3.053	2.636//1.975	-5536.33912494	26.80	
Peroxo pzpz-pypz	3.659	1.401	2.035/2.048//2.031/2.397	2.323//2.044	-5536.36864713	8.27	
Peroxo BS pzpz-pypz	3.517	1.430	2.061/2.049//2.035/2.338	2.326//2.057	-5536.38183397	0.00	0.85
Peroxo Triplett pzpz-pypz	3.402	1.405	2.060/2.081//2.038/2.355	2.271//2.065	-5536.38011979	1.08	2.01

Figure S1. Four possible conformers with bond lengths (Å; black). NBO charges (e^- units; red) and charge transfer energies (in kcal/mol; green); (Gaussian09. TPSSh/6-31g(d) and NBO6.0). The axial position is depicted in blue. whereas the equatorial positions are black.

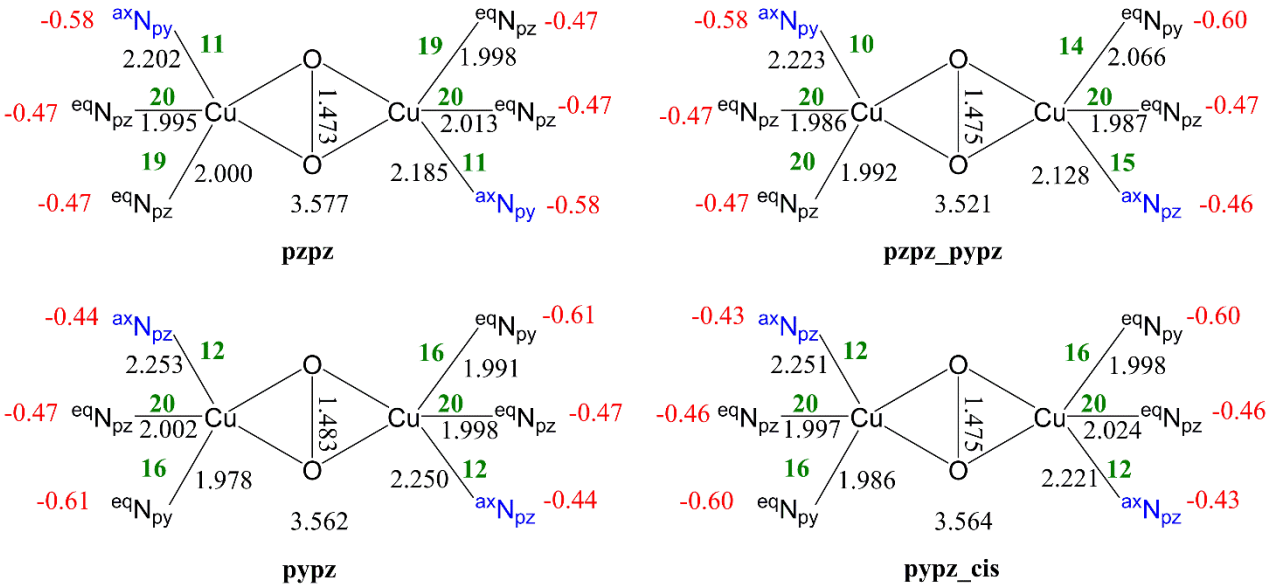

Table S11. Geometric parameters of the four possible P conformers with and without solvent model and with Becke-Johnson damping dispersion (Gaussian09, TPSSh/6-31G(d)).

conformer	Cu…Cu [Å]	O-O [Å]	Cu-N(pz) [Å] left // right	Cu-N(py) [Å] left // right
pzpz	3.577	1.473	1.995/2.000//1.998/2.013	2.202//2.185
pzpz (PCM)	3.563	1.472	1.992/1.997//1.997/2.019	2.168//2.196
pzpz (GD3BJ)	3.537	1.481	1.965/1.976//1.966/1.985	2.175//2.164
pypz	3.562	1.483	2.002/2.253//1.998/2.250	1.978//1.991
pypz (PCM)	3.553	1.485	1.999/2.266//1.996/2.270	1.969//1.978
pypz (GD3BJ)	3.488	1.484	1.973/2.197//1.979/2.162	1.975//1.992
pypz-cis	3.564	1.475	1.997/2.251//2.024/2.221	1.986//1.998
pypz-cis(PCM)	3.560	1.476	1.988/2.271//2.017/2.242	1.979//1.987
pypz-cis (GD3BJ)	3.521	1.477	2.000/2.160//1.975/2.189	1.996//1.981
pzpz-pypz	3.521	1.475	1.986/1.992//2.128/1.987	2.223//2.066
pzpz-pypz (PCM)	3.510	1.522	1.983/1.991//1.992/2.193	2.207//2.008
pzpz-pypz (GD3BJ)	3.499	1.477	1.957/1.979//1.969/2.136	2.189//2.025

Figure S2. TD-DFT-predicted optical spectra of the four conformers of $[Cu_2O_2\{HC(3tBuPz)_2(Py)\}_2]^{2+}$ with TPSSh/6-31g(d). Black: pzpz conformer; red: pypz conformer; green pypz-cis and blue: pzpz-pypz conformer (solid line: without solvent model and dashed line PCM model).

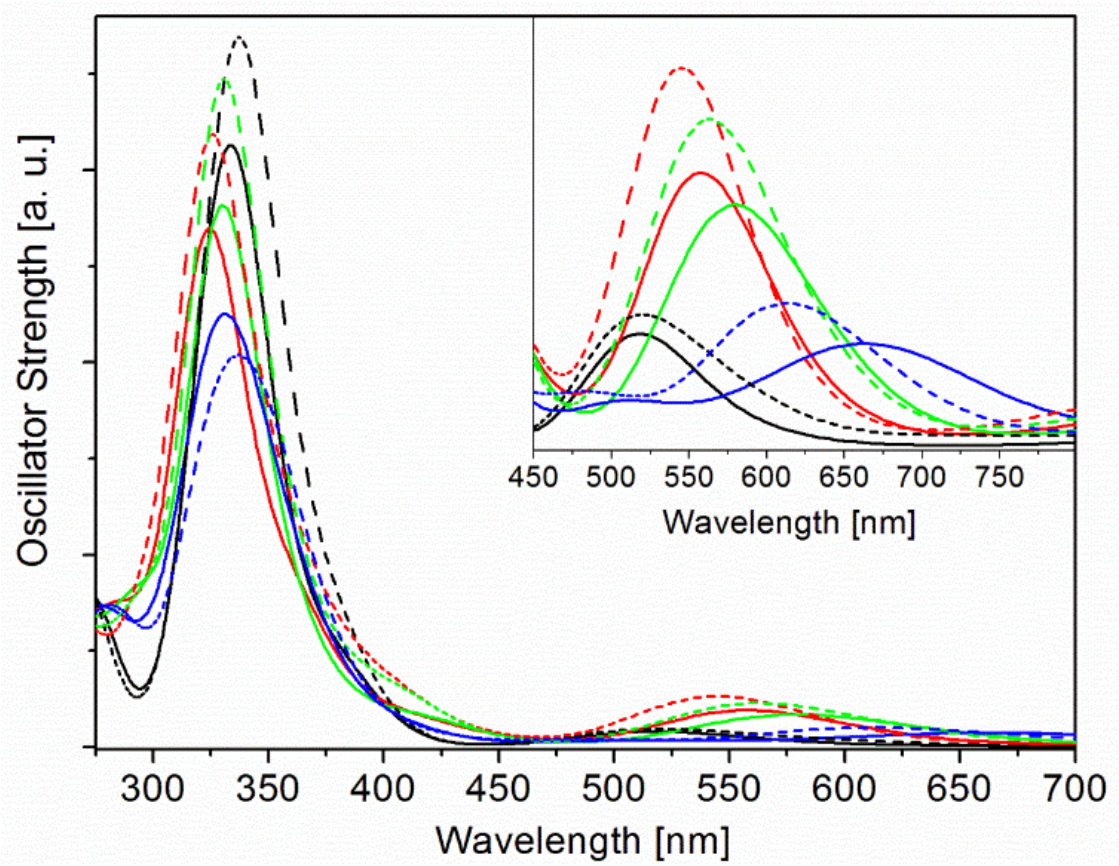

Figure S3. Energy profile of the O (red) and P (black) states of the four conformers (solid line: TPSSh/6-31g(d); dashed line: TPSSh/6-31g(d) with Becke-Johnson dispersion (GD3BJ) and dotted line: TPSSh/6-31g(d) with PCM DCM).

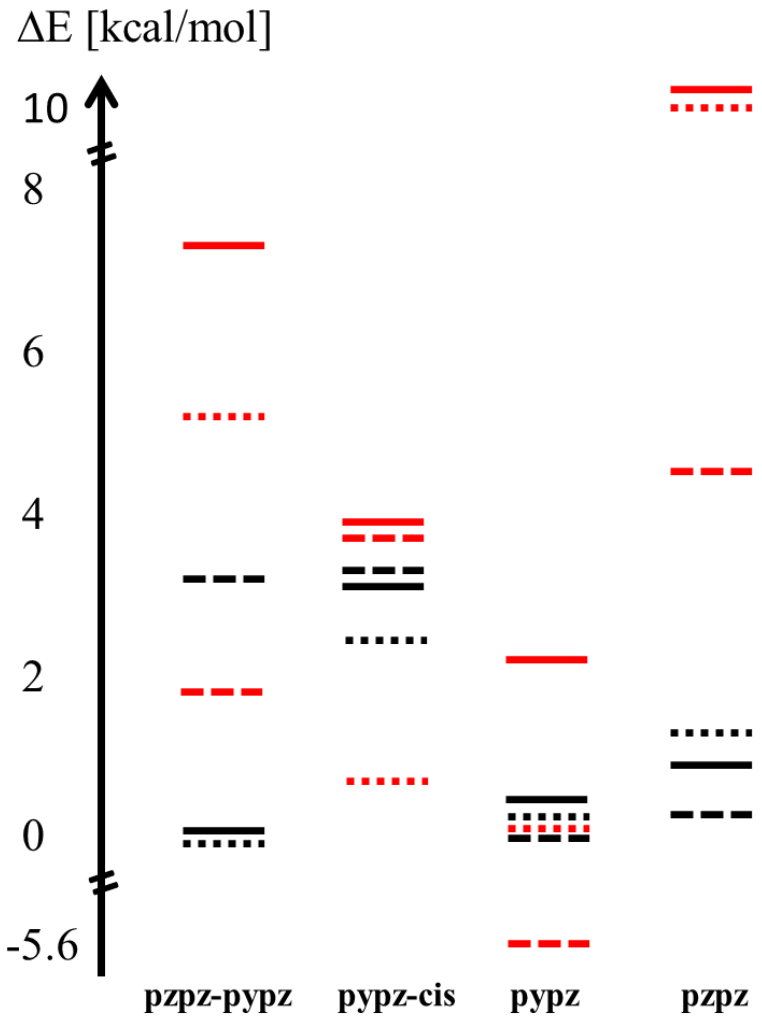

Figure S4. TD-DFT-predicted optical spectra of the four conformers of $[Cu_2O_2\{HC(3tBuPz)_2(Py)\}_2]^{2+}$ with TPSSh/def2-TZVP with solvent DCM (PCM model). Black: pzpz; red: pypz; green: pypz-cis and blue: pzpz-pypz.

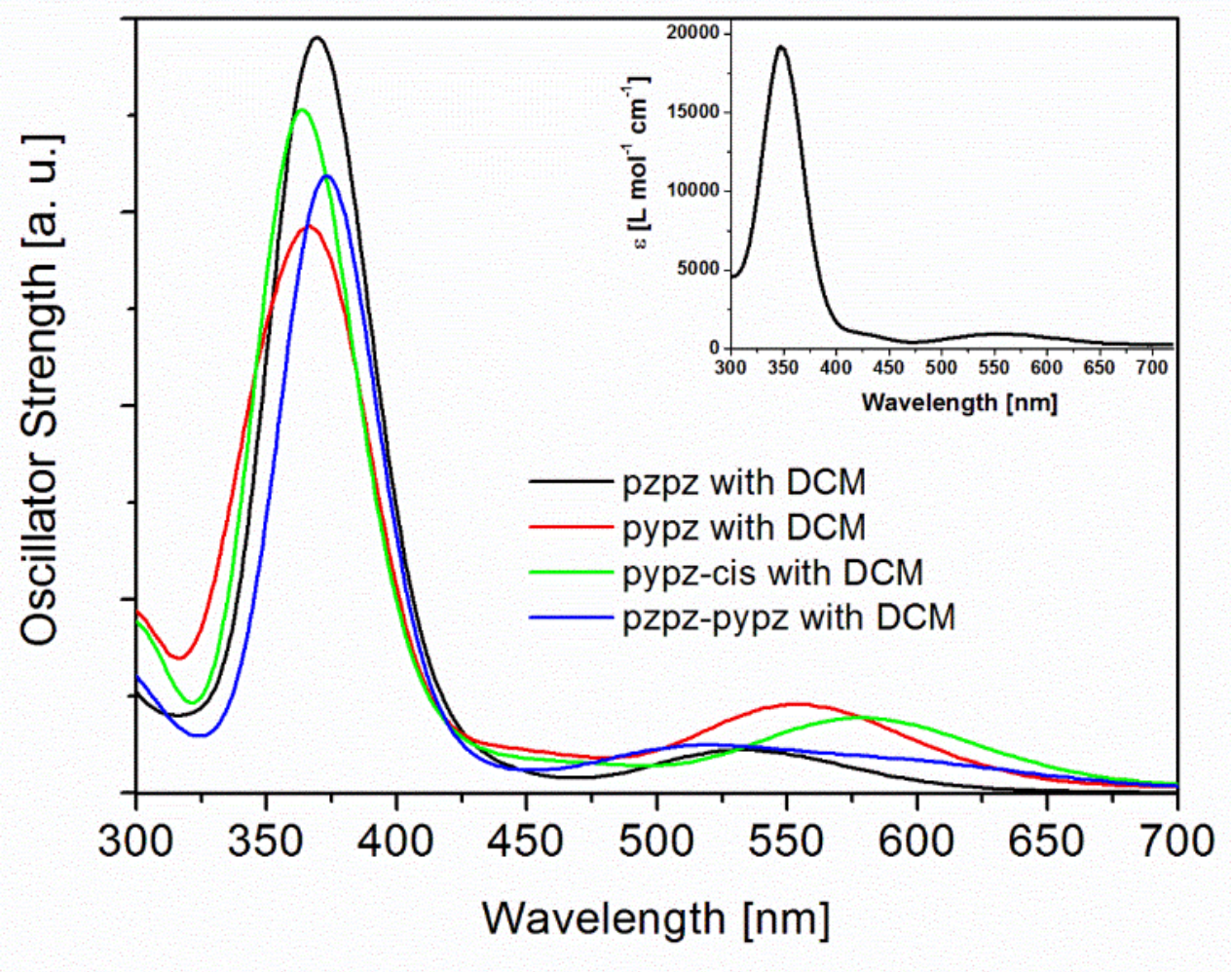

Table S12: FO compositions and energies of Fragment 1 with TPSSh/6-31g(d): Cu_2O_2

FO	Energy [eV]	FO composition
LUFO+3	-11.81	σ^*
LUFO	-16.45	Cu d_{xy} - π_σ^*
HOFO	-17.76	Cu d_{yz} - π_v^*
HOFO-1	-18.73	Cu d_{z2} (+ π_σ)
HOFO-2	-18.78	Cu d_{xz} - π_v
HOFO-3	-18.91	Cu d_{z2}
HOFO-4	-19.04	Cu d_{xy} + σ^*
HOFO-5	-19.07	Cu d_{yz}
HOFO-6	-19.23	Cu d_{xz}
HOFO-7	-19.35	Cu d_{yz} + π_v^* (δ)
HOFO-8	-19.51	Cu d_{x2-y2} - σ
HOFO-9	-19.61	Cu d_{x2-y2} (+ π_σ)
HOFO-10	21.49	Cu d_{xy} + π_σ^*
HOFO-11	-22.55	(Cu d_{xz} +) π_v
HOFO-12	-23.35	σ

Table S13: Fragment orbital descriptions of the two-ligand-fragment pzpz with TPSSh/6-31g(d).

FO	Energy [eV]	FO composition pzpz
LUFO	-1.00	π* of the pyridinyl
HOFO	-5.50	π of the pyrazolyl
HOFO-1	-5.51	π of the pyrazolyl
HOFO-2	-5.57	σ of the pyridinyl (axial) and π of the pyrazolyl
HOFO-3	-5.59	σ of the pyridinyl (axial) and π of the pyrazolyl
HOFO-4	-5.66	π of the pyrazolyl
HOFO-5	-5.67	π of the pyrazolyl
HOFO-6	-5.96	**π of the pyrazolyl** and σ of the pyridinyl
HOFO-7	-5.97	**π of the pyrazolyl** and σ of the pyridinyl
HOFO-8	-6.03	σ of the pyrazolyl
HOFO-9	-6.04	σ of the pyrazolyl
HOFO-10	-6.19	**σ of the pyridinyl** and σ of the pyrazolyl
HOFO-11	-6.23	**σ of the pyridinyl** and σ of the pyrazolyl
HOFO-12	-6.81	π of the pyridinyl
HOFO-13	-6.83	π of the pyridinyl
HOFO-14	-6.93	σ of the pyridinyl and σ of the pyrazolyl
HOFO-15	-6.98	σ of the pyridinyl and σ of the pyrazolyl
HOFO-16	-7.32	π of the pyrazolyl
HOFO-17	-7.33	π of the pyrazolyl
HOFO-18	-7.82	**tert-butyl** and σ of the pyrazolyl
HOFO-19	-7.92	**tert-butyl** and σ of the pyrazolyl
HOFO-20	-7.93	**tert-butyl** and σ of the pyrazolyl
HOFO-21	-8.00	tert butyl
HOFO-22	-8.05	**tert-butyl** and σ of the pyrazolyl
HOFO-23	-8.08	**tert-butyl** and σ of the pyrazolyl
HOFO-24	-8.10	**tert-butyl** and σ of the pyrazolyl
HOFO-25	-8.11	**tert-butyl** and σ of the pyrazolyl
HOFO-26	-8.14	**tert-butyl** and σ of the pyrazolyl
HOFO-27	-8.17	**tert-butyl** and σ of the pyrazolyl
HOFO-28	-8.18	**tert-butyl** and σ of the pyrazolyl
HOFO-29	-8.21	**tert-butyl** and σ of the pyrazolyl
HOFO-30	-8.91	tert-butyl
HOFO-31	-8.96	tert-butyl

Figure S5. Fragment orbitals of the two-ligand-fragment of relevance for the whole pzpz **P** core with TPSSh/6-31g(d).

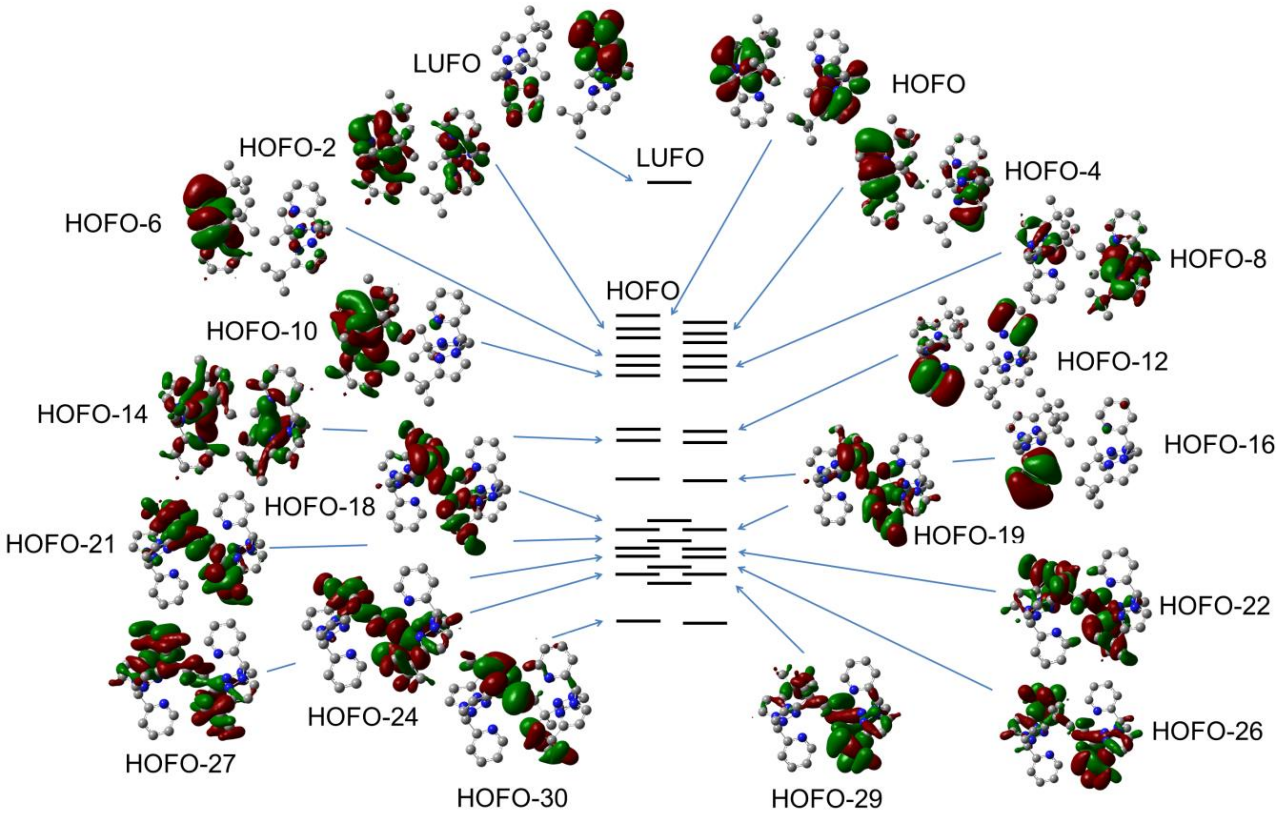

Table S14. Composition of molecular orbitals of fragment orbitals of the pzpz conformer with TPSSh/6-31g(d).

MO	Cu_2O_2 fragment			pzpz		
LUMO+7	73.5% LUFO+3					
LUMO+1				84.7% LUFO+1	12.7% LUFO	
LUMO	81.4% LUFO			7.3% HOFO-8		
HOMO	40.8% HOFO-4	24.9% HOFO		8.6% HOFO-9	7.6% HOFO-1	
HOMO-1	53.3% HOFO-1	8.1% HOFO-2		18.2% HOFO-3		
HOMO-2	46.9% HOFO-3	10.8% HOFO		26.3 HOFO-2		
HOMO-3	53.2% HOFO	21.8% HOFO-4				
	5.3% HOFO-3					
HOMO-4				85.9 HOFO-4	11.2% HOFO-5	
HOMO-5				84.1% HOFO-5	11.7% HOFO-4	
HOMO-6	44.6% HOFO-2	6.4% HOFO-9		15.0% HOFO-3	12.8% HOFO-7	7.8% HOFO-6
HOMO-7	14.9% HOFO-5			32.9% HOFO-1	24.2% HOFO	10.1% HOFO-9
HOMO-8	15.0% HOFO-6	12.1 HOFO-8		38.9% HOFO-6	18.0% HOFO-7	
HOMO-9	9.5% HOFO-7	5.4% HOFO-5		46.9% HOFO	17.2% HOFO-1	9.9% HOFO-8
HOMO-10				27.8% HOFO-10	27.4% HOFO-7	13.4% HOFO-6
				8.8% HOFO-3	8.3% HOFO-11	7.7% HOFO-8
HOMO-11	7.5% HOFO-6			31.8% HOFO-11	16.0% HOFO-2	14.3% HOFO-10
				7.6% HOFO-6		
HOMO-12	27.9% HOFO-2	24.7% HOFO-9		9.6% HOFO-3	5.2% HOFO-7	
HOMO-13	52.3% HOFO-5			17.3% HOFO-1	8.4% HOFO-12	5.4% HOFO-17
HOMO-14				75.7% HOFO-13		
HOMO-15	10.7% HOFO-7			73.2% HOFO-12		
HOMO-16	39.8% HOFO-7			12.6% HOFO-13	11.0% HOFO-12	10.0% HOFO
				6.8% HOFO-18	5.5% HOFO-16	5.4% HOFO-17
HOMO-17	51.1% HOFO-6	28.8% HOFO-8				
	5.5% HOFO-3					
HOMO-18	5.1% HOFO-9			38.5% HOFO-18	11.4% HOFO-20	10.7% HOFO-17
				8.5% HOFO-8		
HOMO-19	43.0% HOFO-8	7.5% HOFO-6		14.8% HOFO-2	6.7% HOFO-6	
	6.1% HOFO-3					
HOMO-20				50.6% HOFO-20	16.4% HOFO-14	14.9% HOFO-18
HOMO-21	47.1% HOFO-9			9.1% HOFO-3	5.7% HOFO-7	5.3% HOFO-18
HOMO-22				68.4% HOFO-19	7.6% HOFO-17	
HOMO-23	5.0% HOFO-5			26.1% HOFO-16	25.8% HOFO-17	17.8% HOFO-22
				6.5% HOFO-15		
HOMO-24				43.9% HOFO-22	16.5% HOFO-16	8.0% HOFO-17
				7.1% HOFO-21	5.4% HOFO-15	
HOMO-25	15.0% HOFO-7			33.5% HOFO-16	23.6% HOFO-17	12.1% HOFO-18
HOMO-26				78.3% HOFO-21	7.6% HOFO-22	
HOMO-27				52.1% HOFO-24	15.7% HOFO-29	9.0% HOFO-28
HOMO-28				24.1% HOFO-26	22.9% HOFO-27	19.4% HOFO-28
				15.8% HOFO-23		
HOMO-29				34.0% HOFO-29	24.0% HOFO-28	17.9% HOFO-25
				10.0% HOFO-23		
HOMO-30				50.8% HOFO-25	14.9% HOFO-23	13.3% HOFO-27
				8.4%H-26		
HOMO-31				31.8% HOFO-26	27.5% HOFO-28	17.8% HOFO-24
HOMO-32				44.4% HOFO-23	37.6% HOFO-27	7.8% HOFO-29
HOMO-33				26.5% HOFO-29	20.1% HOFO-26	16.4% HOFO-25
				14.3% HOFO-27	9.7% HOFO-24	
HOMO-34	13.1% HOFO-3			26.6% HOFO-11	10.2% HOFO-15	7.9% HOFO-2
				5.8% HOFO-7		
HOMO-35	12.2% HOFO-1			29.1% HOFO-10	5.7% HOFO-3	5.6% HOFO-14

		5.3% HOFO-6			
HOMO-36	25.2% HOFO-10	31.3% HOFO-31	9.2% HOFO-30	9.0% HOFO-8	
HOMO-37		64.8% HOFO-30	17.9% HOFO-33		
HOMO-38	7.0% HOFO-10	65.0% HOFO-32	6.2% HOFO-31		
HOMO-39		47.7% HOFO-33	15.6% HOFO-31	11.7% HOFO-32	
		10.2% HOFO-30			
HOMO-40	12.9% HOFO-10	27.8% HOFO-31	19.3% HOFO-33	10.8% HOFO-32	
HOMO-41		27.5% HOFO-40	25.6% HOFO-36	18.3% HOFO-39	
		12.4% HOFO-38			
HOMO-42		33.1% HOFO-38	28.8% HOFO-36	17.2% HOFO-34	
HOMO-43		40.6% HOFO-39	21.4% HOFO-38	15.6% HOFO-35	
		9.7% HOFO-37			
HOMO-44		43.8% HOFO-37	24.5% HOFO-41	8.0% HOFO-35	
HOMO-45		26.8% HOFO-34	18.5% HOFO-40	13.0% HOFO-36	
		9.5% HOFO-43	8.2% HOFO-38	6.1% HOFO-37	
HOMO-46		29.6% HOFO-40	17.0% HOFO-37	15.3% HOFO-36	
		7.9% HOFO-41	7.2% HOFO-38	6.0% HOFO-43	
HOMO-47		25.3% HOFO-41	18.0% HOFO-39	14.1% HOFO-34	
		13.7% HOFO-37	10.6% HOFO-42		
HOMO-48		38.8% HOFO-35	24.5% HOFO-41	9.2% HOFO-42	
		6.1% HOFO-39			
HOMO-49		53.8% HOFO-42	14.6% HOFO-35	9.7% HOFO-43	
HOMO-50		57.8% HOFO-43	17.2% HOFO-34	6.1% HOFO-42	
HOMO-51	17.3% HOFO-4	37.4% HOFO-9	6.1% HOFO-53	5.2% HOFO-19	
HOMO-52	6.7% LUFO+2	33.8% HOFO-14	8.7% HOFO-48	8.1% HOFO-20	
HOMO-53	29.5% HOFO-10	18.7% HOFO-8	15.3% HOFO-52		
HOMO-54	5.3% LUFO+1	33.3% HOFO-15	7.2% HOFO-47	6.5% HOFO-50	

Figure S6. Selected Molecular orbitals of $[Cu_2O_2\{HC(3tBuPz)_2(Py)\}]^{2+}$ in the pzpz conformer with TPSSh/6-31g(d).

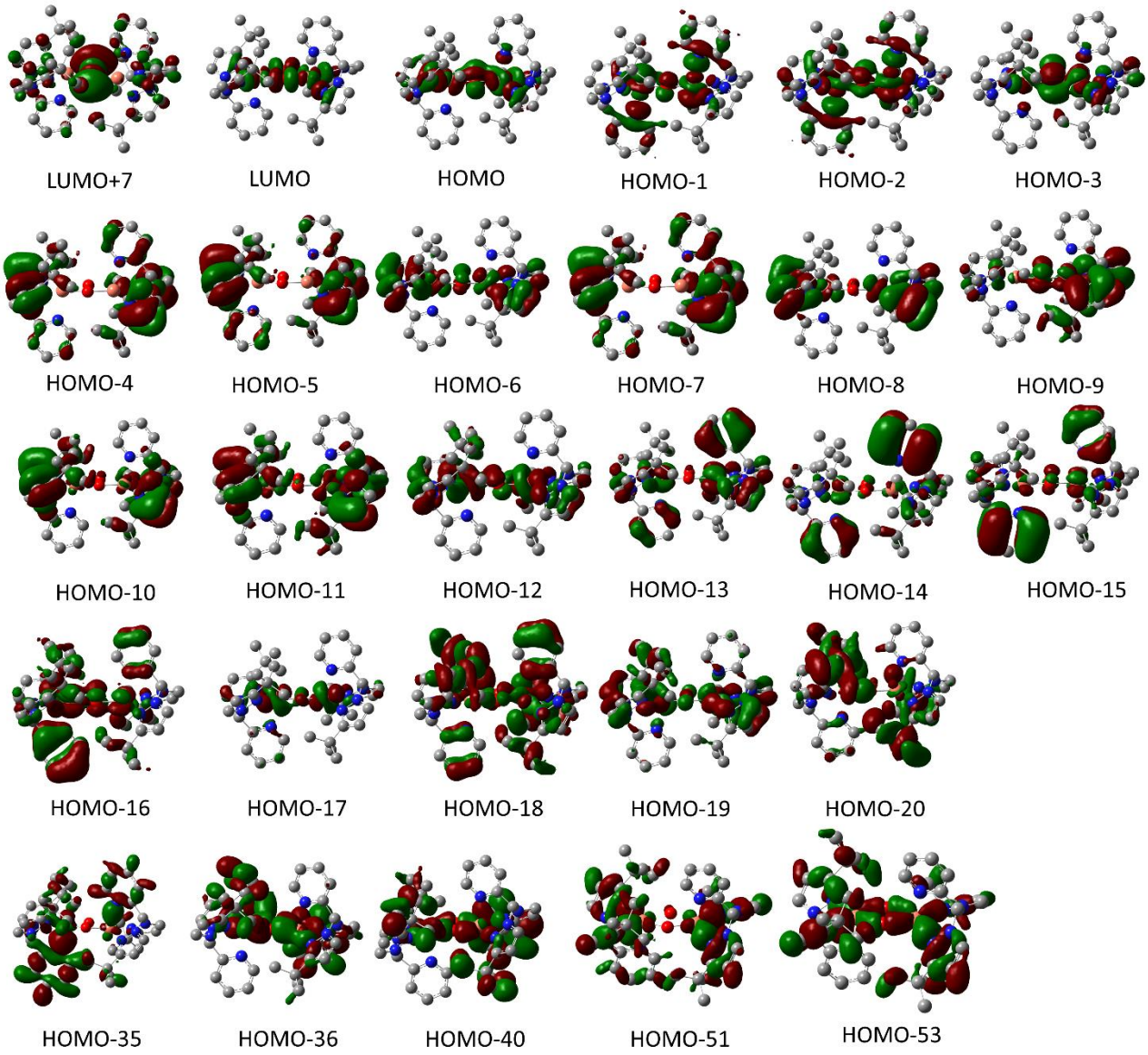

Table S15: MO energies of the pzpz conformer of the **P** core with TPSSh/6-31g(d).

MO	Peroxo	Energy [eV]
226	LUMO +7	-5.18
220	LUMO+1	-6.54
219	LUMO	-8.35
218	HOMO	-10.51
217	HOMO-1	-10.60
216	HOMO-2	-10.79
215	HOMO-3	-10.87
214	HOMO-4	-11.25
213	HOMO-5	-11.26
212	HOMO-6	-11.35
211	HOMO-7	-11.50
210	HOMO-8	-11.54
209	HOMO-9	-11.55
208	HOMO-10	-11.61
207	HOMO-11	-11.65
206	HOMO-12	-11.88
205	HOMO-13	-12.06
204	HOMO-14	-12.12
203	HOMO-15	-12.16
202	HOMO-16	-12.21
201	HOMO-17	-12.22
200	HOMO-18	-12.59
199	HOMO-19	-12.67
198	HOMO-20	-12.72
197	HOMO-21	-12.74
196	HOMO-22	-12.80
195	HOMO-23	-12.83
194	HOMO-24	-12.87
193	HOMO-25	-12.92
192	HOMO-26	-12.97
191	HOMO-27	-13.04
190	HOMO-28	-13.04
189	HOMO-29	-13.14
188	HOMO-30	-13.23
187	HOMO-31	-13.25
186	HOMO-32	-13.27
185	HOMO-33	-13.32
184	HOMO-34	-13.51
183	HOMO-35	-13.53
182	HOMO-36	-13.69
181	HOMO-37	-13.83
180	HOMO-38	-13.85
179	HOMO-39	-13.88
178	HOMO-40	-13.90
177	HOMO-41	-14.10

176	HOMO-42	-14.11
175	HOMO-43	-14.13
174	HOMO-44	-14.15
173	HOMO-45	-14.46
172	HOMO-46	-14.47
171	HOMO-47	-14.50
170	HOMO-48	-14.57
169	HOMO-49	-14.75
168	HOMO-50	-14.83
167	HOMO-51	-14.85
166	HOMO-52	-14.97
165	HOMO-53	-15.06
164	HOMO-54	-15.11

Table S16: Molecular orbital descriptions of the pzpz conformer of the **P** core with TPSSh/6-31g(d).

MO	MO composition pzpz
LUMO +7	σ^*
LUMO +1	π^* of the pyridinyl
LUMO	d_{xy} - π_σ^*
HOMO	π_v^* + σ^* + d – σ of the pyrazolyl
HOMO-1	π_v^* – d – σ of the pyridinyl
HOMO-2	π_v^* – d – σ of the pyridinyl
HOMO-3	π_v^* + σ^* + d – σ of the pyrazolyl
HOMO-4	π of the pyrazolyl
HOMO-5	π of the pyrazolyl
HOMO-6	π_v^* – d – π of the pyrazolyl
HOMO-7	π of the pyrazolyl
HOMO-8	π of the pyrazolyl
HOMO-9	π_v^* and π of the pyrazolyl
HOMO-10	π of the pyrazolyl
HOMO-11	π of the pyrazolyl
HOMO-12	π_v and d and π of the pyrazolyl
HOMO-13	**π of the pyridinyl** and π of the pyrazolyl
HOMO-14	π of the pyridinyl
HOMO-15	π of the pyridinyl
HOMO-16	π_v^* + d und π of the pyridinyl
HOMO-17	d
HOMO-18	π_σ^* + d + π of the pyridinyl
HOMO-19	**π of the pyrazolyl + d** and σ
HOMO-34	σ of the axial pyridinyl + d
HOMO-35	σ of the axial pyridinyl + d
HOMO-36	d_{xy} + π_σ^* – σ of the pyrazolyl
HOMO-40	d_{xy} + π_σ^* – σ of the pyrazolyl
HOMO-51	d_{xy} + σ of the pyrazolyl
HOMO-52	π_σ + d_{xy} + σ of the pyrazolyl
HOMO-53	π_σ^* + d_{xy} + σ of the pyrazolyl
HOMO-54	d_{xy} + σ of the pyrazolyl – σ

Table S17: Fragment orbital descriptions of the two-ligand-fragment pypz with TPSSh/6-31g(d).

FO	Energy [eV]	FO composition pypz
LUFO	-0.97	π* of the pyridinyl
HOFO	-5.52	σ of the eqatorial pyridinyl and the pyrazolyl; π of the axial pyrazolyl
HOFO-1	-5.53	σ of the eqatorial pyridinyl and the pyrazolyl; π of the axial pyrazolyl
HOFO-2	-5.57	σ of the equatorial pyridinyl and the pyrazolyl; π of the axial pyrazolyl
HOFO-3	-5.59	σ of the equatorial pyridinyl and the pyrazolyl; π of the axial pyrazolyl
HOFO-4	-5.64	σ of the equatorial pyridinyl and π of equatorial pyrazolyl and the axial pyrazolyl
HOFO-5	-5.68	π of the equatorial pyridinyl and π of equatorial pyrazolyl and the axial pyrazolyl
HOFO-6	-5.98	σ of the equatorial pyridinyl and π of equatorial pyrazolyl and the axial pyrazolyl
HOFO-7	-5.99	σ of the equatorial pyridinyl and π of equatorial pyrazolyl and the axial pyrazolyl
HOFO-8	-6.11	σ of the equatorial pyridinyl. **σ of the equatorial and the axial pyrazolyl**
HOFO-9	-6.13	σ of the equatorial pyridinyl. **σ of the equatorial and the axial pyrazolyl**
HOFO-10	-6.21	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl
HOFO-11	-6.24	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl
HOFO-12	-6.81	π of the pyridinyl
HOFO-13	-6.82	π of the pyridinyl
HOFO-14	-6.95	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl all six ligands only σ. no π interactions
HOFO-15	-6.98	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl all six ligands only σ. no π interactions
HOFO-16	-7.27	π of the pyridinyl
HOFO-17	-7.28	π of the pyridinyl
HOFO-18	-7.80	tert-butyl
HOFO-19	-7.86	tert-butyl
HOFO-20	-7.94	**tert-butyl**
HOFO-21	-7.99	**tert-butyl**
HOFO-22	-8.05	tert-butyl
HOFO-23	-8.09	tert-butyl and σ of of one axial and one equatorial pyrazolyl
HOFO-24	-8.10	tert-butyl
HOFO-25	-8.12	tert-butyl
HOFO-26	-8.13	tert-butyl
HOFO-27	-8.15	tert-butyl
HOFO-28	-8.18	tert-butyl
HOFO-29	-8.22	tert-butyl
HOFO-30	-8.90	tert-butyl
HOFO-31	-8.96	tert-butyl
HOFO-32	-9.00	tert-butyl
HOFO-33	-9.15	tert-butyl

Figure S7. Fragment orbitals of the two-ligand-fragment of relevance for the whole pypz **P** core with TPSSh/6-31g(d).

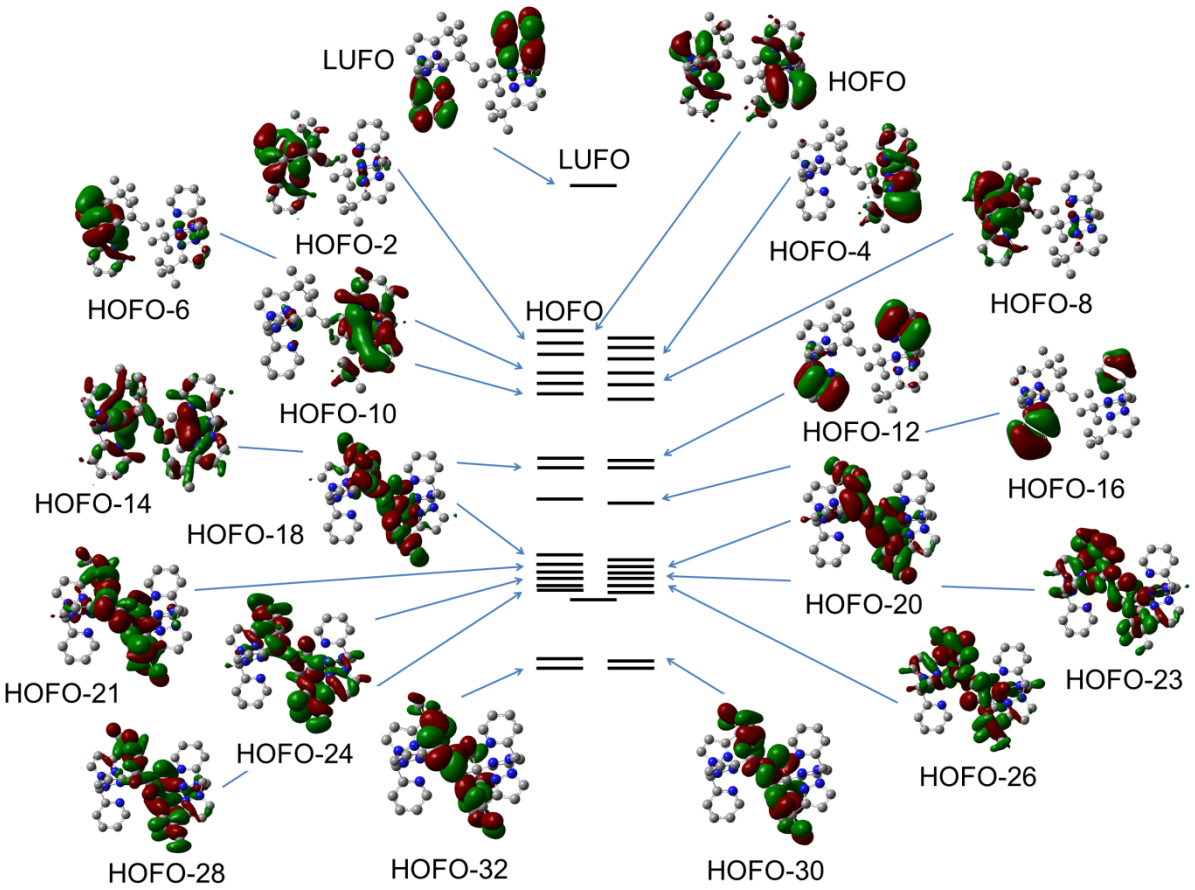

Table S18. Composition of molecular orbitals of fragment orbitals of the pypz conformer with TPSSh/6-31g(d).

MO	Cu_2O_2 fragment		pypz		
LUMO+7	86.6% LUFO+3				
LUMO	78.3% LUFO				
HOMO	42.1% HOFO-4	12.2% HOFO-5	3.5% HOFO-3	8.3% HOFO-1	
	5.5% LUFO+6				
HOMO-1	31.3% HOFO	24.8% HOFO-2	5.1% HOFO		
	9.3% HOFO-1				
HOMO-2	40.1% HOFO	18.8% HOFO-2			
	11.7% HOFO-1				
HOMO-3			75.5% HOFO-4	7.8% HOFO-3	
HOMO-4	31.1% HOFO-3	16.9% HOFO-6	15.2 HOFO		
	7.1% HOFO				
HOMO-5			83.0% HOFO-5		
HOMO-6	10.6% HOFO-2	10.3% HOFO-1	20.5% HOFO-6	17.3% HOFO-2	10.6% HOFO-1
	6.9% HOFO-5		9.3% HOFO-7		
HOMO-7	11.4% HOFO-2		35.5% HOFO-2	16.8% HOFO-1	11.3% HOFO-3
			5.7% HOFO-8		
HOMO-8			30.1% HOFO-7	26.9% HOFO-3	10.5% HOFO-9
			7.0% HOFO-2		
HOMO-9			25.5% HOFO-7	19.9% HOFO-6	14.8% HOFO-9
			13.8% HOFO-10	13.6% HOFO-4	
HOMO-10			32.7% HOFO-8	15.8% HOFO-6	13.9% HOFO-11
			10.1% HOFO-5	7.4% HOFO-10	
HOMO-11	17.6% HOFO-6	14.6% HOFO-7	29.0% HOFO	16.7% HOFO-11	6.3% HOFO-10
HOMO-12	34.2% HOFO-1	17.2% HOFO-4	7.8% HOFO-1		
	13.7% HOFO-5				
HOMO-13	33.8% HOFO-3	20.6% HOFO-6			
	7.4% HOFO-7	5.7% HOFO-8			
HOMO-14	38.0% HOFO-9	25.5% HOFO-5	5.4% HOFO-16	5.1% HOFO-7	5.0% HOFO-1
HOMO-15	50.4% HOFO-8		18.3% HOFO-13	7.0% HOFO-12	5.2% HOFO-17
HOMO-16	14.3% HOFO-8		51.9% HOFO-12	17.6% HOFO-13	
HOMO-17			51.0% HOFO-13	35.6% HOFO-12	
HOMO-18	19.8% HOFO-9	13.6% HOFO-5	9.1% HOFO-19	7.9% HOFO-1	6.2% HOFO-7
	8.4% HOFO-2	5.2% HOFO-4	5.6% HOFO-20		
HOMO-19	29.9% HOFO-7	5.5% HOFO-3	17.1% HOFO-18	8.8% HOFO-6	8.5% HOFO-13
			5.8% HOFO		
HOMO-20	8.9% HOFO-9		27.2% HOFO-20	18.3% HOFO-19	10.1% HOFO-14
			8.8% HOFO-18		
HOMO-21	11.3% HOFO-7		49.5% HOFO-18	6.7% HOFO-20	
HOMO-22			41.8% HOFO-19	38.0% HOFO-20	
HOMO-23			42.3% HOFO-22	21.1% HOFO-21	14.0% HOFO-15
HOMO-24			42.7% HOFO-21	13.2% HOFO-28	12.0% HOFO-24
			8.2% HOFO-23	6.4% HOFO-29	
HOMO-25			37.7% HOFO-28	18.3% HOFO-22	16.3% HOFO-21
			8.8% HOFO-23		
HOMO-26			26.4% HOFO-25	21.9% HOFO-26	14.6% HOFO-23
			14.1% HOFO-24		
HOMO-27			39.7% HOFO-23	25.4% HOFO-26	8.9% HOFO-27
			7.7% HOFO-28		

HOMO-28		36.7% HOFO-29	26.4% HOFO-27	11.7% HOFO-25
		7.2% HOFO-28	5.8% HOFO-22	
HOMO-29		45.2% HOFO-27	31.2% HOFO-29	10.9% HOFO-26
HOMO-30		69.9% HOFO-17		
HOMO-31		35.0% HOFO-36	23.3% HOFO-25	10.3% HOFO-26
		7.2% HOFO-29	5.6% HOFO-24	
HOMO-32		32.2% HOFO-24	20.3% HOFO-16	12.6% HOFO-28
		5.0% HOFO-29	5.0% HOFO-27	
HOMO-33	5.8% HOFO-9	17.6% HOFO-25	16.7% HOFO-26	16.3% HOFO-16
		11.0% HOFO-24	9.3% HOFO-28	6.6% HOFO-23
		6.0% HOFO-22		
HOMO-34		47.3% HOFO-30	15.8% HOFO-32	12.7% HOFO-33
		11.2% HOFO-31		
HOMO-35		52.4% HOFO-32	25.5% HOFO-30	6.9% HOFO-31
HOMO-36		65.5% HOFO-31	12.6% HOFO-32	9.3% HOFO-33
HOMO-37	11.5% HOFO-10	25.2% HOFO-33	13.0% HOFO-30	4.0% HOFO
HOMO-38	8.8% HOFO-10	40.4% HOFO-33	6.1% HOFO-32	
HOMO-39	6.8% HOFO-2	26.8% HOFO-10	7.2% HOFO-43	6.2% HOFO-9
HOMO-40		38.8% HOFO-37	10.6% HOFO-11	8.8% HOFO-40
HOMO-41		45.4% HOFO-38	21.9% HOFO-39	7.0% HOFO-35
HOMO-42		42.8% HOFO-39	12.7% HOFO-34	11.7% HOFO-38
		5.9% HOFO-35	5.0% HOFO-43	
HOMO-43		57.8% HOFO-36	12.8% HOFO-38	
HOMO-44		24.6% HOFO-37	14.7% HOFO-11	
HOMO-45		16.2% HOFO-14	8.9% HOFO-8	7.0% HOFO-36
		6.3% HOFO-38	5.3% HOFO-47	5.2% HOFO-43
		5.2% HOFO-3		
HOMO-46		32.0% HOFO-43	14.2% HOFO-36	8.4% HOFO-42
		5.7% HOFO-34	5.6% HOFO-41	
HOMO-47		60.0% HOFO-40	10.8% HOFO-42	9.6% HOFO-37
HOMO-48	12.4% HOFO-10	23.5% HOFO-42	11.9% HOFO-35	10.4% HOFO-40
		7.1% HOFO-15	6.8% HOFO-41	5.8% HOFO-43
HOMO-49	12.9% HOFO-10	51.0% HOFO-41	9.8% HOFO-34	7.7% HOFO-15
HOMO-50	13.8% HOFO-10	16.7% HOFO-35	13.4% HOFO-42	12.9% HOFO-41
		8.1% HOFO-15	5.3% HOFO-46	
HOMO-51		38.4% HOFO-34	17.1% HOFO-43	9.7% HOFO-38
		6.1% HOFO-41		
HOMO-52		30.5% HOFO-35	19.8% HOFO-42	13.8% HOFO-42
		5.8% HOFO-37		
HOMO-53		18.9% HOFO-14	6.3% HOFO-48	6.2% HOFO-34
		6.1% HOFO-35	5.5% HOFO-19	5.1% HOFO-8
HOMO-54	11.5% HOFO-10	21.5% HOFO-49	11.1% HOFO-15	7.5% HOFO-48
		5.5% HOFO-9		

Figure S8. Selected Molecular orbitals of $[Cu_2O_2\{HC(3tBuPz)_2(Py)\}]^{2+}$ in the pypz conformer with TPSSh/6-31g(d).

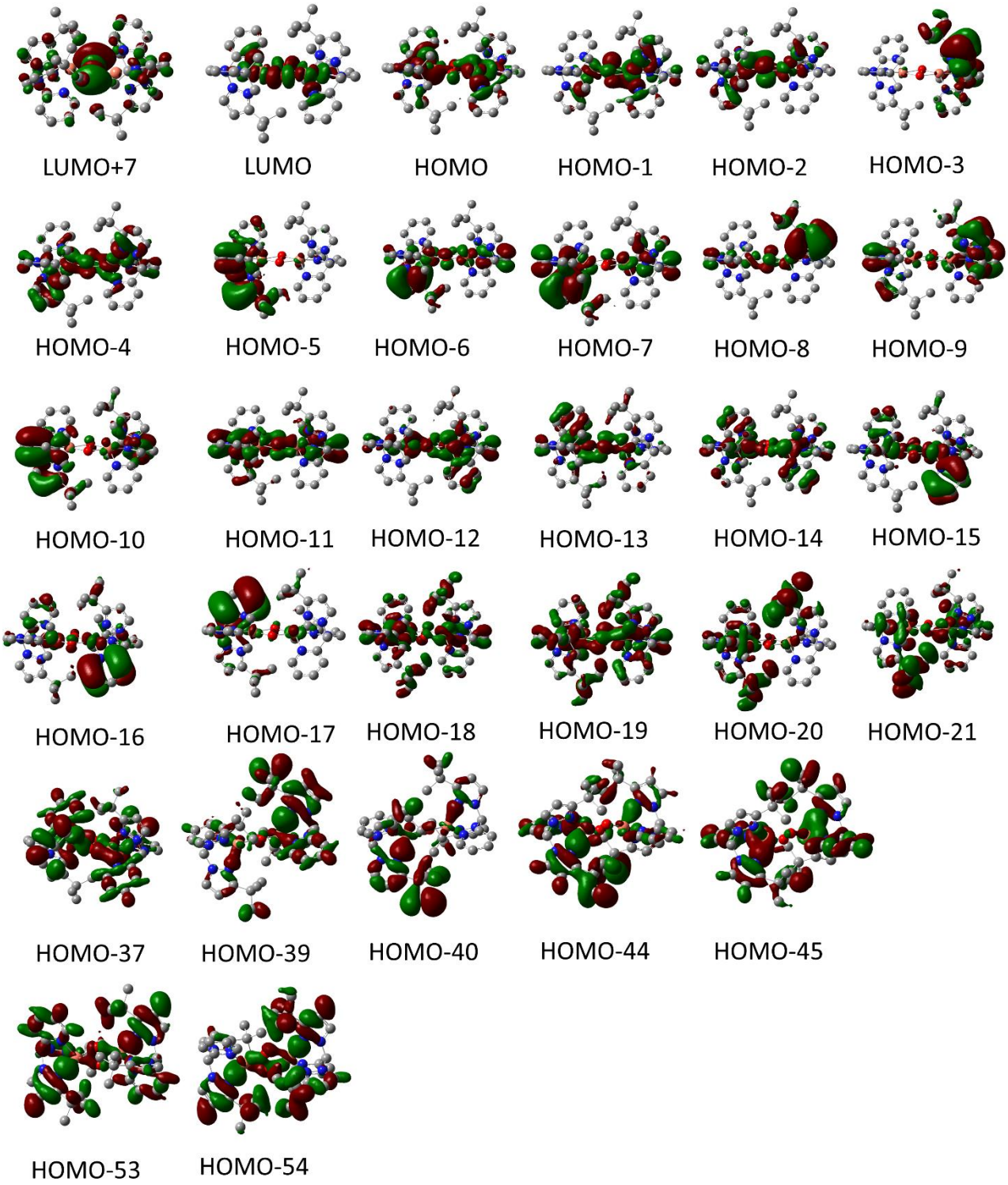

Table S19: MO energies of the pypz conformer of the **P** core with TPSSh/6-31g(d).

MO	Peroxo	Energy in eV
226	LUMO+7	-5.36
220	LUMO+1	-6.84
219	LUMO	-8.44
218	HOMO	-10.58
217	HOMO-1	-10.78
216	HOMO-2	-10.87
215	HOMO-3	-11.02
214	HOMO-4	-11.09
213	HOMO-5	-11.12
212	HOMO-6	-11.33
211	HOMO-7	-11.36
210	HOMO-8	-11.37
209	HOMO-9	-11.54
208	HOMO-10	-11.56
207	HOMO-11	-11.65
206	HOMO-12	-11.80
205	HOMO-13	-11.95
204	HOMO-14	-12.24
203	HOMO-15	-12.34
202	HOMO-16	-12.36
201	HOMO-17	-12.40
200	HOMO-18	-12.48
199	HOMO-19	-12.52
198	HOMO-20	-12.60
197	HOMO-21	-12.61
196	HOMO-22	-12.70
195	HOMO-23	-12.76
194	HOMO-24	-12.84
193	HOMO-25	-12.93
192	HOMO-26	-12.99
191	HOMO-27	-13.03
190	HOMO-28	-13.09
189	HOMO-29	-13.13
188	HOMO-30	-13.19
187	HOMO-31	-13.23
186	HOMO-32	-13.25
185	HOMO-33	-13.27
184	HOMO-34	-13.63
183	HOMO-35	-13.71
182	HOMO-36	-13.81
181	HOMO-37	-13.84
180	HOMO-38	-13.88
179	HOMO-39	-13.96
178	HOMO-40	-14.00
177	HOMO-41	-14.07
176	HOMO-42	-14.09

175	HOMO-43	-14.09
174	HOMO-44	-14.13
173	HOMO-45	-14.23
172	HOMO-46	-14.25
171	HOMO-47	-14.42
170	HOMO-48	-14.50
169	HOMO-49	-14.53
168	HOMO-50	-14.57
167	HOMO-51	-14.89
166	HOMO-52	-14.94
165	HOMO-53	-14.98
164	HOMO-54	-15.13

Table S20: Molecular orbital descriptions of the pypz conformer of the **P** core with TPSSh/6-31g(d)

MO	MO composition pypz
LUMO +7	σ^*
LUMO +1	π^* of the pyridinyl
LUMO	d_{xy} - π_σ^*- σ of the equatorial pyrazolyl and the pyridinyl
HOMO	σ of the equatorial pyrazolyl and σ of the equatorial pyridinyl – d – σ^*
HOMO-1	π_v^* – d – σ of the pyridinyl and σ of the axial pyrazolyl
HOMO-2	π_v^* – d – σ of the pyridinyl and σ of the axial pyrazolyl
HOMO-3	π of the pyrazolyl
HOMO-4	π_v^* + d – σ of the axial and the equatorial pyrazolyl
HOMO-5	π of the pyrazolyl
HOMO-6	π_v^* – d – π of the axial pyrazolyl
HOMO-7	π_v^* – d – π of the axial and the equatorial pyrazolyl
HOMO-8	π_v^* – d – π of the axial pyrazolyl
HOMO-9	**π of the axial and the equatorial pyrazolyl** - π_v^* – d
HOMO-10	π of the axial and the equatorial pyrazolyl
HOMO-11	π_v^* + d – π of the equatorial pyrazolyl
HOMO-12	π_v^* – d – π of the equatorial pyrazolyl – π of the equatorial pyrindinyl
HOMO-13	π_v^* + d – π of the equatorial pyrazolyl
HOMO-14	π_σ + d – π of the equatorial pyrindinyl
HOMO-15	π_v^* – d – π of the equatorial pyrindinyl
HOMO-16	π_v^* – d – π of the equatorial pyrindinyl
HOMO-17	π of the equatorial pyrindinyl
HOMO-18	π_v and d and π of the equatorial pyrazolyl
HOMO-19	π_v^* + d + π of the equatorial and the axial pyrazolyl
HOMO-20	d + π of the equatorial and axial pyrazolyl and **tert-butyl**
HOMO-21	d + π of the equatorial and axial pyrazolyl and **tert-butyl**
HOMO-34	tert-butyl
HOMO-35	tert-butyl
HOMO-36	tert-butyl
HOMO-37	d_{xy} and π_σ^* + σ of the equatorial pyrazolyl + σ of the equatorial pyridinyl
HOMO-39	π_v^* and d + **σ of the axial pyrazolyl + σ of the equatorial pyridinyl**
HOMO-40	d + **σ of the axial pyrazolyl**
HOMO-44	d + **σ of the axial pyrazolyl + σ of the equatorial pyridinyl**
HOMO-45	d + **σ of the axial pyrazolyl + σ of the equatorial pyridinyl**
HOMO-53	π_σ + d + **σ of the equatorial pyrazolyl**
HOMO-54	π_σ* and d + **σ of the equatorial pyrazolyl**

Table S21: FO compositions and energies of Fragment 1 with TPSSh/def2-TZVP and DCM and GD3BJ: Cu_2O_2

FO	Energy [eV]	FO composition
LUFO+3	-3.48	σ^*
LUFO	-8.00	Cu d_{xy} - π_σ^*
HOFO	-10.65	Cu d_{yz} - π_v^*
HOFO-1	-10.65	Cu d_{xz} - π_v
HOFO-2	-10.79	Cu d_{xz} - π_v
HOFO-3	-10.85	Cu d_{xy} –σ^*+ π_σ^*
HOFO-4	-11.02	Cu d_{z2}
HOFO-5	-11.25	Cu d_{yz} - σ^*- π_v^*
HOFO-6	-11.33	Cu d_{yz} + π_v^* (δ)
HOFO-7	-11.37	Cu d_{x2-y2} - σ
HOFO-8	-11.42	Cu d_{xz} + π_σ+ π_v^*
HOFO-9	-11.49	Cu d_{x2-y2} (+ π_σ)
HOFO-10	-13.39	Cu d_{xy} + π_σ^*
HOFO-11	-14.58	(Cu d_{xz} +) π_v
HOFO-12	-15.45	σ

Table S22: Fragment orbital descriptions of the two-ligand-fragment pzpz with TPSSh/def2-TZVP and DCM and GD3BJ.

FO	Energy [eV]	FO composition pzpz
LUFO	-1.38	π* of the pyridinyl
HOFO	-6.04	π of the pyrazolyl
HOFO-1	-6.04	σ of the pyridinyl (axial) and π of the pyrazolyl
HOFO-2	-6.04	π of the pyrazolyl
HOFO-3	-6.05	σ of the pyridinyl (axial) and π of the pyrazolyl
HOFO-4	-6.17	π of the pyrazolyl
HOFO-5	-6.19	π of the pyrazolyl
HOFO-6	-6.47	**π of the pyrazolyl** and σ of the pyridinyl
HOFO-7	-6.47	**π of the pyrazolyl** and σ of the pyridinyl
HOFO-8	-6.57	σ of the pyrazolyl
HOFO-9	-6.59	σ of the pyrazolyl
HOFO-10	-6.69	**σ of the pyridinyl** and σ of the pyrazolyl
HOFO-11	-6.71	**σ of the pyridinyl** and σ of the pyrazolyl
HOFO-12	-7.15	π of the pyridinyl
HOFO-13	-7.18	π of the pyridinyl
HOFO-14	-7.47	σ of the pyridinyl and σ of the pyrazolyl
HOFO-15	-7.53	σ of the pyridinyl and σ of the pyrazolyl
HOFO-16	-7.67	π of the pyrazolyl
HOFO-17	-7.67	π of the pyrazolyl
HOFO-18	-8.20	**tert-butyl** and σ of the pyrazolyl
HOFO-19	-8.31	**tert-butyl** and σ of the pyrazolyl
HOFO-20	-8.33	**tert-butyl** and σ of the pyrazolyl
HOFO-21	-8.39	**tert butyl** and σ of the pyrazolyl
HOFO-22	-8.46	**tert-butyl** and σ of the pyrazolyl
HOFO-23	-8.49	σ of the pyrazolyl
HOFO-24	-8.50	σ of the pyrazolyl
HOFO-25	-8.54	**tert-butyl** and σ of the pyrazolyl
HOFO-26	-8.54	**tert-butyl** and σ of the pyrazolyl
HOFO-27	-8.57	**tert-butyl** and σ of the pyrazolyl
HOFO-28	-8.58	σ of the pyrazolyl
HOFO-29	-8.60	**tert-butyl** and σ of the pyrazolyl
HOFO-30	-9.23	tert-butyl
HOFO-31	-9.28	tert-butyl

Table S23. Composition of molecular orbitals of fragment orbitals of the pzpz conformer with TPSSh/def2-TZVP and DCM and GD3BJ.

MO	Cu_2O_2 fragment		pzpz		
LUMO+9	77.2% LUFO+3		6.6%LUFO+12		
LUMO+1			82.8% LUFO	15.0% LUFO+1	
LUMO	70.3% LUFO	12.9% HOFO	7.2% HOFO-8		
HOMO	77.6% HOFO	11.5% LUFO			
HOMO-1	44.6% HOFO-1		26.7% HOFO-3	10.7% HOFO-1	
HOMO-2	20.0% HOFO-3	15.8% HOFO-4	19.3 HOFO-1	13.4% HOFO-2	9.8% HOFO-3
HOMO-3	23.2% HOFO-3	14.2% HOFO-4	20.3% HOFO-1	13.5% HOFO-2	5.3% HOFO-9
			5.2% HOFO-3		
HOMO-4			97.8 HOFO-4		
HOMO-5			95.6% HOFO-5		
HOMO-6			76.9% HOFO	7.8% HOFO-1	5.6% HOFO-8
HOMO-7	10.7% HOFO-2		36.3% HOFO-7	28.3% HOFO-6	10.9% HOFO-3
HOMO-8			22.7% HOFO-2	21.1% HOFO-9	19.0% HOFO-7
			17.1% HOFO-6	6.3% HOFO-11	
HOMO-9			33.6% HOFO-2	25.4% HOFO-6	14.2% HOFO-7
			8.3 % HOFO-11		
HOMO-10	7% HOMO-1		48.2% HOFO-10	17.2% HOFO-3	7.2% HOFO-8
			6.8% HOFO-7	5.4% HOFO-6	
HOMO-11	12.8% HOFO-4		44.1% HOFO-11	12.0% HOFO-1	5.7% HOFO-6
HOMO-12			81.2% HOFO-13	8.9% HOFO-12	
HOMO-13			88.1% HOFO-12	7.9% HOFO-13	
HOMO-14	70.5% HOFO-2		6.4% HOMO-20		
HOMO-15	25.7% HOFO-6	5.0% HOFO-3	45.7% HOFO-16	5.5% HOHO-17	
HOMO-16	14.8% HOFO-8		65.8% HOFO-17	6.6% HOFO-16	
HOMO-17			62.8% HOFO-18	9.3% HOFO-8	
HOMO-18	24.1% HOFO-5		32.7% HOFO-20	16.2% HOFO-14	
HOMO-19	7.7% HOFO-3	5.8% HOFO-5	54.1% HOFO-19	14.2% HOFO-16	
HOMO-20	36.1% HOFO-5	7.3% HOFO-4	12.5% HOFO-20	11.7% HOFO-19	7.8% HOFO-14
HOMO-21	23.5% HOFO-6	5.15 HOFO-3	20.0% HOFO-22	15.8% HOFO-16	7.6% HOFO-19
			7.2% HOFO-15		
HOMO-22	7.4% HOFO-6		32.4% HOFO-22	14.5% HOFO-21	7.0% HOFO-15
			6.0% HOFO-16	5.1% HOFO-20	5.0% HOFO-19
HOMO-23			57.6% HOFO-21	11.3% HOFO-22	10.7% HOFO-20
HOMO-24	35.5% HOFO-7	12.2% HOFO-8	6.1% HOFO-17	5.2% HOFO-21	
	8.3% HOFO-9				
HOMO-25	7.6% HOFO-9		39.4% HOFO-23	19.1% HOFO-24	5.1% HOFO-21
HOMO-26			46.8% HOFO-24	21.8% HOFO-23	6.2% HOFO-26
			5.7% HOFO-28		
HOMO-27	25.9% HOFO-8	16.4% HOFO-9	18.9% HOFO-28	9.6% HOFO-17	6.8% HOFO-24
HOMO-28	18.5% HOFO-7	8.7% HOFO-8	24.0% HOFO-29	14.8% HOFO-26	
	8.4% HOFO-9				
HOMO-29	14.8% HOFO-7		30.1% HOFO-29	22.0% HOFO-25	8.3% HOFO-26
HOMO-30			46.8% HOFO-26	13.7% HOFO-24	12.2% HOFO-22
			11.5% HOFO-29		
HOMO-31			32.5% HOFO-27	24.4% HOFO-24	14.4% HOFO-29
			6.6% HOFO-23	5.5% HOFO-28	
HOMO-32	7.9% HOFO-9		46.0% HOFO-27	17.3% HOFO-25	
HOMO-33	10.2% HOFO-9		52.8% HOFO-28	7.8% HOFO-23	
HOMO-34	15.2% HOFO-1	7.2% HOFO-9	15.2% HOFO-10	10.0% HOFO-23	8.7% HOFO-25
HOMO-35	22.6% HOFO-4	6.7% HOFO-1	15.1% HOFO-11	5.6% HOFO-15	
HOMO-36	32.4% HOFO-10		13.5% HOFO-8	12.7% HOFO-18	9.3% HOFO-30
			7.0% HOFO-31		
HOMO-37	5.1% HOFO-10		79.5% HOFO-30		

HOMO-38			82.7% HOFO-32		
HOMO-39			71.4% HOFO-31	5.0% HOFO-34	
HOMO-40			87.1% HOFO-33		
HOMO-41			44.7% HOFO-38	33.8% HOFO-34	7.8% HOFO-37
HOMO-42			81.5% HOFO-36	5.3% HOFO-41	
HOMO-43			37.2% HOFO-39	32.7% HOFO-37	9.0% HOFO-35
			5.6% HOFO-34	5.4% HOFO-38	
HOMO-44			45.9% HOFO-37	27.9% HOFO-39	12.4% HOFO-35
HOMO-45			42.0% HOFO-34	40.2% HOFO-38	
HOMO-46			56.2% HOFO-35	27.8% HOFO-39	
HOMO-47			79.7% HOFO-40	7.1% HOFO-37	
HOMO-48			84.8% HOFO-41	6.2% HOFO-36	
HOMO-49			88.8% HOFO-42		
HOMO-50	10.7% HOFO-3	5.0% HOFO-10	28.9% HOFO-9	5.0% HOFO-8	5.0% HOFO-43
HOMO-51			82.6% HOFO-43		
HOMO-52	10.0% LUFO+2		7.0% HOFO-20		
HOMO-53	6.9% LUFO+1	5.4% HOFO-4	27.3% HOFO-15	7.8% HOFO-45	5.6% HOFO-49
HOMO-54	17.7% HOFO-11	5.5% HOFO-10	28.4% HOFO-48	10.1% HOFO-50	5.5% HOFO-51
HOMO-55	14.0% HOFO-11	6.0% HOFO-10	23.0% HOFO-50	10.2% HOFO-46	9.0% HOFO-48
			7.8% HOFO-51		
HOMO-56			58.0% HOFO-44	6.6% HOFO-46	
HOMO-57			43.3% HOFO-49	8.9% HOFO-47	6.6% HOFO-64
HOMO-58			32.9% HOFO-51	13.3% HOFO-52	10.5% HOFO-46
			9.9% HOFO-53	7.6% HOFO-50	5.2% HOFO-48
HOMO-59			44.4% HOFO-47	18.8% HOFO-46	8.4% HOFO-53
HOMO-60			22.6% HOFO-45	20.4% HOFO-46	13.0% HOFO-50
			9.9% HOFO-47	9.8% HOFO-54	8.2% HOFO-49
HOMO-61			23.3% HOFO-54	19.0% HOFO-45	17.6% HOFO-46
			12.2% HOFO-47		
HOMO-62			35.7% HOFO-52	8.1% HOFO-66	6.8% HOFO-51
HOMO-63	10.1% HOFO-11		39.5% HOFO-55	18.9% HOFO-48	12.4% HOFO-52
HOMO-64			49.8% HOFO-53	11.8% HOFO-51	11.0% HOFO-68
HOMO-65			40.1% HOFO-54	19.6% HOFO-45	
HOMO-66	16.7% HOFO-10		20.1% HOFO-50	8.1% HOFO-54	6.9% HOFO-51
			5.7% HOFO-8		

Table S24: MO energies of the pzpz conformer of the **P** core with TPSSh/def2-TZVP and DCM and GD3BJ.

MO	Peroxo	Energy [eV]
228	LUMO +9	-0.85
220	LUMO+1	-2.65
219	LUMO	-4.49
218	HOMO	-6.90
217	HOMO-1	-7.10
216	HOMO-2	-7.34
215	HOMO-3	-7.41
214	HOMO-4	-7.50
213	HOMO-5	-7.52
212	HOMO-6	-7.77
211	HOMO-7	-7.80
210	HOMO-8	-7.85
209	HOMO-9	-7.86
208	HOMO-10	-7.88
207	HOMO-11	-8.05
206	HOMO-12	-8.27
205	HOMO-13	-8.28
204	HOMO-14	-8.50
203	HOMO-15	-8.65
202	HOMO-16	-8.73
201	HOMO-17	-8.90
200	HOMO-18	-9.06
199	HOMO-19	-9.10
198	HOMO-20	-9.14
197	HOMO-21	-9.21
196	HOMO-22	-9.26
195	HOMO-23	-9.29
194	HOMO-24	-9.34
193	HOMO-25	-9.37
192	HOMO-26	-9.39
191	HOMO-27	-9.42
190	HOMO-28	-9.45
189	HOMO-29	-9.47
188	HOMO-30	-9.57
187	HOMO-31	-9.60
186	HOMO-32	-9.61
185	HOMO-33	-9.64
184	HOMO-34	-9.70
183	HOMO-35	-9.80
182	HOMO-36	-9.93
181	HOMO-37	-10.11
180	HOMO-38	-10.18
179	HOMO-39	-10.20
178	HOMO-40	-10.25

177	HOMO-41	-10.50
176	HOMO-42	-10.51
175	HOMO-43	-10.54
174	HOMO-44	-10.55
173	HOMO-45	-10.69
172	HOMO-46	-10.74
171	HOMO-47	-10.76
170	HOMO-48	-10.80
169	HOMO-49	-10.93
168	HOMO-50	-10.95
167	HOMO-51	-10.99
166	HOMO-52	-11.17
165	HOMO-53	-11.33
164	HOMO-54	-11.55
163	HOMO-55	-11.57
162	HOMO-56	-11.70
161	HOMO-57	-11.71
160	HOMO-58	-11.74
159	HOMO-59	-11.77
158	HOMO-60	-11.81
157	HOMO-61	-11.81
156	HOMO-62	-11.85
155	HOMO-63	-11.89
154	HOMO-64	-11.92
153	HOMO-65	-11.95
152	HOMO-66	-11.97

Table S25: Molecular orbital descriptions of the pzpz conformer of the **P** core with TPSSh/def2-TZVP and DCM and GD3BJ.

MO	MO composition pzpz
LUMO +9	σ^*
LUMO	d_{xy} - π_σ*
HOMO	π_v*
HOMO-1	π_v* – d – σ of the pyridinyl – σ of the pyrazolyl
HOMO-2	π_σ* – d – σ of the pyridinyl – σ of the pyrazolyl
HOMO-3	π_σ* – d – σ of the pyridinyl – σ of the pyrazolyl
HOMO-4	**π of the pyrazolyl** and π of the pyridinyl
HOMO-5	**π of the pyrazolyl** and π of the pyridinyl
HOMO-6	π_v* – d – π of the pyrazolyl
HOMO-7	π_v – d **– π of the pyrazolyl**
HOMO-8	π_σ* – d **– π of the pyrazolyl**
HOMO-9	π_σ* – d **– π of the pyrazolyl**
HOMO-10	π of the pyrazolyl –d
HOMO-11	π of the pyrazolyl –d
HOMO-12	π of the pyridinyl
HOMO-13	π of the pyridinyl
HOMO-14	d – π_v
HOMO-15	π of the pyridinyl and d
HOMO-16	π of the pyridinyl and d
HOMO-17	σ of the pyrazolyl –d - π_σ* and tert-butyl
HOMO-18	tert-butyl and d
HOMO-19	tert-butyl and d + π of the pyridinyl
HOMO-20	σ of the pyrazolyl and π of pyridinyl + d + σ
HOMO-21	σ of the pyrazolyl and π of pyridinyl + d + π_v*
HOMO-22	tert-butyl and d
HOMO-23	tert-butyl and d
HOMO-24	π of the pyridinyl and π of the pyrazolyl +d + σ
HOMO-25	tert-butyl and d
HOMO-26	tert-butyl and d
HOMO-27	tert-butyl and d + π / σ of the pyridinyl
HOMO-28	tert-butyl and d + σ
HOMO-29	tert-butyl and d
HOMO-30	σ of the pyridinyl +d and tert-butyl
HOMO-32	σ of the pyridinyl +d and tert-butyl
HOMO-33	σ of the pyridinyl +d and tert-butyl
HOMO-34	d_{yz} + σ of the pyridinyl
HOMO-35	d_{yz} + σ of the pyridinyl
HOMO-36	π_σ* + d_{xy} – σ of the pyridinyl
HOMO-37	π_σ* + d and tert-butyl
HOMO-50	d_{xy} + π_σ* + σ of the pyrazolyl
HOMO-52	σ of the pyrazolyl + d_{xy} + π_σ
HOMO-53	d_{xy} + σ of the pyrazolyl + σ
HOMO-54	d_{xy} + σ of the pyrazolyl + π_v
HOMO-55	d_{xy} + σ of the pyrazolyl + π_v
HOMO-63	d_{xy} + σ of the pyrazolyl + π_v
HOMO-65	σ of the pyrazolyl and σ of the pyridinyl + d_{xy}
HOMO-66	σ of the pyrazolyl + d_{xy} + π_σ^*

Table S26: Fragment orbital descriptions of the two-ligand-fragment pypz with TPSSh/def2-TZVP and DCM and GD3BJ.

FO	Energy [eV]	FO composition pypz
LUFO	-1.38	π* of the pyridinyl
HOFO	-5.99	σ of the equatorial pyridinyl and the pyrazolyl; π of the axial pyrazolyl
HOFO-1	-6.01	σ of the equatorial pyridinyl and the pyrazolyl; π of the axial pyrazolyl
HOFO-2	-6.09	π of the axial and the equatorial pyrazolyl
HOFO-3	-6.11	π of the axial and the equatorial pyrazolyl
HOFO-4	-6.17	π of the axial and the equatorial pyrazolyl and π of the equatorial pyridinyl
HOFO-5	-6.18	π of the axial and the equatorial pyrazolyl and π of the equatorial pyridinyl
HOFO-6	-6.48	σ of the equatorial pyridinyl and π of equatorial pyrazolyl and the axial pyrazolyl
HOFO-7	-6.49	σ of the equatorial pyridinyl and π of equatorial pyrazolyl and the axial pyrazolyl
HOFO-8	-6.61	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl
HOFO-9	-6.66	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl
HOFO-10	-6.70	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl
HOFO-11	-6.77	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl
HOFO-12	-7.14	π of the pyridinyl
HOFO-13	-7.18	π of the pyridinyl
HOFO-14	-7.47	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl all six ligands only σ. no π interactions
HOFO-15	-7.50	σ of the equatorial pyridinyl. σ of the equatorial and the axial pyrazolyl all six ligands only σ. no π interactions
HOFO-16	-7.64	**π of the pyridinyl** and σ of the equatorial and the axial pyrazolyl
HOFO-17	-7.65	**π of the pyridinyl** and σ of the equatorial and the axial pyrazolyl
HOFO-18	-8.17	tert-butyl
HOFO-19	-8.29	tert-butyl
HOFO-20	-8.33	**tert-butyl**
HOFO-21	-8.37	**tert-butyl**
HOFO-22	-8.45	tert-butyl
HOFO-23	-8.48	**tert-butyl**
HOFO-24	-8.49	tert-butyl
HOFO-25	-8.51	tert-butyl
HOFO-26	-8.54	tert-butyl
HOFO-27	-8.56	tert-butyl
HOFO-28	-8.58	tert-butyl
HOFO-29	-8.60	tert-butyl
HOFO-30	-9.23	tert-butyl
HOFO-31	-9.30	tert-butyl
HOFO-32	-9.33	tert-butyl
HOFO-33	-9.38	tert-butyl

Table S27. Composition of molecular orbitals of fragment orbitals of the pypz conformer with TPSSh/def2-TZVP and DCM and GD3BJ.

MO	Cu_2O_2 fragment		pypz		
LUMO+9	79.2% LUFO+3		5.2% LUFO+11		
LUMO	27.0% LUFO	26.5% HOFO			
	17.2% HOFO-3	8.7% HOFO-5			
HOMO	42.7% LUFO	39.8 HOFO	8.0% HOFO		
HOMO-1	19.7% HOFO-4	12.5% HOFO-9	24.3% HOFO-1	8.3% HOFO-2	7.2% HOFO-10
	9.0% HOFO-1				
HOMO-2			67.1% HOFO-4	13.5% HOFO-5	6.9% HOFO-2
HOMO-3			41.1% HOFO-5	17.1% HOFO-4	10.8% HOFO-3
			8.7% HOFO	5.0% HOFO-1	
HOMO-4	6.1% HOFO	6.0% HOFO-3	30.6% HOFO-5	16.3% HOFO-2	11.2% HOFO-6
			9.5% HOFO-1	9.2% HOFO-3	
HOMO-5			38.4% HOFO-2	30.3% HOFO-3	10.7% HOFO-7
HOMO-6	6.1% HOFO-4	5.5% HOFO	22.7% HOFO-3	20.7% HOFO	11.5% HOFO-10
HOMO-7	17.2% HOFO-1		13.0% HOFO-8	12.6% HOFO	9.6% HOFO-2
			8.2% HOFO-7	5.9% HOFO-6	5.0% HOFO-9
HOMO-8	5.2% HOFO-2		31.5% HOFO-7	25.0% HOFO-6	7.8% HOFO-9
			6.4% HOFO-3	6.1% HOFO-8	
HOMO-9			31.8% HOFO-9	26.5% HOFO-7	15.9% HOFO-6
			6.9% HOFO-4		
HOMO-10	8.6% HOFO-2		29.5% HOFO-8	8.7% HOFO-9	8.4% HOFO-1
			7.7% HOFO-11	6.2% HOFO-10	
HOMO-11	8.7% HOFO-1	8.6% HOFO-2	27.8% HOFO-11	8.2% HOFO-6	6.9% HOFO
	8.1% HOFO-6		6.7% HOFO-2		
HOMO-12	16.3% HOFO-2	6.4% HOFO-6	39.9% HOFO-12	10.8% HOFO-13	
HOMO-13	11.2% HOFO-2	9.0% HOFO-6	56.5% HOFO-12	5.0% HOFO-13	
HOMO-14	5.5% HOFO-6		78.9% HOFO-13		
HOMO-15	14.5% HOFO-2	14.0% HOFO-8	15.9% HOFO-17	5-0% HOFO-19	
	8.9% HOFO-5	8.0% HOFO-1			
	5.5% HOFO-9				
HOMO-16	15.0% HOFO-4	8.3% HOFO-5	16.4% HOFO-16	10.8% HOFO-17	7.3% HOFO-14
	6.7% HOFO-3				
HOMO-17	7.4% HOFO-7		21.7% HOFO-20	11.5% HOFO-18	10.2% HOFO-19
			7.6% HOFO-15	5.3% HOFO-21	
HOMO-18	8.0% HOFO-7		20.9% HOFO-22	16.6% HOFO-14	7.0% HOFO-14
			5.7% HOFO-20		
HOMO-19	7.7% HOFO-1		45.4% HOFO-18	7.2% HOFO-20	6.6% HOFO-22
HOMO-20	8.8% HOFO-1		24.1% HOFO-20	13.5% HOFO-21	11.5% HOFO-19
			5.5% HOFO-18		
HOMO-21	33.7% HOFO-8	6.6% HOFO-5	6.8% HOFO-6	5.7% HOFO-20	5.2% HOFO-14
	5.4% HOFO-9				
HOMO-22	6.2% HOFO-7		27.7% HOFO-21	14.0% HOFO-24	14.0% HOFO-23
			6.3% HOFO-18	5.5% HOFO-22	
HOMO-23	22.9% HOFO-7	6.0% HOFO-4	16.0% HOFO-22	8.4% HOFO-25	8.3% HOFO-15
HOMO-24	13.3% HOFO-6	8.5% HOFO-4	10.5% HOFO-25	6.3% HOFO-22	5.5% HOFO-24
	6.5% HOFO-9				
HOMO-25			40.5% HOFO-19	17.2% HOFO-24	14.1% HOFO-21
HOMO-26			57.6% HOFO-23	8.4% HOFO-25	7.1% HOFO-24
			6.3% HOFO-27		
HOMO-27			30.6% HOFO-25	27.2% HOFO-24	20.5% HOFO-26
HOMO-28	13.1% HOFO-7	11.7% HOFO-9	22.0% HOFO-16	7.6% HOFO-28	7.0% HOFO-17

			5.7% HOFO-14		
HOMO-29			38.9% HOFO-29	22.0% HOFO-27	18.3% HOFO-26
HOMO-30			38.5% HOFO-27	28.7% HOFO-26	6.0% HOFO-23
HOMO-31			36.4% HOFO-29	15.6% HOFO-22	12.4% HOFO-25
			7.9% HOFO-26		
HOMO-32			56.7% HOFO-28	14.2% HOFO-27	
HOMO-33	10.2% HOFO-9	9.7% HOFO-7	13.2% HOFO-17	8.4% HOFO-28	6.2% HOFO-16
	8.6% HOFO-6	7.5% HOFO-4			
HOMO-34	17.5% HOFO-5	10.2% HOFO-10	10.5% HOFO	5.4% HOFO-9	
	8.4% HOFO-7				
HOMO-35			53.5% HOFO-31	18.0% HOFO-30	8.7% HOFO-33
HOMO-36	7.8% HOFO-10	5.2% HOFO-9	35.7% HOFO-30	12.2% HOFO-31	6.6% HOFO-1
HOMO-37			79.5% HOFO-32	5.5% HOFO-33	
HOMO-38	11.5% HOFO-9		18.9% HOFO-30	13.8% HOFO-31	8.7% HOFO-1
			6.0% HOFO-9		
HOMO-39			68.1% HOFO-33	6.9% HOFO-31	
HOMO-40	5.0% HOFO-4		14.8% HOFO-10	13.0% HOFO-37	5.0% HOFO-15
HOMO-41	9.3% HOFO-1	5.4% HOFO-6	14.3% HOFO-11	10.8% HOFO-38	5.0% HOFO-33
HOMO-42			25.8% HOFO-39	14.8% HOFO-37	13.8% HOFO-38
			8.8% HOFO-34		
HOMO-43			29.4% HOFO-37	26.8% HOFO-34	14.0% HOFO-36
			7.8% HOFO-38		
HOMO-44			46.5% HOFO-38	24.5% HOFO-39	16.8% HOFO-36
HOMO-45			30.0% HOFO-36	26.1% HOFO-37	24.3% HOFO-39
			5.9% HOFO-35		
HOMO-46			43.5% HOFO-40	13.6% HOFO-42	9.8% HOFO-41
HOMO-47	8.6% HOFO-10		17.1% HOFO-40	10.2% HOFO-45	7.3% HOFO-35
			7.0% HOFO-14	6.1% HOFO-15	
HOMO-48			48.2% HOFO-41	22.6% HOFO-40	5.2% HOFO-34
			5.2% HOFO-43		
HOMO-49			27.7% HOFO-42	15.8% HOFO-34	13.5% HOFO-35
			10.2% HOFO-41	5.5% HOFO-43	5.2% HOFO-36
HOMO-50			35.7% HOFO-35	19.6% HOFO-43	19.5% HOFO-41
			5.9% HOFO-34		
HOMO-51			27.4% HOFO-43	26.9% HOFO-42	15.6% HOFO-34
HOMO-52			24.6% HOFO-43	17.4% HOFO-42	15.7% HOFO-35
			13.5% HOFO-36		
HOMO-53			12.1% HOFO-14	11.1% HOFO-10	6.3% HOFO-15
HOMO-54			30.3% HOFO-50	26.8% HOFO-48	10.8% HOFO-49
HOMO-55			31.0% HOFO-49	14.9% HOFO-50	7.3% HOFO-53
			6.9% HOFO-51		
HOMO-56			26.9% HOFO-44	24.4% HOFO-51	17.7% HOFO-50
			5.4% HOFO-48		
HOMO-57	5.7% HOFO-11		30.4% HOFO-48	16.4% HOFO-51	7.5% HOFO-47
			6.6% HOFO-61	5.0% HOFO-49	
HOMO-58			30.7% HOFO-52	15.9% HOFO-53	7.8% HOFO-45
			6.5% HOFO-48	5.4% HOFO-50	
HOMO-59			23.5% HOFO-45	14.3% HOFO-52	9.8% HOFO-55
			8.2% HOFO-49	5.3% HOFO-48	
HOMO-60			17.2% HOFO-53	12.1% HOFO-46	12.0% HOFO-55
			10.6% HOFO-47	6.8% HOFO-44	6.3% HOFO-57
			5.1% HOFO-52		
HOMO-61	5.0% HOFO-10		19.7% HOFO-52	15.3% HOFO-54	11.3% HOFO-49

HOMO-62		19.2% HOFO-51	13.1% HOFO-44	10.5% HOFO-47
		8.9% HOFO-57	6.6% HOFO-55	6.5% HOFO-58
		5.3% HOFO-46		
HOMO-63		27.7% HOFO-54	19.1% HOFO-46	16.8% HOFO-47
		7.8% HOFO-57		
HOMO-64		17.8% HOFO-54	13.6% HOFO-55	10.2% HOFO-53
		9.7% HOFO-56		
HOMO-65	126% HOFO-11	13.3% HOFO-56	9.6% HOFO-64	9.2% HOFO-58
		8.4% HOFO-47	5.9% HOFO-57	
HOMO-66	5.1% HOFO-11	15.8% HOFO-56	8.9% HOFO-54	8.5% HOFO-58
		8.5% HOFO-46	6.5% HOFO-62	5.7% HOFO-59

Figure S9. Selected Molecular orbitals of $[Cu_2O_2\{HC(3tBuPz)_2(Py)\}]^{2+}$ in the pypz conformer with TPSSh/def2-TZVP and DCM and GD3BJ.

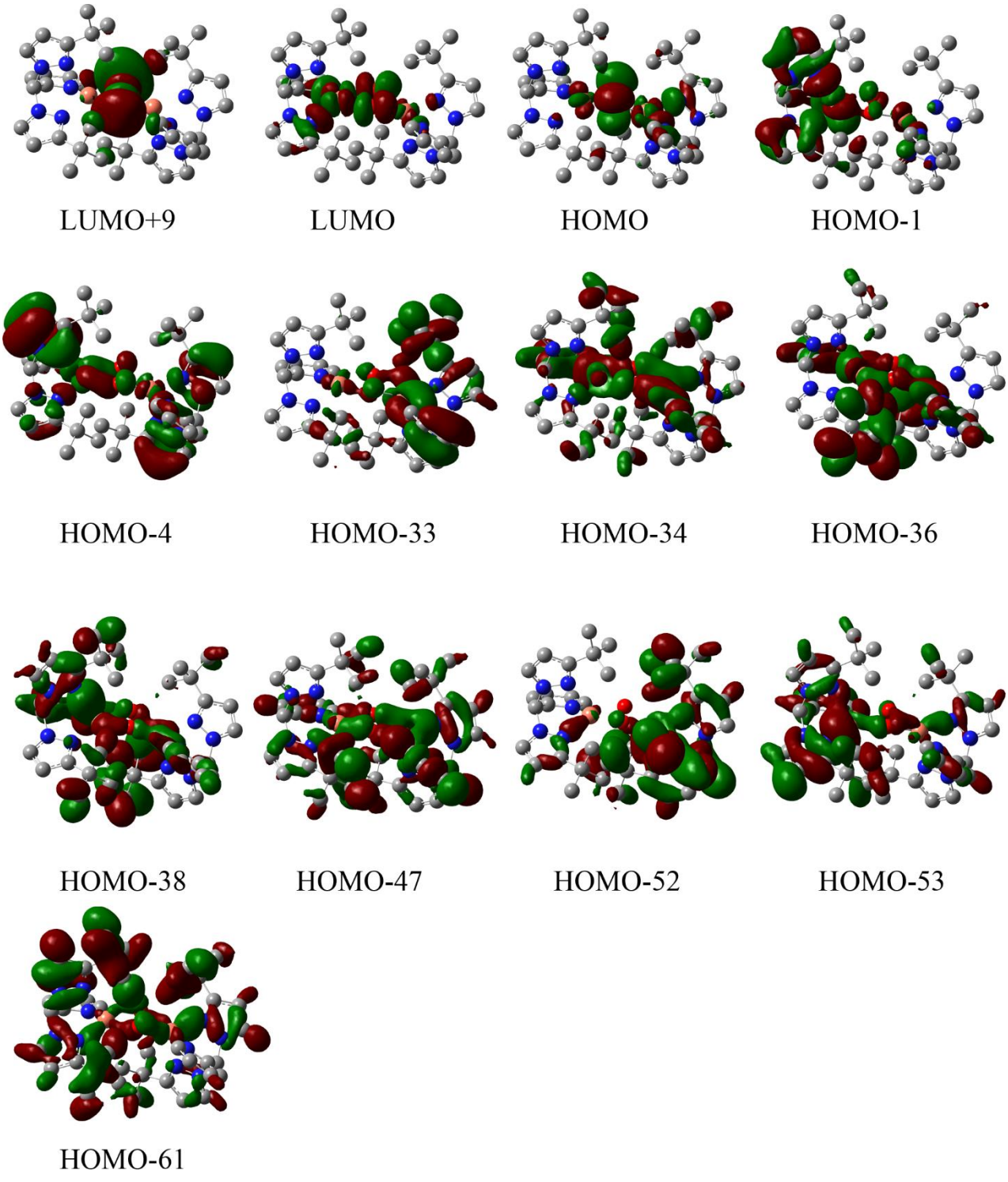

Table S28: MO energies of the pypz conformer of the **P** core with TPSSh/def2-TZVP and DCM and GD3BJ.

MO	Peroxo	Energy in eV
226	LUMO+7	-1.13
220	LUMO+1	-2.94
219	LUMO	-4.46
218	HOMO	-6.92
217	HOMO-1	-7.31
216	HOMO-2	-7.36
215	HOMO-3	-7.39
214	HOMO-4	-7.44
213	HOMO-5	-7.58
212	HOMO-6	-7.67
211	HOMO-7	-7.71
210	HOMO-8	-7.78
209	HOMO-9	-7.82
208	HOMO-10	-7.89
207	HOMO-11	-8.05
206	HOMO-12	-8.44
205	HOMO-13	-8.45
204	HOMO-14	-8.49
203	HOMO-15	-8.72
202	HOMO-16	-8.80
201	HOMO-17	-8.84
200	HOMO-18	-8.98
199	HOMO-19	-9.01
198	HOMO-20	-9.08
197	HOMO-21	-9.12
196	HOMO-22	-9.18
195	HOMO-23	-9.20
194	HOMO-24	-9.22
193	HOMO-25	-9.27
192	HOMO-26	-9.35
191	HOMO-27	-9.38
190	HOMO-28	-9.44
189	HOMO-29	-.947
188	HOMO-30	-9.51
187	HOMO-31	-9.56
186	HOMO-32	-9.61
185	HOMO-33	-9.68
184	HOMO-34	-9.85
183	HOMO-35	-9.99
182	HOMO-36	-10.09
181	HOMO-37	-10.13
180	HOMO-38	-10.17
179	HOMO-39	-10.20
178	HOMO-40	-10.30

177	HOMO-41	-10.37
176	HOMO-42	-10.41
175	HOMO-43	-10.48
174	HOMO-44	-10.51
173	HOMO-45	-10.54
172	HOMO-46	-10.60
171	HOMO-47	-1.070
170	HOMO-48	-10.77
169	HOMO-49	-10.77
168	HOMO-50	-10.82
167	HOMO-51	-11.00
166	HOMO-52	-11.06
165	HOMO-53	-11.12
164	HOMO-54	-11.43
163	HOMO-55	-11.51
162	HOMO-56	-11.59
161	HOMO-57	-11.66
160	HOMO-58	-11.75
159	HOMO-59	-11.77
158	HOMO-60	-11.79
157	HOMO-61	-11.82
156	HOMO-62	-11.89
155	HOMO-63	-11.93
154	HOMO-64	-11.95
153	HOMO-65	-12.08
152	HOMO-66	-12.14

Table S29: Molecular orbital descriptions of the pypz conformer of the **P** core with TPSSh/def2-TZVP and DCM and GD3BJ.

MO	MO composition pypz
LUMO +7	σ^*
LUMO	d_{xy} - π_σ*- σ of the equatorial pyrazolyl and the equatorial pyridinyl
HOMO	σ of the equatorial pyrazolyl and σ of the equatorial pyridinyl – d – π_v*
HOMO-1	π_σ* – d – σ of the pyridinyl and σ of the axial pyrazolyl
HOMO-2	π of the pyrazolyl
HOMO-3	π of the pyrazolyl
HOMO-4	σ of the equatorial pyrazolyl and σ of the equatorial pyridinyl – d + π_σ*
HOMO-5	π of the axial and the equatorial pyrazolyl
HOMO-6	π_v* – d – π of the axial pyrazolyl – σ of the equatorial pyridinyl – σ of the equatorial pyrazolyl
HOMO-7	π_v* – d – π of the axial and the equatorial pyrazolyl
HOMO-8	d – π of the axial and equatorial pyrazolyl
HOMO-9	d – π of the axial and equatorial pyrazolyl
HOMO-10	π of the axial and the equatorial pyrazolyl – d + π_σ*
HOMO-11	π_v* - d – σ of the axial pyrazolyl – π of the equatorial pyrazolyl
HOMO-12	π_v – d **– π of the equatorial pyridinyl**
HOMO-13	π_v* + d **– π of the equatorial pyridinyl**
HOMO-14	d – π of the equatorial pyridinyl
HOMO-15	π_v* – d – π of the equatorial pyridinyl + π_σ*
HOMO-16	d – σ of the axial pyrazolyl **– π of the equatorial pyridinyl**
HOMO-17	**π_σ*– d** – σ of the equatorial pyridinyl
HOMO-18	d – π of the equatorial pyridinyl and tert-butyl
HOMO-21	π of the equatorial pyrazolyl – π of the equatorial pyrindinyl and tert-butyl + d
HOMO-22	tert-butyl – d
HOMO-23	tert-butyl – d –σ
HOMO-24	tert-butyl – d –π_v*
HOMO-28	π of the equatorial pyridinyl and tert-butyl + d
HOMO-32	d – σ and **tert-butyl**
HOMO-33	d + π of the equatorial pyridinyl and tert-butyl
HOMO-34	d_{xy} + π_σ* + σ of the equatorial pyrazolyl + σ of the equatorial pyridinyl
HOMO-35	**tert-butyl** - σ of the equatorial pyridinyl
HOMO-36	d_{xy} + π_σ* + σ of the equatorial pyridinyl
HOMO-37	tert-butyl
HOMO-38	d_{xy} + π_σ* + σ of the equatorial pyridinyl + σ of the axial pyrazolyl
HOMO-39	tert-butyl - σ of the axial pyrazolyl + d
HOMO-40	d + σ of the axial pyrazolyl + σ of the equatorial pyrazolyl + σ of the equatorial pyridinyl
HOMO-41	d + σ of the axial pyrazolyl
HOMO-42	d + σ of the axial pyrazolyl
HOMO-47	d + π_σ* - σ of the equatorial pyrazolyl + σ of the equatorial pyridinyl
HOMO-51	d + σ of the equatorial pyrazolyl
HOMO-52	d + σ of the equatorial pyrazolyl + σ of the equatorial pyridinyl
HOMO-53	d + σ of the equatorial pyrazolyl + π_σ*
HOMO-54	d + σ of the equatorial pyrazolyl + π_σ*
HOMO-55	d + σ of the equatorial pyrazolyl
HOMO-59	d + σ of the equatorial pyrazolyl + π_σ*
HOMO-61	d + σ of the equatorial pyrazolyl - π_v*
HOMO-62	d + σ of the equatorial pyrazolyl – σ and tert-butyl
HOMO-64	d + σ of the equatorial pyrazolyl + π_v^*

HOMO-65	d + σ of the equatorial pyridinyl + σ of the equatorial pyrazolyl + π_v
HOMO-66	d + σ of the equatorial pyridinyl + π_v