Electronic Supporting Information

Zinc-Porphyrins Functionalized with Redox-Active Metal Peripherals: Enhancement of dπ-pπ Interaction Leading to Unique Assembly and Redox-Triggered Remote Switching of Fluorescence†

Masahito Murai,[a, ‡] Manabu Sugimoto,[b] and Munetaka Akita*[a]

[a]*Chemical Resources Laboratory, Tokyo Institute of Technology, R1-27, 4259 Nagatsuta Midori-ku Yokohama 226-8503, Japan*

[b]*Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1, Kurokami, Kumamoto, 860-8555, Japan*

‡*present address: Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushimanaka 3-1-1, Okayama, 700-8530, Japan.*

Table of the Contents page

Table S1. Cartesian coordinates for **1** and $\mathbf{1}^{+}$.

1				$1^{+\cdot}$			
	X	Y	Z		X	Y	Z
Zn	4.453866	0.410893	0.034552	Zn	4.385371	0.481615	-0.008192
N	5.578467	2.099674	0.44916	N	5.452166	2.188872	0.469169
N	2.734015	1.555714	0.114602	N	2.642509	1.598873	-0.01033
N	3.325993	-1.262711	-0.420854	N	3.312355	-1.208806	-0.536618
N	6.167473	-0.749866	-0.01368	N	6.11286	-0.654245	0.035494
C	6.23259	4.235364	1.005708	C	6.044398	4.33323	1.057625
C	5.11236	3.373456	0.679541	C	4.961042	3.453657	0.666539
C	3.761913	3.767609	0.622667	C	3.604419	3.832446	0.52794
C	2.6683	2.914177	0.337899	C	2.546587	2.963015	0.196609
C	1.297973	3.348136	0.203837	C	1.174082	3.371049	-0.002391
C	0.553773	2.241885	-0.089689	C	0.461243	2.249263	-0.307232
C	1.455836	1.122948	-0.142015	C	1.389119	1.14443	-0.308345
C	1.05474	-0.218425	-0.41599	C	1.035928	-0.207923	-0.60005
C	1.956715	-1.318881	-0.516056	C	1.959264	-1.289607	-0.710599
C	1.551074	-2.68135	-0.730399	C	1.59066	-2.654209	-0.997236
C	2.684474	-3.442724	-0.763369	C	2.737506	-3.391712	-0.988455
C	3.800989	-2.547167	-0.575818	C	3.82503	-2.482505	-0.700931
C	5.159754	-2.946631	-0.536436	C	5.177115	-2.85973	-0.581308
C	6.253453	-2.095706	-0.286714	C	6.241741	-1.99008	-0.244659
C	7.650017	-2.488195	-0.29467	C	7.639281	-2.364921	-0.161982
C	8.381721	-1.373153	-0.011218	C	8.333694	-1.241972	0.180656
C	7.4468	-0.286068	0.161599	C	7.371985	-0.172886	0.298096
C	7.798151	1.034124	0.459041	C	7.679696	1.152039	0.62045
C	6.941123	2.128999	0.605624	C	6.802976	2.237471	0.710833
C	7.35822	3.467678	0.951644	C	7.181761	3.580246	1.077712
H	0.529004	-3.00702	-0.834139	H	0.584461	-2.99578	-1.179221
C	3.455549	5.2114	0.880938	C	3.26935	5.27518	0.75335
C	2.742173	5.600348	2.026541	C	2.498347	5.668085	1.859136
C	2.46107	6.945021	2.272721	C	2.193529	7.013186	2.073305
C	2.88694	7.927353	1.376004	C	2.651221	7.986908	1.18315
C	3.595862	7.554708	0.232123	C	3.417456	7.60809	0.078732
C	3.877275	6.20945	-0.012429	C	3.726003	6.263586	-0.133414
C	5.456203	-4.395028	-0.778405	C	5.518682	-4.298176	-0.825509
C	5.206833	-4.981632	-2.03005	C	5.412218	-4.85254	-2.111024
C	5.484795	-6.330223	-2.257238	C	5.737476	-6.190717	-2.338531
C	6.017745	-7.119497	-1.235723	C	6.171248	-6.996806	-1.283993
C	6.270473	-6.549685	0.013748	C	6.279524	-6.456785	-0.000641
C	5.992181	-5.200626	0.239667	C	5.957793	-5.117897	0.22658
H	1.913436	7.2254	3.168971	H	1.604516	7.300755	2.940122
H	3.928315	8.311292	-0.474139	H	3.775747	8.359201	-0.619957
H	5.289316	-6.762748	-3.235177	H	5.657792	-6.601038	-3.341539
H	6.680883	-7.156444	0.816941	H	6.613881	-7.077839	0.825965
H	2.668844	8.974744	1.567537	H	2.415393	9.034166	1.350592
H	6.161644	5.285549	1.249806	H	5.94378	5.382752	1.292146
H	0.951094	4.366777	0.29951	H	0.810486	4.386141	0.062204
H	-0.504281	2.186542	-0.290567	H	-0.584553	2.178935	-0.563401
H	2.415349	4.838612	2.728848	H	2.15047	4.913228	2.558951
H	4.424248	5.92186	-0.906036	H	4.319808	5.971723	-0.995188
H	8.380754	3.772035	1.138269	H	8.186066	3.89869	1.326728
H	2.754776	-4.512784	-0.894529	H	2.841122	-4.453559	-1.15776
H	9.458544	-1.285792	0.065306	H	9.401031	-1.139564	0.330117
H	8.01739	-3.483492	-0.499155	H	8.033217	-3.353016	-0.349402
H	6.183239	-4.762096	1.215175	H	6.040314	-4.701534	1.226836
H	4.798261	-4.368527	-2.828428	H	5.084357	-4.224744	-2.934986
H	6.234584	-8.169806	-1.412105	H	6.425644	-8.038036	-1.461366
Fe	-3.444274	-1.036554	-0.73497	Fe	-3.39406	-1.161254	-0.674281
P	-3.397752	-0.875401	1.552138	P	-3.183577	-0.79205	1.649856
P	-3.777039	1.212039	-0.74553	P	-3.839893	1.135816	-0.80184
C	-0.33818	-0.47284	-0.573637	C	-0.346256	-0.501155	-0.741238

C	-1.555754	-0.684106	-0.655678	C	-1.561433	-0.746044	-0.778644
C	-3.473829	-1.905127	-2.733536	C	-3.698596	-2.155651	-2.608703
C	-3.120211	-2.929705	-1.791432	C	-3.159585	-3.086336	-1.662279
C	-4.203328	-3.09914	-0.891963	C	-4.096088	-3.222124	-0.594632
C	-5.247995	-2.176174	-1.260706	C	-5.230189	-2.375135	-0.881677
C	-4.800028	-1.473063	-2.421864	C	-4.993391	-1.753663	-2.144434
C	-2.752197	0.845028	1.889893	C	-2.593484	0.969351	1.769049
C	-3.414439	1.893798	0.984704	C	-3.376021	1.917258	0.851121
H	-2.851858	1.106882	2.949379	H	-2.626993	1.309107	2.809891
H	-1.685766	0.77637	1.661004	H	-1.54405	0.932179	1.466484
H	-2.775963	2.778346	0.901042	H	-2.78825	2.818924	0.655821
H	-4.368927	2.230454	1.39847	H	-4.309315	2.244766	1.316078
C	-2.234052	-1.910735	2.559892	C	-1.895261	-1.733038	2.577064
C	-4.919585	-0.992458	2.624254	C	-4.614295	-0.895961	2.825062
C	-5.492515	1.879472	-1.028044	C	-5.590654	1.69734	-1.018572
C	-2.762556	2.322847	-1.825008	C	-2.924967	2.154284	-2.035022
C	-2.681727	-1.563082	-3.963275	C	-3.10816	-1.848089	-3.95287
C	-1.900562	-3.796375	-1.876111	C	-1.925102	-3.910557	-1.860427
C	-4.311841	-4.214753	0.112036	C	-4.014605	-4.267597	0.481526
C	-6.641609	-2.153782	-0.695446	C	-6.522127	-2.344451	-0.116781
C	-5.63884	-0.577283	-3.288688	C	-5.99007	-0.976935	-2.951412
H	8.858384	1.231462	0.592321	H	8.725945	1.364474	0.822358
C	-6.51829	1.463216	-0.161762	C	-6.537784	1.370983	-0.032143
C	-5.829117	2.728716	-2.092719	C	-6.022719	2.392789	-2.158455
C	-7.145703	3.161254	-2.27497	C	-7.361805	2.766613	-2.298379
C	-7.830924	1.90191	-0.337333	C	-7.873209	1.749807	-0.171338
C	-8.150155	2.754571	-1.397119	C	-8.289743	2.450483	-1.30629
H	-5.065131	3.059895	-2.787297	H	-5.317947	2.653006	-2.940261
H	-7.38193	3.819357	-3.107214	H	-7.675249	3.309082	-3.185838
H	-6.295891	0.777957	0.650393	H	-6.241876	0.813135	0.851102
H	-8.604132	1.571064	0.351327	H	-8.587495	1.496315	0.607154
H	-9.172657	3.09446	-1.538132	H	-9.32923	2.74586	-1.415131
C	-1.956062	1.77698	-2.830867	C	-2.162319	1.560828	-3.048791
C	-2.77374	3.719403	-1.653974	C	-2.993325	3.559125	-1.970488
C	-1.999866	4.543641	-2.470425	C	-2.311636	4.345063	-2.898122
C	-1.184255	2.602854	-3.652523	C	-1.484224	2.350574	-3.980778
C	-1.203737	3.9856	-3.474478	C	-1.556283	3.741136	-3.90732
H	-3.398638	4.171667	-0.888231	H	-3.592024	4.045966	-1.205443
H	-2.01787	5.620213	-2.32248	H	-2.371859	5.427728	-2.833972
H	-1.90423	0.702028	-2.938072	H	-2.068355	0.483922	-3.085076
H	-0.555841	2.160183	-4.420565	H	-0.890449	1.875273	-4.756301
H	-0.596448	4.627213	-4.107234	H	-1.023846	4.354228	-4.628695
C	-5.436355	-2.259733	2.948799	C	-5.010014	-2.154363	3.31431
C	-5.585642	0.133173	3.134836	C	-5.31709	0.23585	3.26897
C	-6.737078	0.000051	3.917316	C	-6.395082	0.112142	4.150423
C	-6.584017	-2.395958	3.72919	C	-6.086177	-2.278113	4.192516
C	-7.244945	-1.264073	4.21239	C	-6.789115	-1.144567	4.60786
H	-5.207033	1.130807	2.943421	H	-5.022099	1.230583	2.955434
H	-7.227949	0.890163	4.302356	H	-6.916407	1.004231	4.486031
H	-4.918535	-3.151661	2.614212	H	-4.450879	-3.041965	3.039142
H	-6.956158	-3.388893	3.96786	H	-6.366768	-3.260262	4.562357
H	-8.138356	-1.368453	4.821902	H	-7.625316	-1.240017	5.294186
C	-1.270176	-2.704569	1.92443	C	-0.977474	-2.562838	1.918754
C	-2.262263	-1.877327	3.964838	C	-1.793731	-1.578357	3.971744
C	-1.348342	-2.621239	4.711077	C	-0.793961	-2.238859	4.684338
C	-0.354404	-3.449094	2.671914	C	0.020117	-3.227024	2.635968
C	-0.39286	-3.410654	4.065866	C	0.113254	-3.067188	4.018573
H	-3.004006	-1.275027	4.481287	H	-2.497401	-0.947958	4.506869
H	-1.381949	-2.582737	5.796864	H	-0.724702	-2.106243	5.760291
H	-1.220211	-2.702318	0.843198	H	-1.023235	-2.660361	0.84217
H	0.39674	-4.043598	2.159203	H	0.730009	-3.855489	2.106058
H	0.320576	-3.987687	4.648365	H	0.890679	-3.581449	4.576386
H	-6.079041	-1.165104	-4.106833	H	-6.503294	-1.664943	-3.637625
H	-6.460156	-0.115507	-2.73768	H	-6.751318	-0.501615	-2.331945
H	-5.052572	0.225284	-3.746763	H	-5.519693	-0.202641	-3.563131

H	-3.015198	-0.625267	-4.417039
H	-1.613431	-1.469414	-3.740888
H	-2.788664	-2.347297	-4.726927
H	-2.076819	-4.640744	-2.558914
H	-1.040537	-3.240567	-2.256659
H	-1.630162	-4.219298	-0.903886
H	-7.26503	-2.938376	-1.149466
H	-6.651587	-2.315943	0.386901
H	-7.136001	-1.196917	-0.884444
H	-4.367189	-5.182837	-0.404989
H	-3.452677	-4.259354	0.789628
H	-5.218306	-4.124434	0.714813

H	-3.473478	-0.900285	-4.356148
H	-2.015961	-1.806237	-3.916092
H	-3.381645	-2.633452	-4.671154
H	-2.167272	-4.811842	-2.44066
H	-1.158077	-3.360995	-2.410288
H	-1.497299	-4.241576	-0.910722
H	-7.172258	-3.171198	-0.434418
H	-6.364854	-2.443966	0.959856
H	-7.069196	-1.413997	-0.28703
H	-4.137548	-5.263141	0.034529
H	-3.053464	-4.262973	1.004412
H	-4.808937	-4.148147	1.220173

Figure S1. ^{1}H spectrum of **1** observed at 300 MHz in C_6D_6.

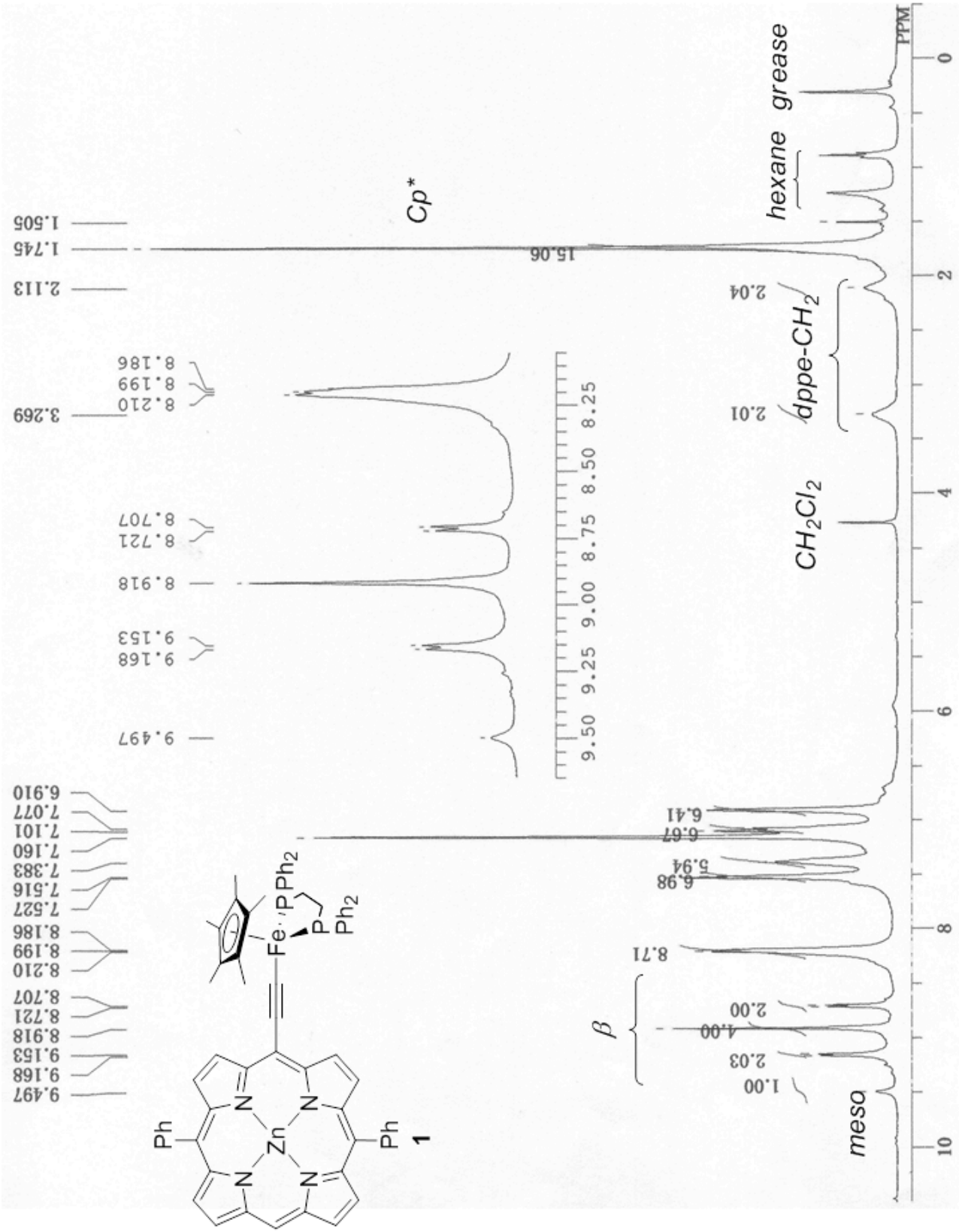

Figure S2. ^{31}P NMR spectrum of **1** observed at 122 MHz in C_6D_6.

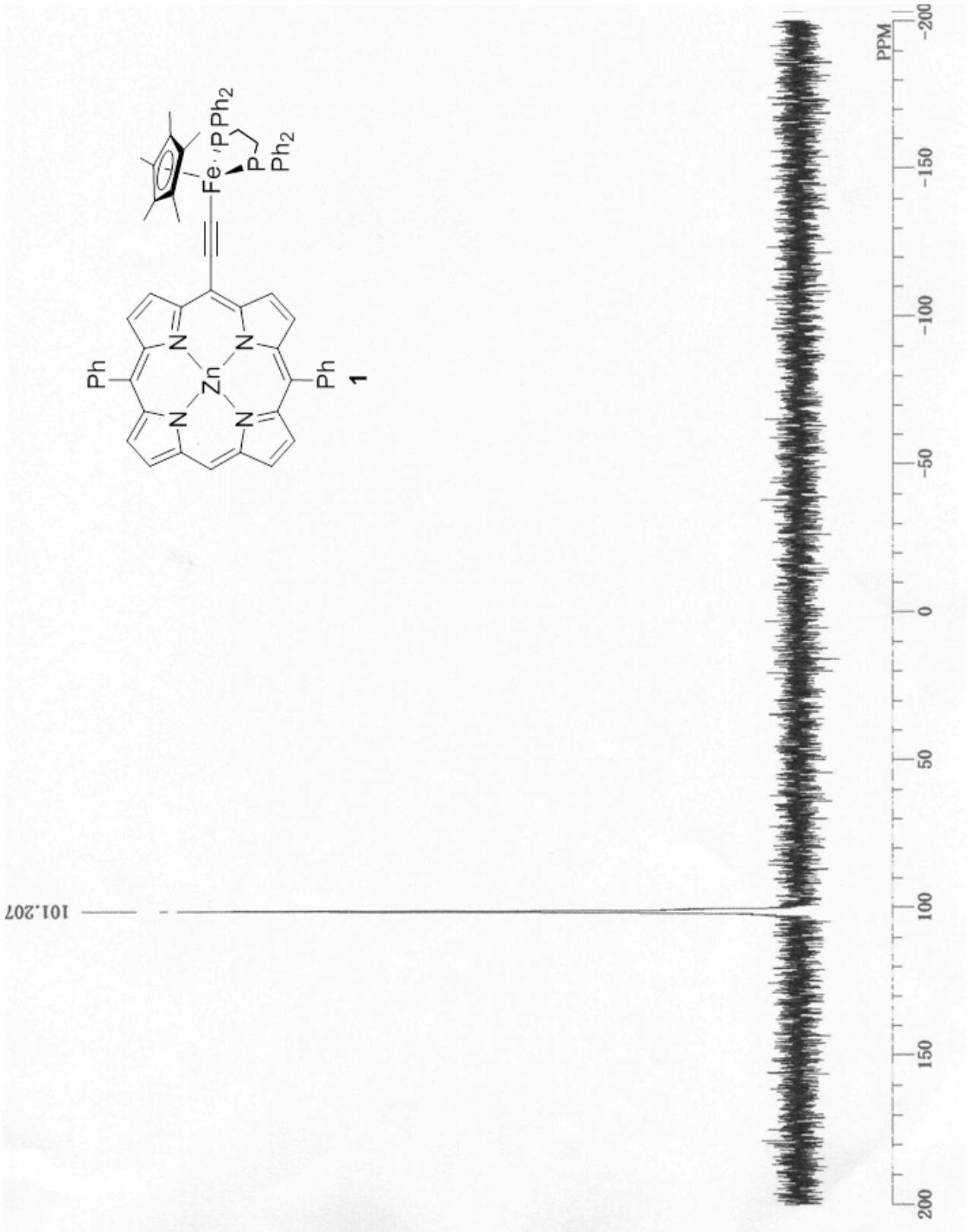

Figure S3. ^{1}H NMR spectrum of **2** observed at 300 MHz in C_6D_6.

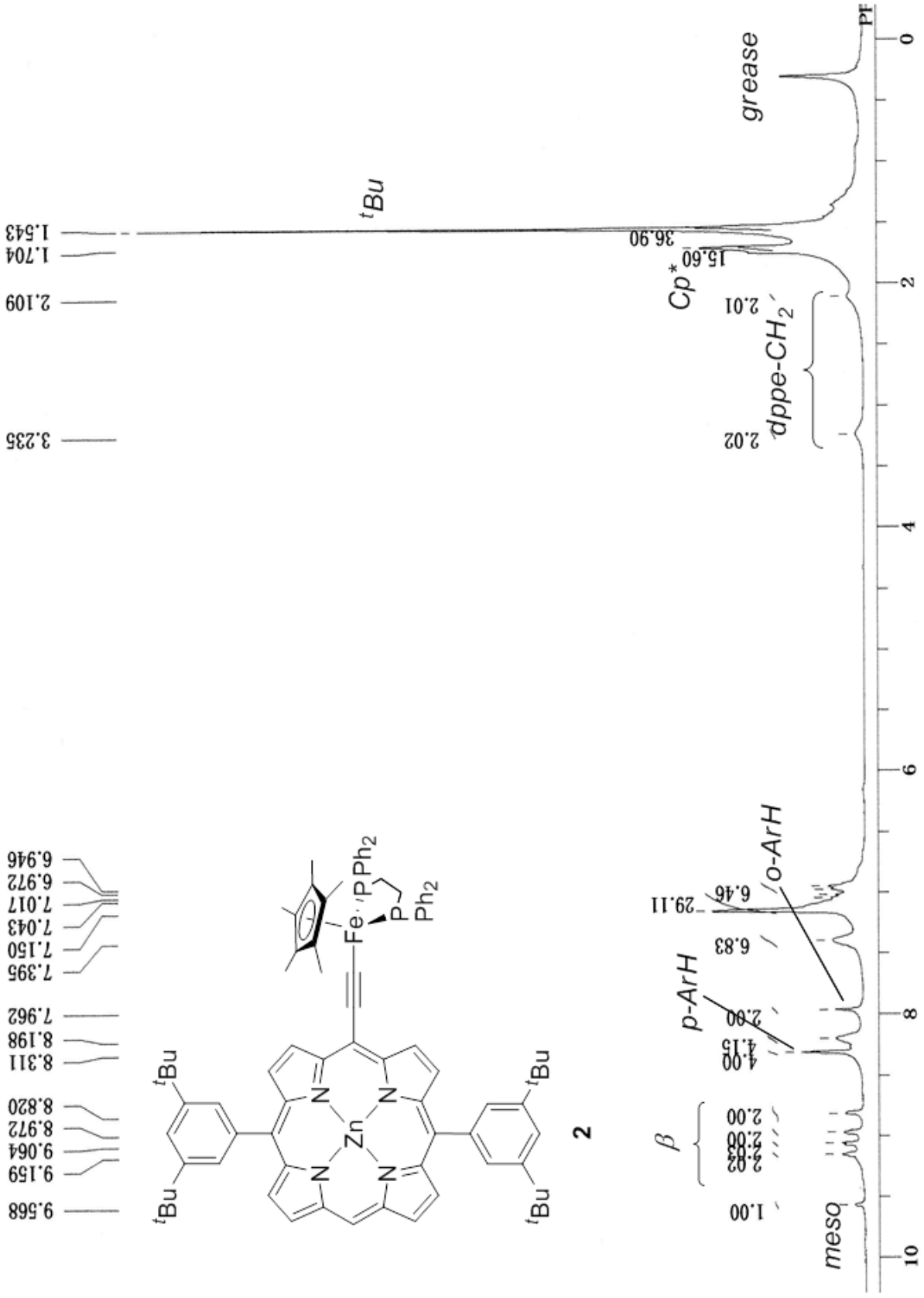

Figure S4. ^{31}P NMR spectrum of **2** observed at 122 MHz in C_6D_6.

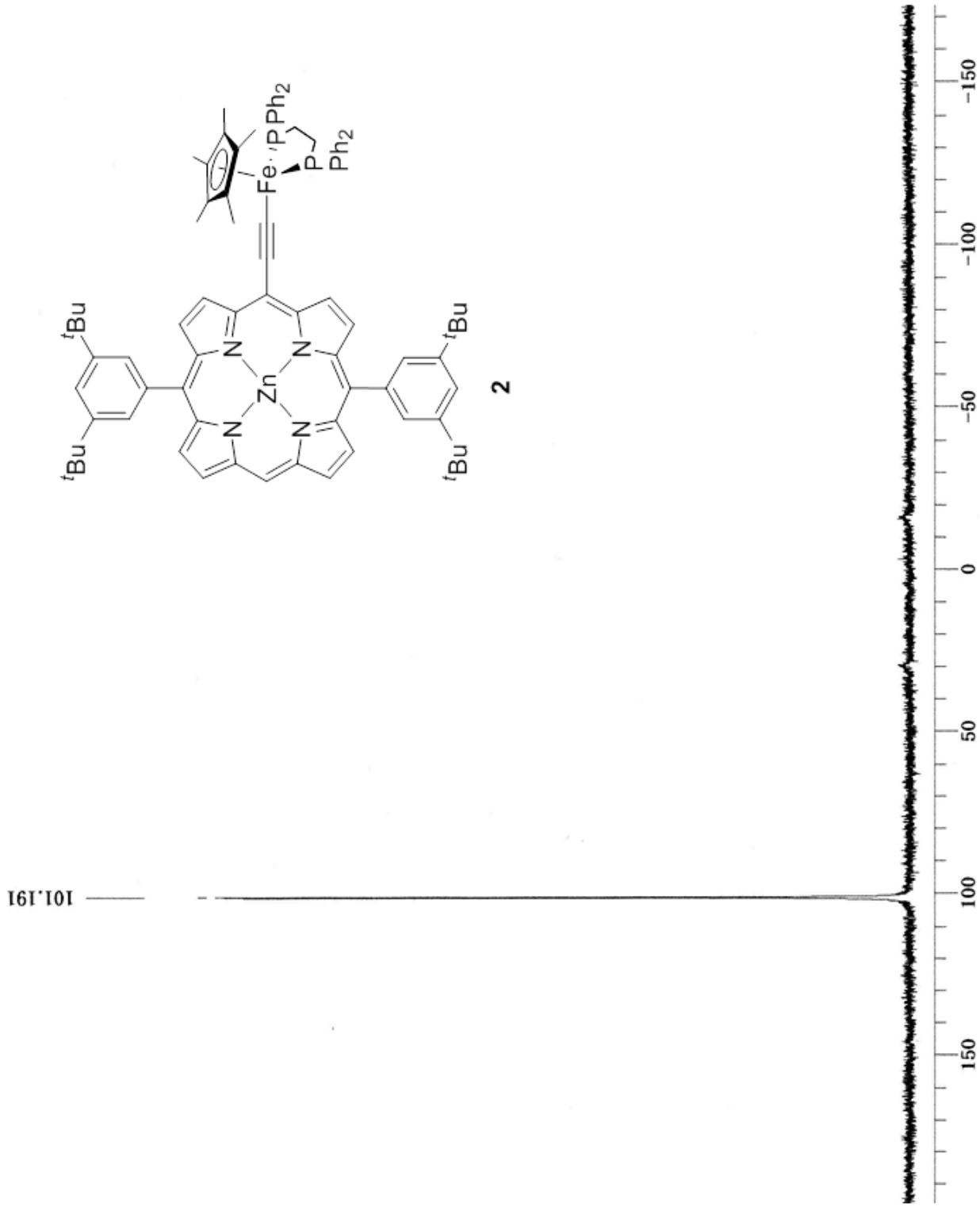

Figure S5. ^{1}H NMR spectrum of **3** observed at 300 MHz in C_6D_6.

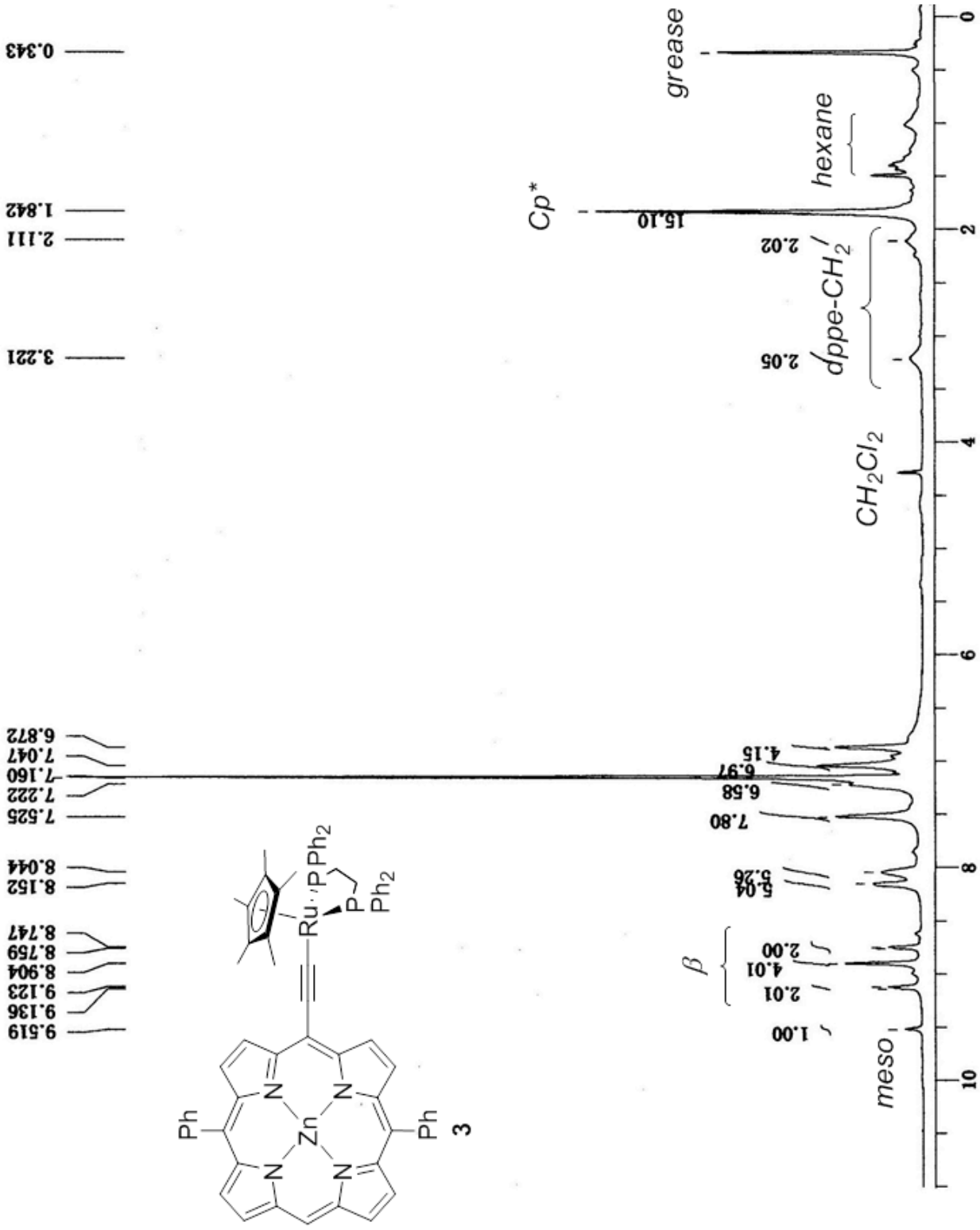

Figure S6. ^{31}P NMR spectrum of **3** observed at 122 MHz in C_6D_6.

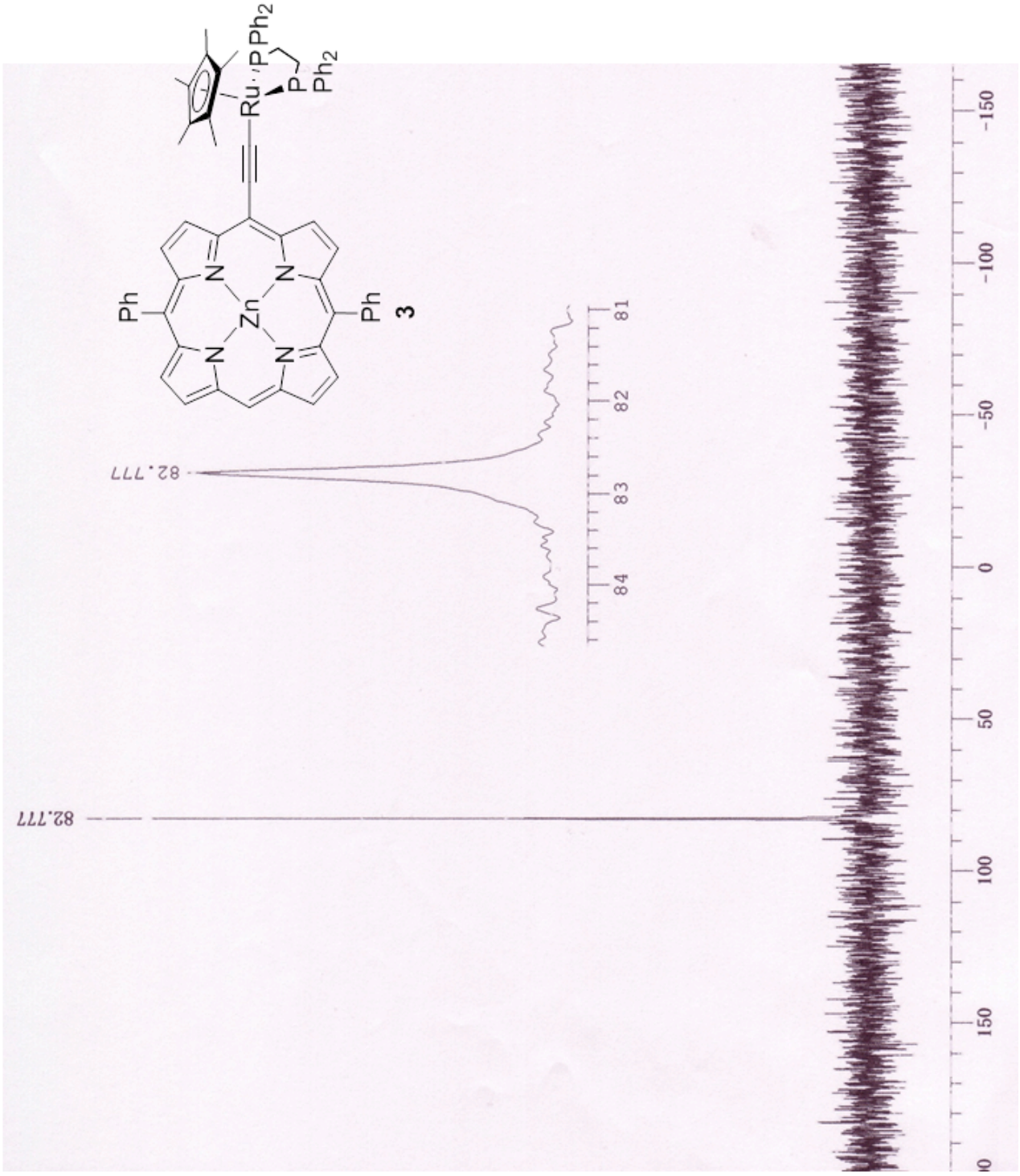

Figure S7. The molecular orbitals of **1**. The contour value is 0.035. A value in a parenthesis indicates the orbital energy level (in hartree).

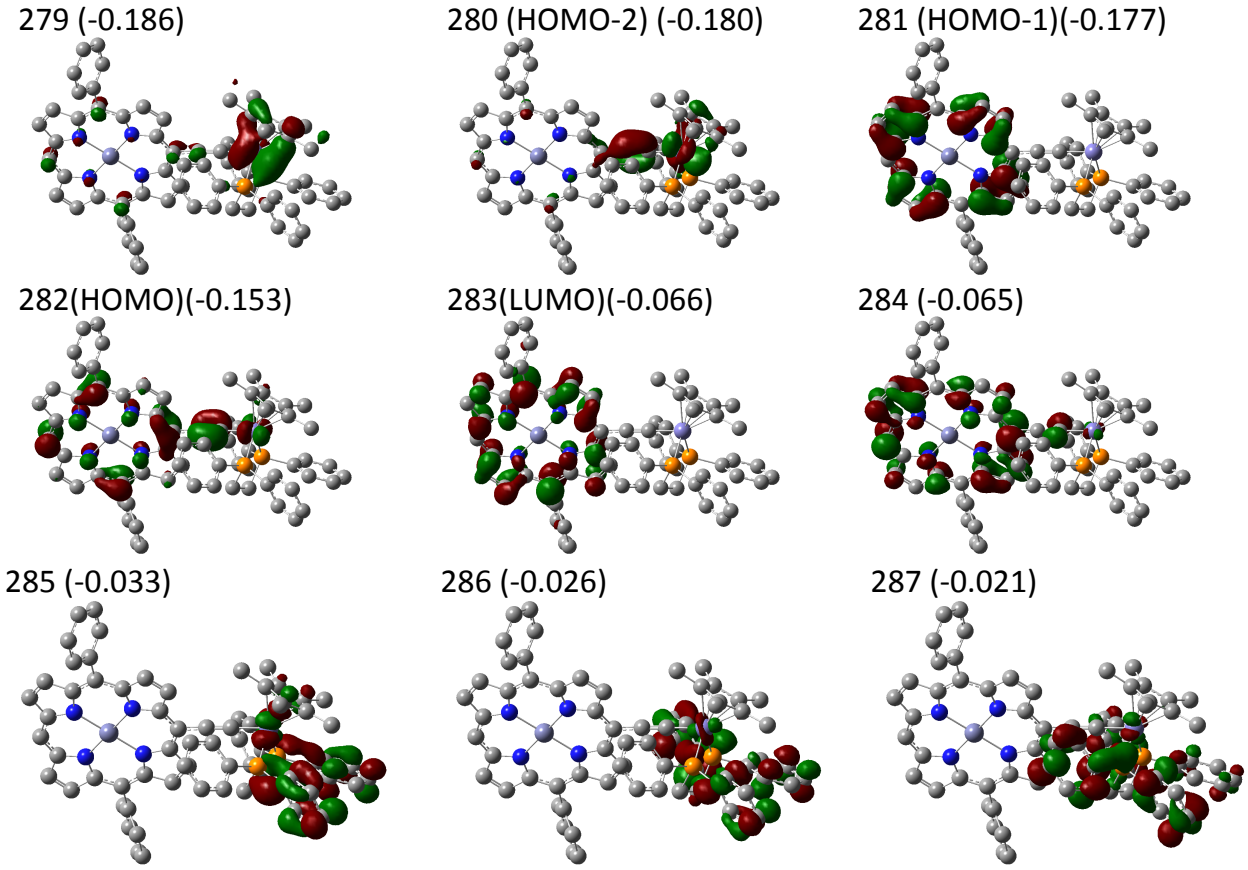

Figure S8. The molecular orbitals $\mathbf{1}^{+\bullet}$ calculated using the restricted open-shell approximation. The contour value is 0.035. A value in a parenthesis indicates the orbital energy level (in hartree).

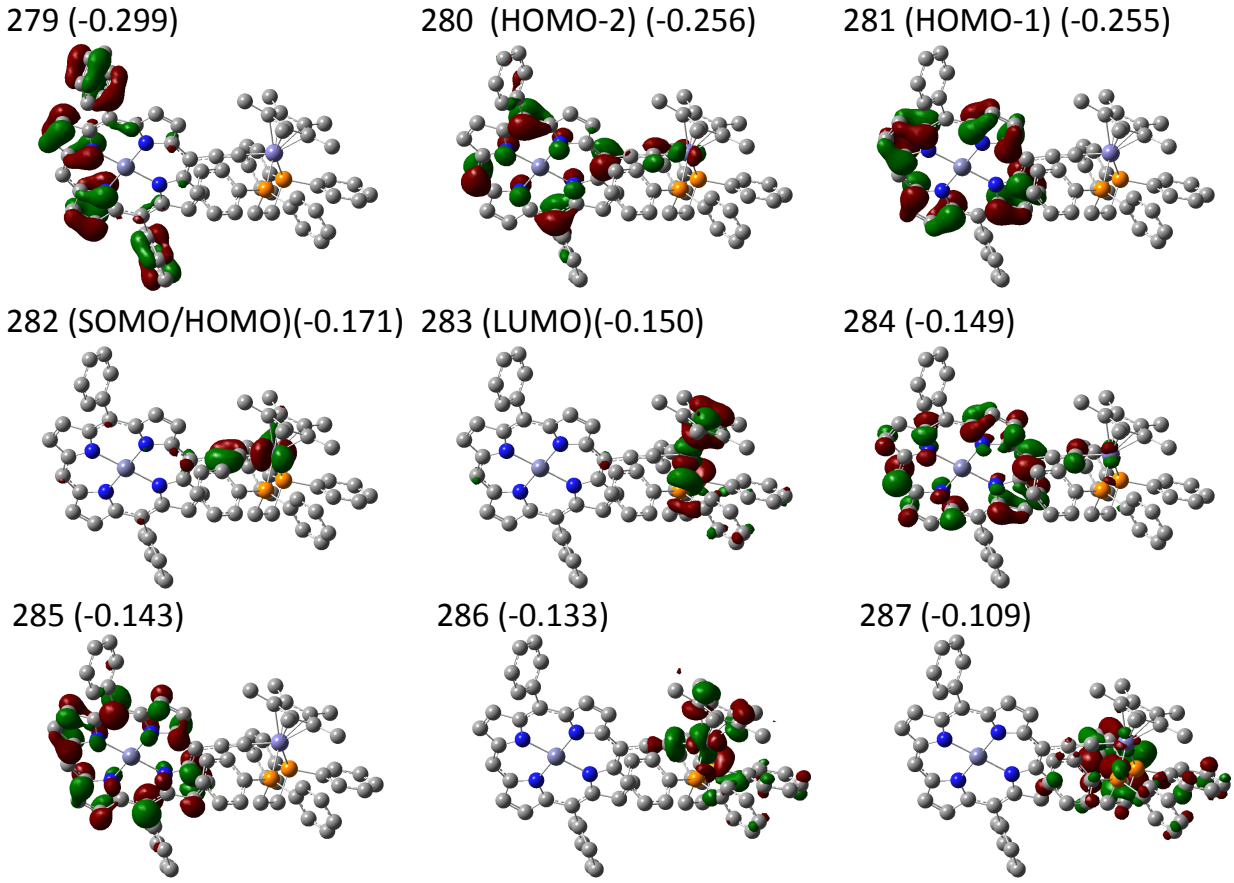

Figure S9. ESI-TOF-mass spectra of **8**.