Electronic Supplementary Information for Dalton Transactions

Supporting Information

Metal-Free and Transition-Metal Tetraferrocenylporphyrins Part 1: Synthesis, Characterization, Electronic Structure, and Conformational Flexibility of Neutral Compounds

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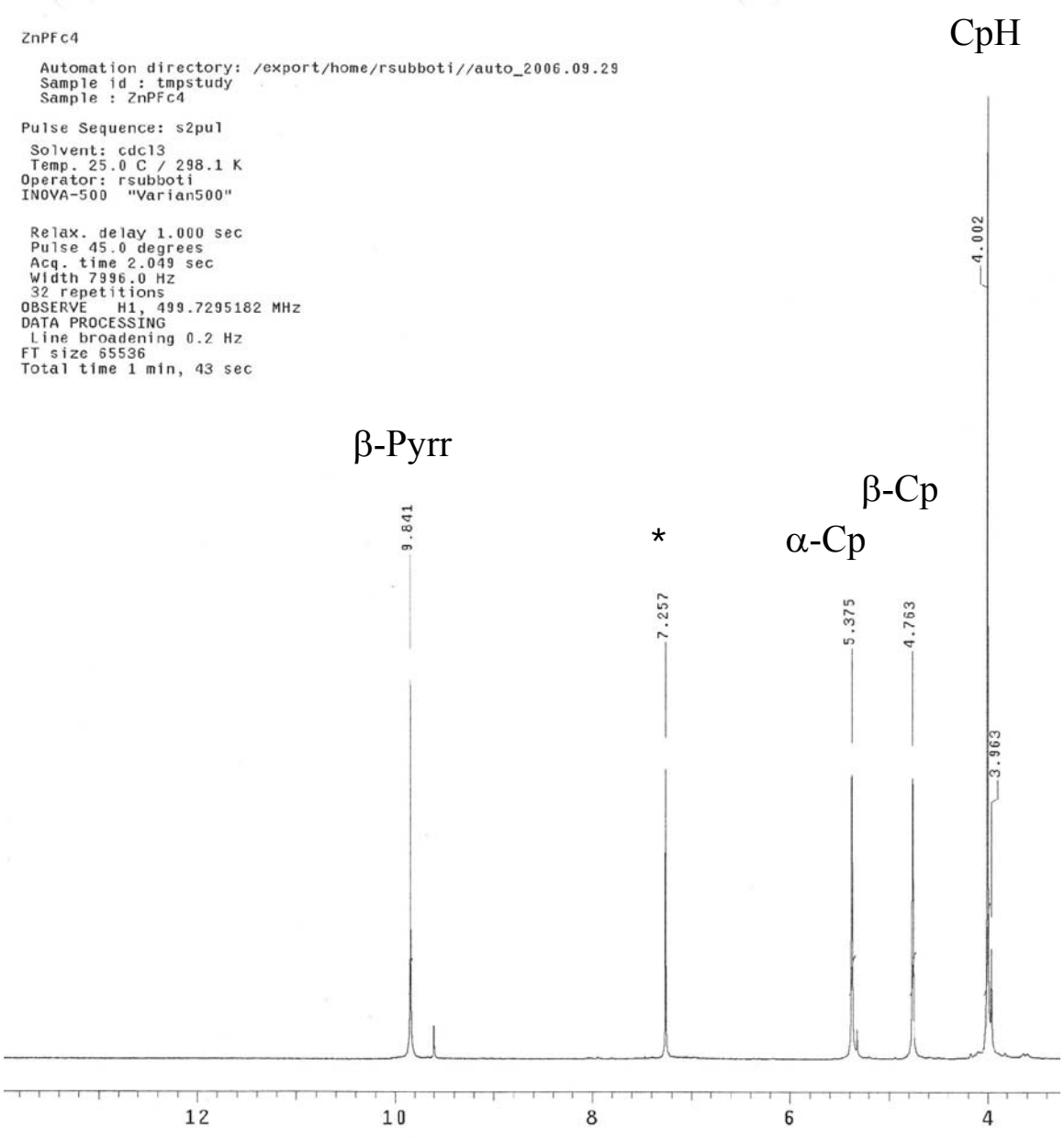
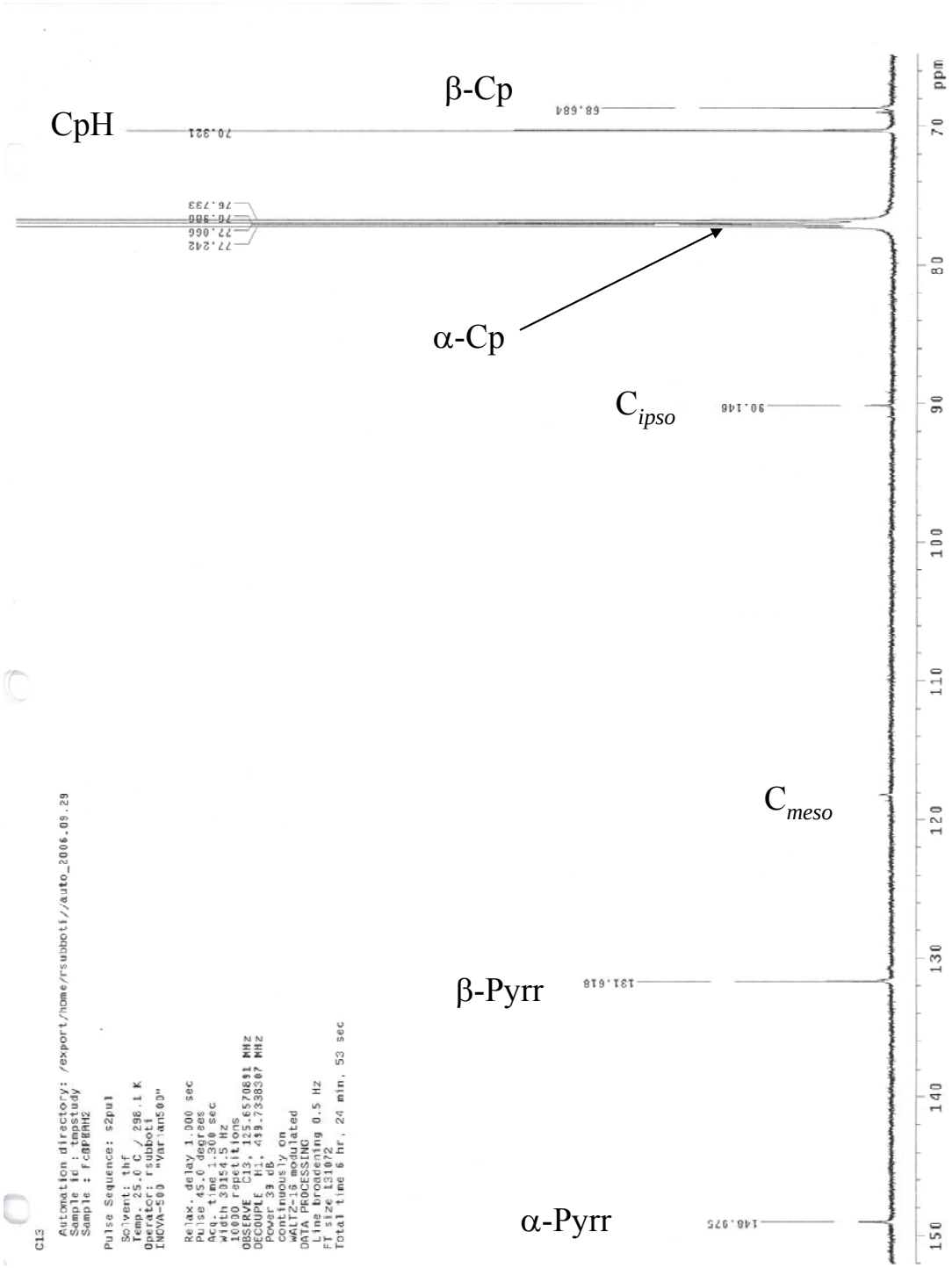


Supporting Information Figure 1. Typical example of ^{1}H and ^{13}C NMR spectra of diamagnetic MTFcP (ZnTFcP) complexes in $CDCl_3$. Solvent labeled with asterisk.



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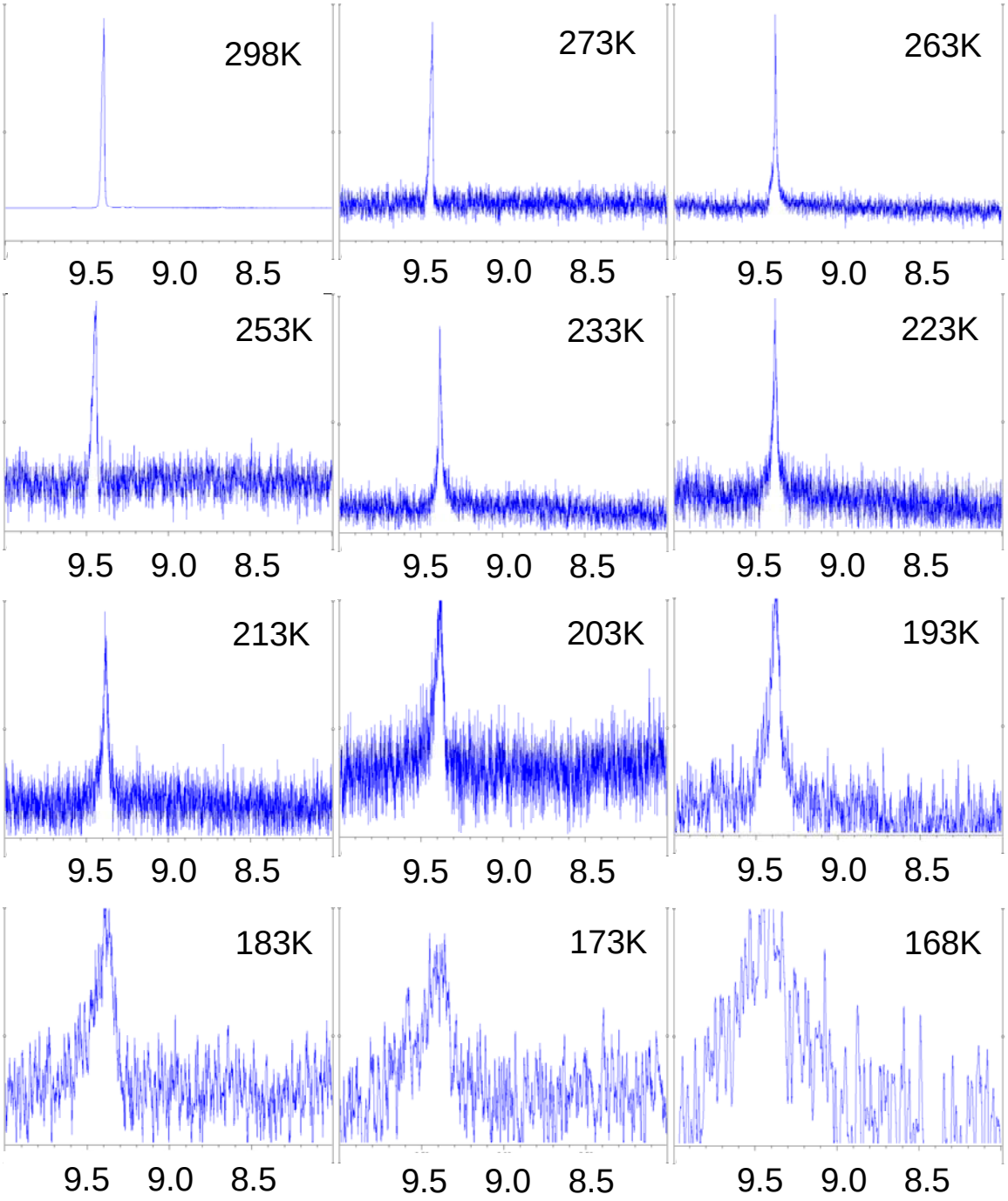
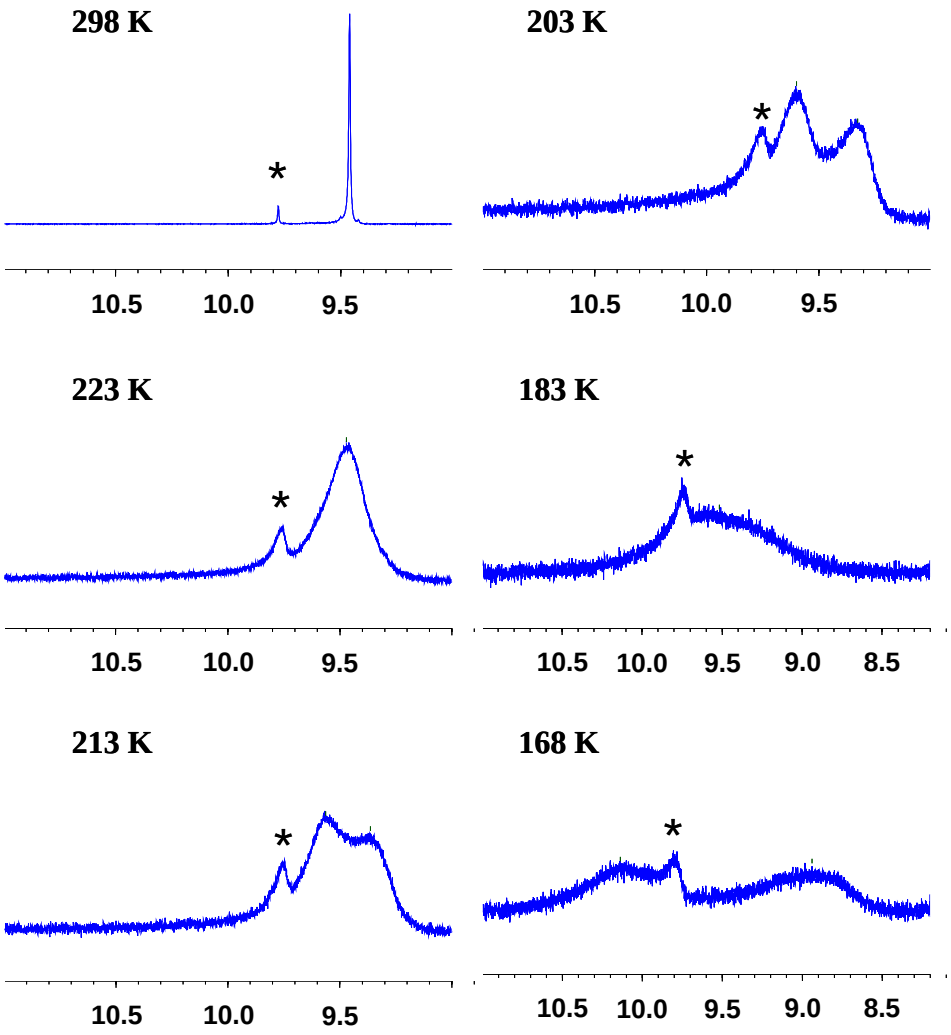
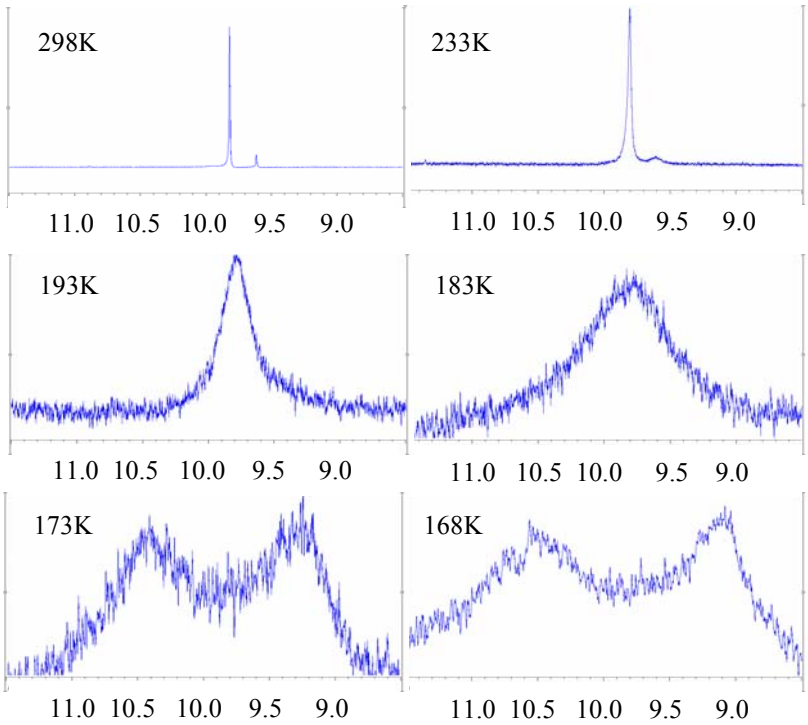


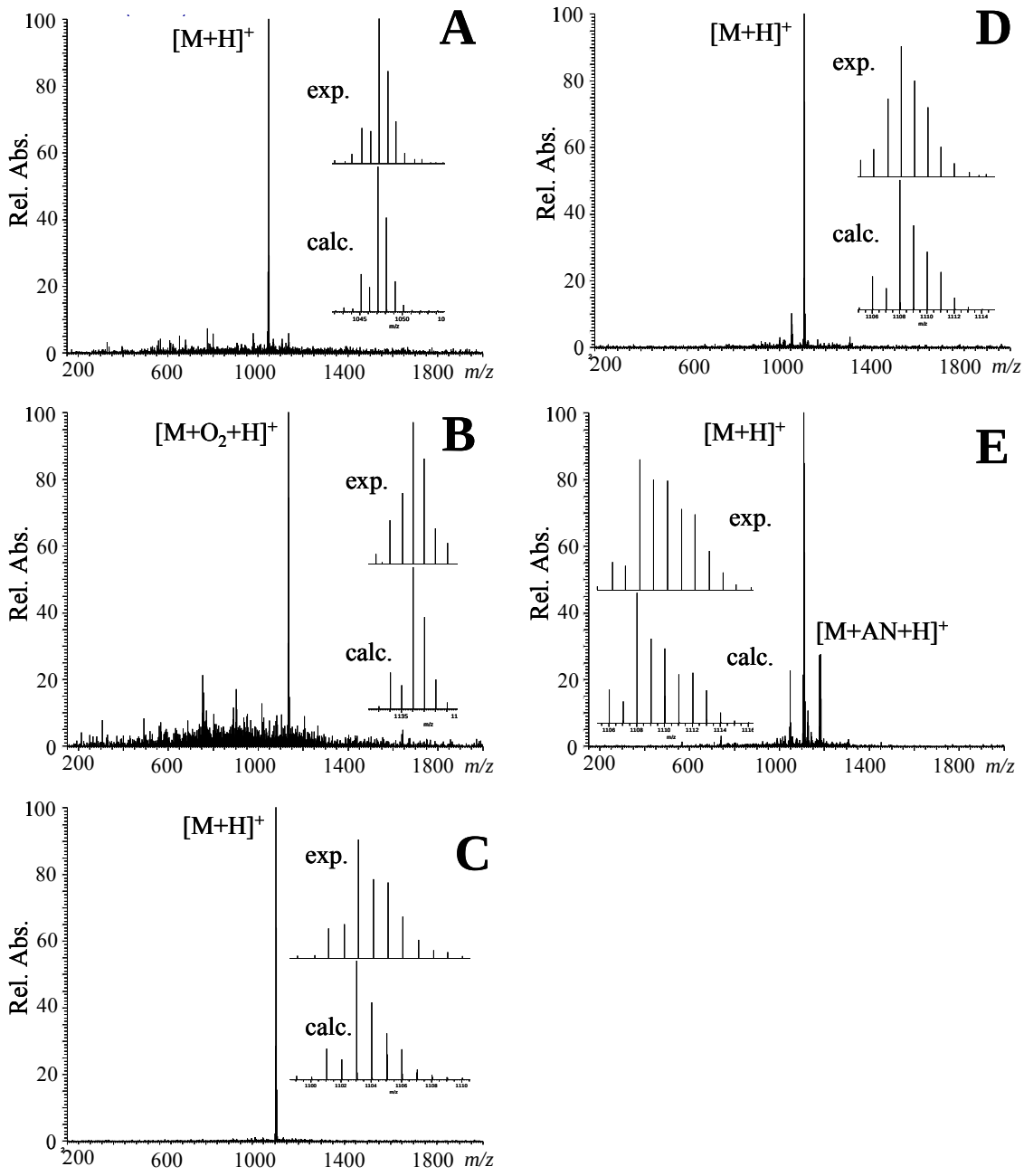
Supporting Information Figure 2. Variable-temperature ^{1}H NMR spectra of NiTFcP in the β-pyrrolic protons region in THF-d8.



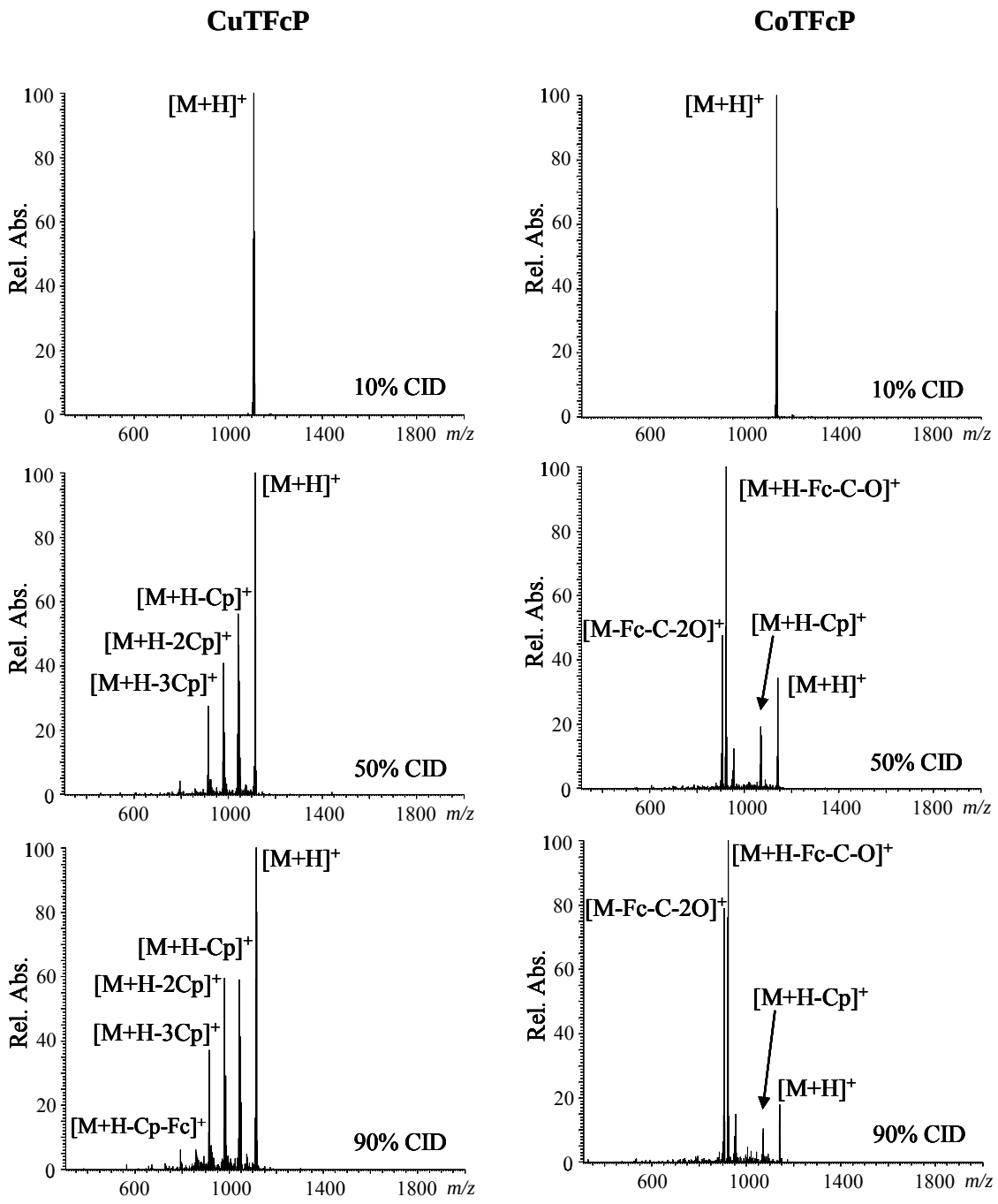
Supporting Information Figure 2. Variable-temperature ^{1}H NMR spectra of H_2TFcP in the β-pyrrolic protons region in THF-d8. Impurity in this particular sample is labeled with asterisk.



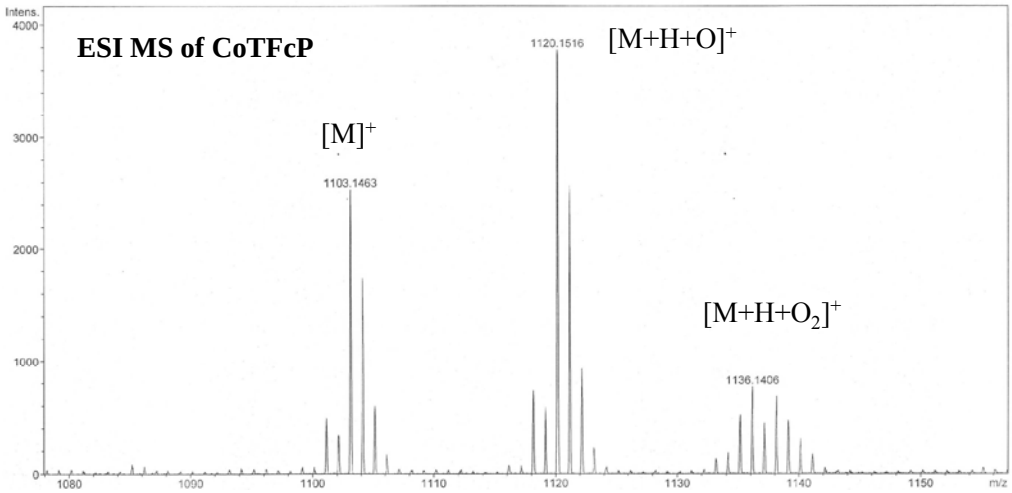
Supporting Information Figure 2. Variable-temperature ^{1}H NMR spectra of ZnTFcP in the β-pyrrolic protons region in THF-d8.

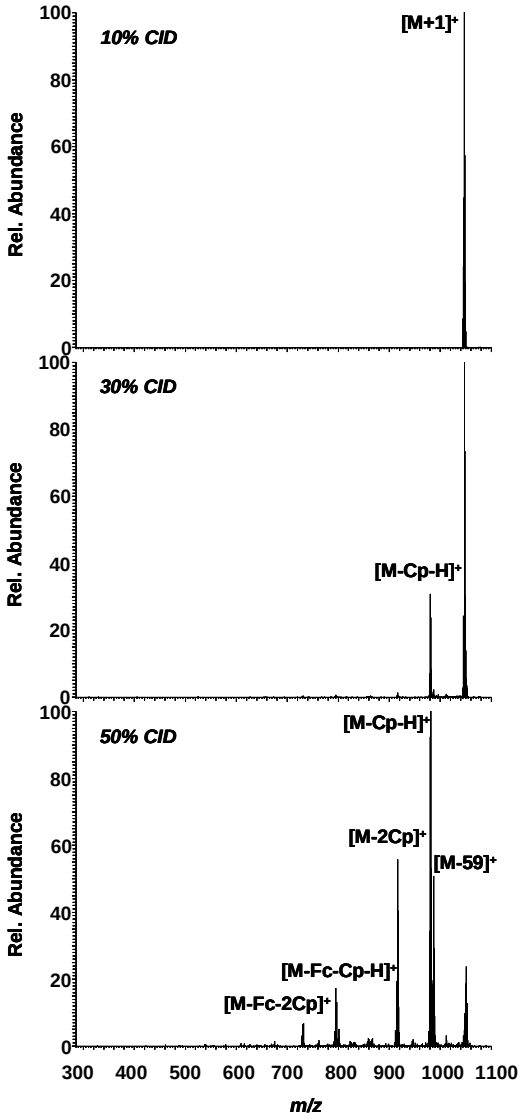


Supporting Information Figure 3. APCI spectra of H_2TFcP (A), CoTFcP (B), NiTFcP (C), CuTFcP (D), and ZnTFcP (E) complexes in THF.

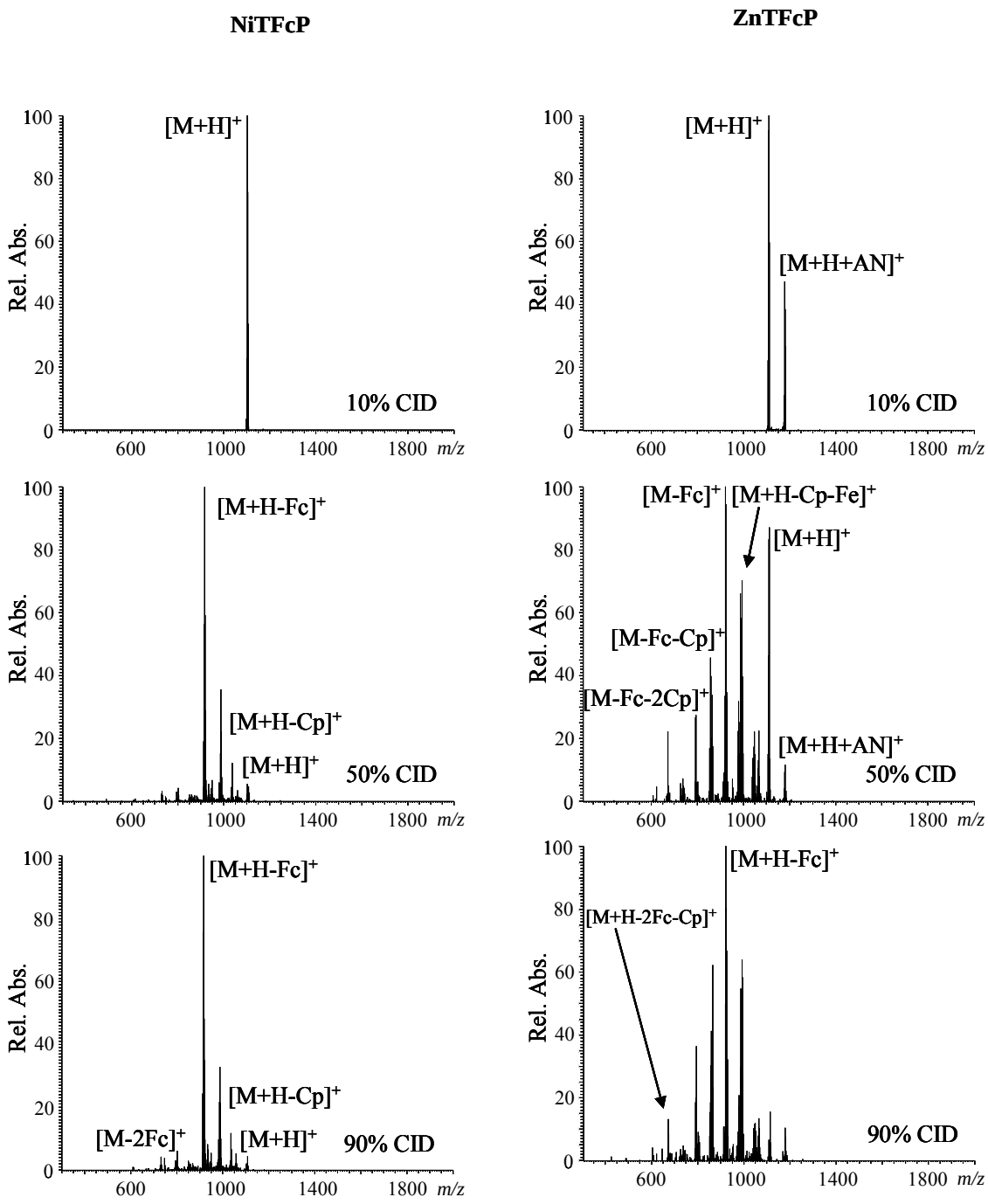


Supporting Information Figure 3. APCI MS/MS spectra of CuTFcP and CoTFcP complexes in THF.





H_2TFcP



Supporting Information Figure 3. ESI spectrum of CoTFcP complex and APCI MS/MS spectra of H_2TFcP, NiTFcP, and ZnTFcP complexes in THF.

Supporting Information Table 1. Calculated (BPW91) atomic orbital contributions to respective molecular orbitals for H_2TFcP and all MTFcP (M = Co, Ni, Cu, and Zn).[a]

H_2TFcP				
E, (eV)	Fe	Fc + Fe	N	Porph
-4.298	81.2	97.8	0.1	2.1
-4.268	78.2	93.4	1.1	5.5
-4.116	78.4	98.3	0.0	1.7
-4.112	77.2	98.4	0.1	1.4
-4.103	68.6	97.5	0.1	2.5
-4.092	61.6	97.7	0.1	2.2
-4.089	66.1	98.0	0.2	1.8
-4.078	66.6	98.0	0.2	1.8
-4.074	57.8	96.8	0.1	3.1
-3.877	**45.6**	**68.4**	**10.6**	**21.0**
-2.620	***9.9***	***21.3***	***10.6***	***68.1***
-2.591	11.8	19.4	10	70.7
-1.668	30.8	49.7	0.5	49.8
-1.228	61.8	94.7	0.5	4.8

CoTFcP											
α set						β set					
E, (eV)	Fe	Fc + Fe	Co	N	Porph	E, (eV)	Fe	Fc + Fe	Co	N	Porph
-4.249	14.3	17.9	54.5	6.4	21.2	-4.013	60.0	97.5	1.3	0.1	1.2
-4.226	73.7	91.0	0.6	1.3	7.1	-4.005	60.1	98.4	0.0	0.0	1.6
-4.015	60.4	98.3	0.0	0.0	1.6	-4.001	60.0	97.9	0.3	0.1	1.7
-4.012	60.8	98.6	0.1	0.1	1.2	-3.992	58.0	97.2	0.0	0.1	2.6
-4.005	59.8	98.2	0.0	0.0	1.7	-3.983	57.4	96.6	0.1	0.1	3.1
-4.001	60.2	98.2	0.0	0.1	1.7	-3.982	57.7	97.1	1.3	0.2	1.5
-3.993	58.1	97.2	0.0	0.2	2.6	-3.932	3.2	5.7	89.7	2.2	2.4
-3.981	58.2	98.2	0.0	0.2	1.6	-3.834	44.2	73.7	3.2	6.6	16.4
-3.981	57.6	97.1	0.1	0.2	2.6	**-3.741**	**1.1**	**2.9**	**67.3**	**2.7**	**27.1**
-3.845	**46.7**	**78.0**	**1.0**	**6.0**	**15**	***-3.341***	***1.5***	***4.4***	***59.7***	***0.6***	***35.2***
-2.545	***7.8***	***20.4***	***1.2***	***10.5***	***67.9***	-2.483	7.9	20.3	5.5	11	63.2
-2.527	***7.9***	***20.5***	***2.6***	***10.7***	***66.1***	-2.401	7.8	19.7	11.7	11.1	57.5
-2.038	0.2	0.7	38.7	36.8	23.8	-1.682	26.3	54.1	0.8	0.4	44.6
-1.684	26.2	53.9	0.8	0.4	44.8	-1.477	1.2	2.8	41.4	31.9	23.8

NiTFcP

E, (eV)	Fe	Fc + Fe	Ni	N	Porph
-4.279	81.4	97.0	0.5	0.2	2.3
-4.248	75.4	92.2	0.4	0.9	6.5
-4.031	59.4	98.2	0.0	0.0	1.8
-4.031	59.4	98.2	0.0	0.0	1.8
-4.027	61.0	98.9	0.1	0.0	0.9
-4.026	59.8	97.9	0.0	0.1	2.0
-4.021	58.1	97.4	0.1	0.2	2.4
-4.021	58.1	97.4	0.1	0.2	2.4
-4.018	57.6	98.3	0.1	0.1	1.6
-3.884	**46.3**	**77.9**	**1.0**	**5.9**	**15.3**
-2.520	***7.6***	***19.9***	***2.3***	***10.8***	***67.0***
-2.520	***7.6***	***19.9***	***2.3***	***10.8***	***67.0***
-2.184	0.1	0.6	36.0	39.7	23.7
-1.667	27.2	56.1	0.5	0.4	43.0

CuTFcP

α set						β set					
E, (eV)	Fe	Fc + Fe	Cu	N	Porph	E, (eV)	Fe	Fc + Fe	Cu	N	Porph
-4.242	74.2	89.2	1.5	2.8	6.5	-4.233	75	92	0.2	1.1	6.7
-4.056	16.4	27.9	20.2	34.9	17.0	-4.014	60.3	98.3	0.0	0.0	1.7
-4.015	60.3	98.3	0.0	0.0	1.7	-4.014	60.3	98.3	0.0	0.0	1.7
-4.015	60.3	98.3	0.0	0.0	1.7	-4.013	61.1	99	0.0	0.0	1.0
-4.014	61.1	98.9	0.0	0.0	1.0	-4.007	60.1	97.7	0.0	0.2	2.1
-4.001	54.2	87.9	3.2	5.4	3.5	-3.992	57.9	97.1	0.0	0.2	2.8
-3.993	57.9	97.1	0.0	0.2	2.7	-3.992	57.9	97.1	0.0	0.2	2.8
-3.993	57.9	97.1	0.0	0.2	2.7	-3.986	58.3	98.3	0.0	0.1	1.6
-3.987	58.4	98.3	0.0	0.1	1.6	**-3.847**	**46.8**	**78.1**	**1.0**	**6.3**	**14.6**
-3.808	**34.5**	**58.4**	**5.4**	**15.4**	**20.9**	***-2.988***	***0.3***	***1.2***	***34.7***	***41.4***	***22.7***
-2.578	***8.3***	***21.3***	***0.5***	***10.1***	***68.1***	-2.558	8.4	21.6	0.6	10.3	67.5
-2.578	***8.3***	***21.3***	***0.5***	***10.1***	***68.1***	-2.558	8.4	21.6	0.6	10.3	67.5
-1.713	26.4	54.1	0.9	0.5	44.5	-1.709	26.6	54.5	0.9	0.5	44.1
-1.331	44.5	95.1	0.0	0.4	4.4	-1.329	44.5	95.1	0.1	0.4	4.4

ZnTFcP

E, (eV)	Fe	Fc + Fe	Zn	N	Porph
-4.267	82.2	97.9	0.1	0.0	2.1
-4.267	42.3	95.5	2.3	0.0	2.1
-4.224	56.6	90.9	0.9	0.4	7.8
-4.008	42.1	96.2	2.0	0.0	1.9
-4.008	48.5	96.5	1.4	0.0	2.1
-4.007	45.8	97.0	1.7	0.0	1.3
-3.998	45.6	95.0	2.0	0.1	2.9
-3.984	52.9	96.0	0.8	0.0	3.2
-3.984	34.7	90.9	3.8	0.0	5.3
-3.977	44.0	94.4	2.4	0.0	3.2
-3.831	**38.0**	**77.2**	**2.0**	**1.5**	**19.3**
-2.599	***25.5***	***39.7***	***0.8***	***1.1***	***58.4***
-2.599	***13.4***	***26.2***	***0.8***	***1.8***	***71.2***
-1.724	30.4	61.5	2.2	0.6	35.8
-1.328	33.8	91.7	2.2	0.2	6.0

a. HOMO is in bold and LUMO(s) is in bold/italic; abbreviations: Fe – all iron centers; Fc + Fe – Cp ligands plus iron centers; N – nitrogen atoms of porphyrins core; Porph – carbon atoms of porphyrin core.

Supporting Information Table 2. Calculated Vertical Excitation Energies of H_2TFcP Using a TDDFT Approach (BPW91).[a]

Transition	λ, nm	*f*	Transitions and expansion coefficients [b]
1	881.05	0.0269	268 → ***270*** 0.30113; **269** → ***270*** 0.49331
2	870.06	0.0495	**269** → ***270*** 0.50609
3	839.35	0.0025	267 → ***270*** 0.58338
4	835.09	0.0027	263 → ***270*** 0.52249; 265 → ***270*** 0.31967
5	832.63	2E-4	266 → ***270*** 0.55347
6	832.08	4E-4	264 → ***270*** 0.63643
7	831.48	1E-3	265 → ***270*** 0.59985
8	825.47	1E-4	262 → ***270*** 0.56044; 267 → 271 -0.38706
9	816.21	0.0171	263 → 271 0.45954; 268 → 271 0.31883
10	815.34	0.0079	265 → 271 0.46396; 268 → 271 0.42384
11	813.55	1E-3	262 → 271 0.40688; 264 → 271 -0.31404; 266 → 271 -0.30416; 267 → 271 0.30166
12	811.19	3E-4	262 → 271 0.41078; 264 → 271 0.54533
13	807.28	0.0428	265 → 271 -0.35653; 268 → ***270*** 0.37930
14	801.63	0.0383	263 → 271 -0.41937; 265 → 271 -0.34201; 268 → 271 0.36539
15	798.4	0.0143	266 → 271 0.49264
16	791.68	1E-3	267 → 271 0.39283
17	738.83	0.0138	261 → ***270*** 0.66210
18	730.31	0.0029	258 → ***270*** 0.54933; 261 → 271 -0.43492
19	729.34	0.0015	259 → ***270*** 0.40826; 260 → ***270*** -0.54148
20	727.38	0.0013	259 → ***270*** 0.52980; 260 → ***270*** 0.39083
21	720.97	0.017	258 → ***270*** 0.42941; 261 → 271 0.51968
22	713.38	0.0018	259 → 271 0.32278; 260 → 271 0.58452
23	712.58	0.0094	258 → 271 0.69280
24	711.1	0.0025	259 → 271 0.59319; 260 → 271 -0.30975
25	618.26	0.0212	256 → ***270*** 0.39130; 257 → 271 0.53951; 257 → ***270*** 0.13797
26	597.9	0.0553	256 → 271 -0.37045; 257 → ***270*** 0.52238; 257 → 271 -0.13016; **269** → ***270*** 0.11499
27	539.16	0.035	**269** → 272 0.67413
28	509.41	0.0149	267 → 272 0.68915
29	508.77	0	268 → 272 0.68434
30	507.34	0.0141	266 → 272 0.68677
31	505.75	2E-4	265 → 272 0.68618
32	505.08	0.0033	264 → 272 0.69057
33	504.77	0	263 → 272 0.68257
34	504.34	0.0066	262 → 272 0.68877
35	472.96	0.0024	261 → 272 0.69155
36	469.55	0.0739	260 → 272 0.58088
37	468.15	0.0188	259 → 272 0.64240
38	467.22	0	258 → 272 0.69522
39	463.56	0.0841	**269** → 274 0.51078
40	462.48	0	**269** → 273 0.66061
41	461.12	0.0188	**269** → 275 0.64308
42	459.31	5E-4	**269** → 276 0.67704
43	458.04	0.1267	**269** → 274 0.36929; **269** → 278 0.40181
44	452.92	0.1047	**269** → 279 0.54218
45	452.84	0	**269** → 277 0.62408
46	451.42	0	255 → ***270*** 0.44275; 255 → 271 0.47243; 269 → 277 0.20036

47	447.64	3E-4	255 → ***270*** 0.46178; 255 → 271 -0.47631; 257 → 272	-0.10926
48	445.28	0.0123	254 → ***270*** -0.33302; **269** → 278 0.47221; 254 → 271 256 → ***270*** -0.11927	-0.27357;
49	440.93	0.0265	254 → ***270*** 0.49172; **269** → 279 -0.30122; 254 → 271 **269** → 278 0.14672	-0.29685;
50	434.97	0.0088	257 → 272 0.62302; 253 → ***270*** -0.23979; 269 → 280	-0.12533
51	433.96	1E-4	268 → 273 0.59480	
52	433.81	7E-4	267 → 273 0.56936	
53	432.89	0.0013	266 → 273 0.49066; 268 → 274 0.39924	
54	432.12	0	267 → 274 0.54578	
55	431.44	0	266 → 274 0.44644; 267 → 275 0.47640	
56	431.33	0.0036	266 → 273 0.32119; 267 → 276 0.51369	
57	430.95	0	265 → 273 0.55750	
58	430.57	0.0037	268 → 275 -0.45732	
59	430.45	0.0024	264 → 273 0.56907; 265 → 274 0.32032	
60	430.38	0	266 → 275 0.47431; 268 → 276 0.44093	

a. HOMO is in bold and LUMOs are in bold/italic; b. only contributions with expansion coefficients larger than 0.3 are shown; more detailed table with contributions is available from the authors upon request.