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Electronic Supplementary Information

The Electronic Structures and Photophysical Properties of Platinum Complexes with CˆNˆN Ligands: Influence of Carborane Substituent

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Captions:

Table S1. The optimized ground-state geometries of complex **1** obtained by different functional levels with the available experimental structure parameters.

		PBE0	B3LYP	M062X	Exp.[a]
Bond length (Å)					
	$Pt-N_1$	2.204	2.156	2.252	2.123
	$Pt-C_{12}$	2.004	1.988	1.972	1.922
	$C_{17}-C_{18}$	1.230	1.230	1.224	1.184
	$Pt-N_2$	2.032	2.007	2.052	1.987
	$Pt-C_{17}$	1.971	1.956	1.958	1.958
	$C_{18}-C_{19}$	1.428	1.425	1.434	1.450
Bond angle (º)					
	N_1-Pt-N_2	77.1	77.9	75.8	78.4
	N_2-Pt-C_{12}	81.7	81.9	82.1	82.1
	$Pt-C_{17}-C_{18}$	177.9	177.9	177.7	176.7
	N_1-Pt-C_{12}	158.8	159.8	157.9	160.5
	N_2-Pt-C_{17}	179.6	179.8	179.9	178.2
	$C_{17}-C_{18}-C_{19}$	179.7	179.4	179.8	178.1
	N_1-Pt-C_{17}	102.4	101.9	104.3	102.0
	$C_{12}-Pt-C_{17}$	98.7	98.3	97.8	97.7

a The experimental value obtains from Reference 19.

Table S2. Simulated absorption spectra of the complex **1** in CH_2Cl_2 obtained by different functional levels with the available experimental spectra.

	PBE0	B3LYP	M062X	Exp.[a]
λ_{abs}/nm	218	226	194	229
	273	283	255	281
	474	506	360	455

[a] The experimental value obtains from Reference 19.

Table S3. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for **1** at the DFT/PBE0 level.

Orbitals	Energy (eV)	MO compositions			
		phbpy	Pt	C≡C-L	Composition contribution>10%
L+6	0.29	76	11	13	Pt+ phbpy + C≡C-L
L+3	-0.36	14	11	75	Pt+ phbpy + C≡C-L
L+1	-1.66	95	3	2	phbpy
L	-2.31	91	6	3	phbpy
H	-5.61	6	19	74	Pt+ C≡C-L
H-1	-6.09	68	32	0	Pt+ phbpy
H-4	-6.83	94	5	1	phbpy
H-6	-7.38	24	36	40	Pt+ phbpy + C≡C-L

[a] H= HOMO; L= LUMO.

Table S4. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for **2** at the DFT/PBE0 level.

Orbitals	Energy (eV)	MO compositions			
		phbpy	Pt	C≡C-L	Composition contribution>10%
L+7	0.24	69	16	14	Pt+ phbpy + C≡C-L
L+5	-0.24	0	0	100	C≡C-L
L+3	-0.53	9	7	84	C≡C-L
L+1	-1.65	95	3	2	phbpy
L	-2.3	91	6	4	phbpy
H	-5.03	2	6	92	C≡C-L
H-1	-6.03	6	18	76	Pt+ C≡C-L
H-2	-6.09	67	33	1	Pt+ phbpy
H-5	-6.83	94	5	2	phbpy
H-11	-7.82	83	4	13	phbpy + C≡C-L

[a] H= HOMO; L= LUMO.

Table S5. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for **3** at the DFT/PBE0 level.

Orbitals	Energy (eV)	MO compositions			
		phbpy	Pt	C≡C-L	Composition contribution>10%
L+2	-1.56	47	2	51	phbpy + C≡C-L
L+1	-1.76	56	2	42	phbpy + C≡C-L
L	-2.36	86	6	8	phbpy
H	-5.7	6	19	75	Pt+ C≡C-L
H-1	-6.13	68	32	0	Pt+ phbpy
H-8	-6.85	94	5	2	phbpy

[a] H= HOMO; L= LUMO.

Table S6. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for **4** at the DFT/PBE0 level.

Orbitals	Energy (eV)	MO compositions			
		phbpy	Pt	C≡C-L	Composition contribution>10%
L+7	0.43	32	41	27	Pt+ phbpy + C≡C-L
L+6	0.2	69	11	20	Pt+ phbpy + C≡C-L
L+3	-0.33	14	11	75	Pt+ phbpy + C≡C-L
L+1	-1.74	96	3	1	phbpy
L	-2.41	92	6	3	phbpy
H	-6.21	70	30	0	Pt+ phbpy
H-1	-6.37	13	36	51	Pt+ phbpy + C≡C-L
H-2	-6.57	14	34	52	Pt+ phbpy + C≡C-L
H-5	-7.84	92	2	6	phbpy
H-6	-8.08	56	43	1	Pt+ phbpy

[a] H= HOMO; L= LUMO.

Table S7. Calculated absorption wavelength (nm)/energies (eV), oscillator strength (ƒ), major contribution and transition characters in CH_2Cl_2 medium at the TD-PBE0 level together with the experimental values of complex **1**-**4**.

	State	λ(nm)/ E(eV)	f	Configuration		Assignment	Exp.[a] (nm)
	S_1	474/2.61	0.1869	H→L (98%)	d(Pt)+π(C≡C-L)→π*(phbpy)	MLCT/LLCT	455
	S_{15}	277/4.47	0.3381	H-4→L+1 (71%)	π(phbpy)→π*(phbpy)	ILCT	
				H→L+3 (17%)	d(Pt)+π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
1	S_{17}	273/4.53	0.3724	H-6→L(11%)	d(Pt)+π(C≡C-L)+π(phbpy)→π*(phbpy)	MLCT/ILCT/LLCT	281
				H-4→L+1(13%)	π(phbpy)→π*(phbpy)	ILCT	
				H→L+3(61%)	d(Pt)+π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
	S_{47}	218/5.66	0.2076	H-1→L+6 (63%)	d(Pt)+π(phbpy)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	229
	T_1	516/2.40	0.0000	H→L (78%)	d(Pt)+π(C≡C-L)→π*(phbpy)	MLCT/LLCT	
	S_1	555/2.24	0.2568	H→L (96%)	π(C≡C-L)→π*(phbpy)	LLCT	
	S_8	346/3.58	0.3099	H-2→L+1 (85%)	d(Pt)+π(phbpy)→π*(phbpy)	MLCT/ILCT	
	S_{10}	329/3.77	0.2958	H-5→L (42%)	π(phbpy)→π*(phbpy)	ILCT	
				H-1→L+1 (21%)	d(Pt)+π(C≡C-L)→π*(phbpy)	MLCT/LLCT	
	S_{11}	327/3.78	0.4347	H-5→L (28%)	π(phbpy)→π*(phbpy)	ILCT	
2				H→L+3 (59%)	π(C≡C-L)→π*(C≡C-L)	ILCT	
	S_{15}	309/4.01	0.2489	H→L+5 (96%)	π(C≡C-L)→π*(C≡C-L)	LLCT	
				H-11→L (17%)	π(phbpy)+π(C≡C-L)→π*(phbpy)	ILCT/LLCT	
	S_{34}	259/4.78	0.1953	H-1→L+3 (52%)	d(Pt)+π(C≡C-L)→π*(C≡C-L)	MLCT/ILCT	
				H→L+7 (17%)	π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
	T_1	530/2.34	0.0000	H→L (78%)	π(C≡C-L)→π*(phbpy)	LLCT	
	S_1	468/2.65	0.3963	H→L (97%)	d(Pt)+π(C≡C-L)→π*(phbpy)	MLCT/LLCT	
	S_5	379/3.27	0.4556	H→L+1 (95%)	d(Pt)+π(C≡C-L)→π*(phbpy)+π*(C≡C-L)	MLCT/ILCT/LLCT	
	S_6	354/3.49	0.4054	H-1→L+1 (16%)	d(Pt)+π(phbpy)→π*(phbpy)+π*(phbpy)	MLCT/ILCT/LLCT	
3				H→L+2 (69%)	d(Pt)+π(C≡C-L)→π*(phbpy)+π*(C≡C-L)	MLCT/ILCT/LLCT	
	S_{28}	277/4.47	0.2198	H-8→L+1 (57%)	π(phbpy)→π*(phbpy)+π*(C≡C-L)	ILCT/LLCT	
				H-8→L+2 (11%)	π(phbpy)→π*(phbpy)+π*(C≡C-L)	ILCT/LLCT	
	T_1	554/2.24	0.0000	H→L (68%)	d(Pt)+π(C≡C-L)→π*(phbpy)	MLCT/LLCT	
				H→L+1(15%)	d(Pt)+π(C≡C-L)→π*(phbpy)+π*(C≡C-L)	MLCT/ILCT/LLCT	
	S_1	437/2.84	0.0048	H→L (95%)	d(Pt)+π(phbpy)→π*(phbpy)	MLCT/LLCT	
	S_{15}	264/4.69	0.1874	H-6→L (15%)	d(Pt)+π(phbpy)→π*(phbpy)	ILCT/LLCT	
				H-5→L (70%)	π(phbpy)→π*(phbpy)	ILCT	
	S_{27}	235/5.29	0.2440	H-5→L+1 (18%)	π(phbpy)→π*(phbpy)	ILCT/LLCT	
				H-2→L+7 (23%)	d(Pt)+π(phbpy)+π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
4				H-1→L+3 (13%)	d(Pt)+π(phbpy)+π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
	S_{38}	219/5.66	0.1868	H-1→L+6 (26%)	d(Pt)+π(phbpy)+π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
				H→L+6 (23%)	d(Pt)+π(phbpy)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
	S_{44}	212/5.85	0.2981	H-2→L+6 (23%)	d(Pt)+π(phbpy)+π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
				H-2→L+7 (12%)	d(Pt)+π(phbpy)+π(C≡C-L)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
				H→L+6 (11%)	d(Pt)+π(phbpy)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/ILCT/LLCT	
	T_1	494/2.51	0.0000	H→L (81%)	d(Pt)+π(phbpy)→d*(Pt)+π*(C≡C-L)+π*(phbpy)	MLCT/LLCT	

[a] The experimental value obtains from Reference 19.

[b] f= oscillator strength. H = HOMO; L= LUMO. The TD-DFT calculations include 50 singlet excited states.

[c] The oscillator strength (f) that are less than or equal to absolute value of 0.1800 are not listed.

Seen from the Table S6, the calculated maximal peak located at around 273 nm for **1** agrees well with the experimental data at 281 nm. In addition, the lowest-lying singlet absorptions at 474 nm are also in good agreement with the experimental values at 455 nm for **1**. As the discrepancies between the evaluated absorption wavelengths and the experimental ones are within the acceptable range, the TD-DFT methods are proved to be reliable in the study of the above complexes.

Table S8. Transition dipole moments $\mu(S_n)$ (Debye) for S_0–S_n transitions, singlet–triplet splitting energies $\Delta E(S_n–T_1)$ (eV) and the SOC matrix elements $\langle T_1|\ H_{SOC}|\ S_n\rangle$ (cm^{-1}) of complexes **1**-**4**.

1				2			
S_n	$\mu(S_n)$	$\Delta E(S_n–T_1)$	$\langle T_1\|\ H_{SOC}\|\ S_n\rangle$	S_n	$\mu(S_n)$	$\Delta E(S_n–T_1)$	$\langle T_1\|\ H_{SOC}\|\ S_n\rangle$
S_1	3.47	0.289	21.645	S_1	4.28	0.178	12.905
S_2	0.81	0.639	445.783	S_2	0.73	0.975	342.644
S_3	0.29	0.648	430.908	S_3	0.30	1.003	317.093
S_4	0.47	1.001	1037.652	S_4	2.93	1.080	14.597
S_5	2.20	1.189	6.209	S_5	0.44	1.332	792.857
S_6	3.37	1.471	195.523	S_6	0.65	1.414	67.797
S_7	2.59	1.584	3.280	S_7	2.45	1.718	14.855
S_8	0.12	1.636	21.179	S_8	3.23	3.233	144.605
S_9	1.33	1.845	24.033	S_9	4.70	4.701	24.147
S_{10}	1.76	1.971	43.438	S_{10}	1.31	1.307	5.334
3				4			
S_n	$\mu(S_n)$	$\Delta E(S_n–T_1)$	$\langle T_1\|\ H_{SOC}\|\ S_n\rangle$	S_n	$\mu(S_n)$	$\Delta E(Sn–T_1)$	$\langle T_1\|\ H_{SOC}\|\ S_n\rangle$
S_1	4.33	0.302	19.751	S_1	0.71	0.315	17.825
S_2	0.74	0.644	406.137	S_2	1.63	0.692	454.186
S_3	0.53	0.661	391.018	S_3	1.46	0.778	548.596
S_4	0.49	1.026	946.558	S_4	0.52	0.880	878.782
S_5	4.47	1.081	11.806	S_5	2.77	1.293	6.697
S_6	1.28	1.316	2.363	S_6	3.32	1.342	50.968
S_7	1.93	1.348	15.339	S_7	1.87	1.644	3.293
S_8	3.12	1.470	169.3913	S_8	0.84	1.756	11.305
S_9	0.87	1.487	48.250	S_9	0.43	1.920	46.648
S_{10}	0.86	1.507	36.288	S_{10}	2.56	2.019	57.769

Figure S1. Potential energy surfaces obtained by scan at PBE0/6-31G* level

Figure S2. The dimer model of complex **1** (left) and **4** (right)

Table S9. The Cartesian coordinates for the optimized structures of **1** in the S_0 and T_1 state.

	S_0			T_1		
C	0.63685200	-3.74243900	-0.62136000	0.60916300	-3.77468900	-0.61091300
N	-0.68244900	-2.12634300	0.54679000	-0.71210000	-2.11748300	0.54804600
C	2.30253600	2.72031300	2.40961200	2.27680600	2.73773800	2.40966600
C	1.58378400	1.59831200	1.98569100	1.56929000	1.61104900	1.97955600
C	3.90269100	-0.81143100	0.15924300	3.88259700	-0.84035100	0.18549000
C	2.96422800	-1.79730200	-0.14323200	2.95310300	-1.81579700	-0.11605700
C	1.64928500	-1.60345500	0.26921800	1.61261900	-1.64177100	0.27384300
N	1.32123400	-0.48542600	0.93895400	1.28703100	-0.48307000	0.94911100
C	3.53288200	0.33423000	0.85480800	3.50790100	0.33660000	0.88291400
C	2.20188700	0.48928700	1.24941000	2.19289500	0.49472500	1.25758300
Pt	-0.57676000	-0.21459100	1.53776800	-0.59221300	-0.21701300	1.51131400
C	-2.42703900	0.04157200	2.11779800	-2.38813200	0.03651600	2.07774300
C	-3.60216500	0.16886200	2.45588600	-3.58109400	0.17379800	2.43873600
C	-4.96226000	0.33183500	2.84864800	-4.90891900	0.33505200	2.83786300
C	-5.38188800	1.48684300	3.53641400	-5.31568400	1.50490500	3.53084900
C	-6.70954300	1.64743600	3.91539600	-6.63349800	1.65952800	3.92113200
C	-7.65173100	0.66272700	3.61952800	-7.57145600	0.66152100	3.63383300
C	-5.92543700	-0.65323200	2.55809500	-5.87355900	-0.66673200	2.55526400
C	-7.25182800	-0.48738600	2.93959400	-7.18788200	-0.49868200	2.95162200
C	0.18581400	1.47484800	2.25496600	0.16990300	1.49505800	2.23235800
C	1.66020800	3.73813600	3.10582900	1.62415500	3.75972900	3.09063700
C	0.29624400	3.63145700	3.37725800	0.25648000	3.65701900	3.34389400
C	-0.42804800	2.51519200	2.95684500	-0.45838000	2.53654700	2.91827300
C	0.51586400	-2.52849100	0.04876500	0.51490900	-2.53353500	0.05608600
C	-0.48490200	-4.54907700	-0.78001000	-0.50631700	-4.56333500	-0.77024300
C	-1.70442200	-4.12470900	-0.26570800	-1.74631800	-4.12063800	-0.26092500
C	-1.75801900	-2.90225800	0.39269800	-1.79039500	-2.90205100	0.38276200
H	1.59569900	-4.05772000	-1.01662700	1.56959200	-4.10097700	-0.99671800
H	3.36576500	2.80579300	2.19866300	3.34316800	2.82094400	2.21371500
H	4.93452100	-0.94176600	-0.15192100	4.91745400	-0.97459500	-0.11462900
H	3.25979400	-2.68783000	-0.68509600	3.25578100	-2.71053900	-0.64983000
H	4.26921100	1.09503800	1.08793400	4.24821200	1.09398000	1.11471200
H	-4.64988800	2.25562400	3.76780500	-4.57660700	2.27017000	3.74611300
H	-7.01124800	2.54752500	4.44500000	-6.94053200	2.55621800	4.45082000
H	-8.68917800	0.79056900	3.91626400	-8.60509400	0.78830600	3.94245600
H	-5.61692500	-1.55013700	2.02805900	-5.56052800	-1.56080900	2.02522400
H	-7.97870000	-1.26067300	2.70425500	-7.92281000	-1.26742600	2.73301000
H	2.22008800	4.60907200	3.43458800	2.18024200	4.63223800	3.42247400
H	-0.20820200	4.42631700	3.92197400	-0.25675500	4.45433300	3.87653900
H	-1.48977700	2.44746200	3.17614200	-1.52337700	2.47329400	3.12520200
H	-0.40273900	-5.49794300	-1.30058700	-0.43106700	-5.51727200	-1.28368300
H	-2.60272200	-4.72339600	-0.36822500	-2.64833200	-4.71296100	-0.36643600

H	-2.67847900	-2.51367200	0.81686100	-2.71601700	-2.51036700	0.79458500

Table S10. The Cartesian coordinates for the optimized structures of **2** in the S_0 and T_1 state.

	S_0			T_1		
C	-8.15252500	-4.37013500	3.16346300	-8.16500400	-4.31825400	2.92695500
N	-9.35727100	-2.49690500	4.03328300	-9.38072500	-2.47638000	3.91619500
C	-6.14418900	2.52232300	4.64368200	-6.17113800	2.48236900	4.92020300
C	-6.91662600	1.36496900	4.50517300	-6.93189300	1.33259500	4.68894600
C	-4.78144700	-1.45687300	3.09197200	-4.77698600	-1.41398400	3.14080800
C	-5.75977000	-2.44997300	3.06543500	-5.74498000	-2.39025200	3.02694600
C	-7.03879300	-2.12689000	3.50862700	-7.06008300	-2.11889400	3.45740500
N	-7.29626400	-0.88154400	3.94386400	-7.31612300	-0.87218100	3.97881500
C	-5.07776600	-0.17802100	3.55004300	-5.08357500	-0.14192300	3.68401200
C	-6.37464200	0.10411300	3.98529200	-6.37572900	0.10508900	4.09992600
Pt	-9.14470300	-0.41955700	4.57712300	-9.16503800	-0.46745700	4.59368300
C	-10.95010000	0.02101900	5.18629200	-10.94406100	-0.06450900	5.18253900
C	-12.10155800	0.25084200	5.55252700	-12.11368000	0.17590800	5.54911300
C	-13.43401100	0.52392100	5.97094000	-13.41116600	0.45841100	5.95224900
C	-13.80347200	1.79188200	6.45951300	-13.74006800	1.70230100	6.56404900
C	-15.10459400	2.06399000	6.85319900	-15.02063600	1.98689400	6.96188500
C	-16.09290600	1.07143700	6.79092600	-16.06436100	1.04564400	6.76272000
C	-14.43757600	-0.46180900	5.90860600	-14.46674700	-0.48011500	5.76637500
C	-15.73594100	-0.19872700	6.31667700	-15.75162500	-0.19668300	6.15153000
C	-8.29780100	1.35340000	4.87167400	-8.32010600	1.29733100	5.02394600
C	-6.71610000	3.68708500	5.14311800	-6.75664400	3.61266300	5.48119100
C	-8.06355900	3.69197200	5.50340900	-8.11131600	3.59313400	5.81328400
C	-8.84077300	2.54090500	5.36850500	-8.87791300	2.44956900	5.58630600
C	-8.20347900	-3.03732100	3.56170200	-8.19033800	-2.99475000	3.42225000
C	-9.29871500	-5.15292000	3.25100300	-9.30509200	-5.08616600	2.93314500
C	-10.47208000	-4.58660000	3.73540700	-10.50607900	-4.53926600	3.44082100
C	-10.45624000	-3.25051300	4.11651700	-10.48358700	-3.24445600	3.91336800
H	-7.22872900	-4.79599200	2.78871600	-7.23522500	-4.72351400	2.53999500
H	-5.09359700	2.52056200	4.36332100	-5.11462000	2.49925500	4.66236800
H	-3.77675800	-1.68629100	2.75075500	-3.76371500	-1.62200800	2.80953900
H	-5.52206800	-3.44453100	2.70731300	-5.49540400	-3.36010600	2.60912000
H	-4.31142500	0.58862400	3.56770400	-4.31525700	0.61839600	3.76887600
H	-13.05314200	2.57572200	6.51219100	-12.95538600	2.44029600	6.69726400
H	-15.36444800	3.05554600	7.21203400	-15.24806400	2.95060000	7.40389700
H	-14.18124700	-1.45281700	5.54447800	-14.23528000	-1.44305400	5.32223000
H	-16.48682300	-0.98195800	6.26924900	-16.53254000	-0.93703800	6.01749600
H	-6.11464700	4.58531100	5.25036500	-6.15946000	4.50314900	5.65834800
H	-8.51332400	4.60214200	5.89366600	-8.57318000	4.47482600	6.25239100
H	-9.88880400	2.56197800	5.65316000	-9.93186000	2.45239200	5.85272400
H	-9.27109500	-6.19345300	2.94338100	-9.28083000	-6.10261200	2.55111700
H	-11.38727300	-5.16209100	3.81988900	-11.42680300	-5.11167000	3.46399500
H	-11.33797600	-2.74873700	4.50251800	-11.37482100	-2.77066200	4.31538500

N	-17.41755800	1.34342200	7.19388300	-17.35169700	1.33232800	7.15404000
C	-18.70466200	3.08588700	8.32298700	-18.58119100	3.26872100	7.98512500
C	-18.95154400	3.86763200	9.44643000	-18.84789000	4.18207300	8.99856100
C	-18.15791900	3.74372300	10.58563500	-18.15536300	4.11613500	10.20714000
C	-17.11548400	2.81817300	10.59054200	-17.19466300	3.12523200	10.40265300
C	-17.66362700	2.14776300	8.32911700	-17.61334000	2.27979300	8.18386600
C	-16.87226300	2.01914200	9.47841000	-16.92447900	2.20208800	9.39841100
C	-18.46789100	0.79435000	5.05681000	-18.56094100	0.62850900	5.14909400
C	-18.50153100	0.81369700	6.45744600	-18.46800300	0.69528600	6.54303000
C	-19.62537800	0.29926600	7.11745200	-19.48459600	0.16425200	7.34242700
C	-20.69363200	-0.21273000	6.38873900	-20.58399000	-0.44054200	6.74411200
C	-19.53328000	0.26403100	4.33700000	-19.66175700	0.01464500	4.56168600
C	-20.65448000	-0.23856600	4.99551600	-20.67524800	-0.52070700	5.35492500
H	-19.31757600	3.19734200	7.43353900	-19.11065500	3.32110500	7.03864200
H	-19.76333900	4.58995400	9.42311200	-19.59533900	4.95373200	8.83918700
H	-18.34905500	4.36100500	11.45870600	-18.36686400	4.83248200	10.99546000
H	-16.49159100	2.70397900	11.47313800	-16.66060200	3.05976300	11.34600500
H	-16.06787600	1.28973000	9.49406700	-16.19197100	1.41537100	9.55293300
H	-17.60307900	1.19725400	4.53804100	-17.77943300	1.06657100	4.53538800
H	-19.65508900	0.30367300	8.20301400	-19.40395200	0.22116200	8.42367900
H	-21.55716100	-0.60761500	6.91755800	-21.36906600	-0.85809300	7.36764900
H	-19.49024600	0.25806800	3.25101500	-19.73237400	-0.03195100	3.47896200
H	-21.48765500	-0.64548900	4.42976300	-21.53562000	-0.99506600	4.89224400

Table S11. The Cartesian coordinates for the optimized structures of **3** in the S_0 and T_1 state.

	S_0			T_1		
C	-20.49453500	1.30742000	5.79782200	-20.67255800	1.05585500	6.09771700
C	-17.55945800	3.58265900	6.03082000	-17.57822000	3.46817100	5.73681500
C	-19.41556500	6.19454300	9.87373100	-19.59428800	6.38709500	9.26403400
C	-18.15822900	3.55428300	7.41688200	-18.20680200	3.55969400	7.10703700
C	-18.51984300	4.77756700	7.98574400	-18.61552000	4.82117800	7.54344300
C	-19.06941000	4.86489100	9.26369700	-19.20354400	5.01486100	8.79230000
C	-19.27208600	3.67592000	9.96313600	-19.40337000	3.89341200	9.59778500
C	-18.37712500	2.34683700	8.12484600	-18.41746300	2.42241900	7.92453900
C	-18.94722800	2.43226900	9.41830200	-19.04066000	2.61146800	9.18425700
B	-17.98754400	0.95268200	7.48107800	-17.97008700	0.98797800	7.45583800
C	-18.84814200	-1.48411900	7.83942800	-18.57151000	-1.46961700	8.07913100
C	-19.04785700	-0.20442400	7.26461900	-18.93488800	-0.25586900	7.44669300
C	-20.21400400	-0.00351100	6.48707200	-20.19248300	-0.19346400	6.79361200
C	-21.12214900	-1.04744000	6.29839800	-21.02011900	-1.31567800	6.76469200
C	-19.79267500	-2.49507600	7.64950000	-19.44326000	-2.56009700	8.05590000
C	-20.93747900	-2.30167600	6.87791100	-20.66771800	-2.51135200	7.39235900
C	-8.50602100	-3.71001700	2.26358100	-8.69563200	-3.24574700	1.70463500
N	-9.70981900	-2.16604700	3.63547000	-9.84550900	-1.82686300	3.28326400
C	-6.40105200	2.22864300	6.00914300	-6.33356000	1.67799400	6.65097400
C	-7.19584100	1.21497700	5.46537800	-7.16279100	0.86453100	5.87246900
C	-5.05903600	-1.08490200	3.30621500	-5.10034900	-1.26444000	3.46687200
C	-6.06001100	-1.97175100	2.91150900	-6.13727500	-1.93902000	2.85092200
C	-7.35337600	-1.75415300	3.37672100	-7.46186800	-1.67652300	3.23991800
N	-7.60117000	-0.70876600	4.18392100	-7.66747500	-0.74346500	4.23314100
C	-5.34674800	-0.01246800	4.14280400	-5.35249100	-0.31197200	4.48480600
C	-6.65853200	0.16863200	4.58754900	-6.65552900	-0.06482700	4.85579700
Pt	-9.47252000	-0.39286700	4.84507200	-9.52476700	-0.35793500	4.79874400
C	-11.29787400	-0.08351200	5.46830000	-11.30055500	-0.00723200	5.36960800
C	-12.46369700	0.08306300	5.82404100	-12.48713500	0.18463800	5.73203100
C	-13.80835900	0.28906400	6.23283200	-13.80315200	0.38847300	6.13664000
C	-14.13176400	1.26249200	7.20076400	-14.11840600	1.36024400	7.12510200
C	-15.44824900	1.47165700	7.57931900	-15.42818400	1.55271700	7.51468300
C	-16.50921600	0.71503000	7.04234500	-16.48346200	0.78251300	6.97574900
C	-14.86102700	-0.46939200	5.67975000	-14.86008500	-0.37770400	5.57352700
C	-16.16939300	-0.26436500	6.08738700	-16.15816300	-0.18720400	6.00040700
C	-8.59568300	1.14793400	5.74404500	-8.57951400	0.90525100	6.03856900
C	-6.96885100	3.19354200	6.83379400	-6.88035700	2.53753400	7.59748500
C	-8.33411300	3.14221700	7.11372300	-8.26383600	2.58584600	7.76862800
C	-9.13378500	2.13286400	6.57573400	-9.09974200	1.77794600	6.99677600
C	-8.54445300	-2.57780900	3.07206500	-8.66006500	-2.26892400	2.72192000
C	-9.67719500	-4.42391500	2.03281600	-9.89941700	-3.75540100	1.27435700
C	-10.86231900	-3.99030900	2.61507100	-11.09596900	-3.29162400	1.86010200

C	-10.83282200	-2.85236900	3.41207000	-11.01137900	-2.33584900	2.85057500
H	-7.57295400	-4.03422500	1.81731200	-7.76630500	-3.59198500	1.26411100
H	-5.33621500	2.27029200	5.79309900	-5.25463000	1.64243200	6.52004000
H	-4.04298800	-1.23484400	2.95461700	-4.07634900	-1.46623100	3.16753000
H	-5.82755300	-2.80512900	2.25924300	-5.92861300	-2.66568100	2.07291400
H	-4.56289000	0.67316600	4.44393200	-4.53011700	0.21040200	4.96058400
H	-13.33164200	1.85208200	7.63998600	-13.31374800	1.94793900	7.55652000
H	-15.67071600	2.23793000	8.31903800	-15.65794400	2.31005600	8.25997000
H	-14.62883700	-1.22120700	4.93025600	-14.62278700	-1.11950200	4.81682000
H	-16.96112700	-0.87093300	5.65226700	-16.95382700	-0.79597300	5.57833000
H	-6.35005500	3.98045700	7.25552400	-6.23007600	3.16672400	8.19901700
H	-8.78048400	3.89605000	7.75821800	-8.69466800	3.25676100	8.50824300
H	-10.19519100	2.10737800	6.80473500	-10.17524900	1.82836100	7.14455900
H	-9.65931600	-5.30863800	1.40428600	-9.92480900	-4.50724400	0.49126300
H	-11.79693000	-4.51798800	2.46042600	-12.06411300	-3.66793800	1.54907400
H	-11.72301700	-2.46182400	3.89480200	-11.89832000	-1.94105800	3.33754200
C	-19.17590000	1.20809000	10.26729300	-19.31765800	1.46326400	10.12278600
C	-17.64073100	-1.80988300	8.68628800	-17.26993400	-1.63830200	8.82626100
C	-21.95312700	-3.39649700	6.70460700	-21.57310200	-3.70961100	7.33916700
H	-19.79562600	1.48255900	4.96989400	-19.95831900	1.40993300	5.34542600
H	-20.40124500	2.15585000	6.48246000	-20.82435400	1.87853000	6.80432800
H	-21.50435900	1.31784600	5.37578600	-21.62219100	0.87068800	5.58613100
H	-16.46364900	3.59492400	6.07104200	-16.48316400	3.47471200	5.79610700
H	-17.87880100	4.48117300	5.49223500	-17.87627600	4.32275700	5.12080100
H	-17.84150400	2.71355900	5.42993300	-17.86165000	2.55779400	5.19930700
H	-19.67497700	6.93203700	9.10719300	-19.82088100	7.05046900	8.42328500
H	-18.56784200	6.60038500	10.44122500	-18.78007000	6.85167600	9.83542700
H	-20.25831200	6.10972800	10.56773000	-20.46987300	6.35058800	9.92049200
H	-18.36914100	5.68987000	7.40976200	-18.47075800	5.67801800	6.88693200
H	-19.70476800	3.71539200	10.96199100	-19.86640700	4.01997800	10.57522800
H	-22.00470700	-0.87177900	5.68471400	-21.97505200	-1.25203600	6.24507700
H	-19.62754400	-3.46386100	8.11959600	-19.15651700	-3.47425600	8.57375000
H	-19.78455000	1.44852300	11.14474400	-19.69604800	1.83252400	11.08107000
H	-18.22730700	0.79576100	10.63507000	-18.41878100	0.87176600	10.33007200
H	-19.67823600	0.41202900	9.70971700	-20.06252900	0.77543600	9.70860700
H	-17.32410300	-0.96873000	9.31012100	-16.93641100	-0.71712100	9.31323000
H	-16.77932100	-2.08259600	8.06538500	-16.46162700	-1.95396000	8.15547400
H	-17.85233900	-2.65638500	9.34787900	-17.36911300	-2.40595900	9.60067500
H	-22.48482600	-3.30224600	5.75214400	-21.40964200	-4.28369600	6.41782900
H	-22.70696900	-3.36465600	7.50211400	-22.62788400	-3.41565700	7.35300400
H	-21.48564400	-4.38605500	6.74059600	-21.39274300	-4.38570600	8.18082500

Table S12. The Cartesian coordinates for the optimized structures of **4** in the S_0 and T_1 state.

	S_0			T_1		
C	-1.28129400	-2.65285700	-1.87741400	-1.21398000	-2.49020600	-1.71984900
C	-1.59851700	-1.42182200	-2.45017100	-1.52619600	-1.25945900	-2.34308200
C	-0.62203400	-0.66701700	-3.10213800	-0.56790700	-0.56407500	-3.04814100
C	1.00510800	-2.38193800	-2.61004400	1.05130900	-2.33572000	-2.51610100
C	0.69541700	-1.11920200	-3.20075500	0.75233000	-1.05986300	-3.16466900
C	4.81108400	1.02440000	-5.42405000	4.74307700	0.94320800	-5.56355900
C	5.12299400	-1.03944100	-4.39111900	5.08851800	-1.12888800	-4.45983100
C	4.33319900	-4.23109100	-2.48951900	4.34743100	-4.23390700	-2.44066700
C	5.10325700	-3.29829300	-3.18319400	5.09489700	-3.34816900	-3.18279400
C	4.48166800	-2.13943000	-3.63774200	4.49435700	-2.15700900	-3.68416000
C	2.39704800	-2.83017900	-2.73200400	2.41672700	-2.81008600	-2.66586500
N	3.17288100	-1.95090300	-3.39944800	3.17294500	-1.95850100	-3.39250500
C	2.98098700	-4.00771500	-2.25870200	2.98196400	-3.98008600	-2.16471300
Pt	2.27952700	-0.27695800	-4.06004700	2.30350300	-0.30132700	-4.07260500
C	1.39967600	1.34249900	-4.69960700	1.43603700	1.33596700	-4.73982100
C	0.87143300	2.36761100	-5.11614200	0.90217300	2.35515500	-5.15756600
B	0.66352000	5.81383500	-7.16255000	0.72468800	5.95834200	-6.91680400
B	-0.96105100	6.37354300	-6.72756700	-0.98455000	6.36765900	-6.68292300
B	0.64030600	4.04474700	-7.21372400	0.84678900	4.20449600	-7.12229000
C	1.15905400	4.89831700	-5.83273200	1.09497800	4.95381500	-5.61132600
B	0.31971100	6.32484900	-5.50172800	0.10796300	6.28634200	-5.28969500
B	-0.75516600	4.95286200	-7.78678900	-0.52024300	5.07148900	-7.81723800
B	-1.33950300	4.01438100	-5.13062700	-1.39989100	3.84831400	-5.36538000
B	-0.99279900	3.50024100	-6.79507400	-0.78267000	3.51853500	-6.99944500
B	-1.31732100	5.78764100	-5.08117900	-1.52443200	5.60598200	-5.16232600
B	0.07941100	4.87617500	-4.51274600	-0.15545900	4.73854000	-4.47195700
C	0.23546300	3.54521700	-5.60663700	0.25720100	3.53172300	-5.64214100
B	-1.98400500	4.93888000	-6.49751900	-1.91432300	4.85456200	-6.72959100
H	1.49894100	6.37180400	-7.79748700	1.59584600	6.62692900	-7.37075900
H	0.92263000	7.22736200	-5.01778500	0.56508100	7.17562100	-4.64762100
H	-1.38090700	7.41226700	-7.13464500	-1.42213400	7.41091400	-7.05832200
H	-3.15194200	4.93021900	-6.73774300	-3.03216200	4.79307800	-7.14004700
H	-1.91935300	3.28650600	-4.39244800	-2.01967100	3.01665500	-4.78615100
H	-1.34119700	2.42945000	-7.17200400	-0.98988600	2.46734200	-7.51156200
H	0.52919900	4.73247500	-3.42661500	0.14608100	4.51877200	-3.34798000
H	-1.02290000	4.95641700	-8.94788900	-0.62032500	5.16892800	-9.00048900
H	-1.98727900	6.39047500	-4.30166800	-2.34408200	6.08663700	-4.44340900
H	1.43539100	3.38592800	-7.79411600	1.76550000	3.65626700	-7.63056700
H	2.20510900	4.77574000	-5.57669200	2.10071900	4.87598700	-5.21465700
N	4.31187200	-0.00634300	-4.73770300	4.24887300	-0.06442400	-4.81620100
C	6.47020200	-1.03542700	-4.73940100	6.44055300	-1.11527500	-4.88644100
C	6.98768200	0.04051500	-5.45277100	6.91555400	-0.07650600	-5.64266900

C	6.14624700	1.08934100	-5.80348600	6.04637100	0.98812800	-5.99768400
C	0.02164500	-3.13186900	-1.95820400	0.06110600	-3.02275200	-1.80615300
H	-2.04436900	-3.23686100	-1.37095000	-1.98434500	-3.02150700	-1.16904600
H	-2.61686900	-1.04526400	-2.38904900	-2.53513300	-0.86519900	-2.25932600
H	-0.88918000	0.28945900	-3.54239800	-0.81407900	0.38003900	-3.52351800
H	4.10536400	1.81148400	-5.66829100	4.03183300	1.72755800	-5.80305800
H	4.79709900	-5.14278700	-2.12620000	4.80846100	-5.13979900	-2.06074300
H	6.15652700	-3.48020900	-3.36001600	6.13983500	-3.55673500	-3.38616800
H	2.38921100	-4.73823700	-1.71904300	2.39691500	-4.67894100	-1.57903800
H	7.11202100	-1.86227900	-4.45819600	7.09391400	-1.93610200	-4.60931800
H	8.03692200	0.05473200	-5.73002100	7.95095700	-0.06870200	-5.96951100
H	6.50874300	1.94612500	-6.36051200	6.39121500	1.82274800	-6.59730400
H	0.26667100	-4.09224300	-1.51127700	0.28330200	-3.96935500	-1.32278800