Electronic Supplementary Information

Alternation of intramolecular electronic transition via deboronation of carbazole-based *o*-carboranyl compound and intriguing 'turn-on' emissive variation

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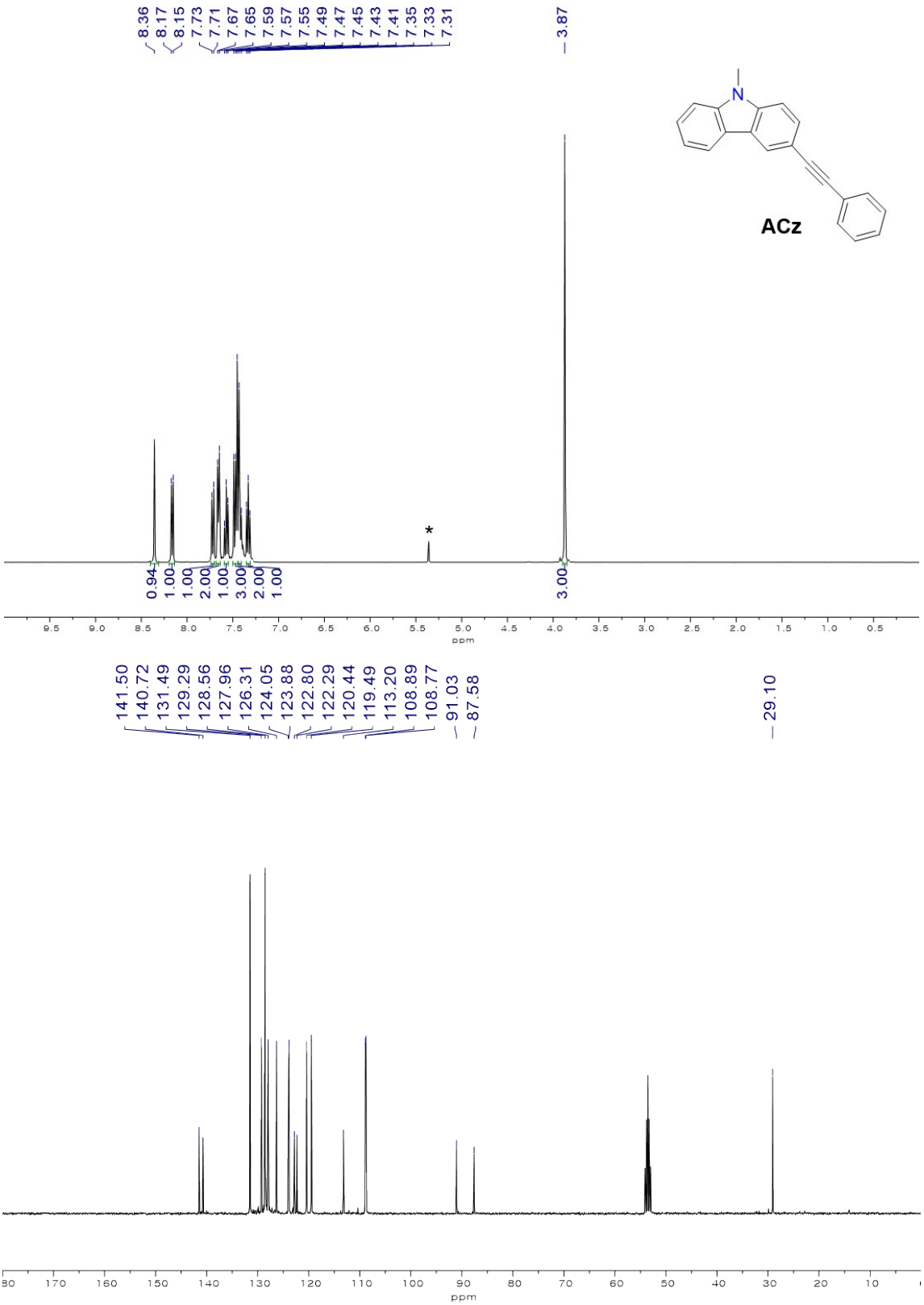

Fig. S1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **ACz** in CD_2Cl_2 (* from residual CH_2Cl_2 in CD_2Cl_2).

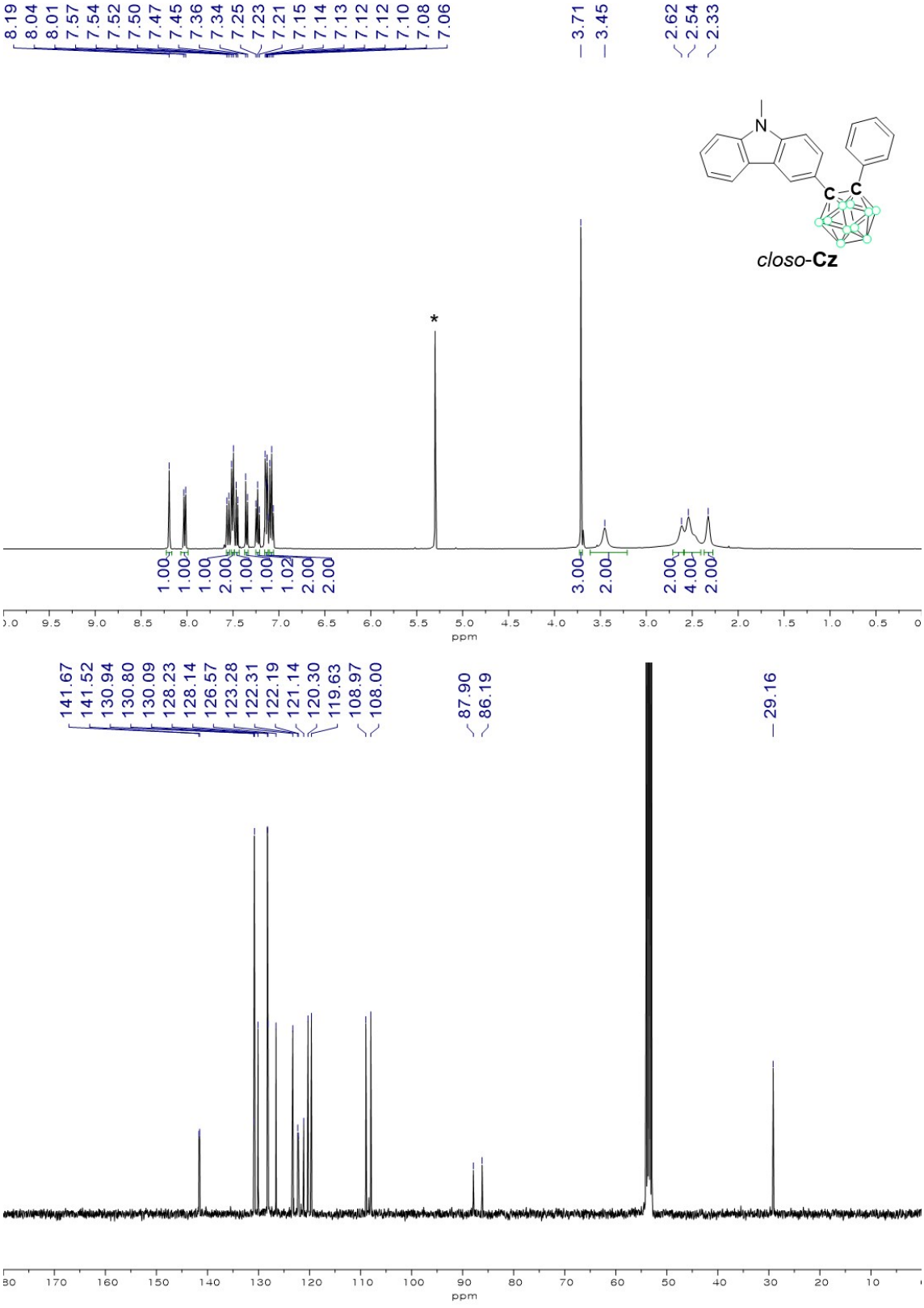

Fig. S2 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of *closo*-**Cz** in CD_2Cl_2 (* from residual CH_2Cl_2 in CD_2Cl_2).

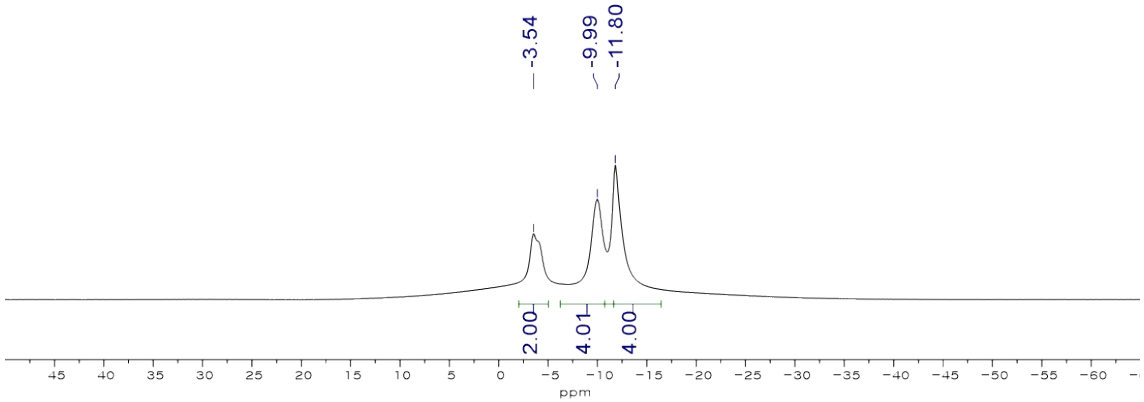

Fig. S3 $^{11}B\{^{1}H\}$ NMR spectra of *closo*-**Cz** in CD_2Cl_2.

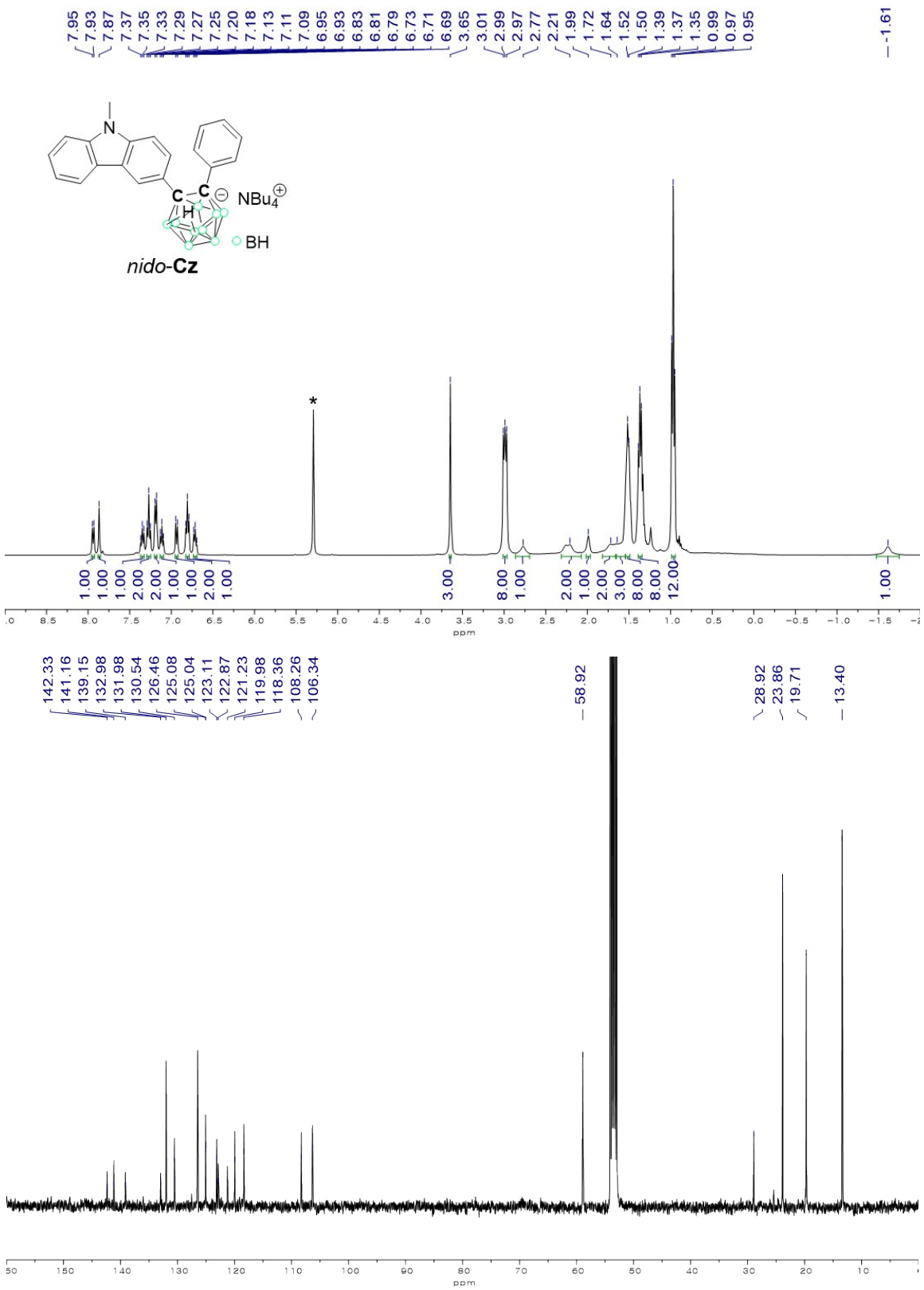

Fig. S4. $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of *nido*-**Cz** in CD_2Cl_2 (* from residual CH_2Cl_2 in CD_2Cl_2).

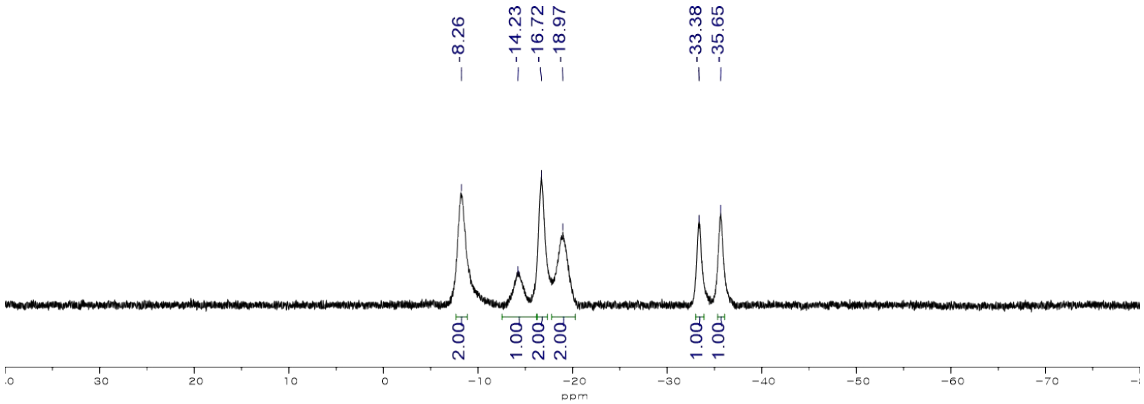

Fig. S5 $^{11}B\{^{1}H\}$ NMR spectra of *nido*-**Cz** in CD_2Cl_2.

Table S1 Crystallographic data and parameters for *closo*-**Cz**

Compound	*closo*-**Cz**
Formula	$C_{21}H_{25}B_{10}N$
Formula weight	399.52
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.573(3)
b (Å)	14.319(3)
c (Å)	13.473(3)
α (°)	90
β (°)	113.15(3)
γ (°)	90
V (Å^3)	2230.3(9)
Z	4
ρ_{calc}(g cm^{-3})	1.190
μ (mm^{-1})	0.061
F(000)	832
T (K)	293(2)
Scan mode	*phi and omega scans*
hkl range	$-16 < h < 16$, $-18 < k < 18$, $-17 < l < 16$
Measd reflns	22194
Unique reflns [R_{int}]	5144 [0.0864]
Reflns used for refinement	5144
Refined parameters	290
R_1[a] (I > 2σ(I))	0.1115
wR_2[b] all data	0.2326
GOF on F^2	1.000
ρ_{fin} (max/min) (e Å^{-3})	1.771, −0.336

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR_2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for *closo*-**Cz**

Compound	*closo*-**Cz**
length (Å)	
C3–C13	1.484(5)
C13–C14	1.749(5)
C14–C15	1.494(5)
angles (°)	
C3–C13–C14	120.2(3)
C13–C14–C15	118.9(3)
C9–N1–C12	108.5(4)
C9–N1–C21	126.8(4)
C12–N1–C21	124.7(4)

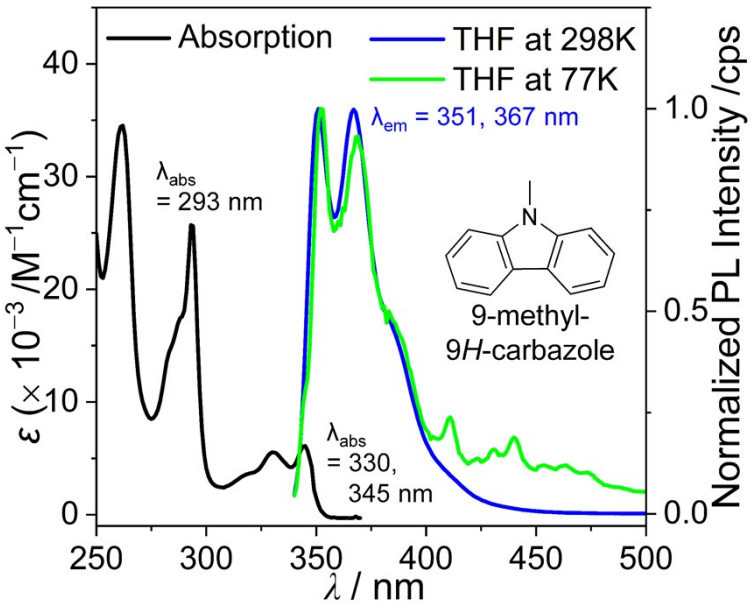

Fig. S6 UV-vis absorption (left side) and PL spectra (right side) for 9-methyl-9*H*-carbazole (λ_{ex} = 330 nm). Black line: absorption spectra in THF (3.0×10^{-5} M), blue and green line: PL spectra in THF (3.0×10^{-5} M) at 298 K and 77 K, respectively.

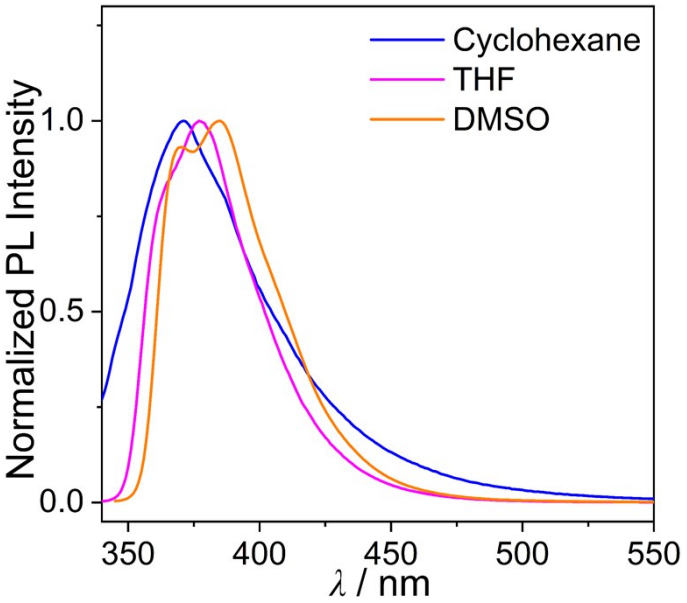

Fig. S7 PL spectra of *nido*-**Cz** (λ_{ex} = 349 nm) in various organic solvents (cyclohexane, THF, and dimethylsulfoxide (DMSO), 3.0×10^{-5} M).

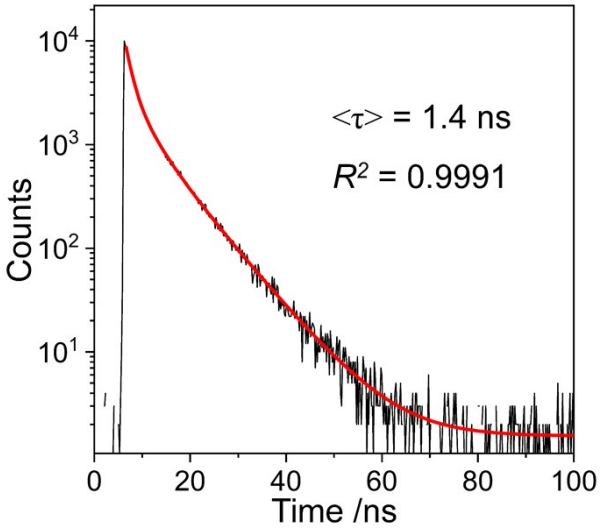

Fig. S8 Emission decay curve for *nido*-**Cz** in THF (3.0×10^{-5} M) detected at each CT based emission maxima at 298 K. Red-line is its single exponential fitting curve for the decay curve.

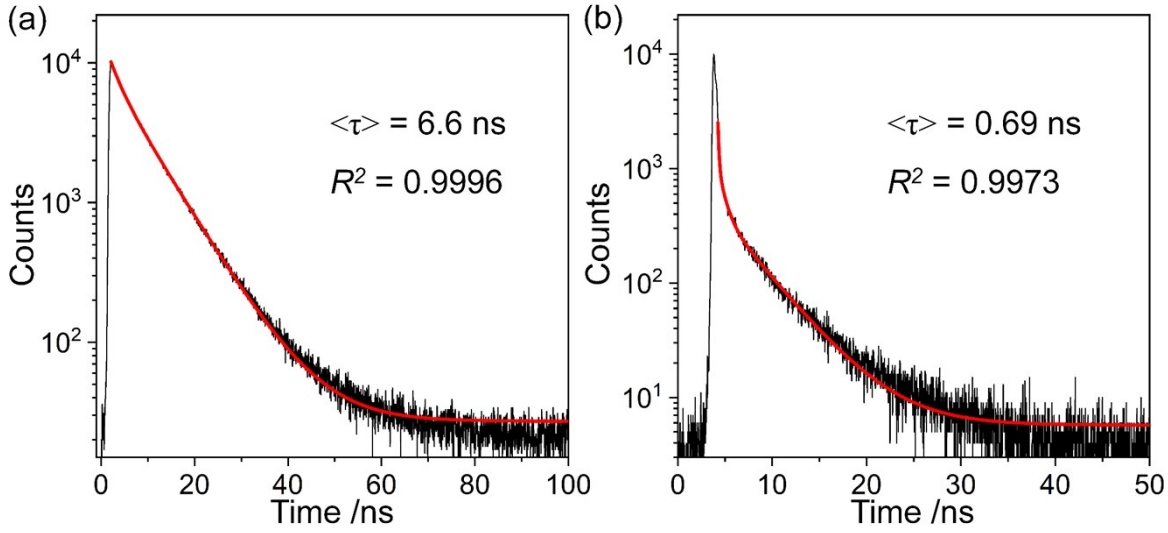

Fig. S9 Emission decay curves for (a) *closo*-**Cz**, and (b) *nido*-**Cz** in the film state (5 wt% doped in PMMA) detected at each CT based emission maxima at 298 K. Each red-line is its single exponential fitting curve for the decay curves.

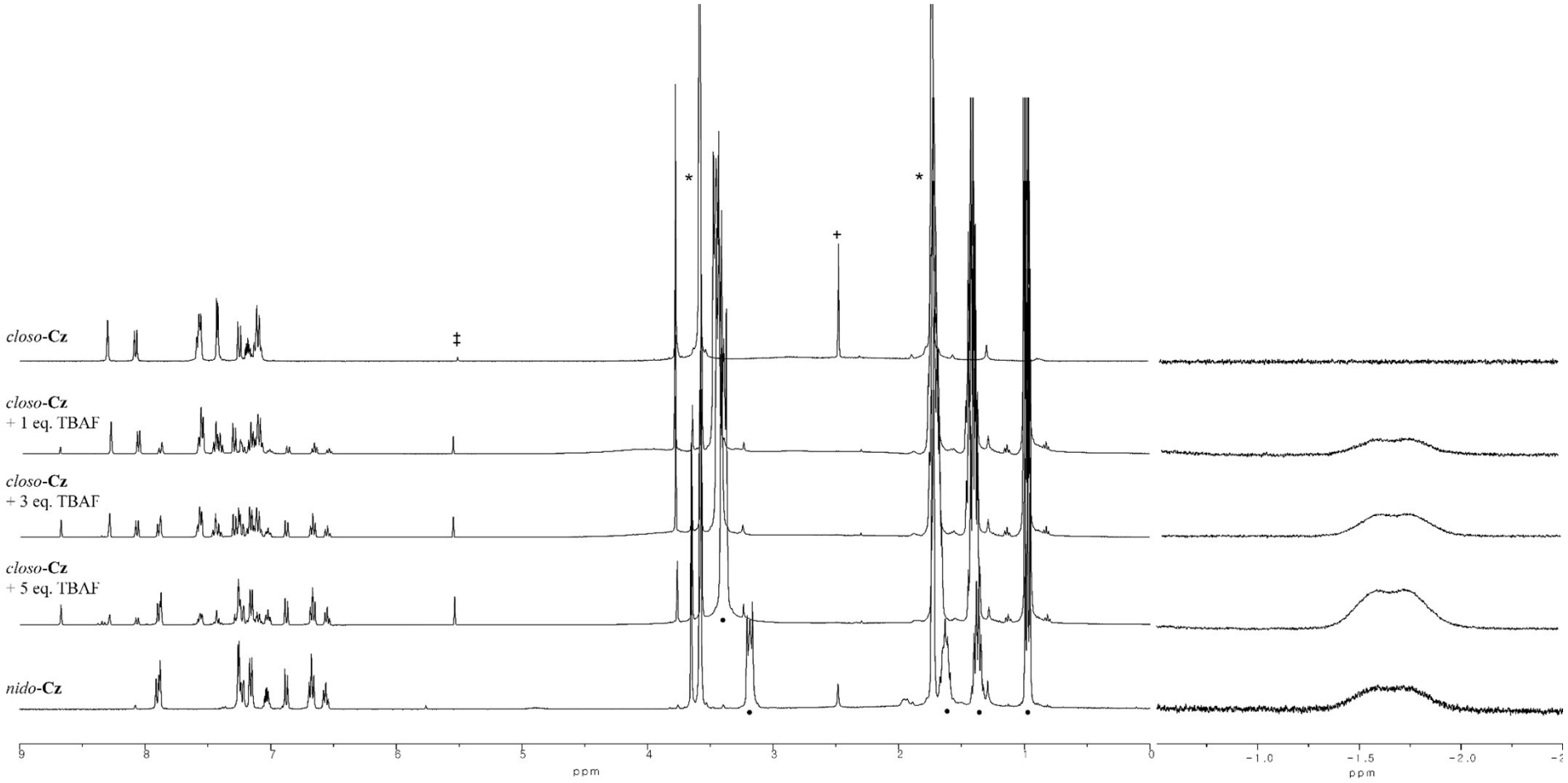

Fig. S10 ^{1}H NMR spectral changes of *closo*-**Cz** upon increasing the amount of added fluoride anions and comparison with that of *nido*-**Cz** in THF-d^8 (* from residual THF in THF-d^8, + from residual H_2O in THF-d^8, ‡ from residual H_2O in CD_2Cl_2, and • from *n*-butyl group from excess TBAF). Each spectrum was measured at 25 °C after 1 hr upon fluoride addition.

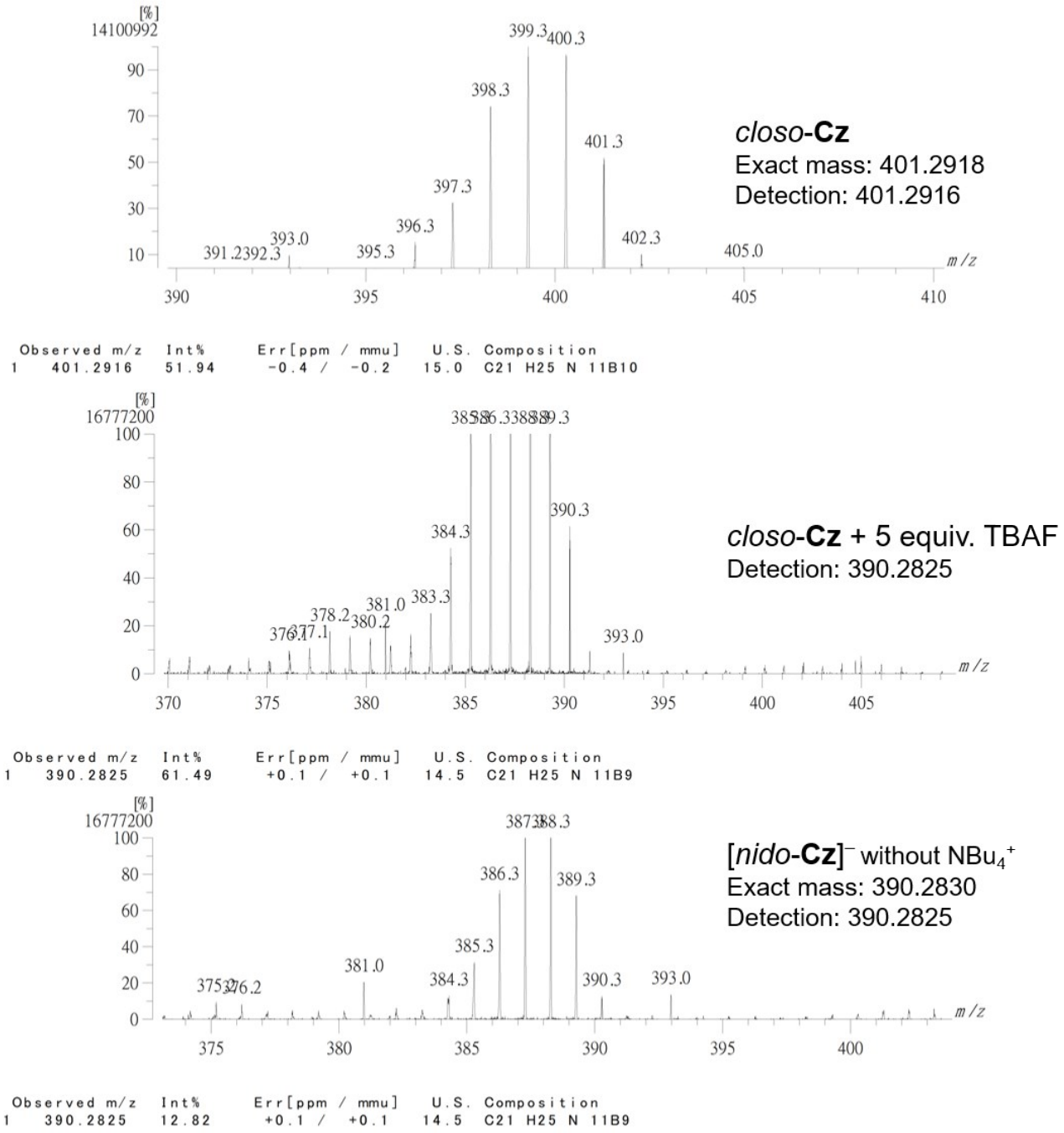

Fig. S11 High resolution (HR)-mass spectroscopy for *closo*-**Cz**, *closo*-**Cz** with 5 equiv. TBAF, and *nido*-**Cz**.

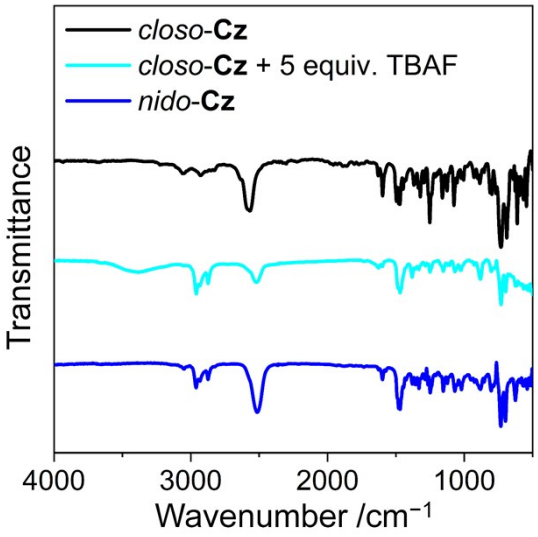

Fig. S12 Infrared (IR) spectra of *closo*-**Cz**, *closo*-**Cz** with 5 equiv. TBAF, and *nido*-**Cz**.

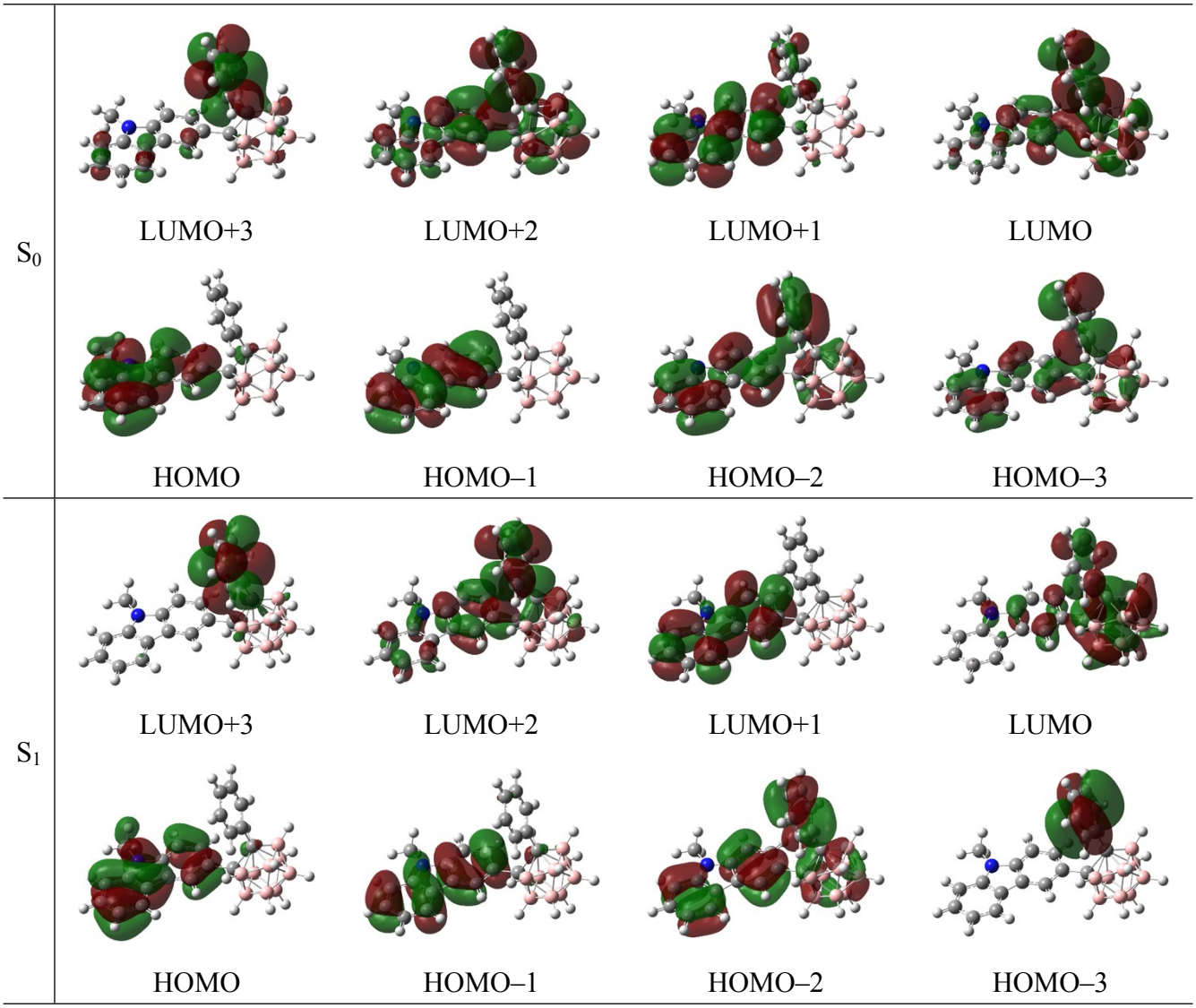

Fig. S13 The selected frontier orbitals of *closo*-**Cz** from B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S3 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for *closo*-**Cz** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	323.51	0.1840	HOMO → LUMO (89.5%)
			HOMO → LUMO+1 (6.5%)
2	314.23	0.0465	HOMO−1 → LUMO (11.0%)
			HOMO → LUMO (7.1%)
			HOMO → LUMO+1 (76.1%)
3	292.11	0.1217	HOMO−1 → LUMO (79.9%)
			HOMO → LUMO+1 (10.3%)
4	280.37	0.0297	HOMO−1 → LUMO (7.0%)
			HOMO−1 → LUMO+1 (46.8%)
			HOMO → LUMO+2 (40.3%)
5	261.18	0.0670	HOMO−1 → LUMO+1 (32.0%)
			HOMO → LUMO+2 (42.9%)
			HOMO → LUMO+3 (18.2%)
			S_1
1	521.20	0.2359	HOMO → LUMO (98.5%)
2	390.37	0.0057	HOMO−1 → LUMO (95.5%)
3	380.91	0.0119	HOMO−2 → LUMO (95.5%)
4	364.58	0.0066	HOMO−3 → LUMO (96.1%)
5	359.48	0.1013	HOMO−5 → LUMO (31.1%)
			HOMO−4 → LUMO (65.1%)

Table S4 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of *closo*-**Cz** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

	E (eV)	carborane phenyl	carborane	carbazole
		S_0		
LUMO+3	−0.44	86.2	7.0	6.8
LUMO+2	−0.60	31.8	19.1	49.2
LUMO+1	−1.09	6.1	4.7	89.2
LUMO	−1.35	21.8	30.1	48.1
HOMO	−5.71	0.1	2.9	97.0
HOMO−1	−6.09	0.2	1.2	98.6
HOMO−2	−7.09	34.8	7.3	57.8
HOMO−3	−7.14	76.7	7.4	15.9
		S_1		
LUMO+3	−0.48	92.0	6.5	1.6
LUMO+2	−0.50	61.1	9.0	29.9
LUMO+1	−1.08	0.7	2.9	96.4
LUMO	−3.35	9.1	84.5	6.3
HOMO	−5.57	0.6	2.7	96.7
HOMO−1	−6.18	1.2	3.6	95.3
HOMO−2	−7.01	36.1	10.9	53.0
HOMO−3	−7.23	98.1	1.7	0.2

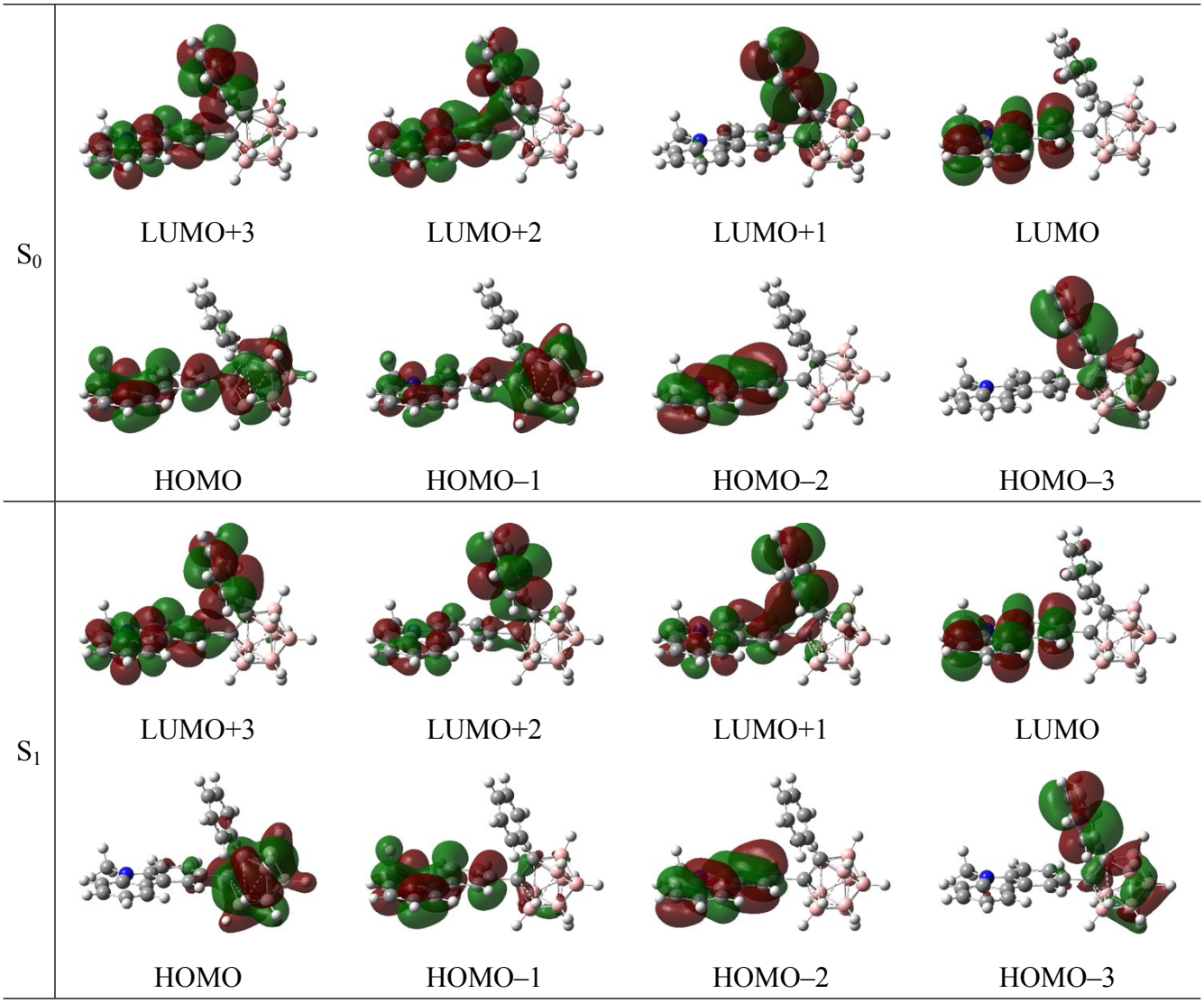

Fig. S14 The selected frontier orbitals of *nido*-**Cz** from B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S5 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for *nido*-**Cz** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	318.09	0.0870	HOMO−1 → LUMO (8.5%)
			HOMO → LUMO (85.5%)
2	306.02	0.0024	HOMO−1 → LUMO (88.6%)
			HOMO → LUMO (9.7%)
3	280.60	0.0750	HOMO−2 → LUMO (72.1%)
			HOMO → LUMO+2 (12.9%)
4	267.90	0.0107	HOMO−1 → LUMO+1 (48.3%)
			HOMO → LUMO+1 (50.1%)
5	260.26	0.0401	HOMO−1 → LUMO+2 (35.5%)
			HOMO → LUMO+2 (53.2%)
			S_1
1	395.55	0.1020	HOMO → LUMO (99.1%)
2	333.59	0.0445	HOMO−1 → LUMO (94.3%)
3	327.41	0.0068	HOMO → LUMO+1 (81.6%)
			HOMO → LUMO+2 (17.0%)
4	316.46	0.0033	HOMO → LUMO+1 (14.8%)
			HOMO → LUMO+2 (79.7%)
5	306.08	0.0031	HOMO → LUMO+3 (90.2%)

Table S6 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of *nido*-**Cz** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

	E (eV)	carborane phenyl	carborane	carbazole
		S_0		
LUMO+3	−0.34	56.8	4.9	38.3
LUMO+2	−0.58	37.5	4.3	58.2
LUMO+1	−0.65	86.4	9.2	4.4
LUMO	−0.83	3.1	1.6	95.3
HOMO	−5.66	0.8	39.4	59.8
HOMO−1	−5.73	0.5	72.4	27.2
HOMO−2	−6.21	1.0	1.8	97.3
HOMO−3	−6.48	79.4	19.2	1.4
		S_1		
LUMO+3	−0.46	44.3	4.4	51.3
LUMO+2	−0.54	77.0	6.0	17.0
LUMO+1	−0.67	61.6	5.9	32.6
LUMO	−1.57	2.2	1.3	96.5
HOMO	−4.93	1.1	96.1	2.8
HOMO−1	−5.71	0.5	4.9	94.6
HOMO−2	−6.13	1.0	1.2	97.8
HOMO−3	−6.77	78.2	19.4	2.4

Table S7 Cartesian coordinates of the ground state (S_0) fully optimized geometry of *closo*-**Cz** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-1.795566	3.831422	0.904956
C	-1.232174	4.362439	-0.255867
C	-2.264652	2.518909	0.922478
C	-1.150292	3.572858	-1.403279
C	-2.174489	1.711337	-0.222285
C	-1.618841	2.260050	-1.388781
C	-2.720355	0.307951	-0.216685
C	-1.643890	-1.051087	0.224812
C	0.156296	-0.580800	1.937052
C	-0.212834	-0.776175	0.585278
C	1.473994	-0.364887	2.319494
C	0.783291	-0.772818	-0.400518
C	2.454859	-0.339945	1.322180
C	2.112851	-0.555417	-0.041911
C	3.349631	-0.492572	-0.792596
C	4.378547	-0.240085	0.153251
C	3.672631	-0.623706	-2.148436
C	5.717910	-0.128946	-0.232928
C	5.004328	-0.507910	-2.538747
C	6.012241	-0.264161	-1.588514
H	-1.875399	4.438291	1.801396
H	-0.866576	5.384557	-0.268186
H	-4.952826	0.879007	0.680615
H	-2.710704	2.130017	1.829294
H	-0.723921	3.976846	-2.316082
H	-2.587756	0.052420	2.280328
H	-4.941457	-1.892408	2.006363
H	-1.558584	1.668339	-2.293596
H	-4.167904	0.560379	-2.205637
H	-5.963290	-1.618545	-0.884936
H	-0.602942	-0.613572	2.708044
H	1.719772	-0.231271	3.367108
H	-2.025042	-2.842985	1.886755
H	0.531622	-0.949397	-1.439067
H	-1.372723	-0.444595	-2.203096
H	-4.124644	-3.953585	-0.127331
H	-3.649710	-2.417460	-2.752174
H	2.896960	-0.815562	-2.884183
H	6.505700	0.050620	0.490869
H	5.270053	-0.609109	-3.586319
H	7.044516	-0.182434	-1.915486
H	-1.240468	-3.161570	-0.999636
B	-4.299968	-0.037481	0.315981
B	-2.887856	-0.506831	1.290401
B	-4.235383	-1.633652	1.088496
B	-3.837493	-0.225359	-1.385528
B	-4.822266	-1.473652	-0.591117
B	-2.567689	-2.235922	1.028830
B	-2.155932	-0.805124	-1.403724
B	-3.758524	-2.824589	-0.153073
B	-3.484190	-1.939628	-1.678748
B	-2.105782	-2.424496	-0.672698
N	3.817510	-0.135965	1.423465
C	4.561231	0.075142	2.652392
H	3.906782	0.519736	3.403186
H	4.969725	-0.862094	3.046477
H	5.383354	0.770206	2.468864

Table S8 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of *closo*-**Cz** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-3.045106	3.807436	0.913272
C	-2.684521	4.477105	-0.259832
C	-3.162399	2.420205	0.926651
C	-2.447551	3.738343	-1.423015
C	-2.925822	1.659204	-0.238268
C	-2.564134	2.351132	-1.414153
C	-3.063451	0.197358	-0.230637
C	-1.280890	-1.313220	0.283570
C	0.473593	-0.578657	1.934708
C	0.120190	-0.900726	0.619127
C	1.779351	-0.187759	2.294059
C	1.112523	-0.844817	-0.382876
C	2.720912	-0.127950	1.283476
C	2.406136	-0.450952	-0.049239
C	3.628073	-0.282388	-0.811502
C	4.642341	0.144678	0.128208
C	3.961099	-0.441366	-2.148625
C	5.975281	0.402779	-0.283681
C	5.277561	-0.183194	-2.546166
C	6.269440	0.233294	-1.618977
H	-3.237571	4.369352	1.822907
H	-2.592069	5.558909	-0.268162
H	-5.187782	-0.017459	0.881619
H	-3.446064	1.913701	1.842820
H	-2.172143	4.246239	-2.343032
H	-2.421749	-0.173901	2.186891
H	-4.410175	-2.577422	2.062008
H	-2.381228	1.790613	-2.324522
H	-4.373566	-0.106978	-2.227658
H	-5.560002	-2.559247	-0.805211
H	-0.280392	-0.625298	2.710965
H	2.013714	0.055779	3.324074
H	-1.492429	-3.095854	1.915708
H	0.864131	-1.104745	-1.405259
H	-1.316149	-0.295247	-1.990387
H	-3.342180	-4.442639	-0.167863
H	-3.152324	-2.718941	-2.733742
H	3.220445	-0.757990	-2.874240
H	6.735329	0.717986	0.420372
H	5.551521	-0.303130	-3.588365
H	7.276564	0.419694	-1.973791
H	-0.689557	-3.171126	-1.153442
B	-4.297971	-0.645920	0.406202
B	-2.619104	-0.759409	1.173106
B	-3.790517	-2.173882	1.128426
B	-3.840376	-0.695461	-1.343334
B	-4.472656	-2.155285	-0.532384
B	-2.064027	-2.536277	1.036327
B	-2.004193	-0.827328	-1.181451
B	-3.162776	-3.264913	-0.154473
B	-3.065855	-2.255195	-1.640218
B	-1.614317	-2.581366	-0.693317
N	4.093707	0.234774	1.360762
C	4.750066	0.631576	2.596407
H	4.245118	1.506201	3.015310
H	4.704962	-0.188589	3.318068
H	5.790443	0.879358	2.400152

Table S9 Cartesian coordinates of the ground state (S_0) fully optimized geometry of *nido*-**Cz** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-2.685870	0.401089	-0.139856
C	-1.863185	-0.979148	-0.033285
B	-4.344454	0.189076	0.331054
B	-3.784619	0.446355	-1.332420
B	-4.483094	-1.563765	0.591630
B	-4.938710	-0.818632	-0.969471
B	-4.014248	-2.382085	-0.945768
B	-3.683780	-1.146334	-2.186803
B	-2.892289	-2.265403	0.417406
B	-2.303823	-1.972936	-1.263892
B	-3.055388	-0.685548	1.159086
H	-4.928786	1.022187	0.950092
H	-4.063659	1.484864	-1.854878
H	-6.069314	-0.792262	-1.355628
H	-5.278618	-2.029263	1.348452
H	-2.740746	-0.466300	2.280338
H	-3.991643	-1.399657	-3.314060
H	-4.509229	-3.430213	-1.234971
H	-2.444075	-3.177586	1.036083
H	-1.539075	-2.764533	-1.724539
C	-1.947861	1.676254	0.190377
C	-1.293259	2.362093	-0.846407
C	-1.897193	2.233825	1.476369
C	-0.605728	3.552106	-0.608297
H	-1.337704	1.957553	-1.852920
C	-1.215808	3.428616	1.718815
H	-2.402928	1.733326	2.294576
C	-0.563295	4.092125	0.678960
H	-0.107288	4.059618	-1.429686
H	-1.198150	3.841058	2.724059
H	-0.032481	5.020985	0.867653
C	-0.004497	-1.298020	1.699585
C	1.333686	-1.300944	2.086928
C	-0.417607	-0.948220	0.395470
C	2.291809	-0.941285	1.135438
H	1.610483	-1.572692	3.100450
C	0.559194	-0.596939	-0.543171
H	-0.756748	-1.578526	2.428278
C	1.910429	-0.581403	-0.184036
H	0.261980	-0.338996	-1.555158
C	4.197472	-0.444543	0.033692
C	3.133255	-0.262777	-0.893096
C	5.528225	-0.204090	-0.325380
C	3.419617	0.153414	-2.198486
C	5.784102	0.209565	-1.632088
H	6.339329	-0.328028	0.384773
C	4.744414	0.386971	-2.562053
H	2.618095	0.295225	-2.918036
H	6.809563	0.402157	-1.934157
H	4.978080	0.711533	-3.571490
N	3.675641	-0.871536	1.248008
H	-2.439444	-0.924689	-2.160746
C	4.437983	-1.114418	2.456466
H	5.425255	-1.502148	2.196617
H	4.562538	-0.204391	3.055740
H	3.931790	-1.867738	3.063312

Table S10 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of *nido*-**Cz** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-2.645836	0.354830	-0.128405
C	-1.854733	-0.948357	0.159251
B	-4.307024	0.186387	0.163442
B	-3.636639	0.174907	-1.478860
B	-4.502829	-1.514560	0.646362
B	-4.834471	-1.022980	-1.038979
B	-3.972800	-2.564386	-0.690827
B	-3.555980	-1.591412	-2.101890
B	-2.862986	-2.190489	0.662971
B	-2.248822	-2.202535	-1.021812
B	-3.126066	-0.549421	1.235561
H	-4.937934	1.129664	0.505299
H	-3.653098	1.050258	-2.275012
H	-5.925407	-0.990986	-1.510687
H	-5.358942	-1.860826	1.391938
H	-2.911944	-0.194140	2.338850
H	-3.767680	-1.912751	-3.223187
H	-4.449917	-3.645696	-0.807781
H	-2.414103	-3.029872	1.366564
H	-1.402360	-2.980645	-1.298667
C	-1.968399	1.691936	0.042310
C	-1.194957	2.212757	-1.005277
C	-2.119663	2.451528	1.208704
C	-0.586637	3.462937	-0.888343
H	-1.075347	1.641182	-1.919118
C	-1.509021	3.703035	1.327763
H	-2.721063	2.070744	2.026748
C	-0.741601	4.211778	0.280268
H	0.009148	3.848960	-1.709938
H	-1.638115	4.277443	2.240343
H	-0.267298	5.184545	0.372189
C	-0.017997	-1.045760	1.882524
C	1.358364	-0.975711	2.255729
C	-0.402653	-0.871947	0.546883
C	2.292372	-0.752333	1.255576
H	1.648676	-1.087457	3.295404
C	0.543855	-0.636079	-0.464740
H	-0.765631	-1.232261	2.644250
C	1.927641	-0.570189	-0.119825
H	0.231520	-0.526387	-1.497615
C	4.214317	-0.405064	0.083218
C	3.124278	-0.354777	-0.852507
C	5.534532	-0.215979	-0.291087
C	3.431899	-0.117240	-2.223113
C	5.812007	0.019870	-1.666525
H	6.338776	-0.238593	0.438721
C	4.766245	0.064294	-2.598328
H	2.639779	-0.075827	-2.965785
H	6.838188	0.170197	-1.988497
H	4.999655	0.246858	-3.646016
N	3.679981	-0.669086	1.348872
H	-2.293083	-1.342996	-2.048974
C	4.439465	-0.777293	2.571944
H	5.436795	-1.167308	2.352751
H	4.550137	0.186285	3.088335
H	3.946592	-1.477758	3.251822