Crystalline Radical Cations of Bis-BN-Based Analogues of Thiele's Hydrocarbon

Zhuofeng Xie,[a] Yuyang Dai,[a] Manling Bao,[a] Zhongtao Feng,[a] Wenjuan Wang,[a] Chunmeng Liu,[a] Xinping Wang,[*b] and Yuanting Su[*a,b]

[a] College of Chemistry, Chemical Engineering and Materials Science, School of Radiation Medicine and Protection, Soochow University, Suzhou 215123, China.

[b.] State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, China.

E-mail: ytsu@suda.edu.cn; xpwang@nju.edu.cn

Contents

1. Synthesis of new compounds and their NMR spectra

General considerations: All experiments were carried out under an argon or nitrogen atmosphere using standard Schlenk or dry glovebox techniques. Solvents were dried over Na metal, K metal, or CaH_2, and were distilled under nitrogen prior to use. Commercially available reagents were purchased from Energy Chemical and used as received. ^{1}H , $^{13}C\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR spectra were obtained with a Bruker AVIII 400 MHz BBFO1 spectrometer at 298K. Chemical shifts (δ) are given in p.p.m. Coupling constants *J* are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. UV-vis spectra were recorded on the Lambda 750 spectrometer at room temperature. Element analyses were performed on an ElementarVario EL III instrument. EPR spectra were obtained using JEOL JES-X320 X-band apparatus. Bromoborane $(HCDippN)_2BBr$ (Dipp = 2,6-diisopropyl) was synthesized according to the literature procedure.[S1]

Synthesis of compound 1

Potassium graphite (0.27 g, 2.0 mmol) was added to the toluene solution of $(HCDippN)_2BBr$ (0.47 g, 1.0 mmol) and pyrazine (0.04 g, 0.5 mmol) at room temperature. The color of the solution changed from yellow to brown and the mixture was stirred for 48 h. After filtration and removal of the solvent, the residue was washed with cooled hexane (5 ml) to afford **1** as a yellow powder (0.18 g, 42%). ^{1}H NMR (C_6D_6 , 400 MHz, 298 K): δ 7.05–6.96(m, 12H, Ar-H), 5.76 (s, 4H, C*H*=C*H*), 4.31 (s, 4H, C*H*=C*H*), 3.25 (sep, 8H, $(CH_3)_2CH$), 1.30 (d, *J* = 8.0 Hz, 24H, $CH(CH_3)_2$), 1.17 (d, *J* = 8.0 Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (C_6D_6 , 400 MHz, 298 K): δ 146.38 (Ar-*C*), 139.51 (Ar-*C*), 127.71 (Ar-*C*H), 123.57 (Ar-*C*H), 118.29 (*C*H=*C*H), 113.94 (*C*H=*C*H), 28.64($(CH_3)_2CH$), 24.65 ($(CH_3)_2CH$), 23.68 ($(CH_3)_2CH$). $^{11}B\{^{1}H\}$ NMR (C_6D_6, 400 MHz, 298 K): δ 19.83 ppm; UV-vis (toluene): λ_{max} = 282, 332, and 398 nm; Elemental analysis for $C_{56}H_{76}B_2N_6$ (%): Calculated:C 78.68, H 8.96, N 9.83; Found: C 78.64, H 8.93, N 9.85.

Synthesis of compound 2

Potassium graphite (0.27 g, 2.0 mmol) was added to the toluene (20 ml) solution of $(HCDippN)_2BBr$ (0.47 g, 1.0 mmol) and quinoxaline (0.065 g, 0.5 mmol) at room temperature. The color of the solution changed from yellow to brown and stirred for 24 h. After filtration and removal of the solvent, the residue was washed with cooled hexane (5 mL) to afford **2** as a yellow powder (0.24 g, 53%). ^{1}H NMR (C_6D_6 , 400 MHz, 298 K): δ 7.11–7.03(m, 12H, Ar-H), 6.17–6.09(m, 4H, Ar-H), 6.02 (s, 4H, C*H*=C*H*), 4.71 (s, 2H, C*H*=C*H*), 3.29 (sep, 8H, $(CH_3)_2CH$), 1.20 (d, J = 8.0 Hz, 24H, $CH(CH_3)_2$), 1.16 (d, J = 8.0 Hz, 24H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6 , 400 MHz, 298 K): δ 145.70 (Ar-*C*), 138.98 (Ar-*C*), 135.82 (*C*=*C*), 128.35 (Ar-*C*H), 127.66 (Ar-*C*H), 123.98 (Ar-*C*H), 121.82 (Ar-*C*H), 119.01 (*C*H=*C*H), 116.38 (*C*H=*C*H), 114.31 (*C*H=*C*H), 28.72 ($(CH_3)_2CH$), 25.83 ($(CH_3)_2CH$), 23.27 ($(CH_3)_2CH$). ^{11}B{^{1}H} NMR (C_6D_6, 400 MHz, 298 K): δ 22.23 ppm; UV-vis (toluene): λ_{max} = 282, 365, and 480 nm; Elemental analysis for $C_{60}H_{78}B_2N_6$ (%): Calculated: C 79.64, H 8.69, N 9.29; Found: C 79.60, H 8.66, N 9.32.

Synthesis of compound $\mathbf{1}^{\cdot+}[SbF_6]^-$

A dichloromethane (5 mL) solution of $AgSbF_6$ (0.07 g, 0.2 mmol) was added dropwise into the dichloromethane (10 mL) solution of **1** (0.17 g, 0.2 mmol) at –30 ^{o}C. The color of the solution immediately changed from yellow to deep green. After slowly warming up to room temperature and stirred overnight, the solvent was removed under vacuum and the resulting residue was washed with hexane (10 ml). After removal of the solvent, $\mathbf{1}^{\cdot+}[SbF_6]^-$ was obtained as a indigo powder (0.16 g, 73%). Single crystals of $\mathbf{1}^{\cdot+}[SbF_6]^-$ suitable for X-ray diffraction studies were grown from the saturated DCM/hexane mixture solution at room temperature. UV-vis (DCM): λ_{max} = 334, 676, 749, and 842 nm; Elemental analysis for $C_{56}H_{76}B_2F_6N_6Sb$ (%): Calculated: C 61.67, H 7.02, N 7.71; Found: C 61.63, H 6.98, N 7.74.

Synthesis of compound $2^{\cdot+}[SbF_6]^-$

A dichloromethane (5 mL) solution of $AgSbF_6$ (0.05 g, 0.15 mmol) was added dropwise into the dichloromethane (10 mL) solution of **2** (0.14 g, 0.15 mmol) at –30 ^oC. The color of the solution immediately changed from yellow to deep green. After slowly warming up to room temperature and stirred overnight, the solvent was removed under vacuum and the resulting residue was washed with hexane (10 ml). After removal of the solvent, $\mathbf{2^{\cdot+}[SbF_6]^-}$ was obtained as a indigo powder (0.13 g, 76%). Single crystals of $\mathbf{2^{\cdot+}[SbF_6]^-}$ suitable for X-ray diffraction studies were grown from the DCM/hexane mixture solution at room temperature. UV-vis (DCM): λ_{max} = 364, 648, 714, and 808 nm; Elemental analysis for $C_{60}H_{78}B_2F_6N_6Sb$ (%): Calculated: C 63.18, H 6.89, N 7.37; Found: C 63.19, H 6.87, N 7.39.

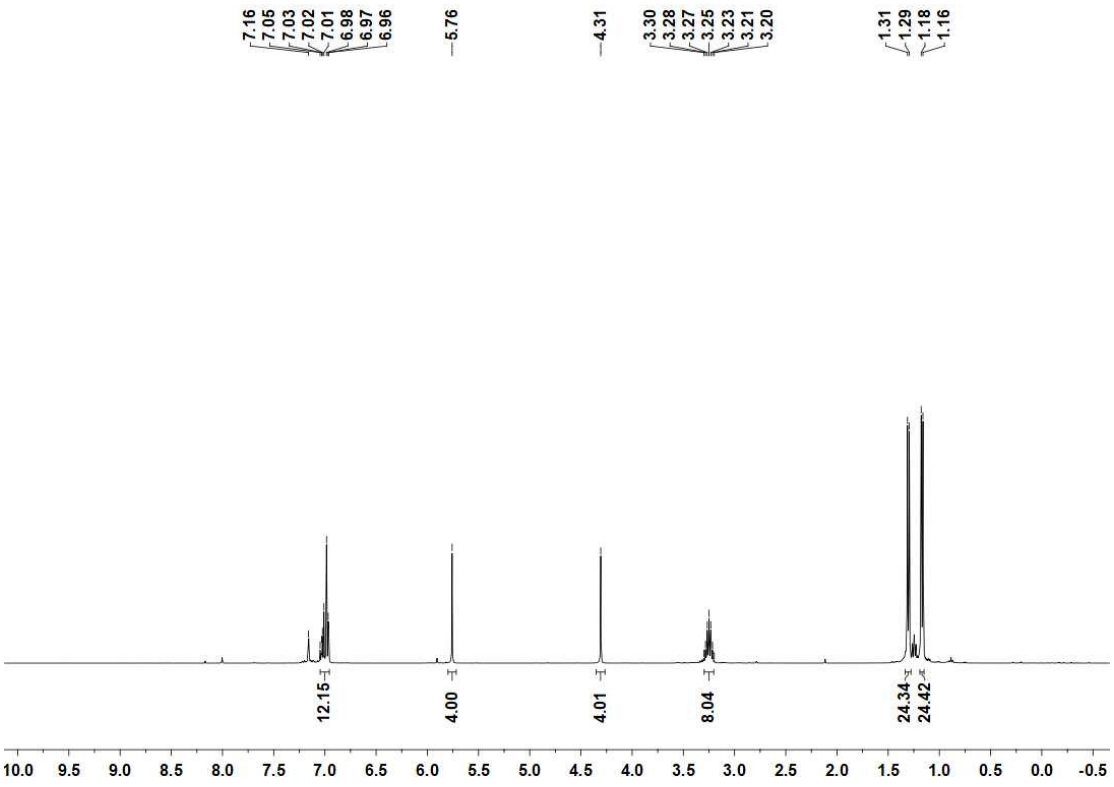


Fig. S1 ^{1}H NMR spectrum of **1** in C_6D_6 at 298 K.

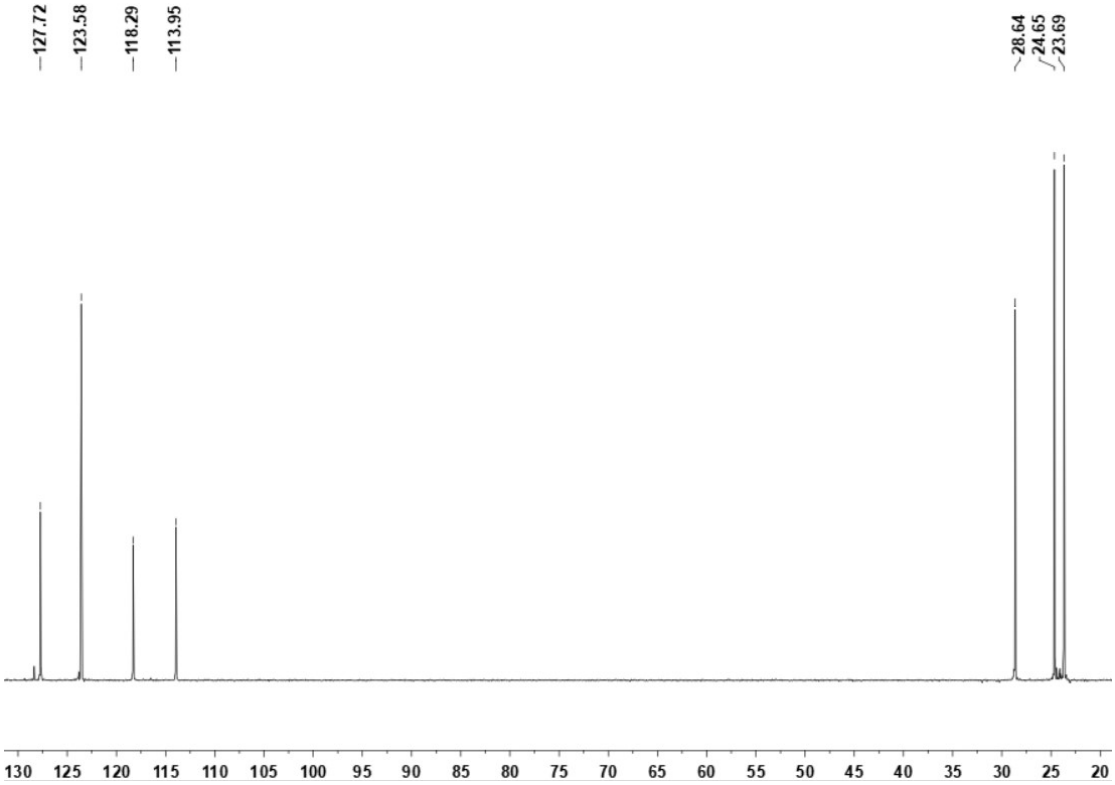


Fig. S2 ^{13}C (DEPT135) NMR spectrum of **1** in C_6D_6 at 298 K.

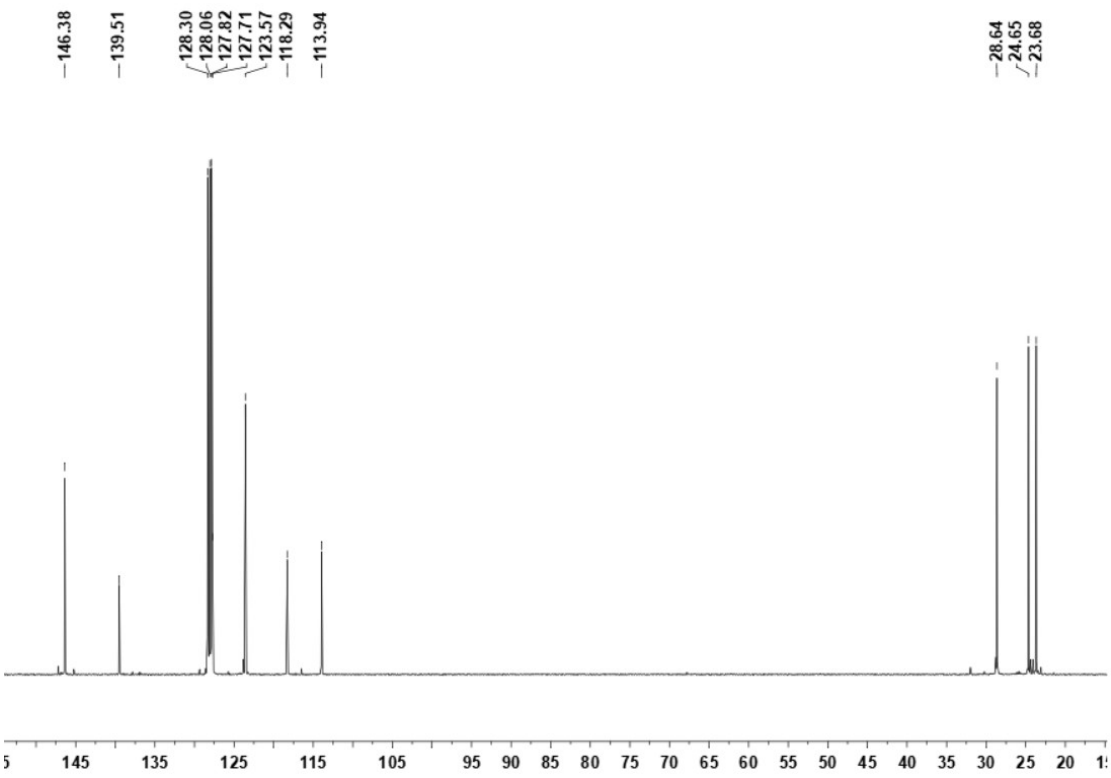


Fig. S3 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 298 K.

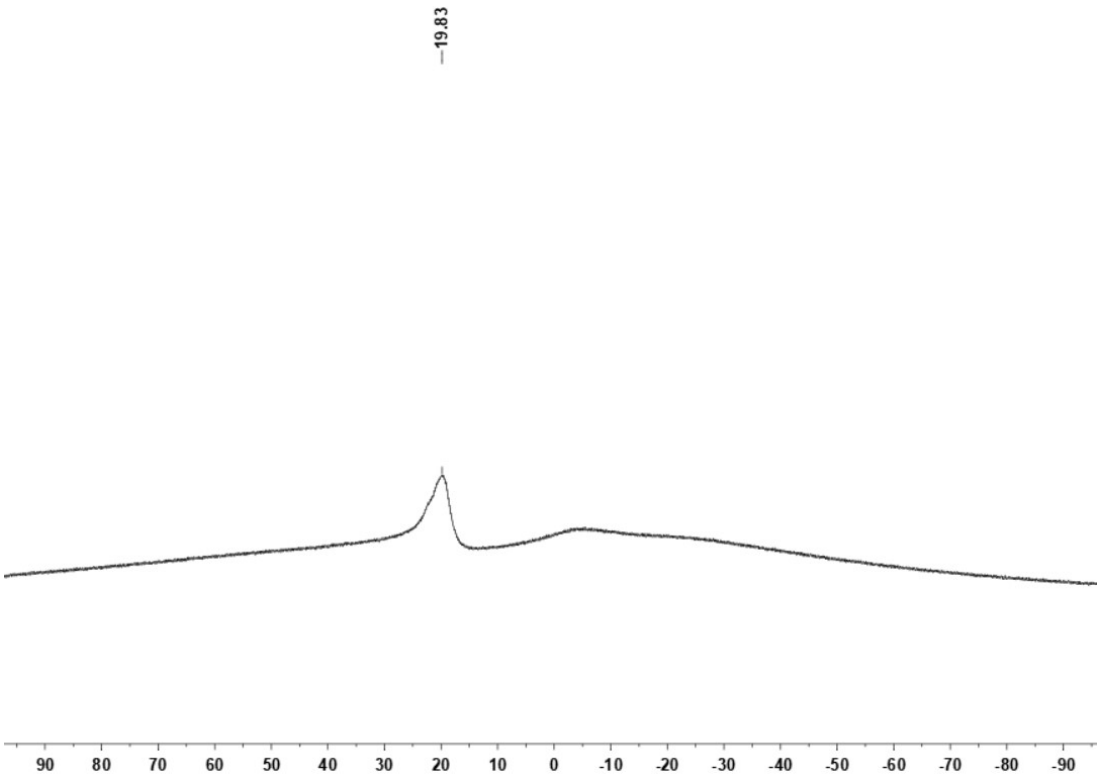


Fig. S4 $^{11}B\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 298 K.

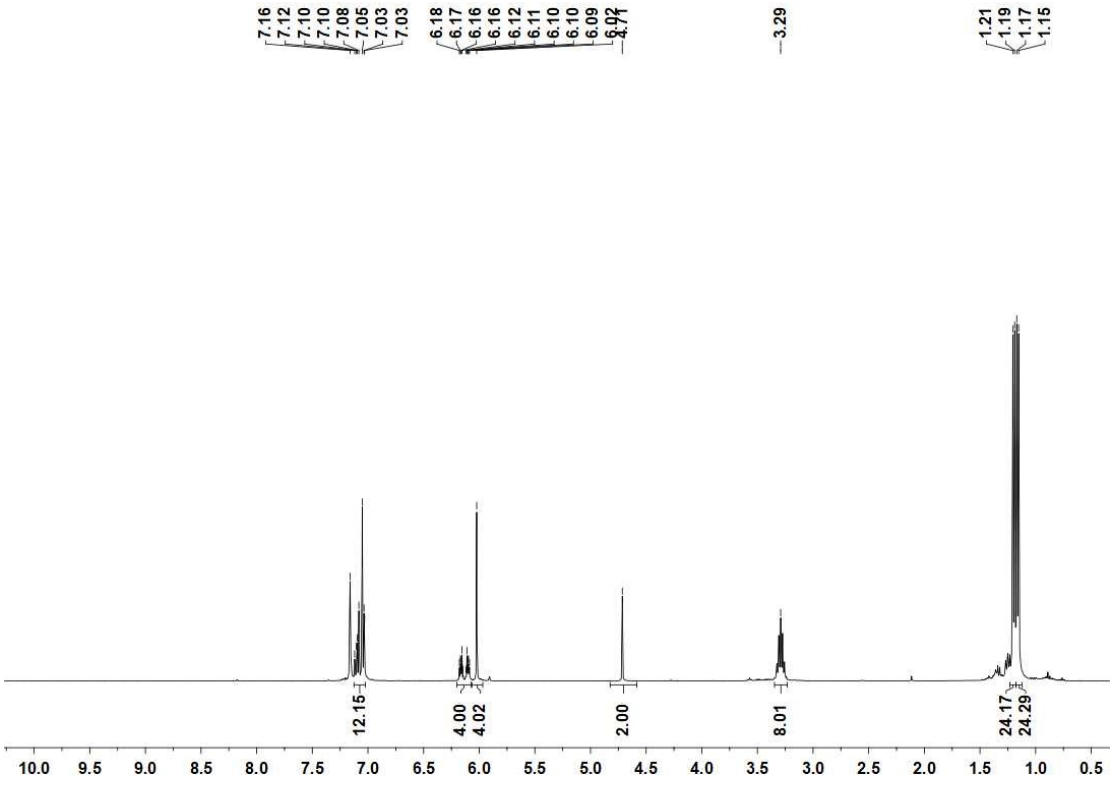


Fig. S5 ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K.

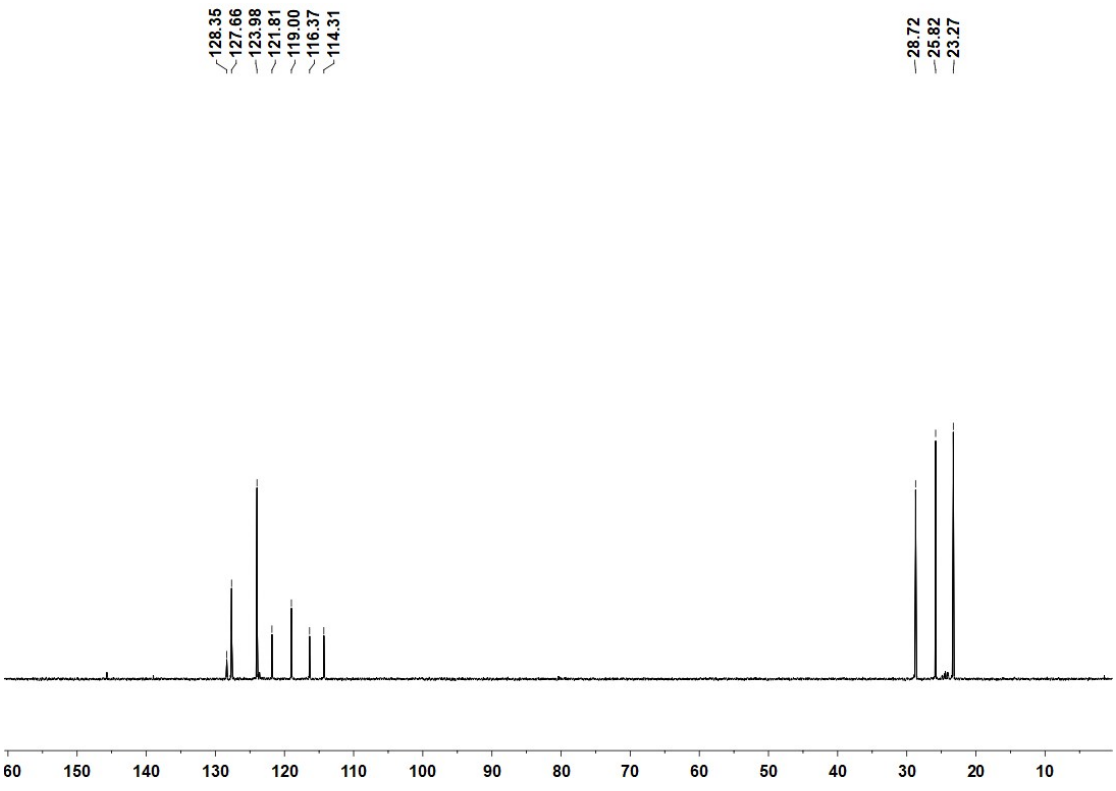


Fig. S6 ^{13}C (DEPT135) NMR spectrum of **2** in C_6D_6 at 298 K.

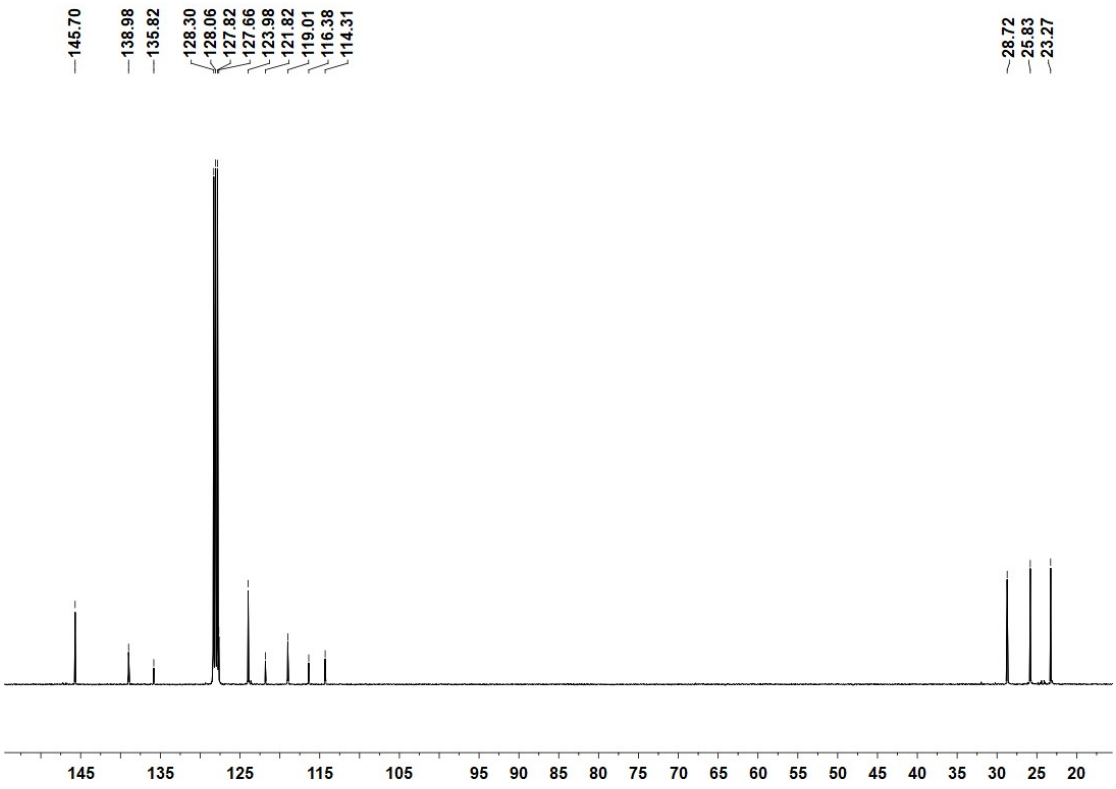


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

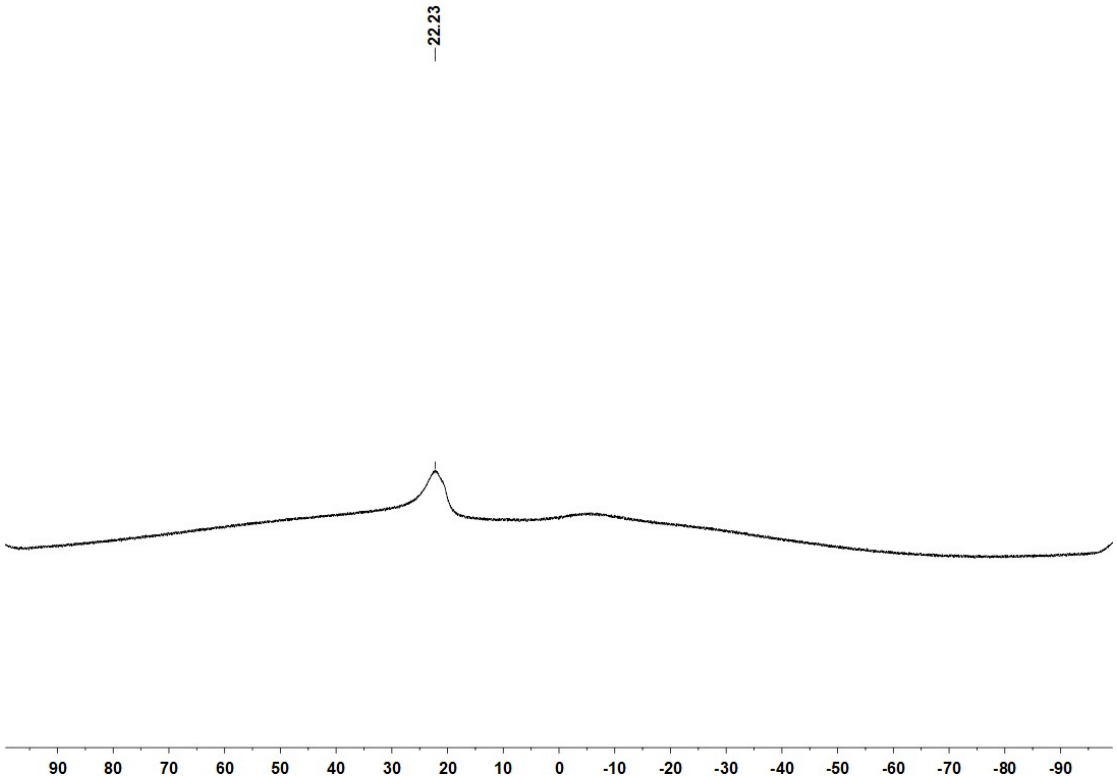


Fig. S8 $^{11}B\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

2. Crystal structural parameters for 1, 2, $1^{\cdot+}[SbF_6]^-$ and $2^{\cdot+}[SbF_6]^-$

For the single crystal X-ray structure analyses the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data for all compounds were collected on a Bruker D8 CMOS detector at low temperatures. The structures were solved by direct methods and all refined on F^2 with the SHELX-2018/3 software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

Table S1. Summary of data collection and structure refinement.

Compounds	**1**	$\mathbf{1}^{+\bullet}$ $[SbF_6]^-$	**2**	$\mathbf{2}^{+\bullet}$ $[SbF_6]^-$
CCDC	2155383	2155384	2155385	2155386
Formula	$C_{56}H_{76}B_2N_6$	$C_{56}H_{76}B_2F_6N_6Sb$	$C_{60}H_{78}B_2N_6$	$C_{60}H_{78}B_2F_6N_6Sb$
Fw	854.84	1090.59	904.90	1140.65
Crystal syst	triclinic	triclinic	monoclinic	orthorhombic
Space group	P-1	P-1	$P2_1/c$	$Pna2_1$
Size, mm^3	0.12 × 0.10 × 0.10	0.20 × 0.14 × 0.10	0.38 × 0.13 × 0.11	0.25× 0.16 × 0.16
T, K	134.0	140.0	136.0	135.00
a, Å	12.5484(10)	10.4503(9)	10.8314(8)	25.5040(18)
b, Å	13.4967(11)	13.9363(12)	13.2692(11)	16.6135(11)
c, Å	17.0112(14)	22.1346(19)	38.304(3)	15.9169(11)
α, deg	69.016(3)	97.006(2)	90	90
β, deg	82.118(3)	103.374(2)	91.671(3)	90
γ, deg	81.640(3)	109.486(2)	90	90
V, $Å^3$	2650.1(4)	2886.1(4)	5502.8(8)	6744.2(8)
Z	2	2	4	4
d_{calcd}, $g•cm^{-1}$	1.071	1.255	1.092	1.123
μ, mm^{-1}	0.302	2.868	0.308	2.468
Reflections collected	48983	44616	54897	74572
Independent reflections	9646	10281	10036	11854
$[R_{int}]$	0.0700	0.0681	0.0589	0.0677
R_1[I>2sigma(I)]	0.0559	0.0491	0.0507	0.0686
wR_2[I>2sigma(I)]	0.1532	0.1319	0.1312	0.2100
R_1[all data]	0.0628	0.0494	0.0605	0.0695
wR_2[all data]	0.1585	0.1322	0.1376	0.2113
GOF	1.063	1.112	1.079	1.028
Largest diff. Peak/hole, $e•Å^{-3}$	0.42/-0.32	1.32/-0.92	0.44/-0.39	1.48/-0.77

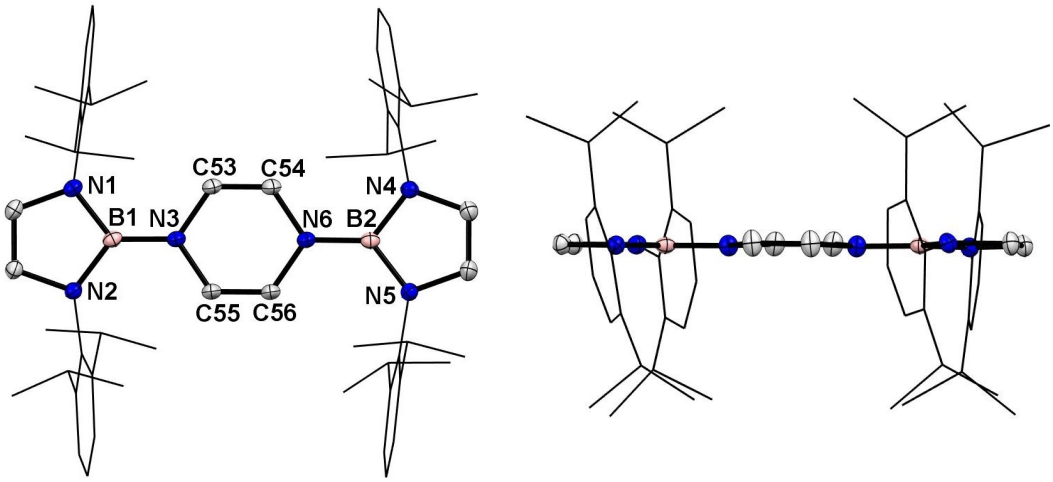


Fig. S9 Solid-state structure **1** with side view. Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): B1–N1 1.4434(19), B1–N2 1.4475(19), B1–N3 1.429(2), B2–N4 1.4462(19), B2–N5 1.4439(19), B2–N6 1.430(2), N3–C53 1.4201(18), N3–C55 1.4144(18), N6–C54 1.4192(18), N6–C56 1.4161(18), C53–C54 1.323(2), C55–C56 1.323(2), N1–B1–N2 104.96(12), N1–B1–N3 127.75(13), N2–B1–N3 127.29(13), N4–B2–N5 104.84(12), N4–B2–N6 127.13(13), N5–B2–N6 128.02(13).

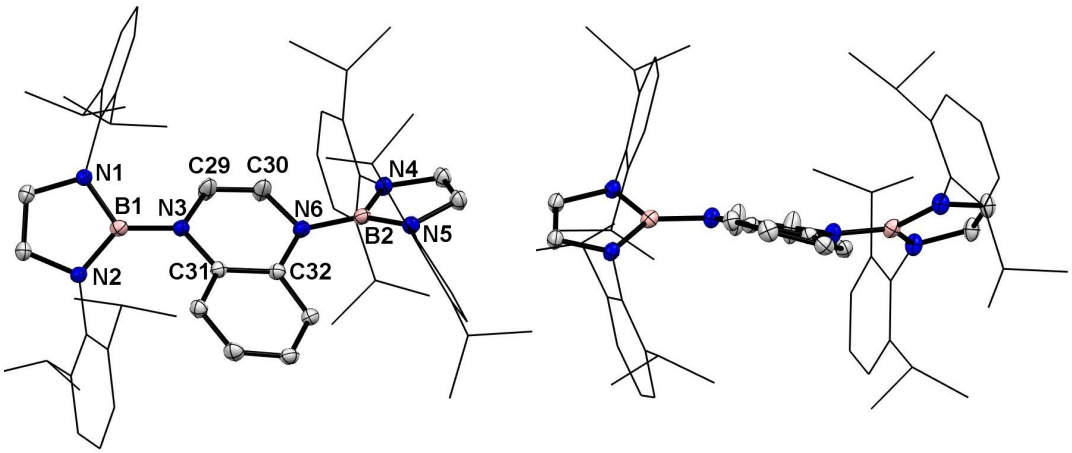


Fig. S10 Solid-state structure **2** with side view. Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): B1–N1 1.437(2), B1–N2 1.441(2), B1–N3 1.455(2), B2–N4 1.446(2), B2–N5 1.445(2), B2–N6 1.449(2), N3–C29 1.407(2), N3–C31 1.4204(19), N6–C30 1.410(2), N6–C32 1.4214(19), C29–C30 1.315(2), C31–C32 1.417(2), N1–B1–N2 104.68(13), N1–B1–N3 124.47(14), N2–B1–N3 130.70(14), N4–B2–N5 104.26(13), N4–B2–N6 123.34(14), N5–B2–N6 132.26(14).

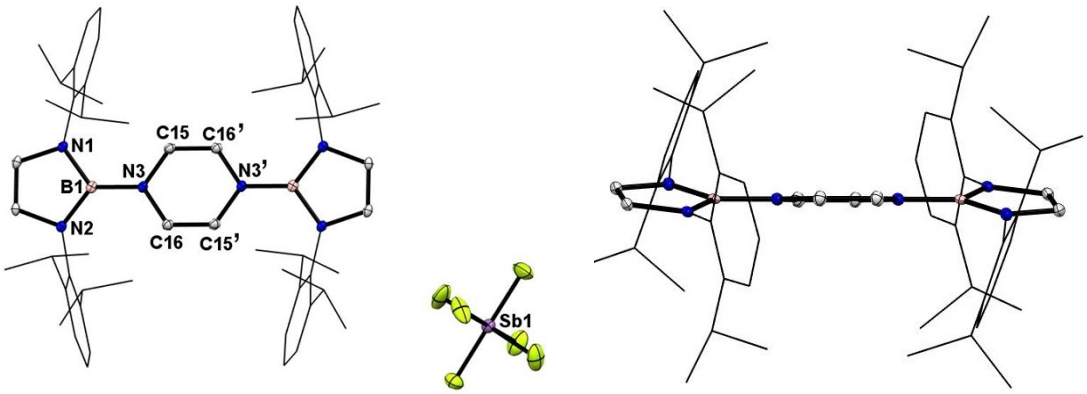


Fig. S11 Solid-state structure $\mathbf{1}^{\cdot+}[\mathbf{SbF_6}]^-$ with side view. Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): B1–N1 1.429(3), B1–N2 1.422(3), B1–N3 1.479(3), N3–C15 1.384(3), N3–C16 1.391(3), C15–C16′ 1.348(4), N1–B1–N2 106.8(2), N1–B1–N3 125.6(2), N2–B1–N3 127.6(2).

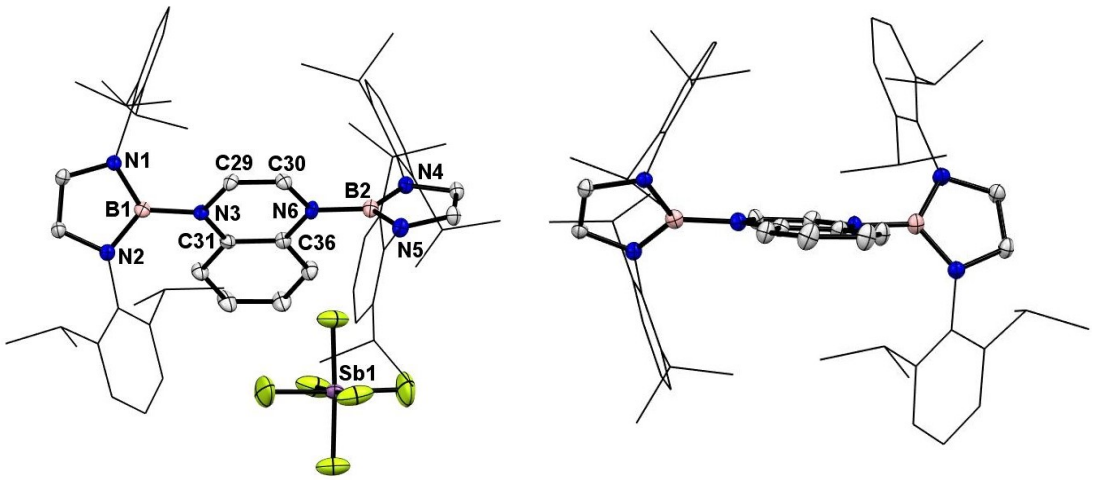


Fig. S12 Solid-state structure $\mathbf{2}^{\cdot+}[\mathbf{SbF_6}]^-$ with side view. Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): B1–N1 1.399(10), B1–N2 1.420(11), B1–N3 1.503(8), B2–N4 1.428(12), B2–N5 1.399(12), B2–N6 1.496(8), N3–C29 1.377(8), N3–C31 1.392(8), N6–C30 1.371(9), N6–C36 1.405(8), C29–C30 1.342(11), C31–C36 1.411(8), N1–B1–N2 107.5(6), N1–B1–N3 124.8(7), N2–B1–N3 127.2(7), N4–B2–N5 107.8(6), N4–B2–N6 127.6(9), N5–B2–N6 124.5(9).

3. Cyclic voltammograms of 1 and 2

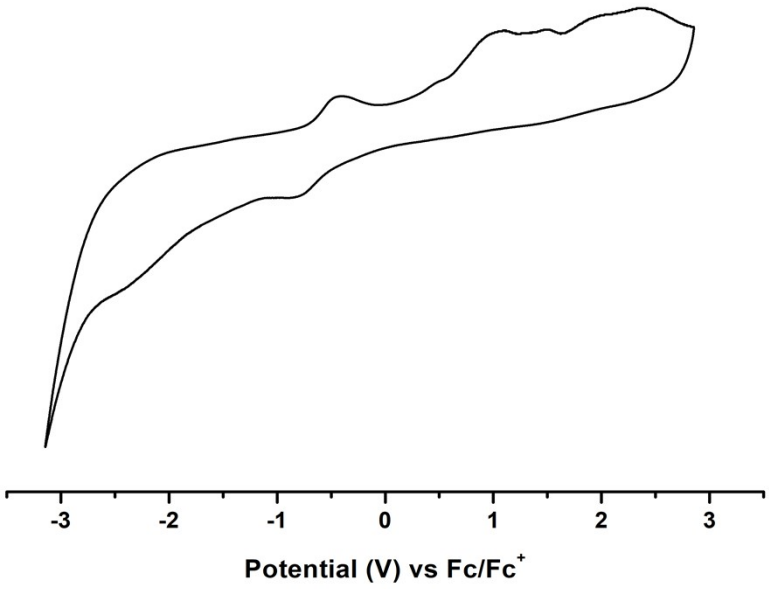


Fig. S13 The cyclic voltammogram of **1** in DCM (0.1 M [^{n}Bu$_4$N][PF$_6$]) measured at a scan rate of 50 mV s^{-1}.

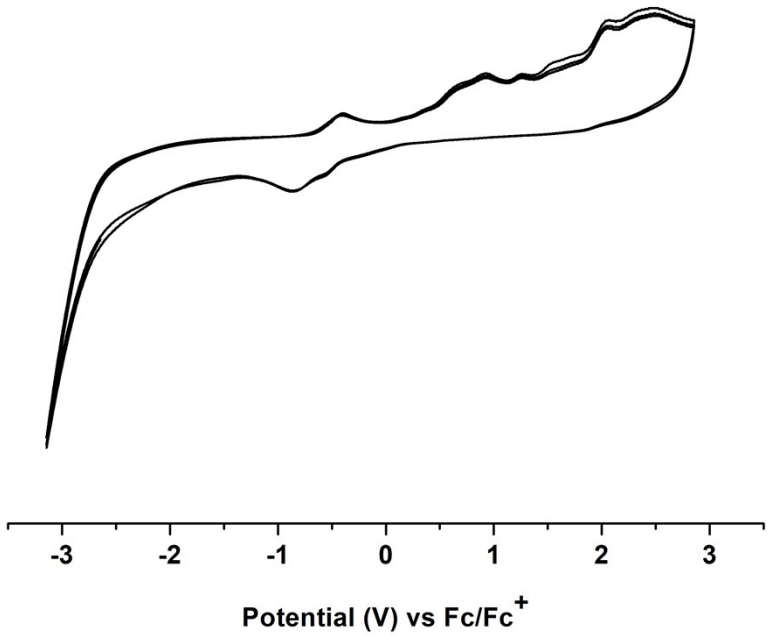


Fig. S14 The cyclic voltammogram of **2** in DCM (0.1 M [^{n}Bu$_4$N][PF$_6$]) measured at a scan rate of 50 mV s^{-1}.

4. UV-vis spectra

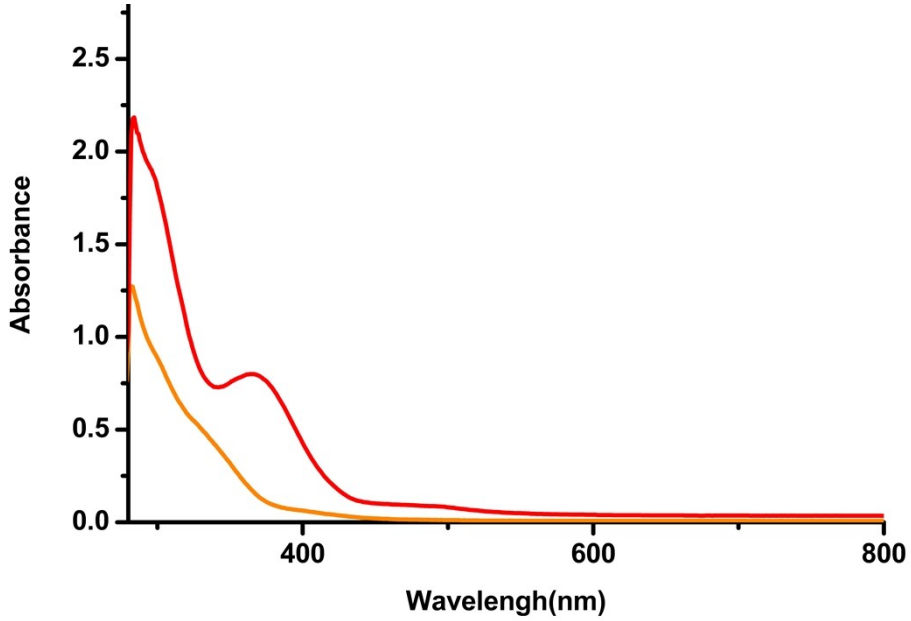


Fig. S15 UV-vis spectra of **1** (orange) and **2** (red) in toluene at room temperature.

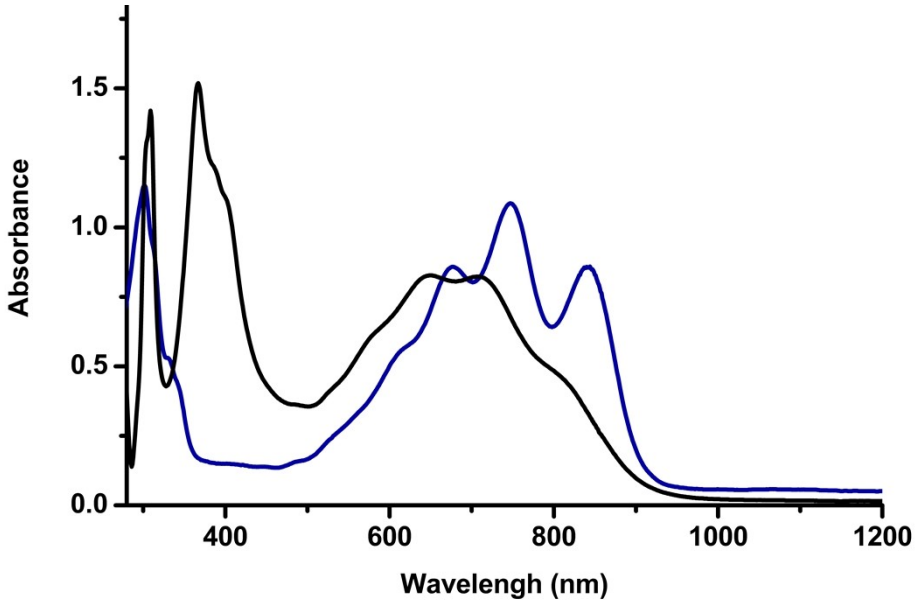
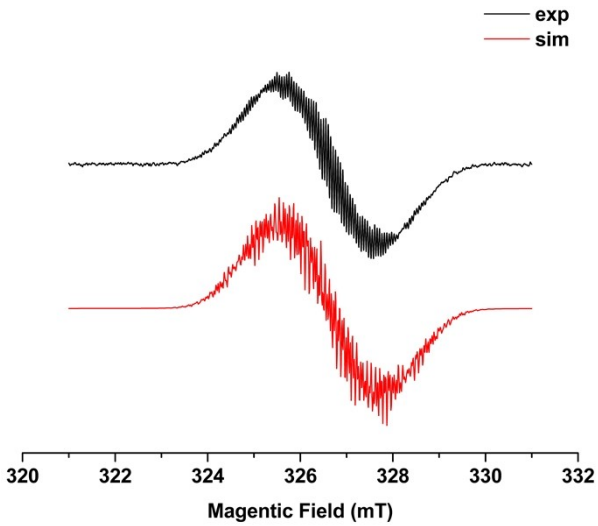


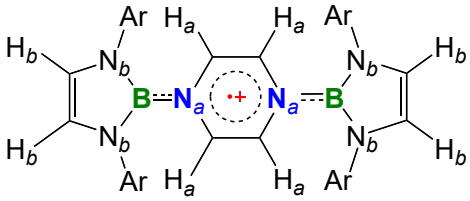
Fig. S16 UV-vis spectra of $\mathbf{1}^{\cdot+}[SbF_6]^-$ (blue) and $\mathbf{2}^{\cdot+}[SbF_6]^-$ (black) in DCM at room temperature.

4. EPR spectra

EPR simulations used the EasySpin package of routines written in MatLAB (The MathWorks, Natick, N.J.) program development environment.[S2]

(a) **(b)**

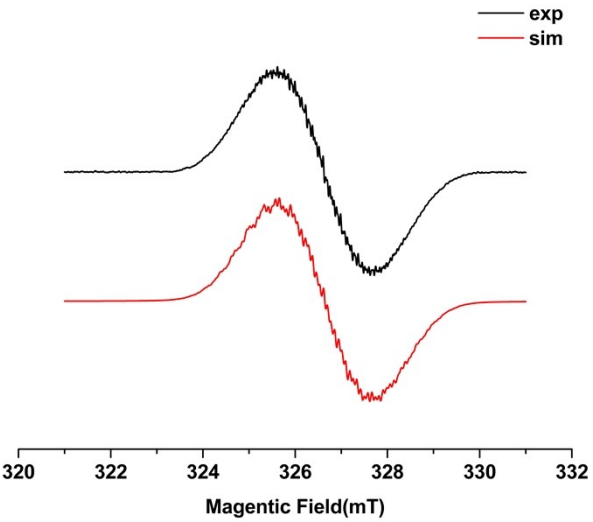


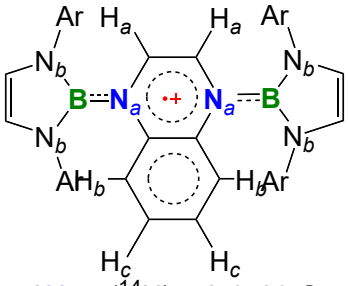


$2N_a$: a(^{14}N) = 2.9452 G;
$4N_b$: a(^{14}N) = 1.8335 G;
2B: a(^{11}B) = 5.4219 G;
$4H_a$: a(^{1}H) = 2.7093 G;
$4H_b$: a(^{1}H) = 1.4258 G

Figure S17 (a) Experimental (black) and simulated (red) EPR spectra of $\mathbf{1}^{\cdot+}[SbF_6]^-$ in DCM at room temperature. (b) Simulated hyperfine couplings.

(a) **(b)**





$2N_a$: a(^{14}N) = 2.4720 G;
$4N_b$: a(^{14}N) = 0.9447 G;
2B: a(^{11}B) = 4.7546 G;
$2H_a$: a(^{1}H) = 5.6761 G;
$2H_b$: a(^{1}H) = 3.8904 G;
$2H_c$: a(^{1}H) = 2.3628 G;

Figure S18 (a) Experimental (black) and simulated (red) EPR spectra of $\mathbf{1}^{\cdot+}[SbF_6]^-$ in DCM at room temperature. (b) Simulated hyperfine couplings.

5. Theoretical calculations

The calculations were performed with the Gaussian 16[S2] program. All of the geometry optimizations for **1** and **2** were performed with the B3LYP, PBE0, and M062X, BH&HLYP functional in conjunction with the def2-svp and 6-311G(d) basis set. All of the geometry optimizations for $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ were performed at the B3LYP/6-311G(d) level. TD-DFT and NICS calculations were conducted under the UB3LYP/6-311G(d) level of theory. The calculated Kohn-Sham orbitals related to the observed transitions are shown in Table S8-S11. To gain further insight into the electronic structures, Multiwfn[S3] and VMD[S4] were also used.

To check the multiconfigurational character, the CASSCF(2,2)/def2-SVP calculations were performed on the model systems $\mathbf{1}^{\mathbf{Me}}$ and $\mathbf{2}^{\mathbf{Me}}$ using the ORCA 4.0.1.2 software.[S5] The singlet diradical index *d* proposed by Neese and coworkers14-15 was calculated, for an *ab initio* CI calculation with the canonical MOs, by the following equation:

$$d = 200\sqrt{\frac{C_0^2 C_d^2}{C_0^2 + C_d^2}}$$

Where c_0^2 is the weight of the closed-shell configuration in the CI wave function and c_d^2 is weight of the double excitation computed.

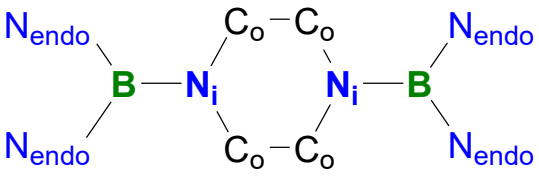
Table S2. Electronic energies (*E* in Hartrees) and relative electronic energies ($\Delta E_{S\text{-}T}$ in kcal/mol) of compound **1** in closed-shell singlet (CS) and triplet (T) states.

Methods	E_{CS}	E_T	$\Delta E_{S\text{-}T}$
B3LYP/def2-SVP	-2555.1106543	-2555.0461742	40.46
B3LYP/6-311G(d)	-2557.4609644	-2557.3946305	41.63
BH&HLYP/def2-SVP	-2553.4605201	-2553.3870525	46.10
PBE0/def2-SVP	-2552.0933548	-2552.0292427	40.23

Table S3. Electronic energies (E in Hartrees) and relative electronic energies ($\Delta E_{S\text{-}T}$ in kcal/mol) of compound **2** in closed-shell singlet (CS) and triplet (T) states.

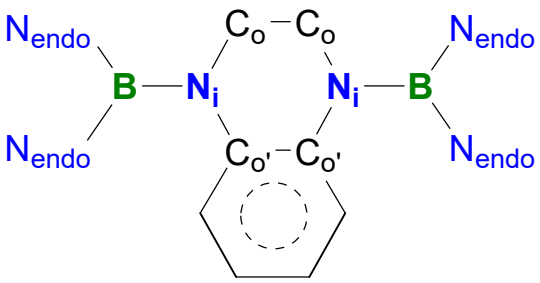
Methods	E_{CS}	E_T	$\Delta E_{S\text{-}T}$
B3LYP/def2-SVP	-2708.5942011	-2708.5227306	44.85
B3LYP/6-311G(d)	-2711.0803500	-2711.0076806	45.60
BH&HLYP/def2-SVP	-2706.8499161	-2706.7711197	49.45
PBE0/def2-SVP	-2705.4037798	-2705.3314936	45.34

Table S4. Experimental and calculated bond lengths (avg., Å) of **1** and $\mathbf{1}^{\cdot+}$ at the (U)B3LYP/6-311G(d) level.



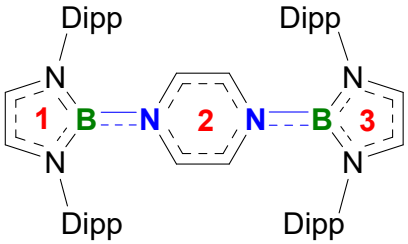
	1-Exp.	**1-CS**	**1-T**	**$1^{\cdot+}$-Exp.**	**$1^{\cdot+}$-Cal.**
$B–N_{endo}$	1.4452(18)	1.456	1.446	1.426(3)	1.438
$B–N_i$	1.429(2)	1.440	1.467	1.479(3)	1.478
$N_i–C_o$	1.4199(18)	1.419	1.385	1.388(3)	1.391
$C_o–C_o$	1.323(2)	1.337	1.409	1.348(4)	1.352
BLA	0.097(2)	0.082	0.024	0.040(4)	0.039

Table S5. Experimental and calculated bond lengths (avg., Å) of **2** and **2**$^{\cdot+}$ at the (U)B3LYP/6-311G(d) level.



	2-Exp.	**2-CS**	**2-T**	**2**$^{\cdot+}$**-Exp.**	**2**$^{\cdot+}$**-Cal.**
$B–N_{endo}$	1.442(2)	1.449	1.438	1.411(10)	1.430
$B–N_i$	1.452(2)	1.464	1.486	1.500(8)	1.502
$N_i–C_o$	1.408(2)	1.414	1.375	1.374(8)	1.370
$N_i–C_{o'}$	1.4209(19)	1.419	1.392	1.398(8)	1.404
$C_o–C_o$	1.315(2)	1.332	1.418	1.342(11)	1.361
$C_{o'}–C_o$	1.417(2)	1.424	1.459	1.411(8)	1.424

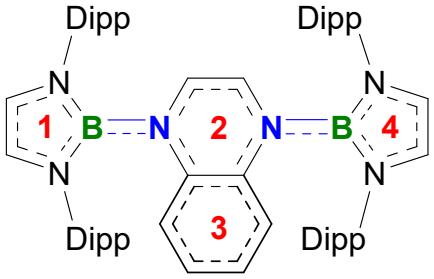
Table S6. NICS(0) and NICS(1) values for **1** and **1**$^{\cdot+}$.



	1	**1**$^{\cdot+}$
Ring 1 NICS (0)	-11.3447	-13.4181
Ring 1 NICS (1)	-4.2795	-5.3488
Ring 2 NICS (0)	12.0403	4.8120
Ring 2 NICS (1)	8.4718	1.3485
Ring 3 NICS (0)	-11.3447	-13.4283

Ring 3 NICS (1)	-4.2795	-5.3488

Table S7. NICS(0), NICS(1) and NICS(1)ZZ for **2** and $\mathbf{2}^{\cdot+}$.



	2	$\mathbf{2}^{\cdot+}$
Ring 1 NICS (0)	-8.5493	-9.0300
Ring 1 NICS (1)	-4.7540	-5.6261
Ring 2 NICS (0)	12.9195	2.6554
Ring 2 NICS (1)	9.2291	-0.2471
Ring 3 NICS (0)	-4.8584	-8.3102
Ring 3 NICS (1)	-6.3255	-10.0403
Ring 4 NICS (0)	-8.5493	-9.0300
Ring 4 NICS (1)	-4.7540	-5.6261

Table S8. CASSCF(2,2)/def2-SVP Energies (in Hartree), HOMO/LUMO occupations, CI vectors and diradicaloid character of $\mathbf{1}^{\mathbf{Me}}$ and $\mathbf{2}^{\mathbf{Me}}$.

		$\mathbf{1}^{\mathbf{Me}}$	$\mathbf{2}^{\mathbf{Me}}$
CI vector	20	0.99194	0.99454
	02	0.00806	0.00546
Occ(HOMO)		1.9839	1.9891
Occ(LUMO)		0.0161	0.0109
CASSCF(2,2)		-841.6164911562	-994.1719416151
d		1.61%	1.09%

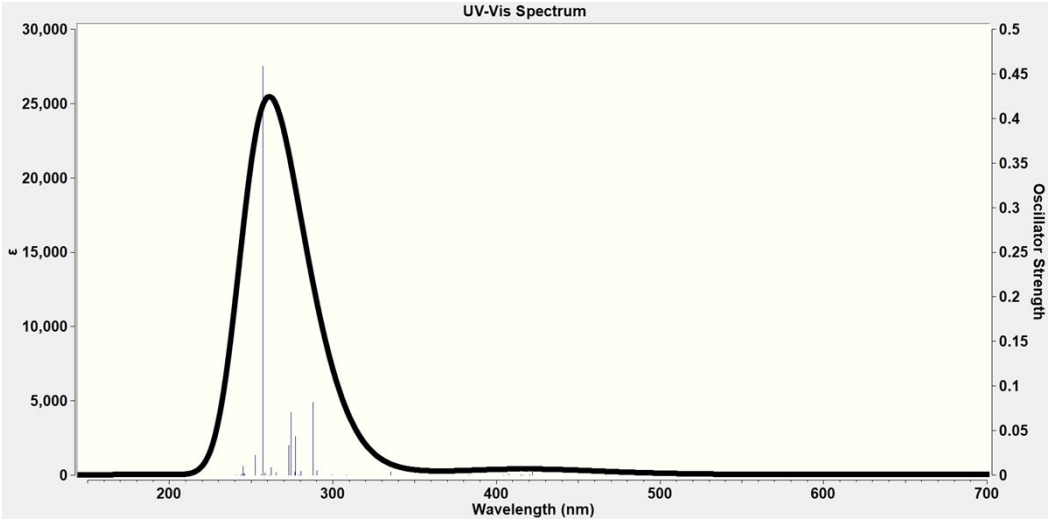


Figure S19. Calculated UV-vis spectrum of **1** at the time-dependent DFT (TD-DFT)//UB3LYP/6-311G(d) level.

Table S9 Calculated absorption properties of **1** including wavelength (nm), oscillator strength (*f*) and the related transition nature

Energy/ev	Wavelength/nm	Oscillator strength/ *f*	Transition nature and contributions
2.9225	424.24	0.0072	HOMO→LUMO +1 (0.70528)
3.6624	338.53	0.0037	HOMO→LUMO +9 (0.68847)
4.2577	291.20	0.0818	HOMO→LUMO +12 (0.69239)
4.7536	260.82	0.4586	HOMO→LUMO +15 (-0.14880) HOMO→LUMO +20 (0.67139)

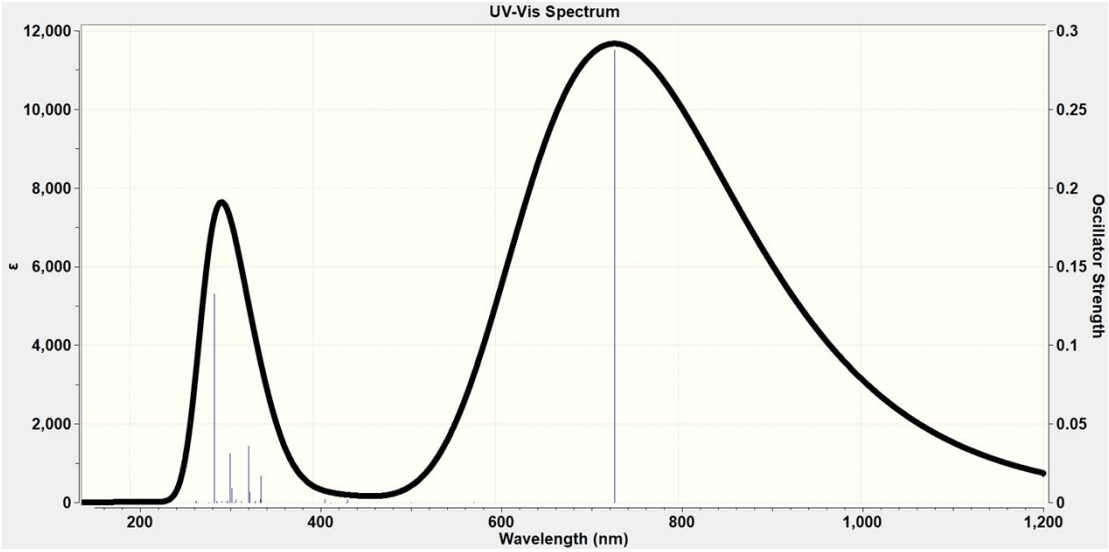


Figure S20. Calculated UV-vis spectrum of $\mathbf{1}^{\cdot+}$ at the time-dependent DFT (TD-DFT)//UB3LYP/6-311G(d) level (SCRF, SMD = DCM).

Table S10 Calculated absorption properties of $\mathbf{1}^{\cdot+}$ including wavelength (nm), oscillator strength (*f*) and the related transition nature

Energy/ev	Wavelength /nm	Oscillator strength/ *f*	Transition nature and contributions
1.6972	730.50	0.2879	SOMO–1 (β)→SOMO (β) (0.99531)
2.8278	438.45	0.0018	SOMO–3(β)→SOMO (β) (0.99749)
4.2388	292.50	0.1329	SOMO–13 (β)→SOMO+1(β) (0.54778) SOMO (α) →SOMO+12 (α) (0.59455)

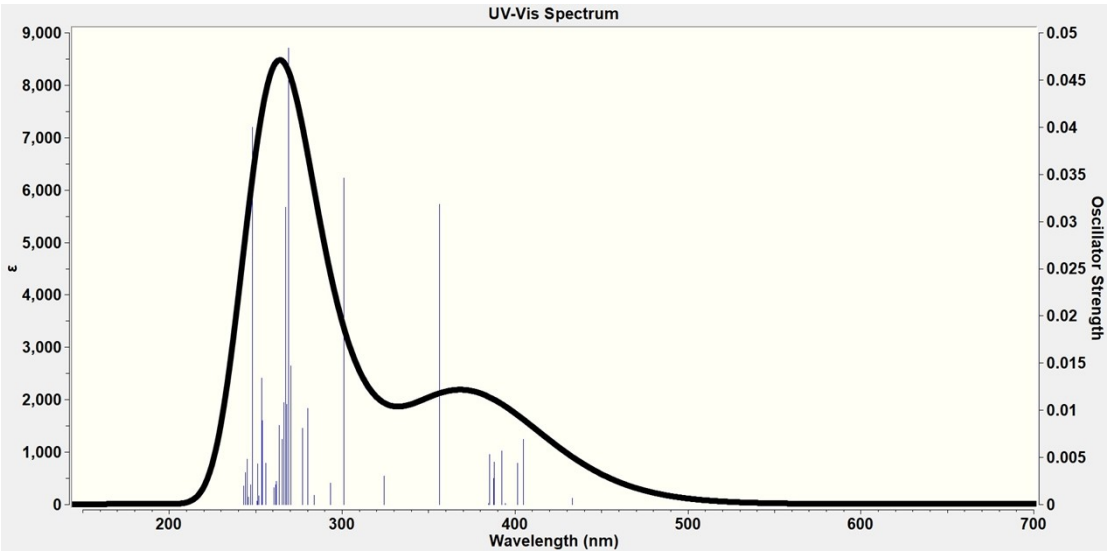


Figure S21. Calculated UV-vis spectrum of **2** at the time-dependent DFT (TD-

DFT)//UB3LYP/6-311G(d) level.

Table S11 Calculated absorption properties of **2** including wavelength (nm), oscillator strength (*f*) and the related transition nature

Energy/ev	Wavelength/nm	Oscillator strength/ *f*	Transition nature and contributions
3.0432	407.41	0.0069	HOMO→LUMO +1 (0.67660)
3.4519	359.18	0.0318	HOMO→LUMO +9 (0.69194)
4.0735	304.37	0.0346	HOMO→LUMO +11 (0.67468)
4.5748	271.02	0.0315	HOMO–1 →LUMO (-0.13157) HOMO–1 →LUMO +1 (0.25866) HOMO –1 →LUMO +3 (0.44573)

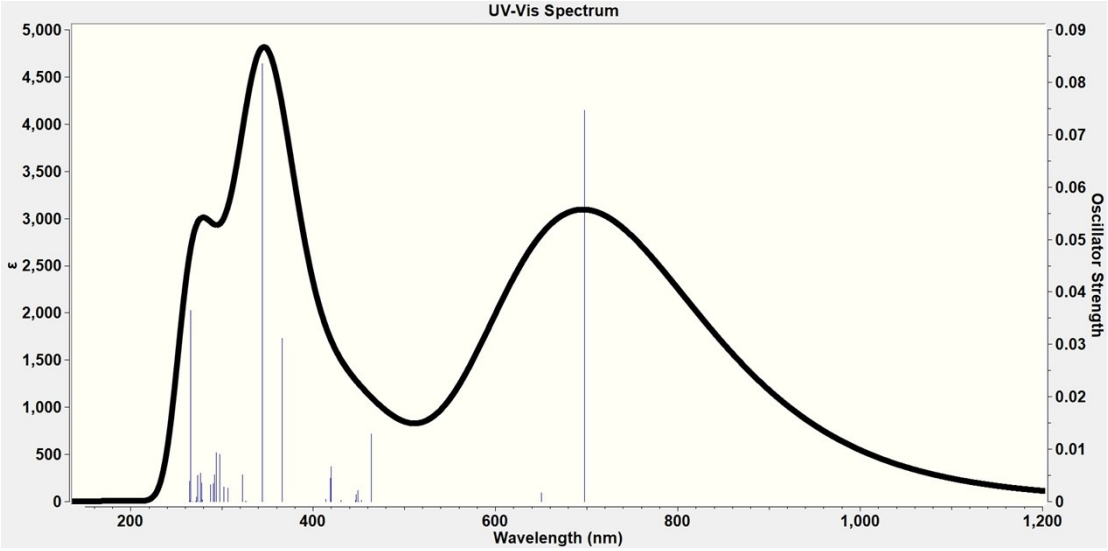


Figure S22. Calculated UV-vis spectrum of $\mathbf{2}^{\cdot+}$ at the time-dependent DFT (TD-DFT)//UB3LYP/6-311G(d) level. (SCRF, SMD = DCM).

Table S12 Calculated absorption properties of $\mathbf{2}^{\cdot+}$ including wavelength (nm), oscillator strength (*f*) and the related transition nature.

Energy /ev	Wavelength /nm	Oscillator strength/ *f*	Transition nature and contributions
1.7630	703.24	0.0746	SOMO–1 (β)→SOMO (β) (0.99719)
2.6278	471.81	0.0129	SOMO–11 (β)→SOMO (β) (-0.53680) SOMO–7 (β)→SOMO (β) (0.57996) SOMO–3 (β)→SOMO (β) (0.56758)

3.5084	353.39	0.0836	SOMO (α)→SOMO+2 (α) (0.83291)
4.5001	275.51	0.0365	SOMO-1 (α)→SOMO+2 (α) (0.56310) SOMO-1 (β)→SOMO+2 (β) (0.67014)

Coordinates for the optimized structure

1-CS at the B3LYP/6-311G(d) level

N	-3.79093600	1.12267100	0.25414400
N	-3.79092700	-1.12268700	-0.25415900
N	-1.45880100	-0.00000300	0.00000700
N	3.79092700	1.12268700	-0.25415600
N	1.45880100	0.00000300	0.00000800
N	3.79093600	-1.12267100	0.25414700
C	-3.55164300	2.48135500	0.64714400
C	3.55162300	2.48137200	-0.64714600
C	-0.66849800	-1.17892100	-0.00242700
H	-1.19965400	-2.11700700	-0.00811800
C	5.11547800	0.65611500	-0.14816300
H	5.95110000	1.31940800	-0.30763700
C	-5.11547800	-0.65611400	-0.14816800
H	-5.95110000	-1.31940600	-0.30764400
C	-3.56775000	3.49838400	-0.33220500
C	-5.11548300	0.65609300	0.14813200
H	-5.95110900	1.31938200	0.30759300
C	3.33613200	2.78250700	-2.00884600
C	5.11548300	-0.65609200	0.14813800
H	5.95110900	-1.31938200	0.30759900
C	3.55164400	-2.48135600	0.64714500
C	-3.33617500	2.78248500	2.00884800
C	-3.34753100	4.81679600	0.07748800
H	-3.35373900	5.61354100	-0.65950000
C	0.66850300	-1.17891800	0.00246100
H	1.19966300	-2.11700200	0.00816600
C	3.11474100	4.11626800	-2.36500700
H	2.94075400	4.36871100	-3.40617700
C	-0.66850300	1.17891800	0.00245300
H	-1.19966300	2.11700100	0.00815100
C	-3.55162200	-2.48137200	-0.64714900
C	-3.11847100	5.12662500	1.41207600
H	-2.94584700	6.15635500	1.70983100
C	3.56773800	3.49839700	0.33220800
C	-3.11479800	4.11624600	2.36501900

H	-2.94083000	4.36868500	3.40619300
C	0.66849700	1.17892100	-0.00243400
H	1.19965400	2.11700700	-0.00813100
C	-3.81699900	3.19945300	-1.80698700
H	-3.89487000	2.11602100	-1.91453500
C	3.34750400	4.81681000	-0.07747600
H	3.35371900	5.61355100	0.65951600
C	3.11842100	5.12664300	-1.41205900
H	2.94578500	6.15637300	-1.70980600
C	3.34530300	1.70783000	-3.09000500
H	3.53245900	0.75008700	-2.60135100
C	-3.34535200	1.70780300	3.09000300
H	-3.53249900	0.75006200	2.60134300
C	-3.56774000	-3.49839700	0.33220400
C	-3.33612900	-2.78250600	-2.00884900
C	3.56775100	-3.49838300	-0.33220600
C	3.33617600	-2.78248800	2.00884900
C	-5.14995500	3.80352600	-2.28514900
H	-5.99000700	3.43985600	-1.68803000
H	-5.34097600	3.53648700	-3.32899100
H	-5.14452900	4.89570700	-2.21850100
C	-3.34750700	-4.81681000	-0.07748100
H	-3.35372400	-5.61355200	0.65951000
B	-2.89931900	-0.00000600	-0.00000100
C	-3.11842200	-5.12664300	-1.41206400
H	-2.94578800	-6.15637300	-1.70981200
C	-3.34529400	-1.70782700	-3.09000700
H	-3.53245100	-0.75008500	-2.60135300
C	3.81701000	3.19946100	1.80698500
H	3.89489300	2.11602800	1.91452500
C	-3.11473900	-4.11626600	-2.36501100
H	-2.94075100	-4.36870900	-3.40618100
B	2.89931900	0.00000600	0.00000100
C	3.34753100	-4.81679600	0.07748500
H	3.35374000	-5.61354000	-0.65950400
C	-2.65192600	3.66640300	-2.69789600
H	-2.53115400	4.75345600	-2.67576900
H	-2.82946800	3.37874200	-3.73859700

H	-1.70425500	3.22070900	-2.38581600
C	-3.81701600	-3.19946200	1.80698000
H	-3.89488800	-2.11602900	1.91452300
C	3.11479900	-4.11624900	2.36501800
H	2.94083000	-4.36869000	3.40619100
C	3.11847100	-5.12662700	1.41207300
H	2.94584600	-6.15635700	1.70982600
C	3.34535300	-1.70780700	3.09000500
H	3.53249800	-0.75006500	2.60134500
C	-5.14998200	-3.80353200	2.28511800
H	-5.99002200	-3.43986200	1.68798300
H	-5.34102300	-3.53649200	3.32895600
H	-5.14455600	-4.89571400	2.21847200
C	-4.48539100	1.93245000	4.09972000
H	-4.36031800	2.86838700	4.65244700
H	-4.51420800	1.11946200	4.83160200
H	-5.45738000	1.96900400	3.60109300
C	1.98593700	1.60164500	-3.80363600
H	1.17781700	1.41116700	-3.09359600
H	1.99750100	0.78206900	-4.52864700
H	1.74236700	2.51859700	-4.34891700
C	3.81700100	-3.19945100	-1.80698700
H	3.89488000	-2.11601800	-1.91453200
C	5.14996700	3.80354400	2.28513100
H	5.99001400	3.43988400	1.68800000
H	5.34100500	3.53650200	3.32896900
H	5.14453100	4.89572500	2.21848900
C	4.48533100	1.93248700	-4.09973300
H	4.36024800	2.86842400	-4.65245500
H	4.51414500	1.11950100	-4.83161800
H	5.45732500	1.96904300	-3.60111500
C	-1.98592300	-1.60164200	-3.80363000
H	-1.17780700	-1.41116700	-3.09358600
H	-1.99748200	-0.78206300	-4.52863900
H	-1.74235200	-2.51859200	-4.34891300
C	-2.65196100	-3.66641000	2.69791200
H	-2.53118900	-4.75346400	2.67579300
H	-2.82952200	-3.37874600	3.73860900

H	-1.70428300	-3.22072000	2.38584900
C	-1.98599200	1.60162100	3.80364600
H	-1.17786400	1.41115000	3.09361300
H	-1.99755900	0.78204100	4.52865300
H	-1.74243200	2.51857100	4.34893400
C	4.48539200	-1.93245300	4.09972100
H	4.36032200	-2.86839100	4.65244500
H	4.51420700	-1.11946700	4.83160500
H	5.45738200	-1.96900300	3.60109300
C	-4.48531700	-1.93248200	-4.09974000
H	-4.36023400	-2.86842100	-4.65245900
H	-4.51412300	-1.11949800	-4.83162800
H	-5.45731400	-1.96903300	-3.60112800
C	2.65194500	3.66639500	2.69791200
H	2.53116300	4.75344700	2.67579400
H	2.82950300	3.37872900	3.73860800
H	1.70427300	3.22069500	2.38584100
C	5.14995200	-3.80353200	-2.28515200
H	5.99000700	-3.43987300	-1.68803100
H	5.34097600	-3.53648900	-3.32899200
H	5.14451700	-4.89571400	-2.21851100
C	1.98599300	-1.60162700	3.80364800
H	1.17786400	-1.41115600	3.09361700
H	1.99755900	-0.78204800	4.52865700
H	1.74243400	-2.51857800	4.34893500
C	2.65192300	-3.66638900	-2.69789500
H	2.53114000	-4.75344200	-2.67576800
H	2.82946700	-3.37873100	-3.73859700
H	1.70425600	-3.22068700	-2.38581500

1-T at the UB3LYP/6-311G(d) level

N	-3.76923300	-1.10121500	-0.32469800
N	-3.76923100	1.10122100	0.32470200
N	-1.42306500	0.00000100	-0.00000100
N	3.76923100	-1.10122100	0.32469900
N	1.42306500	-0.00000100	-0.00000200
N	3.76923400	1.10121500	-0.32469900
C	-3.52524000	-2.44816100	-0.76330000

C	3.52523300	-2.44816700	0.76329900
C	-0.70006400	1.17930700	-0.07753700
H	-1.24906100	2.10359800	-0.08641400
C	5.09096400	-0.64636700	0.19089600
H	5.92565600	-1.29936000	0.39095700
C	-5.09096400	0.64636600	0.19090000
H	-5.92565600	1.29935800	0.39096300
C	-3.61229700	-3.50097400	0.17290800
C	-5.09096500	-0.64635800	-0.19089200
H	-5.92565900	-1.29934900	-0.39095200
C	3.24119500	-2.69405100	2.12225200
C	5.09096600	0.64635800	-0.19089400
H	5.92566000	1.29934900	-0.39095500
C	3.52524100	2.44816100	-0.76330100
C	-3.24120300	-2.69404300	-2.12225400
C	-3.39455600	-4.80571900	-0.28079700
H	-3.45350200	-5.63145500	0.42099000
C	0.70006600	1.17930600	0.07753500
H	1.24906400	2.10359600	0.08641400
C	3.02626600	-4.01651800	2.52141000
H	2.79962700	-4.22929700	3.56113700
C	-0.70006500	-1.17930500	0.07753200
H	-1.24906300	-2.10359600	0.08640900
C	-3.52523400	2.44816600	0.76330300
C	-3.10030600	-5.06486300	-1.61291800
H	-2.93061000	-6.08479400	-1.94411500
C	3.61228900	-3.50097900	-0.17291100
C	-3.02627800	-4.01651100	-2.52141400
H	-2.79964000	-4.22928900	-3.56114200
C	0.70006400	-1.17930600	-0.07753900
H	1.24906100	-2.10359700	-0.08641800
C	-3.93136600	-3.26123800	1.64556400
H	-4.00402900	-2.18302300	1.79893300
C	3.39454400	-4.80572400	0.28079200
H	3.45348800	-5.63145900	-0.42099600
C	3.10029200	-5.06487000	1.61291200
H	2.93059300	-6.08480000	1.94410800
C	3.16582600	-1.57685600	3.15651900

H	3.37754000	-0.63576900	2.64560800
C	-3.16583200	-1.57684700	-3.15651900
H	-3.37754400	-0.63576100	-2.64560700
C	-3.61229400	3.50098000	-0.17290500
C	-3.24119100	2.69404900	2.12225600
C	3.61229800	3.50097400	0.17290800
C	3.24120400	2.69404500	-2.12225500
C	-5.29071300	-3.87161600	2.03358000
H	-6.09887000	-3.47742200	1.41212600
H	-5.53012400	-3.64503800	3.07695400
H	-5.29015800	-4.96015900	1.92330100
C	-3.39455000	4.80572500	0.28079800
H	-3.45349800	5.63146000	-0.42098800
B	-2.89037900	0.00000200	0.00000100
C	-3.10029400	5.06486900	1.61291800
H	-2.93059500	6.08479900	1.94411400
C	-3.16581700	1.57685300	3.15652100
H	-3.37753100	0.63576700	2.64561000
C	3.93135800	-3.26124200	-1.64556700
H	4.00402600	-2.18302700	-1.79893300
C	-3.02626200	4.01651600	2.52141400
H	-2.79962000	4.22929400	3.56114100
B	2.89037900	-0.00000200	-0.00000100
C	3.39455700	4.80571900	-0.28079500
H	3.45350300	5.63145400	0.42099200
C	-2.81445500	-3.77644600	2.57095700
H	-2.69176400	-4.86107900	2.49919300
H	-3.04701400	-3.54172500	3.61422200
H	-1.85414700	-3.31426500	2.33070700
C	-3.93137000	3.26124300	-1.64556000
H	-4.00403400	2.18302800	-1.79892700
C	3.02627900	4.01651300	-2.52141400
H	2.79964200	4.22929200	-3.56114100
C	3.10030700	5.06486500	-1.61291600
H	2.93061100	6.08479500	-1.94411300
C	3.16583400	1.57685000	-3.15652100
H	3.37754500	0.63576300	-2.64560900
C	-5.29071800	3.87162300	-2.03357000

H	-6.09887300	3.47743000	-1.41211200
H	-5.53013300	3.64504400	-3.07694300
H	-5.29016100	4.96016500	-1.92329200
C	-4.23404900	-1.74695700	-4.25168100
H	-4.07756000	-2.65959100	-4.83433800
H	-4.20488900	-0.90359900	-4.94827300
H	-5.23926000	-1.79479600	-3.82467500
C	1.75780800	-1.45945300	3.76647500
H	1.00159900	-1.30602700	2.99336600
H	1.71030000	-0.61259500	4.45777300
H	1.48568700	-2.35840300	4.32810700
C	3.93136600	3.26123600	1.64556400
H	4.00402900	2.18302100	1.79893200
C	5.29070400	-3.87162400	-2.03358300
H	6.09886200	-3.47743500	-1.41212900
H	5.53011500	-3.64504500	-3.07695700
H	5.29014400	-4.96016700	-1.92330700
C	4.23404400	-1.74697000	4.25168000
H	4.07755300	-2.65960400	4.83433600
H	4.20488500	-0.90361300	4.94827300
H	5.23925500	-1.79481000	3.82467300
C	-1.75779500	1.45945100	3.76647100
H	-1.00159000	1.30602800	2.99335900
H	-1.71028300	0.61259300	4.45776800
H	-1.48567400	2.35840100	4.32810300
C	-2.81446200	3.77644900	-2.57095700
H	-2.69176900	4.86108300	-2.49919500
H	-3.04702600	3.54172800	-3.61422100
H	-1.85415400	3.31426700	-2.33071100
C	-1.75781300	-1.45944600	-3.76647400
H	-1.00160400	-1.30602300	-2.99336500
H	-1.71030300	-0.61258700	-4.45777100
H	-1.48569400	-2.35839600	-4.32810700
C	4.23405200	1.74696000	-4.25168100
H	4.07756300	2.65959500	-4.83433800
H	4.20489200	0.90360300	-4.94827400
H	5.23926300	1.79479800	-3.82467400
C	-4.23403000	1.74696400	4.25168700

H	-4.07753700	2.65959900	4.83434300
H	-4.20486700	0.90360700	4.94827900
H	-5.23924200	1.79480400	3.82468400
C	2.81444600	-3.77644400	-2.57096000
H	2.69175000	-4.86107700	-2.49919900
H	3.04700600	-3.54172100	-3.61422500
H	1.85414000	-3.31425900	-2.33070900
C	5.29071300	3.87161500	2.03358100
H	6.09887000	3.47742300	1.41212800
H	5.53012200	3.64503500	3.07695600
H	5.29015600	4.96015800	1.92330400
C	1.75781500	1.45944900	-3.76647700
H	1.00160600	1.30602600	-2.99336900
H	1.71030500	0.61259200	-4.45777500
H	1.48569700	2.35840000	-4.32811000
C	2.81445400	3.77644300	2.57095700
H	2.69176200	4.86107600	2.49919500
H	3.04701200	3.54172000	3.61422200
H	1.85414700	3.31426100	2.33070500

1$^{\cdot+}$

N	-3.76972800	1.10545700	0.31458600
N	-3.76973000	-1.10534000	-0.31468200
N	-1.42773800	0.00005400	-0.00004500
N	3.76991900	1.10533400	-0.31442100
N	1.42787900	0.00000800	0.00007500
N	3.76979400	-1.10544100	0.31490800
C	-3.50615100	2.45399100	0.75591100
C	3.50631900	2.45376800	-0.75602800
C	-0.67587500	-1.17030800	-0.00079100
H	-1.21803300	-2.10229400	-0.00653800
C	5.08643100	0.64992600	-0.18636400
H	5.92215000	1.30214200	-0.38333200
C	-5.08626200	-0.64994200	-0.18683300
H	-5.92194200	-1.30219000	-0.38386500
C	-3.49953900	3.49596300	-0.19646100
C	-5.08626000	0.65008800	0.18666100
H	-5.92193800	1.30234900	0.38365800

C	3.29044400	2.69574600	-2.12841900
C	5.08635700	-0.65008400	0.18720300
H	5.92199800	-1.30232800	0.38441100
C	3.50602600	-2.45391900	0.75627500
C	-3.29040100	2.69625700	2.12827600
C	-3.24370100	4.79304900	0.25877800
H	-3.23692500	5.61542500	-0.44829700
C	0.67599300	-1.17032500	-0.00003300
H	1.21813400	-2.10232700	0.00504000
C	3.03501100	4.01208700	-2.52547500
H	2.86658600	4.22955900	-3.57469600
C	-0.67583700	1.17039100	0.00076200
H	-1.21796900	2.10239300	0.00645200
C	-3.50617300	-2.45384900	-0.75609900
C	-3.00788600	5.05113700	1.60330900
H	-2.81416600	6.06597500	1.93487500
C	3.49977300	3.49595000	0.19612900
C	-3.03505700	4.01268300	2.52508400
H	-2.86674800	4.23038500	3.57427400
C	0.67603100	1.17036700	0.00011600
H	1.21819800	2.10235400	-0.00492700
C	-3.78400200	3.25913800	-1.67713000
H	-3.84906600	2.18069700	-1.83965800
C	3.24385600	4.79292800	-0.25935300
H	3.23713800	5.61545700	0.44754300
C	3.00789400	5.05072800	-1.60391900
H	2.81410000	6.06549100	-1.93567100
C	3.35327600	1.59345700	-3.18083800
H	3.53448000	0.64638600	-2.66753500
C	-3.35331400	1.59415900	3.18089300
H	-3.53407600	0.64693800	2.66771100
C	-3.49972900	-3.49591300	0.19617500
C	-3.29028300	-2.69600100	-2.12846200
C	3.49962800	-3.49599600	-0.19599500
C	3.28984900	-2.69603100	2.12859300
C	-5.14207100	3.86283100	-2.08237700
H	-5.95823600	3.45996600	-1.47786500
H	-5.36239600	3.64348100	-3.13069300

H	-5.14866700	4.94966100	-1.96259900
C	-3.24390000	-4.79296900	-0.25915300
H	-3.23725500	-5.61541100	0.44784600
B	-2.90620200	0.00006500	-0.00006500
C	-3.00793200	-5.05094400	-1.60367900
H	-2.81421800	-6.06576000	-1.93531600
C	-3.35304000	-1.59381900	-3.18099600
H	-3.53394200	-0.64664600	-2.66777300
C	3.78444100	3.25941500	1.67680600
H	3.84915200	2.18099100	1.83960200
C	-3.03495100	-4.01240300	-2.52536000
H	-2.86653100	-4.23001400	-3.57455200
B	2.90634800	-0.00003100	0.00016000
C	3.24355800	-4.79301400	0.25930000
H	3.23694600	-5.61546800	-0.44768400
C	-2.65991300	3.79082000	-2.58445100
H	-2.56471800	4.87800600	-2.52466500
H	-2.86639200	3.54124100	-3.62871200
H	-1.68825000	3.36020500	-2.32628300
C	-3.78435700	-3.25921600	1.67683400
H	-3.84943900	-2.18079000	1.83945200
C	3.03429200	-4.01240100	2.52546200
H	2.86565100	-4.22997900	3.57462400
C	3.00731900	-5.05094600	1.60378900
H	2.81342000	-6.06573600	1.93539900
C	3.35248900	-1.59383000	3.18111600
H	3.53391800	-0.64673800	2.66793300
C	-5.14246800	-3.86294700	2.08187700
H	-5.95856700	-3.46002700	1.47731100
H	-5.36291100	-3.64369200	3.13018800
H	-5.14905600	-4.94976600	1.96200100
C	-4.53118900	1.81398300	4.14839000
H	-4.41392600	2.73517200	4.72543700
H	-4.60162300	0.98644500	4.85972600
H	-5.48183600	1.87791500	3.61351500
C	2.02779200	1.45199700	-3.95036700
H	1.18666700	1.26871300	-3.27575500
H	2.08183600	0.61628100	-4.65352300

H	1.79616800	2.34988600	-4.52941800
C	3.78463200	-3.25934300	-1.67658900
H	3.84933300	-2.18090500	-1.83930000
C	5.14281600	3.86274400	2.08158700
H	5.95871600	3.45940900	1.47703300
H	5.36328800	3.64364900	3.12992600
H	5.14975400	4.94953300	1.96145200
C	4.53072600	1.81336400	-4.14882800
H	4.41301900	2.73436200	-4.72608300
H	4.60111300	0.98565900	-4.85997500
H	5.48155300	1.87768000	-3.61431800
C	-2.02767500	-1.45271500	-3.95079400
H	-1.18636700	-1.26961400	-3.27636200
H	-2.08166000	-0.61700700	-4.65396200
H	-1.79638800	-2.35067000	-4.52987800
C	-2.66036500	-3.79098000	2.58422900
H	-2.56514500	-4.87815600	2.52433200
H	-2.86697100	-3.54151700	3.62849400
H	-1.68868000	-3.36031700	2.32622300
C	-2.02809600	1.45317000	3.95096000
H	-1.18664200	1.27008800	3.27670200
H	-2.08217500	0.61748400	4.65414900
H	-1.79697200	2.35115500	4.53006000
C	4.52964600	-1.81391000	4.14942200
H	4.41165400	-2.73490700	4.72662500
H	4.59994600	-0.98623100	4.86060800
H	5.48061300	-1.87834400	3.61517700
C	-4.53071400	-1.81360200	-4.14874600
H	-4.41327000	-2.73469800	-4.72590200
H	-4.60107400	-0.98597000	-4.85998100
H	-5.48145900	-1.87768100	-3.61406300
C	2.66077100	3.79173300	2.58426700
H	2.56604200	4.87895200	2.52436100
H	2.86735700	3.54221200	3.62852000
H	1.68886000	3.36151100	2.32637000
C	5.14313200	-3.86257800	-2.08109000
H	5.95887100	-3.45924100	-1.47632200
H	5.36383700	-3.64340800	-3.12936500

H	5.15009100	-4.94937500	-1.96102200
C	2.02679900	-1.45230500	3.95028600
H	1.18587700	-1.26892000	3.27545000
H	2.08071300	-0.61663300	4.65350400
H	1.79494800	-2.35021000	4.52922200
C	2.66120900	-3.79165800	-2.58435700
H	2.56657100	-4.87889300	-2.52460200
H	2.86800300	-3.54199700	-3.62853600
H	1.68919800	-3.36156100	-2.32662800

2-CS at the B3LYP/6-311G(d) level

N	-1.44094300	0.13749100	0.07788800
N	-3.91931600	-0.73370800	0.34402900
N	-3.61712300	1.27231300	-0.72734600
N	1.42927100	-0.11193700	0.05982700
N	3.91236100	0.71446200	0.39863900
N	3.60737700	-1.20452700	-0.81570300
C	-0.71498900	-0.02571000	1.28719300
C	0.70123300	-0.17362900	1.27469500
C	-3.83304800	-2.04426100	0.92844900
C	-1.37162800	-0.02128700	2.51492800
H	-2.44317700	0.13480600	2.52736700
C	-3.16912400	2.52708300	-1.26357900
C	3.82563800	1.97464600	1.08706200
C	1.35688000	-0.39611900	2.48300000
H	2.42978800	-0.54500700	2.46959600
C	-5.15716500	-0.23889300	-0.10022600
H	-6.06865500	-0.79201800	0.05719800
C	3.15382300	-2.40410800	-1.46419400
C	-4.34870000	-2.26590200	2.22628800
C	4.28141900	2.07481600	2.42102700
C	2.99431200	-2.41520200	-2.86701500
C	-4.98076200	0.94021400	-0.72883600
H	-5.71744400	1.59227800	-1.17053300
C	-3.06484600	2.68509300	-2.66358200
C	-3.28797400	-3.10484600	0.17296800
C	5.15056300	0.24781300	-0.07028500
H	6.06427300	0.78118800	0.13630800

C	4.97210800	-0.88260900	-0.78440400
H	5.70770000	-1.50366700	-1.27072700
C	0.67479300	-0.42622000	3.70222800
H	1.22131900	-0.60844000	4.62097900
C	-5.01807300	-1.16731000	3.04902200
H	-4.81075800	-0.21063000	2.56422700
C	-0.69228800	-0.21978400	3.71987800
H	-1.24002000	-0.21018200	4.65571700
C	-4.27084600	-3.55540200	2.75912100
H	-4.65944500	-3.74542500	3.75400300
C	3.34316800	3.10783600	0.39686000
C	-3.70234400	-4.59971100	2.04290700
H	-3.64378500	-5.59208100	2.47932300
C	-2.84460900	-2.94569800	-1.27769200
H	-2.87470700	-1.88378600	-1.52516100
C	4.20301400	3.31720800	3.05645500
H	4.54495700	3.41415100	4.08133900
C	-2.88635400	3.59534500	-0.38629800
C	-3.39506000	1.55885500	-3.63937200
H	-3.50635600	0.63885400	-3.06102000
C	-3.22227700	-4.37170200	0.76134900
H	-2.80182000	-5.19787600	0.19771400
C	2.59650900	-3.60687100	-3.47955100
H	2.47208600	-3.63847800	-4.55696400
C	-4.47649000	-1.08620400	4.48770100
H	-4.77962100	-1.94949900	5.08666100
H	-4.86541700	-0.19488600	4.98898600
H	-3.38695600	-1.04018700	4.50701300
C	-2.66700900	3.92826600	-3.16296000
H	-2.58511600	4.07227700	-4.23529300
C	4.89476900	0.89780100	3.17488500
H	4.68527000	-0.01065900	2.60582200
C	3.27264700	-1.18819200	-3.72982200
H	3.39476800	-0.33277600	-3.06156200
C	-0.66194200	0.23189600	-1.09984400
H	-1.20539000	0.39653500	-2.01693700
C	2.92825900	-3.56471700	-0.69464200
C	3.27636000	4.32333500	1.08475400

H	2.90480300	5.20444400	0.57256500
C	3.69433200	4.43125700	2.40347100
H	3.63490000	5.38521300	2.91837000
C	0.66317800	0.09482000	-1.10974400
H	1.21609200	0.17125600	-2.03340900
C	2.35875200	-4.75441200	-2.73459200
H	2.04879600	-5.67000400	-3.22886200
C	-6.54905000	-1.34519000	3.08024300
H	-6.98145600	-1.35643700	2.07765000
H	-7.02062000	-0.52993600	3.63759500
H	-6.82526300	-2.28522200	3.56717300
C	-2.37226600	4.98516400	-2.31165300
H	-2.06177900	5.94239900	-2.71904200
C	2.52446900	-4.72827700	-1.35667500
H	2.34602400	-5.63196000	-0.78329500
C	-2.48163100	4.81469200	-0.93849300
H	-2.25839300	5.64827100	-0.28068500
C	-3.05049700	3.48397600	1.12532200
H	-3.30402100	2.44857000	1.35799000
C	2.97941100	3.07855200	-1.08398600
H	2.95209300	2.03556700	-1.40258600
C	-2.27813100	1.32395400	-4.67246500
H	-2.18103900	2.16210000	-5.36806400
H	-2.49407500	0.43263600	-5.26874700
H	-1.30533800	1.18173100	-4.19542200
C	-4.73573600	1.81209600	-4.35493000
H	-5.55769400	1.92073700	-3.64396100
H	-4.98017600	0.98071400	-5.02315900
H	-4.69666100	2.72446900	-4.95764900
B	-2.89551700	0.21627100	-0.04857100
C	4.59012900	-1.34218500	-4.51332400
H	5.43782500	-1.50846100	-3.84478000
H	4.79867300	-0.44199800	-5.09960300
H	4.54298600	-2.18804200	-5.20578900
C	3.15744100	-3.60764600	0.81199800
H	3.36727000	-2.59022600	1.14562100
C	4.29787300	0.71554900	4.58189100
H	4.60258000	1.51706000	5.26065100

H	4.64438100	-0.22487500	5.02099300
H	3.20752100	0.70072100	4.55815500
B	2.88675600	-0.19813400	-0.06797200
C	2.11357500	-0.86613100	-4.69005000
H	2.00422600	-1.62610200	-5.46869100
H	2.29128700	0.08843700	-5.19416200
H	1.15895200	-0.79886800	-4.16280100
C	-4.21957300	4.35668600	1.61960800
H	-4.03446100	5.41944200	1.43652600
H	-4.36614300	4.22739900	2.69633800
H	-5.15465500	4.09194800	1.11913300
C	6.42717900	1.03483300	3.27148300
H	6.89420700	1.11104000	2.28734500
H	6.86032700	0.16792500	3.77994200
H	6.70673100	1.92789300	3.83836500
C	-3.83025300	-3.65566000	-2.22606100
H	-3.84869100	-4.73544100	-2.05017400
H	-3.54232500	-3.49480200	-3.26973400
H	-4.84910500	-3.28127600	-2.09660900
C	4.07129500	3.77534400	-1.91943800
H	4.15470300	4.83541700	-1.66137000
H	3.83943900	3.71045800	-2.98720600
H	5.05057300	3.31690800	-1.75961300
C	-1.75347800	3.81785500	1.88099700
H	-0.92687800	3.18269700	1.55730700
H	-1.88813100	3.66277100	2.95527300
H	-1.45393800	4.85999200	1.73567700
C	4.39300600	-4.46091300	1.15630600
H	4.25472600	-5.50517500	0.86009800
H	4.58305000	-4.44464000	2.23390800
H	5.28863500	-4.08897600	0.65197200
C	-1.40598400	-3.42975400	-1.51466400
H	-0.69730900	-2.91004800	-0.86819400
H	-1.10485200	-3.24373900	-2.54930100
H	-1.30040700	-4.50347200	-1.33528700
C	1.59681300	3.68216100	-1.37456700
H	0.81270700	3.18510200	-0.80152600
H	1.34951700	3.57352800	-2.43453100

H	1.55869200	4.75054000	-1.14359300
C	1.91912200	-4.09493700	1.58248300
H	1.04387800	-3.47988100	1.36544100
H	2.09883000	-4.04509700	2.66023300
H	1.67024300	-5.13254900	1.34108800

2-T at the UB3LYP/6-311G(d) level

N	1.41099200	0.13324000	-0.05673200
N	3.91837100	-0.67444800	-0.22136400
N	3.56397900	1.45746500	0.54349400
N	-1.41099100	-0.13324100	-0.05673200
N	-3.91836900	0.67444900	-0.22136500
N	-3.56398000	-1.45746300	0.54349700
C	0.72572400	0.07179500	-1.26731500
C	-0.72572100	-0.07180600	-1.26731500
C	3.86030900	-2.04940500	-0.64770200
C	1.38579100	0.17019500	-2.50613900
H	2.46101700	0.31019400	-2.51038600
C	3.06937200	2.73418000	0.98803900
C	-3.86030600	2.04940500	-0.64770800
C	-1.38578800	-0.17021500	-2.50613800
H	-2.46101500	-0.31021400	-2.51038400
C	5.14589700	-0.08151500	0.11521900
H	6.07303700	-0.62204700	0.01461800
C	-3.06937400	-2.73417700	0.98804600
C	4.28344400	-2.39235600	-1.95131500
C	-4.28343700	2.39235100	-1.95132300
C	-2.93075200	-2.97183300	2.37306100
C	4.93822700	1.17564100	0.56053600
H	5.65673300	1.91124900	0.88537500
C	2.93075400	2.97184200	2.37305300
C	3.43962600	-3.03900100	0.26657100
C	-5.14589600	0.08151800	0.11521800
H	-6.07303600	0.62205100	0.01461600
C	-4.93822700	-1.17563700	0.56053700
H	-5.65673400	-1.91124400	0.88537700
C	-0.70800400	-0.09464700	-3.70348900

H	-1.24813900	-0.18303700	-4.63911700
C	4.84056400	-1.36989400	-2.93804800
H	4.62752700	-0.37313800	-2.54608500
C	0.70800700	0.09461800	-3.70349000
H	1.24814100	0.18300300	-4.63911800
C	4.22913900	-3.73641000	-2.33064200
H	4.54457700	-4.02088600	-3.32862700
C	-3.43962600	3.03900400	0.26656300
C	3.77755700	-4.71613900	-1.45738100
H	3.73542000	-5.75303000	-1.77630100
C	3.11527800	-2.73419000	1.72526100
H	3.08244100	-1.65000900	1.84306800
C	-4.22913100	3.73640400	-2.33065400
H	-4.54456800	4.02087700	-3.32864100
C	2.78933400	3.73998800	0.04035900
C	3.26563000	1.91680500	3.42303400
H	3.41088100	0.96555100	2.90635300
C	3.39504000	-4.36638200	-0.17044200
H	3.06763800	-5.14082900	0.51495300
C	-2.49787700	-4.23411800	2.78724000
H	-2.38735100	-4.44025700	3.84664400
C	4.19160500	-1.47073200	-4.32976400
H	4.47785100	-2.39082100	-4.84705500
H	4.51659500	-0.63590700	-4.95823400
H	3.10265800	-1.44743800	-4.26815200
C	2.49787900	4.23412800	2.78722800
H	2.38735500	4.44027200	3.84663200
C	-4.84055700	1.36988500	-2.93805300
H	-4.62752000	0.37313100	-2.54608600
C	-3.26562700	-1.91679200	3.42303700
H	-3.41087800	-0.96554100	2.90635200
C	0.70358100	0.08911200	1.12169700
H	1.26495300	0.10032900	2.04069900
C	-2.78933800	-3.73998900	0.04036900
C	-3.39503900	4.36638300	-0.17045400
H	-3.06763900	5.14083200	0.51493900
C	-3.77755200	4.71613600	-1.45739500
H	-3.73541500	5.75302600	-1.77631900

C	-0.70358000	-0.08910500	1.12169800
H	-1.26495300	-0.10030800	2.04070000
C	-2.20389200	-5.23203900	1.86649600
H	-1.86623800	-6.20561400	2.20836700
C	6.37227900	-1.49495200	-3.05956000
H	6.87042500	-1.37472000	-2.09487200
H	6.76802700	-0.73196900	-3.73686800
H	6.65733300	-2.47355000	-3.45714200
C	2.20389100	5.23204600	1.86648200
H	1.86623800	6.20562200	2.20834900
C	-2.34917200	-4.98246600	0.50948700
H	-2.12578500	-5.77012000	-0.20225100
C	2.34916800	4.98246600	0.50947300
H	2.12577900	5.77011800	-0.20226800
C	2.99196000	3.54170500	-1.45726800
H	3.22329300	2.48926200	-1.62688700
C	-3.11528300	2.73419800	1.72525500
H	-3.08244600	1.65001700	1.84306600
C	2.13048400	1.72021100	4.44360400
H	2.00324400	2.59506600	5.08714600
H	2.34869200	0.86939200	5.09597300
H	1.17406500	1.53440700	3.94969600
C	4.58570800	2.24574000	4.14592500
H	5.41894000	2.32641500	3.44418600
H	4.83421800	1.46478100	4.87113000
H	4.51530900	3.19380600	4.68745700
B	2.88473400	0.29250500	0.04603200
C	-4.58570400	-2.24572400	4.14593200
H	-5.41893700	-2.32640200	3.44419300
H	-4.83421300	-1.46476200	4.87113400
H	-4.51530400	-3.19378800	4.68746700
C	-2.99196900	-3.54171200	-1.45725800
H	-3.22329800	-2.48926900	-1.62688100
C	-4.19159600	1.47071800	-4.32976800
H	-4.47784000	2.39080500	-4.84706300
H	-4.51658600	0.63589100	-4.95823500
H	-3.10264900	1.44742300	-4.26815400
B	-2.88473300	-0.29250400	0.04603200

C	-2.13048000	-1.72019400	4.44360500
H	-2.00323900	-2.59504600	5.08715100
H	-2.34868600	-0.86937200	5.09597100
H	-1.17406100	-1.53439200	3.94969500
C	4.19770300	4.35747800	-1.96163200
H	4.03604400	5.43221700	-1.83462900
H	4.36857100	4.17153800	-3.02641100
H	5.11245200	4.09426800	-1.42387700
C	-6.37227100	1.49494300	-3.05956600
H	-6.87041800	1.37471700	-2.09487800
H	-6.76802000	0.73195800	-3.73687100
H	-6.65732500	2.47354000	-3.45715400
C	4.23615600	-3.25332700	2.64695000
H	4.32581600	-4.34240500	2.59272500
H	4.03134800	-2.98849600	3.68903700
H	5.20565500	-2.82712800	2.37630100
C	-4.23616300	3.25333700	2.64693900
H	-4.32582300	4.34241500	2.59271100
H	-4.03135900	2.98850900	3.68902800
H	-5.20566200	2.82713700	2.37628800
C	1.72698600	3.86667000	-2.26895100
H	0.87277000	3.27803800	-1.92997800
H	1.88538900	3.63720000	-3.32614000
H	1.45849200	4.92500700	-2.19975100
C	-4.19771900	-4.35748100	-1.96161300
H	-4.03606400	-5.43222000	-1.83460500
H	-4.36859000	-4.17154600	-3.02639200
H	-5.11246400	-4.09426400	-1.42385500
C	1.74696000	-3.28199600	2.16024800
H	0.94247000	-2.90301500	1.52783700
H	1.53032900	-2.98327200	3.19050800
H	1.71330200	-4.37462600	2.12854300
C	-1.74696600	3.28200600	2.16024500
H	-0.94247400	2.90302200	1.52783700
H	-1.53033800	2.98328500	3.19050700
H	-1.71330800	4.37463600	2.12853600
C	-1.72700100	-3.86668700	-2.26894500
H	-0.87278000	-3.27805600	-1.92997800

H	-1.88540700	-3.63722000	-3.32613400
H	-1.45851100	-4.92502500	-2.19974200

2$^{\cdot+}$

N	3.53269800	-1.40475400	0.70492100
N	1.41230900	-0.13396900	-0.07603100
N	-3.94162500	-0.59593200	-0.34606100
N	-1.41231200	0.13396500	-0.07602700
N	3.94161600	0.59593000	-0.34611200
N	-3.53268500	1.40478500	0.70490200
C	4.91188200	-1.15390700	0.69270600
H	5.61184400	-1.85619600	1.11573200
C	-0.70807800	0.07275900	-1.28921100
C	1.38234900	-0.16850900	-2.51147900
H	2.45585200	-0.30013300	-2.50958200
C	2.99804700	-2.61893200	1.27299200
C	3.90627700	1.91665500	-0.93032300
C	3.22313900	-1.57286500	3.61975100
H	3.40352500	-0.67663900	3.01955700
C	0.70806000	-0.07287400	-1.28921200
C	-5.15080600	-0.02797400	0.08411400
H	-6.08972600	-0.53276100	-0.07192200
C	5.15080400	0.02799300	0.08406800
H	6.08972000	0.53278100	-0.07199700
C	-2.20834100	4.87594300	1.00732100
H	-1.97590900	5.72803600	0.37794900
C	2.34813000	-3.90445300	3.20208300
H	2.22209400	-4.00341700	4.27460200
C	2.20838300	-4.87591000	1.00747900
H	1.97596500	-5.72803400	0.37814300
C	-0.67690200	0.06783800	1.07851600
H	-1.22092700	0.11672300	2.00864700
C	0.67691300	-0.06773600	1.07851500
H	1.22094900	-0.11653800	2.00864400
C	-3.45990800	-3.00121100	-0.14519400
C	-2.83736200	2.70684100	2.67311000
C	2.11431500	-1.23788200	4.63397800

H	1.96137400	-2.04471200	5.35469200
H	1.15109100	-1.05427300	4.14861600
H	2.37983100	-0.34440800	5.20534200
C	-2.99802500	2.61898200	1.27292500
C	-2.03107100	4.97844200	2.38026500
H	-1.65771000	5.90095500	2.81263500
C	0.69234600	-0.09169900	-3.70879700
H	1.23089300	-0.17143100	-4.64534400
C	-1.38237900	0.16828600	-2.51147900
H	-2.45588100	0.29991500	-2.50958300
C	-4.91187000	1.15394500	0.69271000
H	-5.61182400	1.85625200	1.11571900
C	2.03109700	-4.97834900	2.38042600
H	1.65773800	-5.90084500	2.81283300
C	2.70010100	-3.70431300	0.42332600
C	-3.90630300	-1.91667200	-0.93023900
C	-0.69239000	0.09136500	-3.70879700
H	-1.23094600	0.17101100	-4.64534600
C	4.37192900	2.10371900	-2.25125600
C	-2.34812000	3.90458400	3.20196600
H	-2.22209600	4.00359500	4.27448200
C	2.94835000	-3.67078000	-1.08110100
H	3.23821700	-2.65316400	-1.35270800
C	-6.51265100	-1.08891300	-3.13798700
H	-6.82338300	-2.01749700	-3.62439000
H	-6.94022000	-0.25677500	-3.70420100
H	-6.95852600	-1.07766500	-2.14146400
C	-3.22314500	1.57302100	3.61972900
H	-3.40354500	0.67677200	3.01957500
C	-4.37201500	-2.10377300	-2.25114500
C	6.51251900	1.08880800	-3.13815300
H	6.82324700	2.01739900	-3.62454400
H	6.94005100	0.25667700	-3.70440400
H	6.95843200	1.07752600	-2.14164700
C	3.11200200	2.86862900	1.33445900
H	3.06397100	1.80485700	1.57919700
C	-3.11192200	-2.86858200	1.33453200
H	-3.06386200	-1.80480400	1.57923700

C	-4.97509700	-0.97885100	-3.08966800
H	-4.73469100	-0.02694100	-2.60807200
C	3.45993100	3.00121900	-0.14528300
C	-2.70006200	3.70432400	0.42321500
C	4.53816000	-1.89085400	4.35804400
H	4.82940400	-1.05762500	5.00357900
H	5.35853100	-2.07561400	3.66135500
H	4.43289300	-2.77916600	4.98677400
B	2.89989100	-0.30525600	0.04630600
C	2.83736900	-2.70672900	2.67318000
C	4.97496600	0.97877100	-3.08977500
H	4.73456400	0.02687500	-2.60814800
C	-1.68981400	4.02269400	-1.89305800
H	-1.37210400	5.05508900	-1.72617200
H	-1.88515100	3.91463100	-2.96355800
H	-0.84797000	3.37357600	-1.63921700
B	-2.89989100	0.30526200	0.04631600
C	-3.42529400	-4.26808300	-0.73597100
H	-3.08633100	-5.11821500	-0.15438600
C	-4.53815900	1.89105700	4.35801600
H	-4.43287100	2.77938100	4.98672500
H	-4.82942000	1.05784900	5.00357100
H	-5.35852600	2.07581900	3.66132300
C	-4.41591400	-0.93150800	-4.52339700
H	-4.76466200	-1.77432400	-5.12496200
H	-3.32441400	-0.95289800	-4.53854500
H	-4.74818500	-0.02079700	-5.02905600
C	-2.11432200	1.23806500	4.63396600
H	-1.15109600	1.05444900	4.14861200
H	-2.37983500	0.34460400	5.20535100
H	-1.96138500	2.04491400	5.35466100
C	4.41572600	0.93140600	-4.52348300
H	3.32422700	0.95288200	-4.53859100
H	4.74790900	0.02064500	-5.02911200
H	4.76452100	1.77416600	-5.12509900
C	1.75037400	3.48760400	1.68897800
H	1.74772700	4.57220100	1.55632200
H	1.50467800	3.29505100	2.73708400

H	0.94285000	3.08217400	1.07488300
C	-1.75029300	-3.48757000	1.68902500
H	-1.74766400	-4.57217000	1.55639300
H	-1.50456300	-3.29499700	2.73711800
H	-0.94278100	-3.08216400	1.07489800
C	-4.32419800	-3.39478100	-2.78472800
H	-4.67519000	-3.56690600	-3.79596300
C	4.12432900	-4.58953200	-1.46429400
H	5.03671500	-4.31736800	-0.92815600
H	4.33174700	-4.52169600	-2.53601600
H	3.90599900	-5.63614400	-1.23536200
C	-3.84309800	-4.46587100	-2.04433800
H	-3.81308800	-5.45866700	-2.48109900
C	4.23088800	3.47240800	2.20606200
H	5.19586300	3.00288400	2.00094000
H	4.00873100	3.33506800	3.26837200
H	4.33990200	4.54524500	2.02575300
C	1.68992700	-4.02288700	-1.89295500
H	1.37232200	-5.05531400	-1.72606600
H	1.88526800	-3.91481300	-2.96345400
H	0.84801200	-3.37385300	-1.63913100
C	-2.94828400	3.67072500	-1.08121600
H	-3.23822200	2.65311700	-1.35277200
C	-4.12418400	4.58954400	-1.46448800
H	-5.03660100	4.31748500	-0.92834800
H	-4.33158900	4.52165400	-2.53620900
H	-3.90578000	5.63615500	-1.23562200
C	4.32409700	3.39471400	-2.78486900
H	4.67503900	3.56680800	-3.79612700
C	-4.23078900	-3.47231400	2.20619300
H	-5.19576100	-3.00277200	2.00109700
H	-4.00858700	-3.33495500	3.26849000
H	-4.33983600	-4.54515300	2.02591200
C	3.84304300	4.46582700	-2.04448300
H	3.81302100	5.45861200	-2.48126800
C	3.42530300	4.26807700	-0.73609100
H	3.08637600	5.11822600	-0.15451000

6. References

S1. D. Herrmanndörfer, M. Kaaz, O. Puntigam, J. Bender, M. Nieger, D. Gudat, *Eur. J. Inorg. Chem.*, 2015, 4819−4828.

S2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

S3. T. Lu, F. Chen, *J. Comput. Chem*. 2012, **33**, 580−592.

S4. W. Humphrey, A. Dalke, K. Schulten, *J. Molec. Graphics,* 1996, **14.1**, 33−38.

S5. (a) V. Bachler, G. Olbrich, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 4179–4193; (b) D. Herebian, E. Bothe, F. Neese, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2003, **125**, 9116–9128; (c) D. Herebian, K. E. Wieghardt and F. Neese, *J. Am. Chem. Soc.*, 2003, **125**, 10997–11005; (d) F. Neese, *J. Phys. Chem. Solids*, 2004, **65**, 781–785.