Supporting Information

Cyclic(alkyl)(amino)carbene (CAAC) and Bicyclic (alkyl)(amino)carbene (BICAAC) Derived Glyoxal Radical Cations with Excellent Stability

Bindusagar Das, Ritu Yadav, Ankita Sharma, Tarak Karmakar*, Subrata Kundu*

Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India

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Materials and Methods:

Storage and manipulation of all the air sensitive compounds were performed under an inert atmosphere either in a dinitrogen-filled Jacomex glovebox equipped with a cold-well; or using a dinitrogen Schlenk line using standard techniques. Toluene, hexane, THF were dried over sodium-potassium allov and vacuum distilled over activated 4 Å molecular sieves and stored prior to use. CAAC and BICAAC were prepared from the reported procedure. ^{S1,2} Oxalyl chloride was purchased from Sigma-Aldrich and distilled before use. ¹H and ¹³C{¹H} NMR was recorded using Brucker-DPX-400 or 500 MHz spectrometers and tetramethylsilane (TMS) was used as an internal standard. IR spectra (using KBr pellets) was recorded on Nicolet, Protégé 460 spectrometer. Bruker MicrO-TOF-QII model high-resolution mass spectrometer (HRMS) was used for characterization. Quartz cell of 1mm path length was used for all measurements. Shimadzu UV-2400 double beam spectrophotometer was used for recording UV-visible spectra measurements. EPR data was collected in Bruker EXM plus and simulation was done by Bruker Simfonia software. Fisher-Scientific melting point apparatus was used for recording melting points. Elemental analysis was performed using a Perkin Elmer CHN analyser series III. IR characterization done by Perkin Elmer FTIR spectrometer. All spectroscopic experiments were done at room temperature (25 °C). TGA analysis was performed using a Perkin Elmer TG/DTA SII. Single crystal X-ray diffraction data for compounds 1⁺⁺ [BF₄⁻] and 2⁺⁺ [BF₄⁻] were collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer. ^{S3} The crystals were covered with Paratone-N and mounted on a glass capillary. The data were collected at 302 K using Mo K α radiation ($\lambda = 0.71073$ Å). The integration of data was performed using the SAINT. Empirical absorption correction was applied using SADABS.^{S4} Structural solutions were accomplished by direct methods and refined by fullmatrix least-squares on F² using either SheIXT^{S5} or SheIXL^{S6} incorporated in Olex2^{S7}. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were fixed according to a riding model and were refined isotropically. The high R(int) factors for compounds 1⁺⁺ [BF₄⁻] (0.1699), and 2⁺⁺ [BF₄⁻] (0.1881) may be due to the weak diffracting nature of the crystals. Several attempts were made to get better diffracting crystals (using different solvent combinations and crystallization techniques), but the reported data are the best that we could get. Important crystallographic data are provided in Table S1-6. ^{S8}

Experimental Details:

Synthesis of 1⁺⁺ [BF₄⁻]:



Scheme S1: Synthesis of **1**⁺⁺ [BF₄⁻]

(COCI)₂ (0.04 ml, 0.50 mmol, 1 equiv.) was added to a 30 ml solution of CAAC^{Me2} (300 mg, 1.05 mmol, 2.1 eq) in dry THF in a 100 ml Schlenk flask at 0 °C. The reaction mixture was allowed to warm up to room temperature slowly (2 h) to give a blue solution. Then the solvent was removed by high vacuum and the reaction mixture was washed by 30 mL of hexane (twice). Then the precipitate was dissolved in 5 ml methanol and aqueous NaBF₄ (excess, 5 equiv.) was added to the solution and the reaction mixture was further stir for 2 h to yield blue colour precipitate. The precipitate was then filtered, washed with distilled water (80 ml) followed by diethyl ether to get pure compound in 60% yield. Single crystals were grown from the slow evaporation of water:acetone (1:4) solution. The radical **1**⁺⁺ [BF₄⁻] was NMR silent. UV absorption $\lambda_{max} = 369$ nm (methanol). EPR (microwave frequency = 9.857 GHz) g_{iso} = 2.0060; hyperfine coupling constants: *a*(¹⁴N) = 2.6, 2.4 MHz. Decomp. 230 °C. IR: 1382 (C–O), 1061 (B–F) cm⁻¹. Elemental analysis for C₄₂H₆₂BF₄N₂O₂: C, 70.68; H,8.76; N, 3.92. Found: C, 70.65; H, 8.98; N, 3.75. HRMS (FAB): m/z calcd for [C₄₂H₆₂N₂O₂ (M+H)⁺] 627.4890, found 627.4877.

Synthesis of 2⁺⁺ [BF₄⁻]:



Scheme S2: Synthesis of **2**⁺⁺ [BF₄⁻].

(COCI)₂ (0.04 ml, 0.50 mmol, 1 equiv.) was added to a 30 ml solution of BICAAC (311 mg, 1.05 mmol, 2.1 eq) in dry THF in a 100 ml Schlenk flask at 0 °C. The reaction mixture was allowed to warm up to room temperature slowly (2 h) to give a blue solution. Then the solvent was removed by high vacuum and the reaction mixture was washed by 30 mL of hexane (twice). Then the precipitate was dissolved in 5 ml methanol and aqueous NaBF₄ (excess, 5 equiv.) was added to the solution and the reaction mixture was further stir for 2 h to yield blue colour precipitate. The precipitate was then filtered, washed with distilled water (80 ml) followed by diethyl ether to get pure compound in 60% yield. Single crystals were grown from the slow evaporation of water:acetone (1:4) solution. The radical **2**⁺⁺ [BF₄⁻] was NMR silent. UV absorption $\lambda_{max} = 356$ nm (methanol). EPR (microwave frequency = 9.857 GHz) g_{iso} = 2.0097; hyperfine coupling constants: *a*(¹⁴N) = 1.9, 1.3 MHz. Decomp. 213 °C. IR: 1382 (C– O), 1061 (B–F) cm⁻¹. Elemental analysis for C₄₆H₆₈BF₄N₂O₂: C, 71.95; H, 8.93; N, 3.65. Found: C, 71.02; H, 8.98; N, 3.60. HRMS (FAB): m/z calcd for [C₄₂H₆₂N₂O₂ (M)+] 678.5119., found 678.5170.

Proposed mechanism for the formation of 1**CI- and 2**CI-



Scheme S3: Probable mechanism for the formation of 1"Cl-

We proposed that the formation of 1^{•+} from CAAC and oxalyl chloride involves the formation of 1²⁺ as an intermediate (Step 1, Scheme S3) followed by a spontaneous one electron transfer process from chloride to 1²⁺ to generate 1^{•+} and a chlorine radical (Step 2, Scheme S3). A similar observation was noticed by the Lee group for the formation of NHC stabilized 1,2-dicarbonyl radical.^{S9} We suppose that the reaction mixture contains Cl⁺, which has a propensity to react with the solvent (THF) and produce HCl (Step 3, Scheme S3).^{S10} The produced HCl in the reaction mixture further react with CAAC to produce the byproduct [CAAC-H]⁺Cl⁻ (Step

4, Scheme S3). A similar mechanism can also be proposed for the formation of 2^{++} , when BICAAC was used in the place of CAAC. In this case also we observed the formation of [BICAAC-H]⁺Cl⁻ as a byproduct.

Synthesis of 1²⁺ [BF₄⁻]₂:



Scheme S4: Oxidation of 1"

A mixture of **1**⁺⁺ [BF₄⁻] (100 mg, 0.14 mmol,1 equiv.) and AgBF₄ (27 mg, 0.14 mmol, 1 equiv.) was placed in a 100 mL Schlenk flask and 20 mL of dry THF was added at 25 °C. The solution turned yellow after 10 minutes of stirring, which was further stirred for 1 hour. After that the solvent was removed under vacuum and the compound was washed with (3*10) ml of dry hexane. Then the compound was extracted with 10 ml dry DCM. After filtration of the insoluble residue, the solvent was removed from the solution under vacuum to yield 1^{2+} [BF₄⁻]₂ as yellow crystalline solids (yield 52 %) which was further purified by slow hexane diffusion over DCM solution. HRMS (FAB): m/z calcd for [C₄₂H₆₂N₂O₂] 626.4811, found 626.4821.

Synthesis of 2²⁺ [BF₄⁻]₂



Scheme S5: Oxidation of 2**

A mixture of **2**⁺⁺ [BF₄⁻] (100 mg, 0.13 mmol,1 equiv.) and AgBF₄ (25 mg, 0.14 mmol, 1 equiv.) was placed in a 100 mL Schlenk flask and 20 mL of dry THF was added at 25 °C. The solution turned yellow after 10 minutes of stirring, which was further stirred for 1 hour. After that the solvent was removed under vacuum and the compound was washed with (3*10) ml of dry hexane. Then the compound was extracted with 10 ml dry DCM. After filtration of the insoluble residue, the solvent was removed from the solution under vacuum to yield **2**²⁺ [BF₄⁻]₂ as yellow solids (yield 55%) which was further purified by slow hexane diffusion over DCM solution. HRMS (FAB): m/z calcd for [C₄₂H₆₂N₂O₂ (M+H)] 679.5203, found 679.5150.

Synthesis of 1:



Scheme S6: Reduction of 1"

In a 100ml Schlenk flask 1⁺⁺ [BF₄⁻] (100 mg, 0.14 mmol,1 equiv.) and KC₈ (21 mg, 0.15 mmol,1.1 equiv.) was taken. 10 ml THF was added to it at -78 °C and and the reaction mixture was allowed to warm up to room temperature slowly (3 h) to give a red solution. Then the solvent was removed by high vacuum and the product was extracted by 30 mL of toluene. After filtration of the insoluble residue, the solution was evaporated by high vacuum to obtain a red solid in 62% yield. HRMS (FAB): m/z calcd for $[C_{42}H_{62}N_2O_2 (M+2H)]$ 629.5046, found 629.5032.

Synthesis of 2:



Scheme S7: Reduction of 2**

In a 100ml Schlenk flask **2**⁺⁺ [BF₄⁻] (100 mg, 0.13 mmol,1 equiv.) and KC₈ (19 mg, 0.14 mmol,1.1 equiv.) was taken. 10 ml THF was added to it at -78 °C and the reaction mixture was allowed to warm up to room temperature slowly (3 h) to give a red solution. Then the solvent was removed by high vacuum and the product was extracted by 30 mL of toluene. After filtration of the insoluble residue, the solution was evaporated by high vacuum to obtain a red solid in 62% yield. HRMS (FAB): m/z calcd for [C₄₂H₆₂N₂O₂ (M+2H)] 680.5281, found 680.5225.

UV-Vis Spectroscopy:



Fig. S2 Uv-Visible spectra showing the stability in various mediums.





TGA:



Fig. S4 Thermal gravimetric analysis of 1^{++} [BF₄⁻] and 2^{++} [BF₄⁻].

Cyclic Voltammetry

Cyclic voltammograms were recorded at room temperature with a BioLogic SP-300 potentiostat. The working electrode was a glassy carbon disk (area = 0.02 cm^2), the reference electrode was Ag/AgCl (saturated), and the counter electrode was a platinum wire.



Fig. S5 Cyclic voltammogram of **1**⁺⁺ [BF₄⁻] (left) and **2**⁺⁺ [BF₄⁻] (middle) (5 mM) in dry and degassed acetonitrile with Bu_4NPF_6 (0.1 M) as the supporting electrolyte (scan rate = 0.1 V/s). Differential pulse voltammetry (DPV) of ferrocene (5 mM) (right) against the Bu_4NPF_6 (0.1 M) as the supporting electrolyte (scan rate = 0.1 V/s).



Fig. S6 Multiple oxidative and reductive scan of **1**⁺⁺ and **2**⁺⁺ showing the $E_{1/2}(1^{++})$ oxd/red = 0.69 V / -0.057 V and $E_{1/2}(2^{++})$ oxd/red = 0.683 V / -0.052 V respectively vs Ag/AgCl (saturated). **Magnetic measurements via Evan's method:**

32.431 mg of **1**⁺⁺ [BF₄⁻] and 27.339 mg of **2**⁺⁺ [BF₄⁻] was dissolved in 500µL CDCl₃ (**1**⁺⁺, 0.011 moles/lit; **2**⁺⁺, 0.014 moles/lit) containing hexamethyldisiloxane (HMDSO) as internal standard was taken in a wilmad screw cap NMR tube. HMDSO in CDCl₃ was taken in wilmard coaxial insert stem, and the tube was carefully inserted inside the screw cap NMR tube. 1H NMR of the solution was recorded in Bruker 500 MHz NMR instrument at 25 °C. paramagnetic susceptibility of the radical species **1**⁺⁺ and **2**⁺⁺ was determined using the following equation.^{S11}

$\chi_P = \chi_0 + 3000 \Delta v / 4\pi v_0 c M$

Here χ_0 = diamagnetic susceptibility, Δv = shift of frequency of methyl protons of HMDSO in Hz, v_0 = frequency of the NMR instrument used during the measurement, *c* = concentration of the radical species in mole/lit and *M* = molecular weight of the compounds.

Effective magnetic moment (μ_{eff}) of the radical species **1**⁺⁺ and **2**⁺⁺ were determined using the following equation:

 $\mu_{eff} = (3k_B \chi_P T / N_A \beta^2)^{1/2}$

Where k_B = Boltzmann's constant, T = Temperature, N_A = Avogadro's number = Bohr magneton. The ratio of $3k_B/N_A\beta^2 \approx 8$.

Effective magnetic moment of the radical species **1**⁺⁺ (1.72μ B) and **2**⁺⁺ (1.73μ B) was estimated from the χ_P value and the molecular weight.



Fig. S7 Shift of frequency of methyl protons of HMDSO in ppm.

IR Spectroscopy:



Fig. S8 IR spectrum of **1**^{•+} [BF₄⁻].



Fig. S9 IR spectrum of 1^{2+} [BF₄⁻]₂ (left) and 1 (right).







Fig. S11 IR spectrum of 2^{2+} [BF₄⁻]₂ (left) and 2 (right).

HRMS:



Fig. S12 HRMS of 1^{•+} [BF₄⁻].



Fig. S13 HRMS of **1**²⁺ [BF₄⁻]₂.

													1.4	
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М			Calc	Mass	mDa	PPM	DBE	i-FIT 114.4	Norm 1.178	Conf(%) 30.79	Formula C42 H65	N2 02		

Fig. S14 HRMS of 1.



Fig. S15 HRMS of **2**⁺⁺ [BF₄⁻].

Fig.



HRMS of **2**²⁺ [BF₄⁻]₂.

Fig. S17 HRMS of 2.

Table S1 Crystal Data Collection and Refinement Parameters for 1^{++} [BF₄⁻].



Identification code	CAAC radical 1 ⁻⁺ [BF ₄ ⁻]
Formula weight	713.75
Temperature/K	301.00
Crystal system	triclinic
Space group	P-1
a/Å	9.5562(5)
b/Å	12.4168(7)
c/Å	18.0018(9)
α/\circ	75.944(3)
β/°	87.240(3)
γ/°	75.943(3)
Volume/Å ³	2009.91(19)
Ζ	2
$\rho_{calc}g/cm^3$	1.179
µ/mm ⁻¹	0.083

$$\begin{array}{ll} F(000) & 770.0 \\ Crystal size/mm^3 & 0.18 \times 0.16 \times 0.11 \\ \textbf{Table S2} Crystal data collection and refinement parameters for 2^{**} [BF_4^-]. \\ Radiation & Mo \ K\alpha \ (\lambda=0.71073) \end{array}$$

 2Θ range for data collection/° 3.48 to 56.76



Identification code	
	2 ⁺⁺ [BF ₄]
Formula weight	765.867
Temperature/K	299.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.147(3)
b/Å	19.542(3)
c/Å	12.709(2)
α/°	90
β/°	122.108(4)
γ/°	90
Volume/Å ³	4448.7(12)
Z	4
$ ho_{calc}g/cm^3$	1.143
µ/mm ⁻¹	0.080
F(000)	1652.8
Crystal size/mm ³	0.14 × 0.12 × 0.1
Radiation	Μο Κα (λ = 0.71073)
2O range for data collection/°	3.08 to 56.72
Index ranges	$-28 \le h \le 28, -26 \le k \le 26, -16 \le l \le 16$
Reflections collected	49315
Independent reflections	5549 [R_{int} = 0.0743, R_{sigma} = 0.0697]
Data/restraints/parameters	5549/0/279
Goodness-of-fit on F ²	1.041
Final R indexes [I>=2σ (I)]	R ₁ = 0.0998, wR ₂ = 0.2815
Final R indexes [all data]	R ₁ = 0.1881, wR ₂ = 0.3430
Largest diff. peak/hole / e Å ⁻³	0.85/-0.47

Table S3 Bond Lengths for 1^{++} [BF₄⁻].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
01	C21	1.223(3)	C28	C30	1.522(4)
02	C22	1.278(3)	C28	C29	1.525(4)
N1	C8	1.288(3)	C17	C18	1.521(4)
N1	C9	1.465(3)	C17	C16	1.388(4)
N1	C1	1.551(4)	C1	C4	1.529(5)
N2	C23	1.328(3)	C1	C2	1.515(4)
N2	C31	1.459(3)	C1	C3	1.512(5)
N2	C28	1.524(3)	C5	C4	1.528(4)
C23	C22	1.446(4)	C5	C6	1.535(5)
C23	C24	1.525(4)	C5	C7	1.534(5)
C8	C21	1.528(4)	C33	C34	1.532(5)
C8	C5	1.508(4)	C33	C35	1.534(5)
C31	C39	1.402(4)	C11	C12	1.540(5)
C31	C32	1.397(4)	C11	C13	1.543(5)
C22	C21	1.443(4)	C40	C41	1.521(5)
C39	C40	1.525(4)	C40	C42	1.528(5)
C39	C38	1.393(4)	C18	C20	1.528(5)
C9	C10	1.414(4)	C18	C19	1.544(5)
C9	C17	1.412(4)	C16	C15	1.382(5)
C10	C11	1.518(4)	C14	C15	1.362(5)
C10	C14	1.402(4)	C36	C37	1.362(5)
C32	C33	1.522(4)	C38	C37	1.359(5)
C32	C36	1.399(4)	F2	B1	1.320(6)
C24	C25	1.532(4)	F3	B1	1.337(6)
C24	C27	1.545(4)	F1	B1	1.281(5)
C24	C26	1.542(4)	F4	B1	1.356(6)
C28	C27	1.512(4)			

Table S4 Bond Angles for 1^{++} [BF₄⁻].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	N1	C8	125.6(2)	C29	C28	C27	114.1(3)
C1	N1	C8	111.6(2)	C29	C28	C30	108.5(3)
C1	N1	C9	122.7(2)	C18	C17	C9	125.9(3)
C31	N2	C23	125.7(2)	C16	C17	C9	117.1(3)
C28	N2	C23	113.4(2)	C16	C17	C18	116.9(3)
C28	N2	C31	120.1(2)	C4	C1	N1	100.2(2)

Table S4	4 Bond	Angles	for 1 **	$[BF_4]$].
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Atom	h Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C22	C23	N2	121.7(2)	C2	C1	N1	112.6(3)
C24	C23	N2	110.6(2)	C2	C1	C4	112.0(3)
C24	C23	C22	127.5(2)	C3	C1	N1	109.1(3)
C21	C8	N1	126.7(2)	C3	C1	C4	114.4(3)
C5	C8	N1	114.0(2)	C3	C1	C2	108.4(3)
C5	C8	C21	118.3(2)	C4	C5	C8	101.4(2)
C39	C31	N2	118.0(2)	C6	C5	C8	110.0(3)
C32	C31	N2	119.7(3)	C6	C5	C4	112.5(3)
C32	C31	C39	122.3(3)	C7	C5	C8	110.8(3)
C23	C22	02	122.0(2)	C7	C5	C4	112.8(3)
C21	C22	02	114.2(2)	C7	C5	C6	109.2(3)
C21	C22	C23	123.9(2)	C34	C33	C32	113.4(3)
C8	C21	01	114.1(2)	C35	C33	C32	110.2(3)
C22	C21	01	130.4(3)	C35	C33	C34	109.6(3)
C22	C21	C8	115.4(2)	C12	C11	C10	111.3(3)
C40	C39	C31	124.9(3)	C13	C11	C10	110.5(3)
C38	C39	C31	117.4(3)	C13	C11	C12	109.0(3)
C38	C39	C40	117.6(3)	C41	C40	C39	111.0(3)
C10	C9	N1	119.3(3)	C42	C40	C39	113.1(3)
C17	C9	N1	118.7(3)	C42	C40	C41	110.4(3)
C17	C9	C10	122.0(3)	C28	C27	C24	108.0(2)
C11	C10	C9	126.1(3)	C20	C18	C17	111.7(3)
C14	C10	C9	116.7(3)	C19	C18	C17	111.9(3)
C14	C10	C11	117.1(3)	C19	C18	C20	108.2(3)
C33	C32	C31	124.6(3)	C15	C16	C17	122.1(3)
C36	C32	C31	116.4(3)	C15	C14	C10	122.3(3)
C36	C32	C33	118.7(3)	C37	C36	C32	122.2(3)
C25	C24	C23	114.5(2)	C37	C38	C39	121.4(3)
C27	C24	C23	101.2(2)	C14	C15	C16	119.7(3)
C27	C24	C25	109.3(2)	C5	C4	C1	108.3(3)
C26	C24	C23	109.3(2)	C38	C37	C36	120.2(3)
C26	C24	C25	110.9(2)	F3	B1	F2	104.7(5)
C26	C24	C27	111.3(3)	F1	B1	F2	110.3(4)
C27	C28	N2	101.0(2)	F1	B1	F3	112.1(5)
C30	C28	N2	111.1(2)	F4	B1	F2	111.6(5)
C30	C28	C27	111.1(3)	F4	B1	F3	103.4(4)
C29	C28	N2	111.1(2)	F4	B1	F1	114.1(5)

Table S5 Bond Lengths for 2^{+} [BF₄⁻].

Atom Atom		Length/Å	Aton	n Atom	Length/Å
N1	C1	1.465(4)	B1	F5 ¹	1.507(11)
N1	C13	1.296(4)	B1	F5	1.507(11)
N1	C15	1.531(4)	B1	F6	1.313(11)
01	C14	1.298(5)	B1	F6 ¹	1.313(11)
C1	C6	1.394(5)	C2	C7	1.511(6)
C1	C2	1.402(5)	C2	C3	1.392(6)
C13	C18	1.488(4)	C18	C17	1.561(6)
C13	C14	1.516(5)	C18	C22	1.531(5)
F2	B1	1.360(7)	C18	C19	1.541(7)
F2	F6	1.648(15)	C14	C14 ²	1.345(8)
F2	F6 ¹	1.648(15)	C20	C19	1.530(6)
F4	B1 ¹	1.299(9)	C16	C17	1.531(6)
F4	F3	0.668(19)	C7	C9	1.522(7)
F4	F5	1.52(2)	C7	C8	1.530(6)
C15	C20	1.532(6)	C5	C4	1.340(7)
C15	C16	1.514(6)	C10	C12	1.544(7)
C15	C21	1.512(5)	C10	C11	1.538(6)
C6	C5	1.382(6)	C3	C4	1.373(7)
C6	C10	1.507(6)	C17	C23	1.449(8)
B1	F3 ¹	1.340(14)	F3	F6 ¹	1.44(2)
B1	F3	1.340(14)	F5	F6	0.911(15)

Table S6 Bond Angles for 2** [BF₄⁻] (¹1-X,+Y,1/2-Z; ²3/2-X,1/2-Y,1-Z)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	N1	C1	122.8(2)	F6 ¹	B1	F4	94.7(7)
C15	N1	C1	121.5(2)	F6	B1	F3 ¹	65.8(10)
C15	N1	C13	115.7(2)	F6	B1	F3	125.7(9)
C6	C1	N1	119.0(3)	F6 ¹	B1	F3 ¹	125.7(9)
C2	C1	N1	117.8(3)	F6 ¹	B1	F3	65.8(10)
C2	C1	C6	123.2(3)	F6	B1	F5 ¹	144.8(7)
C18	C13	N1	115.8(3)	F6 ¹	B1	F5	144.8(7)
C14	C13	N1	121.1(3)	F6 ¹	B1	F5 ¹	36.9(7)
C14	C13	C18	122.7(3)	F6	B1	F5	36.9(7)
F6	F2	B1	50.7(4)	F6 ¹	B1	F6	152.1(13)
F6 ¹	F2	B1	50.7(4)	C7	C2	C1	125.1(3)
F6 ¹	F2	F6	101.4(8)	C3	C2	C1	115.9(4)
F3	F4	B1 ¹	79(2)	C3	C2	C7	118.9(4)
F5	F4	B1 ¹	64.0(6)	C17	C18	C13	106.1(3)
F5	F4	F3	127(2)	C22	C18	C13	113.6(3)
C20	C15	N1	106.1(3)	C22	C18	C17	111.9(4)
C16	C15	N1	105.8(3)	C19	C18	C13	107.1(3)

Atom	n Atom	n Atom	Angle/°	Atom	h Atom	n Atom	Angle/°
C16	C15	C20	107.1(3)	C19	C18	C17	106.7(3)
C21	C15	N1	111.5(3)	C19	C18	C22	111.0(4)
C21	C15	C20	112.6(3)	C13	C14	01	118.0(3)
C21	C15	C16	113.3(3)	C14 ²	C14	01	122.3(5)
C5	C6	C1	116.4(4)	C14 ²	C14	C13	119.3(5)
C10	C6	C1	124.9(3)	C19	C20	C15	110.6(3)
C10	C6	C5	118.7(4)	C17	C16	C15	111.8(3)
F4 ¹	B1	F2	125.7(6)	C9	C7	C2	112.6(4)
F4	B1	F2	125.7(6)	C8	C7	C2	111.2(4)
F4	B1	F4 ¹	108.7(11)	C8	C7	C9	109.3(4)
F3 ¹	B1	F2	111.0(7)	C4	C5	C6	122.6(5)
F3	B1	F2	111.0(7)	C12	C10	C6	112.0(4)
F3 ¹	B1	F4	117.0(6)	C11	C10	C6	111.3(4)
F3 ¹	B1	F4 ¹	29.3(8)	C11	C10	C12	109.4(4)
F3	B1	F4 ¹	117.0(6)	C4	C3	C2	121.7(5)
F3	B1	F4	29.3(8)	C16	C17	C18	109.2(4)
F3	B1	F3 ¹	138.0(14)	C23	C17	C18	112.5(4)
F5	B1	F2	92.0(6)	C23	C17	C16	115.3(5)
F5 ¹	B1	F2	92.0(6)	C3	C4	C5	120.1(4)
F5	B1	F4	65.3(9)	C20	C19	C18	110.6(3)
F5	B1	F4 ¹	112.2(6)	B1 ¹	F3	F4	72.0(17)
F5 ¹	B1	F4 ¹	65.3(9)	F6 ¹	F3	F4	127(2)
F5 ¹	B1	F4	112.2(6)	F6 ¹	F3	B1 ¹	56.2(8)
F5 ¹	B1	F3	89.6(9)	B1	F5	F4	50.7(6)
F5	B1	F3 ¹	89.6(9)	F6	F5	F4	109.7(15)
F5 ¹	B1	F3 ¹	89.0(10)	F6	F5	B1	59.9(10)
F5	B1	F3	89.0(10)	B1	F6	F2	53.3(6)
$F5^1$	B1	F5	176.0(13)	F3 ¹	F6	F2	91.9(9)
F6 ¹	B1	F2	76.1(7)	F3 ¹	F6	B1	58.0(6)
F6	B1	F2	76.1(7)	F5	F6	F2	103.9(15)
F6	B1	F4	101.5(7)	F5	F6	B1	83.2(13)
F6 ¹	B1	F4 ¹	101.5(7)	F5	F6	F3 ¹	115.5(16)
F6	B1	F4 ¹	94.7(7)				



Fig. S18 Molecular structures of 1^{2+} [BF₄⁻]₂ and 2^{2+} [BF₄⁻]₂. The data quality of these crystals is not up to the mark (the WR₂ value was above 40% for both the cases due to severe disorder of the BF₄ counter anions), therefore, discussion about 1^{2+} [BF₄⁻]₂ and 2^{2+} [BF₄⁻]₂ are avoided.

DFT Calculations

Input coordinates of the two radicals (1^{•+} and 2^{•+}) were obtained from the experimental X-ray crystal structures. The geometries were optimized at the M062-2x/Def2-SV(P) level of theory using the NWChem software. Structural parameters such as bond distances, angles, and torsions match well with the experimental structures. All positive frequency values obtained from the frequency analyses confirm that the structures are in their corresponding equilibrated state.



Fig. S19 (a) & (b) Experimental and (c) & (d) DFT optimized structures of radicals **1**⁺⁺ and **2**⁺⁺. Comparison between the structural parameters obtained from experiments and DFT calculations are provided in Fig. 2 caption in the main manuscript.

Energy minimization

Method: M062-2x/Def2-SV(P) level of theory^{S12-13} in NWChem software^{S14} **Compound 1⁺⁺** (E^o = -1895.320900 Ha, and G^o = -1894.427217 Ha)







Table S7: Coordinates of optimized structure of 1**.

0	2.546826	-1.111096	-0.665867
0	-0.036923	0.400581	1.091776
Ν	0.143688	-2.749606	0.728621
Ν	0.693485	2.802147	-0.218135
С	1.457637	1.725049	-0.203834
С	1.111577	-1.936071	0.965207
С	-0.747935	2.836429	-0.067138
С	0.964350	0.465082	0.327760
С	1.622055	-0.815772	0.064968
с	-1.533263	2.532187	-1.198071
С	-0.804518	-2.678993	-0.375071
С	-0.402356	-3.130620	-1.651629
с	-1.323144	3.227786	1.158361
с	2.868475	2.041731	-0.690655
С	1.419006	4.055711	-0.652809
С	-2.120741	-2.233075	-0.110305
С	0 173262	-3 961460	1 665166
c	1 922543	-2 293934	2 188319
c C	3 968984	1 463420	0 206746
н	3 780957	1 701194	1 264684
н	4 072402	0 370/03	0.085100
н	4.072402	1 02/618	-0.073662
C C	-0 540516	3 350301	2 456570
ц	0.524044	3 202008	2.400079
 C	1 026515	2 472466	2.229103
	1.020010	-3.473400	-2.001047
	0.072402	-3.301933	-1.1/4133
	-0.972493	1.900415	-2.407500
н	0.122290	1.975091	-2.439334
	2.875589	3.582483	-0.592539
н	3.309370	3.880593	0.373567
н	3.485048	4.036655	-1.385456
C	-2.592634	-1.589577	1.188153
н	-1.754623	-1.585107	1.901839
С	-3.049665	-2.334185	-1.149780
н	-4.074426	-2.004813	-0.971828
С	-1.382443	-3.195529	-2.648298
Н	-1.099930	-3.543491	-3.642966
С	-2.707991	3.411988	1.192987
Н	-3.177981	3.721626	2.128201
С	-2.914613	2.733072	-1.104177
Н	-3.543743	2.514015	-1.968413
С	3.063240	1.571040	-2.144708
Н	3.009096	0.478966	-2.215642
Н	2.318355	2.009758	-2.821892
Н	4.058337	1.893327	-2.484603
С	1.158251	5.201650	0.317203
н	1.453528	4.942356	1.341490
н	1.758885	6.064959	-0.002095
н	0.100671	5.499767	0.307329
С	-2.697102	-2.826832	-2.399843
н	-3.445314	-2.902417	-3.189914

С	0.974516	4.494341	-2.049597
н	1.498926	5.426692	-2.299067
н	1.209247	3.758007	-2.827095
н	-0.104911	4.698745	-2.066405
С	1.080131	-3.437968	2.787622
н	0.455997	-3.044402	3.603028
н	1.707056	-4.239528	3.199933
С	-1.204058	-4.349703	2.170181
н	-1.876096	-4.616191	1.342875
н	-1.086452	-5.235559	2.809978
н	-1.659539	-3.556593	2.772787
с	-3.497827	3.193126	0.069538
н	-4.575409	3.354963	0.118524
с	-1.330207	0.415032	-2.508505
н	-0.966652	-0.117480	-1.615882
н	-2.422353	0.280970	-2.548190
н	-0.897615	-0.062906	-3.400657
С	-0.715527	4.730078	3.121009
н	-0.480633	5.564312	2.448448
н	-1 751236	4 863165	3 466448
н	-0.066452	4 806808	4 005239
c	1 165626	-4 893487	-2 611771
й	0.826960	-5 663459	-1 906945
н	0.584592	-5.000-00	-3 537862
 Ц	0.004092	5.005160	2 858057
 C	0.067243	2 261385	-2.030037
с ц	2 01 5 2 9 0	2.201303	2 7/6726
	-2.013200	1 269567	2 000006
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	-0.340012	2.310000	2 745260
	-1.451090	2.001179	-3.745209
	-2.529740	2.400960	-3.099502
н	-1.258936	3.082510	-3.720332
н	-0.937870	2.175945	-4.619678
	-2.988651	-0.126365	0.943438
н	-2.164695	0.456509	0.516848
н	-3.854488	-0.066463	0.265834
Н	-3.278191	0.344515	1.895080
C	0.770827	-5.130343	0.885294
н	0.847686	-5.996920	1.555745
н	0.112252	-5.404373	0.050116
н	1.770437	-4.908330	0.490068
С	2.011890	-1.081399	3.126451
н	2.607953	-0.275728	2.673119
н	1.016178	-0.682826	3.364052
н	2.507178	-1.390457	4.057930
С	-3.797883	-2.320352	1.799322
н	-4.697289	-2.151240	1.189601
н	-3.657987	-3.404579	1.883249
н	-4.009078	-1.919499	2.801171
С	1.519994	-2.459995	-3.096376
Н	1.008551	-2.618704	-4.057778
н	1.335544	-1.425507	-2.778168
н	2.600066	-2.580032	-3.261253
С	3.339940	-2.738582	1.784008
н	3.330578	-3.565547	1.061884

H3.906008-1.9101791.340312H3.865054-3.0735982.689458

Table S8 Coordinates of optimized structure of 2*+.

Ν 0.639147 2.776206 -0.398293 O 0.219666 0.556421 1.653341 C -0.699893 3.149117 0.034419 С 1.079243 1.557359 -0.330671 С 1.583200 3.783579 -1.001154 С -0.907318 3.552965 1.367006 С -1.729626 3.112437 -0.926614 С 2.433356 1.316213 -0.934124 С 0.291302 0.504216 0.407552 С 1.925822 3.303351 -2.426108 н 1.076000 3.484726 -3.097305 н 2.749400 3.939825 -2.779354 С 2.863288 3.689102 -0.154158 н 3.588983 4.406898 -0.561250 2.632991 4.012124 0.872511 н С 0.995097 5.181459 -1.000365 0.770312 5.528353 0.014391 н н 1.730100 5.864107 -1.447623 н 0.071676 5.233298 -1.588397 С -1.541836 2.646227 -2.365875 н -0.521786 2.253358 -2.476171 С -2.198754 3.965890 1.711230 -2.395383 н 4.289859 2.734327 С 0.173920 3.551630 2.438782 н 1.042432 3.009954 2.040328 С -2.997771 3.539769 -0.520065 н -3.816639 3.534136 -1.241731 С 3.425366 2.251871 -0.162708 н 4.354327 2.225687 -0.754265 С 2.870650 -0.143876 -0.908440 н 2.829982 -0.573171 0.100466 Н 2.231486 -0.754709 -1.561912 н 3.908053 -0.215236 -1.267384 С -3.231835 3.970523 0.780657 н -4.227305 4.306832 1.073282 С 2.327657 1.823494 -2.397013 н 3.302864 1.656841 -2.875908 Н 1.592383 1.193165 -2.917856 С -2.485294 1.493142 -2.723022 -2.270028 0.603297 -2.120922 н -3.540090 1.777163 -2.589288 н -2.346032 1.213898 -3.777199 н С 0.606122 4.972094 2.823673 1.034671 5.534101 Н 1.983007 Н -0.249438 5.548084 3.207047 Н 1.364168 4.930938 3.619095 -0.284082 С 2.797156 3.692347 -1.075549 3.347433 4.222364 н H -0.647270 1.795084 3.436153 н 0.560616 2.689921 4.388098 C -1.737229 3.799616 -3.358630

н	-2.773041	4.168865	-3.324321
н	-1.076696	4.653446	-3.155596
н	-1.540622	3.454350	-4.383828
С	3.725391	1.760672	1.251024
н	4.362834	2.486163	1.775899
н	2.794834	1.644073	1.832754
н	4.249176	0.795855	1.250031
N	-0.639147	-2.776206	0.398293
0	-0 219666	-0 556421	-1 653341
c	0 699893	-3 149117	-0 034419
c	-1 079243	-1 557359	0.330671
c	-1 583200	-3 783579	1 001154
c	0.007318	-3 552065	-1 367006
c	1 720626	3 112/27	0.026614
0	0.400056	4 046040	0.920014
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0	-0.291302	-0.504216	-0.407552
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н	-1.076000	-3.484726	3.097305
н	-2.749400	-3.939825	2.779354
С	-2.863288	-3.689102	0.154158
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н	-2.632991	-4.012124	-0.872511
С	-0.995097	-5.181459	1.000365
н	-0.770312	-5.528353	-0.014391
н	-1.730100	-5.864107	1.447623
н	-0.071676	-5.233298	1.588397
С	1.541836	-2.646227	2.365875
н	0.521786	-2.253358	2.476171
С	2.198754	-3.965890	-1.711230
н	2.395383	-4.289859	-2.734327
С	-0.173920	-3.551630	-2.438782
н	-1.042432	-3.009954	-2.040328
с	2.997771	-3.539769	0.520065
н	3.816639	-3.534136	1.241731
с	-3.425366	-2.251871	0.162708
н	-4 354327	-2 225687	0 754265
c	-2 870650	0 143876	0 908440
н	-2.0700000	0.140070	-0 100466
н	-2 231/186	0.754709	1 561012
н	-3 908053	0.215236	1 267384
 C	2 224025	2 070522	0.790657
	4.007005	-3.970525	4.072292
	4.227305	-4.300032	-1.0/3262
	-2.327657	-1.823494	2.397013
н	-3.302864	-1.656841	2.875908
н	-1.592383	-1.193165	2.917856
С	2.485294	-1.493142	2.723022
н	2.270028	-0.603297	2.120922
Н	3.540090	-1.777163	2.589288
Н	2.346032	-1.213898	3.777199
С	-0.606122	-4.972094	-2.823673
н	-1.034671	-5.534101	-1.983007
н	0.249438	-5.548084	-3.207047
н	-1.364168	-4.930938	-3.619095
С	0.284082	-2.797156	-3.692347
н	1.075549	-3.347433	-4.222364

Н	0.647270	-1.795084	-3.436153
н	-0.560616	-2.689921	-4.388098
С	1.737229	-3.799616	3.358630
н	2.773041	-4.168865	3.324321
н	1.076696	-4.653446	3.155596
н	1.540622	-3.454350	4.383828
С	-3.725391	-1.760672	-1.251024
н	-4.362834	-2.486163	-1.775899
н	-2.794834	-1.644073	-1.832754
н	-4.249176	-0.795855	-1.250031

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