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Supporting Information

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C_4 Cumulene and the Corresponding Air-Stable Radical Cation and Dication**

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Supporting Information

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(S1) Syntheses

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box, unless otherwise stated. The cyclic alkyl(amino) carbene (cAAC) was synthesized according to the literature[S1] and used as a mixture with TfOLi. Solvents were purified with the M-Braun solvent drying system. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus. Electrochemical experiments were performed with an analyzer from Perkin Elmer Model 263A with Mili-GC as working, and Pt as auxiliary, and Ag as the reference electrode, respectively. Decamethylferrocene (DMFe) was used as a standard, and all redox potentials are calculated with respect to the $E_{1/2}$ of the Fc^{+}/Fc redox couple.

Compound 1: To a mixture of CBr_4 (0.66 g, 2 mmol), cAAC: (0.88 g, 2 mmol) and K (0.36 g, 9 mmol) or Li (0.06 g, 9 mmol) in 100 mL Schenk flask was added THF (50 mL) at room temperature. The suspension was vigorously stirred for 48 h to obtain a brown suspension. All the volatiles were removed in vacuum and the brown residue was subjected to sublimation (240 ^{o}C, 0.1 mmHg) to afford **1** as a yellow crystalline solid. Yield: 0.31 g (52 %, based on CBr_4). X-ray quality single crystals of **1** were grown from its toluene solution under -4 ^{o}C in

refrigerator. Sublimating point: 240 °C. UV-visible absorption bands at 535(w), 410 nm. ^{1}H NMR (C_6D_6, 298 K, 500 MHz, δ ppm): 7.19–7.10 (m, 6 H, Ar*H*), 3.13 (sept, 4 H, C*H*Me$_2$, $^3J_{HH}$ = 7 Hz), 1.52 (s, 4 H, CH_2), 1.29 (s, 12 H, NC*Me*$_2$), 1.22 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 7 Hz), 1.12 (s, 12 H, C*Me*$_2$), 0.96 (d, 12 H, CH*Me*$_2$, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (C_6D_6, 298 K, 125 MHz, δ ppm) 176.2($C_{carbene}$), 146.7, 132.4, 124.1, 123.5, 71.2($C_{centroid}$), 49.6, 43.0, 28.9, 28.0, 26.5, 25.7, 25.0, 23.8. Anal(%). calcd for $C_{42}H_{62}N_2$ (594.96) (toluene molecules in the crystals are removed during drying): C, 84.79; H, 10.50; N, 4.71. Found: C, 85.02; H, 10.88; N, 4.97.

Compound 1$^{\cdot+}$TfO$^-$: To a mixture of CBr_4 (0.66 g, 2 mmol), cAAC (0.88 g, 2 mmol) and K (0.27 g, 7 mmol) in a 100 mL Schenk flask was added THF (50 mL) at room temperature. The suspension was vigorously stirred for 36 h. All the volatiles were removed in vacuum and the residue was extracted with a mixture of CH_2Cl_2 and *n*-hexane (1:5, 10 mL, 30 mL). Red crystalline solid was obtained which is NMR-silent. Yield: 0.65 g, 87 % (based on CBr_4). Red crystals of **1$^{\cdot+}$TfO$^-$** were grown from a mixture of CH_2Cl_2 and *n*-hexane at -32 °C. Mp: 205 °C. UV-visible absorption bands at 535(s), 495, 466, 408(s), 388 nm. Anal(%). calcd for $C_{43}H_{62}F_3N_2O_3S$ (744.02): C, 69.41; H, 8.40; N, 3.77. Found: C, 68.98; H, 8.62; N, 3.89. Cyclic voltammogram (CV) shows two reversible one-electron redox cycles at $E_{1/2}$ = -0.313, 0.608 V.

Transformation of 1 to 1$^{\cdot+}$TfO$^-$: To a mixture of **1** (0.06 g, 0.1 mmol), and LiOTf (0.019 g, 0.12 mmol) was added CH_2Cl_2 (10 mL) at room temperature. The suspension was stirred overnight under exposure to air. The color of the solution turned to dark red. Red crystals of **1$^{\cdot+}$TfO$^-$** were obtained from a mixture of CH_2Cl_2 and *n*-hexane (1:2). Yield: 0.07 g (92 %, based on **1**).

Transformation of 1$^{\cdot+}$TfO$^-$ to 1: To a mixture of **1$^{\cdot+}$TfO$^-$** (0.38 g, 0.5 mmol) and K (0.02 g, 0.5 mmol) was added THF (20 mL) at room temperature. The reaction mixture was stirred for 5 h to obtain a slight yellow colored suspension. All the volatiles were removed in vacuum and the residue was extracted with toluene (10 mL). The filtrate was dried in vacuum affording **1** as a yellow NMR-pure powder. Yield: 0.24 g (80 %, based on **1$^{\cdot+}$TfO$^-$**).

Compound 1^{2+}[H(NO$_3$)$_2^-$]$_2$: To **1** (0.12 g, 0.2 mmol) was added concentrated HNO_3 (aq. 68 %, 0.1 g) dropwise under stirring at room temperature. The suspension was stirred for additional 1 h and filtered. Orange crystals of **1^{2+}[H(NO$_3$)$_2^-$]$_2$** were obtained in 41 % yield (0.07 g, based on **1**). Mp: 296 °C (dec.). UV-visible absorption bands at 336 nm (s). Anal(%). calcd for $C_{42}H_{64}N_6O_{12}$ (844.99): C, 59.70; H, 7.63; N, 9.95. Found: C, 59.11; H, 7.91; N, 9.86.

Compound 1^{2+}[B(C$_6$F$_5$)$_4^-$]$_2$: To a mixture of **1$^{\cdot+}$TfO$^-$** (0.15 g, 0.2 mmol) and $CPh_3^+B(C_6F_5)_4^-$ (0.36 g, 0.4 mmol) was added CH_2Cl_2 (20 mL) at room temperature and the suspension was stirred for additional 2 h. White precipitation was formed and the reaction suspension was filtered. Brown red crystals **1^{2+}[B(C$_6$F$_5$)$_4^-$]$_2$** were grown from a mixture of CH_2Cl_2 and *n*-hexane at 0 °C. Yield: 0.11 g, 28 % (based on **1$^{\cdot+}$TfO$^-$**). The possible equation of this reaction is shown as follows:

$$\mathbf{1^{\cdot+}TfO^-} + 2\ CPh_3^+B(C_6F_5)_4^- \longrightarrow \mathbf{1^{2+}[B(C_6F_5)_4^-]_2} + 1/2\ Ph_3C\text{-}(C_6H_5)\text{=}CPh_2 + CPh_3^+TfO^-$$

Mp: 302 °C (dec.). UV-visible absorption bands at 536, 415, 270 nm. ^{1}H NMR (CD_3CN, 298 K, 500 MHz, δ ppm): 7.70–7.40 (m, 6 H, Ar*H*), 2.61 (s, 4 H, CH_2), 2.59-2.39 (m, 4 H, C*H*Me$_2$), 1.65-1.49 (m, 24 H, NC*Me*$_2$ plus CH*Me*$_2$),

1.37-1.22 (d, 12 H, CH*Me*$_2$), 0.79 (s, 12 H, C*Me*$_2$). Anal(%). calcd for $C_{90}H_{62}B_2F_{40}N_2$ (1953.03): C, 55.35; H, 3.20; N, 1.43. Found: C, 55.10; H, 3.08; N, 1.10.

(S2). UV-visible spectra

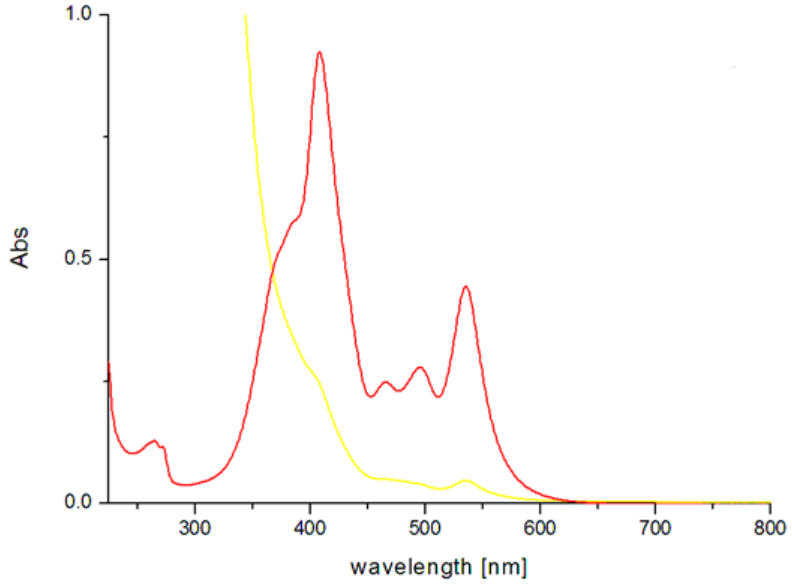


Figure S1 UV-visible spectra of **1** (yellow) and **1**$^{+}$**TfO**$^{-}$ (red) recorded in CH_2Cl_2.

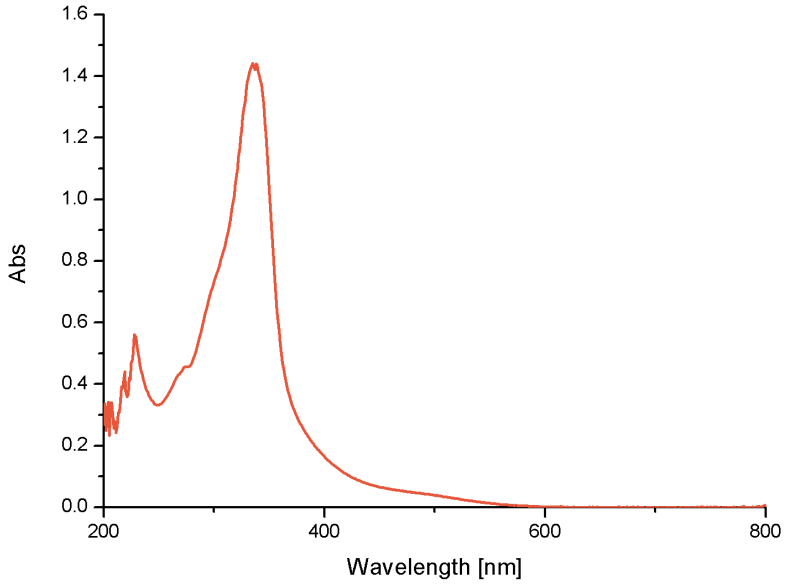


Figure S2 UV-visible spectrum of **1**$^{2+}$**[H(NO$_3$)$_2$**$^{-}$**]$_2$** recorded in CH_2Cl_2.

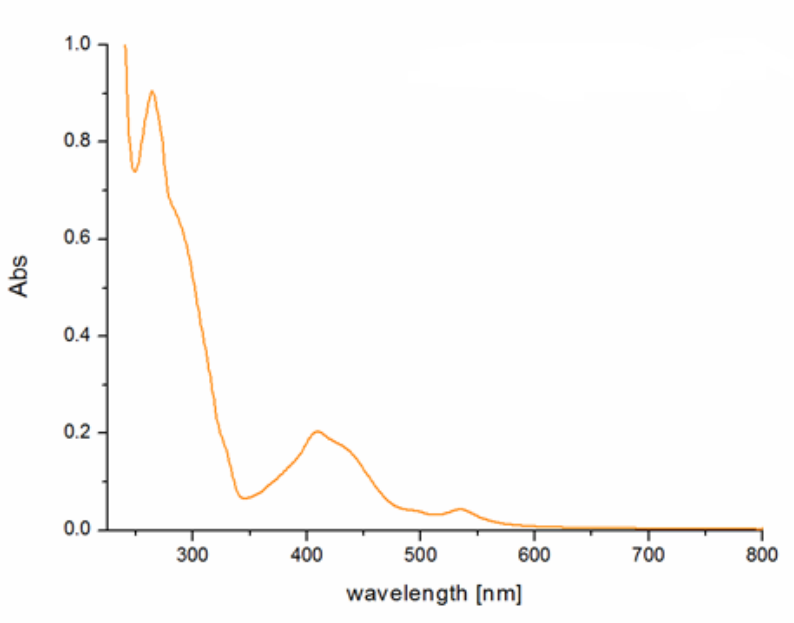


Figure S3 UV-visible spectrum of $\mathbf{1}^{2+}[\mathbf{B}(\mathbf{C_6F_5})_4^-]_2$ recorded in CH_2Cl_2.

(S3). EPR measurement.

EPR spectra in the X band were recorded with a Bruker System EMX and simulated using WinEPR SimFonia. Experimental and simulated EPR spectrum of $\mathbf{1}^{\cdot+}\mathbf{TfO}^-$ is shown as follows:

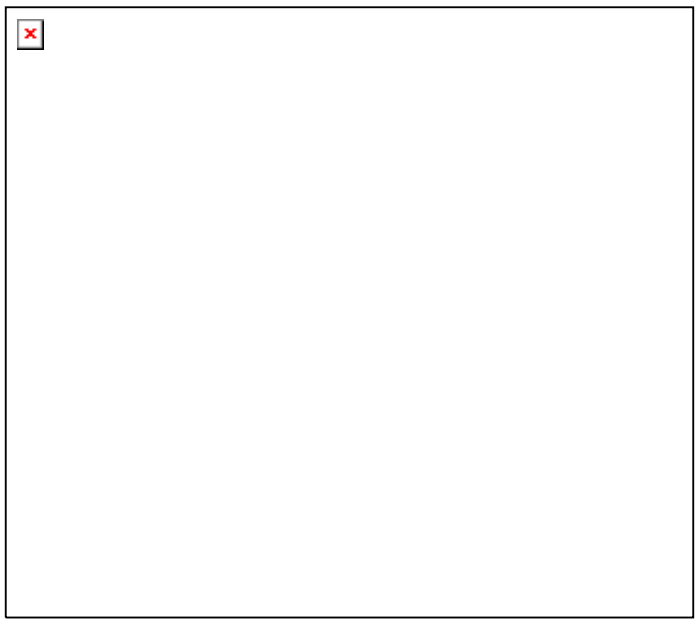


Figure S4 X-band EPR spectrum recorded in THF solution at room temperature for $\mathbf{1}^{\cdot+}\mathbf{TfO}^-$. ($g$ = 2.0032)

(S4). Crystal Structure Determination

Suitable single crystals for X-ray structural analysis of **1**, $\mathbf{1}^{\cdot+}\mathbf{TfO}^{-}$, $\mathbf{1}^{2+}[\mathbf{H(NO_3)_2}^{-}]_2$ and $\mathbf{1}^{2+}[\mathbf{B(C_6F_5)_4}^{-}]_2$ were mounted at room temperature in Paratone N inert oil under nitrogen atmosphere. Single-crystal diffraction data were subsequently collected on two different setups: data for **1**, $\mathbf{1}^{\cdot+}\mathbf{TfO}^{-}$ and $\mathbf{1}^{2+}[\mathbf{B(C_6F_5)_4}^{-}]_2$ were collected at DESY with the PETRAIII accelerator on P11 with a piezo motor driven goniometer. The 6M-Dectris PILATUS[S2] detector was used with standard measurement procedures established at the beamline. A semi-empirical absorption correction with SADABS[S3] was applied after integration with the XDS software[S4] and conversion of the output file with the utility program xds2sad from G. M. Sheldrick. Data for $\mathbf{1}^{2+}[\mathbf{H(NO_3)_2}^{-}]_2$ was collected at an inhouse Agilent diffractometer with Molybdenum SuperNova source. All structures were solved by direct methods.[S5] Except for $\mathbf{1}^{2+}[\mathbf{H(NO_3)_2}^{-}]_2$ the structure models were refined against all data by full-matrix least-squares methods on F^2 with the program shelxl2012.[S6] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were modeled isotropically on calculated positions using a riding model with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

1 crystallized with a disordered toluene in *P*-1 (Figure S5). Because of the low symmetry, two different crystal specimen were measured. Both gave similar figures of merit in refinement. Intensity data were merged, since the phi-scan data-collection procedure did not give full completeness for each of them. Extinction was refined to keep low order reflections, which were affected by instrumental errors of the Pilatus detector.

$\mathbf{1}^{2+}[\mathbf{B(C_6F_5)_4}^{-}]_2$ shows a disorder of the whole cation and sits on an inversion center as displayed in Figure S6. One isopropyl group showed some flexibility, too. Therefore, restraints for several bonds, angles and displacement parameters were used, mainly to model the isopropyl- and methyl- positions and yield chemically reasonable results. In order to get an integer number of atoms in the cell, the site occupancy factors for the disordered parts were kept fixed at the rounded values to which they had converged during the final steps of the refinement.

Several $\mathbf{1}^{\cdot+}\mathbf{TfO}^{-}$ crystals were measured at the synchrotron and could be identified to be the desired compound. The molecule structure of $\mathbf{1}^{\cdot+}\mathbf{TfO}^{-}$ is shown below. (Figure S7) But due to weak scattering the R1-values did not drop below 8%. Data quality of this structure is considerably worse than for the other structures. Despite carrying out the measurement at a temperature of 15 K with an open flow Helium device at the synchrotron, the scattering power of the miniscule crystal samples was low. Nevertheless the connectivity of the compound was determined without doubt. A solvated form of $\mathbf{1}^{\cdot+}\mathbf{TfO}^{-}$, $\mathbf{1}^{\cdot+}\mathbf{TfO}^{-}\cdot\mathbf{THF}\cdot\mathbf{H_2O}$, was grown under the slow evaporation of THF solution of $\mathbf{1}^{\cdot+}\mathbf{TfO}^{-}$, which shows extensive disorders of anion, solvents and the cAAC ring. This is the reason for that the hydrogen atoms of the second site of the water could not be included in the model. The corresponding molecule structure is shown in Figure S8.

An invariom refinement[S7] was carried out for $\mathbf{1}^{2+}[\mathbf{H(NO_3)_2}^{-}]_2$. Starting coordinates were obtained from a refinement with shelxl2012[S6] in which hydrogen atom positions were constrained to idealized positions. These positions were kept, but bond distances were subsequently elongated to values obtained from quantum chemical geometry optimizations in invariom refinement. This aspherical-atom refinement was then carried out with the

program XD[S8], which incorporates the Hansen/Coppens multipole formalism[S9]. The program invariomtool[S10] was used to set up input files for XD including constraints for riding hydrogen treatment. Only isotropic displacement parameters but no positional parameters were hence refined for hydrogen atoms. Quantum chemical computations required for deriving scattering factors were carried out with the program Gaussian[S11]. Invariom refinement led to a reduction of the *R*1(F)-factor from 4.79 % in the independent atom model to 3.54 % with invarioms. The standard deviations of bond lengths and angles and the physical meaning of the anisotropic displacement parameters therefore improve as well, leading to a more accurate structure from the same diffraction data.

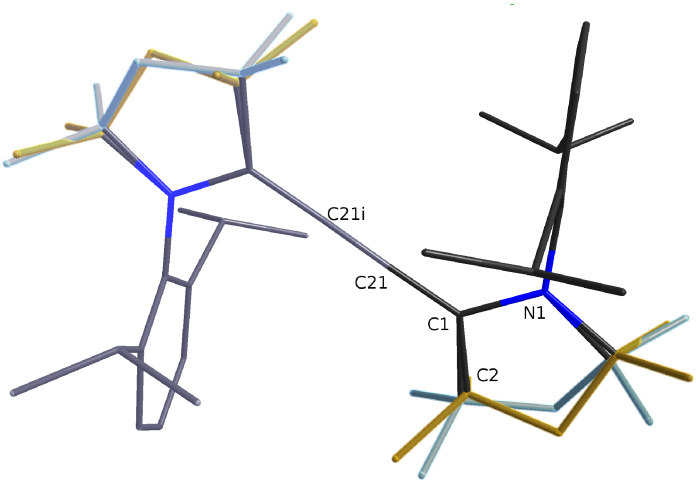
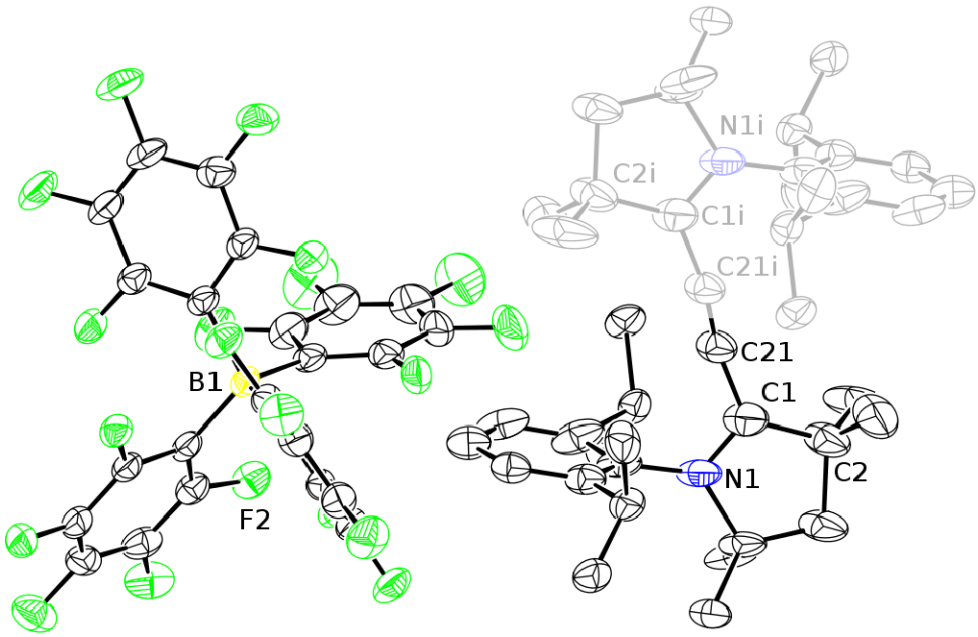
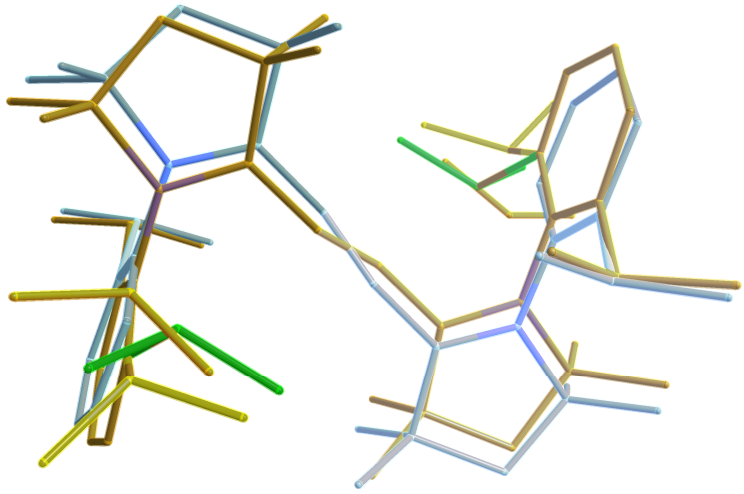


Figure S5 Disordered structure of C_4 backbone of compound **1**. Different parts of the disorder are highlighted in different colors.



(a)



(b)

Figure S6 (a) Molecular structure of compound $\mathbf{1}^{2+}[B(C_6F_5)_4^-]_2$. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Fluorine atoms and the second half of the C_4 unit which is symmetrically generated are displayed in gray. Selected bond lengths (Å) and angles (°) (average values between disordered parts. Calculated values at the M06-2X/SVP level of theory are given in square brackets): N1-C1 1.302(6)[1.288], C1-C21 1.437(4)[1.431], C21-C21i 1.272(11)[1.211]; N1-C1-C2 115.4(6)[114.61], C21-C1-N1 120.0(6)[121.48], C21-C1-C2 124.6(6)[123.90], C21i-C21-C1 158.0(9)[176.82]. (b) Disordered structure of C_4 backbone of $\mathbf{1}^{2+}[B(C_6F_5)_4^-]_2$. Different sites of the disorder are highlighted in different colors. The main molecule occupies the sites with 60% and 40%.

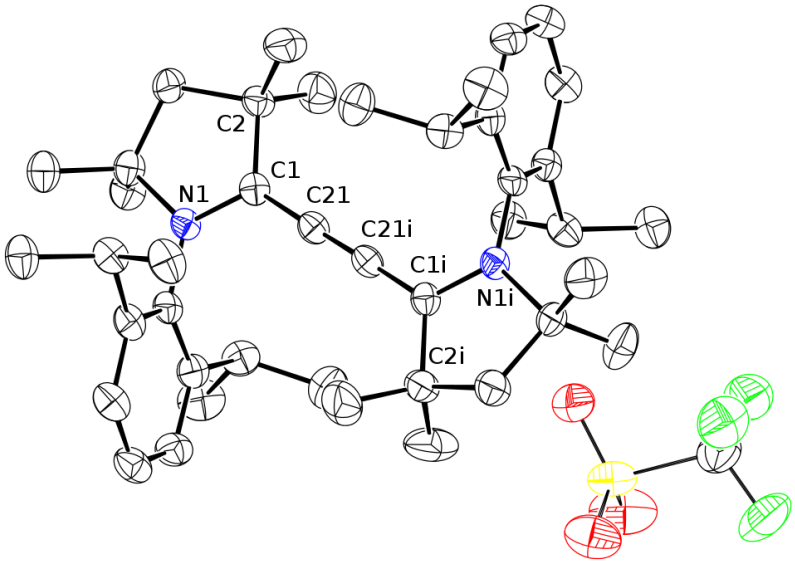


Figure S7 Molecular structure of compound **$1^{+}TfO^{-}$**. White: C; red: O; green: F; yellow: S. Hydrogen atoms are omitted for clarity.

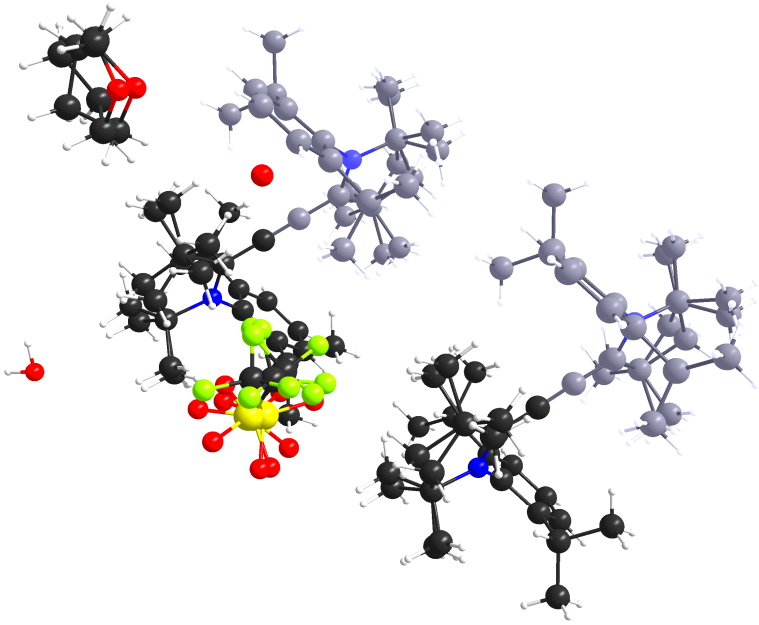


Figure S8 Disordered structure of compound **$1^{+}TfO^{-}\cdot THF\cdot H_2O$**. The second half of each of the C_4 units is symmetrically generated and displayed in gray. Black and gray: C; red: O; blue: N; green: F; yellow: S; white: H. (One asymmetric unit contains one TfO^{-} anion and two halves C_4^{+}. In fact, the molar ratio of C_4^{+} and TfO^{-} in crystal is 1:1.)

Table S1. Crystal data and structure refinements**.**

Compound	**1·2toluene**	**$1^{+}TfO^{-}\cdot THF\cdot H_2O$**	**$1^{+}TfO^{-}$**	**$1^{2+}[H(NO_3)_2^{-}]_2$**	**$1^{2+}[B(C_6F_5)_4^{-}]_2$**
Empirical formula	$C_{56}H_{78}N_2$	$C_{47}H_{71.7}F_3N_2O_5S$	$C_{43}H_{62}F_3N_2O_3S$	$C_{42}H_{64}N_6O_{12}$	$C_{90}H_{62}B_2F_{40}N_2$
CCDC	976141	976142	976143	976144	976145
Molecular weight	779.20	833.82	744.00	844.99	1953.03
Crystal size [mm]	0.30 x 0.17 x 0.12	0.11 x 0.09 x 0.02	0.17 x 0.09 x 0.02	0.320 x 0.260 x 0.220	0.17 x 0.10 x 0.05
Wavelength [pm]	61.992	0.61993	61.99	71.073	49.594
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	*P*-1	$P2_1/n$	*C*2/c
a [pm]	1056.4(8)	1213(3)	915.2(7)	1196.89(2)	2306.6(5) Å
b [pm]	1060.1(7)	2201(6)	1165.4(5)	1524.63(3)	1544.9(3) Å
c [pm]	1189.8(7)	1869(7)	1948.4(7)	1260.48(2)	2511.1(5) Å
α [°]	70.275(4)	90	81.942(12)	90	90
β [°]	74.673(4)	104.6(2)	87.120(12)	103.8880(10)	113.70(3)

γ [°]	76.263(4)	90	79.45(6)	90	90
V [nm^3]	1.1934(14)	4.828(26)	2.0222(19)	2.23290(7)	8.194(3)
Z	1	4	2	4	8
Temperature [K]	120(2)	150(2)	140(2)	100(2)	100(2)
ρ [Mgm^{-3}]	1.084	1.147	1.222	1.740	1.583
μ [mm^{-1}]	0.048	0.088	0.096	0.100	0.077
F (000)	428	1803	802	1264	3944
θ-area [°]	1.619 to 21.913	1.271 to 21.798	0.921 to 21.789	2.108 to 25.182	1.139 to 18.055
Total number of reflect.	27025	51299	10182	27921	49993
Unique reflections	4131	8255	6473	4006	8250
Reflections with $I>2\sigma(I)$					
R_{int}	0.0547	0.0371	0.0416	0.0517	0.0308
Number of restraints	486	526	161	0	347
Parameters	405	848	559	303	847
$R1$ [$I>2\sigma(I)$]	0.0507	0.0568	0.0850	0.035	0.0464
$wR2$ [$I>2\sigma(I)$]	0.1293	0.1744	0.2350	-	0.1313
$R1$ [all data]	0.0513	0.0733	0.1185	0.059	0.0583
$wR2$ [all data]	0.1299	0.1877	0.2592	-	0.1379
GooF	1.144	1.086	1.043	2.247	1.594
Extinction coeff.	1.12(4)	n/a	n/a	n/a	n/a
Largest diff. peak / hole [10^3·e·nm^{-3}]	0.274/ -0.286	0.254 / -0.302	0.617 / -0.311	0.400/ -0.272	0.306 / -0.329

The molecular structure of $\mathbf{1^{2+}[B(C_6F_5)_4^-]_2}$ exhibits a C_4 unit which is severely disordered (Figure S6) and two $B(C_6F_5)_4^-$ anions for balancing the charge. The C21i-C21-C1 bond angle (av. 158.0(9)°) in $\mathbf{1^{2+}[B(C_6F_5)_4^-]_2}$ is more bent than those in **1** (ca. 178.9°), $\mathbf{1^{+}TfO^{-}\cdot THF\cdot H_2O}$ (ca. 176.4°), and $\mathbf{1^{2+}[H(NO_3)_2^-]_2}$ (177.6°). This can be attributed to crystal packing effects. The ^{1}H NMR spectrum of $\mathbf{1^{2+}[B(C_6F_5)_4^-]_2}$ recorded in CD_3CN unambiguously shows characteristic resonances of cAAC, which confirms its diamagnetic property.

(S5) Theoretical calculation

Computational Details:

All calculations were performed with the Gaussian09 suite of program.[S12] Geometries were optimized in gas phase with the global hybrid meta generalized gradient approximation (GGA) to DFT hybrid functional, M06-2X[S13] with SVP[S14] basis set for all atoms. For open-shell structures geometry optimizations were performed at the unrestricted UM06-2X/SVP level. Geometries were fully optimized without symmetry constraints. Harmonic force constant were computed to confirm if the optimized geometries were located at minimum on the potential energy surface. We have also performed single point calculation incorporating higher basis set (TZVP)[S15] for all atoms. Natural Bond Orbital (NBO)[S16] analysis and Mulliken spin density calculations were obtained at M06-2X/TZVP level from the optimized geometries. Wiberg bond indices were also calculated to quantify the bond order.[S17] We have applied Bader's AIM (Atoms-in-molecule) concept[S18] to characterize the electron distributions. Any bonded pair of atoms has a bond path, i.e. a connecting line with maximum electron density. The bond critical point (BCP) is a point on this line where the gradient $\nabla\rho_b$ of the density is equal to zero. The magnitude of the electron density (ρ_b) and its Laplacian ($\nabla^2\rho_b$) at the BCP provide information about the strength and type of bond. The Laplacian indicates whether the density is locally concentrated ($\nabla^2\rho_b<0$) or depleted ($\nabla^2\rho_b>0$). Ellipticities at BCP represent the deviations of the bonding density from cylindrical symmetry. It is quantitatively expressed as $\varepsilon = \lambda_2/\lambda_1-1$, where λ_1 and λ_2 are eigenvalues of the Hessian of ρ at BCP. EPR parameters including the Landé splitting factors (g) and hyperfine coupling constants (*A*) were computed at UB3LYP/TZVP[S19] level. Optimized geometries and orbital diagrams are plotted in the Chemcraft visualization software.[S20]

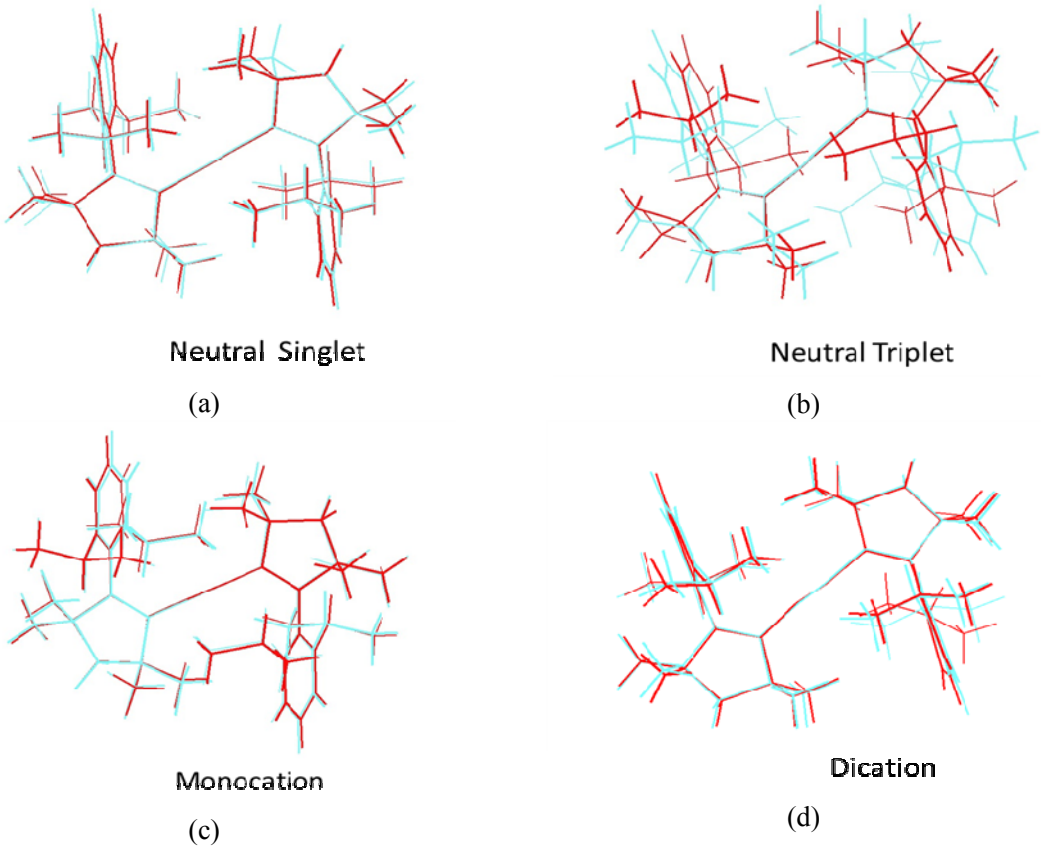


Figure S9 The DFT optimized and X-ray aligned structures of (a) singlet **1**, (b) triplet **1**, (c) cationic radical $\mathbf{1}^{\bullet+}$ and (d) dicationic $\mathbf{1}^{2+}$.

Table S2. Wiberg bond indices (WBI) of the optimized structures at M06-2X/TZVP//M06-2X/SVP level of theory. The values in parentheses are bond distances in Å.

Structure	N1-C1	C1-C21	C21-C21i	C21i-C1i	C1i-N1i
1	1.0694 (1.387)	1.6289 (1.333)	2.0723 (1.272)	1.6289 (1.333)	1.0692 (1.387)
$\mathbf{1}^{\bullet+}$	1.3149 (1.333)	1.3121 (1.375)	2.3424 (1.240)	1.3121 (1.375)	1.3145 (1.334)
$\mathbf{1}^{2+}$	1.6324 (1.288)	1.0863 (1.431)	2.6953 (1.211)	1.0869 (1.431)	1.6316 (1.288)

Table S3. The bond angles (in degrees) along the C1-C21-C21i-C1i framework for the X-ray and the DFT optimized structures.

	1 (Singlet)		**1** (Triplet)		$\mathbf{1}^{\bullet+}$		$\mathbf{1}^{2+}[H(NO_3)_2^-]_2$		$\mathbf{1}^{2+}[B(C_6F_5)_4^-]_2$	
	X-ray	Optimized	X-ray	Optimized	X-ray[a]	Optimized	X-ray	Optimized	X-ray[b]	Optimized

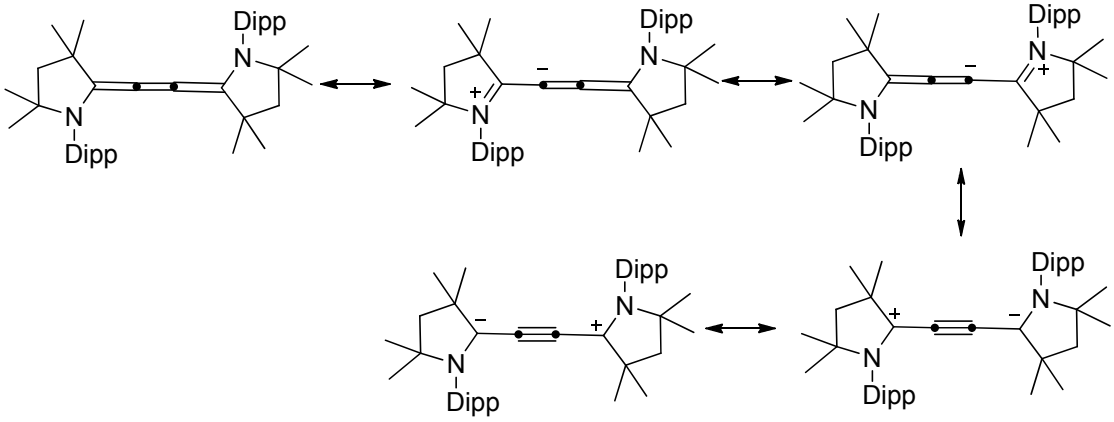
					(av.)					
∠C1C21C21i	178.9	179.2	-	174.3	176.4	178.6	177.6	176.9	158.0	176.9
∠C21C21iC1i	178.9	178.8	-	171.0	176.4	179.1	177.6	176.5	158.0	176.5

(Note: *a,* the data based on compound $\mathbf{1^{\cdot+}TfO^{-}\cdot THF\cdot H_2O}$; *b*, average of the values of the disordered C_4 parts in compound $\mathbf{1^{2+}[B(C_6F_5)_4^{-}]_2}$.)

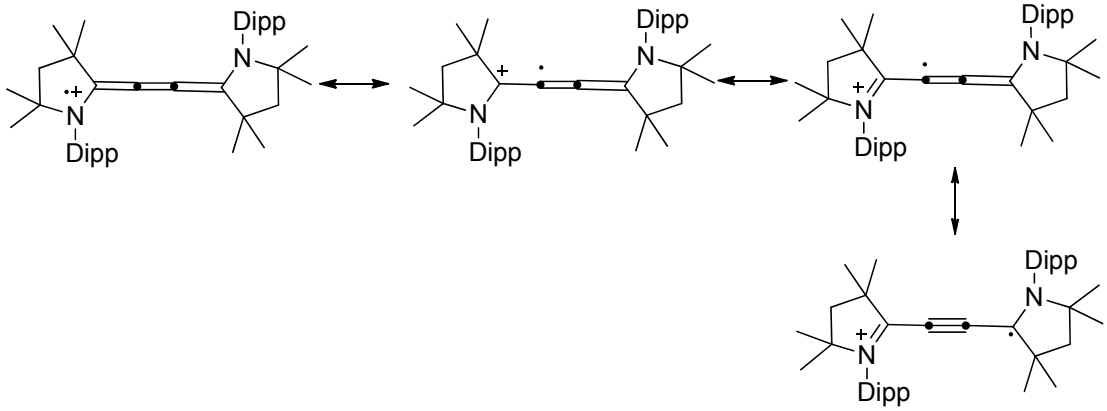
Table S4. Electron density ρ_b (e/Å^3), Laplacian $\nabla^2\rho_b$ (e/Å^5) and ellipticities ε_b at the selected bond critical points of the optimized structures.

Bond	Structure								
	1			**$1^{\cdot+}$**			**1^{2+}**		
	ρ_b	$\nabla^2\rho_b$	ε_b	ρ_b	$\nabla^2\rho_b$	ε_b	ρ_b	$\nabla^2\rho_b$	ε_b
N1□C1	0.296	-0.784	0.146	0.332	-0.852	0.154	0.366	-0.756	0.170
C1□C21i	0.333	-0.936	0.342	0.313	-0.896	0.168	0.286	-0.824	0.027
C21□C21i	0.361	-1.012	0.196	0.383	-1.080	0.143	0.404	-1.140	0.085
C21i□C1i	0.333	-0.936	0.340	0.313	-0.896	0.168	0.286	-0.824	0.027
C1i□N1i	0.296	-0.784	0.145	0.332	-0.852	0.156	0.366	-0.760	0.170

Scheme S1. Canonical forms of **1**.



Scheme S2. Canonical forms of $\mathbf{1^{\cdot+}}$. (partial)



Scheme S3. Canonical forms of $\mathbf{1}^{2+}$.

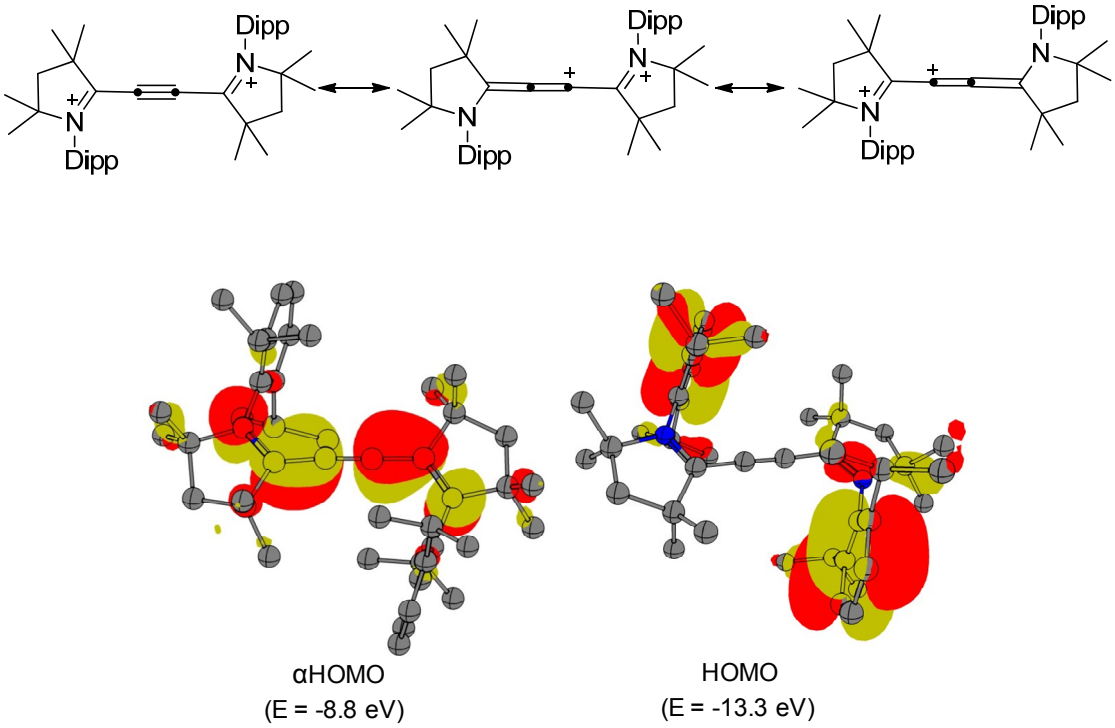
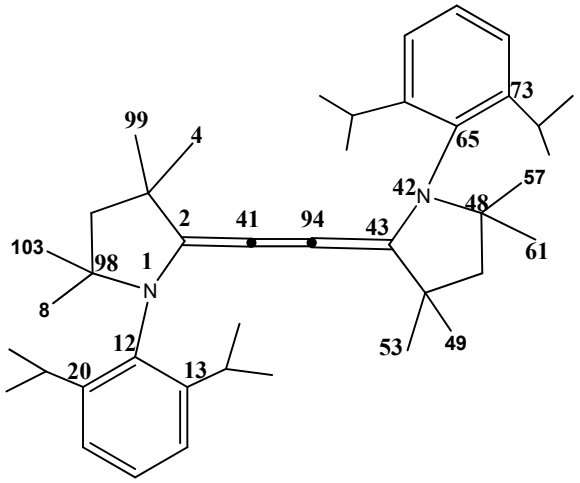


Figure S10 HOMO of $\mathbf{1}^{+}$ (left) and $\mathbf{1}^{2+}$ (right) at M06-TZVP//M06-2X/SVP level.

Calculated EPR result of $\mathbf{1}^{\cdot+}$



C_4 radical cation: $\mathbf{1}^{\cdot+}$

Table S5. Calculated *g*-tensor of $\mathbf{1}^{\cdot+}$ at UB3LYP/TZVP levels.

g_{iso}	g_{xx}	g_{yy}	g_{zz}
2.0028	2.0036	2.0029	2.0021

Table S6. Calculated hyperfine coupling constants (*A* in Gauss) of $\mathbf{1}^{\cdot+}$ at B3LYP/TZVP level.

Atom	A_{iso} (gauss)	A_{xx} (gauss)	A_{yy} (gauss)	A_{zz} (gauss)
N(1)	3.8011	-0.4338	-0.2998	12.1371
C(4)	3.8461	3.5311	3.5541	4.4541
C(8)	2.1009	1.7889	1.8119	1.5009
C(12)	-2.7462	-3.0582	-2.8292	-2.3512
C(13)	2.9087	2.5599	2.7227	3.4427
C(20)	2.9997	2.6467	2.7807	3.5707
C(41)	-2.8141	-7.0681	-5.6781	4.3038
N(42)	3.8046	-0.4313	-0.2963	12.1420
C(48)	-2.3423	-2.6323	-2.3033	-2.0913
C(49)	3.8505	3.5355	3.5585	4.4575
C(53)	2.3064	2.0724	2.1264	2.7484
C(57)	2.1231	1.8101	1.8331	2.7260
C(61)	3.9908	3.5328	3.5698	4.8698
C(65)	-2.7483	-3.0593	-2.8323	-2.3530
C(73)	2.9147	2.5627	2.7317	3.4487
C(94)	-2.8354	-7.1194	-5.6904	4.2675
C(98)	-2.3440	-2.6350	-2.3040	-2.0930
C(99)	2.2468	1.9988	2.0588	2.6828
C(103)	4.0202	3.5612	3.5982	4.9022

Figure S11 (a) Mulliken Spin density values and (b) spin density plots for $\mathbf{1}^{+\cdot}$.

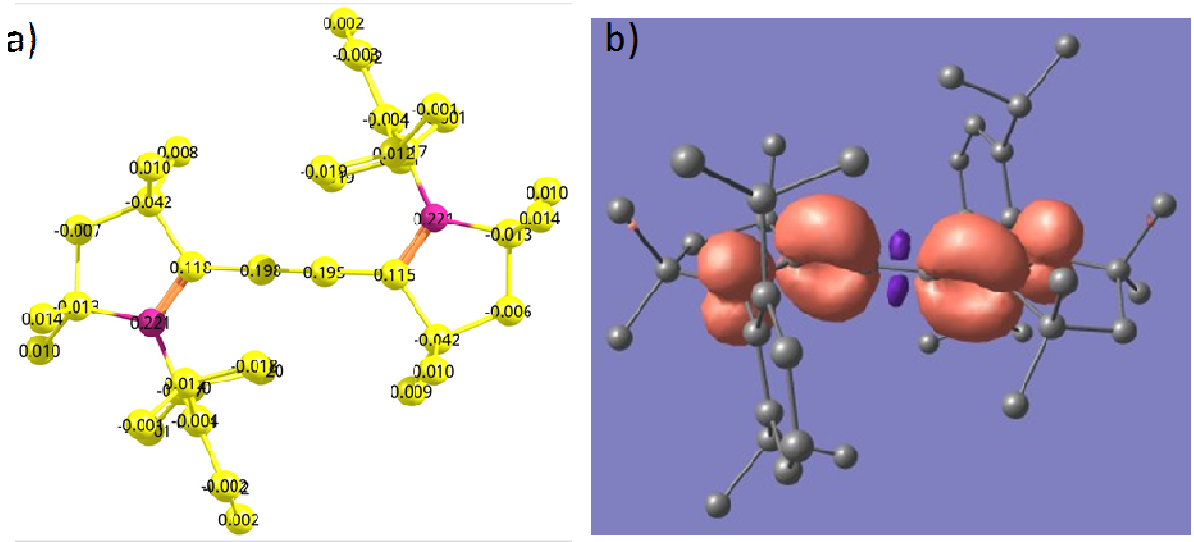


Table S7. Cartesian coordinates (in Å) of the optimized structures at M06-2X/SVP level.

Neutral Singlet:

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XYZ

N	3.346160000	4.957688000	3.308393000
C	2.465141000	5.886006000	3.844455000
C	1.206689000	5.941723000	2.987886000
C	0.077852000	5.154617000	3.669645000
H	-0.257854000	5.695592000	4.565897000
H	0.404970000	4.154331000	3.986328000
H	-0.779175000	5.044004000	2.986788000
C	3.965388000	4.357906000	0.973767000
H	3.589785000	3.870547000	0.062197000
H	4.857044000	3.807589000	1.312284000
H	4.263495000	5.381528000	0.713175000

C	4.582230000	4.695741000	3.962412000
C	4.647961000	3.716178000	4.977066000
C	5.872106000	3.491984000	5.615792000
H	5.937182000	2.731851000	6.397644000
C	7.001011000	4.233551000	5.284124000
H	7.949761000	4.041967000	5.788439000
C	6.908582000	5.242429000	4.331070000
H	7.784999000	5.854353000	4.105433000
C	5.703054000	5.505738000	3.673513000
C	3.414083000	2.971961000	5.457745000
H	2.590169000	3.234156000	4.783503000
C	3.596911000	1.452626000	5.430824000
H	3.904450000	1.095788000	4.437335000
H	2.657304000	0.948543000	5.702135000
H	4.363076000	1.130526000	6.152724000
C	3.016565000	3.448924000	6.859609000
H	2.852664000	4.536431000	6.870169000
H	3.803426000	3.209270000	7.592902000
H	2.088644000	2.953953000	7.185110000
C	5.617164000	6.703032000	2.741712000
H	4.617329000	6.697001000	2.287466000
C	6.663071000	6.646277000	1.625287000
H	6.516405000	7.476106000	0.917725000
H	6.609883000	5.701305000	1.066008000
H	7.681802000	6.737606000	2.032237000
C	5.738233000	8.008390000	3.537041000

H	5.628082000	8.875005000	2.866947000
H	6.723373000	8.080695000	4.025849000
H	4.962665000	8.068338000	4.314731000
C	2.690121000	6.588438000	4.954967000
N	2.261508000	8.904405000	7.638397000
C	3.138476000	7.959428000	7.124848000
C	4.349260000	7.843920000	8.041244000
C	4.234395000	9.150170000	8.860186000
H	4.823846000	9.933525000	8.358849000
H	4.626934000	9.039073000	9.881900000
C	2.748768000	9.575911000	8.858600000
C	4.224548000	6.585877000	8.913215000
H	4.339832000	5.689412000	8.287101000
H	5.009373000	6.574645000	9.685843000
H	3.245630000	6.521963000	9.408849000
C	5.653120000	7.770493000	7.247583000
H	5.648480000	6.891366000	6.582748000
H	5.784944000	8.667212000	6.624460000
H	6.514277000	7.685820000	7.928872000
C	2.598183000	11.096521000	8.768568000
H	2.957512000	11.559423000	9.699255000
H	3.178199000	11.513841000	7.935772000
H	1.541256000	11.374632000	8.634484000
C	2.002869000	9.109417000	10.117250000
H	2.368821000	9.660671000	10.995848000
H	0.925837000	9.309032000	10.013546000

H	2.140020000	8.037715000	10.308507000
C	1.019051000	9.145246000	6.988259000
C	0.954238000	10.099306000	5.948678000
C	-0.272374000	10.317797000	5.313534000
H	-0.337008000	11.060216000	4.514755000
C	-1.402212000	9.585704000	5.663221000
H	-2.351824000	9.768944000	5.157434000
C	-1.309435000	8.596349000	6.636322000
H	-2.186942000	7.992072000	6.877724000
C	-0.104118000	8.348469000	7.301043000
C	2.188194000	10.825925000	5.439831000
H	3.025723000	10.554724000	6.096333000
C	2.018106000	12.347084000	5.463270000
H	1.731360000	12.708488000	6.460998000
H	2.955943000	12.843057000	5.171120000
H	1.240695000	12.670004000	4.753927000
C	2.550776000	10.338704000	4.032079000
H	2.711846000	9.250884000	4.024760000
H	1.746517000	10.572304000	3.315965000
H	3.471129000	10.831042000	3.682098000
C	-0.017186000	7.177992000	8.265549000
H	0.974349000	7.211915000	8.731941000
C	-1.074748000	7.248769000	9.369647000
H	-0.926510000	6.436148000	10.096450000
H	-1.036843000	8.204970000	9.910946000
H	-2.089069000	7.139088000	8.956227000

C	-0.111396000	5.848932000	7.506807000
H	0.009115000	5.002894000	8.200970000
H	-1.093215000	5.746370000	7.016654000
H	0.670752000	5.778753000	6.736491000
C	2.920934000	7.251538000	6.016303000
C	1.699213000	5.271447000	1.684621000
H	2.067575000	6.054019000	1.003235000
H	0.896761000	4.726935000	1.165038000
C	2.878952000	4.342567000	2.051453000
C	0.740544000	7.378658000	2.759205000
H	-0.170836000	7.393694000	2.140926000
H	1.518523000	7.967777000	2.251983000
H	0.514881000	7.867128000	3.721380000
C	2.434656000	2.885733000	2.246954000
H	3.270122000	2.283136000	2.633416000
H	2.121280000	2.457333000	1.283524000
H	1.592771000	2.800309000	2.945781000

Neutral Triplet:

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XYZ

N	3.262041000	4.917472000	3.536691000
C	2.794522000	6.217979000	3.587562000
C	1.923986000	6.535477000	2.381496000
C	0.485781000	6.855373000	2.816817000
H	0.487617000	7.692943000	3.532927000

H	0.007166000	5.997709000	3.309509000
H	-0.127007000	7.138893000	1.946619000
C	3.461809000	3.128231000	1.813151000
H	2.894546000	2.596709000	1.035244000
H	3.853902000	2.385235000	2.523390000
H	4.314027000	3.631537000	1.336429000
C	4.484071000	4.532641000	4.167166000
C	4.471682000	3.856208000	5.400970000
C	5.690586000	3.462188000	5.965619000
H	5.689578000	2.927037000	6.917993000
C	6.897191000	3.756503000	5.345039000
H	7.838811000	3.441191000	5.797692000
C	6.901128000	4.474641000	4.152296000
H	7.852916000	4.731112000	3.683223000
C	5.708502000	4.878599000	3.548882000
C	3.188975000	3.611239000	6.171881000
H	2.363026000	3.986290000	5.554749000
C	2.951865000	2.124072000	6.445283000
H	2.981198000	1.532547000	5.518093000
H	1.970646000	1.971648000	6.920521000
H	3.716553000	1.715963000	7.124234000
C	3.196504000	4.420741000	7.474454000
H	3.290678000	5.496713000	7.259021000
H	4.039228000	4.122339000	8.118189000
H	2.266878000	4.255501000	8.041387000
C	5.762765000	5.736276000	2.295180000

H	4.760193000	5.734475000	1.846443000
C	6.743455000	5.203870000	1.247426000
H	6.658115000	5.786528000	0.318328000
H	6.552143000	4.146463000	1.011496000
H	7.785958000	5.288156000	1.588722000
C	6.094647000	7.186890000	2.668745000
H	6.094316000	7.828307000	1.773593000
H	7.094551000	7.243917000	3.127453000
H	5.364555000	7.586254000	3.388036000
C	3.015124000	7.055225000	4.666367000
N	2.156890000	8.649053000	7.658673000
C	3.289272000	8.387722000	6.907645000
C	4.544470000	8.850342000	7.629844000
C	3.952767000	9.520547000	8.893081000
H	3.925559000	10.612791000	8.751974000
H	4.553167000	9.319552000	9.792696000
C	2.501645000	9.002110000	9.052588000
C	5.459220000	7.660305000	7.956362000
H	5.719195000	7.122772000	7.030890000
H	6.389176000	8.008136000	8.433196000
H	4.973026000	6.944052000	8.633060000
C	5.328626000	9.845039000	6.764879000
H	5.650681000	9.358737000	5.831176000
H	4.709519000	10.714686000	6.499524000
H	6.224460000	10.201911000	7.297090000
C	1.567644000	10.064321000	9.622700000

H	1.896690000	10.331317000	10.637440000
H	1.567818000	10.974531000	9.007248000
H	0.535548000	9.688289000	9.681790000
C	2.448048000	7.751302000	9.940750000
H	2.845625000	7.974143000	10.942279000
H	1.411973000	7.401164000	10.052445000
H	3.037177000	6.933301000	9.501912000
C	0.885675000	8.863018000	7.044643000
C	0.635140000	10.098462000	6.402377000
C	-0.615941000	10.308710000	5.818158000
H	-0.821598000	11.258518000	5.320762000
C	-1.601845000	9.326677000	5.854642000
H	-2.576496000	9.510846000	5.399527000
C	-1.330545000	8.103891000	6.453456000
H	-2.092531000	7.321176000	6.452367000
C	-0.085912000	7.845118000	7.039578000
C	1.704079000	11.170529000	6.272191000
H	2.501856000	10.933103000	6.989063000
C	1.186143000	12.572668000	6.601115000
H	0.686835000	12.602435000	7.580999000
H	2.019996000	13.289999000	6.615783000
H	0.466680000	12.926445000	5.847722000
C	2.322519000	11.129830000	4.869178000
H	2.746876000	10.137887000	4.654906000
H	1.557376000	11.348690000	4.107362000
H	3.121475000	11.881737000	4.774878000

C	0.197917000	6.455516000	7.575934000
H	1.228409000	6.455546000	7.954934000
C	-0.743359000	6.072854000	8.720664000
H	-0.453868000	5.101516000	9.150089000
H	-0.729150000	6.823636000	9.524607000
H	-1.782590000	5.985097000	8.367595000
C	0.126850000	5.434050000	6.435211000
H	0.357570000	4.420867000	6.799886000
H	-0.880966000	5.407749000	5.990470000
H	0.846564000	5.695798000	5.643865000
C	3.241507000	7.708747000	5.702060000
C	2.033393000	5.228598000	1.560326000
H	2.767968000	5.363574000	0.750331000
H	1.077829000	4.947279000	1.093713000
C	2.544475000	4.122777000	2.516601000
C	2.482903000	7.742530000	1.618437000
H	1.877197000	7.954209000	0.723084000
H	3.522121000	7.565848000	1.304412000
H	2.469805000	8.633853000	2.264348000
C	1.381404000	3.361357000	3.168115000
H	1.761937000	2.582036000	3.844205000
H	0.761124000	2.876418000	2.399509000
H	0.746930000	4.039779000	3.756448000

Monocation:

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XYZ

N	3.340229000	4.972123000	3.339830000
C	2.473183000	5.858818000	3.830849000
C	1.227816000	5.969267000	2.970671000
C	0.056174000	5.268205000	3.675499000
H	-0.227579000	5.825690000	4.579607000
H	0.301773000	4.238607000	3.971215000
H	-0.813225000	5.238659000	3.002767000
C	3.975606000	4.309279000	1.018074000
H	3.598623000	3.800498000	0.120074000
H	4.857488000	3.757108000	1.375794000
H	4.281214000	5.321554000	0.727021000
C	4.589255000	4.707467000	4.003595000
C	4.639245000	3.736606000	5.023823000
C	5.867479000	3.522856000	5.658376000
H	5.937016000	2.769392000	6.445371000
C	6.995869000	4.257372000	5.310772000
H	7.946146000	4.068006000	5.812039000
C	6.907507000	5.248361000	4.338738000
H	7.788811000	5.844880000	4.094902000
C	5.703562000	5.507628000	3.677330000
C	3.416620000	2.975530000	5.511959000
H	2.572638000	3.229398000	4.858429000
C	3.621518000	1.458458000	5.461593000
H	3.941412000	1.117364000	4.467164000
H	2.688426000	0.938183000	5.721227000

H	4.387436000	1.138547000	6.183505000
C	3.034410000	3.418862000	6.929402000
H	2.839701000	4.500324000	6.968925000
H	3.839567000	3.187094000	7.643689000
H	2.128004000	2.891923000	7.262158000
C	5.632551000	6.677830000	2.708143000
H	4.639040000	6.675980000	2.238640000
C	6.686545000	6.575082000	1.601973000
H	6.546813000	7.378442000	0.864394000
H	6.635527000	5.610723000	1.077749000
H	7.701718000	6.679462000	2.012221000
C	5.764796000	8.006261000	3.463187000
H	5.678748000	8.851783000	2.764770000
H	6.743774000	8.078222000	3.962425000
H	4.982821000	8.108111000	4.229809000
C	2.696955000	6.567597000	4.988115000
N	2.253643000	8.870355000	7.622964000
C	3.123565000	7.975819000	7.150778000
C	4.366161000	7.882893000	8.016809000
C	4.210995000	9.149962000	8.890119000
H	4.804732000	9.964149000	8.448304000
H	4.574683000	8.991179000	9.914501000
C	2.720380000	9.550998000	8.876260000
C	4.328560000	6.577062000	8.825448000
H	4.427633000	5.713485000	8.152022000
H	5.168981000	6.559052000	9.534295000

H	3.394085000	6.463267000	9.392469000
C	5.636290000	7.912812000	7.163792000
H	5.678135000	7.037420000	6.495861000
H	5.680183000	8.822811000	6.547527000
H	6.521995000	7.891524000	7.815554000
C	2.522954000	11.062056000	8.790738000
H	2.856432000	11.513195000	9.735552000
H	3.107986000	11.511749000	7.979507000
H	1.461307000	11.313871000	8.649999000
C	1.954211000	9.029825000	10.094443000
H	2.299239000	9.569787000	10.986789000
H	0.876677000	9.214530000	9.982535000
H	2.114861000	7.957906000	10.264919000
C	1.000687000	9.112151000	6.957479000
C	0.956906000	10.090025000	5.942668000
C	-0.263812000	10.302783000	5.295209000
H	-0.328398000	11.062165000	4.513477000
C	-1.389860000	9.552337000	5.617401000
H	-2.334327000	9.737303000	5.103694000
C	-1.305796000	8.552306000	6.579873000
H	-2.185306000	7.946414000	6.806520000
C	-0.110895000	8.301148000	7.262274000
C	2.183341000	10.857583000	5.472770000
H	3.022612000	10.604258000	6.135253000
C	1.970330000	12.373142000	5.526243000
H	1.641896000	12.704714000	6.520912000

H	2.902703000	12.899264000	5.275605000
H	1.208590000	12.691976000	4.799569000
C	2.583530000	10.414547000	4.060150000
H	2.783227000	9.333824000	4.024900000
H	1.783347000	10.637362000	3.337394000
H	3.489952000	10.947054000	3.736363000
C	-0.050878000	7.135155000	8.236775000
H	0.935016000	7.143419000	8.717679000
C	-1.118066000	7.242817000	9.330225000
H	-0.984242000	6.445304000	10.075110000
H	-1.079832000	8.210115000	9.850259000
H	-2.127985000	7.132440000	8.908474000
C	-0.175485000	5.798665000	7.495322000
H	-0.095255000	4.961594000	8.204491000
H	-1.151164000	5.718460000	6.991024000
H	0.614751000	5.685575000	6.738880000
C	2.892051000	7.230815000	6.017990000
C	1.694212000	5.242349000	1.687179000
H	2.046395000	5.989508000	0.960280000
H	0.879791000	4.676048000	1.215118000
C	2.872133000	4.321173000	2.072079000
C	0.860479000	7.432025000	2.715675000
H	-0.025554000	7.484142000	2.065891000
H	1.683806000	7.969838000	2.222992000
H	0.624941000	7.945265000	3.662079000
C	2.432396000	2.878526000	2.333248000

H	3.266124000	2.285346000	2.733983000
H	2.120325000	2.426311000	1.381895000
H	1.586592000	2.818086000	3.029689000

Dication:

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XYZ

C	-2.71526	-7.57810	10.00946
H	-3.65505	-7.00724	10.00810
H	-2.44802	-7.84524	11.03871
H	-2.88743	-8.51158	9.45609
C	-2.91490	-4.62398	11.67497
C	-3.87958	-3.67071	12.01376
H	-4.35860	-3.72700	12.99289
C	-4.23777	-2.65696	11.13117
H	-5.00345	-1.93372	11.41507
C	-2.50961	-5.65538	12.71893
H	-1.77427	-6.34324	12.27469
C	-3.70627	-6.48571	13.19731
H	-4.25047	-6.94782	12.36326
H	-4.41915	-5.86175	13.75493
H	-3.36855	-7.28208	13.87518
C	-1.82494	-4.97570	13.91195
H	-0.93365	-4.41051	13.60044
H	-1.51321	-5.72956	14.64880
H	-2.51287	-4.28014	14.41578

C	4.06415	-0.00687	13.00699
H	4.93523	-0.66672	13.12928
H	4.00530	0.33403	11.96678
H	4.22192	0.87792	13.63884
C	4.29559	-2.88297	11.25968
C	5.25732	-3.87244	11.03431
H	5.87948	-3.81679	10.13927
C	5.43678	-4.92255	11.92967
H	6.20628	-5.67272	11.74255
C	4.08898	-1.79585	10.21378
H	3.37819	-1.05578	10.60930
C	5.39243	-1.06328	9.88012
H	5.89236	-0.68332	10.78144
H	6.09841	-1.72668	9.36038
H	5.18988	-0.21474	9.21179
C	3.45613	-2.38229	8.94534
H	2.47467	-2.83282	9.15775
H	3.31415	-1.59638	8.18998
H	4.10343	-3.15650	8.50634
C	0.84765	-3.20769	11.55416
C	1.31098	-2.06086	12.27476
C	0.43960	-0.88744	12.63985
C	1.50679	0.11202	13.14739
H	1.15476	0.67000	14.02477
H	1.72636	0.84194	12.35495
C	2.78431	-0.68821	13.47571

C	-0.55974	-1.34030	13.71962
H	-1.13712	-0.46551	14.05049
H	-1.26660	-2.07760	13.30999
H	-0.06340	-1.77763	14.59731
C	-0.32375	-0.37286	11.41547
H	-0.86140	0.54493	11.69319
H	0.35456	-0.13257	10.58340
H	-1.06525	-1.11055	11.07150
C	2.91454	-1.03646	14.95813
H	1.99670	-1.46970	15.37531
H	3.75226	-1.72565	15.12741
H	3.12701	-0.10717	15.50344
C	3.52729	-2.99724	12.43565
C	4.62831	-5.02584	13.05574
H	4.76062	-5.86755	13.73773
C	3.64040	-4.07561	13.33466
C	2.72622	-4.30619	14.52956
H	2.04609	-3.44814	14.62811
C	1.85609	-5.54954	14.30563
H	1.17638	-5.69510	15.15727
H	1.25057	-5.46059	13.39168
H	2.47869	-6.45237	14.21561
C	3.51055	-4.44565	15.83944
H	2.81912	-4.50355	16.69152
H	4.10927	-5.36773	15.84066
H	4.19862	-3.60686	16.00956

N	2.52903	-1.97112	12.68669
C	0.39687	-4.15153	10.94202
C	-0.07429	-5.31459	10.25355
C	0.82111	-6.40905	9.73557
C	-0.22605	-7.50219	9.41738
H	0.02326	-8.04905	8.49862
H	-0.25081	-8.22915	10.24168
C	-1.60404	-6.81528	9.29885
C	1.54888	-5.86827	8.49030
H	2.13947	-6.68295	8.04838
H	2.24021	-5.05835	8.76402
H	0.85261	-5.49471	7.72651
C	1.84397	-6.84155	10.78999
H	2.45637	-7.65675	10.37931
H	1.35319	-7.21049	11.70186
H	2.51708	-6.01108	11.05861
C	-2.02616	-6.54344	7.85529
H	-1.23177	-6.07979	7.25756
H	-2.92623	-5.91501	7.81775
H	-2.27139	-7.50955	7.39398
C	-2.34159	-4.52097	10.39190
C	-3.61374	-2.55791	9.89214
H	-3.88435	-1.74417	9.21706
C	-2.64117	-3.47953	9.49078
C	-1.93373	-3.26999	8.15919
H	-1.28156	-4.13224	7.96990

C	-1.02918	-2.03206	8.21038
H	-0.25637	-2.12804	8.98746
H	-1.61527	-1.12469	8.42156
H	-0.52755	-1.88914	7.24265
C	-2.92216	-3.16276	6.99298
H	-2.37948	-3.13503	6.03791
H	-3.51359	-2.23831	7.05894
H	-3.62631	-4.00551	6.96643
N	-1.32838	-5.49429	10.01603

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