Supporting Information

Persistent, Highly Localized, and Tunable [4]Helicene Radicals

Aslam C. Shaikh,[a] Jules Moutet,[a] José M. Veleta,[a] Md Mubarak Hossain,[a] Jan Bloch,[b] Andrei V. Astashkin,[a] and Thomas L. Gianetti*[a]

[a] Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, United States.
[b] Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich, Switzerland

*Email: tgianetti@arizona.edu

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I. General information

Unless otherwise stated, the syntheses of radicals were carried out in oven-dried vials or reaction vessels loaded with magnetic stirring bars inside an N₂ filled glove box. Dried solvents and liquid reagents were transferred by oven-dried or hypodermic syringes. Experiments were monitored by analytical thin layer chromatography (TLC), on pre-coated silica gel plates. After elution, plates were revealed under UV light with 254 nm wavelength. Melting points are uncorrected and recorded using digital Buchi Melting Point Apparatus B-540. ¹H and ¹³C NMR spectra and were recorded on Bruker AVII 400/500, spectrometers in deuterated solvents using TMS as internal standard, or the solvent residue signals as secondary standards, and the chemical shifts are shown in δ scales. Multiplicities of the ¹H NMR signals are denoted by s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin (quintet), m (multiplet), br.s (broad singlet)… etc. HRMS (ESI) were performed via LTQ Orbitrap Velos ETD mass-spectrometer (ThermoFisher Scientific, Bremen, Germany). Single-crystal X-ray diffraction data were collected on either a Bruker Kappa APEX II CCD diffractometer using Mo Kα radiation (λ = 0.71073Å) radiation, or a Bruker AXS single-crystal system equipped with a Excillum METALJET liquid gallium X-ray source, kappa goniometer, Oxford 800 series cryostream set to 100 K, and Photon III detector. Image collection, data reduction, and scaling were performed with Bruker AXS APEX3 software. Compounds were drawn using ChemDraw and the assignments of NMR spectra were done on MestReNova. All the chemicals and solvents were purchased from Sigma Aldrich, Fisher Scientific, or VWR and used without further purification. Organic solvents used were dried by using a solvent purification system. The electrolyte tetrabutylammonium hexafluorophosphate (TBAF-PF₆) was recrystallized from ethanol three times prior to use. Compound 1 was prepared according to Laursen report.¹

¹ B. W. Laursen, F. C. Krebs, M. F. Nielsen, K. Bechgaard, J. B. Christensen, and N. Harrit J. Am. Chem. Soc. 1998, 120, 12255-12263
II. General synthetic procedure

II.1 Typical procedures for synthesis of 2-H⁺, 2-NO₂⁺, and 3⁺ - 5⁺

Note: Compound 4⁺ was prepared according to previous report.

Racemic-5,9-bis(3-(dimethylamino)propyl)-1,13-dimethoxy-5,9-dihydro-13bH-quinolino[2,3,4-k/l]acridin-13b-ylium tetrafluoroborate salt (2-H⁺): N,N-dimethylpropane-1,3-diamine (6.28 ml, 49.46 mmol, 25 equiv) was added to a solution of tris(2,6-dimethoxyphenyl)carbenium tetrafluoroborate (1.00 g, 1.99 mmol, 1.0 equiv) in anhydrous acetonitrile (15 ml). The reaction mixture was heated at 85 °C for 12 hours then allowed to cool to room temperature. The crude product precipitated upon addition of Et₂O (~100 ml). The precipitate was filtered and washed several times with Et₂O, dried and collected. Selective precipitation by addition of Et₂O to a solution of crude product in CH₃CN afforded the dimethoxyquinaacidinium tetrafluoroborate salts (1.12 g, 96%).

Grey solid; Melting point: 218-220 °C; Rf = 0.12 (SiO₂, CH₂Cl₂:MeOH (80:20));

¹H NMR (400 MHz, Acetonitrile-d₃) δ = 8.12 (t, J = 8.5 Hz, 1H), 7.88 (dd, J = 8.9, 8.0 Hz, 2H), 7.56 (dd, J = 15.9, 8.7 Hz, 4H), 6.90 (d, J = 8.0 Hz, 2H), 4.71 (ddd, J = 15.6, 9.9, 5.9 Hz, 2H), 4.50 (ddd, J = 15.5, 9.7, 5.9 Hz, 2H), 3.72 (s, 6H), 2.50 (t, J = 6.4 Hz, 4H), 2.28 (s, 12H), 2.12 (m, 4H).

¹³C NMR (125 MHz, Acetonitrile-d₃) δ = 160.58, 143.43, 143.10, 139.90, 137.92, 137.33, 120.25, 113.86, 108.49, 105.86, 103.90, 57.16, 56.46, 48.99, 45.90, 25.14.

¹⁹F NMR (376 MHz, Acetonitrile-d₃) δ = -152.71, -152.66.

HRMS(ESI): m/z = Calcd for C₃₁H₃₉N₄O₂⁺ [M]⁺ 499.3068, found 499.3056.
Racemic-5,9-bis(3-(dimethylamino)propyl)-1,13-dimethoxy-6-nitro-5,9-dihydro-13bH-quinolino[2,3,4-kl]acridin-13b-ylium tetrafluoroborate salt (2-NO2+): To a solution of 2-H+ (500 mg) in CH2Cl2 (10 mL) was added aqueous HNO3 (67%, 3 mL). After 30 min of stirring at 25 °C, the reaction mixture was quenched by addition of aqueous NaOH (1.0 M, 40 mL) and then extracted with CH2Cl2 (3 x 10 mL). Aqueous HBF4 (1.0 M, 10 mL) was added to the combined organic layers, washed with NaOH (1.0 M, 20 mL) again, dried over Na2SO4, and evaporated under vacuum. The solid was precipitated using CH2Cl2 and Et2O solvent mixture. After filtration a dark red solid was obtained (490 mg, 90%). Layering with CH2Cl2 and n-hexanes yielded dark red crystals.

Melting point: 170-172 °C; Rf = 0.12 (SiO2, CH2Cl2:MeOH (80:20));

1H NMR (400 MHz, Methylene Chloride-d2) δ = 8.79 (d, J = 9.6 Hz, 1H), 8.12 (t, J = 8.5 Hz, 1H), 7.99 (t, J = 8.4 Hz, 1H), 7.91 (d, J = 9.6 Hz, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 4.99 (m, 2H), 4.88 (m, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.73 (m, 1H), 2.54 (t, J = 5.9 Hz, 2H), 2.32 (s, 6H), 2.26 (br.s, 2H), 1.95 (m, 1H), 1.81 (m, 1H), 1.69 (m, 2H), 1.52 (s, 6H).

13C NMR (100 MHz, Methylene Chloride-d2) δ = 159.88, 159.58, 141.75, 141.73, 141.27, 141.21, 139.22, 137.75, 136.55, 134.17, 132.03, 120.49, 116.57, 113.95, 109.90, 108.42, 106.69, 105.42, 104.99, 56.35, 56.32, 56.29, 55.35, 54.38, 54.11, 53.84, 53.57, 53.30, 45.73, 44.97, 26.32, 25.88.

19F NMR (376 MHz, Methylene Chloride-d2) δ = -152.48, -152.53.

HRMS(ESI): m/z=Calced for C31H38N5O4+ [M]+ 544.2918, found 544.2911.
Racemic-1,13-dimethoxy-5,9-bis(2-(pyridin-2-yl)ethyl)-5,9-dihydro-13bH-quinolino [2,3,4-kl]acridin-13b-ylium tetrafluoroborate salt (3\(^{+}\)); 2-(pyridin-2-yl)ethan-1-amine (5.97 ml, 49.75 mmol, 25 equiv) was added to a solution of tris(2,6 dimethoxyphenyl)carbenium tetrafluoroborate (1.00 g, 1.99 mmol, 1.0 equiv) in anhydrous acetonitrile (15 ml). The reaction mixture was heated at 85 °C for 12 hours then allowed to cool to room temperature. The crude product precipitated upon addition of Et\(_2\)O (~100 ml). The precipitate was filtered and washed several times with Et\(_2\)O, dried and collected. Selective precipitation by addition of Et\(_2\)O to a solution of the crude product in CH\(_2\)Cl\(_2\) afforded the dimethoxyquinacridinium tetrafluoroborate salts (1.15 g, 92%).

Grey solid; Melting point: 228-230 °C; R\(_f\) = 0.5 (SiO\(_2\), CH\(_2\)Cl\(_2\):MeOH (90:10));

\(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \(\delta = 8.56\) (s, 2H), 8.21 (t, \(J = 8.5\) Hz, 1H), 7.90 (t, \(J = 8.5\) Hz, 2H), 7.77 (d, \(J = 8.5\) Hz, 2H), 7.73 – 7.57 (m, 4H), 7.34 (d, \(J = 7.7\) Hz, 2H), 7.24 (t, \(J = 6.4\) Hz, 2H), 6.93 (d, \(J = 8.0\) Hz, 2H), 5.14 (ddd, \(J = 15.7, 9.5, 6.4\) Hz, 2H), 5.02 – 4.80 (m, 2H), 3.74 (s, 6H), 3.49 (q, \(J = 5.9\) Hz, 4H).

\(^{13}\)C NMR (100 MHz, Acetonitrile-\(d_3\)) \(\delta = 160.59, 158.44, 150.49, 143.10, 138.07, 137.81, 137.48, 124.72, 123.13, 113.98, 108.47, 106.09, 104.04, 56.49, 50.18, 34.83.

\(^{19}\)F NMR (376 MHz, Acetonitrile-\(d_3\)) \(\delta = -151.82\) (dd, \(J = 12.5, 7.3\) Hz).

HRMS(ESI): \(m/z=\text{Calcd for C}_{35}\text{H}_{31}\text{N}_4\text{O}_2^+\ [M]^+\ 539.2442, \text{found 539.2425}\)
Racemic-5-(3-(dimethylamino)propyl)-1,13-dimethoxy-9-(2-(pyridin-2-yl)ethyl)-5,9-
dihydro-13bH-quinolino[2,3,4-k]/acridin-13b-ylium tetrafluoroborate salt (5^+): 2-
(pyridin-2-yl)ethan-1-amine (0.292 mg, 2.3 mmol, 1.2 equiv) was added to a solution of tris(2,6
dimethoxyphenyl)carbenium tetrafluoroborate (1.00 g, 1.99 mmol, 1.0 equiv) in anhydrous
EtOAc (25 ml). The reaction mixture was stirred at room temperature for 1.5 hours. The crude
product precipitated upon addition of hexane (~100 ml). The precipitate was filtered and
washed several times with hexane and collected. Selective precipitation by addition of hexane
to a solution of the crude product in CH₂Cl₂ afforded the 9-(2,6-dimethoxyphenyl)-1,8-
dimethoxy-10-(2-(pyridin-2-yl)ethyl)-9,10-dihydroacridin-9-ylium tetrafluoroborate salts (S1,
1.07 g, 95%).² The first step product (1.0 gm, 1.76 mmol, 1.0 equiv) was dissolved in anhydrous
CH₃CN (15ml) and N,N-dimethylpropane-1,3-diamine (3.3 ml, 26.40 mmol, 15 equiv) was
added. The reaction mixture was heated at 85 °C for 12 hours and then allowed to cool to room
temperature. The crude product precipitated upon addition of Et₂O (~100 ml). The precipitate
was filtered and washed several times with Et₂O and collected. Selective precipitation by
addition of diethyl ether to a solution of the crude product in CH₃CN afforded the
dimethoxyquinacridinium tetrafluoroborate salts (0.94 g, 88%).
Grey solid; Melting point: 218-220 °C; Rf = 0.30 (SiO₂, CH₂Cl₂:MeOH (80:20));
¹H NMR (400 MHz, Chloroform-d) δ = 8.67 – 8.51 (m, 1H), 8.24 (t, J = 8.5 Hz, 1H), 7.91
(ddd, J = 8.9, 8.0, 6.9 Hz, 2H), 7.76 (d, J = 8.5 Hz, 1H), 7.69 (td, J = 7.7, 1.9 Hz, 1H), 7.63 (t,
J = 8.6 Hz, 2H), 7.53 (d, J = 8.9 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.22 (ddd, J = 7.6, 4.8, 1.1
Hz, 1H), 6.86 (dd, J = 8.0, 2.1 Hz, 2H), 5.12 (ddd, J = 15.8, 9.7, 6.7 Hz, 1H), 4.90 (ddd, J =
15.5, 9.7, 6.5 Hz, 1H), 4.81 (ddd, J = 15.5, 9.8, 6.0 Hz, 1H), 4.62 (ddd, J = 15.4, 9.8, 5.9 Hz,

² L. Mei, J. M. Veleta, J. Bloch, H. J. Goodman, D. Pierce-Navarro, A. Villalobos, T. L. Gianetti, *Dalton Trans.* 2020, *doi.org/10.1039/D0DT00419G*. 

S

1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.53 (td, J = 6.2, 3.0 Hz, 2H), 2.58 (t, J = 6.3 Hz, 2H), 2.35 (s, 6H), 2.28 – 2.10 (m, 1H).

13C NMR (100 MHz, Chloroform-d) δ = 159.78, 156.98, 149.82, 142.94, 142.20, 142.14, 138.97, 138.82, 137.73, 137.58, 137.32, 137.17, 124.18, 122.48, 119.23, 113.34, 107.47, 107.40, 105.17, 105.07, 103.22, 103.11, 56.44, 55.83, 45.78, 34.39, 24.82.

19F NMR (376 MHz, Chloroform-d) δ = -151.90 (d, J = 20.3 Hz).

HRMS(ESI): m/z = Calcd for C33H35N4O2+ [M]+ 519.2755, found 519.2743.

II.2 Typical Procedure for synthesis of 2-H·, 2-NO2·, and 3· - 5·

The potassium metal (1.1 equiv) was added to the stirred solution of dimethoxyquinacridinium tetrafluoroborate salts (200 mg, 1 equiv) in anhydrous THF (10 ml). The reaction mixture was stirred at rt for 12 hours and then reaction mixture was filtered and evaporated under vacuum pump. The crude product was triturated 2 times in 5 mL of Et2O then extract with toluene and filtrated again. The filtrate was recrystallized from toluene and hexane layering to afford the radical 2·-5·.

Paramagnetic NMR spectrums were obtained in C6D6 and the spectra are visible in what follows (Figures S14-15). Due to the important paramagnetic character paramagnetic character demonstrated by these species, the complete H attribution could not be completed.

HRMS(ESI) data for radicals:

2-H·: m/z = Calcd for C31H39N4O2: 499.3068, found 499.3068.

2-NO2·: m/z = Calcd for C31H38N5O4: 544.2918, found 519.2893.

3·: m/z = Calcd for C33H35N4O2: 519.2755, found 519.2743.

4·: m/z = Calcd for C35H31N4O4: 539.2442, found 539.2443.

5·: m/z = Calcd for C33H35N4O2: 519.2755, found 519.2743.
Figure S1. HRMS (ESI) spectra of 2-H⁺

Figure S2. HRMS (ESI) spectra of 2-NO₂⁻
Figure S3. HRMS (ESI) spectrum of 3'

Figure S4. HRMS (ESI) spectra of 4'
Figure S5. HRMS (ESI) spectra of 5⁺

III. NMR Spectroscopy data

III.1 NMR spectra of carbenium 2-H⁺

Figure S6. ¹H NMR spectrum of 2⁺ in CD₃CN
Figure S7. $^{13}$C NMR spectrum of 2-H$^+$ in CD$_3$CN

Figure S8. $^{13}$C DEPT-135 NMR spectrum of 2-H$^+$ in CD$_3$CN
Figure S9. $^{19}$F NMR spectrum of 2-H$^+$ in CD$_3$CN

Figure S10. $^1$H–$^1$H COSY spectrum of 2-H$^+$ in CD$_3$CN
Figure S11. $^1$H-$^{13}$C HMBC spectrum of 2-H$^+$ in CD$_3$CN

Figure S12. $^1$H-$^{13}$C HSQC spectrum of 2-H$^+$ in CD$_3$CN
III.2 NMR spectra of carbenium 2-NO$_2^+$

The carbenium 2-NO$_2^+$ has an unresolved $^1$H NMR spectrum in CD$_2$Cl$_2$ at room temperature. Variable temperature (VT) $^1$H NMR spectroscopy analysis of 2-NO$_2^+$ was conducted to resolve the broad signals observed. The sample was prepared in a non-coordinating deuterated dichloromethane and studied over a temperature range of 333 – 193 K (see Figures S13-S14). At room temperature (293 K), $^1$H NMR spectrum shows that the aromatic protons are poorly resolved, and the amino arms are in a rapid exchange suggested by the broad signal at 4.94 ppm. Decreasing the temperature to 193 K results in a sharp and well-defined proton signals (See Figure S15). The presence of the NO$_2$ group result in a low symmetry molecule as exemplified by the aromatic region, the two signals for OMe groups (at 3.77 and 3.73 ppm), two signals for NMe2 groups (2.32 and 1.40 ppm). The assignment of the six methylenic protons of the -nPr-NMe$_2$ arms was successfully carried out using low-temperature $^1$H-$^1$H COSY NMR sequence (see Figure S17). As observed in 2-H$,^+$ the two methylene groups alpha to helicenium scaffold are diasterotopic with the CH$_2$ near the NO$_2$ group resonating at 4.95/3.55 ppm (H$_A$/H$_A'$) and the other resonating at 4.86/4.68 ppm. However, instead of four additional freely rotating methylene groups (-CH$_2$(CH)$_2$NMe$_2$), we observed another set of diasterotopic methylenic protons at 1.92/1.75 ppm (H$_B$/H$_B'$). The presence of diastereostopic H$_B$/H$_B'$ protons along with the large chemical shift difference between the NMe$_2$ groups suggest an interaction between the nitrogen-lone pair of one -nPr-NMe$_2$ arm and the C$^+$ carbocation center (Scheme S1). This interaction is further supported by the presence of a resolved $^1$H NMR spectrum at room temperature for the reported 4-NO$_2^+$ compound containing -nPr arms instead of -nPr-NMe$_2$.³

![Scheme S1. NMe$_2$–C$^+$ interaction](image-url)
Figure S13: $^1$H NMR spectra of $2\text{-NO}_2^+$ in CD$_2$Cl$_2$ between 333 K and 193 K with 10 K increments.

Figure S14: $^1$H NMR of $2\text{-NO}_2^+$ in CD$_2$Cl$_2$ between 333 K and 193 K with 10 K increments.
Figure S15. $^1$H NMR of 2-NO$_2^+$ in CD$_2$Cl$_2$ at 193 K.

Figure S16. $^{13}$C NMR spectrum of 2-NO$_2^+$ in CD$_2$Cl$_2$ at 193 K
Figure S17: $^1$H-$^1$HCOSY NMR spectrum of 2-NO$_2^+$ in CD$_2$Cl$_2$ at 200K and XRD attribution.
III.3 NMR spectra of carbenium $3^+ - 5^+$

Figure S18. $^1$H NMR spectrum of $3^+$ in CD$_3$CN

Figure S19. $^{13}$C NMR spectrum of $3^+$ in CD$_3$CN
Figure S20. $^1$H NMR spectrum of $5^+$ in CD$_3$CN

Figure S21. $^{13}$C NMR spectrum of $5^+$ in CD$_3$CN
III.3 NMR spectra of radical 2' - 5'

The molecules 2'-5' were analyzed by paramagnetic 1H NMR to determine if the pendant arms of the molecule have any effect or interaction with the radical system (see Figure S22-S23). The NMR sequence used to analyze these compounds had a window width of 100 ppm (SW = 100), a scan number of 256 (NS = 256) and a τ1 of 0.1 seconds (D1 = 0.1s).

Due to the pronounced radical nature of these compounds, the aromatic protons of the helicene radical scaffold are not observable. However, the protons of the substituent arms α (N–CH₂–CH₂–R) and β (N–CH₂–CH₂–R) to the helicene core consistently appear broad and shifted at 17 and -7 ppm, respectively, for all radicals. The protons γ (N–CH₂–CH₂–R; R= CH₃, CH₂NMe₂, Py) to the helicene core are less influenced by the radical, and while broad, resonate in the diamagnetic 10-0 ppm region. For 2-H', γ-protons as broad bands of 4 ppm wide centered around 5.71 ppm. The NO₂ electron-withdrawing group on 2-NO₂' is speculated to have a widening effect on this band (from 9 to 2 ppm) still centered on around 5.71 ppm. The pyridinyl protons (π) for 3' and 5' are well-defined at 8.58, 7.38, 6.33 and 6.03 ppm respectively. In scaffold 5', the broad signature of γ-protons at 5.71 ppm is partially hidden by π-protons. The γ-protons on 4' from the n-propyl groups are less affected by the radical system and appeared as a broad peak centered at 2.88 ppm. It thus appears that the nature of the chosen pendant arms has little influence on the radical character of the compounds 2'-5'. Conversely, the substitution of a proton of the helicene core by an electron-withdrawing group induces a modification of the electronic structure of the resulting radical 2-NO₂'.
Figure S22: $^1$H NMR spectra of 2'-5' in C$_6$D$_6$ at 298 K

Figure S23: $^1$H NMR spectra of 2'-5' in C$_6$D$_6$ at 298 K. Impurities are indicated by an asterisk (*)
IV. Single crystal X-ray Diffraction

Table S1 Crystal data and structure refinement for 2-H⁺

| Identification code | CCDC          |
|---------------------|---------------|
|                     | 2-H⁺          |
| Empirical formula   | C₃₂H₄₁BCl₂F₄N₄O₂ |
| Formula weight      | 671.43        |
| Temperature/K       | 100.0         |
| Crystal system      | triclinic     |
| Space group         | P-1           |
| a/Å                 | 11.5110(3)    |
| b/Å                 | 12.4254(3)    |
| c/Å                 | 13.1831(3)    |
| α/°                 | 85.1060(18)   |
| β/°                 | 78.778(2)     |
| γ/°                 | 64.945(3)     |
| Volume/Å³           | 1675.45(8)    |
| Z                   | 2             |
| ρ calc g/cm³        | 1.3308        |
| μ mm⁻¹              | 0.251         |
| F(000)              | 705.0         |
| Crystal size/mm³    | 0.3 × 0.25 × 0.2 |
| Radiation           | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.3 to 52.74 |
| Index ranges        | -16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -17 ≤ l ≤ 18 |
| Reflections collected | 35035     |
| Independent reflections | 6857 [R_{int} = 0.0227, R_{sigma} = 0.0230] |
| Data/restraints/parameters | 6857/0/440 |
| Goodness-of-fit on F² | 1.077       |
| Final R indexes [I>2σ (I)] | R₁ = 0.0460, wR₂ = 0.1040 |
| Final R indexes [all data] | R₁ = 0.0508, wR₂ = 0.1066 |
| Largest diff. peak/hole / e Å⁻³ | 0.37/-0.25 |
### Table S2 Crystal data and structure refinement for 2-H⁺

| Property                          | Value                        |
|-----------------------------------|------------------------------|
| Identification code               | 2-H⁺                         |
| CCDC                              | 2004977                      |
| Empirical formula                 | C₃₁H₃₉N₄O₂                   |
| Formula weight                    | 500.53                       |
| Temperature/K                     | 100.0                        |
| Crystal system                    | orthorhombic                 |
| Space group                       | Pbca                         |
| a/Å                               | 20.1829(5)                   |
| b/Å                               | 10.7314(3)                   |
| c/Å                               | 25.5707(7)                   |
| α/°                               | 90                           |
| β/°                               | 90                           |
| γ/°                               | 90                           |
| Volume/Å³                         | 5538.4(3)                    |
| Z                                 | 8                            |
| ρ calc/cm³                        | 1.201                        |
| μ/mm⁻¹                            | 0.382                        |
| F(000)                            | 2155.0                       |
| Crystal size/mm³                  | 0.12 × 0.1 × 0.05            |
| Radiation                         | GaKα (λ = 1.34138)           |
| 2θ range for data collection/°    | 7.12 to 146.538              |
| Index ranges                      | -27 ≤ h ≤ 24, -13 ≤ k ≤ 14, -32 ≤ l ≤ 31 |
| Reflections collected             | 45766                        |
| Independent reflections           | 7238 [R_int = 0.0549, R_sigma = 0.0405] |
| Data/restraints/parameters        | 7238/6/414                   |
| Goodness-of-fit on F²             | 1.095                        |
| Final R indexes [I>2σ(I)]         | R₁ = 0.0669, wR₂ = 0.1402    |
| Final R indexes [all data]        | R₁ = 0.0906, wR₂ = 0.1506    |
| Largest diff. peak/hole / e Å⁻³   | 0.54/-0.25                   |
Table S3 Crystal data and structure refinement for 2-NO$_2^+$.

| Parameter                              | Value                      |
|----------------------------------------|----------------------------|
| Identification code                    | 2-NO$_2^+$                 |
| CCDC                                   | 2004974                    |
| Empirical formula                      | C$_{31}$ H$_{38}$ N$_5$ O$_4$ |
| Formula weight                         | 544.66                     |
| Temperature/K                          | 100.0                      |
| Crystal system                         | triclinic                  |
| Space group                            | P-1                        |
| a/Å                                    | 10.834(7)                  |
| b/Å                                    | 11.010(7)                  |
| c/Å                                    | 13.357(9)                  |
| $\alpha$/°                             | 71.977(17)                 |
| $\beta$/°                             | 84.217(17)                 |
| $\gamma$/°                            | 64.762(17)                 |
| Volume/Å$^3$                           | 1675.45(8)                 |
| Z                                      | 2                          |
| $\rho$ calc. g/cm$^3$                  | 1.3308                     |
| $\mu$/mm$^{-1}$                        | 0.251                      |
| F(000)                                 | 705.0                      |
| Crystal size/mm$^3$                    | 0.3 × 0.25 × 0.2           |
| Radiation                              | Mo K$\alpha$ ($\lambda = 0.71073$) |
| 2$\Theta$ range for data collection/°  | 6.3 to 52.74               |
| Index ranges                           | -16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -17 ≤ l ≤ 18 |
| Reflections collected                  | 35035                      |
| Independent reflections                | 6857 [R$_{int} = 0.0227$, R$_{sigma} = 0.0230$] |
| Data/restraints/parameters             | 6857/0/440                 |
| Goodness-of-fit on F$^2$               | 1.077                      |
| Final R indexes [I≥2σ (I)]             | R$_1 = 0.0460$, wR$_2 = 0.1040$ |
| Final R indexes [all data]             | R$_1 = 0.0508$, wR$_2 = 0.1066$ |
| Largest diff. peak/hole / e Å$^{-3}$   | 0.37/-0.25                |
| Crystal data and structure refinement for 2-NO$_2^-$  |
|------------------------------------------------------|
| **Identification code**                             |
| CCDC                                                 |
| 2-NO$_2^-$                                           |
| **Empirical formula**                               |
| C$_{31}$ H$_{38}$ N$_5$ O$_4$                        |
| **Formula weight**                                  |
| 544.66                                               |
| **Temperature/K**                                   |
| 100.0                                                |
| **Crystal system**                                  |
| triclinic                                            |
| **Space group**                                     |
| P-1                                                  |
| **a/Å**                                              |
| 10.834(7)                                            |
| **b/Å**                                              |
| 11.010(7)                                            |
| **c/Å**                                              |
| 13.357(9)                                            |
| **α/°**                                              |
| 71.977(17)                                           |
| **β/°**                                              |
| 84.217(17)                                           |
| **γ/°**                                              |
| 64.762(17)                                           |
| **Volume/Å$^3$**                                     |
| 1369.6(16)                                           |
| **Z**                                                |
| 2                                                    |
| **ρ$_{calc}$/g/cm$^3$**                              |
| 1.321                                                |
| **μ/mm$^1$**                                         |
| 0.089                                                |
| **F(000)**                                           |
| 582.0                                                |
| **Crystal size/mm$^3$**                              |
| 0.12 × 0.1 × 0.05                                    |
| **Radiation**                                        |
| GaKα ($λ = 1.34138$)                                |
| **2Θ range for data collection/°**                  |
| 7.12 to 146.538                                      |
| **Index ranges**                                     |
| -27 ≤ h ≤ 24, -13 ≤ k ≤ 14, -32 ≤ l ≤ 31          |
| **Reflections collected**                           |
| 45766                                                |
| **Independent reflections**                         |
| 7238 [R$_{int} = 0.0549$, R$_{sigma} = 0.0405$]     |
| **Data/restraints/parameters**                       |
| 7238/6/414                                           |
| **Goodness-of-fit on F$^2$**                         |
| 1.095                                                |
| **Final R indexes [I>=2σ (I)]**                     |
| $R_1 = 0.0669$, wR$_2 = 0.1402$                     |
| **Final R indexes [all data]**                       |
| $R_1 = 0.0906$, wR$_2 = 0.1506$                     |
| **Largest diff. peak/hole / e Å$^-3$**               |
| 0.54/-0.25                                          |
**Figure S24:** Packing for 2-H⁺ (for clarity hydrogen atoms and solvents molecules have been omitted)

**Figure S25:** Packing for 2-NO₂⁻ (for clarity hydrogen atoms and solvents molecules have been omitted)
Table S5. Characteristic Bond lengths and bond angles for 2-H\textsuperscript{+}, 2-H\textsuperscript{-}, 2-NO\textsubscript{2}\textsuperscript{+} and 2-NO\textsubscript{2}\textsuperscript{-}

| Selected Bonds and distances | 2-H\textsuperscript{+} | 2-H\textsuperscript{-} | 2-NO\textsubscript{2}\textsuperscript{+} | 2-NO\textsubscript{2}\textsuperscript{-} |
|-----------------------------|------------------------|------------------------|-------------------------------|-------------------------------|
| Bonds length (Å)            |                        |                        |                               |                               |
| C1–C2                       | 1.406(2)               | 1.439(2)               | 1.431(1)                      | 1.423(3)                      |
| C1–C3                       | 1.435(3)               | 1.444(2)               | 1.413(1)                      | 1.429(3)                      |
| C1–C4                       | 1.431(3)               | 1.446(2)               | 1.440(1)                      | 1.438(3)                      |
| O1−O2                       | 2.743                  | 2.772                  | 2.659                         | 2.773                         |
| C2–C5                       |                        |                        | 1.435(1)                      | 1.408(3)                      |
| C−NO\textsubscript{2}       |                        |                        | 1.452(1)                      | 1.444(3)                      |
| N2−O (NO\textsubscript{2})  |                        |                        | 1.233(1)/1.235(1)            | 1.226(2)/1.235(2)            |

| Selected Planes Angles      | 2-H\textsuperscript{+} | 2-H\textsuperscript{-} | 2-NO\textsubscript{2}\textsuperscript{+} | 2-NO\textsubscript{2}\textsuperscript{-} |
|-----------------------------|------------------------|------------------------|-------------------------------|-------------------------------|
| (MeO)Ph ^ (MeO)Ph           | 41.93                  | 45.92                  | 38.37                         | 52.05                         |

Figure S26: Distortion angle between aromatic rings MeO-Ph for 2-H\textsuperscript{+}, 2-H\textsuperscript{-}, 2-NO\textsubscript{2}\textsuperscript{+} and 2-NO\textsubscript{2}\textsuperscript{-} (for clarity hydrogen atoms and solvents molecules have been omitted).

Figure S27: Torsion angle between Me\textsubscript{2}N-\textit{n}Pr-N arm and the benzonaphthyridine core for 2-H\textsuperscript{-}, and 2-NO\textsubscript{2}\textsuperscript{-} (for clarity hydrogen atoms and solvents molecules have been omitted)
V. **EPR Spectroscopy**

The continuous wave (CW) electron paramagnetic resonance (EPR) experiments were carried out at the University of Arizona EPR Facility, on the X-band EPR spectrometer Elexsys E500 (Bruker Biospin) equipped with the electron-nuclear double resonance (ENDOR) system and variable temperature nitrogen flow system.

VI. **DFT Computational Details**

Density functional theory (DFT) calculations\(^1\,^2\) were done on a full atom scale using the unrestricted long-range corrected version\(^3\) of the hybrid 1993 Becke three-parameter exchange functional\(^4\,^5\,^6\) and the Lee–Yang–Parr non-local correlation functional\(^7\) (UCAM-B3LYP) implemented in Gaussian 09, revision D.01, software.\(^8\) The internal triple-\(\zeta\) quality basis set 6-311G(d,p) was applied to all atoms. The geometry optimized models were found as minima on the potential energy surface. Molecular orbitals (MO) and self-consistent field (SCF) spin density surfaces were obtained using the cubegen utility in Gaussian 09. All calculations were executed on the Ocelote cluster at the University of Arizona High Performance Computing center.

![Spin density distribution](image)

**Figure S28.** Spin density distribution for the calculated open-shell doublet models of 2–5\(^\cdot\). Surfaces were plotted at a 0.015 isovalue.
Figure S29. Frontier molecular orbital diagram of 2-H* (left) and 2-NO₂* (right) Percentage orbital contribution across the central carbon is also shown. Surfaces were plotted at a 0.04 isovalue.
Figure S30. Frontier MO diagram for the calculated DFT model of 3’. Iso-surfaces corresponding to the alpha orbitals of the model are shown at a 0.04 value. [a] The set of degenerate MOs corresponds to the same $\pi^*$ interaction located in the opposite pyridine moiety.
Figure S31. Frontier MO diagram for the calculated DFT model of 4’. Iso-surfaces corresponding to the alpha orbitals of the model are shown at a 0.04 value.
Figure S32. Frontier MO diagram for the calculated DFT model of 5’. Iso-surfaces corresponding to the alpha orbitals of the model are shown at a 0.04 value.
VII. UV-vis Spectra Analysis

VII.1 UV-vis Spectroscopy under anaerobic conditions

Absorption spectra were recorded on a ThermoScientific Evolution 220 UV-Visible spectrophotometer at 25 °C in analytical-grade solvents (con. 10-5 M). All UV samples for spectroscopy were prepared under an inert atmosphere in a Mbraun Labmaster glovebox maintained at less than 1 ppm O₂. A 3 mL gas-tight cuvette (Quartz Cuvette Self Masking Screw Cap) was used for anaerobic acquisition of spectra. All radicals decay kinetics were studied in the presence of oxygen, solutions of 2'-5' in CF₃-toluene prepared in a N₂-filled glove box were exposed to air and monitored by UV−vis spectroscopy over time.

The compounds 2-H⁺, 3⁺-5⁺ shows similar spectrum with three distinct absorption in the visible regions (λ > 350nm), indicating that the nitrogen bridge substituents have a negligible effect on the transition energy (Figure S29, and Table S6). A sharp peak around 620 nm (ε > 1400), a shoulder at 570 nm (ε > 10000), and a broad absorption around 430 nm (ε > 6000).

![UV-visible absorption spectra for 2⁺-5⁺](image)

**Figure S33.** Combined UV-visible absorption spectra for 2⁺-5⁺

All four radicals, 2-H⁺, 3⁺-5⁺ have a sharp absorption band with the maximum absorbance around 390 nm (ε > 15000), a shoulder at around 450 nm (ε > 5000), and a broad absorption peak around 560 nm (ε > 6000) (Figure S40, and Table S6). The blue shift in absorption bands compared to their cationic analogs indicates the presence of radical character at the central
atom and a reduction in the involvement of the heteroatoms in the molecular framework as well as a remarkably decreased conjugation.

**Figure S34.** Combined UV-visible absorption spectra for 2'-5'.

**Table S6.** Main features of UV-vis spectra of compounds of compounds 2-5 in \(\alpha,\alpha,\alpha\)-Trifluorotoluene

| Compound   | \(\lambda_{\text{max}}\) absorption [nm] (\(\varepsilon\) [M\(^{-1}\).cm\(^{-1}\)]) |
|------------|-----------------------------------------------------------------|
| 2-H\(^+\)  | 435 (6044), 577 (10526), 617 (14431)                              |
| 2-H\(^-\)  | 392 (15936), 445 (5093), 558 (6496)                              |
| 2-NO\(_2\)^+| 417 (18320), 576 (12854)                                         |
| 2-NO\(_2\)^-| 395 (26172), 505 (8116), 604 (1559)                              |
| 3\(^+\)    | 433 (7501), 574 (10987), 612 (14925)                              |
| 3\(^-\)    | 392 (23422), 444 (8061), 554 (9555)                               |
| 4\(^+\)    | 434 (7325), 570 (7706), 613 (10006)                               |
| 4\(^-\)    | 392 (19476), 476 (5245), 556 (7469)                               |
| 5\(^+\)    | 440 (6368), 572 (8705), 615 (11032)                               |
| 5\(^-\)    | 391 (16222), 473 (5229), 557 (7160)                               |
VII.2 Monitoring of radical decay upon exposure to air by UV-vis Spectroscopy.

To quantify the stability of all radicals in the presence of oxygen, solutions of 2•–5• in CF3-toluene prepared in a N2-filled glove box were exposed to air and monitored by UV–vis spectroscopy over time. The absorption spectrum of the cation and their radical analog under N2 atmosphere are shown in Figure S36, S38, S40, S42 and S44. The change in absorption spectroscopy for radical 2-H•, 2-NO2•, and 3•-5• after exposure to air are shown in Figure S37, S39, S41, S43 and S45 respectively, and show a slow decreased with time, reaching the lowest absorption limit within hours.

The first order decay of the absorption of each radical as well as their t1/2 is shown in Figure S35.

Figure S35. Plot of the first order decay of the absorbance for radical 2•-5•.
**Figure S36**: UV–vis spectra (6.8 × 10⁻⁵ M in CF₃-Toluene, room temperature) of 2-H⁺

**Figure S37.** Change of UV-visible absorption spectra for 2-H⁺ (6.8 × 10⁻⁵ M) with time after exposure to air
Figure S38: UV–vis spectra (5.9 × 10^{-5} M in CF3-Toluene, room temperature) of 2-NO2

Figure S39. Change of UV-visible absorption spectra for 2-NO2· (5.9 × 10^{-5} M) with time after exposure to air
**Figure S40**: UV−vis spectra (6.5 x 10⁻⁵ M in CF₃-Toluene, room temperature) of 3

**Figure S41**: Change of UV-visible absorption spectra for 3⁺ (6.5 x 10⁻⁵ M) with time after exposure to air
Figure S42: UV–vis spectra (8.7 × 10⁻⁵ M in CF₃-Toluene, room temperature) of 4

Figure S43. Change of UV-visible absorption spectra for 4⁺ (8.7 × 10⁻⁵ M) with time after exposure to air
**Figure S44:** UV−vis spectra (6.3×10⁻⁵ M in CF₃-Toluene, room temperature) of 5

**Figure S45.** Change of UV-visible absorption spectra for 5⁺ (6.3×10⁻⁵ M) with time after exposure to air
VIII. Cyclic Voltammetry

Note: Cyclic voltammograms of $2^-\rightarrow5^+$ (2 mM) in DCM ([TBA][PF$_6$] 0.1 M) solutions recorded at a platinum working electrode ($n = 0.1\ V/s$) and Ag/Ag$^+$ as internal reference electrode, Fc/Fc$^+$ was used as secondary reference by setting its $E_{1/2} = 0$. The arrows indicate the direction of the scan. All the cyclic voltammograms were recorded at ambient temperature.

VIII.1 CV data for $2^-\rightarrow H^+$

**Figure S46.** A cyclic voltammogram of $2^-\rightarrow H^+$ (2 mM) in CH$_2$Cl$_2$ ([TBA][PF$_6$] 0.1 M) solutions

**Figure S47.** A reversible reduction cyclic voltammogram of $2^-\rightarrow H^+$ (2 mM) in CH$_2$Cl$_2$ ([TBA][PF$_6$] 0.1 M) solutions
VII.2 CV data for 2-\text{NO}_2^+ 

**Figure S48.** A cyclic voltammogram of 2-\text{NO}_2^+ (2 mM) in CH$_2$Cl$_2$ ([TBA][PF$_6$] 0.1 M) solutions

**Figure S49.** A reversible reduction cyclic voltammogram of 2-\text{NO}_2^+ (2 mM) in CH$_2$Cl$_2$ ([TBA][PF$_6$] 0.1 M) solutions
VII.3 CV data for 3⁺

Figure S50. A cyclic voltammogram of 3⁺ (2 mM) in CH₂Cl₂ ([TBA][PF₆] 0.1 M) solutions

Figure S51. A reversible reduction cyclic voltammogram of 3⁺ (2 mM) in CH₂Cl₂ ([TBA][PF₆] 0.1 M) solutions
VIII.4 CV data for 4⁺

Figure S52. A cyclic voltammogram of 4⁺ (2 mM) in CH₂Cl₂ ([TBA][PF₆] 0.1 M) solutions

Figure S53. A first reversible reduction cyclic voltammogram of 4⁺ (2 mM) in CH₂Cl₂ ([TBA][PF₆] 0.1 M) solutions
VIII.5 CV data for 5⁺

**Figure S54.** A cyclic voltammogram of 5⁺ (2 mM) in CH₂Cl₂ ([TBA][PF₆] 0.1 M) solutions

**Figure S55.** A second reversible reduction cyclic voltammogram of 5⁺ (2 mM) in CH₂Cl₂ ([TBA][PF₆] 0.1 M) solutions
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