

Supporting Information

Diphosphane 2,2'-Binaphtho[1,8-*de*][1,3,2]dithiaphosphinine and the easy Formation of a stable Phosphorus Radical Cation†

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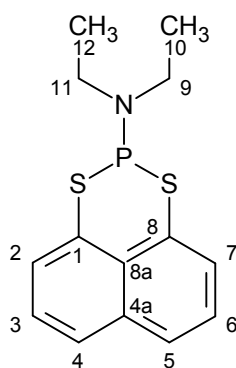
Experimental part

Unless otherwise stated all experiments were carried out under an oxygen- and moisture-free nitrogen or argon atmosphere using standard Schlenk and glovebox techniques and glassware. Dry solvents were collected from a *MBraun Solvent Purification System*. Elemental analyses were performed by Stephen Boyer at the London Metropolitan University. Infrared spectra were recorded for solids as KBr discs in the range 4000–300 cm^{-1} on a Perkin-Elmer System 2000 Fourier transform spectrometer. Transmittance values are qualitatively described as “very strong” (vs), “strong” (s), “weak” (w) and “very weak” (vw). ^1H , ^{13}C and ^{31}P solution-state NMR spectra were recorded on a Bruker Avance 300, Bruker Avance 400 or Bruker Avance 500 spectrometer with chemical shifts (reported in ppm) referenced to external $(\text{CH}_3)_4\text{Si}$ and 85% H_3PO_4 and internally referenced to the carbon nuclei ($^{13}\text{C}\{^1\text{H}\}$) or residual protons (^1H) of the solvent. Assignments of ^{13}C and ^1H NMR spectra were made with the help of ^1H – ^1H COSY and HSQC experiments. Coupling constants (J) are given in Hertz (Hz). Electron ionisation (APCI) mass spectra were carried out by the EPSRC National Mass Spectrometry Service, Swansea. EPR spectra were obtained using a Bruker EMX 10/12 spectrometer operating at ~ 9.5 GHz with 100 kHz modulation. The temperature was controlled via an Oxford ERS900 liquid helium cryostat operated with liquid nitrogen. Measurements were performed in an ELEXSYS Super Hi-Q resonator (Bruker). Samples were prepared under argon and contained in 4 mm OD quartz tubes (Wilmad lab-glass) sealed with rubber septa (Sigma-Aldrich). The EPR spectra of $\mathbf{3}^{*}$ were recorded at 80 K using a 30 mT field sweep centred at 333 mT with 512 points resolution, a time constant and conversion time of 40.96 ms each, a modulation amplitude of 0.05 mT and a microwave frequency of 9.3460 GHz. UV Vis spectrum was obtained on a JASCO V-650 Spectrophotometer on a powdered sample over a 900–200 nm range.

The naphtho[1,8-*cd*]1,2-dithiole precursor was prepared using standard literature procedures.⁵²

Synthesis of 2-(diethylamino)naphtho[1,8-*de*][1,3,2]dithiaphosphinine (1)

To naphtho[1,8-*cd*]-1,2-dithiole (2.00 g, 10.5 mmol) in 125 mL THF a solution of superhydride[®] in THF (1 M, 21.02 mL, 21.02 mmol) was added dropwise while stirring and cooled by an ice bath. The solution turned from orange to yellow under gas production. The solution was then further cooled down to -78 °C followed by the addition of (diethylamino)dichlorophosphine (1.53 mL, 10.5 mmol) while keeping the temperature at -78 °C. The solution was then allowed to warm up to room temperature and stirred for another 18 hours. The solvent was removed *in vacuo* and the residue was redissolved in hexane. After filtration, the solvent was removed *in vacuo*, resulting in a yellow-orange oil which crystallised after a while (2.9 g, 10 mmol, 95%, MP = 39 °C). The compound decomposes in contact with air.

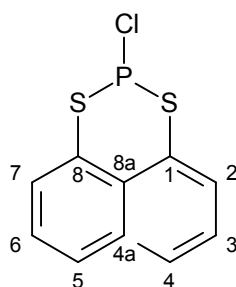


Scheme A1: Numbering-scheme for **1**.

¹H NMR (400.1 MHz, CDCl₃): δ (ppm) = 7.61 (d_t, ³J = 8.3 Hz, ⁴J = 1.2 Hz; 2 H, H-2, H-7), 7.51 (d_d, ³J = 7.4 Hz, ⁴J = 1.3 Hz; 2 H, H-4, H-5), 7.29 (t, ³J = 7.4 Hz; 2 H, H-3, H-6), 3.15 (q, ³J = 7.1 Hz; 4 H, 2 CH₂), 1.03 (t, ³J = 7.1 Hz; 6 H, 2 CH₃). **¹³C NMR** (100.6 MHz, CDCl₃): δ (ppm) = 135.5 (s; C-4a), 130.5 (s; C-2, C-7), 128.8 (d, ²J_{CP} = 11.2 Hz; C-1, C-8), 128.5 (s; C-4, C-5), 128.1 (d, ³J_{CP} = 5.3 Hz; C-8a), 125.8 (s; C-3, C-6), 44.6 (d, ¹J_{CN} = 17.9 Hz; C-9, C-11), 15.1 (d, ²J_{CN} = 4.4 Hz; C-10, C-12). **³¹P NMR** (162.0 MHz, CDCl₃): δ (ppm) = 69.0 (s). **MS** (APCI⁺): *m/z* = 294.0539 ([M+H]⁺). **IR** (KBr): $\tilde{\nu}_{\max}$ (cm⁻¹) = 3423 (w), 3049 (w), 2964 (s), 2925 (s), 2863 (m), 1922 (vw), 1546 (s), 1494 (m), 1453 (m), 1436 (m), 1374 (s), 1359 (s), 1328 (m), 1287 (m), 1199 (vs), 1197 (vs), 1092 (s), 1060 (s), 1019 (vs), 932 (s), 883 (s), 812 (vs), 786 (s), 754 (vs), 660 (s), 578 (m), 549 (m), 522 (m), 505 (s), 472 (m), 448 (m).

Synthesis of 2-chloronaphtho[1,8-de][1,3,2]dithiaphosphinine (**2**)

A solution of 2-(diethylamino)naphtho[1,8-de][1,3,2]dithiaphosphinine (3.5 g, 12 mmol) in 250 mL THF was cooled down to -78 °C. Afterwards trichlorophosphine (1.16 mL, 13.3 mmol) was added dropwise under stirring while keeping the temperature at -78 °C, changing the colour of the solution from orange to a pale yellow. The solution was then allowed to warm up to room temperature and stirred for another 18 hours. The solvent was removed *in vacuo* without exposing the mixture to the atmosphere, leaving a yellow-white solid (2.88 g, 11.2 mmol, 93 % MP = 115 °C). The substance decomposes slowly in contact with air.

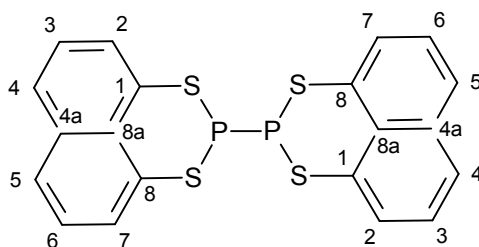


Scheme A2: Numbering-scheme for **2**.

EA (C₁₀H₆CIPS₂): found (%): C 46.94, H 2.27; calc. (%): C 46.79, H 2.36. **¹H{³¹P} NMR** (300.1 MHz, benzene-*d*₆): δ (ppm) = 7.25 (d_t, ³J = 8.2 Hz, ⁴J = 1.1 Hz; 2 H, H-2, H-7), 7.19 (d_t, ³J = 7.3 Hz, ⁴J = 1.3 Hz; 2 H, H-4, H-5), 6.83 (d_t, ³J = 8.2 Hz, ³J = 7.4 Hz; 2 H, H-3, H-6). **¹³C NMR** (75.6 MHz, benzene-*d*₆): δ (ppm) = 135.5 (d, ³J_{CP} = 3.6 Hz; C-8a), 131.8 (d, ³J_{CP} = 3.2 Hz; C-2, C-7), 130.5 (s; C-4, C-5), 126.2 (s; C-3, C-6), 128.8 (s; C-4a), 123.1 (d, ²J_{CP} = 14.0 Hz; C-1, C-8). **³¹P NMR** (121.5 MHz, benzene-*d*₆): δ (ppm) = 72.4 (s). **MS** (APCI⁺): *m/z* = 256.9411 ([M]⁺). **IR** (KBr): $\tilde{\nu}_{\max}$ (cm⁻¹) = 3421 (vs), 2986 (vs), 2819 (s), 2468 (w), 1638 (m), 1545 (w), 1493 (w), 1261 (m), 1200 (vs), 1149 (s), 1021 (vs), 887 (m), 814 (vs), 756 (vs), 547 (w), 489 (vs), 453 (vs).

Synthesis of 2,2'-binaphtho[1,8-*de*][1,3,2]dithiaphosphinine (**3**)

Magnesium (215 mg) was heated to 90°C in a flask under N₂ for three hours and cooled down to RT. A solution of 2-chloronaphtho[1,8-*de*][1,3,2]dithiaphosphinine (1.0 g, 3.9 mmol) in THF (100 mL) was added and stirred for one day under reflux at 70 °C. The mixture was filtered, the solvent evaporated and the residue dissolved in hexane (100 mL) and filtered. The remaining solid was dried *in vacuo* and redissolved in toluene (100 mL). After filtration, the solvent was evaporated and the solid was redissolved in a small amount of THF (20 mL). After another filtration, the residue was dried, and a white solid remained (0.4 g, 0.9 mmol, 23%, MP = 140°C).



Scheme A3: Numbering-scheme for **3**.

¹H NMR (500.1 MHz, CDCl₃): δ (ppm) = 7.83 (d_t, ³J = 8.2 Hz, ⁴J = 1.3 Hz; 4 H, H-2, H-7), 7.70 (d_t, ³J = 7.3 Hz, ⁴J = 1.3 Hz; 4 H, H-4, H-5), 7.43 (d_t, ³J = 8.1 Hz, ⁴J = 7.3 Hz; 4 H, H-3, H-6). **¹³C NMR** (125.8 MHz, CDCl₃): δ (ppm) = 135.7 (s; C-8a), 131.3 (s; C-4, C-5), 130.4 (s; C-2, C-7), 127.4 (s; C-4a), 125.5 (s; C-3, C-6), 124.2 (t, ³J = 8.0 Hz; C-1, C-8). **³¹P {¹H} NMR** (202.5 MHz, CDCl₃): δ (ppm) = -15.1 (s). **MS** (EI): *m/z* = 221.0 ([M/2]⁺), 442.0 ([M]⁺). **IR** (KBr): $\tilde{\nu}_{\max}$ (cm⁻¹) = 3450(w), 3047 (vw), 2964 (vw), 2376 (vw), 2345 (vw), 1545 (m), 1493 (m), 1359 (vw), 1329 (vw), 1316 (vw), 1261 (w), 1201 (m), 1146 (w), 1091 (w), 1056 (w), 1023 (w), 886 (w), 811 (vs), 752 (s), 574 (vw), 547 (w), 509 (w), 490 (m), 388 (w).

Synthesis of the radical cation 3^{•+}

To a solution of 2,2'-binaphtho[1,8-*de*][1,3,2]dithiaphosphinine (20 mg, 0.05 mmol) in 4 mL dried DCM NOBF₄ (10 mg, 0.075 mmol) was added. The solution turned green under gas production and a green precipitate formed. The mixture was stirred for another hour and then filtered, leaving the dark green solid.

MS (ESI⁺): $m/z = 445$ ([M+3H]⁺). **IR** (KBr): $\tilde{\nu}_{\max}$ (cm⁻¹) = 3212 (vs), 2261 (w), 1640 (m), 1461 (vs), 1299 (w), 1197 (m), 1084 (vs), 1057 (vs), 1032 (vs), 884 (w), 809 (s), 652 (w), 548 (m), 533 (m), 522 (m).

Single crystal analysis

Single-crystal **X-ray** diffraction data were collected using either a *Rigaku XtaLAB P200* diffractometer using multilayer mirror monochromated molybdenum K_α radiation source ($\lambda = 71.075$ pm) or a *Rigaku Saturn724* diffractometer using graphite monochromated molybdenum K_α radiation source ($\lambda = 71.075$ pm). Data were collected, solved and refined using SHELXS-97^{S3} and SHELXL-97^{S4} and verified using PLATON.^{S5} Structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. The finalised CIF files were checked with checkCIF.^{S6} Intra- and intermolecular contacts were analysed with Diamond (version 3.2k).^{S7} Thermal ellipsoids are drawn at the 50 % probability level.

Table A.1: Crystallographic and refinement data for **6** and **8**.

	6	8
Formula	C ₁₄ H ₂₂ PS ₂ N	C ₂₀ H ₁₂ P ₂ S ₄
Formula weight [g·mol ⁻¹]	293.37	442.48
Crystal system	orthorhombic	triclinic
Colour	colourless	colourless
Habit	prism	prism
Crystal size [mm]	0.15 × 0.12 × 0.04	0.30 × 0.12 × 0.04
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (19)	<i>P</i> -1 (2)
<i>a</i> [Å]	7.6600(15)	7.5926(15)
<i>b</i> [Å]	13.325(3)	7.7769(16)
<i>c</i> [Å]	14.112(3)	9.5253(19)
α [°]	90	100.33(3)
β [°]	90	112.83(3)
γ [°]	90	105.95(3)
<i>V</i> [Å ³]	1440.4(5)	471.8(3)
<i>Z</i>	4	1
Density calc. [g·cm ⁻³]	1.353	1.557
<i>T</i> [K]	173	173
<i>F</i> (000)	616	226
μ [mm ⁻¹]	0.462	0.675
Absorption correction	multi-scan	multi-scan
Index ranges	-9 ≤ <i>h</i> ≤ 9 -16 ≤ <i>k</i> ≤ 15 -16 ≤ <i>l</i> ≤ 17	-9 ≤ <i>h</i> ≤ 9 -9 ≤ <i>k</i> ≤ 9 -11 ≤ <i>l</i> ≤ 11
θ range [°]	2.102–25.372	2.451–25.375
Reflections collected	17514	7771
Independent reflections	2642	1743
Observed reflections	2139	1538
<i>R</i> _{int}	0.0781	0.0450
Parameters	165	118
Restraints	0	0
Data-to-Parameter ratio	16.0	14.8
Hydrogen atom treatment	constrained	constrained
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0762/0.1470	0.0282/0.0983
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0541/0.1352	0.0309/0.1102
<i>S</i>	1.058	0.876
larg. diff peak/hole [e·Å ⁻³]	1.285/-0.234	0.431/-0.253

Computational Details

Geometry optimization of the structures was carried out in B3LYP using the 6-31G(d) basis set for **3** and UB3LYP using the 6-31+G(d) basis set for **3⁺**. The structures were characterized as minima by frequency calculation. All calculations were done using the Gaussian 09 program package.^{S8}

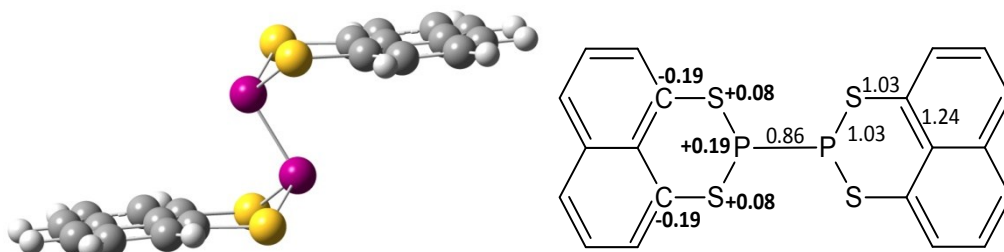


Figure A1: Optimised geometry of **3** (left) and NBO bond orders and charges (bold) (right). Calculated bond lengths (Å) and angles (°) of **3**: P1–P1(i) 2.3018, P1–S1 2.12881, P1–S2 2.12881, S1–C1 1.79876, S2–C8 1.79876, S1··S2 3.23724, S1–P1–S2 98.98824, P1–S1–C1 106.77688, P1–S2–C8 106.77688, S1–P1–P1(i) 101.37630, S2–P1–P1(i) 101.37630. Total energy: -3044.603069 au.

Table A2: Natural bond orbitals (NBOs) with their natural hybrid orbital compositions for the two equal phosphorus atoms in **3**.

NBO	Occupancy	Coefficient	Hybrid	Compositions		
P1 lone pair	1.91814		$sp^{1.27} d^{0.00}$	s(43.96 %)	p(55.93 %)	d(0.10%)
P1-S1	1.96701	0.6529	$sp^{4.31} d^{0.08}$	s(18.56 %)	p(80.04 %)	d(1.40 %)
P1-S2	1.96701	0.6529	$sp^{4.31} d^{0.08}$	s(18.56 %)	p(80.04 %)	d(1.40 %)
P1-P1(i)	1.96239	0.7071	$sp^{4.27} d^{0.04}$	s(18.80 %)	p(80.37 %)	d(0.82 %)
Σ				s(99.88 %)	p(296.38 %)	d(3.72 %)

The hybridisation of each phosphorus atom in **3** involves one sp -rich ($sp^{1.27}$) lone pair orbital and three p -rich ($sp^{4.82}$, $sp^{4.31}$ and $sp^{4.31}$) orbitals. The summation of the compositions confirms that these four hybrid orbitals are mostly consisting of one s -orbital and three p -orbitals, representing an inequivalent sp^3 hybridized phosphorus atom.

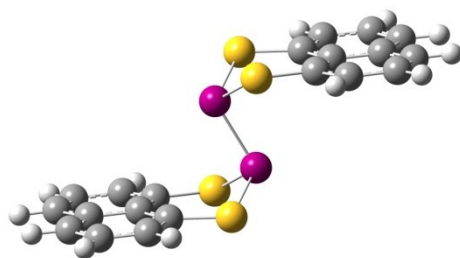


Figure A2: Optimised geometry of **3⁺**. Calculated bond lengths (Å) and angles (°) of **3⁺**: P1–P1(i) 2.28855, P1–S1 2.13199, P1–S2 2.13199, S1–C1 1.78023, S2–C8 1.78023, S1...S2 3.24694, S1–P1–S2 99.190, P1–S1–C1 107.752, P1–S2–C8 107.752, S1–P1–P1(i) 100.609, S2–P1–P1(i) 100.609.

Table A3: Natural bond orbitals (NBOs) with their natural hybrid orbital compositions for the phosphorus atom in the radical cation of **3**.

NBO	Occupancy	Coefficient	Hybrid	Compositions		
P1 lone pair	0.98019		sp ^{0.48} d ^{0.00}	s(67.54 %)	p(32.39 %)	d(0.06%)
P1–S1	0.98395	0.6407	sp ^{7.81} d ^{0.12}	s(11.20 %)	p(87.46 %)	d(1.34 %)
P1–S2	0.98391	0.6407	sp ^{7.81} d ^{0.12}	s(11.20 %)	p(87.47 %)	d(1.33 %)
P1–P1(i)	0.98044	0.7071	sp ^{8.89} d ^{0.07}	s(10.04 %)	p(89.25 %)	d(0.72 %)
Σ				s(99.98 %)	p(296.57 %)	d(3.45 %)
P1(i) lone pair	0.98019		sp ^{0.48} d ^{0.00}	s(67.54 %)	p(32.40 %)	d(0.06%)
P1(i)–S3	0.98394	0.6407	sp ^{7.81} d ^{0.12}	s(11.20 %)	p(87.46 %)	d(1.34 %)
P1(i)–S4	0.98392	0.6407	sp ^{7.81} d ^{0.12}	s(11.20 %)	p(87.47 %)	d(1.33 %)
P1(i)–P1	0.98044	0.7071	sp ^{8.89} d ^{0.07}	s(10.04 %)	p(89.25 %)	d(0.72 %)
Σ				s(99.98 %)	p(296.58 %)	d(3.45 %)

Coordinations of the optimised Structures

3

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radical cation of 3

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 0.0103801202\P,1.1109934029,0.2894500227,-0.0125054382\\Version=AM64L-
 G09RevA.02\State=2-A\HF=-3044.6415699\S2=0.757598\S2-1=0.\S2A=0.750054\RMSD=3.169e-
 09\RMSF=1.577e-05\ZeroPoint=0.2635784\Thermal=0.2858854\Dipole=-0.000027,0.0002296,-
 0.0004343\

UV Vis Spectrum of the radical cation of **3**

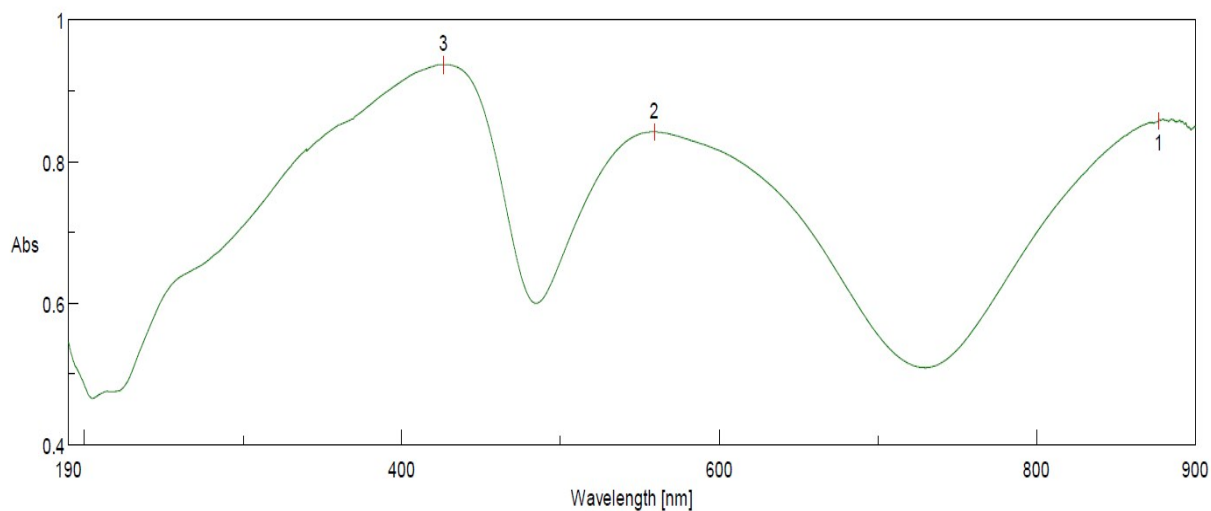


Figure A3: Experimental UV Vis powder spectrum of the radical cation of **3**.

Table A4: Detailed Information of the UV Vis measurement of the radical cation of **3**.

Data array type	Linear data array	Photometric mode	Abs
Data interval	0.1 nm	Measurement range	900–190 nm
Data points	7101	UV/Vis bandwidth	5.0 nm
Response	Medium	Scan speed	200 nm·min ⁻¹
Change source at	340 nm	Light source	D2/WI
Filter exchange	Step	Correction	Baseline

Calculated UV Vis spectrum of the radical cation of **3**

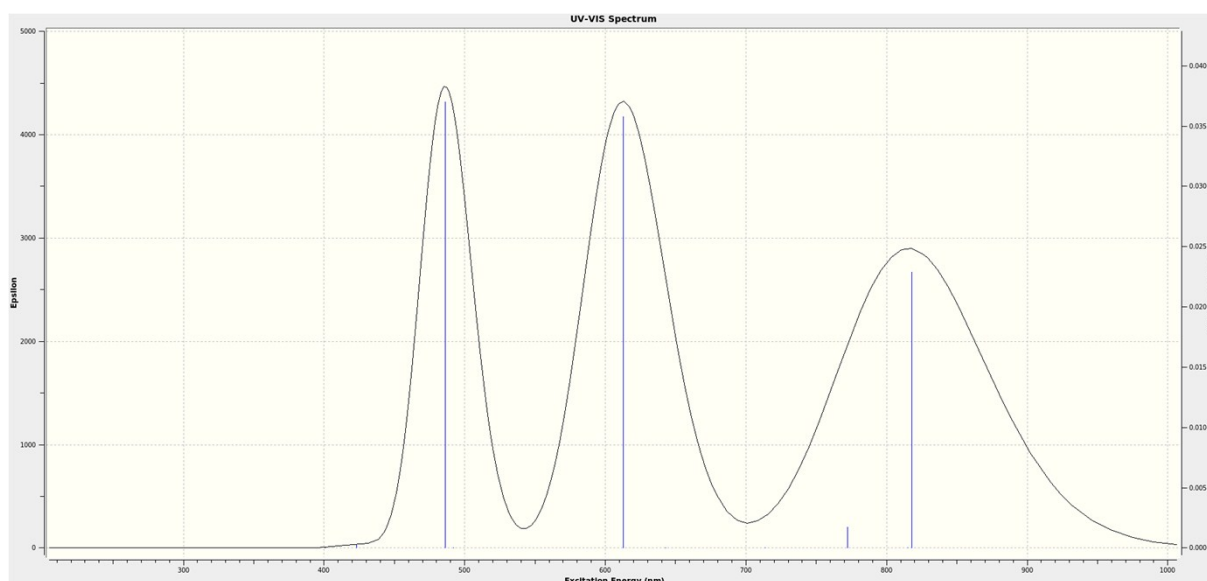


Figure A4: Calculated UV Vis spectrum of the visible area of the radical cation of **3** using the TD UB3LYP/6-31+G(d) basis set.

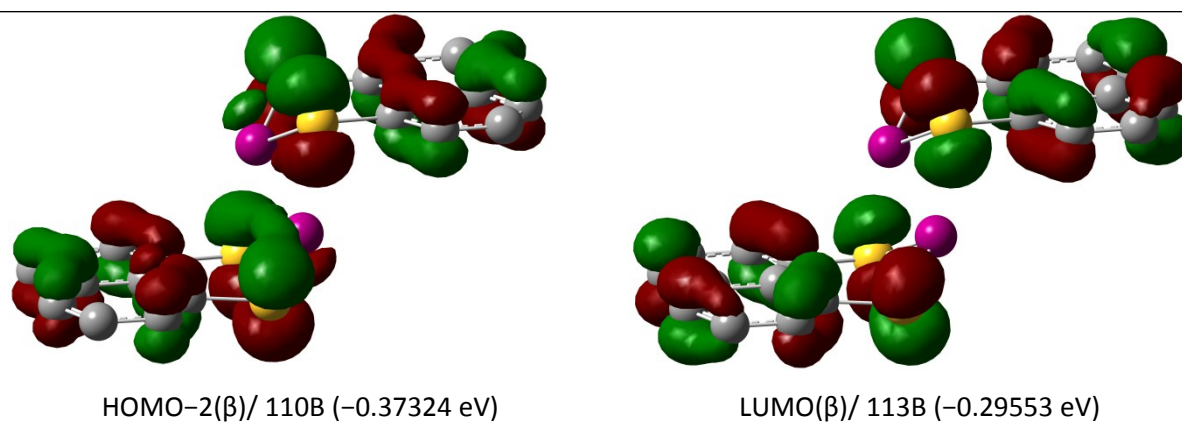
The UV Vis spectrum was calculated using the optimized structure of the radical cation of **3**.

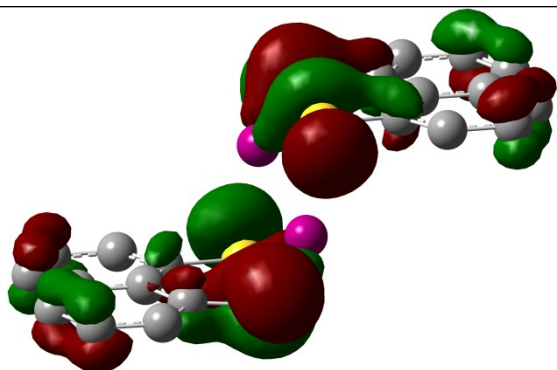
Excited State 3: 2.013-AU 1.5156 eV 818.03 nm f=0.0229 $\langle S^2 \rangle = 0.763$
 110B \rightarrow 113B 0.98657

Excited State 8: 2.030-BU 2.0239 eV 612.61 nm f=0.0358 $\langle S^2 \rangle = 0.780$
 105B \rightarrow 113B 0.98181

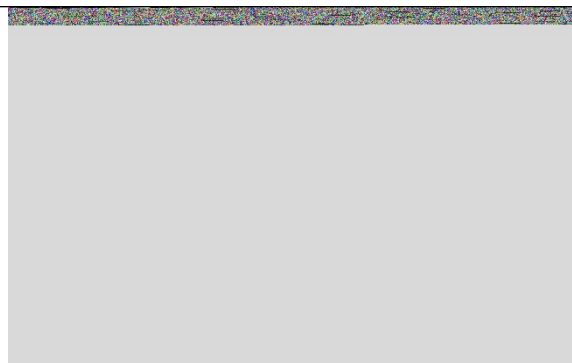
Excited State 10: 3.018-BU 2.5508 eV 486.06 nm f=0.0370 $\langle S^2 \rangle = 2.026$
 113A \rightarrow 114A 0.56903
 112B \rightarrow 115B 0.60774

Table A5: Visualized Kohn-Sham molecular orbitals and their energies of the radical cation **3^{•+}**. Isovalue set at 0.03. Hydrogen atoms are omitted for clarity.

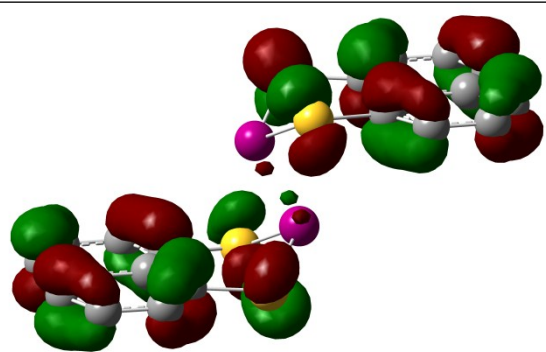




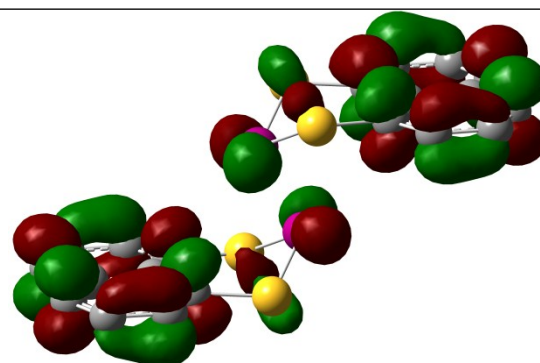
HOMO-7(β)/ 105B (-0.39413 eV)



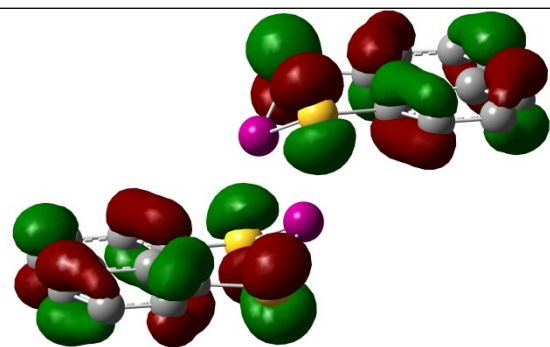
LUMO(β)/ 113B (-0.29553 eV)



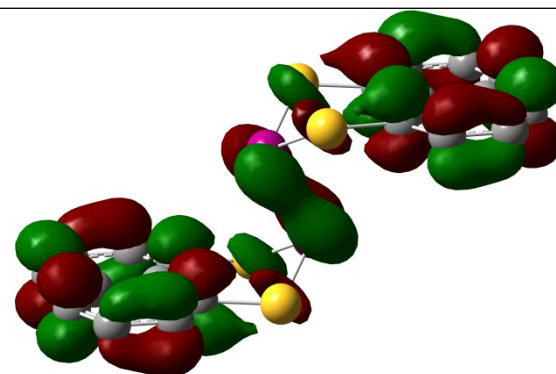
HOMO-1(β)/ 112B (-0.32226 eV)



LUMO+2(β)/ 115B (-0.18100 eV)



HOMO(α)/ 113A (-0.33114 eV)



LUMO(α)/ 114A (-0.19128 eV)

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