Supporting Information for:

Phosphoryl- and Phosphonium-Bridged Viologens as Stable Two- and Three-Electron Acceptors for Organic Electrodes

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General Considerations

$^{31}\text{P}\{^1\text{H}\}$ NMR, $^1\text{H}$ NMR, $^{19}\text{F}\{^1\text{H}\}$ NMR, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker Fourier 300HD, or Bruker Avance (-II,-III) 400 MHz spectrometers. Chemical shifts were referenced to external 85% H$_3$PO$_4$ ($^{31}\text{P}$), C$_6$F$_6$ ($^{19}\text{F}$) and external TMS ($^1\text{H}, ^{13}\text{C}$) or residual non-deuterated solvent peaks ($^1\text{H}, ^{13}\text{C}$). Mass spectra were run on a Finnigan SSQ 7000 spectrometer or a Bruker Daltonics AutoFlex III system. Optical spectroscopy was conducted using a Cary 5000 UV-vis spectrophotometer. Microwave reactions were conducted using an Anton Paar Monowave 200. All electrochemical experiments were conducted on Metrohm Autolab PGSTAT204 potentiostat. Batteries were fabricated using an EL-Cell reusable coin cell apparatus. Calculations were conducted at the B3LYP/6-31+g(d) level of theory using the default solvation model in acetonitrile in Gaussian. TD-DFT calculations were used to calculate the excitation energies from the optimized geometries. Winsim was used to simulate EPR spectra starting from hyperfine coupling data taken from the Gaussian output calculations on each respective molecule. Elemental analysis was performed using an Elementar vario EL cube. Single crystals were coated in Paratone-N oil in the glove-box, mounted on a MiTegen Micromount and placed under an N2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals. Data reduction was performed using the SAINT software package, and an absorption correction was applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least squares on F2 using XL as implemented in the SHELXTL suite of programs. All nonhydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.
Materials

All solvents for the synthesis, battery fabrication, and electrochemical characterization were purchased from Sigma Aldrich, sparged with argon, dried over activated molecular sieves, and stored under argon atmosphere prior to use. All reactions and manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques. PhPCl₂ was purchased from Sigma Aldrich and distilled prior to use. Poly(vinyl endifluoride) (PVDF; Mₚ = 534,000) and Lithium triflate (99.95% purity) were purchased from Sigma Aldrich. TBAPF₆ was purchased from Sigma Aldrich then recrystallized from ethanol and dried under vacuum before use. SWCNTs were purchased from Raymor and used as received. Lithium and Aluminum foil was purchased from Sigma Aldrich and stored under argon. NMR solvents were purchased from Sigma-Aldrich. 3,3’-dibromo-4,4’-bipyridine was prepared to our previously reported procedures. All reactions and manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques.
Calculation and EPR simulation details:

Calculations were conducted using Gaussian \(^{52}\) at the B3LYP/6-31+g(d) level of theory first without a solvation model to optimize the geometry. Energy calculations were conducted using the same level of theory including a default solvation model in acetonitrile on the optimized geometries to calculate orbital geometries, orbital energies, spin densities, spin density maps, and hyperfine coupling constants. TD-DFT calculations were conducted at the B3LYP/6-31+g(d) to calculate the excitation energies using a default solvation model in acetonitrile from the previously optimized geometries. The top ten excitation energies were calculated (triplet and singlet for radicals and singlets only for non-radicals) and the three excitations having the strongest oscillator strength are listed. Simulated EPR spectra are created using the previous DFT calculations to determine the nuclei having the highest spin densities (top 6-9 nuclei), then extracting their hyperfine coupling constants from the respective LOG files. Winsim was used to optimize EPR spectra starting from hyperfine coupling data taken from the Gaussian output calculations on each respective molecule.
**Synthesis of 2,7-diazadibenzophenylphosphole:**

Anhydrous THF (50mL) was added to an oven dried Schlenk flask, charged with a stir bar and 3,3’-dibromo-4,4’-bipyridine (275 mg, 0.88 mmol) under argon gas. The solution was then cooled to -90 °C using an acetone-liquid nitrogen bath. N-butyllithium (2.46 M, 1.80 mmol, 0.730 mL) was then added dropwise over 15 minutes upon which the reaction turned orange. The reaction was then stirred at -90 °C for 1 hour. Dichlorophenylphosphane (165 mg, 0.92 mmol) was added via syringe all at once at -90 °C upon which the reaction turned dark brown. The reaction was immediately placed in a water bath at 40 °C and stirred for 1 hour before removing the solvent under reduced pressure to leave a brown oil. The product was taken up in anhydrous methylene chloride and filtered through celite to remove impurities. The solvent was removed under reduced pressure to give 2,7-diazadibenzophenylphosphole as a pale yellow air sensitive solid (150 mg, 0.57 mmol, 65 %). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 9.106 (s, 2H), 8.806 (d, $J = 5$ Hz, 2H), 7.931 (d, $J = 5$ Hz, 2H), 7.359 (m br., 1H), 7.287 (m br., 4H) ppm. $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$: -16.012 ppm. The material was characterized by NMR (matching previous literature reports)$^3$ and used immediately in the next step without further purification due to its air and moisture sensitivity.
Synthesis of 2,7-diazadibenzophenylphosphole sulfide:

Anhydrous methylene chloride (20 mL) was added to an oven dried Schlenk flask charged with a stir bar and 2,7-diazadibenzophenylphosphole (259 mg, 0.99 mmol). An excess of sulfur was added (50 mg) and the reaction was refluxed for 16 hours. The solvent was removed under reduced pressure and the product was dissolved in anhydrous acetonitrile and filtered to remove excess sulfur. Acetonitrile was removed under reduced pressure to yield a pale yellow solid (203 mg, 0.69 mmol, 70 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 9.01 (d br., $J = 4$ Hz, 2H), 8.95 (dd, $J = 3$ Hz, 5 Hz, 2H), 7.84 (d br., $J = 4$ Hz, 2H), 7.72 (m br., 2H), 7.56 (m br., 1H), 7.45 (m br., 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 153.7, 151.2 (d, $J = 12$ Hz), 146.7 (d, $J = 16$ Hz), 132.9 (d, $J = 3$ Hz), 132.1, 131.2, 130.9 (d, $J = 12$ Hz), 129.2 (d, $J = 12$ Hz), 128.3, 116.7 (d, $J = 6$ Hz) ppm. $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$: 39.3 ppm. HRMS (ESI, m/z): [M+H]$^+$ calcd for: C$_{16}$H$_{12}$N$_2$PS, m/z = 295.0459; Found [M+H]$^+$ m/z = 295.0447, $\Delta = 4.0671$ ppm.
Synthesis of phenylphosphaviologen sulfide (PVS)

An oven dried Schlenk flask is charged with 2,7-diazadibenzophenylphosphole sulfide (0.480 g, 1.63 mmol), anhydrous methylene chloride (25 mL) and a stir bar. Methyl triflate (0.670 g, 4.10 mmol) was added all at once and the reaction was stirred at 35 °C for 16 hours under argon after which a pale yellow precipitate formed. The product was decanted and washed with anhydrous methylene chloride (2 x 15 mL) and anhydrous diethyl ether (2 x 15 mL) to yield a pale yellow powder (773 mg, 76 %). X-ray quality crystals were formed by slow evaporation of an acetonitrile solution of PVS. $^1$H NMR (400 MHz, CD$_3$CN) $\delta$: 9.18 (d, $J = 6$ Hz, 2H), 9.08 (d, $J = 6$ Hz, 2H), 8.90 (dd, $J= 2$ Hz, $J= 6$ Hz, 2H), 7.81 (m br., 3H), 7.62 (m br., 2H), 4.40 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CD$_3$CN) $\delta$: 150.2, 149.4, 149.070 (d, $J = 12$ Hz), 146.4 (d, $J = 18$ Hz), 136.5, 135.6, 133.6 (d, $J = 3$ Hz), 130.9 (d, $J = 12$ Hz), 128.7 (d, $J = 15$ Hz), 123.7 (d, $J = 7$ Hz), 116.3, 48.3 ppm. $^{31}$P NMR (161 MHz, CD$_3$CN) $\delta$: 40.4 ppm. $^{19}$F NMR (376 MHz, CD$_3$CN) $\delta$: 79.31 ppm. HRMS (ESI, m/z): [M - 2 triflates (C$_2$F$_6$O$_6$S$_2$)]$^{2+}$ calcd for: C$_{18}$H$_{17}$SN$_2$P, m/z = 162.0425; Found [M - 2 triflates (C$_2$F$_6$O$_6$S$_2$)]$^{2+}$, m/z = 162.0419, $\Delta = -3.7027$ ppm. Elemental Analysis (C$_{20}$H$_{17}$F$_6$O$_6$S$_3$N$_2$P): C: Expected 38.59 %, Found 38.86 %, S: Expected 15.45 %, Found 14.59 %, N: Expected 4.50 %, Found 5.56 %, H: Expected 2.752 %, Found 2.097 %.
Synthesis of methylphenylphosphaviologen (PVM):

A solution of 2,7-diazadibenzophenylphosphole (150 mg, 0.57 mmol) dissolved in anhydrous chlorobenzene (6 mL) was added to an oven dried microwave vial charged with a stir bar under Argon. Methyl triflate (0.540 g, 3.9 mmol) was added via syringe and the flask was placed in a microwave reactor and heated to 180 ºC for 10 minutes, reaching a maximum pressure of 6 bar, then cooled to 55 ºC. This process was repeated 3 times to give an off-white precipitate in a yellow solution. Under argon, the chlorobenzene was decanted and the product was washed with anhydrous methylene chloride (2 x 5 mL), anhydrous diethyl ether (2 x 5mL), and anhydrous tetrahydrofuran (2 x 5mL). The product was then taken up in acetonitrile and filtered using a syringe filter into a tared Schlenk flask. Acetonitrile was removed under reduced pressure to yield an off-white crystalline solid (240 mg, 0.34 mmol 52 %). Please note this material is air and light sensitive in solution, forming the radical species which may broaden NMR signals. ¹H NMR (700 MHz, CD₃CN) δ: 9.67 (d, J = 6 Hz, 2H), 9.28 (d, J = 6 Hz, 2H), 9.05 (dd, J = 2 Hz, J = 6 Hz, 2H), 8.00 (m br., 3H), 7.77 (m br., 2H), 4.50 (s, 6H), 3.24 (d, J_C-P = 16 Hz) ppm. ¹³C NMR (176 MHz, CD₃CN) δ: 154.8, 154.6, 151.7, 139.0, 135.6, 131.9, 127.0, 126.6, 123.1, 121.3, 51.3. ³¹P NMR (161 MHz, CD₃CN) δ: 36.3 ppm. ¹⁹F NMR (376 MHz, CD₃CN) δ: 79.31 ppm. HRMS (ESI, m/z): [M - 3 triflates (C₃F₉O₉S₃)]²⁺ calcd for: C₁₉H₂₀N₂P, m/z = 153.5682; Found [M - 3 triflates (C₂F₆O₆S₂)]²⁺ ,m/z =153.5675, Δ = -4.5582 ppm. Elemental Analysis: (C₁₉H₂₀F₁₉O₉S₃N₂P) C: Expected 35.02 %, Found 34.92 %, S: Expected 12.75 %, Found 11.92 % N: Expected 3.71 %, Found 4.22 %, H: Expected 2.671 %, Found 1.960 %. 

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**Reaction conditions for incomplete methylation of PVM:**

An oven dried Schlenk flask is charged with 2,7-diazadibenzophenylphosphole (0.7 mmol), anhydrous methylene chloride (15 mL) and a stir bar. Methyl triflate (0.670 g, 4.10 mmol) was added all at once and the reaction was stirred at 35 °C for 16 hours under argon after which a pale yellow precipitate formed. The product was decanted and washed with anhydrous methylene chloride (2 x 15 mL) and anhydrous diethyl ether (2 x 15 mL) to yield a pale yellow powder. $^1$H and $^{31}$P NMR showed methylation on the pyridines but no P-methylation, which would be evidenced in $^1$H NMR by a doublet at 3.2 ppm with strong C-P coupling, which is seen in PVM but not in this product mixture. $^{31}$P NMR indicated a trivalent phosphorus with a phenyl substituent having a peak at 5.36 ppm rather than 36 ppm expected for quaternized phosphorus observed for PVM synthesized using microwave procedures. NMR was taken on the product without further purification.

$^1$H NMR (400 MHz, MeOD-d$_4$) δ: 9.63 (s, 2H), 9.25 (d, J = 6 Hz, 2H), 9.16 (d, J = 6 Hz, 2H), 7.47 (m br., 3H), 7.44 (m br., 2H), 4.45 (s, 6H) ppm. $^{31}$P NMR (161 MHz, MeOD-d$_4$) δ: 5.4 ppm.

An alternate procedure using 2,7-diazadibenzo(N-pyrrolidonyl)phosphole, which replaces the phenyl substituent for the more electron donating pyrrolidine, hopefully making the phosphorus more susceptible to reaction with electrophiles. An oven dried Schlenk flask is charged with 2,7-diazadibenzo(n-pyrrolidonyl)phosphole (0.5 mmol), anhydrous methylene chloride (15 mL) and a stir bar. Methyl triflate (2.10 mmol) was added all at once and the reaction was stirred at 35 °C for 16 hours under argon after which a pale yellow precipitate formed. The product was decanted and washed with anhydrous methylene chloride (2 x 15 mL) and anhydrous diethyl ether (2 x 15 mL) to yield a beige powder. $^1$H NMR showed methylation on the pyridines but no, or very slight, P-methylation, which would be evidenced by a doublet at ~3-4 ppm with strong C-P coupling seen in PVM. $^{31}$P NMR indicated a trivalent phosphorus, having a peak at -15 ppm rather than 36 ppm measured for PVM synthesized using microwave procedures. NMR was taken on the product without further purification.

$^1$H NMR (400 MHz, CD$_3$CN) δ: 9.39 (s, 2H), 8.93(d, 2H), 8.88 (d, 2H), 4.49 (s, 6H), 3.26 (q, 4H), 1.83 (q, 4H) ppm. $^{31}$P NMR (161 MHz, CD$_3$CN) δ: -12.4 ppm, $^{19}$F NMR (376 MHz, CD$_3$CN) δ: 79.2 ppm.
Electrochemistry:

Cyclic Voltammetry and Differential Pulse Voltammetry were conducted on a 10mg/mL solution in dry, degassed acetonitrile containing 0.1M TBAPF₆ under flowing argon. A typical three-electrode cell was used with glassy carbon as a working electrode, Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. CV was done at a 100mV/s scan rate and DVP was done at a 5 mV step width and 25 mV amplitude with 100 ms pulse width. Spectro-electrochemistry was conducted in a 1 mg/mL solution of dry, degassed acetonitrile containing 0.1M TBAPF₆ using a OTTLE cell having a Pt wire working electrode and counter electrode, and a sliver wire quasi reference electrode. Experiments were conducted at room temperature in combination with a Cary 5000 UV-Vis spectrophotometer.
Chemical Reductions for optical spectroscopy and EPR:

In the glove box, dilute phosphaviologen sulfide (PVS\textsuperscript{++}) and methyl phosphaviologen (PVM\textsuperscript{+++}) were prepared in THF (0.05 mg/mL). In 2 separate vials, zinc powder and lithium metal were added to solutions of PVS\textsuperscript{++} to generate the radical cation (PVS\textsuperscript{+}) and neutral species (PVS), respectively. The PVS\textsuperscript{++} is pale yellow-colourless, PVS\textsuperscript{+} appears dark blue, and the PVS appears bright orange, similar to previous experiments with phosphaviologen oxides.\textsuperscript{3} From a solution of PVM\textsuperscript{+++} in acetonitrile, the radical dication PVM\textsuperscript{++} can be prepared by adding CuBr. Unreduced PVM\textsuperscript{+++} is colorless, whereas PVM\textsuperscript{++} is pale yellow. The second and third reduction of PVM\textsuperscript{+++} occur at very similar potentials, so both the mono-cation radical (PVM\textsuperscript{+}) and neutral radical (PVM) forms of PVM\textsuperscript{+++} can be formed using Zn metal as a reductant, since the reductions occur stepwise. Doubly reduced PVM\textsuperscript{+} appears dark purple whereas triply reduced PVM is yellow/green. To isolate PVM\textsuperscript{+}, Zn powder is added to a solution of PVM\textsuperscript{+++} in THF and the solution is left stirring for 10 minutes, or until the solution reaches its darkest purple state, then filtered to remove excess Zn. The triply reduced neutral radical, PVM, forms if excess Zn is left in the solution for over 24 hours, and the solution can be used in further optical or EPR experiments as is.
**CW-EPR Measurements on chemically reduced phosphaviologens:**

The chemically reduced species were diluted in THF and transferred into airtight NMR tubes. A Bruker X-band CW EMX EPR spectrometer equipped with a 10” electromagnet and an ER 4119HS resonator was applied for signal detection. The parameters set for the EPR measurements in this study were: a microwave frequency of 9.34 GHz, a microwave power between 20-26 db, a modulation amplitude between 0.25-1.0 Gauss, a sweep width of 102.4 Gauss, a sweep time of 60 s, a receiver gain between 40-74 db, a scan number between 2-10, a modulation frequency of 100 kHz, a modulation phase of 0 or 180 degrees, a time constant of 0.01 ms, and a points per modulation amplitude of 10. The spectra were recorded at 298 K. Simulated EPR spectra were created using WinSim beginning from hyperfine coupling constants calculated using Gaussian with a B3LYP/6-31+g(d) basis set.
**Electrode Preparation**

SWCNT and **PVM** were suspended/dissolved in *N*-methyl-2-pyrrolidone (NMP) at 20 mg/mL by sonicating for 15 minutes and stirred at 90 °C for 1 hour. A separate solution of 20 mg/mL of PVDF in NMP was prepared and stirred at 90 °C until it dissolved. Subsequently, a PVDF solution is added to the **PVM**:SWCNT solution to create a 20 wt% PVDF, 40 wt% **PVM**, and 40 wt % SWCNT composite. This solution is sonicated for 15 minutes and stirred at 90 °C for 1 hour. 0.2 mL of the slurry is evenly spread over the electrode (Al foil) and dried at 90 °C in a glove box. The electrode is then dried under vacuum at 90 °C for 72 hours before being used in a battery. The total amount of material per electrode is around 10 mg, giving an areal density of 5 mg/cm².
Battery Testing

The battery is assembled using an EL-cell ECC-ref reusable test cell in a coin cell geometry using a lithium reference and saturated lithium triflate in TEGDME as the electrolyte. A lithium foil of diameter 18 mm was used as the anode, an 18 mm diameter glass fiber separator (EL-cell) was used to prevent short circuiting, and an 18mm diameter disc of 200 micron thick aluminum foil was used as the cathodic current collector. Li coins were cut using an ECC Li-punch press and Al foil coins were cut using an EL-cut from EL-cell. A battery architecture consisted of lithium foil: glass fiber impregnated with 0.35 mL electrolyte: PVM:SWCNT:PVDF 40:40:20 on Al foil. The electrode was sealed in the cell inside of a glove box with an argon atmosphere before being used in cyclic voltammetry and battery cycling experiments. Current densities for different C-rates were calculated by assuming that PVM has a specific capacity of 107 mAh/g including the triflate counterion or 267 mAh/g excluding counterions.
Figure S1. Cyclic voltammetry on a solution of PVM (10 mg/mL in a 0.5M TBAPF$_6$/MeCN electrolyte, 100mV/s scan rate) showing the reversibility and peak to peak difference of each individual reduction. The small peak to peak difference indicates excellent electrochemical reversibility.
Figure S2. Cyclic voltammetry on a solution of PVS (10 mg/mL in a 0.5M TBAPF₆/MeCN electrolyte, 100mV/s scan rate) showing the reversibility and peak to peak difference of each individual reduction. The small peak to peak difference indicates excellent electrochemical reversibility.
Figure S3. A) Cyclic voltammetry on a battery consisting of PVM as the active electrode material (red, 5 mV/s scan rate) and on PVM in solution (dashed, 100mV/s scan rate). Poor electrode kinetics are indicated by the broad current peaks and high over-potential compared to the CV in solution. B) Charge discharge curves of PVM batteries at varying discharge rates. Although plateaus (shoulders) in the charging and discharging curves are observed near the potentials predicted by the redox reactions of PVM, the observed capacity is roughly 30% of the theoretical capacity (31 mAh/g observed v.s. 107 mAh/g theoretical with triflate counterions, 76 mAh/g observed v.s. 262 mAh/g excluding counterions) at 1C, indicating most of the electrode material is dissolved in the electrolyte solution. The electrolyte solution was made to be saturated in triflate anions to prevent dissolution using the common ion effect, however this strategy was not highly effective. Small molecules are highly soluble in most electrolyte solvent systems, so a strategy of tethering PVM to polymer or insoluble composite should allow electrodes made from this material to exhibit closer to their theoretical capacity.
Figure S4. Optical absorption spectra of PVS (solid black line) and PVM as dilute solutions in acetonitrile (0.5 mg/mL). There are no prominent absorption features in the visible range for each of the unreduced molecules.
Figure S5. Spectro-electrochemistry in a 0.1M TBAPF₆/acetonitrile electrolyte on A) PVS and B) PVM. Spectroelectrochemistry on PVS initially shows the colorless dication. The radical cation absorbance (~600 nm) emerges at -0.15 V vs. Ag/AgCl, then begins to fade at more strongly reducing potentials as the neutral species absorbance (400 nm) becomes prominent (Figure 3A). Spectroelectrochemistry on PVM initially shows the colorless trication. As more strongly reducing potentials are scanned, an absorbance tail due to the radical dication 350 nm begins to emerge, followed by the biradical cation absorbance (~600 nm), then the neutral radical absorbance (390 nm) at -0.3 V vs. Ag/AgCl. (Figure 3B). The absorbance of the biradical cation (~600 nm) and the neutral radical (390 nm) are observed concurrently as the reactions occur at similar redox potentials.
Figure S6. DFT calculations of orbitals and orbital energy on optimized geometries of the tri-cationic form of PVM. Calculations were conducted at the B3LYP/6-31+g(d) level of theory using the Gaussian.
Figure S7. DFT calculations of alpha and beta orbitals and orbital energies on optimized geometries of the singly reduced di-cationic radical form of PVM. Calculations were conducted at the B3LYP/6-31+g(d) level of theory using the Gaussian.
Figure S8. DFT calculations of alpha and beta orbitals and orbital energies on optimized geometries of the doubly reduced mono-cationic biradical form of PVM. Calculations were conducted at the B3LYP/6-31+g(d) level of theory using the Gaussian.
Figure S9. DFT calculations of alpha and beta orbitals and orbital energies on optimized geometries of the triply reduced neutral radical form of PVM. Calculations were conducted at the B3LYP/6-31+g(d) level of theory using the Gaussian.
Figure S10. DFT calculations orbitals and orbital energies on optimized geometries of the unreduced di-cationic form of PVS (left) and the doubly reduced neutral form of PVS (right). Calculations were conducted at the B3LYP/6-31+g(d) level of theory using the Gaussian.
Figure S11. DFT calculations of alpha and beta orbitals and orbital energies on optimized geometries of the singly reduced mono-cationic radical form of PVS. Calculations were conducted at the B3LYP/6-31+g(d) level of theory using the Gaussian.
Figure S12. Calculated and optimized hyperfine coupling constants and calculated spin density on the indicated atoms for PVS radical cation. Spin density is delocalized around the viologen core.

| Atom   | Calculated Coupling (mT) | Optimized Coupling (mT) | Calculated Spin Density |
|--------|--------------------------|--------------------------|-------------------------|
| 1 (H 1)| 6.6877                   | 7.7403                   | 0.0109                  |
| 2 (C 13)| 4.1465                 | 3.3572                   | 0.1202                  |
| 3 (H 1)| 3.7611                   | 3.8100                   | 0.059                   |
| 4 (N 14)| 3.4744                  | 3.9589                   | 0.1455                  |
| 5 (C 13)| 2.1585                 | 1.9150                   | 0.0575                  |
| 6 (C 13)| 1.3937                 | 2.2478                   | 0.0777                  |
| 7 (S 33)| 1.0408                 | 1.2418                   | 0.0179                  |
| 8 (C 13)| 0.9420                 | 1.8637                   | 0.0928                  |
Figure S13. Calculated and optimized hyperfine coupling constants and calculated spin density on the indicated atoms for PVM radical dication. Significant spin density exists around the phosphorus center.

| Atom | Calculated Coupling (mT) | Optimized Coupling (mT) | Calculated Spin Density |
|------|--------------------------|--------------------------|------------------------|
| 1 (C 13) | 5.2543                   | 6.9591                   | 0.1270                 |
| 2 (C 13) | 4.5063                   | 3.5987                   | 0.1461                 |
| 3 (C 13) | 3.8300                   | 3.5987                   | 0.0400                 |
| 4 (H 1)  | 4.9166                   | 2.3218                   | 0.0079                 |
| 5 (H 1)  | 4.8333                   | 2.3218                   | 0.0078                 |
| 6 (H 1)  | 0.1877                   | 2.1961                   | 0.0007                 |
| 7 (H 1)  | 0.1836                   | 0.3580                   | 0.0007                 |
| 8 (N 14) | 3.0994                   | 1.2120                   | 0.1330                 |
Figure S14. Calculated and optimized hyperfine coupling constants and calculated spin density on the indicated atoms for PVM biradical mono-cation. Spin density is delocalized around the viologen core and the phosphorus center.

| Atom | Calculated Coupling (mT) | Optimized Coupling (mT) | Calculated Spin Density |
|------|--------------------------|-------------------------|------------------------|
| 1 (C 13) | 10.7355 | 3.5632 | 0.0245 |
| 2 (C 13) | 4.4589 | 4.5171 | 0.3290 |
| 3 (H 1) | 2.1121 | 2.4905 | 0.0071 |
| 4 (H 1) | 2.0780 | 2.2124 | 0.0071 |
| 5 (C 13) | 1.8296 | 2.2827 | 0.1741 |
| 6 (C 13) | 1.5818 | 2.5366 | 0.1399 |
| 7 (N 14) | 1.0778 | 1.2505 | 0.1015 |
| 8 (C 13) | 1.0178 | 1.0254 | 0.1285 |
| 9 (H 1) | 0.2143 | 1.1930 | 0.0010 |
Figure S15. Calculated and optimized hyperfine coupling constants and calculated spin density on the indicated atoms for PVM neutral radical. Significant spin density exists around the phosphorus center.
Table S1. Cartesian coordinates for the optimized structure of

Input orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | -4.304408   | -1.739474   | 0.256837    |
| 2             | 6             | 0           | -2.935572   | -1.974832   | 0.321145    |
| 3             | 6             | 0           | -2.061455   | -0.957575   | -0.072888   |
| 4             | 6             | 0           | -2.599940   | 0.265826    | -0.527646   |
| 5             | 6             | 0           | -3.974016   | 0.448789    | -0.563164   |
| 6             | 1             | 0           | -5.033483   | -2.486684   | 0.548769    |
| 7             | 1             | 0           | -2.591485   | -2.941715   | 0.677345    |
| 8             | 1             | 0           | -4.450983   | 1.368508    | -0.885791   |
| 9             | 6             | 0           | -0.578081   | -0.982966   | -0.069029   |
| 10            | 6             | 0           | 0.004349    | 0.221       | -0.521108   |
| 11            | 6             | 0           | 0.258707    | -2.029375   | 0.329725    |
| 12            | 6             | 0           | 1.384046    | 0.356992    | -0.549757   |
| 13            | 6             | 0           | 1.635130    | -1.841061   | 0.272195    |
| 14            | 1             | 0           | -0.117328   | -2.983859   | 0.684531    |
| 15            | 1             | 0           | 1.893826    | 1.259831    | -0.869857   |
| 16            | 1             | 0           | 2.336670    | -2.615620   | 0.567966    |
| 17            | 6             | 0           | -6.289539   | -0.367914   | -0.213925   |
| 18            | 1             | 0           | -6.709263   | -1.080037   | -0.928784   |
| 19            | 1             | 0           | -6.692058   | -0.547909   | 0.785439    |
| 20            | 1             | 0           | -6.513095   | 0.651172    | -0.526951   |
| 21            | 6             | 0           | 3.668457    | -0.538063   | -0.187458   |
| 22            | 1             | 0           | 4.057098    | -0.712653   | 0.818435    |
| 23            | 1             | 0           | 4.069486    | -1.277015   | -0.885512   |
| 24            | 1             | 0           | 3.928483    | 0.466816    | -0.517742   |
| 25            | 7             | 0           | -4.801470   | -0.552376   | -0.172448   |
| 26            | 7             | 0           | 2.174731    | -0.671901   | -0.154929   |
| 27            | 15            | 0           | -1.275862   | 1.446548    | -1.026371   |
| 28            | 6             | 0           | -1.268373   | 1.632005    | -2.837942   |
| 29            | 1             | 0           | -2.150033   | 2.196475    | -3.160162   |
| 30            | 1             | 0           | -0.366981   | 2.167207    | -3.155507   |
| 31            | 1             | 0           | -1.283503   | 0.643136    | -3.306629   |
| 32            | 6             | 0           | -1.251171   | 2.989736    | -0.144576   |
| 33            | 6             | 0           | -1.249571   | 2.993268    | 1.270841    |
| 34            | 6             | 0           | -1.234902   | 4.203742    | -0.869073   |
| 35            | 6             | 0           | -1.231663   | 4.208235    | 1.947004    |
| 36            | 1             | 0           | -1.262006   | 2.066134    | 1.839805    |
| 37            | 6             | 0           | -1.217062   | 5.410671    | -0.170683   |
| 38            | 1             | 0           | -1.235547   | 4.223023    | -1.954521   |
| 39            | 6             | 0           | -1.215504   | 5.413983    | 1.228359    |
| 40            | 1             | 0           | -1.230138   | 4.221635    | 3.032827    |
| 41            | 1             | 0           | -1.204262   | 6.346801    | -0.720911   |
| 42            | 1             | 0           | -1.201496   | 6.358848    | 1.764411    |
Table S2. Cartesian coordinates for the optimized structure of

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms)   |
|---------------|---------------|-------------|---------------------------|
|               |               |             | X  | Y  | Z  |
| 1             | 6             | 0           | 2.964529 | -2.604212 | -0.570379 |
| 2             | 6             | 0           | 1.615017 | -2.829124 | -0.631498 |
| 3             | 6             | 0           | 0.711711 | -1.825582 | -0.189464 |
| 4             | 6             | 0           | 1.297699 | -0.609140 | 0.318797  |
| 5             | 6             | 0           | 2.659922 | -0.435950 | 0.346244  |
| 6             | 1             | 0           | 3.690921 | -3.339943 | -0.896085 |
| 7             | 1             | 0           | 1.266132 | -3.778929 | -1.022716 |
| 8             | 1             | 0           | 3.140372 | 0.469504  | 0.701585  |
| 9             | 6             | 0           | -0.710597| -1.826019 | -0.189511 |
| 10            | 6             | 0           | -1.297367| 0.609957  | 0.318753  |
| 11            | 6             | 0           | -1.613250| -2.830101 | -0.631646 |
| 12            | 6             | 0           | -2.659696| -0.437589 | 0.346064  |
| 13            | 6             | 0           | -2.962906| -2.830101 | -0.631646 |
| 14            | 1             | 0           | 3.140372 | 0.469504  | 0.701585  |
| 15            | 1             | 0           | 3.688820 | -3.342170 | -0.896441 |
| 16            | 6             | 0           | 4.961346 | -1.249816 | -0.070118 |
| 17            | 1             | 0           | 5.407933 | -2.021557 | 0.562017  |
| 18            | 1             | 0           | 5.353319 | -1.329699 | -1.087225 |
| 19            | 1             | 0           | 5.203814 | -2.689999 | 0.334126  |
| 20            | 1             | 0           | 4.960585 | -1.252814 | -0.070595 |
| 21            | 1             | 0           | 5.352349 | -1.332646 | -1.087788 |
| 22            | 1             | 0           | 5.406820 | -2.024991 | 0.561255  |
| 23            | 1             | 0           | 5.203694 | -0.270254 | 0.333888  |
| 24            | 7             | 0           | 3.490912 | -1.419434 | -0.092457 |
| 25            | 7             | 0           | 3.490048 | -1.421568 | -0.092739 |
| 26            | 7             | 0           | -0.000191| 0.531189  | 0.869736  |
| 27            | 6             | 0           | -0.000317| 0.697605  | 2.685980  |
| 28            | 1             | 0           | 0.892140 | 1.235721  | 3.021103  |
| 29            | 1             | 0           | -0.893408| 1.234674  | 3.021092  |
| 30            | 1             | 0           | 0.000241 | -0.303925 | 3.125656  |
| 31            | 6             | 0           | -0.000595| 2.139366  | 0.069155  |
| 32            | 6             | 0           | 0.000296 | 2.200964  | -1.339668 |
| 33            | 6             | 0           | -0.001905| 3.322220  | 0.832681  |
| 34            | 6             | 0           | -0.000102| 3.441181  | -1.972755 |
| 35            | 1             | 0           | 0.001285 | 1.293017  | -1.937991 |
| 36            | 6             | 0           | -0.002284| 4.558354  | 0.184003  |
| 37            | 1             | 0           | -0.002582| 3.295456  | 1.917857  |
| 38            | 6             | 0           | -0.001386| 4.617797  | -1.212216 |
| 39            | 1             | 0           | 0.000593 | 3.492743  | -3.057348 |
| 40            | 1             | 0           | -0.003270| 5.471769  | 0.770994  |
| 41            | 1             | 0           | -0.001679| 5.582465  | -1.711267 |
| 42            | 1             | 0           | -0.001679| 5.582465  | -1.711267 |
Table S3. Cartesian coordinates for the optimized structure of

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 6             | 0           | X: 2.960880, Y: -2.597208, Z: -0.590479 |
| 2             | 6             | 0           | X: 1.596290, Y: -2.812502, Z: -0.661697 |
| 3             | 6             | 0           | X: 0.710136, Y: -1.812949, Z: -0.194225 |
| 4             | 6             | 0           | X: 1.284364, Y: -0.607652, Z: 0.351190 |
| 5             | 6             | 0           | X: 2.668615, Y: -0.442360, Z: 0.397223 |
| 6             | 1             | 0           | X: 3.681247, Y: -3.329663, Z: -0.935545 |
| 7             | 1             | 0           | X: 1.233342, Y: -3.745519, Z: -1.077142 |
| 8             | 1             | 0           | X: 3.163467, Y: 0.441666, Z: 0.777079 |
| 9             | 6             | 0           | X: -0.709833, Y: -1.813071, Z: -0.194210 |
| 10            | 6             | 0           | X: -1.284258, Y: -0.607877, Z: 0.351224 |
| 11            | 6             | 0           | X: -1.595824, Y: -2.812779, Z: -0.661659 |
| 12            | 6             | 0           | X: -2.668536, Y: -0.442825, Z: 0.397288 |
| 13            | 6             | 0           | X: -2.960451, Y: -2.597724, Z: -0.590408 |
| 14            | 1             | 0           | X: -1.232724, Y: -3.745739, Z: -1.077100 |
| 15            | 1             | 0           | X: -3.163713, Y: 0.441118, Z: 0.777144 |
| 16            | 1             | 0           | X: -3.680696, Y: -3.330300, Z: -0.935468 |
| 17            | 6             | 0           | X: 4.948863, Y: -1.282391, Z: -0.046029 |
| 18            | 1             | 0           | X: 5.399726, Y: -2.076024, Z: 0.557107 |
| 19            | 1             | 0           | X: 5.354819, Y: -1.320377, Z: -1.061274 |
| 20            | 1             | 0           | X: 5.194635, Y: -0.317290, Z: 0.397887 |
| 21            | 6             | 0           | X: -4.948641, Y: -1.283126, Z: -0.046179 |
| 22            | 1             | 0           | X: -5.354314, Y: -1.319847, Z: -1.061590 |
| 23            | 1             | 0           | X: -5.399614, Y: -2.077552, Z: 0.555820 |
| 24            | 1             | 0           | X: -5.194605, Y: -0.318619, Z: 0.398919 |
| 25            | 7             | 0           | X: 3.488455, Y: -1.443107, Z: -0.080323 |
| 26            | 7             | 0           | X: 3.488215, Y: -1.443722, Z: -0.080223 |
| 27            | 15            | 0           | X: -0.000035, Y: 0.494643, Z: 0.876247 |
| 28            | 6             | 0           | X: -0.000056, Y: 0.824275, Z: 2.691991 |
| 29            | 1             | 0           | X: 0.891723, Y: 1.385934, Z: 2.988733 |
| 30            | 1             | 0           | X: -0.891971, Y: 1.385712, Z: 2.988749 |
| 31            | 1             | 0           | X: 0.000066, Y: -0.141222, Z: 3.204697 |
| 32            | 6             | 0           | X: -0.000175, Y: 2.143968, Z: 0.075688 |
| 33            | 6             | 0           | X: -0.000132, Y: 2.182639, Z: -1.329757 |
| 34            | 6             | 0           | X: -0.000337, Y: 3.346318, Z: 0.801741 |
| 35            | 6             | 0           | X: -0.000240, Y: 3.406348, Z: -1.997612 |
| 36            | 1             | 0           | X: -0.000011, Y: 1.255564, Z: -1.898297 |
| 37            | 6             | 0           | X: -0.000447, Y: 4.570369, Z: 0.127255 |
| 38            | 1             | 0           | X: -0.000374, Y: 3.344793, Z: 1.887059 |
| 39            | 6             | 0           | X: -0.000398, Y: 4.601066, Z: -1.269167 |
| 40            | 1             | 0           | X: -0.000202, Y: 3.429199, Z: -3.083669 |
| 41            | 1             | 0           | X: -0.000570, Y: 5.496941, Z: 0.694368 |
| 42            | 1             | 0           | X: -0.000484, Y: 5.554269, Z: -1.790439 |
**Table S4.** Cartesian coordinates for the optimized structure of

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 2.971872 -2.606878 -0.592568 |
| 2             | 6             | 0           | 1.625407 -2.835182 -0.663522 |
| 3             | 6             | 0           | 0.687714 -1.849702 -0.198980 |
| 4             | 6             | 0           | 1.282211 -0.615555  0.363558 |
| 5             | 6             | 0           | 2.656209 -0.440370  0.404208 |
| 6             | 1             | 0           | 3.705568 -3.329127 -0.933210 |
| 7             | 1             | 0           | 1.278064 -3.776202 -1.079100 |
| 8             | 1             | 0           | 3.140396  0.451196  0.786200 |
| 9             | 6             | 0           | -0.686696 -1.850077 -0.199014 |
| 10            | 6             | 0           | -1.281897 -0.616297  0.363590 |
| 11            | 6             | 0           | -1.623819 -2.836065 -0.663620 |
| 12            | 6             | 0           | -2.655998 -0.441863  0.404138 |
| 13            | 6             | 0           | -2.970417 -2.608505 -0.592732 |
| 14            | 1             | 0           | -1.275936 -3.776897 -1.079170 |
| 15            | 1             | 0           | -3.140704  0.449418  0.786137 |
| 16            | 1             | 0           | -3.703697 -3.331149 -0.933432 |
| 17            | 6             | 0           | 4.943721 -1.257213 -0.042180 |
| 18            | 1             | 0           | 5.419863 -2.039011  0.565742 |
| 19            | 1             | 0           | 5.370056 -1.294780 -1.054115 |
| 20            | 1             | 0           | 5.185265 -0.286239  0.396332 |
| 21            | 6             | 0           | -4.943028 -1.259858 -0.042588 |
| 22            | 1             | 0           | -5.369142 -1.297246 -1.054626 |
| 23            | 1             | 0           | -5.418908 -2.042120  0.564937 |
| 24            | 1             | 0           | -5.185135 -0.289173  0.396252 |
| 25            | 7             | 0           | 3.502385 -1.426847 -0.075943 |
| 26            | 7             | 0           | -3.501602 -1.428788 -0.076098 |
| 27            | 15            | 0           | -0.000146  0.461531  0.879976 |
| 28            | 6             | 0           | -0.000407  0.886291  2.697284 |
| 29            | 1             | 0           | 0.893086  1.457740  2.975098 |
| 30            | 1             | 0           | -0.894404  1.456981  2.975041 |
| 31            | 1             | 0           | -0.000034 -0.060960  3.242648 |
| 32            | 6             | 0           | -0.000444  2.151486  0.085550 |
| 33            | 6             | 0           | 0.000104  2.180729 -1.318527 |
| 34            | 6             | 0           | -0.001467  3.365961  0.788847 |
| 35            | 6             | 0           | -0.000287  3.395209 -2.005131 |
| 36            | 1             | 0           | 0.000838  1.241881 -1.868079 |
| 37            | 6             | 0           | -0.001893  4.584720  0.101318 |
| 38            | 1             | 0           | -0.001919  3.376320  1.874311 |
| 39            | 6             | 0           | -0.001291  4.600901 -1.295189 |
| 40            | 1             | 0           | 0.000178  3.402334 -3.092314 |
| 41            | 1             | 0           | -0.002681  5.518893  0.658117 |
| 42            | 1             | 0           | -0.001616  5.548212 -1.828765 |
Table S5. Cartesian coordinates for the optimized structure of

| Center Number | Atomic Number | Type | Coordinates (Angstroms) X | Y | Z |
|---------------|---------------|------|--------------------------|---|---|
| 1             | 6             | 0    | 2.967484                | -2.571365 | -0.729823 |
| 2             | 6             | 0    | 1.600215                | -2.753639 | -0.864728 |
| 3             | 6             | 0    | 0.740411                | -1.753996 | -0.393353 |
| 4             | 6             | 0    | 1.287331                | -0.598194 | 0.194364  |
| 5             | 6             | 0    | 2.661408                | -0.475434 | 0.312579  |
| 6             | 1             | 0    | 3.688756                | -3.306072 | -1.070623 |
| 7             | 1             | 0    | 1.242750                | -3.667560 | -1.327635 |
| 8             | 1             | 0    | 3.140473                | 0.379040  | 0.778518  |
| 9             | 6             | 0    | -0.739797               | -1.754244 | -0.393395 |
| 10            | 6             | 0    | -1.287137               | -0.598606 | 0.194303  |
| 11            | 6             | 0    | -1.599240               | -2.754117 | -0.864876 |
| 12            | 6             | 0    | -2.661243               | -0.476240 | 0.312299  |
| 13            | 6             | 0    | -2.966608               | -2.572223 | -0.730203 |
| 14            | 1             | 0    | -1.241459               | -3.667903 | -1.327806 |
| 15            | 1             | 0    | -3.140657               | 0.378081  | 0.778518  |
| 16            | 1             | 0    | -3.687571               | -3.307157 | -1.071139 |
| 17            | 6             | 0    | 4.955679                | -1.331213 | -0.001928 |
| 18            | 1             | 0    | 5.298624                | -2.063795 | 0.732700  |
| 19            | 1             | 0    | 5.425694                | -1.515691 | -0.969633 |
| 20            | 1             | 0    | 5.196720                | -0.324840 | 0.337981  |
| 21            | 6             | 0    | -4.955144               | -1.332843 | -0.001350 |
| 22            | 1             | 0    | -5.426475               | -1.529636 | -0.965924 |
| 23            | 1             | 0    | -5.295649               | -2.057190 | 0.742574  |
| 24            | 1             | 0    | -5.197239               | -0.322796 | 0.326745  |
| 25            | 7             | 0    | 3.476873                | -1.453154 | -0.150063 |
| 26            | 7             | 0    | -3.476390               | -1.454166 | -0.150548 |
| 27            | 15            | 0    | -0.000105               | 0.556239  | 0.881648  |
| 28            | 6             | 0    | -0.000347               | 2.074266  | -0.103286 |
| 29            | 6             | 0    | -0.000403               | 2.034328  | -1.511408 |
| 30            | 6             | 0    | -0.000508               | 3.304835  | 0.572690  |
| 31            | 6             | 0    | -0.000614               | 3.225561  | -2.234226 |
| 32            | 1             | 0    | -0.000277               | 1.087282  | -2.047892 |
| 33            | 6             | 0    | -0.000721               | 4.492574  | -0.163058 |
| 34            | 1             | 0    | -0.000478               | 3.332474  | 1.658697  |
| 35            | 6             | 0    | -0.000776               | 4.453691  | -1.559559 |
| 36            | 1             | 0    | -0.000659               | 3.199902  | -3.319972 |
| 37            | 1             | 0    | -0.000844               | 5.445342  | 0.357815  |
| 38            | 1             | 0    | -0.000947               | 5.379797  | -2.126782 |
| 39            | 16            | 0    | -0.000155               | 0.680584  | 2.823927  |
**Table S6.** Cartesian coordinates for the optimized structure of

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 6             | 0           | X: 2.963169, Y: -2.537681, Z: -0.763422 |
| 2             | 6             | 0           | X: 1.613729, Y: -2.723678, Z: -0.903268 |
| 3             | 6             | 0           | X: 0.712157, Y: -1.751124, Z: -0.387556 |
| 4             | 6             | 0           | X: 1.290506, Y: -0.604052, Z: 0.252772 |
| 5             | 6             | 0           | X: 2.644587, Y: -0.475661, Z: 0.374847 |
| 6             | 1             | 0           | X: 3.687071, Y: -3.251782, Z: -1.135500 |
| 7             | 1             | 0           | X: 1.263622, Y: -3.619248, Z: -1.405900 |
| 8             | 1             | 0           | X: 3.115946, Y: 0.361524, Z: 0.878212 |
| 9             | 6             | 0           | X: -0.711354, Y: -1.751429, Z: -0.387616 |
| 10            | 6             | 0           | X: -1.290237, Y: -0.604609, Z: 0.252683 |
| 11            | 6             | 0           | X: -1.612475, Y: -2.724345, Z: -0.903422 |
| 12            | 6             | 0           | X: -2.644377, Y: -0.476776, Z: 0.374627 |
| 13            | 6             | 0           | X: -2.962012, Y: -2.538902, Z: -0.763707 |
| 14            | 1             | 0           | X: -1.261959, Y: -3.619757, Z: -1.406050 |
| 15            | 1             | 0           | X: -3.116141, Y: 0.360194, Z: 0.877973 |
| 16            | 1             | 0           | X: -3.687198, Y: -3.253306, Z: -1.135870 |
| 17            | 6             | 0           | X: 4.944875, Y: -1.321483, Z: 0.043817 |
| 18            | 1             | 0           | X: 5.282620, Y: -2.012172, Z: 0.822956 |
| 19            | 1             | 0           | X: 5.447952, Y: -1.555418, Z: -0.897488 |
| 20            | 1             | 0           | X: 5.195134, Y: -0.300623, Z: 0.334358 |
| 21            | 6             | 0           | X: -4.944245, Y: -1.323586, Z: 0.043762 |
| 22            | 1             | 0           | X: -5.447458, Y: -1.560659, Z: -0.896659 |
| 23            | 1             | 0           | X: -5.281149, Y: -2.012301, Z: 0.825028 |
| 24            | 1             | 0           | X: -5.195233, Y: -0.302073, Z: 0.331396 |
| 25            | 7             | 0           | X: 3.487706, Y: 1.430085, Z: -0.134595 |
| 26            | 7             | 0           | X: 3.487064, Y: -1.431525, Z: -0.134953 |
| 27            | 15            | 0           | X: -0.000126, Y: 0.525705, Z: 0.924104 |
| 28            | 6             | 0           | X: -0.000420, Y: 2.030085, Z: -0.117818 |
| 29            | 6             | 0           | X: 0.000094, Y: 1.933122, Z: -1.520230 |
| 30            | 6             | 0           | X: -0.001203, Y: 3.288598, Z: 0.497260 |
| 31            | 6             | 0           | X: -0.00183, Y: 3.091136, Z: -2.297542 |
| 32            | 1             | 0           | X: 0.000716, Y: 0.961443, Z: -2.009051 |
| 33            | 6             | 0           | X: -0.001477, Y: 4.445206, Z: -0.287878 |
| 34            | 1             | 0           | X: -0.001571, Y: 3.356966, Z: 1.581544 |
| 35            | 6             | 0           | X: -0.000970, Y: 4.348013, Z: -1.681094 |
| 36            | 1             | 0           | X: 0.000217, Y: 3.014586, Z: -3.381357 |
| 37            | 1             | 0           | X: -0.002078, Y: 5.419707, Z: 0.192168 |
| 38            | 1             | 0           | X: -0.001180, Y: 5.248799, Z: -2.288627 |
| 39            | 16            | 0           | X: -0.000283, Y: 0.818300, Z: 2.861301 |
Table S7. Cartesian coordinates for the optimized structure of

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | 2.971970    | -2.490393   | -0.823204   |
| 2             | 6             | 0           | 1.638108    | -2.679193   | -0.978455   |
| 3             | 6             | 0           | 0.689462    | -1.735746   | -0.425287   |
| 4             | 6             | 0           | 1.294105    | -0.605115   | 0.288681    |
| 5             | 6             | 0           | 2.633435    | -0.477530   | 0.426588    |
| 6             | 1             | 0           | 3.705836    | -3.180107   | -1.226126   |
| 7             | 1             | 0           | 1.300180    | -3.552487   | -1.528923   |
| 8             | 1             | 0           | 3.094164    | 0.333499    | 0.982273    |
| 9             | 6             | 0           | -0.687804   | -1.736338   | -0.425401   |
| 10            | 6             | 0           | -1.293523   | -0.606247   | 0.288495    |
| 11            | 6             | 0           | -1.635556   | -2.680590   | -0.978724   |
| 12            | 6             | 0           | -2.632979   | -0.479806   | 0.426200    |
| 13            | 6             | 0           | -2.969603   | -2.492940   | -0.823664   |
| 14            | 1             | 0           | -1.296802   | -3.553582   | -1.529162   |
| 15            | 1             | 0           | -3.094486   | 0.330817    | 0.981833    |
| 16            | 1             | 0           | -3.702810   | -3.183278   | -1.226718   |
| 17            | 6             | 0           | 4.918374    | -1.382973   | 0.212966    |
| 18            | 1             | 0           | 5.121697    | -2.018931   | 1.087837    |
| 19            | 1             | 0           | 5.517698    | -1.742831   | -0.629587   |
| 20            | 1             | 0           | 5.231630    | -0.361084   | 0.443027    |
| 21            | 6             | 0           | -4.917047   | -1.387336   | 0.212506    |
| 22            | 1             | 0           | -5.516015   | -1.748228   | -0.629851   |
| 23            | 1             | 0           | -5.119634   | -2.023118   | 1.087678    |
| 24            | 1             | 0           | -5.231404   | -0.365678   | 0.442109    |
| 25            | 7             | 0           | 3.509175    | -1.387024   | -0.148943   |
| 26            | 7             | 0           | -3.507865   | -1.390031   | -0.149496   |
| 27            | 15            | 0           | -0.000238   | 0.501334    | 0.945519    |
| 28            | 6             | 0           | -0.000825   | 2.001136    | -0.131945   |
| 29            | 6             | 0           | 0.000473    | 1.858188    | -1.529304   |
| 30            | 6             | 0           | -0.002698   | 3.281504    | 0.432115    |
| 31            | 6             | 0           | -0.000115   | 2.987378    | -2.349430   |
| 32            | 1             | 0           | 0.001923    | 0.867026    | -1.976190   |
| 33            | 6             | 0           | -0.003284   | 4.411424    | -0.392398   |
| 34            | 1             | 0           | -0.003618   | 3.382165    | 1.514162    |
| 35            | 6             | 0           | -0.001999   | 4.266676    | -1.781616   |
| 36            | 1             | 0           | 0.000895    | 2.869623    | -3.430302   |
| 37            | 1             | 0           | -0.004725   | 5.402997    | 0.053601    |
| 38            | 1             | 0           | -0.002447   | 5.145615    | -2.421740   |
| 39            | 16            | 0           | -0.000665   | 0.937773    | 2.876477    |
Figure S16. $^1$H and $^{31}$P NMR of PVS precursor in deuterated chloroform.
Figure S17. $^{13}$C NMR of PVS precursor in deuterated chloroform.
Figure S18. $^1$H and $^{31}$P NMR of PVS in deuterated acetonitrile.
Figure S19. $^{13}$C NMR and $^{19}$F NMR of PVS in deuterated acetonitrile.
Figure S20. $^1$H and $^{31}$P NMR of PVM in deuterated acetonitrile. Crude NMR contains * ethyl acetate, ** methyl triflate, and *** chlorobenzene.
Figure S21. $^{13}$C NMR and $^{19}$F NMR of PVM in deuterated acetonitrile.
**Figure S22.** Calculated absorptions of the three redox states of PVS and the absorption spectra of the isolated redox states using chemical reductions. TD-DFT calculations were conducted at the B3LYP/6-31+g(d) level of theory to calculate the excitation energies using a PCM solvation model in acetonitrile from the previously optimized geometries. The ten lowest energy absorptions are calculated (singlets and triplets for radicals, singlets only for non-radicals) and the four energies having the highest calculated oscillator strength are shown.
**Figure S23.** Calculated absorptions of the three redox states of PVM and the absorption spectra of the isolated redox states using chemical reductions. TD-DFT calculations were conducted at the B3LYP/6-31+g(d) level of theory to calculate the excitation energies using a PCM solvation model in acetonitrile from the previously optimized geometries. The ten lowest energy absorptions are calculated (singlets and triplets for radicals, singlets only for non-radicals) and the three energies having the highest calculated oscillator strength are shown.
**Figure S24.** Molecular structure of PVS in the solid state (50% probability) with and without triflate counterions, and its packing structure (some hydrogen atoms are omitted for clarity).
| Table S8. Crystal data and structure refinement for PVS |
|------------------------------------|
| **Identification code** | PVS |
| **Empirical formula** | C_{20}H_{17}N_{2}O_{6}F_{6}PS_{3} |
| **Formula weight** | 622.530 |
| **Temperature/K** | 173.0 |
| **Crystal system** | orthorhombic |
| **Space group** | Pnma |
| **a/Å** | 13.0226(5) |
| **b/Å** | 16.7841(6) |
| **c/Å** | 11.5890(4) |
| **α/°** | 90 |
| **β/°** | 90 |
| **γ/°** | 90 |
| **Volume/Å³** | 2533.04(16) |
| **Z** | 4 |
| **ρ_{calc}/g/cm³** | 1.632 |
| **μ/mm¹** | 0.441 |
| **F(000)** | 1266.8 |
| **Crystal size/mm³** | 0.6 × 0.2 × 0.2 |
| **Radiation** | Mo Kα (λ = 0.71073) |
| **2θ range for data collection/°** | 4.7 to 56.56 |
| **Index ranges** | -21 ≤ h ≤ 20, -27 ≤ k ≤ 26, -18 ≤ l ≤ 17 |
| **Reflections collected** | 51293 |
| **Independent reflections** | 3242 [R_{int} = 0.1396, R_{sigma} = 0.0648] |
| **Data/restraints/parameters** | 3242/0/185 |
| **Goodness-of-fit on F²** | 1.061 |
| **Final R indexes [I>=2σ (I)]** | R₁ = 0.1182, wR₂ = 0.3110 |
| **Final R indexes [all data]** | R₁ = 0.1331, wR₂ = 0.3368 |
| **Largest diff. peak/hole / e Å⁻³** | 1.24/-2.00 |
### Bond Lengths for PVS

| Atom | Atom | Length/Å |
|------|------|----------|
| P1   | S1   | 1.474(4) |
| P1   | C1   | 1.790(7) |
| P1   | C7   | 1.807(4) |
| S2   | O2   | 1.429(5) |
| S2   | O1   | 1.442(6) |
| S2   | O3   | 1.413(6) |
| S2   | C13  | 1.771(8) |
| N1   | C11  | 1.340(5) |
| N1   | C10  | 1.352(5) |
| N1   | C12  | 1.480(5) |
| C11  | C7   | 1.378(5) |
| C8   | C8   | 1.475(7) |

### Bond Angles for PVS

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C1   | P1   | S1   | 113.4(3) |
| C7   | P1   | S1   | 118.01(19) |
| C7   | P1   | C1   | 107.23(18) |
| C7   | P1   | C7   | 90.3(2) |
| O1   | S2   | O2   | 113.9(3) |
| O3   | S2   | O2   | 116.0(5) |
| O3   | S2   | O1   | 114.8(6) |
| C13  | S2   | O2   | 105.7(4) |
| C13  | S2   | O3   | 103.2(5) |
| C10  | N1   | C11  | 122.0(3) |
| C12  | N1   | C11  | 119.7(4) |
| C7   | C11  | N1   | 118.3(3) |
| C9   | C8   | C7   | 119.8(3) |
| C2   | C1   | P1   | 118.9(6) |
Figure S25. Molecular structure of PVM in the solid state (50% probability) with and without triflate counterions showing residual acetonitrile from recrystallization, and its packing structure and its packing structure (some hydrogen atoms are omitted for clarity).
Table S9. Crystal data and structure refinement for PVM

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | PVM                                        |
| Empirical formula               | C_{24}H_{23}F_{9}N_{3}O_{9}PS_{3}          |
| Formula weight                  | 795.60                                     |
| Temperature/K                   | 173.0                                      |
| Crystal system                  | triclinic                                  |
| Space group                     | P-1                                        |
| a/Å                             | 9.5784(5)                                  |
| b/Å                             | 11.1999(6)                                 |
| c/Å                             | 15.6039(8)                                 |
| α/°                             | 102.532(2)                                 |
| β/°                             | 90.622(2)                                  |
| γ/°                             | 97.933(2)                                  |
| Volume/Å³                       | 1616.98(15)                                |
| Z                               | 2                                          |
| ρ_{calc}g/cm³                   | 1.634                                      |
| μ/μm⁻¹                          | 0.385                                      |
| F(000)                          | 808.0                                      |
| Crystal size/mm³                | 0.15 × 0.05 × 0.05                         |
| Radiation                       | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/° | 5.078 to 52.744                            |
| Index ranges                    | -11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 19 |
| Reflections collected           | 8700                                       |
| Independent reflections         | 5924 [R_{int} = 0.0388, R_{sigma} = 0.0809]|
| Data/restraints/parameters      | 5924/0/446                                 |
| Goodness-of-fit on F²           | 1.037                                      |
| Final R indexes [I>=2σ(I)]     | R₁ = 0.0845, wR₂ = 0.2022                 |
| Final R indexes [all data]     | R₁ = 0.1394, wR₂ = 0.2603                 |
| Largest diff. peak/hole / e Å⁻³| 1.79/-1.11                                 |
## Bond Lengths for PVM

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| P1   | C18  | 1.802(6) | N1   | C11  | 1.347(8) |
| P1   | C8   | 1.814(6) | N1   | C13  | 1.476(8) |
| P1   | C2   | 1.777(6) | F6   | C23  | 1.323(8) |
| P1   | C1   | 1.774(6) | F8   | C24  | 1.327(9) |
| S3   | O7   | 1.432(4) | C9   | C8   | 1.382(8) |
| S3   | O8   | 1.432(5) | C9   | C14  | 1.475(8) |
| S3   | O9   | 1.445(5) | C9   | C10  | 1.391(9) |
| S3   | C24  | 1.807(8) | C18  | C17  | 1.386(8) |
| S2   | O6   | 1.435(5) | C18  | C14  | 1.396(8) |
| S2   | O4   | 1.430(5) | C8   | C12  | 1.379(8) |
| S2   | O5   | 1.439(5) | C14  | C15  | 1.389(8) |
| S2   | C23  | 1.812(9) | C2   | C7   | 1.386(9) |
| S1   | O1   | 1.412(6) | C2   | C3   | 1.397(9) |
| S1   | O2   | 1.386(6) | C16  | C15  | 1.373(9) |
| S1   | O3   | 1.473(7) | F3   | C22  | 1.387(12) |
| S1   | C22  | 1.797(10)| C10  | C11  | 1.374(9) |
| F5   | C23  | 1.352(9) | F2   | C22  | 1.324(11)|
| F4   | C23  | 1.330(9) | C7   | C6   | 1.374(10)|
| F7   | C24  | 1.338(9) | C3   | C4   | 1.394(10)|
| F9   | C24  | 1.306(9) | F1   | C22  | 1.255(11)|
| N2   | C17  | 1.348(7) | C4   | C5   | 1.371(11)|
| N2   | C16  | 1.332(8) | C6   | C5   | 1.392(11)|
| N2   | C19  | 1.481(8) | C20  | N3   | 1.077(10)|
| N1   | C12  | 1.354(8) | C20  | C21  | 1.449(14)|
### Bond Angles for PVM

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C18  | P1   | C8   | 90.7(3) | C12  | C8   | P1   | 127.3(5) |
| C2   | P1   | C18  | 111.0(3) | C12  | C8   | C9   | 121.4(6) |
| C2   | P1   | C8   | 114.4(3) | C18  | C14  | C9   | 113.0(5) |
| C1   | P1   | C18  | 114.5(3) | C15  | C14  | C9   | 127.6(6) |
| C1   | P1   | C8   | 111.4(3) | C15  | C14  | C18  | 119.4(6) |
| C1   | P1   | C2   | 113.1(3) | C7   | C2   | P1   | 119.3(5) |
| O7   | S3   | O8   | 115.7(3) | C7   | C2   | C3   | 121.4(6) |
| O7   | S3   | O9   | 115.5(3) | C3   | C2   | P1   | 119.3(5) |
| O7   | S3   | C24  | 103.9(3) | N1   | C12  | C8   | 117.7(6) |
| O8   | S3   | O9   | 113.2(3) | N2   | C16  | C15  | 121.9(6) |
| O8   | S3   | C24  | 102.7(3) | C11  | C10  | C9   | 117.3(6) |
| O9   | S3   | C24  | 103.6(4) | C16  | C15  | C14  | 118.0(6) |
| O6   | S2   | O5   | 114.6(3) | C6   | C7   | C2   | 119.2(7) |
| O6   | S2   | C23  | 102.5(3) | C4   | C3   | C2   | 118.2(7) |
| O4   | S2   | O6   | 115.9(4) | N1   | C11  | C10  | 122.1(6) |
| O4   | S2   | O5   | 115.4(3) | C5   | C4   | C3   | 120.4(7) |
| O4   | S2   | C23  | 102.9(3) | F7   | C24  | S3   | 110.4(5) |
| O5   | S2   | C23  | 102.7(4) | F9   | C24  | S3   | 111.9(6) |
| O1   | S1   | O3   | 111.8(4) | F9   | C24  | F7   | 108.0(6) |
| O1   | S1   | C22  | 105.6(4) | F9   | C24  | F8   | 108.7(7) |
| O2   | S1   | O1   | 119.6(5) | F8   | C24  | S3   | 111.0(5) |
| O2   | S1   | O3   | 111.0(5) | F8   | C24  | F7   | 106.6(7) |
| O2   | S1   | C22  | 104.8(5) | C7   | C6   | C5   | 120.1(7) |
| O3   | S1   | C22  | 102.0(5) | C4   | C5   | C6   | 120.6(7) |
| C17  | N2   | C19  | 118.9(5) | N3   | C20  | C21  | 176.5(12) |
| C16  | N2   | C17  | 121.9(5) | F5   | C23  | S2   | 110.9(5) |
| C16  | N2   | C19  | 119.1(5) | F4   | C23  | S2   | 111.9(5) |
| C12  | N1   | C13  | 118.9(6) | F4   | C23  | F5   | 105.4(6) |
| C11  | N1   | C12  | 121.8(5) | F6   | C23  | S2   | 112.7(6) |
| C11  | N1   | C13  | 119.3(6) | F6   | C23  | F5   | 107.1(6) |
| C8   | C9   | C14  | 113.6(5) | F6   | C23  | F4   | 108.5(7) |
| C8   | C9   | C10  | 119.6(6) | F3   | C22  | S1   | 106.1(8) |
| C10  | C9   | C14  | 126.8(6) | F2   | C22  | S1   | 113.4(7) |
| C17  | C18  | P1   | 128.5(5) | F2   | C22  | F3   | 101.9(8) |
| C17  | C18  | C14  | 120.0(6) | F1   | C22  | S1   | 115.8(7) |
| C14  | C18  | P1   | 111.4(4) | F1   | C22  | F3   | 106.5(9) |
| N2   | C17  | C18  | 118.7(6) | F1   | C22  | F2   | 111.7(10) |
| C9   | C8   | P1   | 111.3(4) |
**Figure S26.** Viologen and PVM disproportionation and comproportionation reactions. These reactions occur at similar rates with viologens on electrode surfaces, leading to the observation of two similar reduction peaks in CV.\textsuperscript{4,5} For PVM, disproportionation of the biradical cation occurs at a much higher rate than comproportionation, leading to the two reduction peaks to merge since the neutral radical forms once the biradical cation forms. This disparity in these reactions in PVM compared to viologens may be attributed to the strong propensity for biradical species to dimerize, and to the higher concentration of PVM at the electrode surface, making dimerization more favourable compared to more dilute optical experiments and for viologens. Comproportionation may not occur for PVM due to the extremely low concentration of the radical dication once the biradical cation begins to form at -0.3 V vs. Ag/AgCl. Viologens were developed for electrochromic applications, where it was desirable to increase the separation of redox reactions to more selectively access specific coloured redox states. The more recent development of viologens for batteries have opposite requirements, and having both redox reactions at the same or similar potentials would allow for more stable operating voltages.
Figure S27. Cyclic voltammetry at various scan rates is used to extract diffusion coefficients and a dimensionless parameter ($\gamma$) using the peak-to-peak separation of each redox peak and the peak current at each scan rate. The electron transfer rates ($k_{tr}$) are extracted by the slope of a linear best fit. The second reduction is well modelled as a two electron process and the first reduction is well modelled as a single electron process. Both reactions exhibit high rate constants of electron transfer. $D =$ diffusion coefficient (cm/s), $n =$ # of electrons, $F =$ Faradays constant (C/mol), $v =$ scan rate (mV/s), $R =$ ideal was constant (J/(mol*K)), $T =$ temperature (K).
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