Viologen Analogues

3,7-Diazadibenzophosphole Oxide: A Phosphorus-Bridged Viologen Analogue with Significantly Lowered Reduction Threshold**

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4,4'-Bipyridine (1) and its N-alkylated congeners^[1] are classic organic building blocks that have been utilized in a variety of fields, such as photochemistry,^[1b] electrochemistry,^[1c] solarenergy conversion,^[1d] and as bridging ligands in metallosupramolecular assemblies, or molecular wires.^[1e] Methylviologen \mathbf{MV}^{2+} , or paraquat, easily accessible from 4,4'-bipyridine by methylation (Scheme 1), is frequently used as a photo-

$$N \xrightarrow{2 \text{ MeX}} Me = N \xrightarrow{+} Me = N \xrightarrow{+} N^{+} Me \xrightarrow{+} e^{-} MV^{+} \xrightarrow{+} e^{-} MV^{+}$$

$$1 \qquad X = \text{OTf, Br, Cl} MV^{2+} 2 X^{-}$$

Scheme 1. Synthesis and reduction of methylviologen (**MV**²⁺).

chemical probe,^[2a] an electrochemical label,^[2b] or a cosensitizer in studies concerning the electron-transport processes or oxidative damage in DNA.^[3]

The high practical value of \mathbf{MV}^{2+} is based on its pronounced electron-acceptor character and the change between intense colors (purple and orange) for the radical cation (\mathbf{MV}^{++}), and the neutral species (\mathbf{MV}), respectively, that make the reduction event(s) easily detectable by optical spectroscopy or even the naked eye.^[1a]

In the context of systematic studies on phosphoruscontaining π -conjugated materials for organic electronics, our group^[4] and others^[5] could confirm the highly tunable, favorable electron-acceptor features that are attributable to the electronic nature of phosphorus. Recently we have extended our studies toward π -conjugated phospholes with pyridine units as integral part of the scaffold and were able to establish the highly functional nature, as well as the pronounced electron-accepting features of these systems, particularly for the phosphole oxides.^[6]

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We now report the synthesis and characterization of a 3,7diazadibenzophosphole oxide, which can be considered a phosphorus-bridged viologen precursor, and its subsequent conversion into the dimethylated phospha- MV^{2+} species. Our study shows that incorporation of the bridging phosphoryl group dramatically enhances the electron-acceptor features of the scaffold, while maintaining MV^{2+} -analogue stability and responses.

To synthesize the title compound using our established method towards ring-fused phospholes,^[7] 3,3'-dibromo-4,4'bipyridine (**3**) had first to be prepared on a synthetically useful scale. Despite the fact that compound **3** had been reported before, the procedure outlined was tedious only providing **3** in very low yield and analytical amounts.^[8] To gain access to the starting material **3** in synthetically useful amounts, we applied an Ullmann coupling^[9] of 3-bromopyridine (**2**) to afford the target bipyridine in moderate yield (44%; Scheme 2). Remarkably, the reaction involves only



Scheme 2. Synthesis and reactivity of 3,7-diazadibenzophosphole oxide **4**: a) 1. LDA (-85 °C, THF), 2. CuCl₂, 3. air. b) 1. 2 *n*BuLi (-85 °C, THF), 2. PhPCl₂, 3. H₂O₂ (excess, CHCl₃). c) 2 MeOTf, CH₂Cl₂, room temperature.

inexpensive starting materials and was proven to be scalable, so that bipyridine **3** could be obtained on a gram scale within two days. Multinuclear NMR spectroscopy, mass spectrometry and elemental analysis confirmed the formation of compound **3**. In addition, single-crystals, suitable for X-ray crystallography were also obtained (see the Supporting Information).

The best results for the synthesis of **4** were obtained by treatment of **3** with two equivalents *n*BuLi at -85 °C in THF (Scheme 2);^[10] diazadibenzophosphole oxide **4** was isolated in 49 % yield as colorless solid. The ³¹P NMR resonance of **4** ($\delta^{31}P = 33.6$ ppm) agrees well with that observed for the 3-azadibenzophosphole oxide analogue ($\delta^{31}P = 34.0$ ppm)^[6] and dibenzophosphole oxide ($\delta^{31}P = 31.4$ ppm).^[11a] Single crystals, suitable for X-ray crystallography, were obtained from a

concentrated solution of **4** in ethanol upon evaporation.^[12] The structure (Figure 1) exhibits a planar backbone with small C–C and C–N bond-length alternation and shows essentially equidistant endo- and exocyclic P–C bond lengths



Figure 1. Molecular structure of **4** (left) and packing (right) in the solid state (thermal ellipsoids set at 50% probability, H atoms are omitted for clarity). See the Supporting Information for detailed metric parameters.

that are in good agreement with the reported 1-aza-, and 4-azadibenzophosphole oxide,^[6] as well as dibenzophosphole oxide.^[11b]

The packing in **4** shows a layered motif with two different face-to-face interactions. The layers with the O-atoms pointing toward each other show a strong π -stacking interaction with a distance of 3.41 Å, whereas the layers with the phenyl rings pointing toward one another show weaker face-to-face interactions with a distance of 3.61 Å.

The photophysical features of **4** were investigated by UV/ Vis spectroscopy in dichloromethane (Table 1). The spectrum (Supporting Information) shows an absorption profile with a maximum at $\lambda_{max} = 276$ nm and a molar absorptivity of $\varepsilon_{276} =$ 10750 Lmol⁻¹cm⁻¹, as well as shoulders at 305 nm and 269 nm; the onset of absorption is found at $\lambda_{onset} = 330$ nm. The photophysical features are comparable to those observed for the azadibenzophosphole oxides.^[6]

Table 1: Photophysical and electrochemical features of 3-5 and MV²⁺.

Compd	$\lambda_{\max}{}^{[a]}$ [nm]	$\varepsilon [Lmol^{-1}cm^{-1}]$	$E_{\rm red}^{\rm [b]}$ [V]	$E_{\rm ox}^{\rm [b]}$ [V]
3	272	5340	-2.58	0.48, 0.95
4	276	10750	-1.85, -2.47	0.81
5	288	17720	-0.51, -1.00	_
MV ^{2+[17]}			-1.09, -1.52	_

[a] Dichloromethane, $c \approx 10^{-5}$ M. [b] CH₃CN, NBu₄PF₆ as supporting electrolyte, vs. Fc/Fc⁺.

The electrochemical characteristics of **4** were probed via cyclic voltammetry (CV), performed in acetonitrile solution at different scan rates and referenced versus Fc/Fc⁺ (Fc = [(η -C₅H₅)₂Fe] see the Supporting Information). The cyclic voltammograms show a reversible reduction at $E_{\text{red1,1/2}} = -1.85$ V ($E_{\text{LUMO}} = -2.95$ eV). Furthermore, another irreversible reduction is observed at $E_{\text{red2,1/2}} = -2.47$ V; an irreversible oxidative wave can be found at $E_{\text{ox,peak}} = 0.81$ V (Table 1). The first reduction occurs at a lower potential

compared to 3-azadibenzophosphole oxide ($\Delta E = 0.29 \text{ V}$),^[6] due to the presence of the second nitrogen within the scaffold of **4**. Since the material revealed reversible one-electron reduction events, assessed by the separation between anodic and cathodic peak potentials, its electron-transfer constant $k_{\rm ET}$ was evaluated.^[13] 3,7-Diazadibenzophosphole **4** shows a lower $k_{\rm ET} = 2.01 \times 10^{-4} \text{ cm s}^{-1}$ than those observed in the azadibenzophospholes,^[6] probably due to the less polar backbone structure, resulting in lower mobility in an electric field. Nevertheless, the obtained $k_{\rm ET}$ value indicates sufficiently fast electron-transfer processes that are beneficial for an application in electronic devices,^[14] well within the range of previously reported phosphadiazole-oxide, thiadiazole, thiadiazole-oxide and -dioxide fused phenanthrenes, and pyrenes.^[15]

After having established synthetic access to the 3,7diazadibenzophosphole oxide 4, its reactivity towards transition metals was investigated. Due to the analogy of the backbone of 4 to 4,4'-bipyridine, the synthesis of a supramolecular square (see Supporting Information), analogous to a compound reported by Fujita and co-workers,^[16] was attempted. However, no reaction was observed upon mixing of 4 with $[Pd(bipy)(NO_3)_2]$, and slow heating resulted in decomposition to unidentified products, as confirmed by NMR spectroscopy and MALDI-TOF mass spectrometry. The lack of success can be explained by the electronwithdrawing effect of the phosphoryl group, making 4 a weak N-donor system not capable of coordination to two Pd²⁺ centers. Furthermore, owing to the distortion of the backbone, the arrangement of the N donors in 4 is such that the formation of an ideal square complex is not possible, the geometry of the product would be a distorted square with considerable ring strain. Alternatively, the synthesis of a coordination polymer was attempted by treatment of 4 with 0.9 equivalents of K₂[PtCl₄], affording a poorly soluble, bright orange solid. Despite the fact that ¹H and ³¹P NMR spectroscopy and UV/Vis spectroscopy, as well as MALDI-TOF spectrometry (see the Supporting Information) suggest the formation of oligomeric species, the insolubility of the material precluded a clear assignment of its structure. However, note in this context that the analogous reaction using the related monodentate 3-azadibenzophosphole (L) as ligand cleanly results in the formation of the $[Pt(L)_2Cl_2]$ complex.^[6]

3,7-Diazadibenzophosphole oxide **4** was subsequently converted into the methylviologen analogue **5** (Scheme 2). In stark contrast to the metal complexation, the reaction of **4** proceeded cleanly by addition of two equivalents of methyl triflate, providing phospha- MV^{2+} **5** in good yield (79%) as colorless solid. In addition to multinuclear NMR spectroscopy and CHN analysis, the formation of **5** was confirmed by X-ray crystallography (Figure 2). Single crystals were obtained from a concentrated solution of **5** in ethanol upon cooling to $0^{\circ}C.^{[12]}$

Note that the triflate anions are disordered over two positions and only the major component is shown. Due to the symmetry, both pyridinium rings and triflate anions are equivalent. The triflate anions are located on top of the annelated backbone, resulting in a short contact between O12

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Figure 2. Molecular structure of **5** (left) and packing (right) in the solid state (thermal ellipsoids set at 50% probability, H atoms are omitted for clarity). See the Supporting Information for detailed metric parameters.

and N1 (2.86 Å). The bond lengths observed in **5** are in good agreement with those of **4**. In the packing diagram, no face-to-face interactions are observed due to the position of the anions, preventing close contacts between the π systems, in favor of dipolar interactions.

The photophysical features of the phospha-MV²⁺ **5** were investigated via UV/Vis spectroscopy. The absorption profile is featureless with a maximum at $\lambda_{max} = 288$ nm and a molar absorptivity of $\varepsilon_{288} = 17720 \text{ Lmol}^{-1}$, comparable to that of **4** (Table 1). Cyclic voltammetry of **5** revealed two reversible reductions at $E_{red1,1/2} = -0.51$ V ($E_{LUMO} = -4.29$ eV) and $E_{red2,1/2} = -1.00$ V, respectively (Figure 3).



Figure 3. Cyclic voltammograms of **5** in CH₃CN solution at varying scan rates (10, 20, 50, 100, 200, 500, 1000, 1500, and 2000 mV s⁻¹; peak height increases with increasing scan rate). NBu₄PF₆ as supporting electrolyte; referenced vs. Fc/Fc⁺.

The separate electrochemical events result from sequential one-electron reduction of the individual pyridinium moieties. The reduction potentials of **5** are significantly lower than those of both, the starting material **4** and the parent \mathbf{MV}^{2+} ($E_{\text{red1,1/2}} = -1.09$ V and $E_{\text{red2,1/2}} = -1.52$ V, vs. Fc/ Fc⁺),^[17] as a result from the methylation and incorporation of the phosphole oxide, respectively. Both modifications decrease the energy of the LUMO-levels, facilitating the reduction. The electron-transfer rates were determined to be $k_{\rm ET1} = 1.93 \times 10^{-3} \,{\rm cm \, s^{-1}}$ and $k_{\rm ET2} = 1.71 \times 10^{-3} \,{\rm cm \, s^{-1}}$, respectively.^[14] Compared to **4**, the methylated congener **5** shows increased electron-transfer rates, probably due to the charges, resulting in a high mobility in an electric field.

As mentioned above, MV^{2+} and analogues have been shown to be useful redox-active photochemical probes to investigate electron-transfer processes from DNA intercalators (i.e., ruthenium complexes or ethidium) to $MV^{2+,[2a,3a]}$ The reduction events on MV^{2+} result in an increase of the absorption in the visible range of the spectrum and are monitored by UV/Vis spectroscopy.^[2a] To investigate the suitability of **5** for studies of this kind, the spectroelectrochemical features were examined. As shown in Figure 4,



Figure 4. Spectroelectrochemistry of compound 5 in acetonitrile at $E=0.0 \vee (--), -0.6 \vee (\cdots, 5_{red1}), and -1.1 \vee (---, 5_{red2}) \vee s. Fc/Fc^+$. Inset: magnification of the visible-light region.

without applied potential (0.0 V), the phospha-MV²⁺ **5** shows no significant absorption in the visible range of the spectrum. After application of a potential (-0.6 V), resulting in the reduction of **5** to the corresponding monocation radical **5**_{red1}, the absorption in the visible range of the optical spectrum is significantly increased over a wide spectral window, as expected for the reduced monocation radical. **MV**⁺⁺ (the product for reduction of **MV**²⁺) also shows a broad absorption over the whole visible range of the spectrum, due to its charge-transfer nature, with a maximum at $\lambda_{abs} = 605$ nm.^[18] The second reduction, resulting in the formation of the neutral **5**_{red2}, leads to a slightly decreased absorptivity (Figure 4).

However, even after applying a higher potential (-1.1 V), the absorption remains significantly higher than that of the dication **5**. These results, in combination with its solubility in water, show that the phospha-MV²⁺ **5** is well suited for an application as redox-active photochemical probe, due to its significant change in the absorption profile upon reduction. Its advantage over parent \mathbf{MV}^{2+} lies in the decreased (i.e., less negative) reduction potentials (**5**: $E_{\text{red1},1/2} = -0.51 \text{ V}$, $E_{\text{red2},1/2} = -1.00 \text{ V}$; \mathbf{MV}^{2+} : $E_{\text{red1},1/2} = -1.09 \text{ V}$, $E_{\text{red2},1/2} = -1.52 \text{ V}$, vs. Fc/Fc⁺), inherently leading to increased sensitivity and wider scope of useable excited-state electron donors with low-lying LUMO levels.

To better understand the electronic and photophysical characteristics, DFT calculations (B3LYP/6-31G*) have been performed on the diazadibenzophosphole oxide **4**, the dimethylated congener **5**, and the corresponding native species **1** and \mathbf{MV}^{2+} .^[19,20] The geometries were fully optimized and the orbital energies determined (Table 2).

Table 2: Frontier orbital energies [eV] and (character) for 1, 4, 5, and $MV^{2+,[19]}$

Orbital	1	4	5 ^[a]	$\mathbf{MV}^{2+[\mathbf{a}]}$
LUMO	-2.02 (π*)	-2.60 (π*)	-4.18 (π*)	-3.77 (π*)
НОМО	-7.40 (n _N)	-7.37 (π)	-7.45 (π _{Ph})	-8.96 (π)
HOMO-1	-7.45 (n _N)	-7.39 (n _N)	-7.61 (π _{Ph})	-8.97 (π)
HOMO-2	-7.57 (π)	-7.50 (n _N)	-8.58 (op)	-8.99 (π)

[a] Only the cationic portion was calculated using PCM solvation.^[20]

The LUMO energy of 4 is significantly stabilized in comparison with 4,4'-bipyridine 1 ($\Delta E \approx 0.6 \text{ eV}$), while the HOMO energy level essentially remains the same, despite a switch in character from n_N to π . The energy differences between HOMO, HOMO-1, and HOMO-2, representing either the nitrogen lone pairs or the π system (see Supporting Information), are minor in both compounds, which supports the fact that the general reactivity of 4 toward methylation is not compromised; the phosphoryl bridge largely introduces increased electron-acceptor features to the system. While the correlation between computational results for 4 with the experimental electrochemical data is fair (from CV: $E_{LUMO} =$ -2.95 eV; calculated: $E_{\text{LUMO}} = -2.60 \text{ eV}$), the calculated LUMO level of dication 5 ($E_{LUMO} = -4.18 \text{ eV}$) agrees very well with that determined by CV ($E_{LUMO} = -4.29 \text{ eV}$);^[20] as expected, it is significantly stabilized compared to that of 4 $(\Delta E \approx 1.6 \text{ eV})$, but also that of \mathbf{MV}^{2+} ($\Delta E \approx 0.4 \text{ eV}$). The character of the LUMO in 5 is very similar to that for 4 and MV^{2+} , representing a quinoidal π^* system. It is interesting to note, however, that the HOMO level of 5 shows no contribution from the main π system, only the π system of the exocyclic phenyl ring is represented; the same is true for the HOMO-1. Since MV^{2+} does not have this structural feature, the essentially degenerate HOMO, HOMO-1, and HOMO-2 involve the π system, however at lower energy than the corresponding orbitals for 5 ($\Delta E \approx 0.4$ –1.5 eV).

In conclusion, we have successfully synthesized 3,3'dibromo-4,4'-bipyridine in reasonable quantities for the first time, which has allowed us to access a novel phosphorusbridged viologen analogue. Owing to the pronounced electron-acceptor character of the phosphoryl bridge, the compound shows reversible reduction features, but only a limited capacity to act as a rigid bidentate ligand for transition-metal species through the nitrogen centers. However, methylation of the nitrogen centers is clearly possible, providing the watersoluble phospha-MV²⁺ **5** with a further lowering of the reduction potentials. This species can be reversibly reduced in two steps and the reduction can be monitored by optical spectroscopy, as the reduction events correlate well with the formation of strongly absorbing charge-transfer species, similar to those observed for the parent **MV**²⁺ system. Importantly, the reduction of the system can be achieved at significantly lower potential ($\Delta E_{\rm red} > 0.5$ V) than for the parent viologen system, owing to the planarized geometry, as well as the electron-withdrawing nature of the phosphoryl bridge. Our studies suggest considerable practical value of the new system, for example, in the context of electron-transfer processes with weaker electron donors. Verifying studies with corresponding transition-metal complexes and species of biochemical relevance are currently underway.

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- [12] Crystal data for 4: ($C_{16}H_{11}N_2OP$): $M_r = 278.24$, T = 173(2) K, triclinic, space group $P\bar{1}$, a = 7.6072(4), b = 9.5827(3), c =10.0206(5) Å, $\alpha = 87.971(3)$, $\beta = 72.078(2)$, $\gamma = 67.961(2)^{\circ}$, V =641.59(5) Å³, Z=2, $\rho_{\text{calcd}} = 1.440 \text{ Mg m}^{-3}$, $\mu = 0.210 \text{ mm}^{-1}$, $\lambda =$ 0.71070 Å, $\theta_{\text{max}} = 27.56^{\circ}$, 9205 measured reflections, 2867 [*R*-(int) = 0.0921] independent reflections, GOF on $F^2 = 1.158$, $R_1 =$ 0.0552, $wR_2 = 0.1473 \ (I > 2\sigma(I)), R_1 = 0.0661, wR_2 = 0.1660$ (for all data), largest difference peak and hole 0.351 and $-0.409 \text{ e} \text{ Å}^{-3}$; Crystal data for **5**: (C₂₀H₁₇F₆N₂O₇PS₂): $M_r =$ 606.45, T = 173(2) K, orthorhombic, space group *Pnma*, a =b = 16.7820(6),c = 11.5768(4) Å, 13.0018(4), V =2526.01(15) Å³, Z = 4, $\rho_{calcd} = 1.595 \text{ M gm}^{-3}$, $\mu = 0.363 \text{ mm}^{-1}$, $\lambda = 0.71070 \text{ Å}, \ \theta_{\text{max}} = 27.48^{\circ}, \ 14507 \text{ measured reflections}, \ 2985$ [R(int) = 0.0681] independent reflections, GOF on $F^2 = 1.153$, $R_1 = 0.0644, wR_2 = 0.1776 (I > 2\sigma(I)), R_1 = 0.0833, wR_2 = 0.2064$ (for all data), largest difference peak and hole 0.536 and $-0.437 \text{ e} \text{ Å}^{-3}$. The intensity data were collected on a Nonius KappaCCD diffractometer with graphite monochromated $Mo_{K_{\alpha}}$ radiation. The structure was solved by direct methods (SHELXTL) and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included by using a riding

model. CCDC 820571, 820572-820573 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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