

A Convenient *N*-Arylation Route for Electron-Deficient Pyridines: The Case of π -Extended Electrochromic Phosphaviologens

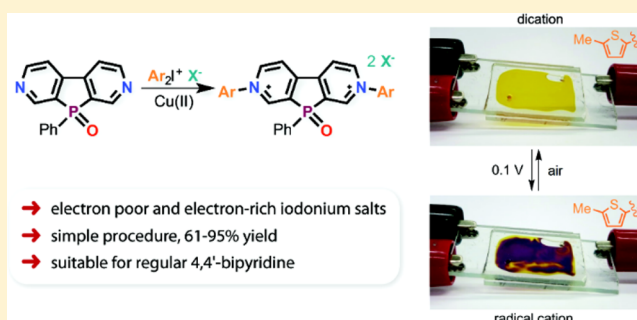
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Supporting Information

ABSTRACT: A simple and representative procedure for the synthesis of *N,N'*-diarylated phosphaviologens directly from both electron-rich and electron-poor diaryliodonium salts and 2,7-diazadibenzophosphole oxide is reported. The latter are electron-deficient congeners of the widely utilized *N,N'*-disubstituted 4,4'-bipyridinium cations, also known as viologens, that proved to be inaccessible by the classical two-step route. The single-step preparation method for phosphaviologens described herein could be extended to genuine viologens but reached its limit when sterically demanding diaryliodonium salts were used. The studied phosphaviologens feature a significantly lowered reduction threshold as compared to all other (phospha)viologens known to date due to the combination of an extended π -system with an electron deficient phosphole core. In addition, a considerably smaller HOMO–LUMO gap was observed due to efficient π -delocalization across the phosphaviologen core, as well as the *N*-aryl substituents, which was corroborated by quantum chemical calculations. Detailed characterizations of the singly reduced radical species by EPR spectroscopy and DFT calculations verified delocalization of the radical over the extended π -system. Finally, to gain deeper insight into the suitability of the new compounds as electroactive and electrochromic materials, multicolored proof-of-concept electrochromic devices were manufactured.

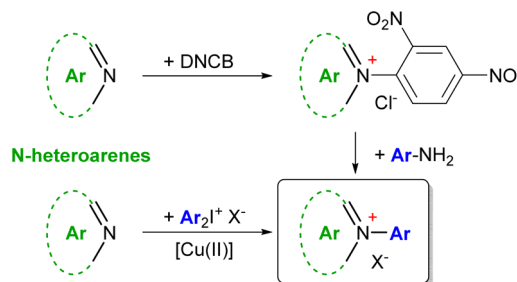


INTRODUCTION

The application of organic π -conjugated materials in a wide range of contemporary technological areas has rapidly increased in recent years.¹ However, purely carbon-based scaffolds with strongly electron-accepting properties are still few and far between and typically suffer from distinct drawbacks.² The replacement of selected carbon atoms within the organic framework by main-group heteroatoms such as B,³ N,⁴ P,⁵ or S⁶ has emerged as a potent tool to bypass these disadvantages. In addition, further extension of the π -system, i.e., further decrease of the energy gap, can be realized by *N*-arylation of incorporated N-heteroarene structures.

Though *N*-alkylation of such nitrogen centers can typically be achieved with alkyl halides or triflates,⁷ direct *N*-arylations are not as simple because of the lower electrophilicity of aryl halides as compared to alkyl halides. *N*-Arylations thus mostly rely on the Zincke reaction⁸ (Scheme 1, top), which exploits the strongly electron-deficient character of 2,4-dinitrochlorobenzene (DNCB). This reagent furnishes the formation of, for example, corresponding imidazolium⁹ or (bi)pyridinium salts,¹⁰ which can in turn be converted to the desired *N*-arylated derivatives by treatment with electron-rich aryl amines (Scheme 1). These quaternized N-heteroarenes are vigorously sought-after for their utilization in diverse areas ranging from synthetic

Scheme 1. Top: Zincke Reaction (DNCB: 2,4-Dinitrochlorobenzene);⁸ Bottom: Modified Nesmeyanov Reaction^{13,14}



chemistry and catalysis, to electrochemistry and materials science.¹¹ Therefore, new synthetic routes are constantly being developed,¹² but the most promising proved to be the rediscovery¹³ of a largely unnoticed reaction reported by Nesmeyanov in 1957,¹⁴ which utilizes the superior arylation properties of diaryliodonium salts.¹⁵ Crivello and Lee refined the Nesmeyanov protocol by introducing a copper(II) catalyst

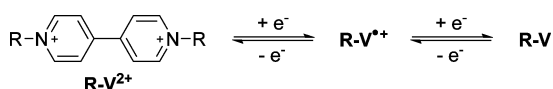
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(Scheme 1, bottom) and thereby successfully accessed *N*-phenylated pyridine, isoquinoline, and acridine.¹³ This methodology was recently proven to be tolerant toward functional groups such as acetyl, formyl, ester, and hydroxyl,¹⁶ and was extended to simplify the access to unsymmetrical imidazolium and triazolium salts.¹⁷

N,N-Disubstituted 4,4'-bipyridinium dications (also known as viologens; $R-V^{2+}$, Scheme 2) constitute another important

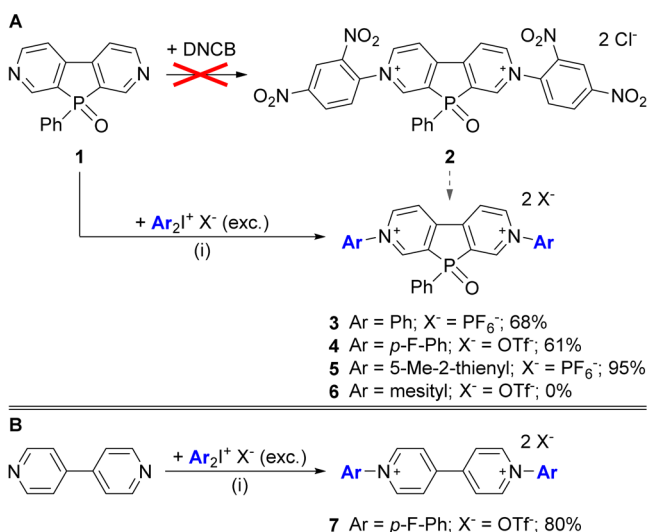
Scheme 2. Viologen $R-V^{2+}$ and Reduction to Its Radical ($R-V^{\bullet+}$) and Neutral Form ($R-V$)



class of quaternized *N*-heteroarenes which have so far only been arylated via the Zincke reaction.¹⁰ Viologens are of particular interest because of their pronounced electron-acceptor qualities and the intense color changes upon switching between their three different and highly stable redox states as dication ($R-V^{2+}$), radical cation ($R-V^{\bullet+}$) and neutral species ($R-V$, Scheme 2).¹⁸ These features can be tuned at will by altering the substituents on the nitrogen centers and render viologens suitable for applications spanning from photochemistry¹⁹ and solar energy conversion,²⁰ molecular wires²¹ and switches,²² to electrochromic devices such as self-dimming mirrors, displays and smart windows.²³

To further advance these developments, an access to a library of viologen species with enhanced physicochemical properties is crucial. Thus, our group has of late investigated the design of new π -conjugated, ring-fused phosphaviologens such as *N,N'*-dimethylated (**Me-PV**)²⁴ and *N,N'*-dibenzylated (**Bn-PV**)²⁵ ditriflate salts of 2,7-diazadibenzophosphole oxide (**1**, Scheme 3A) via *N*-alkylation. While the characteristic electrochromic and redox behaviors remained comparable to those of corresponding viologens, the electron affinity of the *N,N'*-dialkylated congeners of **1** increased dramatically by 0.3–0.5 V

Scheme 3. Failure of the Zincke Reaction between the Electron-Deficient Phosphole **1 and DNCB (A, Top) and Successful Two-Fold *N*-Arylation of **1** (A, Bottom) As Well As of Parent 4,4'-Bipyridine (B)**



(i): Cu(OAc)₂·H₂O (8 mol %), DMF, 40–100 °C, 4–36 h.

for each of the two reduction steps. This lowering of the LUMO (lowest unoccupied molecular orbital) energy level can be explained by an efficient phosphorus-centered $\sigma^*-\pi^*$ hyperconjugation²⁴ and leads to promising electron-acceptor properties.

As an exemplary study for a universal *N*-arylation of electron-deficient pyridines, we herein report a straightforward method to arylate the nitrogen centers in **1** via the modified Nesmeyanov protocol shown in Scheme 1. The scope of this addition is elucidated by reactions with varying diaryliodonium salts. Detailed spectroscopic characterizations, supported by quantum chemical calculations, shed light on the physicochemical properties of the obtained dicationic π -extended phosphaviologens.

RESULTS AND DISCUSSION

Reactivity of **1 toward *N*-Arylations.** In a first attempt, the best-established Zincke reaction for the *N*-arylation of 4,4'-bipyridines was considered to expand the π -system of **1** (Scheme 3A). However, the essential nucleophilic addition of DNCB to generate the phosphaviologen **2** did not proceed. The high electrophilicity of DNCB does not compensate for the severely reduced basicity of **1**²⁵ as compared to that of 4,4'-bipyridine. Even a neat reaction in DNCB with stoichiometric amounts of silver triflate, to trigger the precipitation of AgCl, could not force any addition reaction. While disappointing, these observations are in line with the already described hindered *N*-benzylation of **1** that has also been attributed to the low basicity of the phosphoryl-bridged 4,4'-bipyridine.²⁵

To overcome the weak nucleophilicity of **1**, the high nucleofugacity of a hypervalent iodine group in diaryliodonium salts with noncoordinating counterions such as PF₆⁻ or OTf⁻, respectively, was exploited via the modified Nesmeyanov protocol. The best results for the reaction of **1** with the most basic diaryliodonium salt Ph₂I⁺PF₆⁻ (Scheme 3A) could be obtained following the approach from Guo and You et al. using Cu(OAc)₂·H₂O as a catalyst and DMF as the solvent at elevated temperatures.¹⁶ The formation of **3** was readily followed by NMR spectroscopy: The ³¹P resonance experienced a high-field shift from 31.2 to 28.4 ppm and the ¹H NMR resonances for the pyridine protons were shifted from 8.0 (H-3,6), 8.9 (H-4,5), and 9.0 ppm (H-1,8) to lower fields at 9.1 (H-3,6), 9.4 (H-4,5), and 9.6 ppm (H-1,8), respectively. Furthermore, the presence of only three pyridine proton resonances, as well as the proton integral ratios between the signals for the phenyl and pyridine protons, confirmed the symmetrically substituted scaffold in **3**, with one added phenyl group to each of the nitrogen atoms.

To assess the capability of this procedure for the *N*-arylation of electron-deficient pyridines we first chose an electron-poor and an electron-rich diaryliodonium salt as reaction partners for **1**. The corresponding *p*-fluorophenyl- (**4**) and 5-methyl-2-thienyl-substituted (**5**; Scheme 3A) phosphaviologens were obtained in 61% and 95% yield, respectively, and unequivocally identified by multinuclear NMR spectroscopy. Similar trends as already described for compound **3** were detected in the ¹H and ³¹P{¹H} NMR spectra and thus do not merit further discussion. However, the reaction kinetics varied quite significantly for *N*-arylations with the different hypervalent iodonium species. On the one hand, the addition of the electron-rich 5-methyl-2-thienyl moiety proceeds readily at 40 °C (compound **5**, Scheme 3A); higher temperatures solely promote side and decomposition reactions. The electron-poor *p*-fluorophenyl substituent

Table 1. Optical and Electronic Properties of the New N,N' -Diarylated (3–5) and Already Known Phosphaviologens (Me-PV and Bn-PV) As Well As the Reference Viologen Ph-V²⁺

compd	$E_{1/2}^{\text{red1}}$ [V] ^a	$E_{1/2}^{\text{red2}}$ [V] ^a	λ_{max} [nm] (ϵ [M ⁻¹ cm ⁻¹]) ^b	λ_{onset} [nm] ^b	E_G^{opt} [eV] ^c (calcd) ^d	$E_{\text{HOMO}}/E_{\text{LUMO}}$ [eV] ^e (calcd) ^d	λ_{max} [nm] {radical cation} ^f	λ_{max} [nm] {neutral} ^g
3	-0.42	-0.77	345 (22 100)	425	2.9 (3.2)	-7.3/-4.4 (-7.5/-4.3)	458, 591, 647, 780	455
4	-0.42	-0.75	263 (8100), 351 (7700)	425	2.9 (3.1)	-7.3/-4.4 (-7.4/-4.3)	290, 448, 586, 639, 785	420 ^g
5	-0.38	-0.71	462 (23 100)	550	2.3 (2.6)	-6.7/-4.4 (-6.9/-4.3)	543, 663, 774	449
Me-PV ^h	-0.60	-1.03	288 (17 700) ⁱ	380	3.3 (3.3)	-7.5/-4.2 (-7.5/-4.2)	406, 581, 634	408
Bn-PV ^h	-0.53	-0.97	257 (10 700), 298 (8270) ^j	350	3.5 (3.3)	-7.8/-4.3 (-7.4/-4.1)	415, 584, 636	402
Ph-V ²⁺	-0.68 ^k	-0.94 ^k	314 (21 000) ^l	–	– (3.7)	–/-4.1 (-7.6/-3.9)	250, 318, 377, 437, 627, 644, 664, 713 ^m	442, 446 ⁿ

^aCV in DMF solution with [nBu₄N][PF₆] as supporting electrolyte (0.05 M), referenced to Fc/Fc⁺. ^bUV–vis absorption in CH₃CN. ^cEnergy gap values were calculated from the onset wavelengths (λ_{onset}) of the absorption spectra. ^dTheoretical calculations have been carried out at the B3LYP/6-31G(d) level with a PCM solvation model (CH₃CN) by using the GAUSSIAN09 suite of programs; ref 28. ^eEnergy levels vs vacuum level were calculated from CV data ($E_{\text{LUMO}} = -4.8 \text{ eV} - E_{1/2}^{\text{red1}}$; Fc/Fc⁺ = -4.8 eV vs vacuum level) and from the optically determined energy gap ($E_{\text{HOMO}} = E_{\text{LUMO}} - E_G^{\text{opt}}$). ^fAbsorption maxima in CV solution using spectroelectrochemistry. ^gChemically reduced with Li metal in DMF solution. ^hRef 25. ⁱIn CH₂Cl₂. ^jIn MeOH. ^kIn THF with [nBu₄N][PF₆] as supporting electrolyte (0.10 M), referenced to Fc/Fc⁺; ref 26. ^lIn DMSO; ref 26. ^mIn CH₃CN; ref 26. ⁿIn THF; ref 26.

ent on the other hand, is being transferred slowest and a large excess of 12 equiv of the iodonium salt (*p*-F-Ph)₂I⁺OTf⁻ is needed to achieve complete 2-fold addition to generate **4**. These results match previous observations that electron-rich diaryliodonium salts react more readily than electron-deficient ones.¹⁶

In the present case, this decreased reactivity of the iodine(III) derivatives is even more problematic for sterically demanding reagents: Dimesityliodonium triflate does not transfer its mesityl moiety to **1** at all and the formation of **6** could not be observed (Scheme 3A), while the starting materials are, however, consumed entirely.²⁷ NMR spectroscopy, elemental analysis, and MALDI mass spectrometry data indicate that a transfer of mesityl groups does not occur; the two nitrogen centers are in fact protonated instead, at least to some degree. Remarkably, it was also impossible to mesitylate the parent 4,4'-bipyridine with dimesityliodonium triflate. By contrast, Guo, You, and co-workers were able to synthesize a mesitylated imidazolium salt in good yields under these conditions, even without explicit O₂-removal.¹⁶ For the systems described herein, conducting the experiments in degassed and carefully dried DMF as well as under inert atmosphere proved to be beneficial both for the yields as well as the workup of the reactions. This can be attributed to the extremely low-lying reduction potentials of **3–5** (vide infra) that cause the partial reduction to their radical cations during their synthesis, which was concluded from severely broadened signals in the ¹H and ³¹P{¹H} NMR spectra. On the other hand, trace amounts of water do not obstruct the reaction as no difference was observed between employing the monohydrate Cu(OAc)₂·H₂O or the dried form Cu(OAc)₂ as catalyst. We thus assume that the in situ formed radical cations react with molecular oxygen and form follow-up products, which hinder the reaction, likely by deactivating the copper catalyst.

To emphasize its general applicability, our *N*-arylation method was finally extended to parent 4,4'-bipyridine by converting it to the literature-known *N,N'*-bis(*p*-fluorophenyl)-bipyridinium ditriflate¹⁰ (**7**; Scheme 3B). Under these conditions, the desired product was obtained in a simple one-step synthesis in 80% yield even though (*p*-F-Ph)₂I⁺OTf⁻ proved to be the least reactive of the employed iodonium salts.

Electrochemistry. The electrochemical characterization of the phosphaviologens **3–5** was performed via cyclic voltammetry (CV) in DMF and the results are summarized in Table 1. The dicationic compounds exhibit two reduction waves separated by 0.35 V, on average. Complete electrochemical reversibility was verified using scanning speeds ranging from 10 mV/s to 1000 mV/s as can be seen in the representative cyclic voltammograms of **3** in Figure 1; only the thienyl-substituted **5**

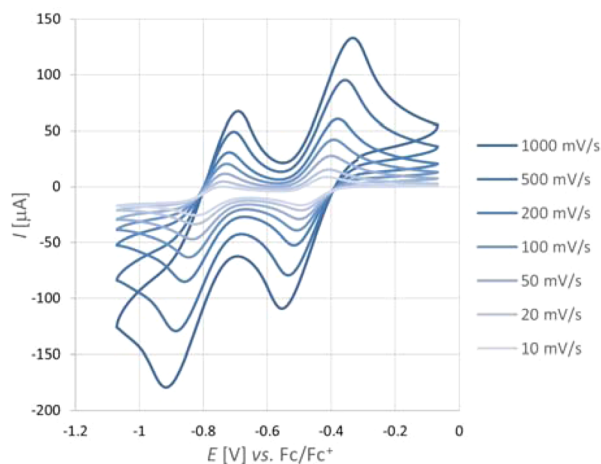


Figure 1. Cyclic voltammograms of **3** at different scan rates in DMF solution with [nBu₄N][PF₆] as supporting electrolyte (0.05 M), referenced to Fc/Fc⁺.

shows some signs of quasi-reversibility at higher scanning rates (see the Supporting Information). As compared to the previously reported *N,N'*-dimethylated (Me-PV)²⁴ and *N,N'*-dibenzylated phosphaviologens (Bn-PV),²⁵ the first electron injection is facilitated by 0.1–0.2 V and the second by 0.2–0.3 V vs Fc/Fc⁺ (Table 1). This efficient lowering of the LUMO energy levels is a direct consequence from the extension of the π -system by *N*-arylation of the phosphaviologen moiety. The incorporation of the phosphole oxide center itself leads to a drop of the LUMO energy level by 0.3 eV as opposed to the parent *N,N'*-diphenyl viologen²⁶ Ph-V²⁺ (Table 1). Moreover, CV measurements of the protonated side-product, that was formed during the reaction between **1** and dimesityliodonium

triflate, emphasize the need for *N*-alkyl or *N*-aryl substituents because of a limited reversibility and a hindered reduction by at least 0.5 V (see the [Supporting Information](#)).

In addition to these anticipated results, we also came across two unexpected findings: (i) The most electron-rich phosphaviologen **5** features the lowest lying LUMO energy level with a first reduction at -0.38 V vs Fc/Fc⁺, and (ii) the introduction of the electron withdrawing *p*-F-Ph moiety (**4**) did not alter the LUMO energy level as compared to phenyl-substituted species **3**. In contrast, in the case of regular viologens the latter actually does facilitate the electron injection by 0.1 V.²⁸

Photophysical Properties. The photophysical properties of **3–5** were investigated via UV–vis absorption spectroscopy in acetonitrile ([Table 1](#)). While solutions of **3** and **4** are colorless and accordingly show absorptions exclusively in the UV region with maxima around 350 nm, λ_{max} of **5** is red-shifted to 462 nm in the visible range of the optical spectrum ([Figure 2](#); see [Figure 4](#) for pictures of **4** and **5** in solution).

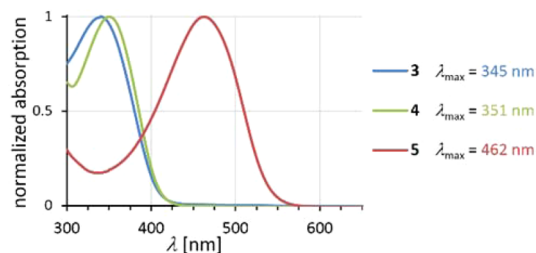


Figure 2. Normalized UV–vis absorption spectra of the phosphaviologens **3–5** in acetonitrile.

This change in absorption is accompanied by a reduced energy gap from 2.9 eV (**3**, **4**) to 2.3 eV (**5**) and can be explained with the strong electron-donating character of the thienyl substituents. In conjunction with the CV data, these energy gaps resemble a significant raise of the HOMO (highest occupied molecular orbital; see [DFT Calculations](#) below) energy levels from -7.3 eV in **3** and **4** to -6.7 eV in **5** ([Table 1](#)). This can also be visualized by taking possible resonance structures of **5** into consideration where one of the two positive formal charges is located on one of the sulfur atoms (see the [Supporting Information](#) and discussion of the Mulliken charges below), which essentially reflects a significant Charge Transfer (CT) character for **5** in the ground state. These resonance structures exhibit less aromatic character and are a reason for the increased HOMO energy level. On the other hand, the reduced steric strain of a five-membered thienyl ring provides a better coplanarity of the *N*-aryl substituent with the 2,7-diazadibenzophosphole core (see [DFT Calculations](#) section below). The latter effect will likely improve the delocalization of the electron density across the π -system in the LUMO and decrease the energy thereof, leading to the notably reduced energy gap of 2.3 eV for **5**. Nevertheless, compounds **3** and **4** already display a noteworthy smaller energy gap than **Me-PV** and **Bn-PV** due to their extended π -systems.

The UV–vis absorption of **5** was additionally measured in different solvents to elucidate the effect of the solvent polarity on the absorption maximum and to confirm the presence of a CT ground state (see the [Supporting Information](#) for an overlay of the different absorption spectra). Upon dissolution in a more polar solvent like DMF, λ_{max} of **5** is shifted

hypsochromically to 443 nm. The absorption maximum in the rather nonpolar solvent CH₂Cl₂ can be found at 487 nm and corresponds to a shift of 2000 cm⁻¹. This indicates a pronounced negative solvatochromism owing to the highly polar ground state of the dicationic **5**. DFT-derived Mulliken charges support this interpretation with strongly positive shares on the phosphorus, sulfur, C-1,8, and C-3,6 atoms, as well as negative portions primarily on the oxygen and nitrogen atoms (see the [Supporting Information](#) for a graphical plot of the Mulliken charge distribution in **5**).

Spectroelectrochemistry characterizations were carried out in DMF to monitor the transitions from the dications **3–5** to the radical cations **3'–5'** and finally to the neutral species **3''–5''**. Upon application of a voltage that just induces the reduction to the radical cations, strong chromism effects can be observed for all the phosphaviologens. The monoreduced phosphaviologens were colored either intensely green (**3'**, **4'**) or purple (**5'**; see [Figure 4](#)), resulting from strong and multiple absorptions in the visible spectrum. As already observed by UV–vis spectroscopy for the dications, the thienyl-substituted radical cation **5'** behaves significantly different from the two phenyl-derived compounds **3'** and **4'**. The absorption spectra of the latter two show an intense single absorption at about 450 nm, a series of peaks that represent a vibrational fine structure with a maximum at about 650 nm, and a weak absorption in the near-IR region at about 780 nm ([Figure 3A](#), and the [Supporting](#)

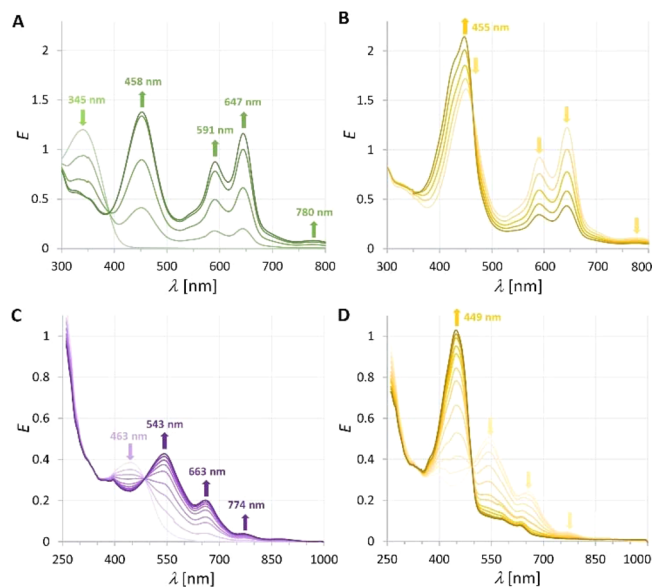


Figure 3. Spectroelectrochemistry of **3** (top) and **5** (bottom) in DMF for their first (A and C) and second reductions (B and D).

[Information](#)). This peak pattern closely resembles that of the radical cation of **Bn-PV**²⁵ and, to a minor extent, that of the monoreduced parent viologen **Ph-V**^{•+}.²⁶ By comparison, thienylated **5'** exhibits the strongest absorption at 543 nm and shows additional local maxima at 663 nm and in the near-IR at 774 nm ([Figure 3C](#)). Upon further reduction to the neutral derivatives, however, the absorption spectra of phenyl- and thienyl-based (phospha)viologens **3''**, **5''**, and **Ph-V**²⁶ become very similar, leading to only one major absorption at about 450 nm that is responsible for their yellow/brown colors ([Figure 3B/D](#); [Table 1](#)). Following the transition **4' → 4''** did

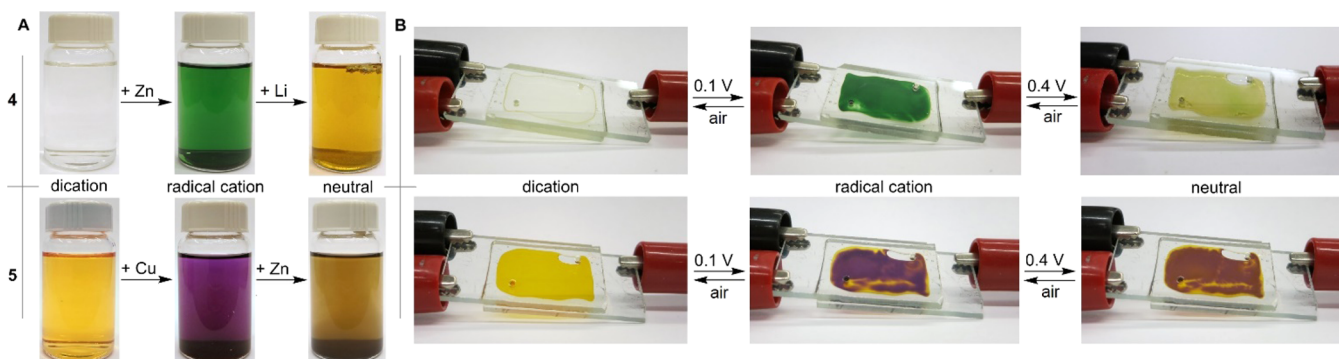


Figure 4. Chemochromism (A) and reversible electrochromism (B) of the phosphaviologens **4** (top row) and **5** (bottom row) in acetonitrile solutions. The proof-of-concept devices in B were assembled as already described elsewhere.²⁵

not reveal an analogous trend but only the extinction of all absorption features and no rise of any new signals.

It should be noted that the apparent color changes between the different redox states $3-5 \rightarrow 3'-5'$ can also be achieved via chemical reduction with zinc (**3**, **4**) or copper dust (**5**; Figure 4A). Nondried and nondegassed acetonitrile solutions of all generated radicals $3'-5'$ kept their colors for several hours under air which proves the high stability of these π -extended phosphaviologen-centered radicals. Much to our surprise, the treatment of an acetonitrile solution of **5** with Zinc dust induced a complete reduction to the brown neutral species **5''** (Figure 4A). In contrast to the already discussed spectroelectrochemical findings, the chemically reduced sample of **4''** does show the typical absorption band at 420 nm (see the Supporting Information for a spectrum in DMF solution) which is similar to those of the dicationic species **3''** and **5''**. At this point it is, however, not apparent where these differences in the chemical and electrochemical reduction of **4** stem from and further detailed studies are necessary.

DFT Calculations. To further corroborate the experimental findings, DFT calculations at the B3LYP/6-31G(d) level of theory with a PCM solvation model²⁹ have been performed for the new phospholes **3-5** and genuine Ph-V^{2+} (see the Supporting Information for further details). The results are in agreement with the trends observed by CV and UV-vis spectroscopy, but the HOMO-LUMO gaps of the arylated species are systematically overestimated by 0.3 eV (Table 1). For all of these compounds, similar HOMO and LUMO orbital distributions are clearly visible. As such, the characteristics of the LUMOs for all these compounds are essentially the same and correspond to a varying degree of delocalization across the *N*-aryl substituents and the central (phospha)viologen core. Additionally, the LUMOs of the phosphorus-based compounds **3-5** exhibit the already mentioned $\sigma^*-\pi^*$ hyperconjugation and are thus significantly lower in energy than the LUMO of Ph-V^{2+} . According to the calculations the dihedral angle between the *N*-aryl substituent and the 2,7-diazadibenzophosphole core amounts to 34° in **5** while it is widened to 50° for **3** and 47° for **4**, respectively. Therefore, a better delocalization of the charge density is granted in the LUMO of **5**, which leads to its significantly decreased energy gap.

In addition to DFT calculations that back up the properties of the synthetically accessed compounds, the potential scope of electronic fine-tuning possibilities was evaluated by calculating two additional, representative π -extended phosphaviologens. To this end, a strongly electron deficient *N,N'*-bis(perfluorophenyl) derivative (**8**) as well as another electron

donating *N,N'*-bis(*p*-methoxyphenyl) substituted compound (**9**), with expectedly similar dihedral angles, were investigated (see the Supporting Information).

Because of the pronounced electron-withdrawing effect of the perfluorophenyl groups in derivative **8**, the LUMO energy (-4.6 eV) is lower than that of the other two phenyl congeners **3** and **4**. Moreover, the π -system of the scaffold is also lowered considerably, and found in the degenerate HOMO-2 and HOMO-3 orbitals at -7.7 eV. HOMO and HOMO-1 that largely reflect the *P*-phenyl substituent have energies of -7.6 and -7.7 eV, respectively. In this compound, the dihedral angle between the *N*-aryl substituent and the 2,7-diazadibenzophosphole core amounts to 51° , in line with the other two phenyl-extended species. This electronic distribution with a $\pi-\pi^*$ energy gap of 3.2 eV clearly reflects the absence of any donor elements in the scaffold, and does suggest somewhat similar photophysics to compounds **3** and **4**, however, accompanied by a slightly lowered reduction threshold for **8** that suggests that the reduction properties in these systems are somewhat dominated by the phosphaviologen core.

A different picture was provided by the DFT calculations of **9**: Because of the donor-character of the *p*-methoxyphenyl substituents, its HOMO comprising the π -system is primarily centered on the donor parts of the molecule. This destabilizes the HOMO in a similar fashion to **5**, and corresponds to a CT scenario that is reflected in resonance structures with a positive charge on the oxygen atom (see the Supporting Information for a simple resonance structure analysis). In comparison to **5**, the relatively stronger donor capabilities of the methoxy groups in **9** are counterbalanced by the larger dihedral angle of 47° between the donor and acceptor moiety planes which leads to a HOMO energy level of -6.7 eV (**5**: -6.9 eV). The LUMO of **9** (-4.2 eV), which is largely located in the central phosphaviologen core, comprising the π^* -system, is slightly higher in energy than those of the other relatives. This leads to a HOMO-LUMO ($\pi-\pi^*$) energy gap of 2.6 eV, similar to that of **5**, and ultimately suggests very similar photophysics and redox properties for **9**, despite the large dihedral angle discrepancy.

Radical Characterization. With this knowledge at hand, we next characterized the chemically reduced radicals $3'-5'$ by EPR spectroscopy at room temperature in acetonitrile. Even though the radicals are fairly stable, degassed acetonitrile solutions were used to avoid any interactions with molecular triplet oxygen. For all compounds $3'-5'$ the *g*-factor values were determined to 2.002–2.003 as expected for purely organic radicals. The spectra were collected with varying parameter

settings, such as modulation amplitudes as small as 0.05 G in order to record even smallest hyperfine couplings that are often observed for viologens.^{18,26} While the spectra of 3' and 4' are very similar and do only show little fine structure, the EPR spectrum of 5' features a very distinct coupling pattern with hyperfine interactions as small as 0.6 G (Figure 5A, and the

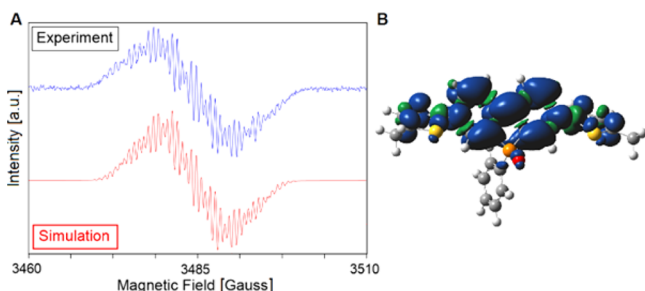


Figure 5. EPR spectrum of 5' (A; see the Supporting Information for experimental and simulation details) and spin density of the cationic portion of 5' (B3LYP/6-31G(d) level of theory).

Supporting Information). To gain deeper insight into the nature of the radicals, DFT calculations were performed again at the B3LYP/6-31G(d) level of theory with a PCM solvation model (see the Supporting Information for details).²⁹ To our satisfaction, the resulting spin density distributions clearly confirmed a complete spin delocalization across the extended π -systems of the N,N' -diarylated phosphaviologens with strong contributions on the aryl substituents (Figure 5B, and the Supporting Information). Furthermore, the SOMOs (singularly occupied molecular orbitals) of the radical species 3'–5' bear a close resemblance to the LUMOs of the dicationic 3–5. With the calculated isotropic Fermi contact couplings, all spectra could successfully be simulated. The largest hyperfine couplings were assigned to the phosphorus atom (4.7 G (5), 5.2 G (3, 4)), to the nitrogen atoms (2.8 G (5), 3.6 G (3, 4)), and to several protons of the conjugated system (up to 2.1 G; see the Supporting Information for detailed simulation parameters).

Electrochromic Device Fabrication. In order to demonstrate the feasibility of the new phosphaviologens as electroactive and electrochromic materials, we tested them in a proof-of-concept device introduced by us earlier.²⁵ This simple setup consists of two FTO-coated glass plates and an acetonitrile solution of the respective compound in between without any added electrolyte. A potential difference of 0.1 V was applied to these two glass electrodes and is followed by a complete color change to the corresponding color of the individual radicals (Figure 4). This process is reversed over time by the diffusion of air into the cell. For the phenyl-based systems 3 and 4, a switching between colorless and green occurs (Figure 4B) that matches the typical behavior for viologens.^{10,18} By contrast, the color of the thienyl-substituted phosphaviologen 5 interchanges between yellow and purple. Moreover, a reversible transition between the green (3', 4') and purple radical cations (5'), respectively, and the different shades of yellow/brown of the neutral species 3''–5'' can be achieved by applying higher voltages of 0.4 V (Figure 4B, and the Supporting Information).

CONCLUSIONS

The inability of DNCB to add to electron-deficient pyridines such as the phosphoryl-bridged 4,4'-bipyridine 1 highlights the need for an alternative N -arylation method. In this study, we

were able to extend the π -system of 1, and electron-deficient pyridines in general, via the Cu(II)-catalyzed Nesmeyanov protocol. This method proved to be compatible with both electron-poor as well as electron-rich diaryliodonium salts but hit its limits when sterically demanding iodine(III) compounds were employed. Next to straightforward reaction conditions and simple workup by precipitation, another beneficial attribute of this protocol is the possibility to access π -extended parent viologens $R-V^{2+}$ as well. Especially 4,4'-bipyridinium salts with electron-deficient N -aryl substituents like 7 are difficult to synthesize via the classical Zincke reaction and can now be prepared in just one step. The key features of viologens, i.e., the reversible chemical and/or electronic reduction to intensely colored and highly stable radicals, are preserved in the resulting N,N' -diarylated phosphaviologens 3–5. At the same time, their LUMO energy levels are efficiently lowered by at least 0.15 eV as opposed to all known phosphaviologens and by as much as 0.3 eV in comparison to corresponding parent viologens. This in turn improves the suitability of these compounds for use as electron-accepting materials. The thienyl-substituted dicationic species 5 proved to be a special case due to its significantly diminished energy gap and hence its absorption in the visible range of the optical spectrum, due to the presence of the terminal donor moieties and improved conjugation throughout the overall planarized scaffold, as verified through DFT calculations. The efficient chemo- and electrochromism of 5 lead to a switching between yellow and purple colors and has not been achieved for viologens yet. This is the first example of a (phospha)viologen that can not only dim the light by changing from colorless (dication) to colored (radical cation and neutral species) but that can actually switch between different colors for all three states and is thus even more interesting for applications in multicolored displays. Investigations of more sophisticated electrochromic cell designs with this promising new material are currently underway.

EXPERIMENTAL DETAILS

General Methods. Reactions were carried out under nitrogen atmosphere using Schlenk techniques unless otherwise specified. Bis(*p*-fluorophenyl)iodonium triflate,³⁰ bis(5-methyl-2-thienyl)iodonium hexafluorophosphate,³¹ and 2,7-diazadibenzophosphole oxide (1)²⁴ were prepared according to previously reported literature procedures. DMF was dried over molecular sieves and degassed with nitrogen prior to use. Anhydrous Cu(OAc)₂ was generated by heating turquoise-colored Cu(OAc)₂·H₂O to 100 °C for 24 h under vacuum until the color has completely switched to green. All other reagents were purchased from Sigma-Aldrich and used without further purification. NMR solvents were purchased from Cambridge Isotope Laboratories or Sigma-Aldrich. ³¹P{¹H} NMR, ¹H NMR, ¹⁹F{¹H} NMR, and ¹³C{¹H} NMR were recorded on Bruker Avance (-IL,III) 400 MHz spectrometers. Chemical shifts were referenced to external 85% H₃PO₄ (³¹P), C₆F₆ (¹⁹F) and external TMS (¹H, ¹³C) or residual nondeuterated solvent peaks (¹H, ¹³C). Mass spectra were run on a Finnigan SSQ 7000 spectrometer or a Bruker Daltonics AutoFlex III system. Elemental analyses were performed in the Department of Chemistry at the University of Calgary. EPR was measured using a Bruker EMX 10/12 instrument at room temperature in dry degassed acetonitrile using a flat cell. The EPR parameters for the experiments are as follows: modulation frequency = 100 kHz, modulation amplitude = 1.0 G (3, 4) or 0.2 G (5), time constant = 20.48 ms, conversion time = 81.92 ms, center field = 3485 G, sweep width = 60.0 G (4) or 50.0 G (3, 5), microwave attenuation = 12 dB (4) or 10 dB (3, 5), microwave power = 12.69 (4) or 20.12 mW (3, 5), no. of points = 2048, and no. of averaged scans = 8. Thermogravimetric Analysis (TGA) was performed on a TA-Instruments Q50 instrument. Cyclic voltammetry (CV) analyses were performed on an Autolab

PGSTAT302 instrument, with a polished glassy carbon electrode as the working electrode, a Pt-wire as counter electrode, and an Ag wire as reference electrode, using ferrocene/ferrocenium (Fc/Fc^+) as internal standard. CV experiments were performed in DMF solution with tetrabutylammonium hexafluorophosphate (0.05 M) as supporting electrolyte. Spectroelectrochemical experiments were carried out in the previously mentioned CV solutions with the same CV analysis setup and monitored with a UV-vis/NIR Cary 5000 spectrophotometer.

***N,N'*-Diphenyl-2,7-diazadibenzophosphole oxide di(hexafluorophosphate) (3).** 2,7-Diazadibenzophosphole oxide **1** (402 mg, 1.44 mmol, 1 equiv), diphenyliodonium hexafluorophosphate (1770 mg, 4.15 mmol, 3 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (13 mg, 0.065 mmol, 5 mol %), and DMF (50 mL) were added to a Schlenk flask with a magnetic stir bar. The reaction mixture was stirred for 4 h at 100 °C. The volatiles were removed, the algae blue oil was taken up in acetone/chloroform/diethyl ether (1:1:1), and filtered. The resulting blue solid was taken up in chloroform (250 mL) and acetone (50 mL) and vigorously stirred for 2 h. Once filtered the resulting beige-colored solid was washed with cold water and dried under a vacuum. Yield: 68% (709 mg, 0.981 mmol). ^1H NMR (400 MHz, CD_3CN) δ 9.57 (ddd, $J = 6.2, 1.3, 0.8$ Hz, 2H), 9.40 (dt, $J = 6.5, 1.3$ Hz, 2H), 9.07 (dd, $J = 6.5, 1.8$ Hz, 2H), 7.94–7.74 (m, 13H), 7.68–7.60 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) δ 151.1 (d, $J = 14.9$ Hz), 150.4, 146.7 (d, $J = 16.9$ Hz), 142.4, 135.1 (d, $J = 2.8$ Hz), 134.7 (d, $J = 102.7$ Hz), 132.5, 132.1 (d, $J = 12.4$ Hz), 130.7, 129.5 (d, $J = 14.3$ Hz), 125.1 (d, $J = 7.5$ Hz), 124.6, 123.5 (d, $J = 111.1$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CD_3CN) $\delta = -72.9$ (d, $J = 706.7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN) $\delta = 28.4, -144.7$ (hept, $J = 706.8$ Hz). Decomposition temperature (TGA) 170 °C. Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{F}_{12}\text{N}_2\text{O}_3$ (722.39): C, 46.23; H, 3.14; N, 3.87. Found: C, 46.55; H, 2.93; N, 3.54. HRMS (ESI) m/z calcd for $[\text{M} - \text{PF}_6]^+$ 577.1033, found 577.1019.

***N,N'*-Bis(*p*-fluorophenyl)-2,7-diazadibenzophosphole oxide ditriflate (4).** 2,7-Diazadibenzophosphole oxide **1** (74 mg, 0.266 mmol, 1 equiv), bis(*p*-fluorophenyl)iodonium triflate (1496 mg, 3.209 mmol, 12 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (4 mg, 0.02 mmol, 8 mol %), and DMF (30 mL) were added to a Schlenk flask with a magnetic stir bar. The reaction mixture was stirred for 36 h at 100 °C until all iodonium salt was consumed. The volatiles were removed, the brown oil was taken up in CH_2Cl_2 (30 mL) and diethyl ether (10 mL) was added. The precipitated brown solid was filtered off and washed with diethyl ether. The solid was once more taken up in CH_2Cl_2 (30 mL) and diethyl ether was added (5 mL). The precipitated olive colored solid was filtered off, washed with CH_2Cl_2 , and dried at 80 °C under a vacuum. Yield: 61% (125 mg, 0.163 mmol). ^1H NMR (400 MHz, CD_3CN) δ 9.60 (d, $J = 6.4$ Hz, 2H), 9.41 (d, $J = 6.4$ Hz, 2H), 9.13 (dd, $J = 6.4, 2.1$ Hz, 2H), 8.02–7.92 (m, 2H), 7.92–7.86 (m, 4H), 7.82 (t, $J = 6.9$ Hz, 1H), 7.66–7.61 (m, 2H), 7.56–7.47 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) δ 165.4 (d, $J = 252.5$ Hz), 152.3 (d, $J = 15.6$ Hz), 151.6, 148.1 (d, $J = 17.2$ Hz), 139.6, 136.3 (d, $J = 3.2$ Hz), 134.6 (d, $J = 105.7$ Hz), 133.2 (d, $J = 12.9$ Hz), 130.4 (d, $J = 14.7$ Hz), 128.2 (d, $J = 9.8$ Hz), 126.0 (d, $J = 7.8$ Hz), 123.2 (d, $J = 118.2$ Hz), 122.3. $^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CD_3CN) $\delta = -79.2, -108.5$ (d, $J = 36.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN) δ 30.4. Decomposition temperature (TGA) 170 °C. Anal. Calcd for $\text{C}_{30}\text{H}_{19}\text{F}_8\text{N}_2\text{O}_7\text{PS}_2$ (766.57): C, 47.01; H, 2.50; N, 3.65. Found: C, 39.13%; H, 2.78; N, 3.59. HRMS (MALDI) m/z calcd for $[\text{M} - \text{OTf}]^+$ 617.0723, found 617.0743.

“*” represents incomplete combustion. Note, the phosphaviologen scaffold tends to systematically provide low carbon values, as already observed for methylated²⁴ and benzylated²⁵ phosphaviologens as well as for related aza-dibenzophospholes.^{5h}

***N,N'*-Bis(5-methyl-2-thienyl)-2,7-diazadibenzophosphole oxide di(hexafluorophosphate) (5).** 2,7-Diazadibenzophosphole oxide **1** (22 mg, 0.079 mmol, 1 equiv), bis(5-methyl-2-thienyl)iodonium hexafluorophosphate (200 mg, 0.415 mmol, 5 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (1.5 mg, 0.0075 mmol, 9 mol %), and degassed DMF (5 mL) were added to a Schlenk flask with a magnetic stir bar. The reaction mixture was stirred for 36 h at 40 °C. The volatiles were

removed, the red residue was taken up in THF (10 mL) and a mixture of CH_2Cl_2 /diethyl ether (1:1; 10 mL) was added. The precipitated deep orange solid was filtered off, washed with CH_2Cl_2 , and dried at 80 °C under a vacuum. Yield: 95% (57 mg, 0.075 mmol). ^1H NMR (400 MHz, CD_3CN) $\delta = 9.47$ (d, $J = 6.4$ Hz, 2H), 9.30 (d, $J = 6.4$ Hz, 2H), 8.92 (dd, $J = 6.4, 1.9$ Hz, 2H), 7.91–7.78 (m, 3H), 7.68–7.61 (m, 2H), 7.57 (d, $J = 3.5$ Hz, 2H), 7.01 (d, $J = 3.5$ Hz, 2H), 2.63 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) $\delta = 150.1$ (d, $J = 14.8$ Hz), 148.9, 145.9, 145.6 (d, $J = 17.2$ Hz), 139.3, 135.1 (d, $J = 3.2$ Hz), 134.8 (d, $J = 102.2$ Hz), 132.1 (d, $J = 12.4$ Hz), 129.7, 129.5 (d, $J = 14.4$ Hz), 126.5 (d, $J = 3.1$ Hz), 125.0 (d, $J = 7.7$ Hz), 123.5 (d, $J = 115.8$ Hz), 14.9. $^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CD_3CN) $\delta = -72.9$ (d, $J = 706.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN) $\delta = 27.9, -144.6$ (hept, $J = 706.5$ Hz). Decomposition temperature (TGA) 180 °C. Anal. Calcd for $\text{C}_{26}\text{H}_{21}\text{F}_{12}\text{N}_2\text{O}_3\text{PS}_2$ (762.49): C, 40.96; H, 2.78; N, 3.67. Found: C, 39.16%; H, 2.96; N, 3.38. HRMS (MALDI) m/z calcd for $[\text{M} - 2\text{PF}_6]^+$ 472.0833, found 472.0840.

“*” represents incomplete combustion. Note, the phosphaviologen scaffold tends to systematically provide low carbon values, as already observed for methylated²⁴ and benzylated²⁵ phosphaviologens as well as for related aza-dibenzophospholes.^{5h}

Reaction of **1 with Dimesityliodonium Triflate (Attempted Synthesis of Compound **6**).** 2,7-Diazadibenzophosphole oxide **1** (39 mg, 0.14 mmol, 1 equiv), dimesityliodonium triflate (355 mg, 0.690 mmol, 5 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2 mg, 0.01 mmol, 8 mol %), and DMF (20 mL) were added to a Schlenk flask with a magnetic stir bar. The reaction mixture was stirred for 24 h at 110 °C until no dimesityliodonium triflate was left (NMR control). The volatiles were removed, the dark red oil was taken up in acetonitrile (10 mL) and CH_2Cl_2 (10 mL) and the product was precipitated upon addition of diethyl ether (25 mL). The precipitated brown solid was filtered off, washed with diethyl ether, and dried at 80 °C under a vacuum. Yield: 26 mg.

Analytical data point toward the formation of the *N,N*-diprotonated phosphaviologen derivative and thus the yields tentatively amount to 32% (26 mg, 0.045 mmol). ^1H NMR (400 MHz, CD_3CN) $\delta = 9.25$ (d, $J = 5.6$ Hz, 2H), 9.16 (dd, $J = 6.0, 1.5$ Hz, 2H), 8.79 (dd, $J = 6.1, 1.4$ Hz, 2H), 7.81–7.75 (m, 3H), 7.62–7.59 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN) $\delta = 153.08$ (d, $J = 16.0$ Hz), 149.78 (s), 145.94 (d, $J = 15.5$ Hz), 135.73 (d, $J = 3.1$ Hz), 133.69 (d, $J = 104.1$ Hz), 132.70 (d, $J = 12.1$ Hz), 130.51 (d, $J = 14.1$ Hz), 125.75 (d, $J = 114.1$ Hz), 124.35 (d, $J = 7.1$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CD_3CN) $\delta = -79.3$. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN) $\delta = 28.6$. Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{F}_6\text{N}_2\text{O}_2\text{PS}_2$ (578.39): C, 37.38; H, 2.27; N, 4.84. Found: C, 37.44; H, 2.56; N, 4.72. HRMS (MALDI) m/z calcd for $[\text{M} - \text{H} - 2 \text{OTf}]^+$ 279.0682, found 279.0674.

A control experiment of **1** with triflic acid at –40 °C did not lead to the observation of the same species but rather to the decomposition of **1** due to the strong acidity of TfOH.

***N,N'*-Bis(*p*-fluorophenyl)bipyridinium ditriflate (7).** 4,4'-Bipyridine monohydrate (50 mg, 0.29 mmol, 1 equiv), bis(*p*-fluorophenyl)iodonium triflate (535 mg, 1.15 mmol, 4 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (4 mg, 0.02 mmol, 8 mol %), and DMF (20 mL) were added to a Schlenk flask with a magnetic stir bar. The reaction mixture was stirred for 36 h at 100 °C until all iodonium salt was consumed. The volatiles were removed, the dark yellow solid was taken up in acetonitrile (10 mL), chloroform was added (10 mL) and the desired product was precipitated upon addition of diethyl ether (20 mL), and filtered. Once filtered the resulting beige colored solid was washed with diethyl ether (10 mL) and dried under a vacuum. Yield: 80% (148 mg, 230 mmol). NMR data match previous reports of this compound in the literature.³²

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06413.

^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, details and additional plots of UV-vis spectroscopy, electro-

chemical measurements, chemo- and electrochromism, EPR spectroscopy, and DFT calculations. (PDF)

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Notes

The authors declare no competing financial interest.

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