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1 A Highly Stable Organic Radical Cation

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8 **S** Supporting Information

9 **ABSTRACT:** Functionalization of a methylviologen with four methyl
 10 ester substituents significantly facilitates the first two reduction steps. The
 11 easily generated radical cation showed markedly improved air stability
 12 compared to the parent methylviologen, making this derivative of interest
 13 in organic electronic applications.

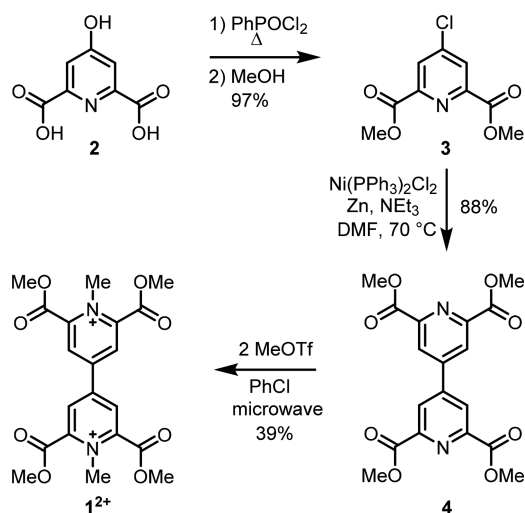


14 **A**mong the strong, organic-based electron acceptors,
 15 quaternized derivatives of 4,4'-bipyridine, also known as
 16 viologens, are promising candidates for applications in organic
 17 electronics,¹ molecular machines,² and as functional materials.³
 18 Interest in this family of acceptors stems from their simple
 19 preparation, stability, and three, distinctly colored, redox
 20 states.⁴ Stable organic acceptors for which the first reduction
 21 potential is near 0 V, or even positive, are highly desirable for
 22 practical applications.² Tuning the potential of viologen
 23 derivatives is commonly achieved by changing the N-
 24 substituent (either alkyl or aryl) or the counteranions.^{5,6}
 25 Another more effective strategy that significantly facilitates the
 26 first reduction compared to that of methyl viologen (MV²⁺)
 27 utilizes the introduction of main-group element^{7–11} or
 28 carbon¹² bridges between the pyridyl moieties of the viologen
 29 framework. Few other reports describe the functionalization of
 30 the viologen's carbon skeleton with electron-withdrawing
 31 groups as a method to alter its electronic properties.¹³

32 Herein, we describe two remarkable features of a viologen
 33 (**1**²⁺) bearing methyl ester groups at the 2,2',6,6' positions.
 34 Not only do these four electron-withdrawing groups
 35 significantly facilitate both reduction potentials but they also
 36 stabilize the radical cation in organic solution, even in the
 37 presence of oxygen. Although viologen radical cations can be
 38 stabilized as dimers under argon at low temperature⁴ or in
 39 host–guest systems,¹⁴ and air-stable viologen radical cations
 40 encapsulated in catenanes have been reported by Stoddart,¹⁵
 41 there are no other examples of simple viologen derivatives in a
 42 stable radical-cation state.

43 The tetraester viologen **1**²⁺ was synthesized in three steps
 44 starting from chelidamic acid^{16,17} **2** (Scheme 1), which was
 45 transformed to the methyl ester of the chloropyridine

Scheme 1. Synthesis of the Tetraester Viologen **1**²⁺



derivative **3** by subsequent treatment with PhPOCl₂ and 46
 MeOH.¹⁸ After optimization of the previously reported 47
 coupling conditions by Oda et al.,¹⁹ chloropyridine **3** 48
 underwent clean homocoupling that afforded bipyridine **4** in 49
 88% yield. Quaternization of the nitrogen atoms of the 50
 bipyridine required harsh conditions, indicating the weak 51
 nucleophilic character of the pyridine nitrogen atoms. 52
 Treatment of **4** with methyl triflate (MeOTf) under microwave 53
 irradiation afforded viologen **1**²⁺ as its triflate salt in 39% yield. 54

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55 Single crystals of the dicationic species were obtained by
 56 slow diffusion of Et₂O in MeCN. In the solid-state structure²⁰
 57 of **1**²⁺ (Figure 1), the bipyridinium rings are twisted with a 32°

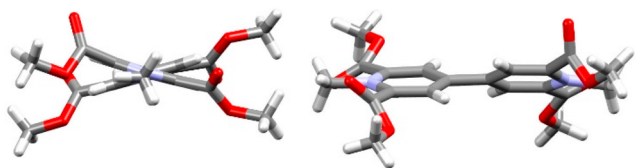


Figure 1. Side views of the viologen **1**²⁺ in the solid state. Triflate anions and solvent molecules have been omitted for clarity.

58 dihedral angle that is closer to the 36° twist of 1,1'-
 59 diphenylviologen²¹ than to the nearly coplanar structures
 60 observed for most 1,1-dialkylviologen dications. The structure
 61 of **1**²⁺ also shows the possible formation of intramolecular
 62 hydrogen bonds between the ester groups and the N-methyl
 63 substituents (2.1–2.5 Å) or the pyridine protons (~2.4 Å)
 64 (see Supporting Information).

65 The redox properties of **1**²⁺ were investigated by electro-
 66 chemical methods. Cyclic voltammetry (CV) on a glassy
 67 carbon electrode in CH₃CN solutions with tetrabutylammo-
 68 nium hexafluorophosphate (TBAPF₆; 0.1 M) as supporting
 69 electrolyte showed three reversible reductions (Figure 2a). The
 70 first two one-electron reductions at -0.27 and -0.50 V versus
 71 Fc⁺/Fc are, respectively, attributed to the formation of the
 72 radical cation **1**^{•+} and the neutral **1**⁰. The third reduction
 73 detected from the CV at -1.90 V versus Fc⁺/Fc is a two-
 74 electron event that generates **1**²⁻. This reduction was almost
 75 absent in rotating disk electrode experiments (Figure 2b),
 76 suggesting that the neutral form (**1**⁰) undergoes a relatively
 77 slow chemical reaction once formed. It is also possible that the
 78 generated **1**²⁻ species is sparingly soluble in the 0.1 M TBAPF₆
 79 CH₃CN medium. Controlled-potential coulometry at -0.37
 80 and at -0.60 V versus Fc⁺/Fc resulted in the respective
 81 exchange of 0.97 and 1.85 electrons per molecule of compound
 82 **1**.

83 The first two reductions of **1**²⁺ are shifted by +560 and +740
 84 mV, respectively, compared to those of MV²⁺ ($E_{\text{red1},1/2} = -0.83$
 85 V and $E_{\text{red2},1/2} = -1.24$ V vs Fc⁺/Fc) under the same
 86 experimental conditions. The significantly less cathodic values

of these potentials are attributed to the presence of the four
 87 electron-withdrawing ester groups. When the same ester
 88 groups are appended to an aryl ring at the quaternized
 89 nitrogen atoms of a viologen, the electronic effects are less
 90 pronounced⁶ than in **1**²⁺. Hence, conjugation effects also play a
 91 role in tuning the redox properties, as supported by the small
 92 contribution of the ester group in the density functional theory
 93 (DFT)-generated singly occupied molecular orbital (SOMO)
 94 (Figure 3 and Supporting Information).

95 f3

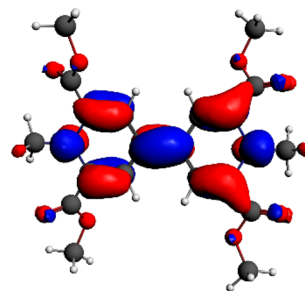


Figure 3. ADF view drawing of the Kohn–Sham SOMO of the radical cation **1**^{•+}.

The colorless divalent viologen **1**²⁺ mainly absorbs at 278
 96 nm (Figure 4, blue spectrum). Upon one-electron reduction,
 97 this absorbance decreases in intensity, while new absorption
 98 bands grow at 334, 417, 769, and 852 nm (shoulder) for the
 99 green radical cation **1**^{•+} (Figure 4, green spectrum and
 100 Supporting Information). The absence of absorption bands
 101 in the near-infrared (NIR) indicates that π -dimers do not
 102 form⁴ in solution at 1×10^{-3} M and suggests that the radical
 103 cation is stabilized only by the four electron-withdrawing ester
 104 groups. We attribute the broadness of the absorption centered
 105 at 769 nm to the coexistence of several possible conformations
 106 of the ester groups, as seen in DFT calculations, or to
 107 vibrational states.²² The second reduction generates a red,
 108 neutral viologen species **1**⁰ that absorbs at 492 nm (Figure 4,
 109 red spectrum). Aside from indicating the absence of π -dimer
 110 formation, an interesting feature of the UV–vis–NIR
 111 monitoring of the three species **1**²⁺, **1**^{•+}, and **1**⁰ is their
 112 individually addressable character and readability at specific
 113 wavelengths. Reversible changes of the absorptions at 278, 417, 114

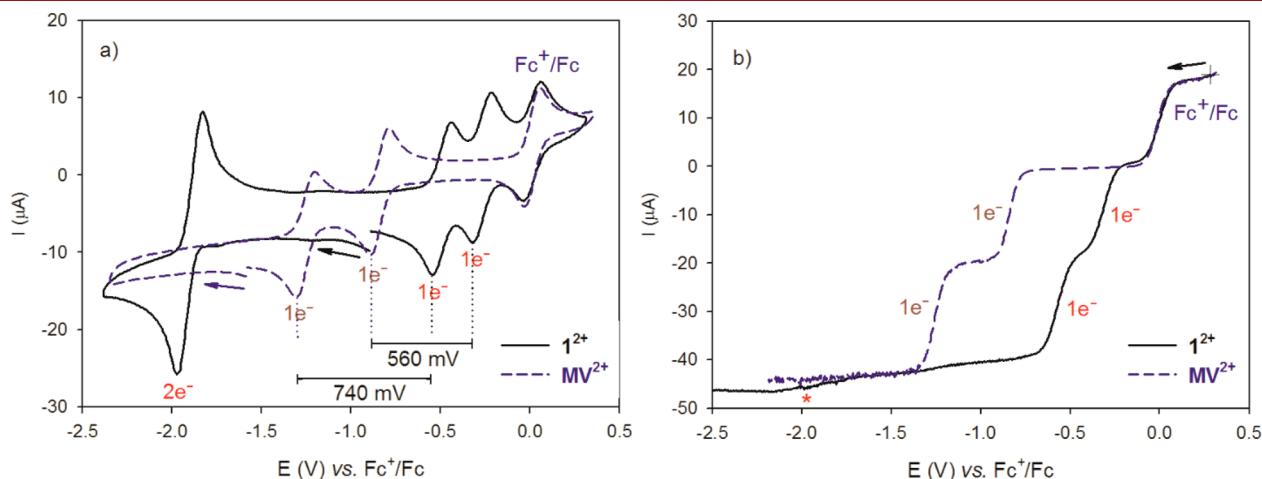


Figure 2. CV (a) and rotating disk electrode voltammetry (b) of **1**²⁺ and MV²⁺ in CH₃CN + 0.1 M TBAPF₆; working electrode = glassy carbon, pseudoreference = Pt, counter electrode = Pt, internal reference = Fc. (a) $\nu = 0.1$ V/s; (b) $\nu = 0.02$ V/s, rotation: 1000 rpm.

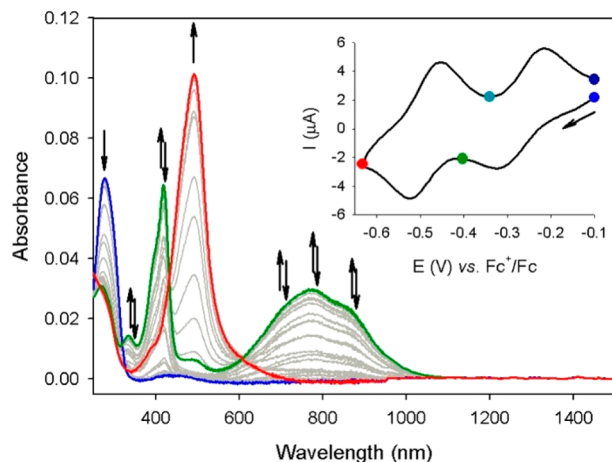


Figure 4. UV-Vis-NIR monitoring of the reduction of 1^{2+} . (inset) Corresponding CV at scan rate of 0.01 V s^{-1} . Solution ($c = 1 \times 10^{-3} \text{ M}$) of 1^{2+} in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAPF}_6$ recorded with an optically transparent thin-layer (0.2 mm) electrochemical cell equipped with an Au mini-grid WE and CaF_2 optical windows, reference AgCl/Ag .

115 492, and 769 nm over several reduction-oxidation cycles
 116 confirmed the reversibility of the redox interconversion
 117 features of the three redox states (see [Supporting Information](#)).
 118 Electron paramagnetic resonance (EPR) studies confirmed
 119 the paramagnetic, radical character of $1^{\cdot+}$. The reaction of 1^{2+}
 120 with 1 equiv of ascorbic acid yielded a well-resolved EPR
 121 spectrum ([Figure 5](#)) centered at $g = 2.0032$ corresponding to

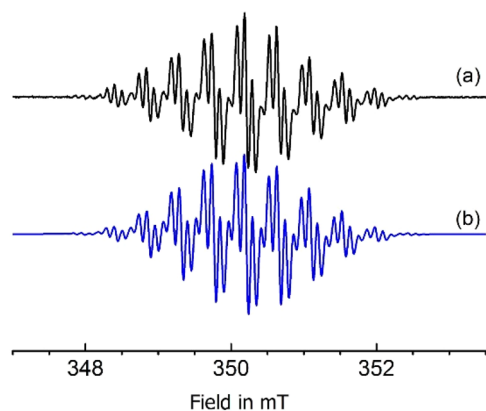


Figure 5. X-band EPR spectrum of $1^{\cdot+}$ (a) in CH_3CN at 10^{-3} M at room temperature; (b) simulated spectrum.

122 two sets of four and six equivalent protons ($A_1(^1\text{H}) = 0.11 \text{ mT}$,
 123 $A_2(^1\text{H}) = 0.43 \text{ mT}$), respectively, and one set with two
 124 equivalent nitrogen atoms ($A_1(^{14}\text{N}) = 0.45 \text{ mT}$). The same
 125 spectrum was obtained by electrolysis. The colorless solution
 126 turned green upon one-electron reduction to generate the
 127 radical cation $1^{\cdot+}$. After the second reduction, the solution
 128 turned red, and the intensity of the EPR spectrum decreased
 129 gradually to give the silent neutral species 1^0 .

130 The air stability of the radical cation $1^{\cdot+}$ over time was also
 131 investigated by EPR ([Figure 6](#)). After the radical cation was
 132 generated by coulometry in MeCN, samples of the solution of
 133 $1^{\cdot+}$ were transferred to EPR tubes purged with argon or open
 134 to air. The argon sample was stable for more than 40 h. Even
 135 after three months, the intensity of the EPR spectrum of the
 136 same solution remained constant. For samples under air, the

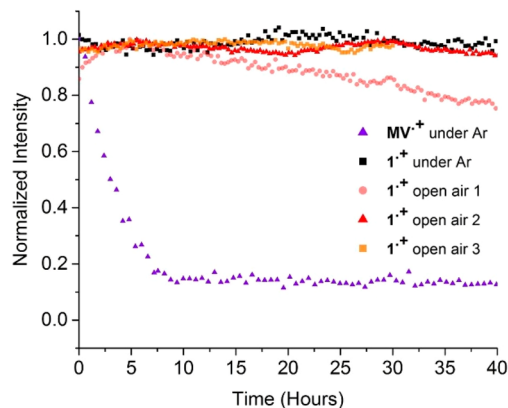


Figure 6. Double integrated EPR spectrum of $1^{\cdot+}$ and $\text{MV}^{\cdot+}$ in CH_3CN at $1 \times 10^{-3} \text{ M}$ at room temperature under Ar and open to air.

intensity of the EPR signal of $1^{\cdot+}$ remained relatively stable 137
 over 40 h in two cases. In the third case ([Figure 6](#), $1^{\cdot+}$ open air 138
 3), the intensity of the EPR signal increased initially over the 139
 first 5 h and then decreased by $\sim 25\%$ after 40 h. We assign the 140
 initial increase to the presence of some diamagnetic dimeric 141
 species $(1^{\cdot+})_2$ that dissociate into paramagnetic $1^{\cdot+}$ monomers 142
 within the first few hours. The presence of oxygen in the 143
 samples exposed to air was confirmed by a broad EPR signal 144
 (see [Supporting Information](#)). Under the same experimental 145
 conditions, the $\text{MV}^{\cdot+}$ reference compound was considerably 146
 less stable under argon, as demonstrated by the rapid decay²³ 147
 of the EPR signal within a few hours ([Figure 6](#)). In the 148
 presence of air, $\text{MV}^{\cdot+}$ was very unstable, and no EPR signal was 149
 observed. Together, these data confirmed the high stability of 150
 $1^{\cdot+}$. 151

Despite the stability of the radical cation, we were unable to 152
 grow single crystals of sufficient quality for X-ray diffraction. 153
 Thus, optimizations of the geometries of 1^{2+} and $1^{\cdot+}$ were 154
 performed without any symmetry restriction. For the dication 155
 1^{2+} , the twist between the pyridinium rings was reproduced 156
 (33° vs 32°), and the accord between experimental and 157
 calculated geometry remained quite satisfactory. A large 158
 highest occupied molecular orbital-lowest unoccupied molec- 159
 ular orbital (HOMO-LUMO) energy gap was calculated 160
 (4.60 eV) for 1^{2+} , but the LUMO was stabilized by 0.7 eV 161
 compared to MV^{2+} . These calculations corroborate with the 162
 electrochemical data. 163

When the dication 1^{2+} is reduced to $1^{\cdot+}$, the optimized 164
 geometrical parameters provide a more planar structure with a 165
 value of dihedral angle of 15° . This twist is higher than the 6° 166
 and 11° observed in the two independent molecules of the X- 167
 ray structure of $\text{MV}^{\cdot+}$.²⁴ Comparison of these data suggests less 168
 electronic delocalization in $1^{\cdot+}$ than in $\text{MV}^{\cdot+}$. The calculated 169
 ^1H and ^{14}N isotropic constants (see [Supporting Information](#)) 170
 are in close agreement with the experimental values. As shown 171
 by the SOMO illustrated in [Figure 3](#), the unpaired electron is 172
 essentially localized on the pyridine rings, on both N-methyl 173
 groups, and only slightly on the tetraester substituents. This 174
 observation supports the stabilizing effect of the four electron- 175
 withdrawing ester groups on the radical cation. 176

In conclusion, the tetraester derivative of methylviologen is a 177
 strong electron acceptor that converts easily and reversibly into 178
 its radical cation species. Because of the electron-attracting 179
 effect of the ester groups, the radical species is stable for 180
 months under argon and for hours in the presence of oxygen. 181

182 These features are of great interest from the perspective of air-
183 operating electrochromic devices and molecular switches.
184 Isolation and investigations of I^{*+} as a solid material are in
185 progress.

186 ■ ASSOCIATED CONTENT

187 S Supporting Information

188 The Supporting Information is available free of charge on the
189 ACS Publications website at DOI: [10.1021/acs.orglett.8b03579](https://doi.org/10.1021/acs.orglett.8b03579).

191 Experimental procedures, spectro-electrochemical and
192 EPR spectra, hyperfine coupling constants, calculated
193 molecular orbitals, X-ray crystal data (PDF)

194 Accession Codes

195 CCDC 1846774 contains the supplementary crystallographic
196 data for this paper. These data can be obtained free of charge
197 via www.ccdc.cam.ac.uk/data_request/cif, or by emailing
198 data_request@ccdc.cam.ac.uk, or by contacting The Cam-
199 bridge Crystallographic Data Centre, 12 Union Road,
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209 All authors have approved the final version of the manuscript.

210 Notes

211 The authors declare no competing financial interest.

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