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Viologen embedded polyaromatic hydrocarbons (VPAH²⁺): synthesis, computational, photophysical, and electrochemical characterizations of 3,8-diazaphenanthrenyl viologens

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ABSTRACT

Several new dicationic viologen sensitizers are synthesized and characterized both photo- and electrochemically. Benzo-annulation of methyl viologen increases its fluorescence lifetime by a factor of 6.6. Similar lifetime increases were observed for methylated derivatives, that have the added advantage of enhanced solubilities. These electron transfer sensitizers can oxidize organic substrates with oxidation potentials of approximately 2.4 eV and lower.

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Introduction

Viologens have been known and studied since 1882 when Weidel and Russo¹ first reported the synthesis of the 4,4'-viologen, methyl viologen, or paraquat, MV^{2^+} . However, interest in these compounds did not pique until the mid 1950s when it was revealed that diquat, DQ^{2^+} , functioned as a potent herbicide.² In more recent years these fascinating molecules have found use in a wide-range of applications including as components of photochromic/electrochromic materials,³ in supramolecular assemblies,⁴ in molecular machines,⁵ and as electron shuttles⁶ and sensors.⁷

$\underbrace{-N}_{\oplus}\underbrace{N}_{\oplus}\underbrace{N}_{\oplus}$

Organic dications have also been used as electron transfer photosensitizers since the initial photo-induced electron transfer produces a radical-cation/radical-cation pair (Eq. 1) whose rapid repulsive separation competitively inhibits energy wasting return electron transfer.⁸ Viologens (V^{2*}) are especially attractive for this application because of the remarkable stability of both their dication and radical-cation redox partners. (Eq. 2) Unfortunately,¹ $(\mathbf{MV}^{2*})^*$ has a singlet lifetime of 1.00 ± 0.04 ns in acetonitrile precluding all but ultrafast quenching events.⁹

$$\left(V^{2} \oplus \right)^{*} + M \longrightarrow \left[V_{\bullet}^{\oplus} \right]_{\mathsf{M}}^{\oplus} \frac{\mathsf{k}_{\mathsf{sep}}}{\mathsf{fast}} V_{\bullet}^{\oplus} + \mathsf{M}_{\bullet}^{\oplus}$$
(1)

$$\underbrace{\bigoplus_{n \in \mathbb{Z}} (M_{n})}_{\text{dication}} \underbrace{\bigoplus_{n \in \mathbb{Z}} (M_{n})}_{\text{radical cation}} \underbrace{\bigoplus_{n \in \mathbb{Z}} (M_{n})}_{\text{neutral}} \underbrace{\bigoplus_{n \in \mathbb{Z}} (M_{n})}_{\text{neutral}} (2)$$

We report here a photophysical, computational, and electrochemical study of viologens $1^{2+}-4^{2+}$. The results demonstrate that extending the π -system of MV^{2+} by ring fusion is a viable strategy to produce new viologens with attributes more suitable for their use as electron transfer sensitizers.¹⁰

Results and discussion

The syntheses of $1^{2+}-4^{2+}$ are depicted in Scheme 1. The first step involves a Pd-catalyzed cross coupling between two equivalents of the 3-bromopyridine and triethoxyvinylsilane in water to give the 1,2-bis-(3-pyridyl)ethenes in modest 19.6–56.8% yields.¹¹ The Mallory photocyclizations¹² occurs in very good 84% and 78% yields to give the 3,8-diazaphenanthrenes **2** and **4**, respectively. The absence of a methyl group on the pyridyl rings α to nitrogen and *ortho* to the vinyl group in the ethenes allowed alternative photocyclizations to give 1,8- and 1,10-diazaphenanthrenes that reduced the yields of the desired 3,8-isomers **1** and **3** to 60% and 30%, respectively. (See Supplementary material) Treatment of the 3,8-diazaphenanthrenes with excess Meerwein's salt, (CH₃)₃OBF₄, gave





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the viologens, 1^{2+} , 2^{2+} , 3^{2+} , and 4^{2+} , that were purified by trituration with methanol.

The geometries of 1^{2^+} , 2^{2^+} , 3^{2^+} , and 4^{2^+} at the DFT B3LYP/6-311 +G(2d,p) computational level do not differ significantly. However, as anticipated the C–N bond lengths in the viologens are 0.034 ± 0.011 Å longer than the corresponding C–C bonds in all their carbon phenanthrene homologs, and the *peri* methyl–hydrogen interaction in 2^{2^+} destabilizes it by 4.8 kcal/mol in comparison to its 3^{2^+} isomer. The most unexpected computational outcome is the observation that the H₁–H₁₀ distance decreases by 6% in the series $1^{2^+} > 3^{2^+} > 2^{2^+} > 4^{2^+}$ from 2.137 Å to 2.006 Å. A similar decrease of 4% and 3% is also observed in the corresponding methyl substituted 3,8-diazaphenanthrene (1–4) and phenanthrene series suggesting that methyl buttressing interactions play the critical role in changing the through space H₁–H₁₀ distance.

The photophysical data for $1^{2+}-4^{2+}$ are given in Table 1. The UV-vis spectra are characterized by $S_0 \rightarrow S_1$ transitions centered at 368, 363, 380, and 386 nm, for 1^{2+} , 2^{2+} , 3^{2+} , and 4^{2+} , respectively, with vibrational spacing of 1200 to 1600 cm⁻¹ as anticipated for several in-plane C-H bend and ring breathing modes. (Fig. 1a) In addition, all 4 viologens also exhibit vibrationally rich $S_0 \rightarrow S_2$ transitions centered at 278 (1^{2+}), 284 (2^{2+}), 287 (3^{2+}), and 292 nm (4^{2+}). These assignments were verified with remarkable precision by TD-DFT (Time Domain Density Functional Theory) calculations predicting the wavelength of the $S_0 \rightarrow S_1$ transitions to within 5, 2, and 8 nm for 1^{2+} , 2^{2+} , and 4^{2+} , respectively. The calculated $S_0 \rightarrow S_1$ transition in 3^{2+} deviated somewhat from these very precise predictions and was 26 nm bathochromic of the observed value. The HOMO \rightarrow LUMO determinant is the dominant

Table 1	
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Photophysical data for diazaphenanthrenyl viologens $1^{2*}-4$
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	1 ²⁺	2 ²⁺	3 ²⁺	4 ²⁺
$\lambda_{UV-vis}(\varepsilon)^{b}$	387(5700)	390(7900)	400(7400)	406(7600)
	367(4800)	371(6900)	380(6100)	386(6700)
	350(2400)	355(3100) 336(800)	361(3000)	368(3400)
$\lambda_{\rm F}^{\rm b}$	407	408	419	424
λ_{Phos}^{b}	429	415	430	416
Stokes shift ^c	1270	1131	1134	1046
$\tau_{\rm F}^{\ \rm d}$	6.6 ± 0.1	5.7 ± 0.1	6.1 ± 0.2	4.8 ± 0.1
$arPsi_{ m F}$	0.34 ± 0.01	0.38 ± 0.01	0.30 ± 0.01	0.29 ± 0.01
$k_{\rm F}^{\rm e}$	$5.2 imes 10^7$	$6.7 imes 10^7$	$4.9 imes 10^7$	$6.0 imes 10^7$
$E(S_1)^f$	72.4	71.7	69.9	68.9
$E(T_1)^f$	68.4	68.9	66.8	68.6

^a In CH₃CN.

^b In nm.

^c In wavenumbers (cm⁻¹).

^d In nanoseconds (ns).

 $^{\rm e}$ In s⁻¹.

^f In kcal/mol.



Figure 1. Absorption spectra for viologens and phenanthrenes.

(96-97%) contributor to the excited state density or wave function for the $S_0 \rightarrow S_1$ absorption bands. The wavelengths of $S_0 \rightarrow S_2$ bands were all predicted to within 8 to 17 nm of the observed values. The dominant contributors to these higher energy absorption bands are the HOMO \rightarrow LUMO + 1 transitions (71% to 85%) with less significant contributions from the HOMO – 1 \rightarrow LUMO and HOMO – 2 \rightarrow LUMO transitions.

The diazaphenanthrenes **1–4** also exhibit $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ vibrational clusters very similar to that observed in the viologens. (Fig. 1) The effects of N-methylation of 1–4 on the wavelengths of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are very different. The $S_0 \rightarrow S_1$ transitions experience bathochromic shifts of (calculated/observed) +45 nm/+30 nm, +48 nm/+23 nm, +51 nm/+32 nm, and +55 nm/ +38 nm for the conversions of 1, 2, 3, and 4 to 1²⁺, 2²⁺, 3²⁺, and 4²⁺, respectively. In dramatic contrast, the $S_0 \rightarrow S_2$ transitions are very insensitive to N-methylation exhibiting very small shifts of (calculated/observed) +3nm/-1 nm, +2 nm/-2 nm, -3 nm/0 nm, -3 nm/-2 nm for the conversions of 1, 2, 3, and 4 to 1²⁺, 2²⁺, 3²⁺, and **4**²⁺, respectively. The reason for this stark difference is evident upon examination of the orbitals involved in the transitions. The N-methyl groups in the HOMO and LUMO + 1 orbitals that are involved in the $S_0 \rightarrow S_2$ transitions are located at nodes on the orbital surface and would not be expected to influence orbital energy. On the other hand, the nitrogen atoms bearing the N-methyl groups in the LUMOs, which are important players in the $S_0 \rightarrow S_1$ transitions, have substantial orbital coefficients. Consequently, the N-methyl group would influence the energy of the LUMO but not the HOMO substantially changing the HOMO-LUMO gap and as a result the wavelengths of the $S_0 \rightarrow S_1$ transitions.

All the viologens fluoresce and phosphoresce (Table 1 and Fig. 1a). The fluorescence spectra are reasonable mirror images of the absorption spectra but with broadened vibrational fine structure. The phosphorescence spectra exhibit well-defined vibrational fine structure that allows easy assignment of the 0-0 band. (Fig. 1a inset) Consequently, the singlet energies, $E(S_1)$, were determined from the crossing point of the absorption and fluorescence spectra and the triplet energies, $E(T_1)$, from the 0–0 band in the phosphorescence spectra. The singlet triplet energy gaps in the viologens are very small and decrease with addition of methyl groups from 4.0 kcal/mol in 1²⁺ to only 0.3 kcal/mol in tetra-methylated 4²⁺. (Table 1) The phenanthrenes also all fluoresce but at shorter wavelengths (see Table S1 in the Supplementary material) leading to singlet energies 7.7 to 8.4 kcal/mol higher than that of the corresponding viologen. (80.1, 79.6, 77.7, and 77.3 kcal/mol for 1, 2, 3, and **4**, respectively) The Stokes shifts for the viologens are approximately twice as large as for the corresponding phenanthrene (Table S1) reflecting a larger magnitude relaxation of the Franck Condon populated excited singlet state.

The fluorescence lifetimes for $1^{2+}-4^{2+}$ are factors of 4.8 to 6.6 times larger than observed in methyl viologen, MV^{2+} . The Einstein equation¹³ ($\langle x^2 \rangle = 6Dt$), where *D* is the diffusion coefficient (estimated as 2×10^{-5} cm² s⁻¹),¹⁴ and $\langle x^2 \rangle$ is the mean squared molecular displacement, predicts that an excited viologen with a lifetime of 6 ns can migrate approximately 85 Å within its lifetime. Consequently, we conservatively anticipate that diffusive encounter of the viologen sensitizer and the substrate will readily occur at substrate concentrations greater than 10^{-2} M.¹⁵

The fluorescence quantum yields for the viologens and the phenanthrenes (Table S1 in Supplementary material) are very similar and fall in the narrow range of 0.26 to 0.38. The magnitude of the rate constants of fluorescence, $k_F = \Phi_F/\tau_F$ [(3.5–7.3) × 10⁷ s⁻¹], are those anticipated for a $\pi\pi^*$ character of the S₁ excited state.

The reduction potentials for the viologens appear at -0.45, -0.58, -0.52, and -0.62 V for reduction to the radical cation and at -0.94, -1.07, -0.96, and -1.19 V versus SCE for reduction to the neutral redox partners in 1^{2+} , 2^{2+} , 3^{2+} , and 4^{2+} , respectively. (see Supplementary information for the CV curves) The value for reduction to the radical cation for the unsubstituted phenanthrenyl viologen 1²⁺ is remarkably close to that reported for methyl viologen $(-0.45^{16} \text{ and } -0.43 \text{ V}^{17} \text{ vs SCE})$. On the other hand, the reductions to both the radical cation and the neutral redox partners become more difficult when hydrogens on the phenanthrene ring are replaced with electron donating methyl groups. The 60 mV more difficult reduction to the radical cation and 110 mV more difficult reduction to the neutral redox partner in 2^{2+} than in 3^{2+} can be attributed to antibonding interactions with the methyl groups on the 4,7-carbons that raises the energy of the electron accepting LUMO (Fig. 2). Similar destabilizing interactions are absent with the methyls residing on the 2,9-carbons. The reduction to the neutral redox partner is chemically irreversible or at best quasi-irreversible in 1²⁺ and in 3²⁺, which lack methyl groups on the 4,7carbons.

We do not know precisely why the 2-electron reduced viologens 1^0 and 3^0 are kinetically less stable than those formed in the reductions of 2^{2+} and 4^{2+} . The neutral redox partners exists as *syn*- and *anti*-isomers¹⁸ (Fig. 3) and are stable for all four viologens at the B3LYP/6-311+G(2d,p) computational level. The length of the formally double bond between the two six-membered nitrogen containing rings in the neutral redox partners are nearly identical in all four compounds (1^0 1.372 Å; 2^0 1.374 Å; 3^0 1.373 Å; and 4^0 1.376 Å) and only slightly shorter than in **MV**⁰ (1.380 Å). However, the deviation from planarity is greatest for 2^0 ($\Theta_{MeNC4Me}$: *syn* 23.1⁰; *anti* 22.4) and 4^0 ($\Theta_{MeNC4Me}$: *syn* 32.2⁰; *anti* 32.1⁰) and smaller for 1^0 (Θ_{MeNC4H} : *syn* 17.1⁰; *anti* 16.8⁰) and 3^0 (Θ_{MeNC4H} :



Figure 2. Methyl antibonding interactions in 2²⁺, 3²⁺, and 4²⁺. B3LYP/6-311+G(2d, p).



Figure 3. Syn- and anti-deformations in 2-electron reduced viologens.

syn 18.9^o; *anti* 18.7^o) that lack methyl groups on the 4 and 7 positions of the phenanthrene nucleus. For comparison, the corresponding dihedral angles in \mathbf{MV}^{0} are 17.5^o for the *syn*- and 16.5^o for the *anti*-isomer (see Supplementary material for more structural information).

Conclusion

The viologen sensitizers described here are sufficiently soluble for use in polar solvents (CH₃CN, H₂O), which are known to support electron transfer processes.¹⁹ For example, viologen **3²⁺** sensitizes decomposition of tetraphenyloxirane in acetonitrile²⁰ (see Supplementary information for details). They are easy to handle and stable to irradiation in the absence or presence of substrate for at least 2 h, and in contrast to pyrylium based dications are very resistant to hydrolysis.²¹ Electrochemically they form the radicalcations in reversible/quasi-reversible processes that allow measurement of thermodynamically significant reduction potentials. The S₁ states of 1^{2+} , 2^{2+} , 3^{2+} , and 4^{2+} are thermodynamically capable of oxidizing organic substrates with oxidation potentials lower than 2.68, 2.53, 2.51, and 2.37 eV, respectively. The T₁ states of 1^{2+} , 2^{2+} , 3^{2+} , and 4^{2+} are thermodynamically capable of oxidizing organic substrates with oxidation potentials lower than 2.51, 2.41, 2.38, and 2.35 eV, respectively. In addition, the triplet excited states and radical-cation/radical-cation pairs have the added advantages of long lifetimes that will enhance their migration lengths and suppress energy wasting return electron transfer.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.08. 049.

References and notes

- 1. Weidel, H.; Russo, M. Monatshefte 1882, 3, 850–885.
- (a) Summers, L. A.O In Advances in Heterocyclic Chemistry; Katritzky, A. R., Ed.; Academic Press: Orlando, FL, 1984; Vol. 35, pp 281–374; (b) Summers, L. A. The Bipyridinium Herbicides; Academic Press: NY, New York, 1980; (c) Monk, P. M. S. The Viologens, Physicochemical Properties, Synthesis and Applications of the Salts of 4.4'-Bipyridine; Wiley: Chichester, UK, 1998; (d) Sliwa, W. Heterocycles 1991, 32, 2241–2273.
- 3. Barltrop, J. A.; Jackson, A. C. J. Chem. Soc. Perkin Trans. II 1984, 367-371.
- (a) Barnes, J. C.; Jurícek, M.; Strutt, N. L.; Frasconi, M.; Sampath, S.; Giesener, M. A.; McGrier, P. L.; Bruns, C. J.; Stern, C. L.; Sarjeant, A. A.; Stoddart, J. F. J. Am. *Chem. Soc.* 2012, 135, 183–192; (b) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. Angew. Chem., Int. Ed. Engl. 1988, 27, 1547–1550.
- (a) Fahrenbach, A. C.; Zhu, Z.; Cao, D.; Liu, W.-G.; Li, H.; Dey, S. K.; Basu, S.; Trabolsi, A.; Botros, Y. Y.; Goddard, W. A.; Stoddart, J. F. *J. Am. Chem. Soc.* 2012, 134, 16275–16288; (b) Cantekin, S.; Markvoort, A. J.; Elemans, J. A. A.; Rowan, A. E.; Nolte, R. J. M. *J. Am. Chem. Soc.* 2015, 137, 3915–3923.
- 6. Harris, C.; Kamat, P. V. ACS Nano 2009, 3, 682–690.
- (a) Li, H.-Y.; Wei, Y.-L.; Dong, X.-Y.; Zang, S.-Q.; Mak, T. C. W. Chem. Mater. 2015, 27, 1327–1331; (b) Kaur, K.; Mittal, S. K.; Kumar, S. K. A.; Kumar, A.; Kumar, S. Anal. Methods 2013, 5, 5565–5571.

- (a) Clennan, E. L.; Liao, C.; Ayokosok, E. J. Am. Chem. Soc. 2008, 130, 7552–7554;
 (b) Clennan, E. L.; Welch, W.; El-Idreesy, T. T.; Arulsamy, N. Can. J. Chem. 2015, 93, 414–421.
- Peon, J.; Tan, X.; Hoerner, J. D.; Xia, C.; Luk, Y. F.; Kohler, B. J. Phys. Chem. A 2001, 105, 5768–5777.
- **10.** A singlet lifetime of 10.4 ns has been reported for *N,N'*-2,7-diazapyrenium dication but the generality of this observation has not been demonstrated. Ballardine, R.; Credi, A.; Gandolfi, M. T.; Giansante, C.; Marconi, G.; Silvi, S.; Venturi, M. *Inorg. Chim. Acta* **2007**, *360*, 1072–1082.
- (a) Gordillo, A.; de Jesús, E.; López-Mardomingo, C. Chem. Commun. 2007, 4056–4058; (b) Gordillo, A.; Ortuño, M. A.; López-Mardomingo, C.; Lledós, A.; Ujaque, G.; de Jesús, E. J. Am. Chem. Soc. 2013, 135, 13749–13763.
- 12. Mallory, F. B.; Mallory, C. W. Org. React. 1984, 30, 1-456.
- 13. Ellison, E. H.; Thomas, J. K. Langmuir 2001, 17, 2446–2454.
- 14. Valencia, D. P.; González, F. J. Electrochem. Commun. 2011, 129–132.
- 15. This is based on the observation that at 0.01 M when two molecules are placed at the center of a cube to maximize intermolecular distances a viologen sensitizer placed at a vertex in an ensemble of those cubes must diffuse at most 48 Å to encounter one of eight substrate molecules in adjacent cubes, which is considerably shorter than its maximum diffusion length of 85 Å.
- Ammon, U.; Chiorboli, C.; Dümler, W.; Grampp, G.; Scandola, F.; Kisch, H. J. Phys. Chem. A 1997, 101, 6876–6882.
- 17. Nunn, I.; Eisen, B.; Benedix, R.; Kisch, H. Inorg. Chem. 1994, 33, 5079-5085.
- These two isomers are nearly identical in energy with energy differences of only 0.006–0.11 kcal/mol.
- Gould, I. R.; Moser, J. E.; Armitage, B.; Farid, S. Res. Chem. Intermed. 1995, 21, 793–806.
- Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. J. Photochem. 1984, 26, 167–181.
- (a) Reynolds, G. A.; VanAllan, J. A. J. *Heterocycl. Chem.* **1969**, *6*, 623–626; (b) El-Idreesy, T. T.; Clennan, E. L. J. Org. Chem. **2011**, *76*, 7175–7179.