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Authors: Gang He, Guoping Li, Letian Xu, Weidong Zhang, Kun Zhou, Yousong Ding, Fenglin Liu, and Xiaoming He

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Narrow Band Gap Chalcogenoviologens for Electrochromism and Visible-Light-Driven Hydrogen Evolution

Guoping Li,^[a] Letian Xu,^[a] Weidong Zhang,^[a] Kun Zhou,^[a] Yousong Ding,^[a] Fenglin Liu,^[a] Xiaoming He,^[b] and Gang He^{*[a]}

Abstract: A series of electron-accepting chalcogen-bridged viologen with narrow HOMO–LUMO band gaps and low LUMO levels is reported. The optoelectronic properties of chalcogenoviologens can be readily tuned *via* heavy atoms substitution (S, Se and Te). Herein, *in-situ* electrochemical spectroscopy was performed on the proof-of-concept electrochromic devices (ECD). E-BnV²⁺ (E = Se, Te) was used in visible-light-driven hydrogen evolution due to the strong visible light absorption. Remarkably, E-BnV²⁺ was not only used as a photosensitizer, but also as an electron mediator, providing a new strategy to explore photocatalysts. The higher apparent quantum yield of Se-BnV²⁺ could be interpreted in terms of different energy levels, faster electron-transfer rates and faster formation of radical species.

The research and application of viologen analogs (RV²⁺) have developed rapidly,^[1] particularly in fields such as electrochromic display devices (ECD),^[2] metallosupramolecular assemblies,^[3] host-guest complexes,^[4] solar-to-fuel conversion,^[5] energy storage^[6] and many other utilities.^[7] The widespread use of viologen analogs results from their unique properties, that is, different redox states of these analogs can donate or accept electrons, participate in the coordination from reversible redox reaction and change color between purple and orange,^[8]

The substitution of specific carbon atoms in the purely carbonbased scaffolds by main-group heteroatoms has drawn significant attention due to their unique synergistic electrical and optical properties.^[9] In recent years, several groups have made efforts to combine heteroatoms and viologens. For example, rigid phosphaviologens (P-RV)^[10], doubly phosphorus-bridged viologen (DPMV)^[11] or disulfide viologen^[12] were developed by doping P or S into viologen scaffolds, which showed enhanced electrochemical and electrochromic properties.^[13] By incorporation of silole/germole or thiazole with viologen, the solidstate phosphorescent dipyridinometalloles^[14] and fluorescent bipyridinium thiazolothiazole derivatives^[15] have been reported. Evidently, combination of main group elements and viologen is an efficient strategy to develop viologen derivatives with broad promising applications.

 [b] Prof. Dr. X. He
 School of Chemical Science and Engineering, Tongji University, Shanghai, 200092 (China)
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Conditions: [a] 1. n-BuLi (-85 °C, THF). 2. °S₂Cl₂, 'SeCl₂, 'TeCl₄, then Na₂S solutio [b] MeOTf, DCM. [c] benzyl bromide, 25 °C. [d] MeOTf, DCM.

 $\label{eq:scheme1.} \textbf{Scheme 1.} Synthesis of chalcogenoviologens.$

Typically, polythiophene tends to generate p-doping charges and capture photons which improves electrical conductivity, electrochromism and drive photocatalysis.^[16] As members of the chalcogen family, heavier Se and Te atoms have special properties compared to S atom in terms of greater mass and polarizability, which are expected to improve the electron mobilities.^[17] It can be envisioned that introducing heavier chalcogen atoms (Se and Te) into viologen skeleton should significantly perturb the electronic structures of novel viologen derivatives. Based on this consideration, we have now focused on the synthesis of chalcogen-bridged viologens (chalcogenoviologens, E-RV²⁺), which combine the nature of viologen and chalcogenophene and extend their applications in electrochromic devices and visible-light-driven hydrogen evolution.

The synthesis of chalcogenoviologens were obtained by treatment of 1^[10a] with "BuLi, followed by addition of S₂Cl₂,^[18] $\text{SeCl}_2^{[19]}$ or $\text{TeCl}_4.^{[20]}$ Thieno[2,3-c:5,4-c']bipyridine (2a) was obtained in 36% yield;^[21] selenopheno[2,3-c:5,4-c']bipyridine (2b) and telluropheno[2,3-c:5,4-c']bipyridine (2c) were synthesized for the first time with the moderate yield of 44% and 57%, respectively. Low-field shift of ¹H resonances was observed from 9.28 to 9.18 on the α -pyridine protons with the introduction of heavier atoms. Chalcogen-bridged bipyridine 2 was converted into the chalcogen-MV2+ 3 via reaction with methyl triflate (MeOTf), which were obtained as a solid (3a: off-white, which was reported previously,^[22] 3b: dark green, 3c: dark red) in a high yield of ca. 80%. We hypothesized that the basicity of the nitrogen centers of 2 would increase along with the introduction of electron-donating chalcogen contrary to 3,7-diazadibenzophosphole oxide,[10b] so that the N-benzylation reaction could carry out at room temperature instead of microwave conditions. The strong association of 2 with trifluoroacetic acid (TFAH) verified our prediction (Figure S1-S3). Based on this, we quaternized the

[[]a] G. Li, L. Xu, W. Zhang, K. Zhou, Y. Ding, Dr. F. Liu, Prof. Dr. G. He Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an, Shaanxi Province, 710054 (China) E-mail: ganghe@mail.xjtu.edu.cn.

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nitrogen atoms *via* benzylation in mild conditions, resulting in dicationic salts **4a/4b/4c** with moderate yields (70-81%). More soluble **5a/5b/5c** were synthesized by anion exchanges between **4a/4b/4c** and excess MeOTf (Scheme 1).

The formations of these compounds were also confirmed by Xray crystallography (Figures 1, S6-S10). Single crystal structure of 2c exhibits a planar backbone with two similar Te-C bond lengths (*i.e.*, 2.10 Å), the packing in 2c shows a strong Te-Te interaction (i.e., 3.99 Å) as well as a layered motif with two different face-to-face interactions (Figure 1b). Single crystals of 3b, 3c, 4c and 5c were obtained from their concentrated acetonitrile solutions. The packing in 3b shows Se-O interactions, however no Se-Se interactions were found. Strong interactions from both Te-Te and Te-O bonds can be observed from the packing in 3c, which showed a similar packing model to 2c. In the structure of 5c, it is worth noting that the triflate anions are disordered over two positions, in which the one is interacting closely with the π system of bipyridine skeleton at a distance of 3.09 Å, while the other triflate anion displays Te-O interaction at a distance of 3.06 Å (Figure 1a). Compared to 3c, there are no face-to-face interactions or close contacts between the skeletons in 5c due to the presence of bulky benzyl groups. TGA analysis indicated that chalcogen-bridged viologens are all stable under 200 °C (Figure S4 and S5).



Figure 1. Crystal structure of (a) **5c** and (b) **2c** (thermal ellipsoids set at 50% probability, H atoms are omitted for clarity). (c) Cyclic voltammograms of **5c** (c = 10^{-3} M) in DMF solution, [*n*-Bu₄N][PF₆] (0.1 M) as supporting electrolyte, vs. Fc/Fc⁺. (d) UV-vis spectra of chalcogen-BnV²⁺ in DMF, c~ 10^{-4} M; extrapolated optical band gaps (E₉) are shown as insets.

The electrochemical characteristics of chalcogenoviologens were probed *via* cyclic voltammetry (CV, Figure S11), and the results were summarized in Table S6. For example, **2c** presents redox potential $E_{red1,1/2}$ = -2.11 V (E_{LUMO} = -2.69 eV) and $E_{red2,1/2}$ = -2.56 V. All dicationic species show two reversible one-electron reductions due to the presence of bipyridine skeleton. The reduction potentials of new chalcogen-BnV²⁺ were measured for **5a** ($E_{red1,1/2}$ = -0.60 V and $E_{red2,1/2}$ = -1.05 V), **5b** ($E_{red1,1/2}$ = -0.63 V and $E_{red2,1/2}$ = -0.68 V and $E_{red2,1/2}$

-1.10 V). The reduction potentials of 5a/5b/5c (Figure 1c and S11) were significantly lower than those of both the starting materials 2a/2b/2c and chalcogen-MV²⁺ (3a/3b/3c). Although 5 had 70-150 mV higher reduction potential than P-BnV, the first reduction events were still 60-140 mV lower than the corresponding parent analog, 1,1'-bis(benzyl)-4,4'-bipyridinium salt (BnV), and showed desirable electron-accepting characters (Figure S13a). This was attributed to a more rigid and conjugated structure due to the introduction of heteroatoms. Clearly, both the ionization and incorporation of the chalcogen decrease the energy of the LUMOlevels, facilitating the reduction reaction. From the electrontransfer constants of **5a** ($k_{\text{ET1}} = 1.17 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1}$ and $k_{\text{ET2}} = 2.13$ × 10⁻² cm·s⁻¹), **5b** (k_{ET1} = 1.55 × 10⁻² cm·s⁻¹ and k_{ET2} = 2.16 × 10⁻² cm·s⁻¹), and **5c** ($k_{\text{ET1}} = 0.93 \times 10^{-2} \text{ cm·s}^{-1}$ and $k_{\text{ET2}} = 1.67 \times 10^{-2}$ cm·s⁻¹), it is clear that the electron-transfer rates of 5b are faster than 5a and 5c (Nicholson method, Table S7). Notably, in 5c, there is another semi-reversible reductive wave at -2.66 V due to the introduction of tellurophene rings: this is in a good agreement with the reported dibenzo[b,d]tellurophene (DPhTe) and the precursor 2c. This demonstrates the existence of extra redox centers of Te-BnV2+ (Scheme S1).

The UV-vis spectra of chalcogenoviologens were studied to evaluate their light absorption properties (Figures S12 and 1d), and their photophysical data were summarized in Table S6. The maximum absorptions of 2a/2b/2c in DMF were measured to be 345, 355 and 385 nm, respectively. The HOMO-LUMO energy gaps were calculated to be 3.50 (2a) to 3.38 (2b) to 3.08 eV (2c). The maximum absorptions for chalcogen-BnV²⁺ 5a/5b/5c in DMF solution were observed at 395, 422 and 491 nm. There is a pronounced redshift of optical absorption from 5a to 5b to 5c, compared to precursors 2 and 3 (Figure S13b). This change in absorption is accompanied by a reduced energy gap from 3.00 (5a) to 2.78 (5b) to 2.33 eV (5c). These results can be explained by the stronger electron-donating character of the chalcogen atoms and decrease in aromaticity from S-viologen to Se-viologen to Te-viologen.^[16b] Additionally, this transformation is in good agreement with the first singlet excitation energy obtained by time-dependent DFT (TD-DFT) calculations (Figure S28-S42). Raised HOMO levels are also observed from 5a to 5b to 5c because the electronegativity of the heteroatom is inversely proportional to the HOMO of the heterocycles. Compared to the known P-BnV, chalcogenoviologens showed raised HOMO levels and narrowed band gaps, while keeping electron-accepting characters, which is destined to be extraordinary for applications.

We used the proof-of-concept ECD aiming to verify electrochromic and photophysical behaviors of **5a/5b/5c**. Fluorine-doped tin oxide (FTO)-coated glasses were utilized as the electrodes and **5a/5b/5c** were used as active components (Figure S15 and 2a). For **5c**, with the applied potential of -1 V, the absorption in the visible region increased and the color gradually changed to dark blue (Figure 2c) due to the formation of radical species (**5c'**). This process resembles chemical reduction of Zn. Moreover, the decreased absorption in the visible region was observed due to the accumulation of neutral species **5c**" by applying higher voltages of -2 V (Figure 2d); this process corresponds to the chemical reduction of Na. Similarly, electrochromism and identical absorption profiles of **5a** and **5b** were observed (Figure S16–S20). Reversibility of color change was displayed using etched FTO glass or diffusion of air into the

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Figure 2. (a) Solution-based ECD with 5c. (b) Gel-based ECD with 5c. (c) Spectroelectrochemistry of 5c for first reduction and chemical reduction with Zn is shown as the inset. (d) Spectroelectrochemistry of 5c for second reduction and chemical reduction with Na is shown as the inset. (e) EPR spectrum and spin densities of radical species of chalcogen-BnV²⁺ (5a', 5b' and 5c').

cell. The CV stability test of **5c** indicated good electronic stability even after 400-scan cycles, and the slight transmittance changes for ECD of **5c** at 661 and 730 nm showed good electrochromic switching (Figure S17). In gel-based ECD, lower voltages were needed due to the presence of a thinner material layer with higher electrical conductivities (Figure 2b).

Interestingly, chalcogen-BnV2+ showed weak fluorescence in DMF solutions (Figure S21, lifetime (r) for 5a: 8.93 ns; 5b: 5.39 ns and **5c**: 5.18 ns). The quantum yields ($\Phi_{\rm F}$) were all less than 1%, due to the strong heavy atom effect. When radical species 5c' were exposed to air, emission intensity gradually increased and the maximum emission wavelength was redshifted until reaching the wavelength of the original dication 5c. This process was also monitored by UV-vis spectroscopy and ¹H NMR (Figure S23). The same trends were also observed in 5a and 5b, suggesting most of the radical species converted to original dication over time in air (Figure S22). Simultaneously, radical characters of radical species were evaluated via electron paramagnetic resonance (EPR) spectroscopy. The resulting signal displayed a considerable amount of hyperfine coupling (Figure 2e), suggesting delocalization of the radical over a large portion of the molecular scaffold. 5a', 5b' and 5c' had expected g-factor values of 2.0031, 2.0042 and 2.0049, respectively, supporting the organic nature of the radicals. Typically, the spin density on the chalcogen element is gradually increased from 5a' to 5b' to 5c', which was confirmed through DFT calculations (insets of Figure 2e). The SOMO of the radical cations are similar to the LUMO of the dicationic species, and the radicals are delocalized and stabilized over the whole π -system of the scaffold.

Considering of the strong visible light absorption of Se/Te-BnV ($\lambda > 400 \text{ nm}$) in combination with their facile radical formation properties, visible-light-driven hydrogen evolution system was designed to uncover the new application of viologens. Previous investigations show that Ru(bpy)₃²⁺ or polythiophene^[5b] derivatives (PT) can be used as photosensitizers and MV²⁺ served as an electron relay for photoreduction of water.^[23] In our tests, Se-BnV²⁺ (**5b**) and Te-BnV²⁺ (**5c**) possessed similar properties to the photosensitizer. Meanwhile, **5a'/5b'/5c'** have sufficient driving forces for H⁺ reduction based on their negative

LUMO levels (Figure S25). Therefore, the water-soluble E-BnV²⁺ was used both as a photosensitizer and as an electron mediator (Figure 3a). In contrast to reported systems based on MV or P-RV, this system does not require an additional photosensitizer. EDTA was used as a sacrificial electron donor and colloidal platinum particles stabilized by polyvinylpyrrolidone (colloids of PVP-Pt) as a catalyst. The proposed mechanism was shown in Figure S26. Firstly, the E-BnV²⁺ was excited to excited states (E-BnV^{2+*}) under visible light, where E-BnV^{2+*} accepted one electron from EDTA and changed to radical cation E-BnV⁺⁺. Then H⁺ was reduced to hydrogen on the surface of PVP-Pt and E-BnV⁺⁺ was oxidized to E-BnV²⁺ to finish the catalytic cycle.^[24]

Taking 5b as an example, a mixture of 5b (5 mmol), EDTA (50 mmol), colloidal PVP-Pt (4 mg) and 1 mL distilled water were sealed in a Pyrex bottle. After bubbling with argon for 30 minutes, the bottle was exposed to the xenon lamp with a filter ($\lambda > 400$ nm) at 100 mW. The hydrogen quantity was calculated according to the H₂ normalized curves (Figure S24). The plots of the hydrogen generation are shown in Figure 3b. Hydrogen can continuously generate for more than ten hours (total about 13.03 μ mol of H₂, hydrogen generation rate: 0.31 mmol·h⁻¹·g⁻¹), and apparent quantum yield (AQY) was 1.71×10^{-3} , which is higher than the previously reported results (Table S8). For Te-BnV²⁺ (5c), hydrogen was generated for more than twenty-two hours with the total amount of ca. 4.73 µmol (the first twelve hours was listed in Figure 3b, hydrogen generation rate: 0.056 mmol·h⁻¹·g⁻¹), and lower AQY of 3.39×10^{-4} compared to **5b**. For S-BnV²⁺ (**5a**), there was only 0.12 µmol hydrogen generated after thirty hours, while there was no hydrogen evolution in the case of BnV²⁺.

To understand this phenomenon, the formation speeds of radical species were investigated in the absence of PVP-Pt. As shown in Figure 3c, the radical species, **5b'** were generated much faster than **5c'** (1 min vs. 2 h), while **5a'** and BnV' did not form under this condition. This is attributed to the more negative HOMO level of **5b** compared to **5c**. In HOMO level, in case of **5b** the electrons are distributed over the entire skeleton in contrast to the solely bypiridine part (in particular, Te atom) in case of **5c**. Furthermore, **5b** showed faster electron-transfer rates than **5c**. This may lead to capture of more photon flux from the solar

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spectrum to further improve hydrogen evolution efficiency in **5b**. Thus, the subtle electron properties, the faster formation of radical species and electron-transfer rates^[23b] led to higher AQY and increased hydrogen generation of Se-BnV²⁺ (**5b**) than Te-BnV²⁺ (**5c**). The hydrogen generation of **5b** exhibits decent cycle stability due to the simplified catalytic process (Figure S27).



Figure 3. (a) Schematic diagram for photoinduced hydrogen production from water. (b) Time-dependent hydrogen generation from aqueous solution under xenon lamp. (c) Total hydrogen generation of active components; changed colors as the time go by under xenon lamp are shown as insets.

In conclusion, a series of novel chalcogenoviologens were successfully synthesized by combining the viologen with chalcogenophenes. By introducing different chalcogen atoms (S, Se and Te), the HOMO-LUMO band gaps narrowed gradually, along with increased HOMO levels, which caused the red-shift of absorptions to the visible range. The multiple redox peaks were found (especially for 5c), which were promising in many electronrelated fields. The proof-of-concept solution-based/gel-based ECD were fabricated successfully and their electrochemical performance was studied in situ. These results lay a solid foundation for flexible low-voltage electrochromic devices and relevant research is in progress. In addition, the water-soluble Se- BnV^{2+} (5b) and Te-BnV²⁺ (5c) were first used as both a photosensitizer and as an electron mediator for visible-light-driven hydrogen evolution due to their high visible light absorption and optimal energy levels, which provide a new strategy for developing organic photocatalysts. Research on other applications of chalcogenoviologens is currently underway.

Keywords: viologen • chalcogenoviologens • electrochromism • visible region • hydrogen evolution

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