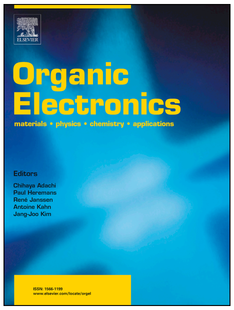

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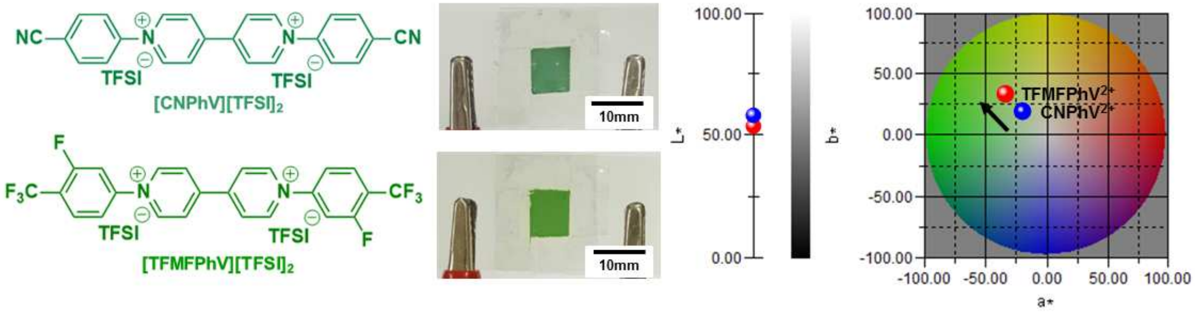
"Graphical Abstract"



Novel Viologen Derivatives for Electrochromic Ion Gels Showing a Green-Colored State with Improved Stability

Hwan Oh, Dong Gyu Seo, Tae Yong Yun, Seong Been Lee, Hong Chul Moon[*]

Department of Chemical Engineering, University of Seoul, Seoul 02504, Republic of Korea

* Corresponding authors. E-mail: hcmoon@uos.ac.kr (H.C.M)

Abstract

We successfully synthesized a novel viologen derivative (1,1'-bis(3-fluoro-4-(trifluoromethyl)phenyl)-4,4'-bipyridinium bis(trifluoromethylsulfonyl)imide, (TFMFPhV)(TFSI)$_2$ exhibiting a green-colored state. We selected cyanophenyl viologen (CNPhV^{2+}), a conventional electrochromic (EC) chromophore with a green color indication, to compare EC performance. Ion gels consisting of poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-*co*-HFP) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI][TFSI]) were employed as a solid-state electrolyte for EC devices (ECDs). In comparison to CNPhV^{2+}-containing devices, the ECDs with TFMFPhV^{2+} showed higher transmittance contrast, larger coloration efficiency, faster coloration and bleaching responses, and better coloration/bleaching operational stability. Cyclic voltammetry revealed that the more stable redox behavior of TFMFPhV^{2+} is the origin of the outstanding ECD performance.

Keywords

Electrochromism; Ion Gel; Viologen; Zincke Reaction; Electrochemical Display

1. Introduction

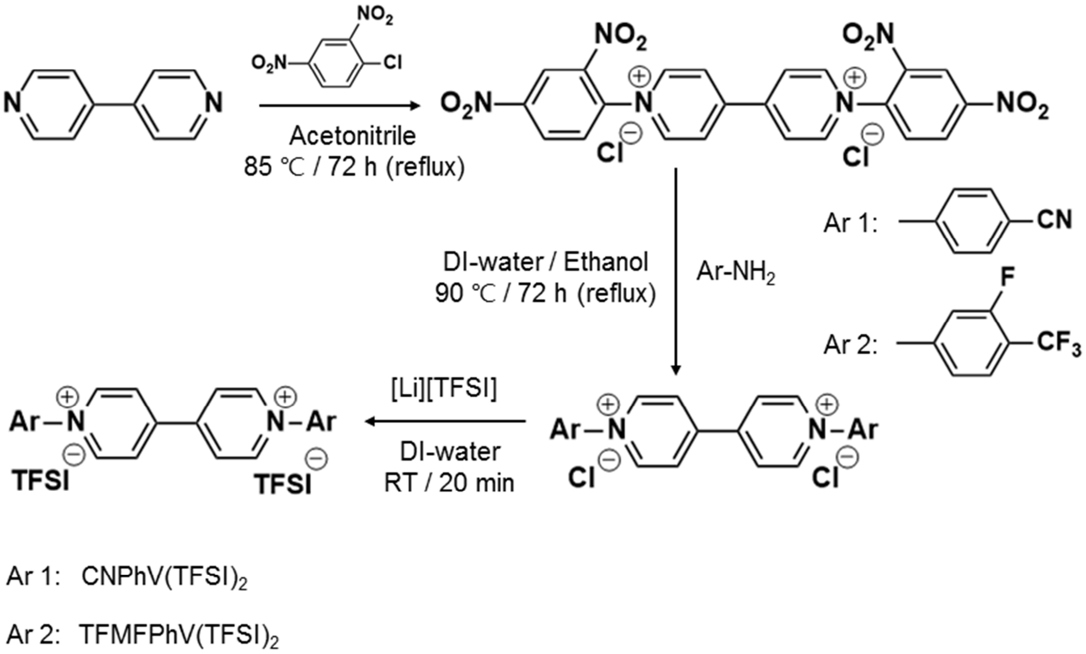
Electrochromism (EC) corresponds to reversible changes in transmittance and color by redox reactions when appropriate electrical stimuli are applied across electrochemical cells [1–9]. In addition to the modulation of optical properties, EC devices (ECDs) exhibit characteristic low voltage operation and low power consumption. Thus, ECDs have been employed in diverse applications such as smart windows for cars or buildings, anti-glare car rear-view mirrors, protective eyewear, and information displays [10,11]. There are a number of chemical EC-active chromophores [6–9]. In general, ECDs based on conducting polymers or metal oxides are composed of multiple layers, including ion conductive electrolytes and ion storage layers, in addition to the EC layer. In contrast, small organic materials can provide a much simpler device configuration (namely, an EC layer between two electrodes) because both colored and bleached species are dissolved in the electrolyte layer.

One representative organic EC material is 1,1’-disubstituted-4,4’-bipyridinium salt (viologen), in which EC properties can be tuned by selecting various substituents. For example, when the substituents are alkyl groups, bluish colored states are induced [8,12]. More abundant colors can be obtained with functionalized phenyl substituents, although the synthetic processes, including the Zincke reaction, are relatively more complex. For example, the radical cation of the 1,1’-bis(4-cyanophenyl)-4,4’-bipyridinium (CN-PhV^{2+}) is a typical EC chromophore with a green colored state [13–15]. However, CN-PhV^{2+} could form a dimer in hydrophilic electrolytes due to strong π-π stacking or spin pairing [16]. The dimer exhibited a quasi-reversible characteristic, which leads to an aging process [17-20]. This process impacts device operational stability. Recently, Kao et al. demonstrated greenish ECDs with improved device coloration/bleaching stability based on phenyl viologen (PV) and vinyl benzyl viologen (VBV), in which the VBV moieties were thermally cured with MMA to prevent dimerization [21]. However, purity of the greenish colored state was not high according to the CIELAB color coordinate of $L^*= 40.9$, $a^* = –9.7$, $b^* = –19.0$. Therefore, the development of a new EC chromophore is essential to realizing pure and stable greenish ECD pixels for display applications.

In this work, a novel viologen derivative, 1,1’-bis(3-fluoro-4-(trifluoromethyl)phenyl)-4,4’-bipyridinium(TFMFPhV^{2+}), with a greenish colored state was successfully synthesized via the Zincke reaction, and was employed in ECDs based on ion gels consisting of copolymers (poly(vinylidene fluoride-*co*-hexafluoropropylene), PVDF-*co*-HFP) and ionic liquids (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMI][TFSI]). To verify device performance, a TFMFPhV^{2+}-containing ECD was compared with one including CN-PhV^{2+}. For both devices, the change in color to green commenced at similar applied voltages: –0.13 V (CNPhV^{2+}) and –0.20 V (TFMFPhV^{2+}). However, when we evaluated color purity based on the CIELAB coordinates, a more negative a* value (namely, closer to the green component) was obtained from the ECD including TFMFPhV^{2+} (L*= 51.5, a*= –34.1, b*= 29.8) in comparison to the CNPhV^{2+}-containing device (L*= 54.7, a*= –22.8, b*= 18.8). With respect to device dynamics, much faster coloration and bleaching responses were observed in TFMFPhV^{2+}-containing ECDs: t_c ~22 s for coloration at –0.35 V, t_b ~32 s and ~10 s for bleaching under open-circuit and short-circuit conditions, respectively. In addition to slower responses, the incomplete recovery from the colored state to the original bleached state was detected from the ECD with CNPhV^{2+} due to poor redox reversibility of the EC chromophore. This feature significantly affects coloration/bleaching cycling behaviors. The CNPhV^{2+}-based device rapidly deteriorated. For example, ~72% of the initial ΔT was lost after 1 h working. Although a continuous 24 h operation cut transmittance contrast (ΔT) in half, colored and bleached states were clearly distinguishable for TFMFPhV^{2+}-containing ECDs. Overall, TFMFPhV^{2+} has high potential as a stable green EC component for display applications.

2. Experimental

2.1 Materials



Scheme 1. Synthetic routes of CNPhV(TFSI)$_2$ and TFMFPhV(TFSI)$_2$.

All materials were purchased from Sigma-Aldrich and used as received without further purification unless otherwise noted. The synthetic route and molecular structure of EC materials (CNPhV(TFSI)$_2$ and TFMFPhV(TFSI)$_2$) are given in Scheme 1. In brief, a mixture of 4,4'-bipyridine (32 mmol, 1 eq) and 2,4-dinitrochlorobenzene (128 mmol, 4 eq) dissolved in dry acetonitrile (80 mL) was refluxed for 72 h, and the resulting yellowish solution was cooled to room temperature and filtered. Bright yellow precipitates were obtained, and washed with anhydrous acetonitrile. The crude products were recrystallized from DI-water/acetone and dried in vacuum for 24 h, producing yellow-green products (1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride, DNPhVCl$_2$). The DNPhVCl$_2$ (1.78 mmol, 1eq) was dissolved in 50% aqueous ethanol (40 mL) and an ethanol solution (10 mL) of 4-aminobenzonitrile (10.68 mmol, 6eq) was added dropwise. After refluxing for 72 h, the solution was cooled to room temperature. The reddish solution was evaporated by a rotary evaporator to remove the excess ethanol. The additional DI water (200 mL) was introduced and stirred for 1 h at room temperature. The solution was filtered and the filtrate was evaporated, producing 1,1'-bis(2,4-cyanophenyl)-4,4'-bipyridinium dichloride, $CNPhVCl_2$. For an anion exchange, a solution of excess lithium bis(trifluoromethanesulfonyl)imide [Li][TFSI] in DI water reacted with the aqueous $CNPhVCl_2$ solution for 20 min at room temperature. The precipitated $CNPhV(TFSI)_2$ was collected and dried in vacuum for 24 h. An ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMI][TFSI]) was synthesized by an anion exchange reaction between 1-ethyl-3-methylimidazolium chloride [EMI][Cl] and an excess amount of [Li][TFSI] in DI water [22].

2.2 Preparation of EC gels and ECDs

The EC ion gels and ECDs were prepared in ambient air. First, all components of the gel, including redox active materials [$CNPhV(TFSI)_2$ or $TFMFPhV(TFSI)_2$ (cathodic species) + dmFc (anodic species)], copolymers (poly(vinylidenefluoride-*co*-hexafluoropropylene), PVDF-*co*-HFP), and room temperature ionic liquids (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMI][TFSI]) at a pre-determined weight ratio of 2 or 3:4:36 were fully dissolved in acetone at 50 ^{o}C. The equimolar cathodic and anodic species were mixed. The prepared homogeneous solution was cast onto a slide glass and dried in ambient air. The residual acetone was then fully removed in vacuum. The EC gel was placed on ITO-coated glass (sheet resistance: 10 Ω/sq, Asahi Glass Co.) via a "cut-and-stick" method [23,24]. The fabrication of ECDs was completed by placing another ITO-coated glass on the gel, which was firmly fixed using 88-μm-thick, double-sided tape. Fig. S1 in the Supporting Information showed the whole fabrication process by the "cut-and-stick" strategy.

2.3 Device characterization

The cyclic voltammograms were recorded on a potentiostat (Wave Driver 10, Pine

Instrument) at a sweep rate of 50 mV/s, where a platinum disk, Ag wire, and ITO-coated glass were employed as the working, reference, and counter electrode, respectively. The redox potentials of $CNPhV^{2+}$ and $TFMFPhV^{2+}$ were calculated according to the redox potential of an internal standard, $dmFc^{+}$/dmFc. The variation of the UV-vis absorption spectra of the ECDs were measured by a UV-vis spectrometer (V-730, Jasco) from 400 to 850 nm at a scan speed of 400 nm/min. The applied DC voltage was supplied by a Sourcemeter (Keithley 2400, Tektronix). Transient current and transmittance profiles were recorded by a combination of the UV-vis spectrometer and potentiostat. CIELAB color coordinates of ECDs in colored and bleached states were estimated using Spectra Magic NX software (CM-S100w, Konica Minolta). The L* represents the lightness of the color, and a* and b* correspond to the positions of the color; green (–) to red (+) and blue (–) to yellow (+), respectively.

3. Results and discussion

Fig.1a depicts a schematic diagram of ECDs and chemical structures of components in EC gels. Because both EC chromophores (cathodic species) and dimethyl ferrocene (anodic species) were dissolved in the gel (electrolyte), the ECD can be simply fabricated by inserting an EC gel between two ITO-coated glasses. The prepared ion gels were based on P(VDF-*co*-HFP) and [EMI][TFSI] at a weight ratio of 1:9 because the resulting gel electrolyte exhibited high ionic conductivity (~6.7 mS/cm) and good mechanical moduli ($>10^4$ pa) at room temperature [25]. Fig. 1b displays the change in UV-vis spectra of the ECDs including $CNPhV^{2+}$ and two representative photographs of the device in bleached and colored states. No absorption peaks were observed under –0.13 V except a peak at ~450 nm arising from the dmFc in the gel. Before coloration occurred, the device was slightly yellowish in the bleached state due to the dmFc. The dmFc served as an anodic species, such as ferrocene [26], hydroquinone [27,28], and potassium ferrocyanide [29], which is essentially required for low-voltage electrochemical devices. As the applied voltage increased, the device absorbed a broad range of wavelengths and showed characteristic peaks at ~596 and 655 nm. The corresponding device indicated a green colored state (see Fig. 1b). For example, the CIELAB coordinates (L*, a*, b*) at –0.23 V were (54.7, –22.8, 18.8). While the yellowish bleached state was the same for the TFMFPhV^{2+}-containing ECD (Fig. 1c), the coloration to green commenced at a slightly higher voltage of –0.20 V than the ECD CNPhV^{2+}. However, when we estimated the color coordinates of the induced green, the a* remarkably shifted to a negative value [i.e. (L*, a*, b*) ~ (51.5, –34.1, 29.8)]. This implies that a purer green color was realized using the synthesized TFMFPhV^{2+}. To determine the operation type of the device, we disassembled the ECD including TFMFPhV^{2+} after coloration. As a result, we could observe green-colored gel without any residual solids on the electrodes (see Fig. S2 in the Supporting Information). Based on the bleached (TFMFPhV^{2+}) and colored species (TFMFPhV$^{+\bullet}$) dissolved in the gel, we conclude that the ECDs including TFMFPhV^{2+} correspond to the Type I ECD.

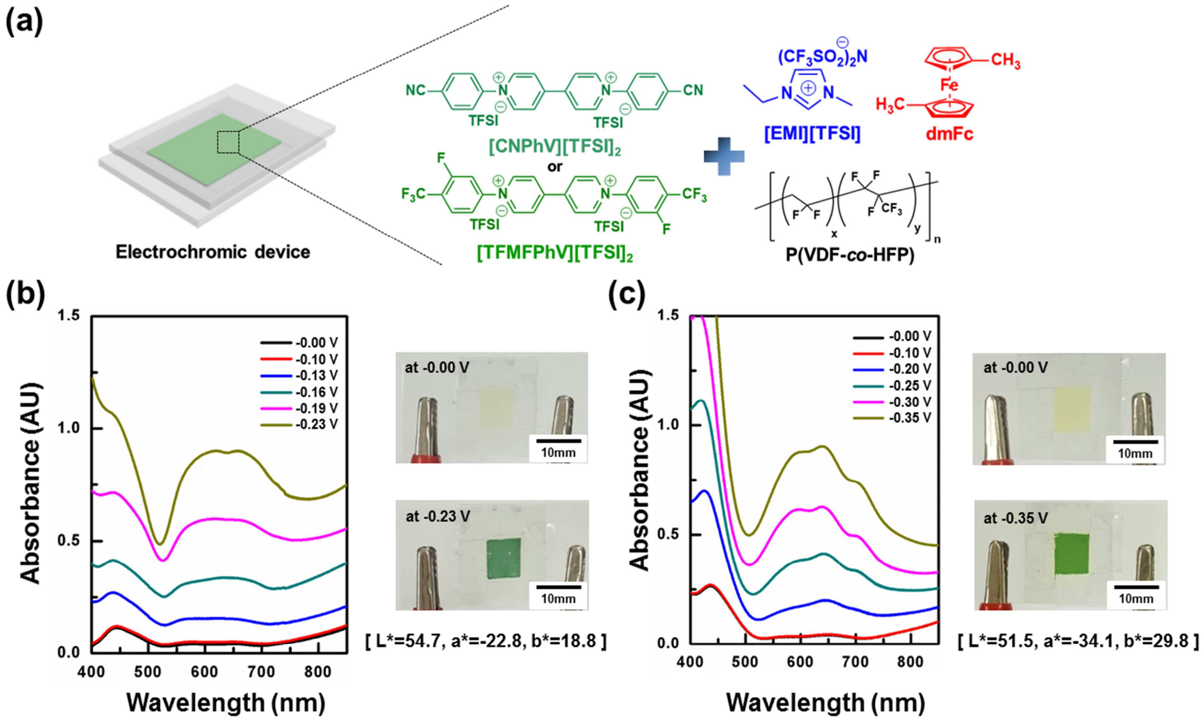


Fig. 1. (a) ECD configuration (left) and molecular structures of components in the EC gels (right). Dependence of UV/vis spectra on the applied voltages and two representative photographs of the bleached and colored states for ECDs based on (b) CNPhV^{2+} and (c) TFMFPhV^{2+}.

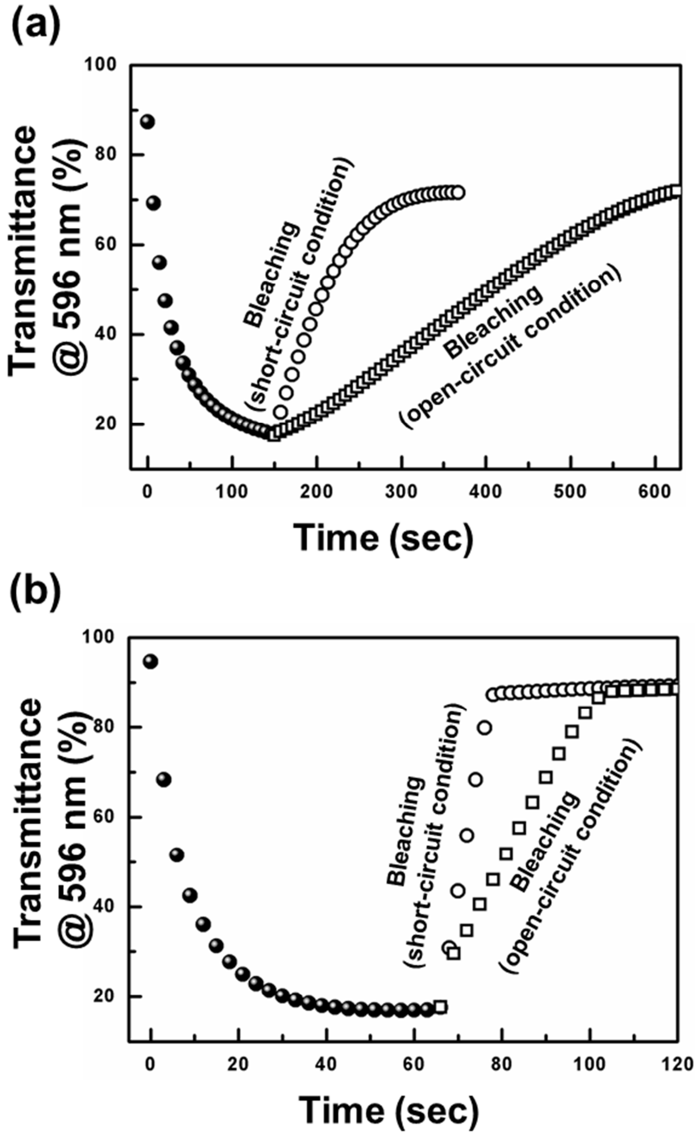


Fig. 2. Transient transmittance profiles of ECDs containing (a) CNPhV^{2+} at 596 nm and –0.23 V and (b) TFMFPhV^{2+} at 596 nm and –0.35 V, respectively.

To understand device dynamics, we recorded transient transmittance profiles at 596 nm that corresponds to the wavelength for one of characteristic peaks (Fig. 2a and 2b). When –0.23 V was applied, the transmittance of the ECD containing CNPhV^{2+} decreased gradually. The coloration time, defined as the time interval to reach 90% ($\Delta t_{90\%}$) of the total transmittance change, was ~74 s. On the other hand, the bleaching times were measured as ~398 s and ~122 s at open- and short-circuit conditions, respectively. The three-times faster transmittance recovery under shorting was quite predictable. Under the open-circuit condition, a pathway toward the non-colored state (namely, CNPhV^{2+}), i.e., chemical bleaching by a reaction between $CNPhV^{+\bullet}$ and $dmFc^{+}$ in bulk, is the only one available. When the circuit is shorted, a relatively rapid direct re-oxidation of $CNPhV^{+\bullet}$ (or $dmFc^{+}$) simultaneously occurs near the electrode. As a result, faster bleaching behavior was achieved under the short-circuit condition, which is in agreement with the behaviors of previously reported gel-based Type I ECDs [25,26]. In contrast, the ECD including $TFMFPhV^{2+}$ showed faster response times: Δt_c ~22 s at –0.35 V for coloration and Δt_b ~10 s (short-circuit condition) and ~32 s (open-circuit condition) for bleaching. In addition, good reversibility of coloration/bleaching cycles (see Fig. 2b) was also observed. Specifically, the transmittance level of the bleached state was nearly recovered by either open- or short-circuit conditions. These high transmittance changes (ΔT ~73%) can be favorably compared to other green-colored ECDs based on viologens. Recently, Chang et al. reported that the solid-state ECDs composed of heptyl-viologen, phenyl-viologen, and UV-cured electrolyte did not exhibit remarkable performance degradation after 3000 switchings, but the initial ΔT values at 610 nm and 438 nm were smaller than reported here: ~55.8% and ~48.9%, respectively [30]. Li et al. fabricated ECDs based on 1-(9-hexyl-9H-carbazole)-1'-(propylphosphonic acid)-4,4'-bipyridinium dichloride and 4-(diphenylamino)phenyl)methylphosphonic acid) exhibiting high stability, but those also gave relatively lower ΔT (~63% at 670 nm) [31].

The coloration efficiency (η), which is defined by the change in optical density (ΔOD) per injected charge density (Q), can also be extracted from Fig. 3. Although the coloration voltage was slightly higher, $TFMFPhV^{2+}$ demanded a smaller amount of charge for coloration of the specific area. By the linear fit on Fig. 3a and 3b, the η values for $CNPhV^{2+}$ and $TFMFPhV^{2+}$ were determined as ~73.92 cm^2/C at –0.23 V and ~79.39 cm^2/C at –0.35 V, respectively, which lie on the η range of analog viologen systems reported by other groups. For example, Kavanagh et al. reported a relatively lower η (~10.7 cm^2/C at 610 nm) of solid-state ECDs based on photo-polymerized gel networks containing viologen-based ionic liquids [32]. The UV-cured EC gel including ferrocene/nonyl viologen ($Fc/NV(BF_4)_2$) also provided a lower η of ~36.2 cm^2/C at 605 nm [33]. The ECDs composed of the methyl viologen (MV^{2+}) and graphene quantum dot (GQD) in a poly(vinyl alcohol) (PVA) matrix showed an η of 65

cm^2/C [34]. In contrast, two asymmetric viologens (Ethyl/CNPh- and benzyl/CNPh-viologen) exhibited higher η values: 118 cm^2/C and 180 cm^2/C under application of –0.80 V, respectively, although overall coloration potentials were larger than ours [35].

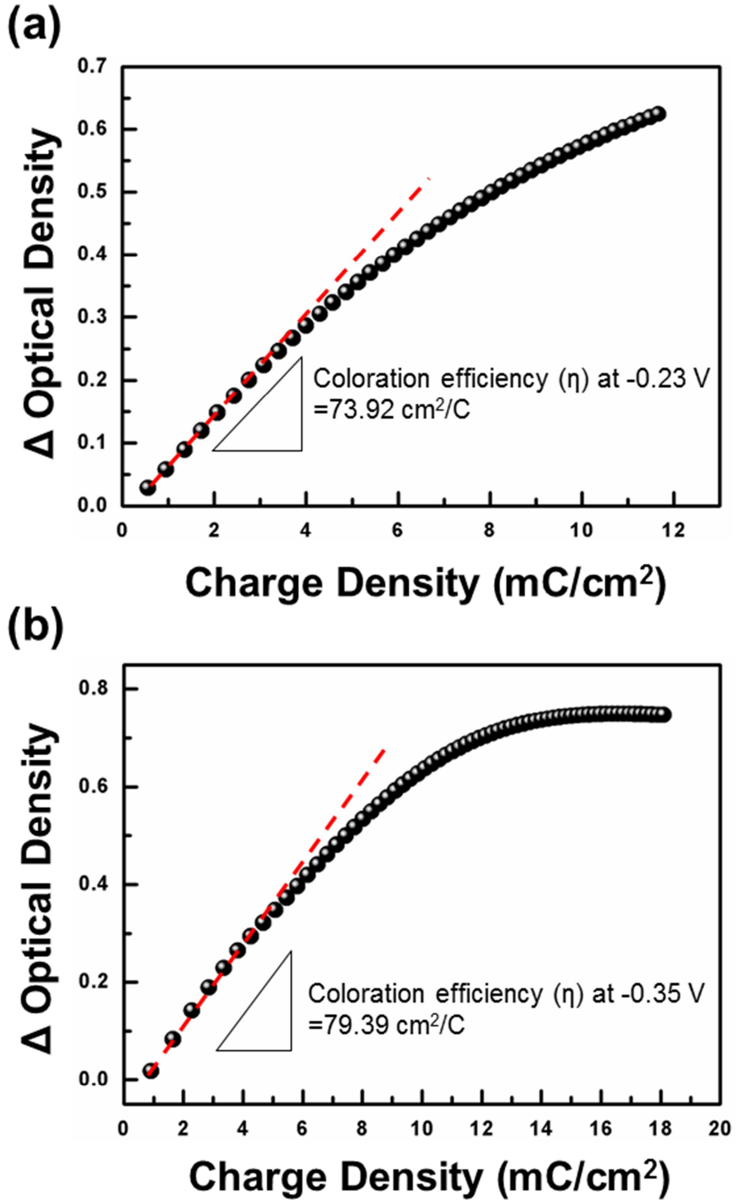


Fig. 3. Charge density dependence of the change in optical density for ECDs containing (a) $CNPhV^{2+}$ and (b) $TFMFPhV^{2+}$, where the coloration efficiency (η) was extracted from the slope of the linear zone.

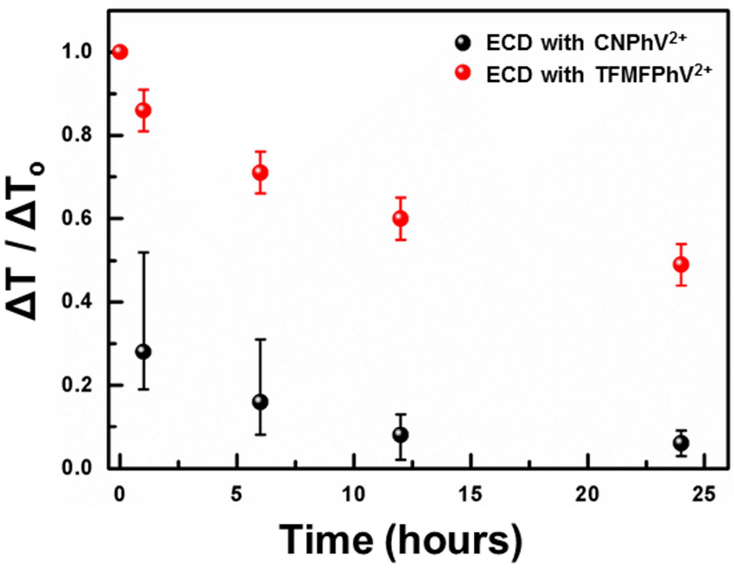


Fig. 4. The normalized transmittance variation of ECDs containing CNPhV^{2+} (black) and TFMFPhV^{2+} (red) as a function of time.

One of the required features for ECDs is to minimize drops in device performance even after continuous coloration and bleaching cycles. We plotted the variation of normalized transmittance (ΔT) over time (Fig. 4). For the device with CNPhV^{2+}, a dramatic reduction (~72%) from the initial value (ΔT_o) was observed at an early stage (~1 hour), followed by further degradation up to ΔT of 0.06. Alternatively, only a ~14% decrease of ΔT_o occurred from the TFMFPhV^{2+}-containing ECD. Although the ΔT_o level was halved, the distinct EC transition between colored and bleached states was shown even after 24 h operation.

To reveal the origin of the difference in device stability, cyclic voltammograms (CVs) of ECDs containing either CNPhV^{2+} or TFMFPhV^{2+} were obtained (Fig. 5a and b). Herein, the dmFc functioned as the internal standard material as well as the anodic species. Thus, the redox potentials of the EC materials were calculated on the basis of that of the dmFc^{+}/dmFc. The redox peaks at –0.23 V for the CNPhV^{2+}/CNPhV$^{+\bullet}$ –0.35 V for TFMFPhV^{2+}/TFMFPhV$^{+\bullet}$ were determined by taking the midpoint potentials, which are consistent with the coloration voltage. However, the CNPhV^{2+} did not clearly show the anodic peak, by which the corresponding cathodic peak abruptly decreased as the voltage sweep proceeded (Fig. 5a). This supports the irreversible bleaching behavior (see Fig. 2a) and poor operational stability (Fig. 4) of the resulting device. On the other hand, quite symmetric anodic/cathodic peaks were detected with TFMFPhV^{2+}. As a result, a smaller decrease in both peaks was induced, although the cathodic peak was relatively more depressed. This result indicates that the electrochemical stability of EC chromophores is intimately related to ECD performance.

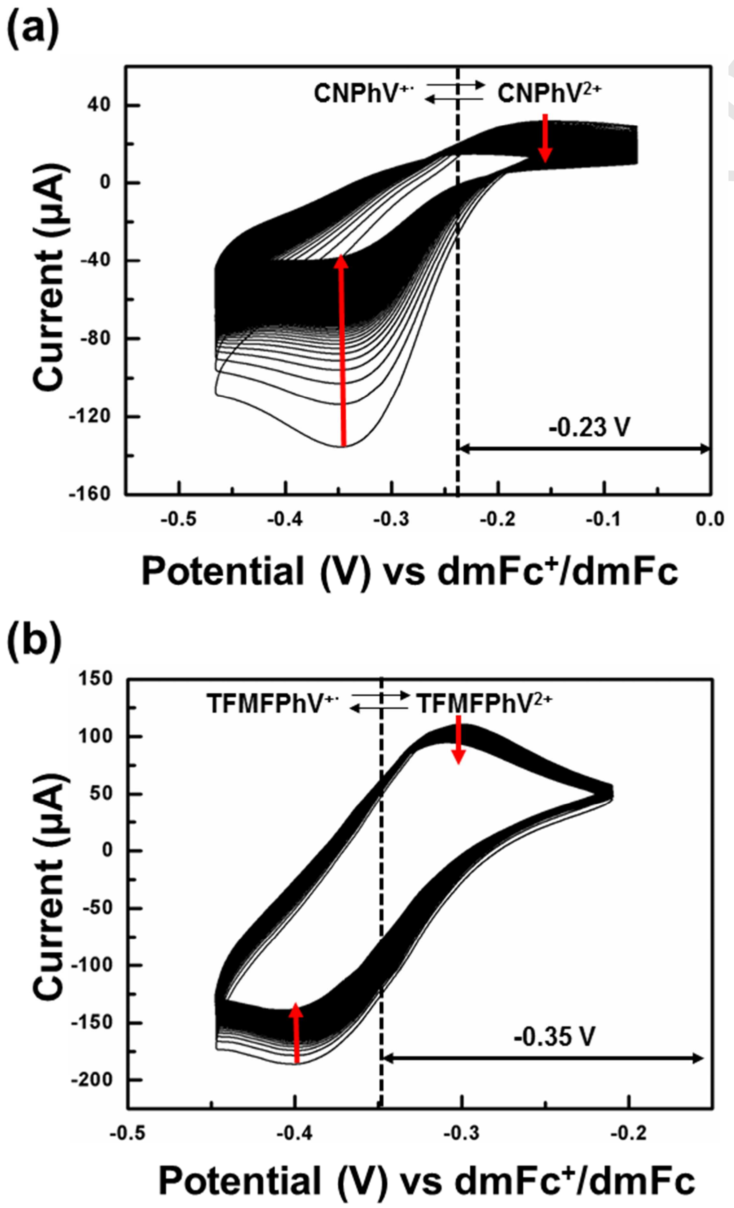


Fig. 5. Cyclic voltammograms (CVs) of EC gels containing (a) CNPhV^{2+} and (b) TFMFPhV^{2+} during 100 continuous voltage sweeps at a rate of 50 mV/s, in which a platinum disk, Ag wire, and ITO-coated glass were utilized as the working, reference, and counter electrodes, respectively.

4. Conclusion

We successfully developed a new EC material (TFMFPhV^{2+}) showing green-colored states. For comparative purposes, a typical EC chromophore exhibiting green color, CNPhV^{2+}, was chosen. Both devices based on the CNPhV^{2+} and TFMFPhV^{2+} exhibited a low-voltage operation characteristic; coloration occurred at –0.13 V and –0.20 V, respectively. Compared to the ECDs containing CNPhV^{2+}, the ECDs with TFMFPhV^{2+} showed higher color purity, faster response times, higher coloration efficiency, and improved operational stability. All these features were attributed to the better electrochemical stability of the TFMFPhV^{2+}. Overall, the results indicate the TFMFPhV^{2+} can be a promising EC candidate for ion gel-based electrochemical displays.

Acknowledgements

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Highlights

· A novel electrochromic material is designed and synthesized via the Zincke reaction.

· The ion gel-based ECDs with very simple configuration are successfully demonstrated.

· The performance of ECD containing $TFMFPhV^{2+}$ is compared to that with $CNPhV^{2+}$.

· The $TFMFPhV^{2+}$ shows better cyclic stability and higher color purity.