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Electrochromism of a Bipolar Reversible Redox-Active Ferrocene–Viologen Linked Ionic Liquid

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A ferrocene–viologen linked "bipolar" type redox-active ionic liquid ([FcC$_{11}$VC$_1$][TFSI]$_2$) was synthesized as an electrochromic (EC) material that functions without any other additives: solvent, supporting electrolyte and sacrificial agent. The efficiency of a prototype symmetrical EC cell was 70 cm^{2}C^{-1} at 1.0 V. The EC process was stable even after over 10000 potential cycles.

Electrochromic (EC) materials change their colour markedly and rapidly upon applying electrode potential or adding a redox agent.[1] The innovation of EC materials is of profound importance in the development of electronic devices such as electronic displays and optical sensors. Usually, liquid EC materials are multi-component solutions that fill the separated anodic and cathodic compartments of an EC cell. Realization of a single-component compartment-free liquid EC device is eagerly awaited. In such a device, the novel EC material should play the three roles simultaneously as reductant, oxidant, and electrolyte (ionic or electronic conductor).

Viologen derivatives are strongly blue ($\lambda \approx 600$ nm, $\varepsilon \approx 1.6\times10^4$ M^{-1}cm^{-1})[2] because of one electron reduction and are among the most frequently used cathodic EC materials. When the cathodic compartment of an EC cell is filled with a viologen solution, the anodic compartment should be filled with an electron donor to compensate the reaction charge. Viologens are often combined with ferrocene as an anodic material to compensate electrochemically reduction of viologens.[3] Nishikitani and coworkers used a ferrocene–viologen (Fc-V)-linked bipolar redox-active molecule to realize stable EC performance and they used the material in a compartment-free EC cell.[4] The V-Fc-linked molecule has been used in both liquid-phase and quasi-solid-state EC devices. However, these EC devices still consist of multi-component, because a liquid solvent or solid electrolyte is required. In liquid devices, the volatilization of liquid materials is an inevitable problem. In solid-state devices, we confront a difficulty in attaining effective electronic contacts between the solid electrolyte, EC material, and electrodes. To overcome such problems, we develop an ionic liquid (IL), a salt of a V-Fc-linked bipolar IL, as a single-component EC material.

ILs composed of cations and anions behave as not only a non-volatile solvent but also an electrolyte.[5] Functionalization of a constituent ion of an IL with a redox-active unit provides us with a redox-active ionic liquids (RAILs), a type of task-specific IL[6], as a solvent-free and supporting electrolyte-free electrochemically active material.[7–9] RAILs based on viologens[7] and ferrocenes[8] have been reported. For instance, we synthesized a viologen RAIL with two bis(trifluoromethane-sulfonyl)imide (TFSI) counter anions and explored its ionicity characteristics.[7j,k] Kavanagh and coworkers prepared a viologen IL bearing a trioctylphosphonium cation and investigated its EC behavior.[7h] However, this RAIL required dimethoxyacetophenone as an additive sacrificial agent.

The Fc-V-linked molecule remains cation unless the viologen unit becomes neutral (FcV^0 in Fig. 1a) by two-electron reduction. A bis(fluoroalkanesulfonyl)imide salt of the Fc-V-linked molecule should behave as a bipolar additive-free EC material. In the molecule, the V$^{+\bullet}$/V^{++} redox undergoes intense colour change and the Fc/Fc$^+$ redox couple drives counter electrode process (Fig. 1a). An electrolyte-free EC material has already been constructed that consists of a graphene quantum dot–viologen composite system.[10] However, bipolar RAILs in which electron acceptor and donor units are combined in one molecule have not yet been reported. In this communication, we describe the synthesis of a Fc-V-linked bipolar RAIL, its electrochemistry, and additive-free EC performance in a simple two-electrode EC cell without a compartment separation.

The synthesis of Fc-V-linked RAIL was described in ESI†. X-ray fluorescence and mass spectrometry analyses revealed that the Fc-V linked RAIL ([FcC$_{11}$VC$_1$][TFSI]$_2$) did not contain Br$^-$ or I$^-$. The melting point of [FcC$_{11}$VC$_1$][TFSI]$_2$ determined by differential scanning calorimetry was 52 °C (see Fig. S1, ESI†). Once melted [FcC$_{11}$VC$_1$][TFSI]$_2$ remained in a viscous liquid state even at temperatures below its melting point. Long-lived

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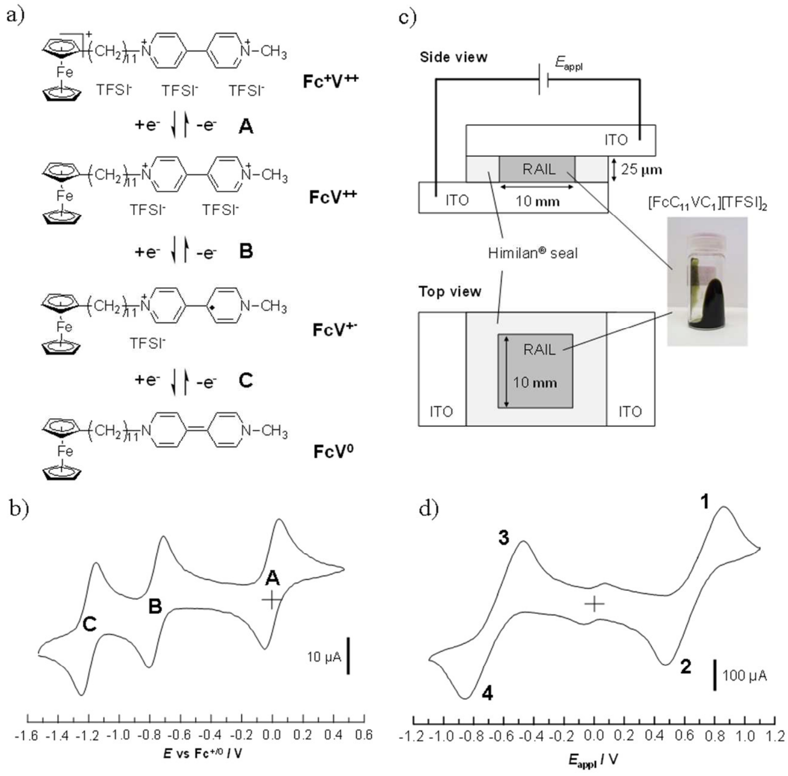

Fig.1 a) Redox behavior of $[FcC_{11}VC_1][TFSI]_2$. X^- stands for TFSI anion. b) Cyclic voltammogram of 1.0 mM $[FcC_{11}VC_1][TFSI]_2$ in acetonitrile at room temperature with a three-electrode configuration. Scan rate is 100 mV s^{-1}. c) Structure of the ITO two-electrode electrochromic cell. d) Cyclic voltammogram of neat $[FcC_{11}VC_1][TFSI]_2$ in the two-electrode cell at room temperature. Scan rate is 20 mV s^{-1}.

supercooled liquid states have been found for many ILs[11] including previously reported viologen type RAIL ($[C_4VC_7][TFSI]_2$) below its melting point (52 °C).[7j]. Because the viscous liquid state of $[FcC_{11}VC_1][TFSI]_2$ remained for several months even in a refrigerator at 4 °C. We can handle $[FcC_{11}VC_1][TFSI]_2$ as an IL at room temperature lower than the melting point.

Cyclic voltammograms (CVs) of 1.0 mM $[FcC_{11}VC_1][TFSI]_2$ in acetonitrile containing 0.1 M potassium TFSI as the supporting electrolyte were measured with a three-electrode configuration (see ESI† for detail condition). Fig. 1b shows the CV obtained at a sweep rate of 0.10 V・s^{-1}. Three consecutive one-electron transfer reactions of $[FcC_{11}VC_1][TFSI]_2$ were observed as three sets of quasi-reversible redox waves with midpoint potentials at $E_{m,A}$ = 0 V (standard of the potential), $E_{m,B}$ = –0.752 V, and $E_{m,C}$ = –1.200 V, corresponding to $Fc^{+/0}$ (peak A in Fig. 1a), $V^{++/+\cdot}$ (peak B), and $V^{+\cdot/0}$ (peak C) in this order. The peak separations of all the three redox couples were approximately 0.090 V at 0.10 V・s^{-1}. The position of $E_{m,B}$ was approximately 0.080 V more positive than the formal potential of a reported Fc-V-linked compound;[4] the difference is attributed to the different counter anions of the two materials.

The CV measurement of neat $[FcC_{11}VC_1][TFSI]_2$ melt was carried out using a symmetrical two-electrode EC cell consisting of two indium tin oxide (ITO) glass substrates with the electrode area defined using Himilan® thermal fusion bonding film (DuPont™). The separation of the two parallel ITO substrates was 25 μm (Fig. 1c). Fig. 1d shows the CV of neat $[FcC_{11}VC_1][TFSI]_2$ without any additives. Four peaks were observed at ±0.860 and ±0.474 V. The midpoint potential between peak 1 and 2 was 0.667 V and that between peak 3 and 4 was −0.667 V, corresponding approximately to the potential difference between the oxidation of the Fc unit (0 V) and the first reduction potential of the V^{++} unit (−0.752 V), as illustrated in Fig. 1b. The peak separation for both couple was 0.386 V at 20 mV・s^{-1}, which is much greater than the theoretical separation for reversible one-electron redox electrochemistry, presumably because of the resistance between the two ITO electrodes originating from the high viscosity of $[FcC_{11}VC_1][TFSI]_2$.

A difference absorption spectrum of the EC cell containing only neat $[FcC_{11}VC_1][TFSI]_2$ electrolyzed at 0.7 V is depicted in Fig. 2a, and that obtained following electrolysis at 1.0 V is displayed in Fig 2d. The voltage of 0.7 V is under the midpoint potential difference ($|E_{m,B}$ - $E_{m,A}|$ in Fig. 1b), whereas the voltage of 1.0 V is over the difference (see Fig. 1d). Note that the reference absorption spectrum, which was subtracted from the absorption spectra at constant potentials after the potential steps from 0 V, was obtained at 0 V. In both figures, two bands were observed at 550 and 880 nm, and the absorbance difference (ΔAbs) of the bands increased with the electrolysis time. These two bands are assigned to the $V^{+\bullet}$ dimer.[2] The peak maxima of the bands were at longer wavelength compared with those of the $V^{+\bullet}$ dimers reported previously.[3a,7h,10,12] This difference would be caused by the different concentrations of viologen and dielectric surroundings in the EC cells. A shoulder was also observed at 600 nm, corresponding to the $V^{+\bullet}$ monomer.[2] Fig. 2b shows the time course of ΔAbs at 550, 600, and 880 nm for neat $[FcC_{11}VC_1][TFSI]_2$ electrolyzed at 0.7 V. In Fig. 2b, the increases in ΔAbs_{550} and ΔAbs_{600} were almost the same until over 10 s, whereas a longer electrolysis time resulted in a faster increase of ΔAbs_{550} than that of ΔAbs_{600}, suggesting the acceleration of the dimerization of the $V^{+\bullet}$ species. This acceleration is attributable to the high concentration of $[FcC_{11}VC_1][TFSI]_2$ (1–2 M for a viologen IL[7j,k]) and its high viscosity (several Pa・s for a viologen IL[7j] around room temperature). The time courses of ΔAbs and electric charge (Q) for the electrolysis of neat $[FcC_{11}VC_1][TFSI]_2$ at 0.7 V both took 100 s to reach diffusion-controlled linear regions with respect to $t^{1/2}$ (Fig. 3b and c, respectively), suggesting that a time period of 100 s is needed to reach local redox equilibria at both electrode/solution

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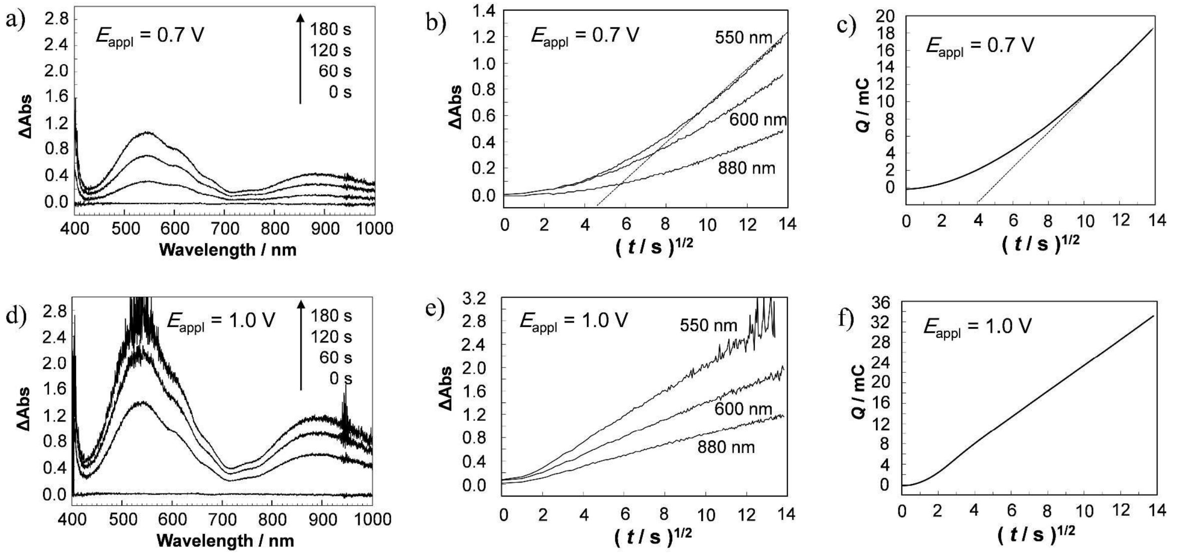

Fig.2 Electrolysis of neat $[FcC_{11}VC_1][TFSI]_2$. a, d) Absorption spectra, b, e) time courses of the absorbance at 550, 600 and 880 nm, and c, f) time course of the electric charges at E_{appl} = 0.7 (a, b, c) and 1.0 V (d, e, f). The dotted lines in b) and c) show the linear regions of ΔAbs_{550} and Q as visual guides.

interfaces, which is represented by $[V^{++}]_c[Fc]_a/[V^{+\bullet}]_c[Fc^{+\bullet}]_a$ = constant, where the subscript "*c*" and "*a*" indicates the concentration at the cathode and anode surface. After the potential has been applied for 100 s, infinite planar diffusion processes of the redox species control the redox reaction at both electrodes. In contrast, both ΔAbs and *Q* of neat $[FcC_{11}VC_1][TFSI]_2$ electrolyzed at 1.0 V reached the region linear to $t^{1/2}$ in 1 s (Fig. 2e and 2f, respectively), indicating that totally diffusion-controlled situations were established. In other words, the maximum rate of EC coloration controlled by diffusion is attained in a very short time when a voltage ca. 0.3 V greater than the midpoint voltage (0.7 V) is applied.

Here we should mention two intrinsic drawbacks of the Fc-V-linked IL EC device. First, the EC device is weakly coloured even before the potential application, because the ferrocene unit is only a weak brown ($\lambda \approx 440$ nm, $\varepsilon \approx 1\times10^2$ $M^{-1}cm^{-1}$)[12]. Second, theoretically only a quarter of the total Fc-V-linked molecules are coloured, and their colour fades through the charge recombination between $V^{+\bullet}$ and $Fc^{+\bullet}$ unless a potential is continuously applied. In other words, continuous electrolysis is needed to keep the coloured state of this device. Nevertheless, the former drawback can be overcome by decreasing the thickness of the Fc-V liquid phase. Meanwhile, the latter drawback may be avoided by restricting the electrolysis time to shorter than several minutes to prevent the mutual contact of the edges of the diffusion layers of $V^{+\bullet}$ and $Fc^{+\bullet}$. In fact, the charge recombination reaction, which should result in the saturation of absorbance, was not observed experimentally in the first 100 s (see Fig. 2b and 2e).

Fig. 3 shows the response of the EC cell to a repeated potential-step electrolysis between 0 and 1.0 V every 30 s. Before electrolysis, the colour of the EC cell was light brown, originating from $[FcC_{11}VC_1][TFSI]_2$ (Fig. 3a). The colour contrast of the device responded clearly to the potential cycles. At 1.0 V, the device turned dark purple, mainly originating from the $V^{+\bullet}$ dimer species. Subsequent holding of the potential at 0.0 V resulted in a rapid decrease of the colour contrast. The gradual decrease in the recovery of the contrast was attributed to the residual coloured species ($V^{+\bullet}$) away from the ITO electrode surface. Colour contrast between 0 V and 1 V decreased with potential step cycles. The complete decolouration of this EC cell can be observed by a long enough hold time at 0 V. This issue also should be overcome by decreasing the thickness of the Fc-V liquid phase to achieve more rapid decolouration. The time course of the initial potential cycles is shown in Fig. S2 (ESI†). However, the linear relationship between *Q* and ΔAbs

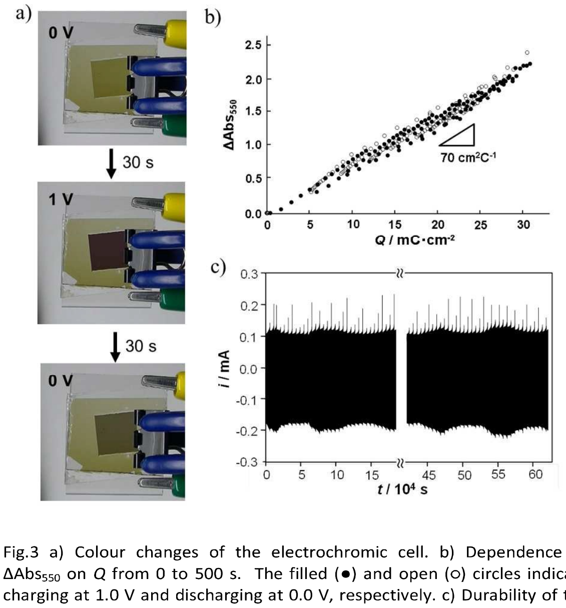

Fig.3 a) Colour changes of the electrochromic cell. b) Dependence of ΔAbs_{550} on *Q* from 0 to 500 s. The filled (●) and open (○) circles indicate charging at 1.0 V and discharging at 0.0 V, respectively. c) Durability of the electrochromic cell (10000 cycles) during applied potential step (E_{appl} = 0.0 and 1.0 V) cycles every 30 s.

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(Fig. 3b) indicates that the residual coloured species can be recovered by holding the potential for a longer period. The coloration efficiency (η = ΔAbs(λ)/ΔQ, slope of Fig. 3b) of this EC cell at 550 nm was 70 cm^2C^{-1} at 1.0 V. This value is the almost same as that obtained for a ion-gel EC cell consisting of viologen (78 cm^2C^{-1} at 0.80 V and 605 nm).[13] On the other hand, our value is larger than that of a solid-state EC cell consisting of viologen-type IL (10.7 cm^2C^{-1} at 0.84 V and 610 nm)[7h] and polymeric ionic liquid consisting viologen system (38.6 cm^2C^{-1} at 1.2 V and 605 nm)[3c] but smaller than those of a viologen-modified TiO_2 EC cell (270 cm^2C^{-1} at 1.2 V and 608 nm)[14] and ZnO nanowire EC cell (196 cm^2C^{-1} at 2.0 V and 608 nm)[15]. The EC cell in the present work, while exhibiting middle-ranking efficiency, possesses a simple structure (ITO/Fc-V/ITO) without the need for any additives or compartments. Remarkably, the EC cell was durable for more than 10000 alternating potential cycles without any degradation (Fig. 3c). Therefore, $[FcC_{11}VC_1][TFSI]_2$ is an attractive material for EC devices.

Conclusions

In conclusion, we proposed an electrochromic RAIL, ferrocene-viologen linked ionic liquid ($[FcC_{11}VC_1][TFSI]_2$), for a simple EC cell without any other additives: solvent, supporting electrolyte, and sacrificial agent. We synthesized $[FcC_{11}VC_1][TFSI]_2$ and demonstrated that it functions as a single-component liquid EC material in a compartment-free two-electrode EC cell. As the EC device, we built a prototype symmetrical, optically-transparent cell. Remarkable properties of $[FcC_{11}VC_1][TFSI]_2$ as an EC material include: (i) its non-volatile properties allowed construction of a solvent- and electrolyte-free electrochemical system; (ii) the EC cell containing $[FcC_{11}VC_1][TFSI]_2$ was durable for at least 10000 potential cycles without any degradation. These results suggest that V-Fc-linked RAILs are competent candidate EC materials. At the present stage, however, the EC cell did not show the good contrast after several dozen potential step cycles because of the slow alternate response of the EC cell. Recently, viologens have exerted the potential of energy storage because of their high energy density in aqueous solution systems.[16] The energy density should depend on the concentration of viologens. Viologen-based RAILs contains a high concentration reaching *ca*. 1.5 M of viologen. Therefore, Fc-V-linked RAILs can be also used for energy storage in electrolyte- and solvent-free systems. To achieve a more rapid response and clear contrast, the viscosity of Fc-V-linked RAILs needs to be lowered and the EC cell system should be optimized. These investigations are currently in progress in our laboratory.

Notes and references

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