Electronic Supplementary Information

Remarkable Effect of Bromide Ion upon Two-Dimensional Faradaic Phase Transition of Dibenzyl Viologen on an HOPG Electrode Surface: Emergence of Two-Step Transition

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Cyclic voltammograms of dBV in KF and KI aqueous solutions

Typical CVs for dBV at an HOPG electrode in 0.30 M KF and 0.30 M KI solutions are shown in Fig. S1.

In KF solution (Fig. S1-a), dBV exhibited a single-step phase transition around -295 mV. The amounts of $dBV^{\bullet+}$ formed through reduction was obtained as being 2.2×10^{-10} mol cm^{-2} from the CV. This value is consistent with the coverage of 2D condensed monolayer $dBV^{\bullet+}$ on an HOPG electrode surface in KCl solution.

In KI solution, CVs of dBV was elusive and varied sample-to-sample. One of the typical CVs that exhibited two cathodic peaks (Pc1 and Pc2) and two anodic peaks (Pa1 and Pa2) is shown in Fig. S1-b. For the two couples of Pc1-Pa1 and Pc2-Pa2, Γ (Pc1) = Γ (Pa1) = 0.8 × 10^{-10} mol cm^{-2} and Γ (Pc2) = Γ (Pa2) = 0.3 × 10^{-10} mol cm^{-2} were obtained. The sum, 1.2 × 10^{-10} mol cm^{-2}, much less than those obtained in KF, KCl, and KBr (0.30 M) solutions, was in line with one monolayer formation of $dBV^{\bullet+}$ flat-lying adsorption orientation with a *face-on* configuration. Note that this CV was short-lived. In a short time even under open-circuit condition, emergence a number of shoulders and small peaks, peak broadening and decay of Γ were observed.
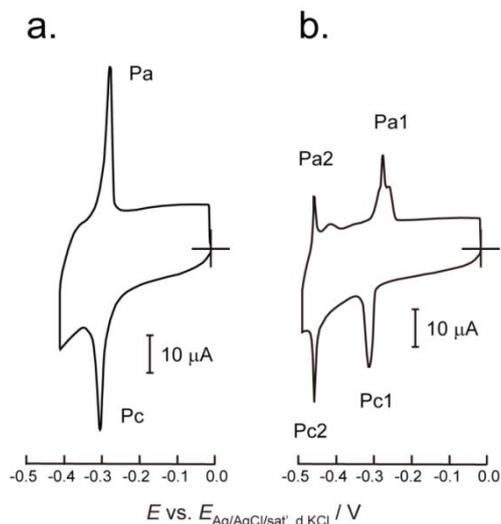
Fig. S1 Cyclic voltammograms for an HOPG electrode in the H-M configuration ($A = 1.44$ cm^2) with 0.1 mM dBV^{2+} 2Br$^-$ + 0.30 M KF (a) or KI (b) solutions at $v = 50$ mV s^{-1}.

Cyclic voltammograms (CVs) for dBV^{2+} 2Br$^-$ free of Cl$^-$ solution

Typical CVs for various concentrations of KBr (C_{KBr}) at $v = 5$ mV s^{-1} are shown in Fig. S2.

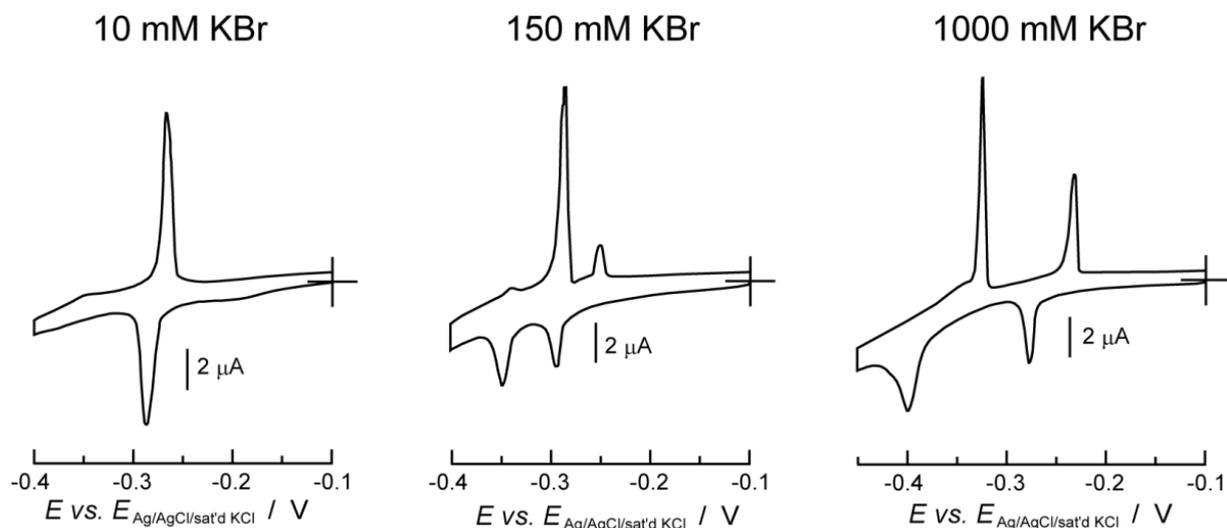**Fig. S2** Collection of cyclic voltammograms for an HOPG electrode ($A = 1.44$ cm^2) at $v = 5$ mV s^{-1} in the H-M configuration with 0.1 mM dBV^{2+} 2Br$^-$ containing 10 mM, 150 mM, or 1000 mM KBr solutions.

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UV-Vis absorption spectrum of dBV in aqueous solution

Figure S3 shows the absorption spectra of $dBV^{\bullet+}$ in phosphate buffer solution.   In the buffered aqueous solution (pH = 7.0) of 1.0 mM dBV^{2+} $2Br^-$ + 0.10 M KBr, added was approximately 5 equivalents of sodium hydrosulfite powder reductant to obtain the sample solution.   To prevent $dBV^{\bullet+}$ from dimerization, the sample was heated around 50 ºC.   The color of $dBV^{\bullet+}$ solution was blue while warm (dashed line), whereas it was violet at room temperature (solid line).   The solute of warm solution is monomer-$dBV^{\bullet+}$ (blue), while that in the cool solution is exclusively of dimer-$dBV^{\bullet+}$ (violet).   Such a highly temperature dependent monomer-dimer equilibrium is a common phenomenon for the several $V^{\bullet+}$ in aqueous solution [1].
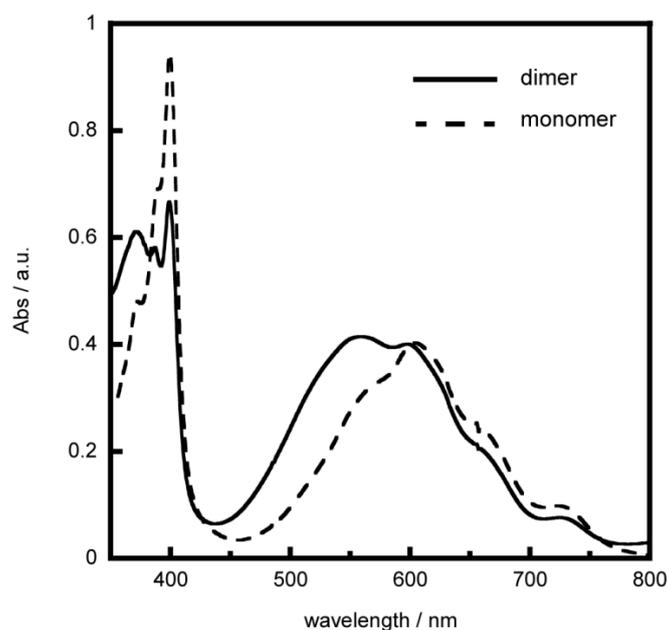

Figure S3.   Absorption spectra of the aqueous solutions of $dBV^{\bullet+}$ dimer (solid line) and $dBV^{\bullet+}$ monomer (dashed line) forms.

Simulation for electroreflectance spectrum

In all the simulations of electroreflectance spectra (ERS), the protocol of simulation was the same as described in our previous paper [2,3].

Figure S4 shows the simulated ERS using solution absorption spectrum of dBV$^{\bullet+}$. As for the solid line, the state at the positive side of the potential modulation is an HOPG surface fully covered with Phase-OX and that at the negative side is an HOPG surface fully covered with a monolayer of dBV$^{\bullet+}$-dimer.

As for the dashed line, the state at the negative side is an HOPG surface covered with a monolayer of dBV$^{\bullet+}$-monomer. For both two spectra, flat-lying longitudinal bipyridinium axis of dBV$^{\bullet+}$ on the HOPG surface is assumed.

Figure S5 shows the experimental ERS at HOPG/dBV-KCl solution (solid lines) and simulated ERS using solution absorption spectrum of dBV$^{\bullet+}$ in dimer forms (dashed line). The real part of the latter is the same as solid line in Fig. S4 so that the state at the positive side of the potential modulation is an HOPG surface fully covered with Phase-OX and that at the negative side is an HOPG surface fully covered with a monolayer of dBV$^{\bullet+}$-dimer. The presumed bipyridinum orientation was the same as above.

Figure S6 shows two simulated ERS.

As for the solid line, from the reflection spectrum of 0.30 ML submonolayer of dBV$^{\bullet+}$ monomer (Phase-M) representing the positive side of the potential modulation, reflectance spectrum of 1.0 ML of dBV$^{\bullet+}$ dimer (Phase-Red) representing the negative side of the potential modulation was subtracted. In order to realize the coverage ratio of 1:3, the reflection spectrum of Phase-Red was multiplied by 3.0 before subtraction.

As for the dashed line, the reflectance spectrum of 0.30 ML submonolayer of dBV$^{\bullet+}$ monomer was used again for Phase-M, but for Phase-Red, 1.0 ML of dBV$^{\bullet+}$ monomer (Phase-Red) representing the negative side of the potential modulation was used.
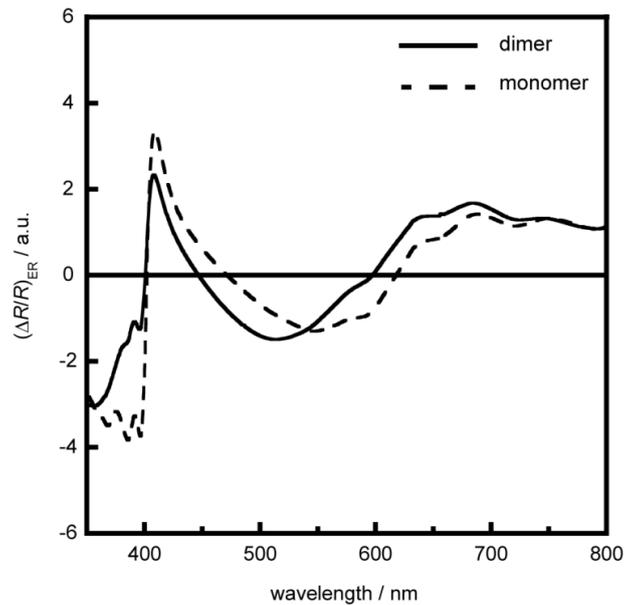
Figure S4. Simulated ERS (real part) using solution absorption spectra of dBV$^{\bullet+}$, both in dimer forms (solid line) and in monomer forms (dashed line). The interconversion of the state is between Phase-Ox (at the positive potential side) and dBV$^{\bullet+}$ adlayer (at negative potential side). For details, see text.
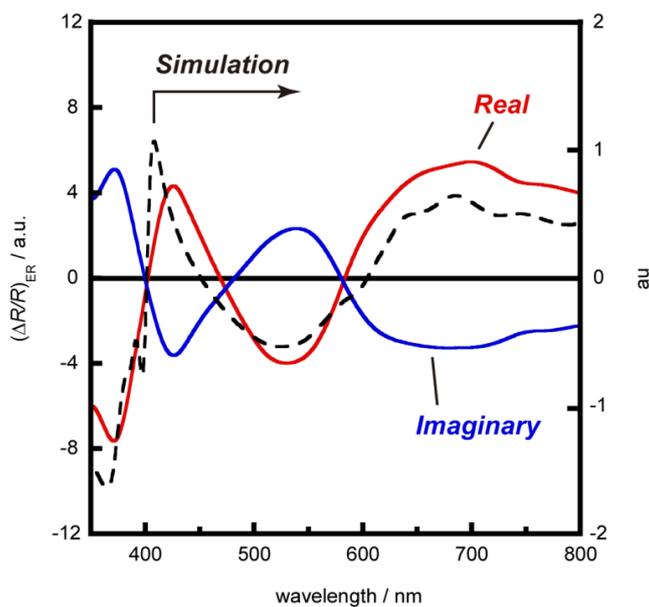

Figure S5. Experimental ERS at HOPG/dBV-KCl solution (solid line) and simulated ERS using solution absorption spectrum of dBV$^{\bullet+}$ dimer forms (dashed line). The simulated one is the same as solid line in Fig.S4.
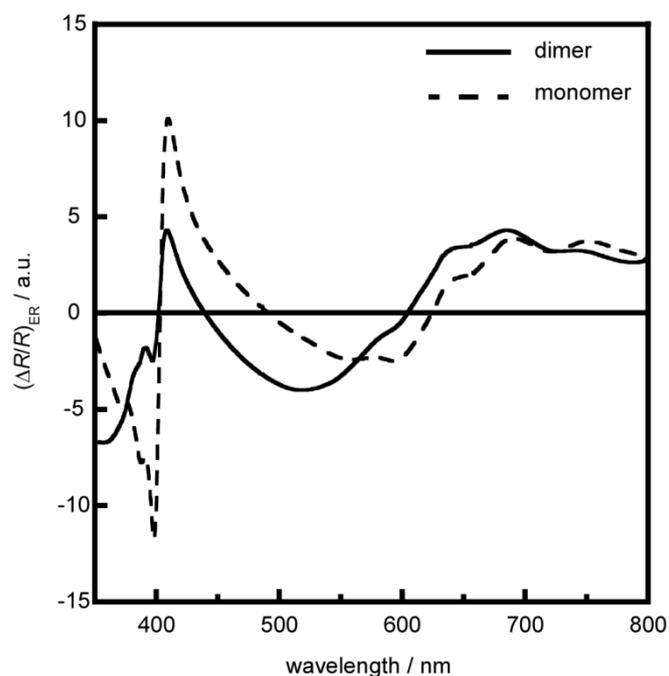
Figure S6. Solid line: simulated ERS (real part) obtained by subtraction of the reflectance spectrum of 1.0 ML of dBV$^{\bullet+}$ dimer (Phase-Red) from 0.30 ML of dBV$^{\bullet+}$ monomer (Phase-M). Dashed line: simulated ERS (real part) obtained by subtraction of the reflectance spectrum of 1.0 ML of dBV$^{\bullet+}$ monomer (Phase-Red) from 0.30 ML of dBV$^{\bullet+}$ monomer (Phase-M).

Reference

[1] P. M. S. Monk, The Radical Cation: Dimer Formation, in: The Viologens: Physicochemical Properties, Synthesis, and Applications of the Salts of 4,4'-bipyridine, John Wiley & Sons, Chichester, England, 1989, pp. 115-131.

[2] T. Sagara, UV-visible Reflectance Spectroscopy of Thin Organic Films at Electrode Surfaces in: R. C. Alkire, D. M. Kolb, J. Lipkowski, P. N. Ross (Eds.) Advances in Electrochemical Science and Engineering, vol. 9, Wiley-VCH, Weinheim, 2006, pp. 47-95.

[3] T. Sagara, S. Tanaka, Y. Fukuoka, N. Nakashima, Study of the voltammetric spike response of heptyl viologen at a HOPG electrode horizontally touched to a gas/heptyl viologen aqueous solution interface, Langmuir 17 (2001) 1620-1629.