

Supporting information for:

Interfacial Structure at the Quaternary
Ammonium-Based Ionic Liquids|Gold
Electrode Interface Probed by
Surface-Enhanced Infrared Absorption
Spectroscopy: Anion Dependence of the
Cationic Behavior

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S1 SEIRA spectra of vibrational bands for anions

The assignment of the bands are listed in Table S1. The SEIRA spectra for the anion bands at the Au interface of the three IIs in the present study are shown in Fig.S1 ($[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$), S2 ($[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$), and S3 ($[\text{N}_{441}^+][\text{C}_1\text{C}_1\text{N}^-]$).

Table S1: Assignment of the vibration modes for anions.

Symbol	Mode	Peak position (cm^{-1})	Integ. region (cm^{-1})
$\nu_{\text{as}}(\text{SO})$	asym. stretching of SO	1350-1353	1287-1390
$\nu(\text{CF})$	sym./asym. stretching of CF_2/CF_3	1186-1189 ^a	1255-1165

^a For $\text{C}_1\text{C}_1\text{N}^-$. Several overlapping peaks are discernible for $\text{C}_4\text{C}_4\text{N}^-$.

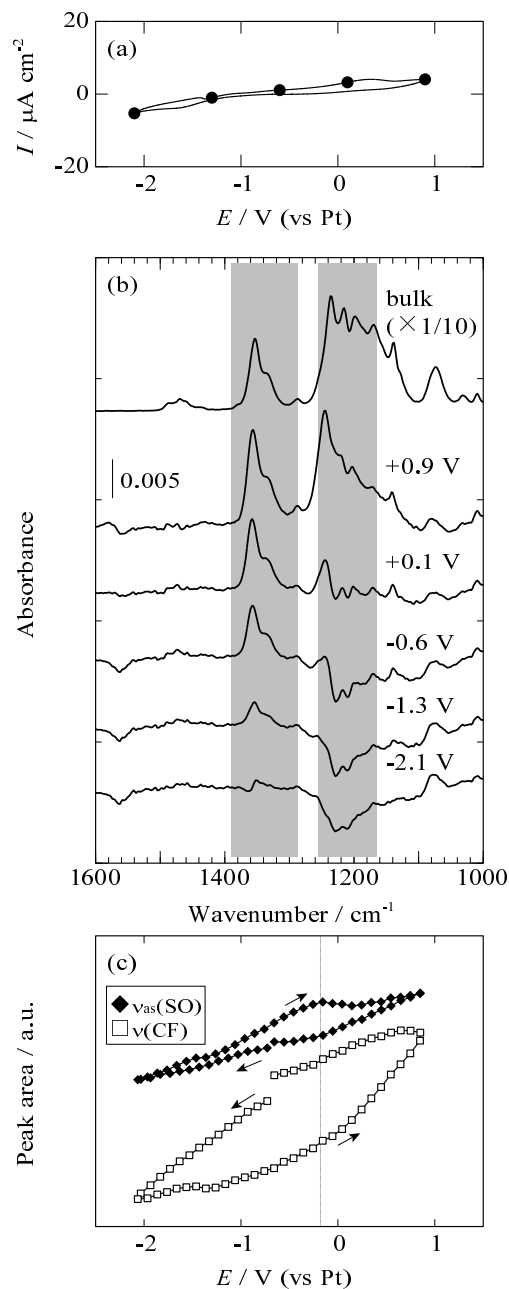


Figure S1: (a) Cyclic voltammogram at 2 mV s^{-1} and (b) SEIRA spectra at the $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]|\text{Au}$ interface and IR spectrum for the bulk $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]$. The SEIRA spectra were recorded at the potentials shown in (a) as solid circles during the CV. Reference spectrum for the SEIRAS was taken before the potential scan at the initial potential, -0.6 V . (c) voltabsorptograms at the $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]|\text{Au}$ interface for the SO and CF stretching vibrational bands: $\nu_{\text{as}}(\text{SO})$ (solid diamond) and $\nu(\text{CF})$ (open square). The negative peak at 1580 cm^{-1} in (b) would be due to trace impurity.

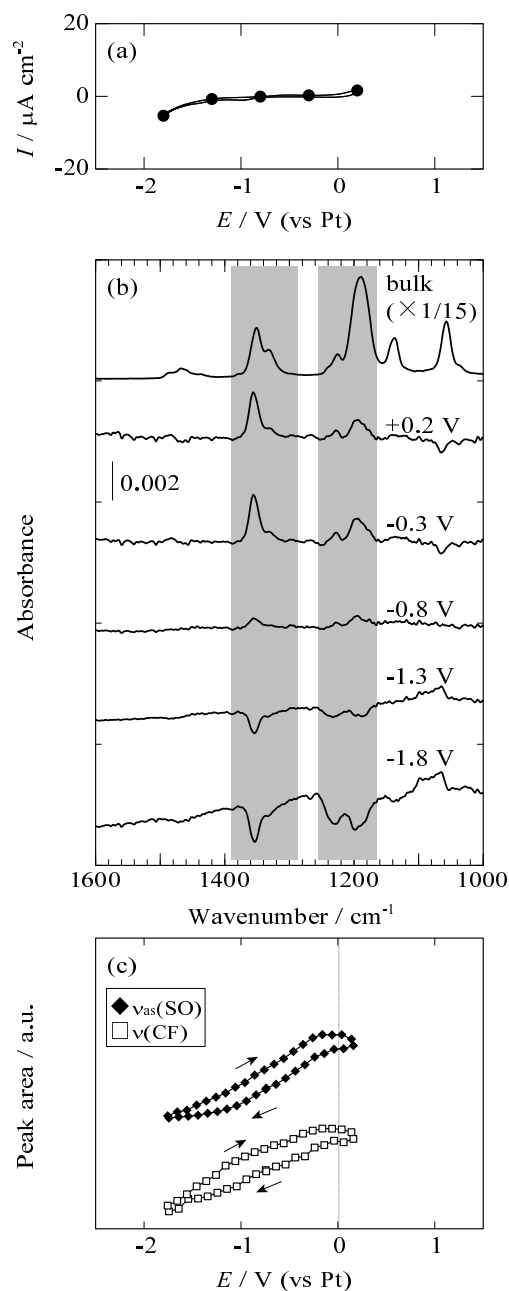


Figure S2: (a) Cyclic voltammogram at 2 mV s^{-1} and (b) SEIRA spectra at the $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface and IR spectrum for the bulk $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]$. The SEIRA spectra were recorded at the potentials shown in (a) as solid circles during the CV. Reference spectrum for the SEIRAS was taken before the potential scan at the initial potential, -0.6 V . (c) voltabsorptograms at the $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface for the SO and CF stretching vibrational bands: $\nu_{\text{as}}(\text{SO})$ (solid diamond) and $\nu(\text{CF})$ (open square).

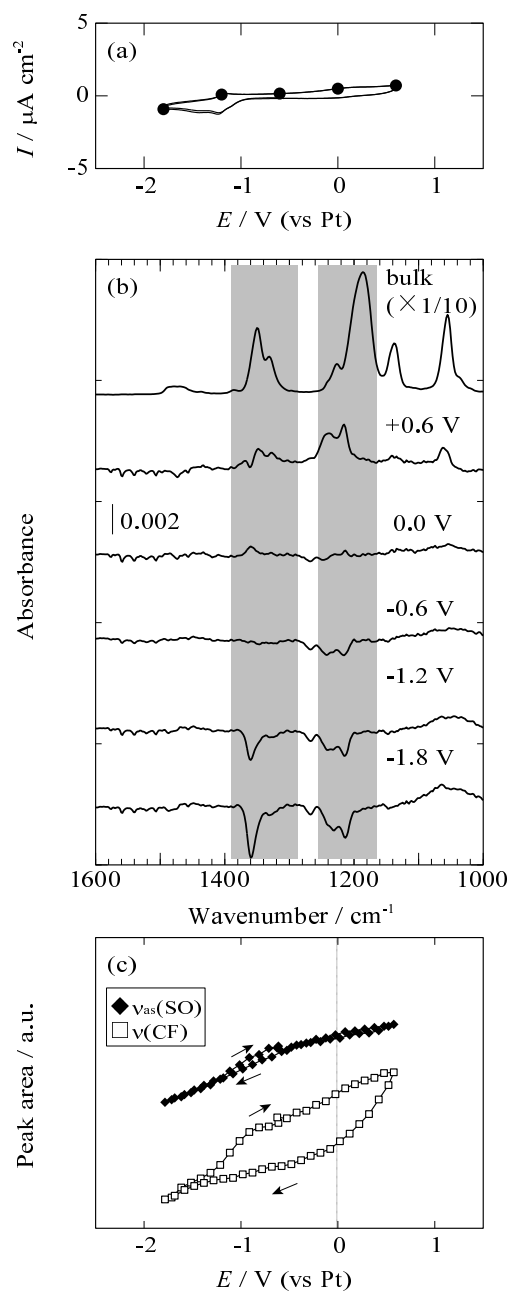


Figure S3: (a) Cyclic voltammogram at 2 mV s^{-1} and (b) SEIRA spectra at the $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface and IR spectrum for the bulk $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]$. The SEIRA spectra were recorded at the potentials shown in (a) as solid circles during the CV. Reference spectrum for the SEIRAS was taken before the potential scan at the initial potential, -0.6 V . (c) voltabsorptograms at the $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface for the SO and CF stretching vibrational bands: $\nu_{\text{as}}(\text{SO})$ (solid diamond) and $\nu(\text{CF})$ (open square). The strong band at 1190 cm^{-1} in the bulk spectrum in (b) is shifted and observed at 1213 cm^{-1} in the SEIRA spectra, owing to the large dispersion of the refractive index.^{S1-S3}

S2 Voltabsorptograms for $[\text{N}_{8881}^+][\text{C}_2\text{C}_2\text{N}^-]$ and $[\text{N}_{8881}^+][\text{C}_0\text{C}_0\text{N}^-]$

In this section, voltabsorptograms for the cation bands and anion bands at the gold interface of $[\text{N}_{8881}^+][\text{C}_2\text{C}_2\text{N}^-]$ and $[\text{N}_{8881}^+][\text{C}_0\text{C}_0\text{N}^-]$ are shown in Fig.S4 and Fig.S5, respectively.

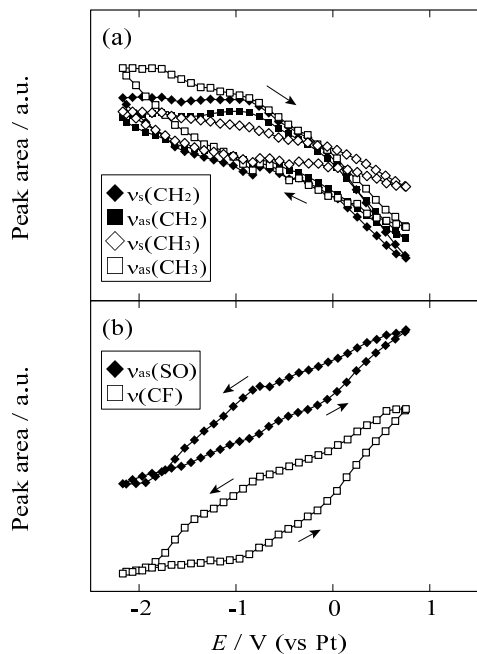


Figure S4: Voltabsorptograms at the $[\text{N}_{8881}^+][\text{C}_2\text{C}_2\text{N}^-]|\text{Au}$ interface (a) for the four CH stretching vibrational bands: $\nu_s(\text{CH}_2)$ (solid diamond), $\nu_s(\text{CH}_3)$ (open diamond), $\nu_{as}(\text{CH}_2)$ (solid square), and $\nu_{as}(\text{CH}_3)$ (open square) and (b) for the SO and CF stretching vibrational bands: $\nu_{as}(\text{SO})$ (solid diamond) and $\nu(\text{CF})$ (open square). Scan rate: 2 mV s^{-1} .

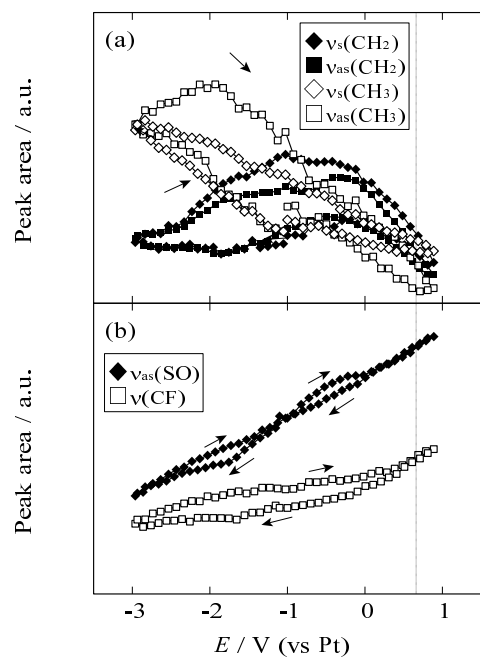


Figure S5: Voltabsorptograms at the $[\text{N}_{8881}^+][\text{C}_0\text{C}_0\text{N}^-]|\text{Au}$ interface (a) for the four CH stretching vibrational bands: $\nu_s(\text{CH}_2)$ (solid diamond), $\nu_s(\text{CH}_3)$ (open diamond), $\nu_{as}(\text{CH}_2)$ (solid square), and $\nu_{as}(\text{CH}_3)$ (open square) and (b) for the SO and CF stretching vibrational bands: $\nu_{as}(\text{SO})$ (solid diamond) and $\nu(\text{CF})$ (open square). Scan rate: 2 mV s^{-1} .

S3 A model for the voltabsorptogram at IL|electrode interfaces

The model used for the voltabsorptogram simulation will be described in this section. In SEIRAS, the molecules closer to the electrode surface receive higher enhancement for the absorption. The distance dependence of the enhancement is steep and the enhancement becomes substantially zero (no absorption) when the molecule is several nm apart from the electrode.^{S4,S5} The absorbance A of a vibrational mode in an ion i ($i = +, -$) of IL may be represented as,

$$A = P \int_0^\infty dx c_i(x) G(x) \quad (\text{S-1})$$

where x is a coordinate along the surface normal of the IL|electrode interface with $x = 0$ for the electrode surface and $x > 0$ for the IL phase, $c_i(x)$ is the local concentration of the ion i , and $G(x)$ is the enhancement factor.^{S5} Note that P is a parameter composed of variables other than $c_i(x)$ and $G(x)$, and that we neglect the effect of the ionic orientation (the direction of the transition dipole moment of the vibrational mode). In an electromagnetic model for SEIRAS, rough electrode film was reasonably modeled as an assembly of metal island and A is suggested to be proportional to the distance of a molecule from the metal island center powered by -6 . So G can be written as,

$$G(x) = \frac{r_{\text{metal}}^6}{(x + r_{\text{metal}})^6} \quad (\text{S-2})$$

where r_{metal} is the radius of the metal island, and $G(x)$ is normalized to fulfill $G(0) = 1$ and $G(\infty) = 0$. In the present calculation we set $r_{\text{metal}} = 5$ nm taken from previous discussion.^{S4}

A voltabsorptogram is the potential dependence of A and the potential dependence comes from $c_i(x)$ ($G(x)$ is related to the electric field at frequencies of infrared light, not to the static and electrochemical electric field). To calculate $c_i(x)$ and its potential-dependence, we per-

formed a model calculation for the electrical double layer (EDL) at the IL|electrode interface. We adopted the EDL model proposed by Oldham,^{S6} instead of the Gouy-Chapman-Stern model used for the EDL for conventional electrolyte solutions, to incorporate the excluded volume effect between IL ions. A possible concern of the Oldham model is that the model does incorporate lattice saturation effect, taking into account the excluded volume between ions in EDL, but does not incorporate overscreening effect in which not counter-ions but co-ions become rich in the second ionic layer. This imperfection may cause a change in the slope of the model voltabsorptogram, however, the model voltabsorptogram will keep the behavior semi-quantitatively.

We define the potential at the IL|electrode interfaces as $\phi(q, x)$, with a reference that $\phi(q, \infty) = 0$, where q is the surface charge density on the electrode surface. The relationship of the potential with the experimental potential, $E(q)$, is,

$$\phi(q, 0) \equiv \phi_0(q) = E(q) - E_{pzc} \quad (\text{S-3})$$

where E_{pzc} is the potential of zero charge for the IL|electrode interface evaluated using the immersion method. Note that we neglect any specific adsorption because we have no evidence of the existence from the measured CVs.

The potential profile can be represented as an inverse function, i.e., $x(\phi, q)$, with the decomposition to two parts (diffuse layer and inner layer).^{S6}

$$x(\phi, q) = \begin{cases} d_2 - \text{sgn}(q)\kappa^{-1} \int_{\phi_2(q)}^{\phi} d\left(\frac{F\phi'}{RT}\right) \frac{1}{\sqrt{2 \ln \left[\cosh \left(\nu \frac{F\phi'}{RT} \right) \right]}} & (x \geq d_2, \text{diffuse layer}) \\ d_2 \frac{\phi - \phi_0(q)}{\phi_2(q) - \phi_0(q)} & (0 \leq x \leq d_2, \text{inner layer}) \end{cases} \quad (\text{S-4})$$

where $\phi_0(q) = \phi(q, 0)$, $\phi_2(q) = \phi(q, d_2)$, $\kappa^{-1} = \sqrt{\frac{RT\epsilon\epsilon_0}{2F^2c_0}}$ is the Debye length and sgn is the sign function. For the definition of the other variables, see Table S2.

The x dependence of the concentrations for ion i, $c_i(x)$ is obtained again using ϕ as a

Table S2: Parameters in the EDL calculation.

Symbol	Definition	Value	Unit
ϵ	Relative permittivity in IL	10	—
c_0	Ionic concentration in IL bulk	1350 ^a	mol m ⁻³
d_2	Inner layer thickness in IL	5	Å
ν	Absolute value of charge number for ions	1	—
T	Absolute temperature	298.15	K
R	Gas constant	8.314	J K ⁻¹ mol ⁻¹
F	Faraday constant	96485	C mol ⁻¹
ϵ_0	Vacuum permittivity	8.8542	F m ⁻¹

^aCalculated using the molecular weight and the density of [N₈₈₁⁺][C₄C₄N⁻].

parameter, as follows,

$$c_i(x(\phi, q)) = c_0 \frac{\exp\left(-\text{sgn}(\nu_i)\nu_i \frac{F\phi}{RT}\right)}{\cosh\left(\nu_i \frac{F\phi}{RT}\right)} \quad (x \geq d_2, \text{diffuse layer}) \quad (\text{S-5})$$

Therefore, the absorbance becomes,

$$A = P \int_{d_2}^{\infty} dx \frac{r_{\text{metal}}^6}{(x + r_{\text{metal}})^6} c_0 \frac{\exp\left(-\text{sgn}(\nu_i)\nu_i \frac{F\phi}{RT}\right)}{\cosh\left(\nu_i \frac{F\phi}{RT}\right)} \quad (\text{S-6})$$

We set the lower limit of the integration region as d_2 , the inner layer thickness over which the representative points of ions cannot get close to the electrode surface. This “representative point” idea from the EDL theory will lead to some error because ions have finite sizes in reality. Similar to the model imperfection due to the lack of the overscreening effect described above, however, the semi-quantitative discussion in the text will still be valid.

We calculated the potential dependence of A by numerically solving the above equations with Mathematica. Figure 3 shows the voltabsorptogram for cation and anion and Fig.S6 shows a typical $c_i(x)G(x)$ profiles.

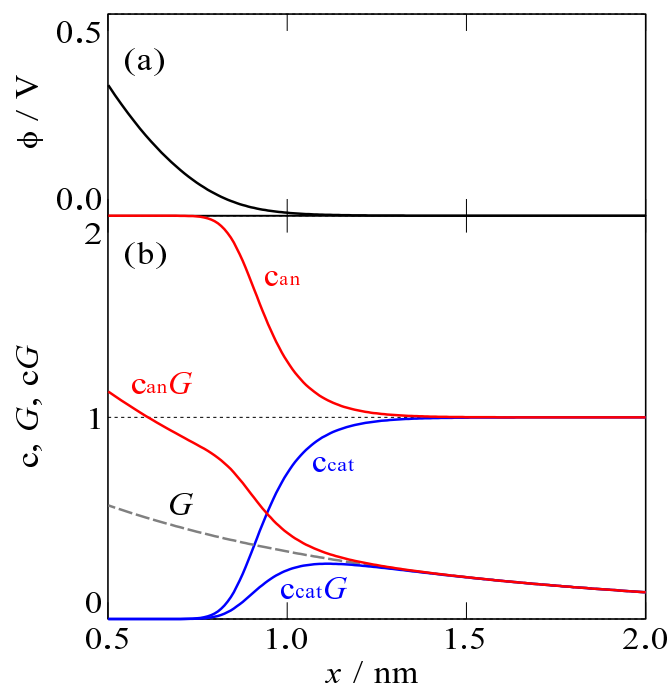


Figure S6: (a) Potential and (b) normalized concentration ($\mathbf{c} = c(x)/c_0$), enhancement factor (G), and their product ($\mathbf{c}G$) as a function of x , the distance from the electrode surface at IL|electrode interface.

S4 SEIRA spectra for the water stretching region

The SEIRA spectra for the water stretching region at the Au interface of the three ILs are shown in Fig.S7. Broad O-H stretching band due to potential-dependent accumulation of trace water at the interface^{S7} is observed at 3050-3600 cm^{-1} . The four peaks around 3600-3700 cm^{-1} are due to the fluctuation of the water vapor concentration in the IR light path inside the FT-IR spectrometer.

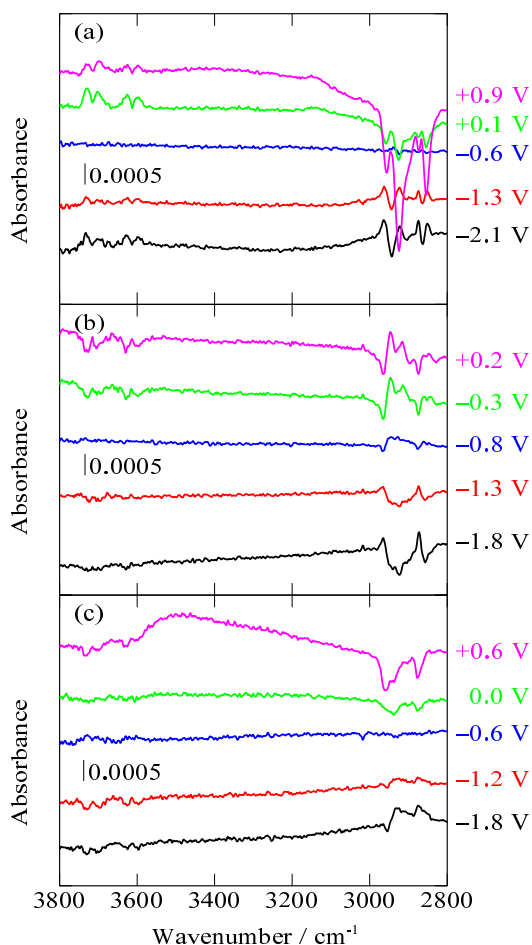


Figure S7: SEIRA spectra for the O-H stretching region at the Au interface of (a) $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]$, (b) $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]$, and (c) $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]$, simultaneously recorded with those in Figs. (a) 2, (b) 4, and (c) 5. Reference spectra were taken at (a) -0.6 V, (b) -0.8 V, and (c) -0.8 V, during the CV.

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