

Supporting Information

“In-water” Dehydration reaction of Aromatic Diol on Inorganic Surface

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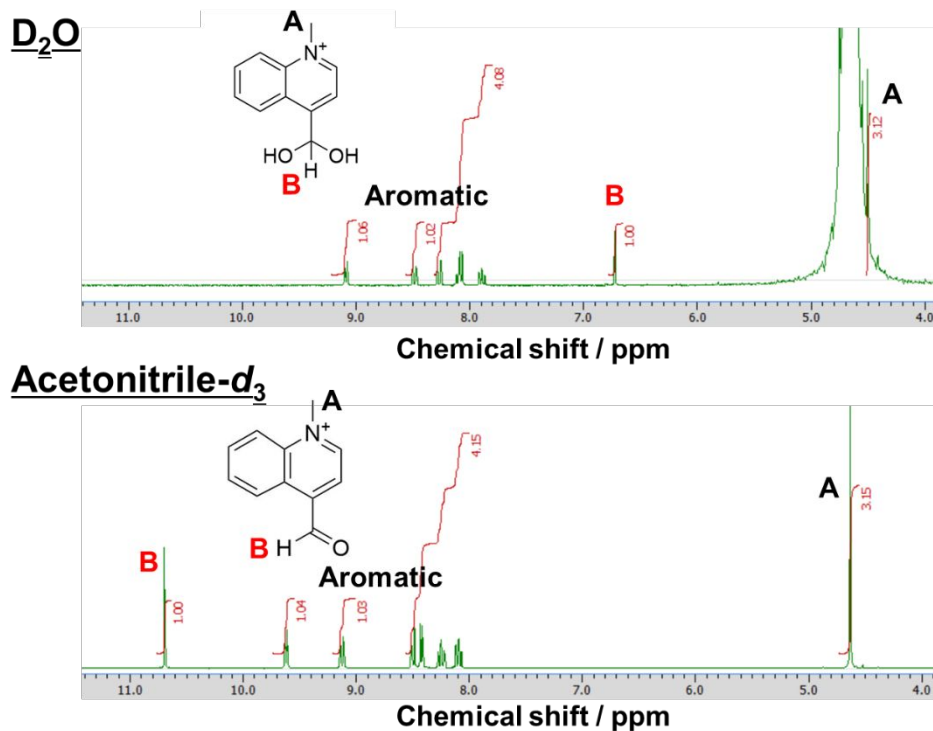


Figure S1. ^1H NMR spectra of $\text{MQu}^+\text{PF}_6^-$. In D_2O (top) and $\text{acetonitrile-}d_3$ (bottom).

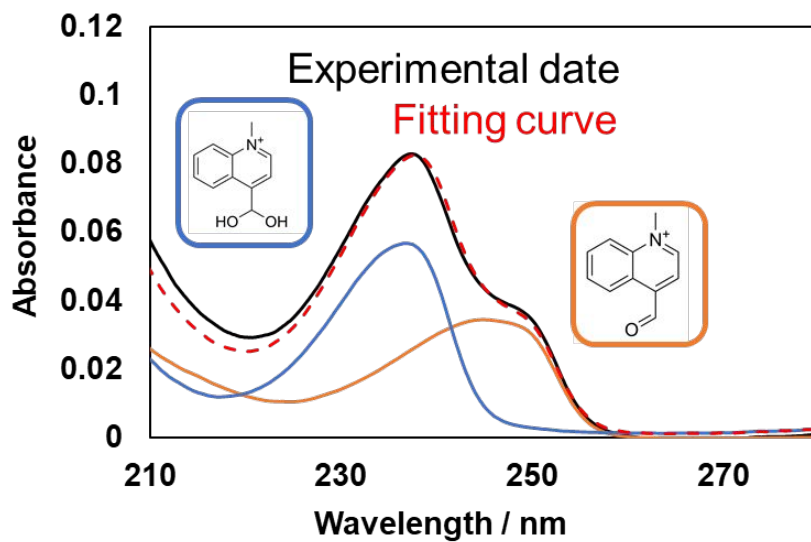


Figure S2. Fitting curve on experimental spectrum for Figure 3b. Water content was 1.0 % (v/v). Fitting curve (red broken line) = MQu^+ -Diol (blue solid line) + MQu^+ -Aldehyde (orange solid line) and experimental spectrum (black solid line).

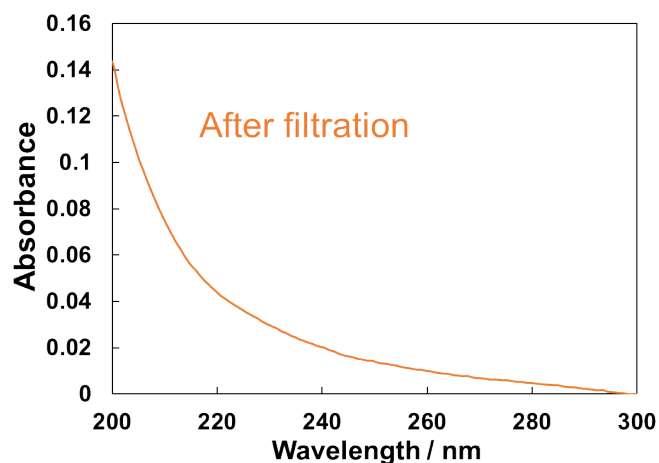


Figure S3. Absorption spectrum of filtrate after filtration experiment of MQu⁺ adsorption experiment on sap1.2 dispersion.

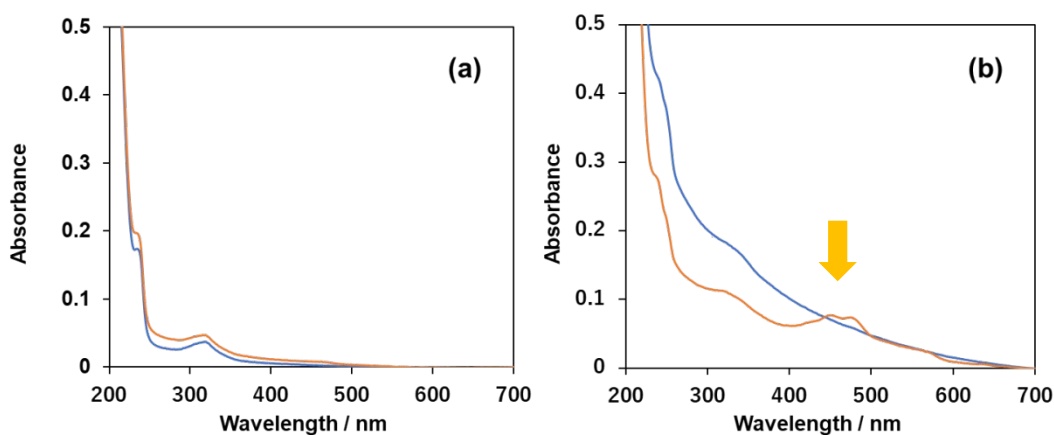


Figure S4. Results of Ehrlich reaction between MQu⁺-Aldehyde and pyrrole. Absorption spectra of each reaction solution at 0 hour (blue) and 10 hours (orange) from the start of the reaction in water. (a) [MQu⁺]₀ = 1.2×10^{-6} mol L⁻¹, [pyrrole] = 1.2×10^{-5} mol L⁻¹ and pH = 1. (b) [MQu⁺]₀ = 1.2×10^{-6} mol L⁻¹, [sap1.2] = 1 g L⁻¹, [pyrrole] = 1.2×10^{-5} mol L⁻¹ and pH = 1.

Ehrlich reaction is a color reaction of pyrrole and aldehyde in dilute hydrochloric acid solution. Without saponite nanosheet, the reaction did not proceed because MQu⁺ was diol form. On the other hand, the absorption band at 400-500 nm that was attributed as a product of this reaction, were observed in the saponite dispersion. The absorption band at 300-320 nm is the absorption band of MQu⁺.

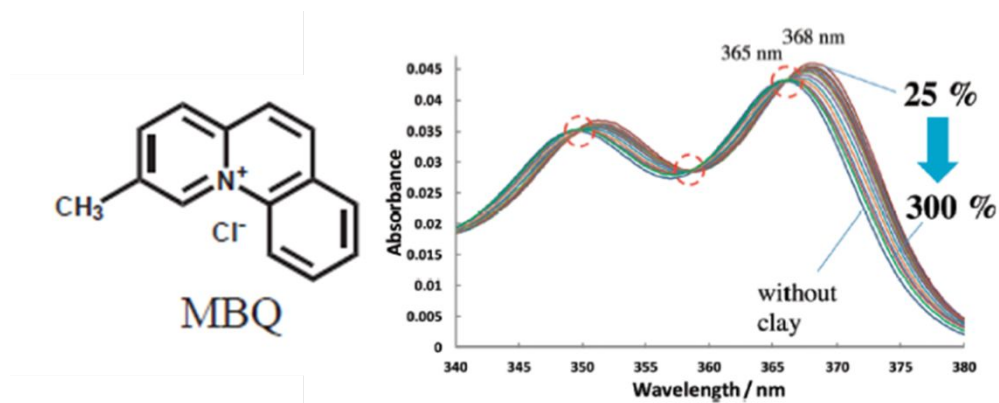


Figure S5. The molecular structure of 2-methylbenzo[c] quinolizinium chloride (MBQ) and the absorption spectra of mixture of 2-methylbenzo[c] quinolizinium chloride (MBQ) and saponite in water. [MBQ] = 3.3×10^{-6} M and [saponite] = 1.33×10^{-5} - 1.1×10^{-6} eq/L.³⁰

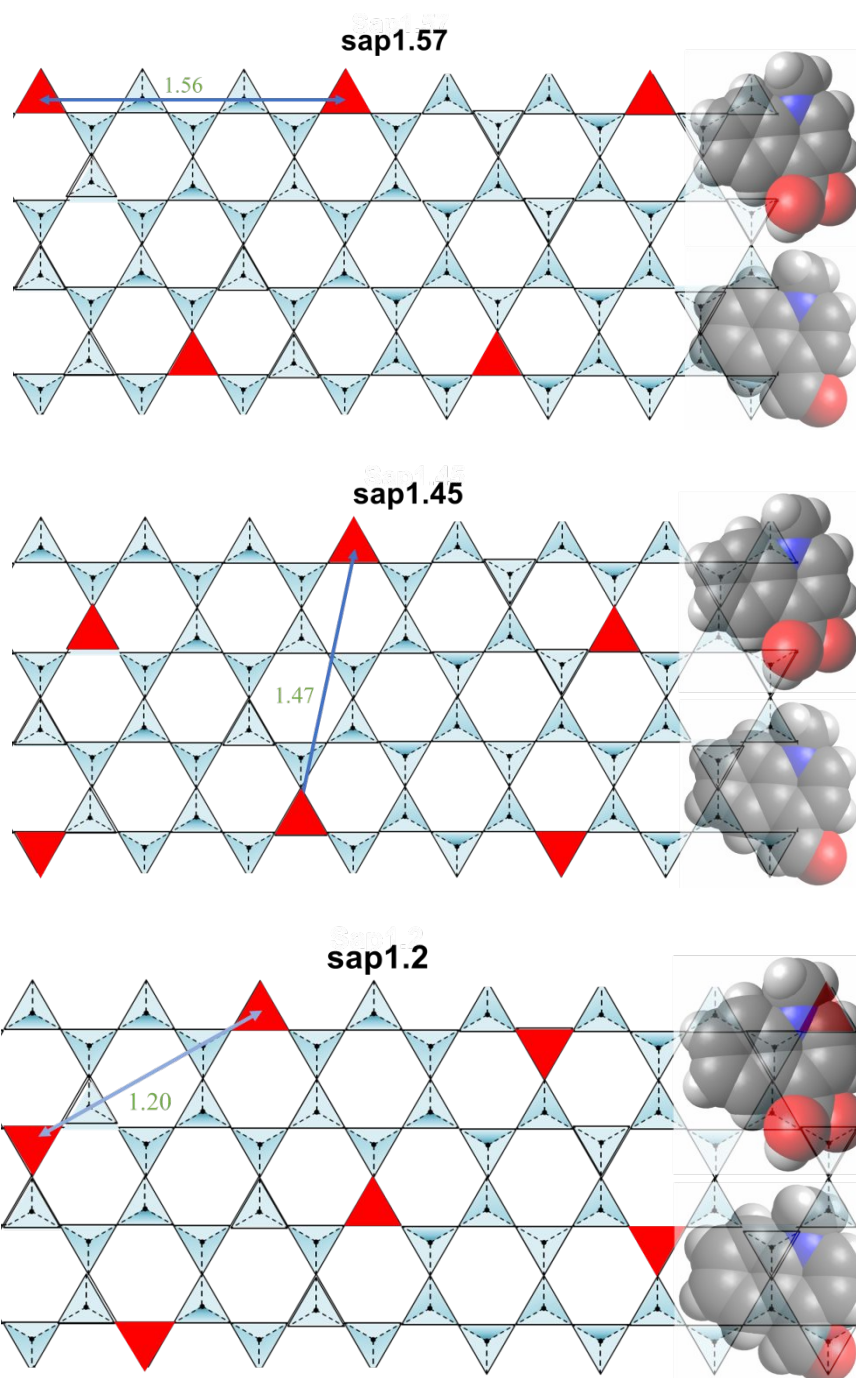


Figure S6. Relationship between molecular sizes of MQu⁺ (top one is diol and bottom one is aldehyde) and the charge distance of each clay surface. The blue triangle represents the Si and the red triangle represents the Al tetrahedral unit that generates the negative charge on the surface.

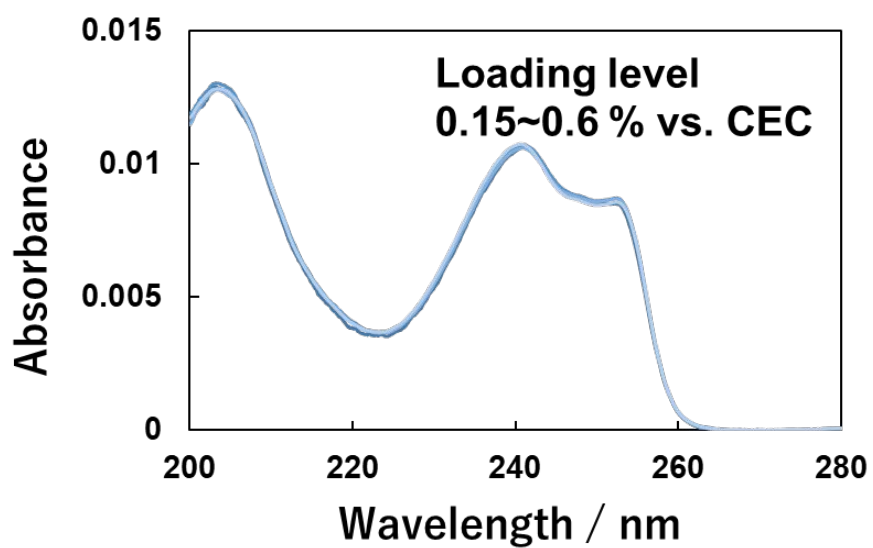


Figure S7. Absorption spectra of MQu^+ in sap1.2 dispersion at loading level = 0.15, 0.3, 0.45, 0.6% vs CEC.

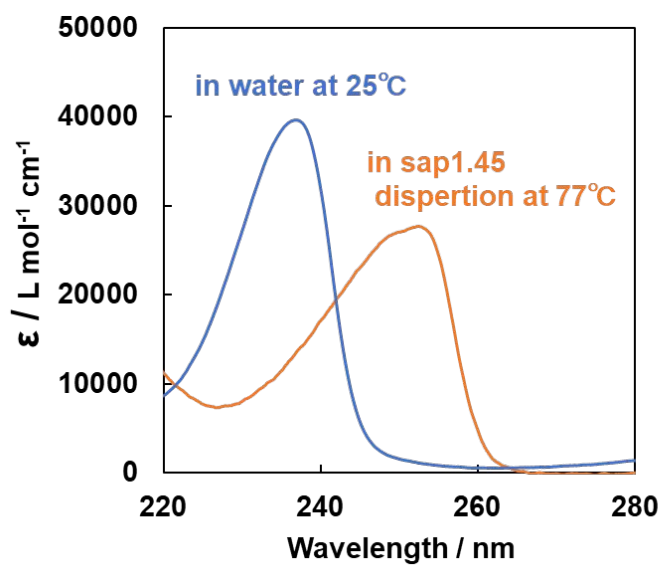


Figure S8. Absorption coefficient of MQu^+ -Aldehyde in Sap1.45 dispersion at 350 K (orange line) and of MQu^+ -Diol in water at 298 K.

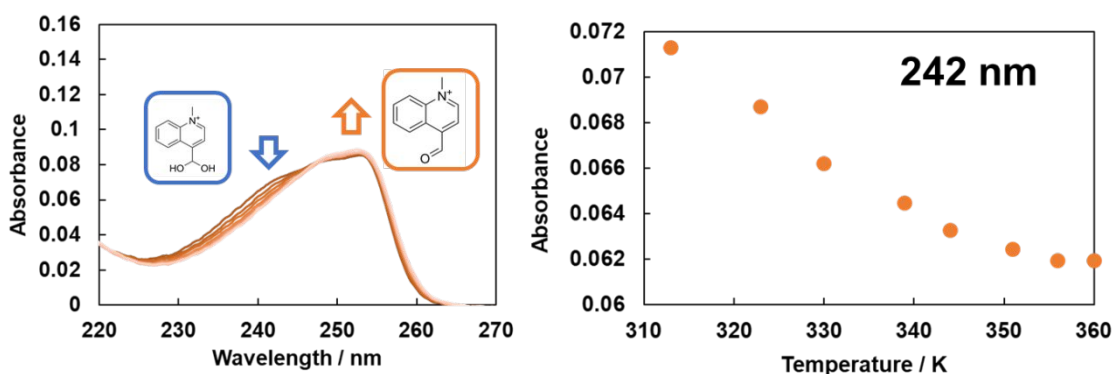


Figure S9. Absorption spectrum change that indicated the temperature dependence of MQu⁺ equilibrium at 313~360 K.

The fitting curve composed of two spectra of MQu⁺ measured in water and acetonitrile as basis functions by least squares method did not match to the measured spectrum in the saponite dispersion. This result indicates that the shape of absorption spectra of MQu⁺ in the saponite dispersion are different from those in solution.

From this results, getting pure spectrum of MQu⁺-Aldehyde adsorbed on saponite surface was attempted. It was confirmed by heating experiment that MQu⁺-Aldehyde was isolated (Figure S8). This equilibrium was affected by temperature. The number of chemical species of left side of this equilibrium equation is one, while that of right side is two (Figure 2). Thus, the higher the temperature, the more the equilibrium shifted to right side to stabilize entropically. The absorption spectrum at 357 K was used as a pure spectrum of the adsorbed MQu⁺-Aldehyde because there was no change in these spectra shape above 357 K. sap1.45 nanosheet was used in this heating experiment because the isolated spectrum was not obtained even at 368 K in the case of on sap1.2. The vibration structure in this spectrum is same as the spectrum in Figure 5.

When the spectrum of MQu⁺-Diol measured without saponite in water is used as a basis spectrum for adsorbed MQu⁺-Diol on saponite surface, the misfitting near 240 nm in the fitting procedure was not observed. This suggests that, in the case of MQu⁺-Diol, the immobilization with adsorption is smaller than that in the case of MQu⁺-Aldehyde.

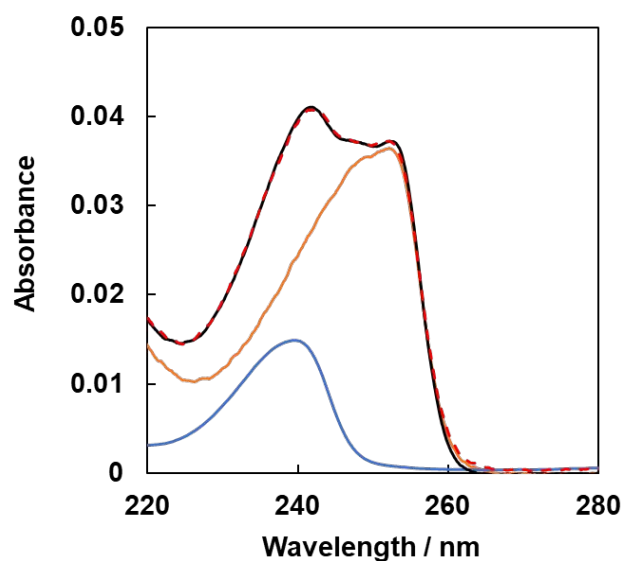


Figure S10. Fitting results on experimental spectrum on sap1.2 surface shown in Figure 5. Fitting curve (red broken line) = MQu⁺-Diol (blue solid line) + MQu⁺-aldehyde (orange solid line) and experimental spectrum (black solid line).

In this fitting calculation, these basis spectra (orange(*f1*) and blue solid line(*f2*)) was shifted in the wavelength axis direction. Thus, the function of the fitting curve (*F(λ)*: red broken line) was expressed as an equation shown below,

$$F(\lambda) = A f_1(\lambda + a) + B f_2(\lambda + b)$$

For strict fitting, it is better to exchange wavelength to wavenumber. However, the range of spectra shift from original state is small (within 5 nm), thus, the error caused by conversion operation in nm can be ignored.

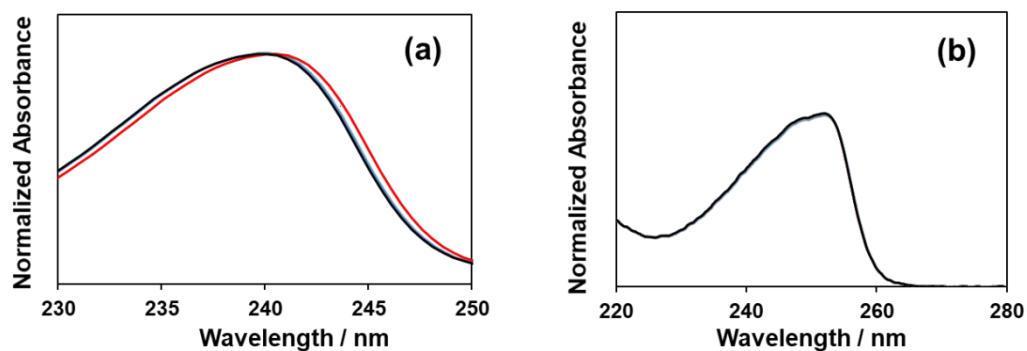


Figure S11. The basis absorption spectra of MQu⁺-Diol (a) and MQu⁺-Aldehyde (b) used for the fitting operation shown in Figure S10 and S17. sap1.2 (black), sap1.45 (blue), sap1.57 (red).

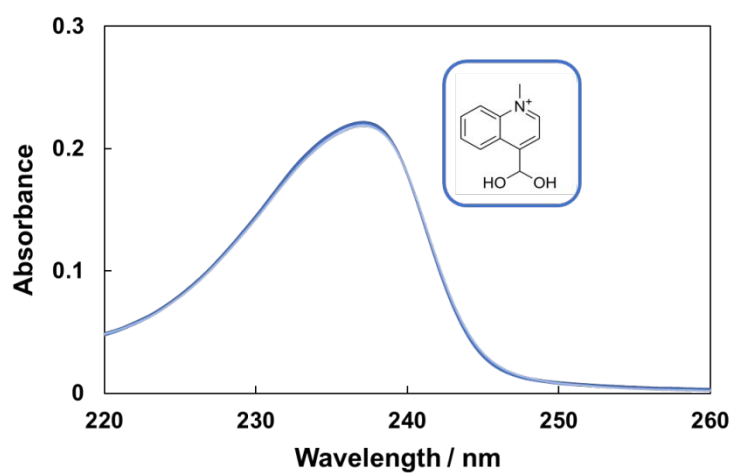


Figure S12. Absorption spectra of MQu⁺ in acidic aqueous solution. Values of pH were 2, 3 and 6.

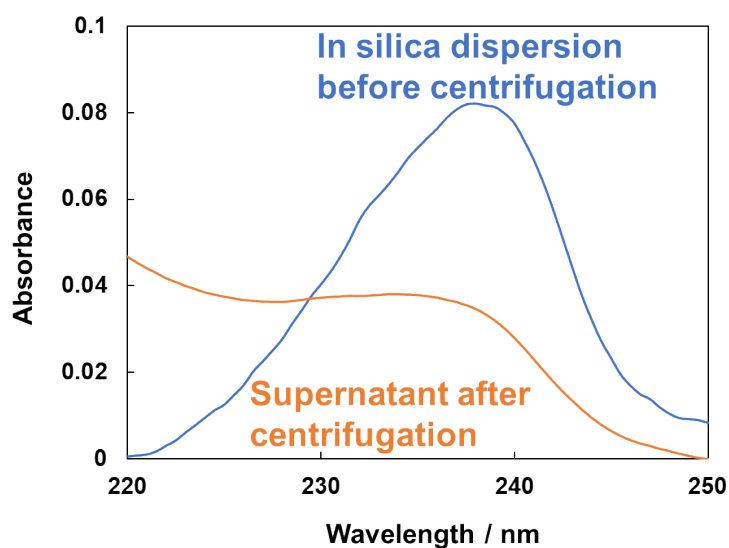


Figure S13. Absorption spectra of MQu⁺ in the spherical silica dispersion (blue line) and the supernatant of the dispersion after centrifugation for 1 hour at 14000 rpm (orange line).

To check the adsorption ratio, a separation experiment of adsorbed and non-adsorbed components of MQu⁺ on the silica surface was conducted using a centrifuge for 1 hour at 14000 rpm. As a result, most of MQu⁺ molecules was adsorbed on the silica surface. Additionally, the λ_{max} of MQu⁺ shifted to 239 nm from 237 nm by the adsorption on silica in water.

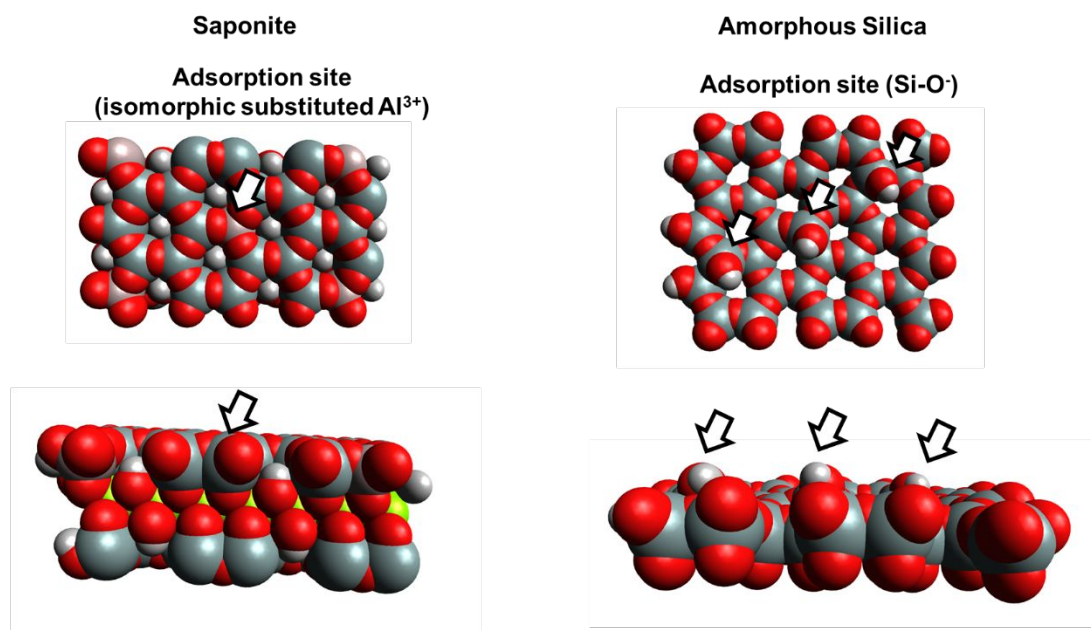


Figure S14. The surface models of saponite and amorphous silica and the plausible adsorption site of each surface.

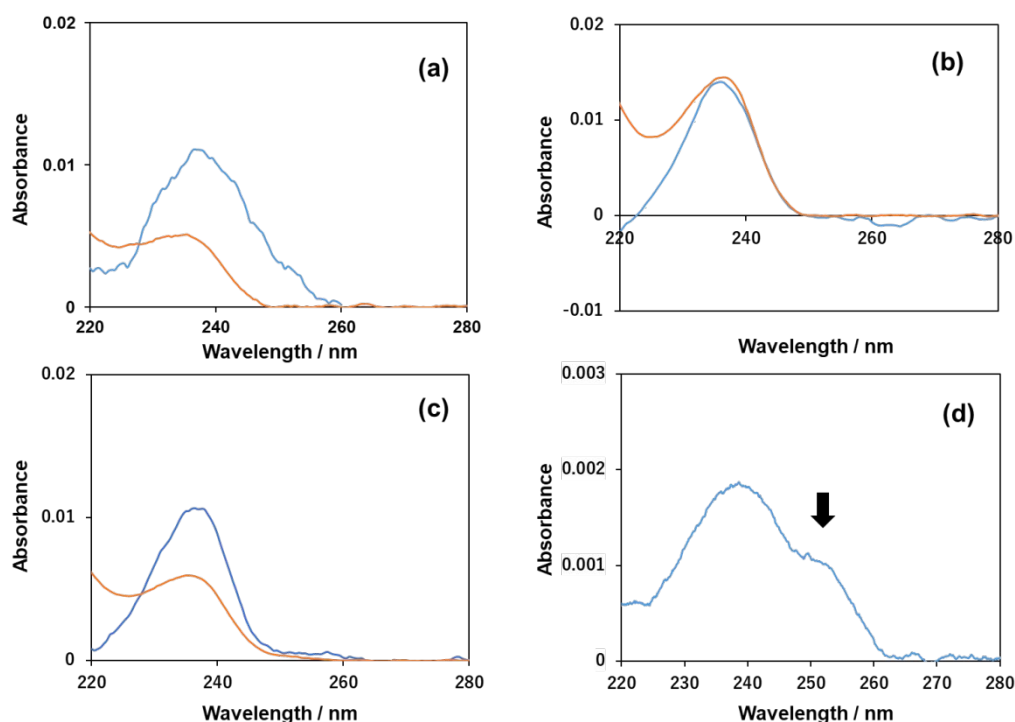


Figure S15. Absorption spectra of MQu^+ in several adsorbent dispersion (blue line). (a) IR124 Na (cation exchange polymer), (b) agarose gel, (c) zeolite (molecular sieves 3A), (d) fluorohectorite. Absorption spectra of supernatant of these dispersions after a centrifugation for 30 minutes at 14000 rpm were also shown (orange line).

Separation experiment of adsorbed and non-adsorbed components of MQu^+ on the several adsorbents were conducted in the same manner as that for the spherical silica dispersion. Figure S15(a) and (c) shows that the part of MQu^+ dissolved in these solutions was adsorbed on these surfaces. Figure S15(b) shows that agarose did not interact with MQu^+ .

In the case of fluorohectorite, the particle is too small to be precipitated by the centrifugation method. Thus, the absorption spectrum of the supernatant could not be observed here. However, the absorption peak at about 250 nm that was attributed to MQu^+ -Aldehyde was confirmed. This indicates that a part of MQu^+ was adsorbed on the surface as MQu^+ -aldehyde.

The zeta potential, the mechanism of charge generation, flatness of the surface of each substance were summarized in Table S1.

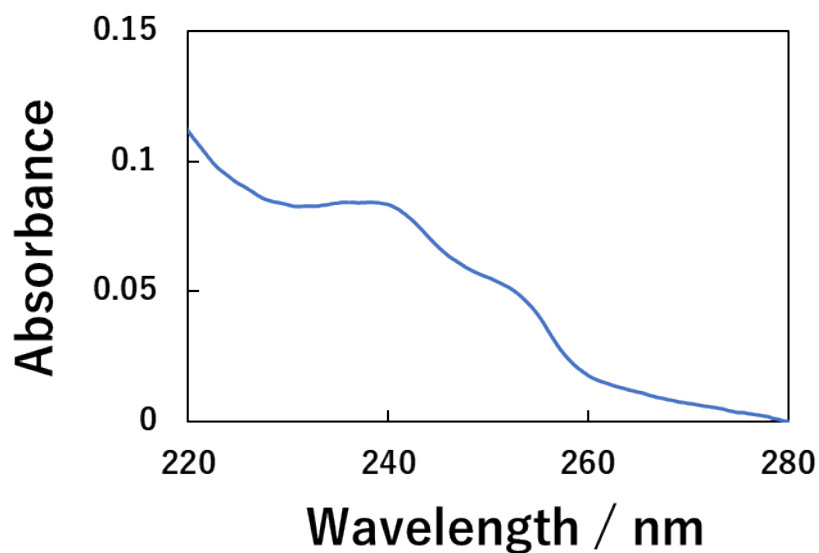


Figure S16. Absorption spectrum of MQu⁺ intercalated between the restacked sap1.2 layers. The sample preparation method is described below.

At first, the sap1.2 dispersion where MQu⁺ is adsorbed at the 0.6 % vs. CEC loading was prepared and was filtrated under the reduce pressure. The clay-MQu⁺ composite gel was obtained by this procedure. Then, this restacked clay gel was transferred to a quartz plate. Finally, the absorption measurement of the composite gel was conducted in a quartz cell that was filled up with distilled water.

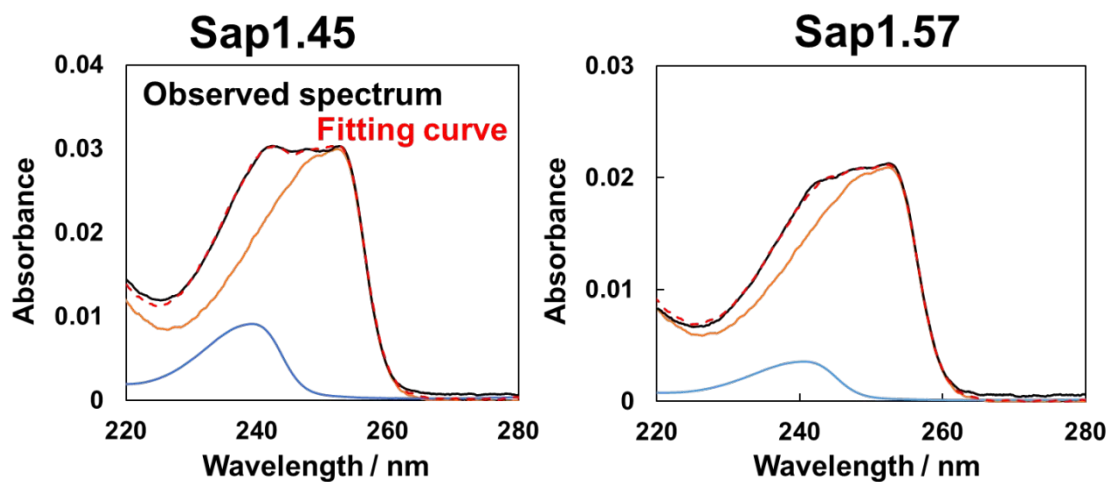


Figure S17. Fitting results on experimental spectra on sap1.45 and sap1.57 surface shown in Figure 6. Fitting curve (red broken line) = MQu^+ -Diol (blue solid line) + MQu^+ -Aldehyde (orange solid line) and experimental spectrum (black solid line). $[\text{MQu}^+] = 0.6\%$ vs. CEC for each clay.

The concentrations of MQu^+ were different for each clay but were same ratio for negative charge on each clay surface. It means that $[\text{MQu}^+]$ loading level / % vs. CEC are same for each clay.

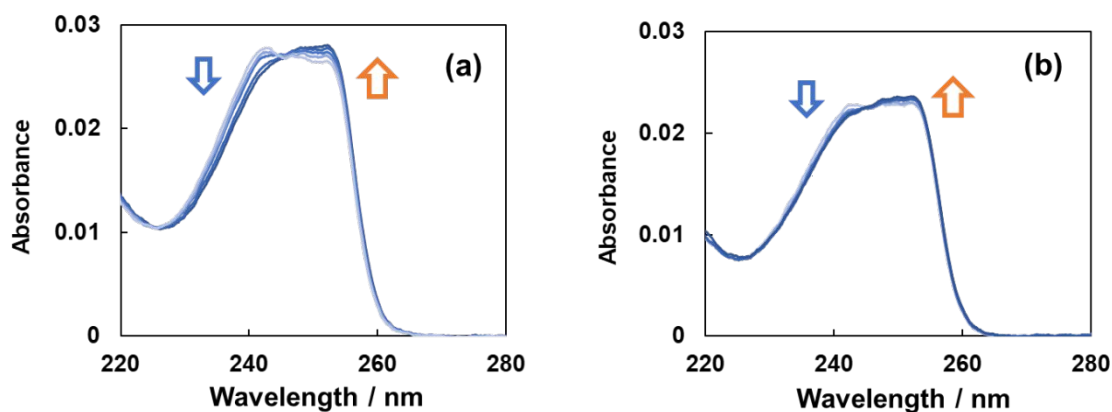


Figure S18. Effect of temperature on the absorption spectra of MQu⁺ adsorbed on (a) sap1.45 and (b) sap1.57 nanosheet surface. Temperature range; (a) 298 ~ 318 K. (b) 301 ~ 313 K. (a) Concentration condition; [MQu⁺] = 1.4×10^{-6} M. [sap1.45] = 33 mg / 100 mL. Loading level: 0.6 % vs. CEC. (b) [MQu⁺] = 1.2×10^{-6} M. [sap1.45] = 33 mg / 100 mL. Loading level: 0.6 % vs. CEC.

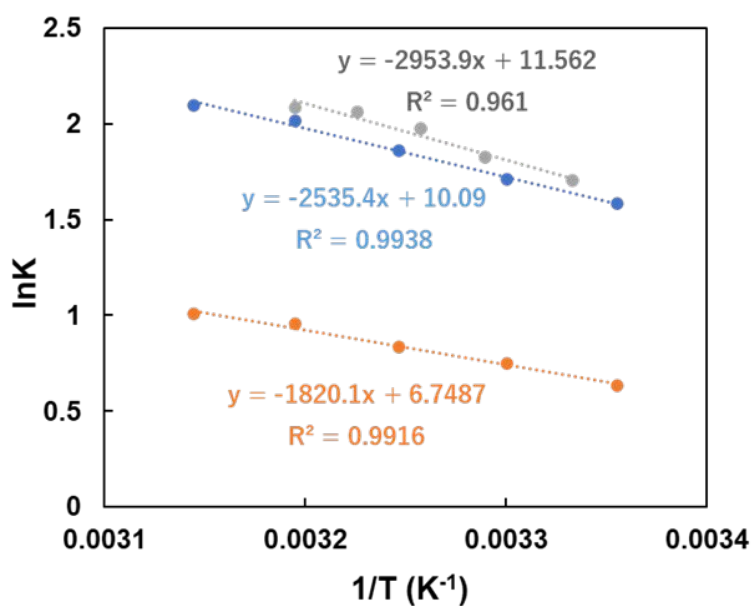


Figure S19. van't Hoff plot from results in Figure 7 and Figure S10. On sap1.2 (orange), sap1.45 (blue) and sap1.57 (gray).

Table S1. The character of each adsorbent such as, flatness of the surface, zeta potential, mechanism of charge generation and the results for water dehydration.

	Flatness of the surface	Zeta potential /mV (pH = 6~7)	Mechanism of charge generation	Aldehyde formation
Saponite ⁴²	○	-50 ± 5	Isomorphic substitution of Al ³⁺ with Si ⁴⁺	○
Fluorohectorite ⁴³	○	-25 ± 5	Isomorphic substitution of Li ⁺ with Mg ²⁺	○
IR124 Na (Polystyrene latex) ³⁹	×	-60 ± 10	-SO ₃ ⁻	×
Zeolite A type (K ⁺) ⁴⁰	×	-35 ± 5	Isomorphic substitution of Al ³⁺ with Si ⁴⁺	×
Amorphous silica ⁴¹	×	-35 ± 5	SiO ⁻	×