

Photocontrol of the adsorption behavior of phenol for an azobenzene-montmorillonite intercalation compound†

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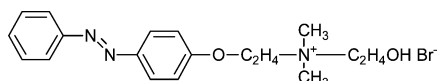
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Intercalation of phenol into an azobenzene-montmorillonite intercalation compound was successfully controlled by photoirradiation.

Smectite group of layered clay minerals has been applied in a wide range of scientific research due to their two-dimensional expandable interlayer space, large surface area, cation exchange ability and stability.^{1–5} Among possible properties of smectites, the adsorptive ones for various cationic species are well-known.^{6,7} The resulting cation exchanged smectites show modified adsorptive properties, notably organoammonium-exchanged smectites have been applied as adsorbent for non-ionic organic compounds both from vapor and from water.^{2,8} It is worth mentioning as a merit of the smectite derived adsorbents that the combination of hosts with different layer charge density and guests with different molecular geometry led controlled adsorptive properties.^{7–9} Here we report a novel photoresponsive adsorbent, which shows reversible intercalation and deintercalation of phenol by photoirradiation. This was achieved by the complexation of a smectite with a photochromic dye, *p*-(ω -dimethylhydroxyethylammonioethoxy)azobenzene bromide (abbreviated as AZ⁺Br[–]; Scheme 1). Phenol was intercalated into the AZ⁺-montmorillonite, by UV irradiation and was deintercalated by subsequent visible light irradiation. To our knowledge, this is the first example of photoresponsive adsorbent derived from a natural resource, smectite clay. The reversible intercalation and deintercalation behavior of phenol triggered by irradiation can be applied to a construction of a smart adsorbent for a wide range of applications including environmental purification.

AZ⁺-montmorillonite was prepared from sodium-montmorillonite (Kunipia F; obtained from Kunimine Ind. Co., cation exchange capacity of 119 meq/100 g clay¹⁰) by the cation exchange reaction with AZ⁺Br[–] as reported previously.¹¹ Intercalation of phenol into the AZ⁺-montmorillonite was conducted by mixing the AZ⁺-montmorillonite and neat phenol at the mass ratio of 4 : 1 (phenol : AZ⁺-montmorillonite). The mixture was ground with an agate mortar and a pestle at room temperature for 15 min. The basal spacing of the AZ⁺-montmorillonite (Fig. 1a) increased from 1.8 nm to 2.6 nm (Fig. 1b) by the mixing the AZ⁺-montmorillonite and neat phenol, indicating that phenol was intercalated into the interlayer space of the AZ⁺-montmorillonite.

Upon UV irradiation¹² of the AZ⁺-montmorillonite-phenol for 30 min, a new diffraction peak with *d* value of 3.2 nm emerged (Fig. 1c). This indicates that phenol was intercalated into the interlayer space of the AZ⁺-montmorillonite further. Extending UV irradiation period (30 min) did not cause further change in the XRD



Scheme 1 The molecular structure of *p*-(ω -dimethylhydroxyethylammonioethoxy)azobenzene bromide.

† Electronic supplementary information (ESI) available: The change in the XRD pattern of the AZ⁺-montmorillonite-phenol with UV irradiation time to 30 min (Fig. S1) and the reversible change in the XRD pattern of the AZ⁺-montmorillonite-phenol upon UV and visible light irradiation (Fig. S2). See <http://www.rsc.org/suppdata/cc/b3/b312962d/>

pattern. Irradiation of visible light¹² for 30 min led the decrease in the basal spacing to the value identical to that (2.6 nm) seen before UV irradiation (Fig. 1b), indicating the deintercalation of phenol. Reversible change in the basal spacing was observed repeatedly (Fig. S1).†

The change in the absorption spectrum of the AZ⁺-montmorillonite-phenol upon irradiation with UV and visible light is shown in Fig. 2.¹³ The absorbance of *trans*-isomer (342 nm) of AZ⁺ decreased and the band due to *cis*-isomer appeared at 433 nm by UV irradiation of the AZ⁺-montmorillonite-phenol, indicating *trans-cis* photoisomerization of AZ⁺. The reaction reached the

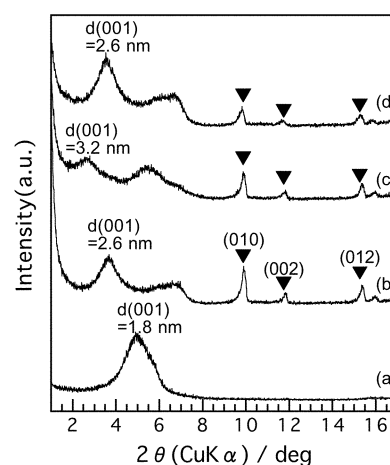


Fig. 1 XRD patterns of (a) AZ⁺-montmorillonite and (b)–(d) AZ⁺-montmorillonite-phenol (mass ratio of 4 : 1 (added phenol : AZ⁺-montmorillonite)). Patterns (b) and (c) were recorded before and after UV irradiation for 30 min, respectively. Pattern (d) was recorded after visible light irradiation for 30 min subsequent to UV irradiation. Peaks indicated with triangle are diffractions from pure phenol.

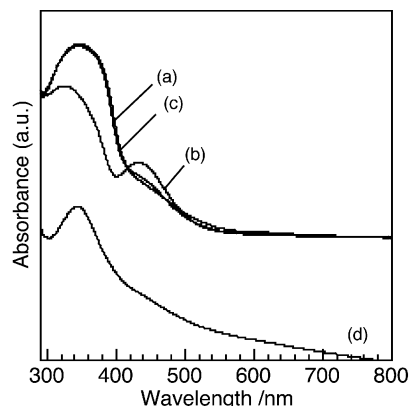


Fig. 2 Change in the UV-vis absorption spectrum of the AZ⁺-montmorillonite-phenol prepared at the mass ratio of 4 : 1 (phenol : AZ⁺-montmorillonite) (a) before and (b) after UV irradiation for 10 min. Spectrum (c) was recorded after visible light irradiation for 10 min subsequent to UV irradiation. Spectrum (d) is the AZ⁺-montmorillonite intercalation compound.

photostationary state by UV irradiation for 10 min (Fig. 2b) under the experimental conditions employed in this study. On the other hand, it took 30 min for the change in the XRD pattern (Fig. S2).† The difference (10 min for the spectral change and 30 min for the structural change) was thought to be due to the diffusion of phenol into the interlayer space. The absorption spectrum (Fig. 2a) was recovered upon subsequent visible light irradiation for 10 min (Fig. 2c), indicating *cis*-to-*trans* photoisomerization of AZ⁺ in the interlayer space. Similar to the intercalation, the deintercalation of phenol took 30 min. Reversible spectral change was also repeatedly observed. Considering the changes in the absorption spectrum and the XRD pattern, the reversible intercalation and deintercalation of phenol were thought to be caused by the *trans*-*cis* isomerization of the intercalated AZ⁺. The more polar nature¹⁴ of *cis*-AZ⁺ compared to *trans*-AZ⁺ was thought to cause the intercalation of phenol.

The absorption maximum for the AZ⁺-montmorillonite intercalation compound was observed at 345 nm, which was slightly red shifted from the value observed for monomeric AZ⁺ (342 nm) in a dilute ethanol solution of AZ⁺Br⁻ (1.0×10^{-5} M).¹¹ The chromophore interacts to give aggregates and the dye-dye interactions cause both bathochromic and hypsochromic spectral shifts depending upon the microstructures.^{15,16} According to Kasha's molecular exciton theory,¹⁷ the observed bathochromic shift of the absorption band of the AZ⁺-montmorillonite intercalation compound was ascribable to the formation of a J-aggregate. We have discussed the aggregation of a series of cationic azo dyes in the interlayer space of layered silicates from the nanostructures and the spectral shifts of the π - π^* absorption bands.^{11,16,18} Considering the gallery height of the AZ⁺-montmorillonite (0.8 nm = 1.8–1.0 nm) and the size of AZ⁺ (1.9 nm for the molecular long axis), the intercalated AZ⁺ were thought to form an interdigitated monolayer with the molecular long axis inclined to the silicate layer to give a J-aggregate in the interlayer space.¹¹ After the intercalation of phenol, the absorption band appeared at 342 nm corresponding to that of monomeric AZ⁺ (342 nm), suggesting the deaggregation of AZ⁺ by the intercalated phenol.

The reversible intercalation and deintercalation of phenol occurred only when excess phenol was present (the diffraction peaks due to excess phenol were seen in Figure 1). When excess phenol was absent, no change in the basal spacing (2.6 nm) upon UV and visible light irradiation was observed. As an example, the XRD patterns of the AZ⁺-montmorillonite-phenol prepared at the mass ratio of 0.6 : 1 (phenol : AZ⁺-montmorillonite) are shown in Figure 3. This indicates that the amount of added phenol is identical to the amount of intercalated phenol in the interlayer space of the *trans*-AZ⁺-montmorillonite. Supposing that the increase in the gallery height (0.6 nm) upon UV irradiation corresponds to the volume of intercalated phenol, the amount of intercalated phenol can be estimated to be 0.33 g (0.035 mol) g⁻¹ montmorillonite $\{ (0.6 \text{ nm (gallery height)}) \times (3.5 \times 10^{20} \text{ nm}^2 \text{ g}^{-1} \text{ montmorillonite (half of surface area of montmorillonite)}) \} / \{ (0.10 \text{ nm}^3 \text{ (volume of phenol molecule)}) \times 6 \times 10^{23} \}$ upon UV irradiation. Taking into the adsorbed amount of AZ⁺ on montmorillonite (0.33 g g⁻¹ clay) into consideration, the amount of intercalated phenol induced by UV irradiation was estimated to be 0.24 g (0.026 mmol) g⁻¹ AZ⁺-montmorillonite. These observations supported the idea that the change in the basal spacing was caused by the intercalation and the deintercalation of phenol.

This paper demonstrated that the adsorptive properties of the AZ⁺-montmorillonite intercalation compound could be controlled by UV and visible light irradiation. Studies on the intercalation of various organic species into AZ⁺-layered silicate intercalation compounds under light irradiation are being done in our laboratory

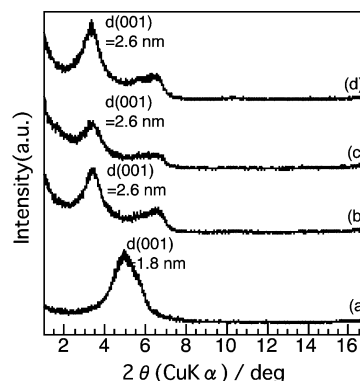


Fig. 3 XRD patterns of (a) AZ⁺-montmorillonite and (b)–(d) AZ⁺-montmorillonite-phenol (mass ratio of 0.6 : 1 (added phenol : AZ⁺-montmorillonite)). Patterns (b) and (c) were recorded before and after UV irradiation for 30 min, respectively. Pattern (d) was recorded after visible light irradiation for 30 min subsequent to UV irradiation.

to obtain more quantitative understanding on the change in the adsorptive properties.

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- 12 The photochemical reaction of the intercalated AZ⁺ was conducted by UV and visible light irradiation with a 150 W high pressure Hg-Xe lamp. (Hamamatsu Photonics Co.) A band pass filter, TOSHIBA D-35, the transmittance centered at 360 nm, was used for isolating the UV light. For the *cis*-*trans* backward reactions, a sharp cut filter, HOYA L42 (cut off wavelength is 420 nm) was used to obtain visible light.
- 13 The AZ⁺-montmorillonite-phenol obtained was smeared on a glass substrate and was subsequently put on another glass substrate to record UV-vis absorption spectra.
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