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Naked-Eye Discrimination of Methanol from Ethanol Using Composite Film of Oxoporphyrinogen and Layered Double Hydroxide

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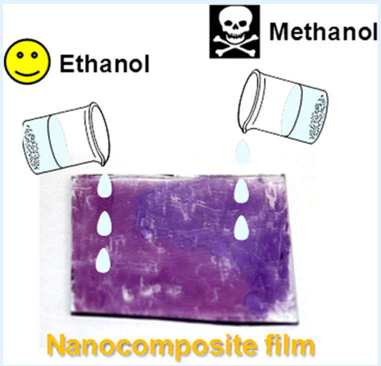
Supporting Information

ABSTRACT: Methanol is a highly toxic substance, but it is unfortunately very difficult to differentiate from other alcohols (especially ethanol) without performing chemical analyses. Here we report that a composite film prepared from oxoporphyrinogen (OxP) and a layered double hydroxide (LDH) undergoes a visible color change (from magenta to purple) when exposed to methanol, a change that does not occur upon exposure to ethanol. Interestingly, methanol-induced color variation of the OxP-LDH composite film is retained even after removal of methanol under reduced pressure, a condition that does not occur in the case of conventional solvatochromic dyes. The original state of the OxP-LDH composite film could be recovered by rinsing it with tetrahydrofuran (THF), enabling repeated usage of the composite film. The mechanism of color variation, based on solid-state ^{13}C−CP/MAS NMR and solution-state ^{13}C NMR studies, is proposed to be anion transfer from LDH to OxP triggered by methanol exposure.



KEYWORDS: *sensor, porphyrinoid, clay mineral, layered double hydroxide, alcohol, organic−inorganic composite*

INTRODUCTION

Methanol and ethanol are becoming increasingly important substances as liquid fuels because of the development of technologies for direct-methanol-fuel-cells (DMFC)[1] and biomass ethanol[2] so that these alcohols will become more widely used by the public in the near future. Both methanol and ethanol are colorless liquids, which cannot be differentiated by sight alone. However, methanol is a highly toxic substance, which can cause serious illnesses upon ingestion.[3] In the absence of proper analytical instrumentation (e.g., gas chromatograph, NMR, mass spectrometry, electrochemistry) or other chemical testing facilities, a facile, nontoxic, and cost-effective methodology for discriminating between methanol and ethanol is required.

Color variation of dyes depending on the polarity of solvents is known as solvatochromism,[4,5] while color variation of metal−ligand complexes also occurs when the metal cation interacts with or coordinates to solvent molecules,[6] and these visible color variations are of practical use for discriminating solvents. However, there are only a few dyes that exhibit when dissolved in methanol or ethanol a visible difference in color because methanol[7] and ethanol[8] are chemically very similar. Reichardt's betaine represents a class of charge-transfer dye which exhibit highly sensitive solvatochromism sufficient for the naked-eye discrimination between methanol and ethanol.[9] However, that solution system may not be very convenient for practical use because it entails the waste of a certain amount of solvent for dye dissolution and, in addition, solvents must be removed in order to recycle the sensor.

Dye-loaded inorganic materials have attracted attention due to potential functionalities that are not available from the pristine dye substance.[10−13] In particular, clay minerals are some of the most attractive inorganic host materials because of their two-dimensional (2D) interlayer nanospaces where dye molecules tend to be assembled and oriented leading to the observation of unique photofunctionalities.[14−19] In this study, we report that a composite film of oxoporphyrinogen (OxP) and layered double hydroxide (LDH) exhibits visible color

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change (from magenta to purple) when exposed to methanol (Figure 1), whereas film color does not vary for ethanol and other common solvents (e.g., propanol, acetone, THF, and toluene). The composite film can be used repeatedly and might be applicable as a "test paper" for methanol detection.

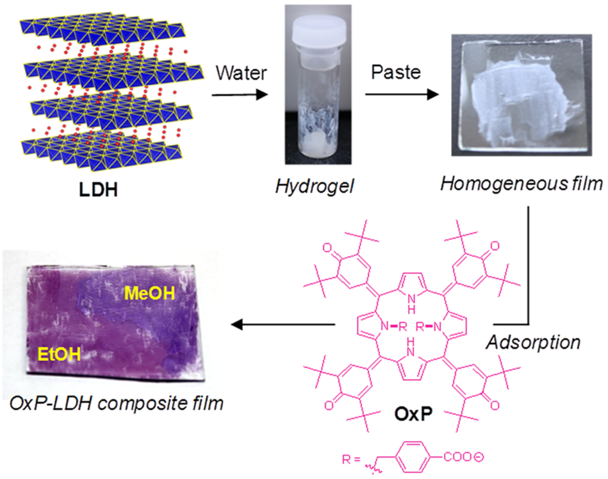

Figure 1. Schematic illustration for the preparation of OxP-LDH composite film demonstrating visible color variation when exposed to methanol or ethanol.

RESULTS AND DISCUSSION

OxP[20−22] is a class of organic dye synthesized by the two-electron oxidation of the corresponding porphyrin derivative.[23−25] OxPs bind various guest molecules at their pyrrolic-NH as well as quinonoid C═O, leading to variation of their π-electronic structure through tautomeric processes.[26] We have previously reported that OxPs are variously available as sensing probe molecules for anions,[27−29] organic solvents,[27] water,[30] and chiral molecules.[31,32] On the other hand, LDH is a synthetic clay mineral of general formula $M^{II}_{1-y}M^{III}_{y}(OH)_2(X^{n-})_{y/n}\cdot mH_2O$, where M and X represent metal cation and counteranion, respectively, and $y = 0.2{-}0.33$ and $m = 1{-}3y/2$.[33−35] LDH consists of alternating layers of positively charged $M^{II}_{1-y}M^{III}_{y}(OH)_2$, negatively charged anion $(X^{n-})_{y/n}$, and mH_2O. Anions inserted in the interlayer space of LDH are exchangeable by anion-exchange reactions.[36−38] In this study, we used acetate (OAc) type LDH (i.e., $MgAl_3(OH)_8(OAc)\cdot 2H_2O$) because a homogeneous film can be prepared when it is dried from a hydrogel paste.[39]

OxP used in this study is modified with two carboxylate units at two pyrrolic-N positions (Figure 1) to enable the adsorption of OxP into LDH by an anion-exchange reaction. LDH film prepared on a glass substrate was soaked in an OxP solution (in ethanol) for 1 h, resulting in a stained LDH film with a magneta color. After washing with ethanol and THF, the composite film OxP-LDH was obtained (Figure 1). During several washings with different solvents, OxP remains contained in the OxP-LDH composite film, indicating that OxP is strongly adsorbed on the LDH film.

The X-ray diffraction (XRD) pattern of LDH did not change upon loading of OxP indicating that OxP is not inserted within the interlayer space of LDH, but is rather adsorbed at the surface of LDH particles (Figure 2). OxP is a rather large molecule (M_w = ca. 1400 g/mol), so that its inclusion with displacement of acetate anions from LDH might be energetically unfavored due to its low charge density.

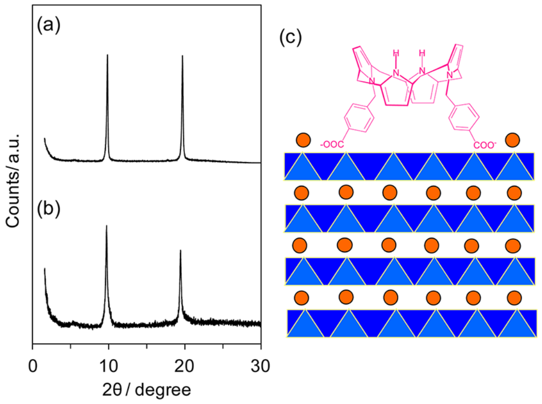

Figure 2. XRD pattern of AcO-LDH (a) before and (b) after adsorption of OxP measured under dry N_2 atmosphere (CuK_α radiation; λ = 0.154 nm). (c) Proposed adsorption structure of OxP on LDH. OxP is attached at the surface not within the interlayer space of LDH. Blue framework and orange balls denote hydroxide layers and anions, respectively. Interlayer water is omitted for clarity.

As shown in Figure 3a, UV−vis spectra and the color of OxP dissolved in methanol and ethanol (other solvents, see Figures S1−S3 in the Supporting Information) are virtually identical. Thus, OxP alone cannot be used to discriminate methanol from ethanol. On the other hand, OxP-LDH composite film undergoes a visible color change (from magenta to purple) when immersed in liquid methanol but not when immersed in

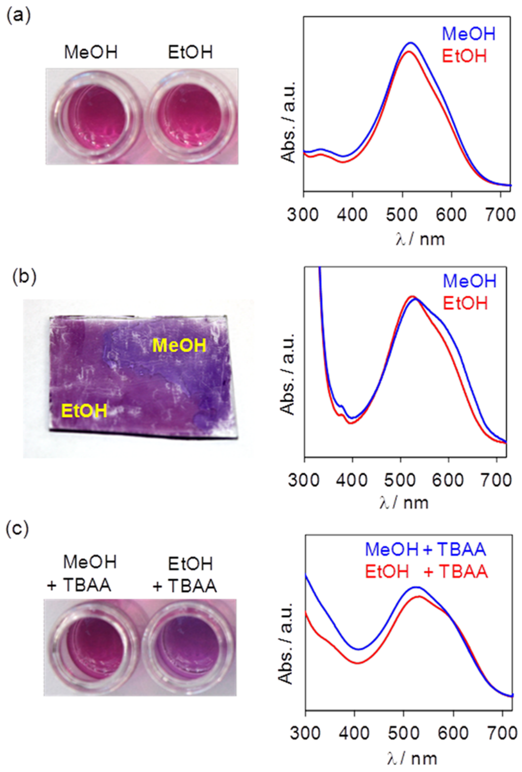

Figure 3. (a) Photograph and UV−vis spectra of OxP dissolved in methanol or ethanol. (b) Photograph and UV−vis spectra of OxP-LDH composite film under exposure to methanol or ethanol. (c) Photograph and UV−vis spectra of OxP dissolved in methanol or ethanol in the presence of TBAA.

ethanol (Figure 3b). Also, immersion of OxP-LDH in methanol does not cause leaching of OxP from the LDH support. The UV−vis spectrum of OxP-LDH composite film reveals that adsorption at 600 nm increases after exposure to methanol (Figure 3b), which is also typical of OxP upon binding with anion species in solution (Figure 3c).[27]

Interestingly, color variation of OxP-LDH composite film caused by methanol is retained even after the removal of methanol under reduced pressure. Solvatochromism is usually a reversible process since it is based on variation of the electronic state of dye molecules depending on prevailing polarity, which may be determined by solvent identity.[4,5] In addition, as indicated by XRD measurements (Figure 2), OxP is not inserted within the interlayer spacing of OxP, so that the color variation of OxP-LDH composite film by methanol must not be based on the anisotropic orientation of OxP molecules within the interlayer spaces of LDH as reported by Takagi et al.[40,41] On the other hand, the starting color of OxP-LDH could be recovered by rinsing it with THF. Previous X-ray crystal structure studies revealed that OxP has a saddle-shape conformation with face-to-face pyrrolic N-Hs binding solvent molecules through hydrogen-bonds.[27,42] These results suggest that the color variation of OxP-LDH composite film caused by methanol is not due to solvent polarity but to the binding of a nonvolatile guest species to OxP. The guest molecule can subsequently be displaced by hydrogen bond-accepting volatile THF solvent molecules leading to the recovery of the original state of the OxP-LDH composite film (i.e., magenta colored).

This “nonvolatile” memory effect for color variation of OxP-LDH composite is quite unique and enabled us to apply solid-state ^{13}C−CP/MAS NMR spectroscopy to the OxP-LDH composite film in its color-varied purple state in order to probe the mechanism of color variation volatile solvents tend to evaporate during solid-state NMR measurements due to frictional heat of the rotating sample at high speed. Additionally, it requires several days for accumulation of low sensitivity ^{13}C NMR signals. As shown in Figure 4a, the solid-state ^{13}C−CP/MAS NMR spectrum of OxP-LDH composite film around 130 ppm, which correspond to sp^2 carbons, demonstrates a relatively enhanced signal intensity following color variation due to methanol (i.e., to purple), implying that the π-electronic structure of OxP has been altered. Solution-state ^{13}C NMR spectra were measured in the presence and absence of tetrabutylammonium acetate (TBAA), and sums of the NMR signal intensities in the indicated spectral area ($\sum$) were compared (Figure 4b, c). It is obvious that the sum of NMR signal intensities ($\sum$) around 130 ppm are enhanced in the presence of TBAA, which is similar to the case of solid-state ^{13}C−CP/MAS NMR spectroscopy of OxP-LDH following methanol treatment. Even though analytical methods that can be applied to OxP-LDH composite film are limited, these NMR results imply a mechanism of color variation of OxP as follows. (i) Methanol causes the transfer of acetate anion (on the surface or at interlayer) from LDH to OxP, leading to variation of OxP-color. Actually, methanol is known as an appropriate solvent for anion-exchange reactions of the LDH series.[43,44] (ii) In contrast, ethanol is not sufficiently polar to facilitate the transfer of LDH anion to OxP. (iii) Anions remain hydrogen-bonded to OxP even after drying of methanol so that color variation is retained. (iv) Excess THF can be used to displace with-bonded anions, leading to recovery of the original state of the OxP-LDH film.

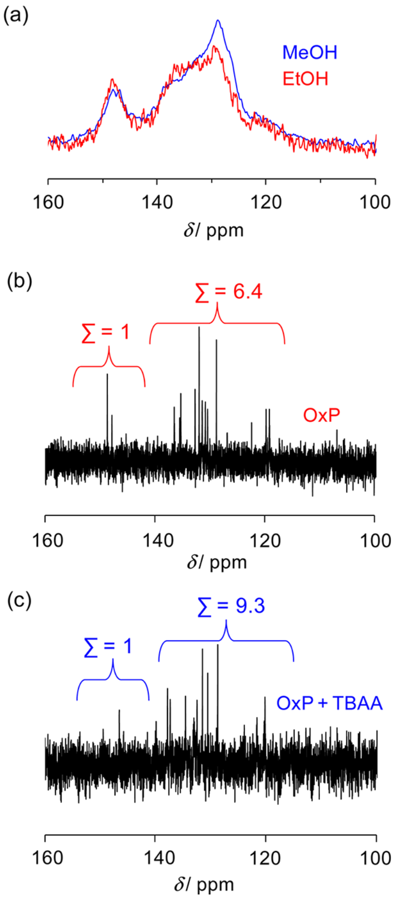

Figure 4. (a) Solid-state ^{13}C−CP/MAS NMR spectra (in the region of sp^2 carbons) of OxP-LDH composite powders after drying from methanol (blue line) and ethanol (red line) suspensions. (b) Solution-state ^{13}C NMR spectrum of OxP in the absence of TBAA. Sum of NMR signal intensities in the indicated spectral area is denoted as $\sum$. (c) Solution-state ^{13}C NMR spectrum of OxP in the presence of 2 equivalents of TBAA.

CONCLUSION

In conclusion, we have demonstrated a unique molecular event of OxP occurring at an interface of layered double hydroxide, which might be applied in a sensing system because of the visible color variation upon methanol exposure. The sensing activity is based on the interaction between acetate anions and OxP which selectively occurs in the presence of methanol. Our system makes a rapid and convenient method for analyzing liquids suspected of being methanol prior to their use or storage with an emphasis on improving public safety.

METHODS

Preparation of OxP-LDH Composite. OxP[30] and AcO-LDH[45] were prepared as previously reported. AcO-LDH (100 mg) was added to degassed distilled water (1 mL). The resulting hydrogel was smoothly pasted onto a glass slide (2.5 cm × 3 cm), and subsequently immersed into a solution of OxP (1 wt %, in ethanol) for 1 h. After adsorption of OxP onto LDH, the complex was washed with ethanol and THF, and then dried in vacuum for 12 h. The film thickness was ca. 20 μm, and OxP loading was estimated to be ca. 0.02 wt %.

High-Resolution Solid-State NMR Experiments. High-resolution solid-state NMR experiments were carried out at 125.7 MHz for ^{13}C, using a JEOL ECA500 spectrometer equipped with a high power amplifier for proton decoupling and a CP/MAS (cross-polarization/magic angle spinning) probe. Spectra were externally referenced to the methyl carbon signal of hexamethylbenzene (17.4 ppm relative to TMS). Samples were packed as powders in a ZrO rotor (⌀ = 4 mm). The MAS frequency was set at 15 kHz and sample temperature was 300 ± 3 K. Contact time was 2 ms, with a pulse delay of 5 s.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, methods, and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(7) Methanol: colorless, mp = −97.0 °C, bp = 64.7 °C, d = 0.79 g cm^{-3}, nD (at 20 °C) = 1.33, dipole moment = 1.70 D, dielectric constant = 33, pK_a = 15.5.

(8) Ethanol: colorless, mp = −114.3 °C, bp = 78.4 °C, d = 0.799 g cm^{-3}, nD (at 20 °C) = 1.36, dipole moment = 1.69 D, dielectric constant = 24.6, pK_a = 15.9.

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