Hybridization of layered zirconium phosphate with azo compounds and its photoresponsivity and adsorption of rare earth elements

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1. Introduction

Inorganic layered materials can often accommodate various ions and molecules into their interlayer space. Generally, inorganic layered materials can be classified as one of three types: intrinsically anionic layers with complementary cations, intrinsically cationic layers with complementary anions, or uncharged layers. Among them, layered zirconium phosphate, an anionic layer compound, adopts a layered structure composed of PO₄ tetrahedra and ZrO₆ octahedra as well as complementary protons between the layers. Two types of layered zirconium phosphate, α- and γ-type (α-ZrP and γ-ZrP) form with different crystal structures.¹,² However, the chemical formula of both phosphate materials can be expressed as Zr(PO₄)₃n·H₂O (where n = 1 for α-ZrP and n = 2 for γ-ZrP) and the complementary protons are present in both phosphates. The protons can be easily replaced with other cations via ion exchange reaction and coordinated with basic organic molecules via acid-base reaction. Thus, zirconium phosphate has been applied as an ion exchanger, adsorbent, catalyst, and ion conductor.³–⁵ Furthermore, it has been used for removing specific components with high selectivity for alkali metals. Generally, both α- and γ-ZrP can be used as suitable host materials for intercalation of these ions.

Intercalation treatments of azo compounds were performed in the interlayer space of α- and γ-zirconium phosphates (ZrP). X-ray diffraction patterns confirmed that the intercalation of the azo compounds into α-ZrP occurred via an octylamine intercalated intermediate. CHN elemental analysis indicated that the azo compounds were substituted for pre-intercalated octylamine. In contrast, all azo compounds tested except for p-hydroxyazobenzene were directly intercalated into the interlayer space of γ-ZrP without octylamine. Photoisomerization of p-aminooazobenzene and p-hydroxyazobenzene included in γ-ZrP was observed along with their reversibility, as determined by alternate ultraviolet and visible photoirradiation for 30 min. The adsorption competency of the prepared materials for rare earth cation significantly increased depending on the azo molecule density.

Key-words : Layered zirconium phosphate, Azo compounds, Intercalation, Photoresponsivity, Adsorption

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Herein, we aimed to prepare organic–inorganic hybrids intercalated with azo compound in the interlayer space of \( \alpha \)- and \( \gamma \)-ZrP. The structure of the prepared organic–inorganic hybrids was evaluated and their photoresponsivity to irradiation by UV and visible light was characterized. Finally, the adsorption properties of rare earth elements to the prepared materials were also examined.

2. Experimental procedures

2.1 Hybridization of \( \alpha \)- and \( \gamma \)-zirconium phosphate with two types of photoresponsive organic molecules

Intercalation of three azobenzene-based molecules, p-aminoazobenzene (AB), chrysoideine (CH), and p-hydroxy-azobenzene (HAB), was achieved by refluxing. Figure 1 shows schematic illustrations of the structures of AB, CH, and HAB. The intercalation was performed as follows. First, 100 mL of distilled water was added to a three-necked flask as a solvent. The starting materials, \( \alpha \)- or \( \gamma \)-ZrP were added to the flask to a final concentration of 0.2 mol/L and stirred to achieve proper dispersion. Subsequently, each azobenzene molecule was added with a molar ratio of \( \alpha \)- or \( \gamma \)-ZrP:azoazobenzene of 1:2. The mixed solution was subsequently refluxed at 80°C for 48 h. Toluene was used instead of water as a solvent for the intercalation of HAB. After the treatment, the resulting mixture was filtered and washed using more solvent.

2.2 Characterization

The intercalation degree of the guest azo molecules was estimated via X-ray diffraction (XRD) using Cu K\( \alpha \) radiation with a wavelength of 0.15418 nm (RINT-2000, Rigaku). The amount of included water molecules was measured by thermogravimetry–differential thermal analysis (TG–DTA; Thermo Plus 8120, Rigaku). The amount of organic content in the hybrids was measured by CHN elemental analysis (MT-5, Yanaco). Fourier transform infrared (FT-IR) spectroscopy was used to confirm the presence and bonding state of organic molecules by KBr method.

To probe the photoresponsive properties of the organic–inorganic hybrids, photoisomerization experiments with the three azobenzene hybrids were performed as follows. An arbitrary amount of azobenzene hybrid sample was dispersed in 3 mL of acetonitrile in a quartz glass cell. These solutions were subsequently irradiated by wavelength-controlled light from a Xe short arc lamp (PE300B UV, Excelitas) for 30 min.10),11) To control the wavelength, cutoff filters were used. The sharp cutoff filters were used to remove wavelengths of <340 and >385 nm for UV irradiation. The cutoff was set to <450 and >550 nm for the visible light irradiation. After alternate irradiation at each wavelength, the absorption spectra of the samples were measured using a UV–vis spectrophotometer (V-550, JASCO).

The hybrid samples were examined for adsorption competency towards rare earth cations. The hybrid sample was placed into an aqueous solution containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb with a total concentration of 6000 mg/L (500 mg/L for each metal). The ratio of the sample to solution was fixed at 10 g/L. The mixed solution was shaken at 25°C for 48 h. Subsequently, the concentrations of each rare earth metal were measured by inductively coupled plasma (ICP-OES; PS3500DDII, Hitachi High-Technologies).

After the adsorption treatments, the samples were examined for their chemical state using X-ray absorption fine structure (XAFS) measurements in BL14B2 (SPRING8). In these measurements, the samples were pelletized via uniaxial pressing at 10 MPa. Then, the pelletized sample was arranged on the axis of an X-ray monochromated by Si(311). K absorption edges were measured via transmission mode. The measured data were analyzed by Athena.14)

3. Results and discussion

3.1 Structural characterization of the \( \alpha \)- and \( \gamma \)-ZrP azo compound hybrids

The host compound for dye accommodation should exhibit a wide transparent range for UV and visible light because the intercalated dye should be exposed to the irradiated light of any wavelength. Therefore, the absorption
of the host or mother compounds of $\alpha$- and $\gamma$-ZrP in the UV and visible wavelength ranges was evaluated by UV–vis spectroscopy with an integrated sphere. Figure 2 shows the UV–vis spectra of the $\alpha$- and $\gamma$-ZrP, showing relatively high reflectance of around 80% and few absorptions for both spectra. This indicated that zirconium phosphate was a suitable host material for azo compounds.

Figure 3(a) shows the XRD patterns of $\alpha$- and $\gamma$-ZrP, as well as the corresponding azobenzene intercalated composites. Not all azobenzene molecules could be inserted into the interlayer space of $\alpha$-ZrP. In contrast, AB and CH were intercalated into $\gamma$-ZrP, as shown in the corresponding XRD patterns. The interlayer distance increased by approximately 0.5 and 2.3 nm for the CH- and AB-introduced samples, respectively. The molecular lengths of CH and AB are approximately 1.46 nm, and it was hence supposed that CH lied flat on the layer and AB formed a bilayer slab.

To promote the intercalation, Oc was intercalated in the host beforehand to form an intermediate as a starting material. Figure 3(b) shows the XRD patterns of the $\alpha$- and $\gamma$-ZrP with Oc and the azo compound. From the XRD patterns of $\alpha$- and $\gamma$-ZrP(Oc), varying increases in the interlayer space were observed at approximately 2.0 and 1.4 nm, respectively. After introduction of AB, CH, and HAB, the interlayer distance increased slightly for $\alpha$-ZrP(Oc), indicating that the azobenzene was intercalated by replacing some of the Oc. For $\gamma$-ZrP, AB, CH, and HAB addition resulted in a slightly increased interlayer distance by 0.6–0.8 nm, where some of the Oc was likely substituted by the azobenzene. These patterns confirmed that all azo compounds can be intercalated directly and/or with the prior addition of Oc. Generally, coexisted Oc is unnecessary for the photoisomerization of the azobenzene. Therefore, we choose one sample for each combination (with and without Oc) by the rule with a priority of direct intercalation. Consequently, only the samples where the azo molecules were intercalated; $\alpha$-ZrP(Oc-AB), $\alpha$-ZrP(Oc-CH), $\gamma$-ZrP(Oc-AB), $\gamma$-ZrP(CH), and $\gamma$-ZrP(Oc-HAB) were analyzed, hereafter.

To investigate the chemical composition of the prepared hybrids, CHN and TG–DTA analyses were conducted. Table 1 shows the obtained chemical compositions of the hybrids. The Oc contents in $\alpha$-ZrP(Oc) and $\gamma$-ZrP(Oc) were 1.88 and 0.76 per mol of $\alpha$- and $\gamma$-ZrP, respectively. The Oc molecules likely formed bilayers and monolayers in the interlayer space of the $\alpha$- and $\gamma$-ZrP, respectively. The measured expansions of the interlayer spacings were 2.0 and 1.4 nm, which could be regarded as the bilayer and monolayer, respectively. In terms of the amounts of azo compounds, AB showed the largest intercalation amount in both $\alpha$- and $\gamma$-ZrP. For $\alpha$-ZrP-based samples, the AB, CH, and HAB contents were 0.73, 0.44, and 0.59 per mol of $\alpha$-ZrP, respectively, and the Oc content decreased to 1.55 per mol of $\gamma$-ZrP(Oc). Thus, some of the Oc were replaced by the azo compound and the others remained or were released during hybridization. For the $\gamma$-ZrP-based sample, the amounts of intercalated AB, CH, and HAB

![Figure 3](attachment:image3.png)

**Fig. 3.** XRD patterns of $\alpha$- and $\gamma$-ZrP, and their intercalated samples; (a) without octylamine and (b) with octylamine. Interlayer distance is also shown.

### Table 1. Chemical compositions of the hybrids

| samples               | x (azo comp.) | y (Oc) | m (H2O) | filling ratio |
|-----------------------|---------------|--------|---------|---------------|
| $\alpha$-ZrP(Oc)      | —             | 1.88   | 0.94    | 0.62          |
| $\alpha$-ZrP(Oc-AB)   | 0.73          | 0.49   | 0.57    | 0.38          |
| $\alpha$-ZrP(Oc-CH)   | 0.44          | 0.30   | 0.69    | 0.24          |
| $\alpha$-ZrP(Oc-HAB)  | 0.59          | 0.36   | 1.43    | 0.31          |
| $\gamma$-ZrP(Oc)      | —             | 0.76   | 0.81    | 0.49          |
| $\gamma$-ZrP(AB)      | 1.26          | —      | 0.98    | 0.56          |
| $\gamma$-ZrP(CH)      | 0.39          | —      | 1.21    | 0.82          |
| $\gamma$-ZrP(Oc-HAB)  | 0.66          | 0.25   | 1.22    | 0.42          |

General formula:

$\text{Zr(PO}_4\text{)}_{n-1}\text{(H}_2\text{PO}_4\text{)}_{n-2}(\text{azo compound})\text{O}_x\text{·mH}_2\text{O}$

($\alpha$-ZrP: $n = 1$, $\gamma$-ZrP: $n = 2$)
were 1.26, 0.39, and 0.66, respectively. A bilayer of azo molecules was formed in AB and HAB samples. Charge density within the interlayer space of the \( \alpha \)- and \( \gamma \)-ZrP was calculated to be approximately 0.120 and 0.089 nm\(^2\)/e, respectively. The cross-sectional areas were also estimated from these lengths and volume of each molecule as 0.127, 0.135, and 0.126 nm\(^2\) for the AB, CH, and HAB samples, respectively. Since these areas are larger than the charge densities of the \( \alpha \)- and \( \gamma \)-ZrP, bilayers or lacking monolayer textures should be generated due to charge compensation. Therefore, the filling ratios were calculated from the volumes of the azo molecules and composition, as listed in Table 1. For the \( \gamma \)-ZrP-based samples, the filling ratio was larger than that of the \( \alpha \)-ZrP-based samples. Particularly for the \( \gamma \)-ZrP(CH), >80% of the interlayer space was filled by the CH molecules due to the small interlayer space. This filling ratio and conformation of the molecules affected the photoisomerization of the azo molecules and adsorption of cationic species in the interlayer space.

FT-IR measurements were performed to confirm the bonding state and presence of guest molecules in the zirconium phosphate. Figure 4 shows the FT-IR spectra of the hybrid samples. The two peaks at 3400–3600 cm\(^{-1}\) were attributed to \( \text{O-H} \) of the interlayer water and the absorption peak at 1050 cm\(^{-1}\) to P–O.\(^{15}\) In the spectrum of the Oc intermediate and azobenzene hybrids, the peak at 3400–3600 cm\(^{-1}\) broadened. This behavior implied that the water conformation broadened.\(^{15}\) The peak assigned to the P–OH group slightly shifted toward lower wavenumbers likely due to the coordination bond between P–OH and the amine group. By introducing Oc, the two peaks attributed to C–H stretching vibration emerged at approximately 2800–3000 cm\(^{-1}\) derived from the alkyl chain.\(^{16,17}\)

By introducing CH and AB, the C–N stretching vibration of the aromatic primary amine was observed at 1250–1340 cm\(^{-1}\), C–C stretching vibration from the benzene ring at 1400–1500 cm\(^{-1}\), and stretching vibration derived from N=N of the azo group at approximately 1600 cm\(^{-1}\).\(^{16,17}\) Because the amino group of azobenzene was confirmed to coordinate with the proton from the P–OH group to generate \( \text{NH}_3^+ \), the azobenzene molecules were intercalated into the negatively charged layer of the zirconium phosphate.

### 3.2 Photoisomerization of the azobenzene hybrids

To confirm the absorption corresponding to \( \pi-\pi^* \) and n–\( \pi^* \) transitions derived from the trans and cis isomers and their isomerization reactions, UV–vis absorption spectra of the prepared hybrids were measured. Figures 5(a)–5(f) shows the absorption spectra of the samples before and after the alternative irradiation of UV and visible light for 30 min. From the spectra of the sample before irradiation, \( \pi-\pi^* \) absorption (350–450 nm) was observed for all hybrid samples. In addition, the n–\( \pi^* \) absorption (450–500 nm) was observed as a small shoulder for the AB and HAB intercalated samples, and as a large peak for the CH sample. To understand the cis-trans isomerization within the interlayer space of the \( \alpha \)- and \( \gamma \)-ZrP, UV–vis spectra of the photo-irradiated hybrids with UV and visible light were measured. In the \( \alpha \)-ZrP(Oc-AB) spectra after UV irradiation, the absorbance originating from the trans-isomer (at 385 nm) decreased [Fig. 5(a)]. Upon additional irradiation with visible light for 30 min, the absorbance of the 385 nm band attributed to the trans-isomer increased. Upon further continuous irradiation under the same conditions, a similar change was observed, confirming the reversibility of the photoisomerization of \( \alpha \)-ZrP(Oc-AB). Similar absorption changes for \( \gamma \)-ZrP(AB) (at 385 nm) and \( \gamma \)-ZrP(Oc-HAB) (at 345 nm) were also observed [Figs. 5(d) and 5(f)]. Particularly, the two \( \gamma \)-ZrP hybrid samples showed significant changes and increases in absorbance by alternating UV and visible light irradiation. This indicated that the azo group changed to a purer trans-isomer than that present in the as-prepared hybrid. Consequently, AB can be isomerized in both \( \alpha \)- and \( \gamma \)-ZrP, whereas HAB can be isomerized only in \( \gamma \)-ZrP irrespective of the filling ratio. For CH, isomerization was difficult because of the two amino groups with electron donating behavior. In this case, the absorption energy of \( \pi-\pi^* \) decreased and n–\( \pi^* \) could not be separately identified.

From these spectra, apparent photoisomerization behavior can be clear in the hybrids, \( \alpha \)-ZrP(Oc-AB), \( \gamma \)-ZrP(AB), and \( \gamma \)-ZrP(Oc-HAB). Therefore, the apparent photoisomerization quantum yield in these three hybrids was estimated from these UV–VIS spectra similar to the method reported by Stranius et al.\(^{18}\). For the calculation, the absorbance values at 385 nm (AB) and 345 nm (HAB) were used for formation of cis form, and those at 480 nm (AB) and 450 nm (HAB) were used for formation of trans
Figure 6 shows differential absorption spectra of these selected samples. From these spectra, the effect of a small absorption in the starting ZrP can be canceled. At a glance, the main absorption peaks at 350 nm are always negative for $\gamma$-ZrP(Oc-HAB). The reason is attributed to that the initial state of HAB dye is complete trans; the other dyes are a mixture of trans and cis form. The differential absorption of the $\gamma$-ZrP(Oc-AB) is around 4–10 times smaller than those of the other samples. Such small absorption may result from slow photoisomeric reaction. The apparent quantum yields from cis to trans are estimated as $3.0 \times 10^{-2}$, $2.0 \times 10^{-1}$, and $1.5 \times 10^{-1}$ for $\alpha$-ZrP(Oc-AB), $\gamma$-ZrP(AB), and $\gamma$-ZrP(Oc-HAB), respectively. Those from trans to cis form are $9.0 \times 10^{-4}$, $7.9 \times 10^{-2}$, and $5.8 \times 10^{-2}$, respectively. The $\gamma$-ZrP(AB) shows maximum quantum yields which are around half of the azobenzene reported value in the literature. The small quantum yield may result from the existence of the host layered material.

Fig. 6. Differential absorption spectra of azobenzene intercalated compounds before and after irradiation for 30 min; (a) $\alpha$-ZrP(Oc-AB), (b) $\alpha$-ZrP(Oc-CH), (c) $\alpha$-ZrP(Oc-HAB), (d) $\gamma$-ZrP(AB), (e) $\gamma$-ZrP(CH), and (f) $\gamma$-ZrP(Oc-HAB).

Fig. 7. The amount of rare earth adsorption for the prepared $\alpha$-ZrP(Oc-AB), $\alpha$-ZrP(Oc-HAB), $\gamma$-ZrP(AB), $\gamma$-ZrP(Oc-HAB), and $\gamma$-ZrP samples.
3.3 Adsorption of rare earth elements and their incorporation into the interlayer space

Previously, photoisomerization behavior was examined and the $\alpha$-ZrP(Oc-AB), $\gamma$-ZrP(AB), and $\gamma$-ZrP(Oc-HAB) species could be formed and they exhibited photoisomerization. These results indicate that the azo groups may not be fixed in the interlayer space. The free lone pair on the azo group can affect the adsorption of cationic species via coordination bonding. Therefore, the adsorption of rare earth elements was examined. Figure 7 shows the relationships between the ionic radius and adsorption degree of rare earth cations by the hybrids. In these curves, four ridges which were derived from the tetrad effect were observed. Generally, the effect with upward ridges in terms of the adsorption amount implies that the ionicty of the rare earth element decreased upon adsorption. That is, the rare earth elements showed decreased ionicty upon adsorption and ion exchange and/or sorption by weak interactions.

Comparing all samples, the absorption by $\gamma$-ZrP(AB) was conspicuously lower than those of the other samples. The ionic equivalent amount of $\gamma$-ZrP and $\gamma$-ZrP(AB) derived from the ion exchange of H$^+$ was calculated to be approximately 2.08 and 0.77 mmol/g, respectively. These values can be converted to 267 and 99 mg/L per lanthanoid cation when the equimolar amounts of the 12 lanthanoid elements were assumed to be adsorbed. Thus, $\gamma$-ZrP(AB) showed significantly increased competency for rare earth adsorption of approximately 3.6 times that of the theoretical value determined by H$^+$ exchange. Since the adsorption amounts of each lanthanoid element were approximately 370 mg/L on average, the excess adsorption (over that of H$^+$ exchange) of approximately 270 mg/L resulted from the presence of the intercalated AB molecules. That is, the lone pair on the azo group likely adsorbed the lanthanoid cations (include lanthanum) by complex formation.

In these experiments, only $\gamma$-ZrP(AB) showed additional adsorption of cations likely due to the abundant 2–3 times that of the other compounds. After adsorption treatments, the amounts of azo compounds remaining were measured. The value $x$ indicates the amount of the azo molecules remaining, with values of approximately 90, 95, and 99% for $\alpha$-ZrP(Oc-AB), $\gamma$-ZrP(AB), and $\gamma$-ZrP(Oc-HAB), respectively. Therefore, the azo molecules were not replaced by the lanthanoid cations.

To analyze the state of the adsorbed rare earth elements, La K XAFS was measured as a representative adsorbed element. Figure 8 shows the X-ray absorption near edge structure (XANES) curves of the lanthanoid element-adsorbed $\gamma$-ZrP(AB) and reference materials. The adsorption edges are very similar, indicating the existence of trivalent La in all samples. In contrast, the curve slightly differed in the larger energy range. The difference was caused by different coordination of the La atoms. The curves of $\gamma$-ZrP and $\gamma$-ZrP(AB) were similar and differed from those of the other samples. These curves confirmed that $\gamma$-ZrP(AB) is similar to $\gamma$-ZrP. Thus, these XANES curves provide strong evidence for the lack of formation of La(NO$_3$)$_3$ and La(OH)$_3$ within the samples. That is, the free lone pair of the azo molecules in the limited intercalating space with a relatively large density can affect the adsorption of rare earth cations.

4. Conclusions

Azobenzenes and layered zirconium phosphate were hybridized by refluxing. The azobenzene molecules used were AB, CH, and HAB for hybridization of the layered zirconium phosphate. The hybrids were examined for photoisomerization upon alternate irradiation of UV and visible light, as well as for their ability to adsorb rare earth elements. The relationships between photoisomerization and adsorption of rare earth elements and the texture of hybrids were also probed. The major conclusions were as follows.

1. For $\alpha$-ZrP, no azobenzene compounds could be hybridized directly using the methods described herein. Pre-intercalation by Oc provided sufficient interlayer space where all azobenzenes (AB, CH, and HAB) could be intercalated.
2. For $\gamma$-ZrP, AB and CH could be intercalated directly into the interlayer space, whereas HAB could only be intercalated to the Oc-intercalated intermediate.
3. Photoisomerization of the azo compounds intercalated within ZrP was confirmed for only AB and HAB molecules irrespective of the volume of the interlayer space.
4. Lanthanoid elements could be effectively adsorbed by the prepared photoisomerization-active hybrid. Particularly, $\gamma$-ZrP(AB) showed an extraordinarily efficient adsorption.
5. From the chemical compositions and XANES results, the lone pair in the azo groups likely affected the adsorption of the lanthanoid elements.
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References
1) J. M. Troup and A. Clearfield, Inorg. Chem., 16, 3311–3313 (1977).
2) D. M. Poojary, B. Shpeizer and A. Clearfield, J. Chem. Soc. Dalton, 111–113 (1995).
3) L. Szirtes, J. Megyeri, L. Riess, E. Kuzmann and K. Havancsák, Radiat. Phys. Chem., 73, 39–44 (2005).
4) R. Thakkar and U. Chudasama, J. Sci. Ind. Res., 68, 312–318 (2009).
5) T. Takei, K. Iizuka, A. Miura, S. Yanagida, N. Kumada, E. Magome, C. Moriyoshi and Y. Kuroiwa, Langmuir, 32, 9993–9999 (2016).
6) B. Casanas, A. Diaz, C. Barbosa, C. Ramos, C. Collazo, E. Meléndez, C. Queffelec, F. Fayon, A. Clearfield, B. Bujolli and J. L. Colón, J. Organomet. Chem., 791, 34–40 (2015).
7) T. Takei, N. Kumada, N. Kinomura, H. Nakayama and M. Tsuhako, Mater. Res. Bull., 43, 111–119 (2008).
8) R. Hoppe, G. Alberti, U. Costantino, C. Dionigi, G. Schulz-Ekloff and R. Vitani, Langmuir, 13, 7252–7257 (1997).
9) E. Brunet, M. J. Mata, O. Juanes and J. C. Rodrigues-Ubis, Chem. Mater., 16, 1517–1522 (2004).
10) M. Ogawa, H. Kimura, K. Kuroda and C. Kata, Clay Sci., 10, 57–59 (1996).
11) M. Ogawa, T. Ishii, N. Miyamoto and K. Kuroda, Appl. Clay Sci., 22, 179–180 (2003).
12) C. Montagner, M. Bacci, S. Bracci, R. Freeman and M. Picollo, Spectrochim. Acta A, 79, 1669–1680 (2011).
13) T. Takei, Q. Dong, Y. Yonesaki, N. Kumada and N. Kinomura, Langmuir, 27, 126–131 (2011).
14) B. Ravel and M. Newville, J. Synchrotron Radiat., 12, 537–541 (2005).
15) A. F. Ali, A. A. Hanna and A. E. Gad, Phosphorus Res. Bull., 22, 32–40 (2008).
16) H.-N. Kim, S. W. Keller and T. E. Mallouk, Chem. Mater., 9, 1414–1421 (1997).
17) J. Coates, “Interpretation of Infrared Spectra, A Practical Approach, in Encyclopedia of Analytical Chemistry”, Ed. by R. A. Meyres, John Wiley & Sons, Ltd, Chichester, UK (2006) pp. 1–23.
18) K. Stranius and K. Börjesson, Sci. Rep., 7, 41145 (2017).
19) I. Kawabe, Geochem. J., 26, 309–335 (1992).
20) I. Kawabe, Geochem. J., 33, 267–275 (1999).