ORIGINAL ARTICLE

Organic/inorganic fusion materials: cyclodextrin-based polymer/CaCO₃ hybrids incorporating dye molecules through host–guest interactions

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In this work, fluorescent and azo dyes were incorporated into CaCO₃ and cyclodextrin (CD)-based network polymer thin-film hybrids through host–guest interactions. The hybrid films were prepared on poly(CD)s by a one-pot CaCl₂ and Na₂CO₃ solution process in the presence of poly(acrylic acid). The hybrid-thin films containing fluorescent dyes demonstrate homogeneous fluorescence. The photoisomerization of azo dyes is observed in the solid thin-film hybrids.

INTRODUCTION

Biomineralization is the process by which living organisms produce hard tissues.[1,2] During this process, living organisms deposit inorganic materials with elaborate structures under mild conditions.[3–6] It is therefore promising to mimic the mechanisms of biomineralization in the development of new environmental friendly approaches for synthesis of inorganic materials.[7–11] Among biominerals, CaCO₃ has attracted particular attention [8–18] because it is the most abundant biomineral in nature.[1] Biomimetic control of CaCO₃ material crystallization under mild conditions has been extensively reported.[8–23] These approaches achieved crystallization that mimics the biomineralization process by adding organic molecules to the CaCO₃ crystallization solution.[24–26]

Our previous studies focused on preparing CaCO₃ thin films[9,22,27–41] and other organic/inorganic hybrids.[42–44] To induce CaCO₃ thin-film crystals in the presence of soluble electrolytes, we utilized insoluble polymers as matrices. Through this approach, CaCO₃ thin-film hybrids were obtained on a variety of hydrophilic matrices including chitin,[27–30] chitosan,[31,32] poly(vinyl alcohol) (PVA),[33–38] pullulan[39,40] and polymer brushes.[41] However, further functionalization of these organic/inorganic hybrids with hydrophobic molecules is difficult[45–48] because of the hydrophilicity of both the inorganic crystals and the matrices. Thus, the current study aims to use cyclodextrin (CD) as a functional molecule host in the CaCO₃ thin films to introduce functional hydrophobic molecules.

CDs are characterized by a hydrophilic exterior and a hydrophobic central cavity (Figure 1).[49,50] They can accommodate hydrophobic molecules while maintaining outer surface hydrophilicity.[49–54] Accordingly, we expect that matrices containing CDs will induce thin-film growth of CaCO₃ while allowing for incorporation of hydrophobic molecules if the CD cavities are not hindered after crystallization. In the present study, hybrid films with host–guest

interaction-incorporated fluorescent and azo dyes (Figure 2) were prepared on **poly(CD)s** (Figure 1b) through a one-pot CaCl₂ and Na₂CO₃ solution process in the presence of poly(acrylic acid).

EXPERIMENTAL PROCEDURE

Materials

α-CD, β-CD, ethylene glycol diglycidyl ether (EDGE), bromoethane, sodium 6-(p-toluidino)naphthalene-2-sulfonate (**D1**), rhodamine B (**D2**), ammonium 8-anilinonaphthalene-1-sulfonate (**D3**), eosin Y (**D4**), dansyl-L-phenylalanine (**D5**), fluorescein (**D6**), anthracene-9-carboxylic acid (**D7**) and 1-aminopyrene (**D8**) were obtained from Tokyo Kasei (Tokyo, Japan). D₂O was utilized as the solvent for nuclear magnetic resonance (NMR) and was obtained from Acros Organics (Bridgewater, NJ, USA). Calcium chloride, ammonium carbonate and all other solvents were purchased from Wako (Tokyo, Japan). All reagents were utilized without further purification.

Characterization

¹H NMR spectra were recorded on a JNM-LA400 spectrometer (JEOL, Tokyo, Japan) with D₂O as the solvent. Chemical shifts were referenced to the solvent residual peak (δ 4.79 p.p.m.). Crystal samples were coated with platinum for scanning electron microscopy observation using a Hitachi E-1030 ion sputter (Hitachi, Tokyo, Japan). Scanning electron microscopy images were obtained on a Hitachi S-4700 field-emission scanning electron microscopy (Hitachi). Ultraviolet–visible (UV) spectra were obtained on a V-670 UV spectrophotometer (Jasco, Tokyo, Japan) equipped with an integrating sphere. Circular dichroism spectra were obtained on a J-820 spectropolarimeter (Jasco). Irradiation of thin-film hybrids was carried out using a SP-9 light source (Ushio, Tokyo, Japan). U360 and Y44 filters (Hoya, Tokyo, Japan) were employed to obtain UV and Vis irradiation.

Synthesis of poly(CD)s and preparation of poly(CD) matrices

Solutions of **poly(α-CD)** and **poly(β-CD)** were synthesized following the previously reported method but with minor modifications.[55] α-CD (6.85 g, 7.05 × 10⁻³ mol) or β-CD (8 g, 7.05 × 10⁻³ mol) was dissolved in an aqueous
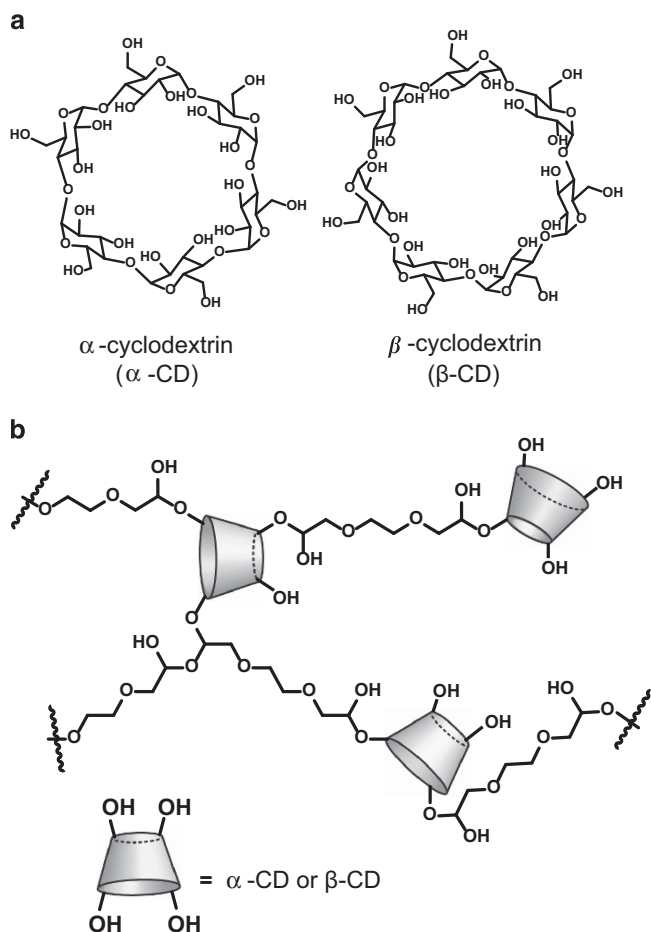
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Figure 1 Chemical structures of (**a**) α- and β-cyclodextrin and (**b**) **poly (cyclodextrin)** matrices.

Figure 2 Functional dyes utilized in the present study.

solution of NaOH (20 ml, 1 M). EDGE (5 ml, 2.43×10^{-2} mol) was subsequently added into the solution. The mixture was stirred at 70 °C for 1 h, precipitated, washed with methanol and dried under vacuum to provide **poly (α-CD)** (4.73 g, 45%) or **poly(β-CD)** (4.85 g, 37%). ¹H NMR of **poly(α-CD)** (D₂O, 400 MHz): δ 5.35–4.85 (1-H of α-CD, ¹H), 4.30–3.20 (2,3,4,5,6-H of α-CD and H of EDGE, 12.92H). ¹H NMR of **poly(β-CD)** (D₂O, 400 MHz): δ 5.35–4.85 (1-H of α-CD, 1H), 4.30–3.20 (2,3,4,5,6-H of α-CD and H of EDGE, 14.4H).

To prepare **poly(CD)** matrices, **poly(CD)s** were dissolved in dimethylsulfoxide at 16 wt%, and the resulting solutions were spin coated (2000 r.p.m., 30 s) onto glass substrates. The matrices were then air dried and annealed at 180 °C for 30 min to insolubilize them and thoroughly washed with deionized water. PVA matrices were prepared as previously described.[35]

Crystallization of CaCO₃

Crystallization was performed using a previously reported method with minor modification.[37] Briefly, the supersaturated solution of CaCO₃ was prepared by mixing a solution of Na₂CO₃ (40 mM) and a solution of CaCl₂ (40 mM) and poly(acrylic acid) (0.24 wt%; 1:1 v/v). Vessels containing polymer matrices and freshly prepared supersaturated CaCO₃ solutions (4 ml) were placed in an FMU-131I incubator (Fukushima, Tokyo, Japan) with the temperature set to 25 °C. Samples were removed from the solution after 1 day and dried for characterization.

Synthesis of sodium 4-ethoxy-4′-azobenzene sulfonate (D9)

D9 was synthesized using the method reported by Bazuin and co-workers.[56] Sodium 4-hydroxyazobenzene-4′-sulfonate (1.04 g, 3.46×10^{-3} mol), anhydrous
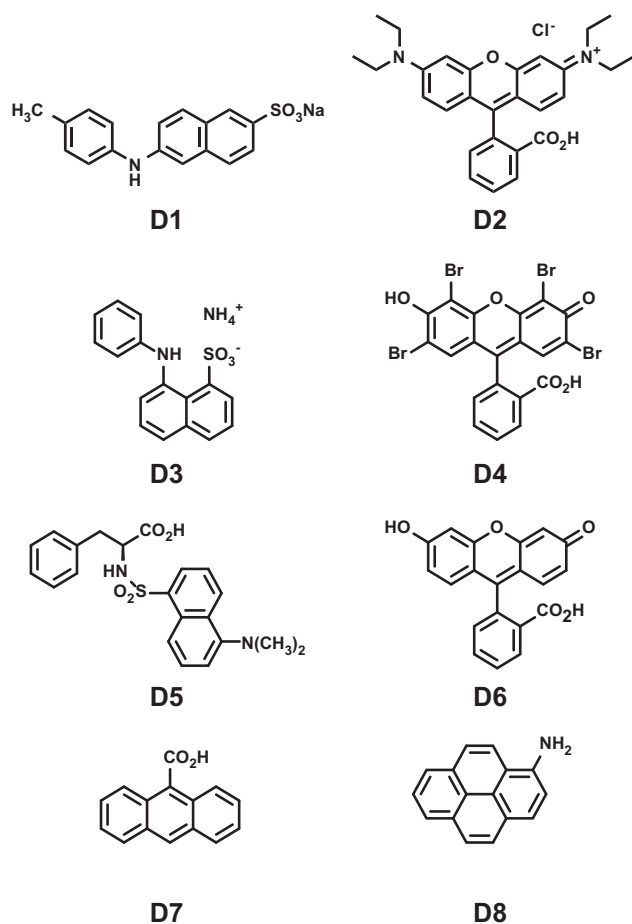
potassium carbonate (1.43 g, 3 eq.) and bromoethane (3.76 g, 10 eq.) were added to anhydrous DMF (20 ml). The mixture was stirred at 80 °C for 2 days. Next, the mixture was centrifuged to remove insoluble substances. The supernatant was precipitated with acetone three times. The final precipitate was rinsed with small amounts of water and dried under vacuum, resulting in an orange powder (0.32 g, yield 27%). ¹H NMR (D₂O, 400 MHz): δ 1.36 (t, $J = 7.25$ Hz, 3H), 4.16 (q, $J = 7.25$ Hz, 2H), 7.06–7.13 (m, 2H), 7.76–7.97 (m, 6H).

Incorporation of dyes into thin-film hybrids of CaCO₃/poly(CD)

Aqueous solutions (0.5 mM) were prepared for **D1**, **D2**, **D3**, **D4** and **D5**. Solutions (0.5 mM) of **D6**, **D7** and **D8** were prepared in mixtures of methanol and water (1:1 v/v). **D9** was dissolved in pure water (5 mM).

Thin-film hybrids of CaCO₃/**poly(CD)** were immersed in the dye solutions for 1 h and then washed extensively with water to remove excess or weakly bound dye molecules.

RESULTS AND DISCUSSION

Solutions of **poly(CD)** in dimethylsulfoxide were utilized to prepare thin-film matrices of **poly(CD)** by crosslinking CDs[55] with EDGE (Figure 1). The amounts of CDs in the **poly(CD)** solutions were roughly estimated by comparing integrations over the ranges of 5.35–4.85 (1-H of CDs) and 4.30–3.20 (2,3,4,5,6-H of CDs and H of EDGE) in the ¹H NMR spectra. The **poly(α-CD)** matrix was estimated to contain 65 wt% of α-CD, corresponding to 3.0 residual EDGEs per α-CD unit. The β-CD content in the polymer was calculated to be 61 wt% based on the EDGE ratio (4.2 residues per β-CD).
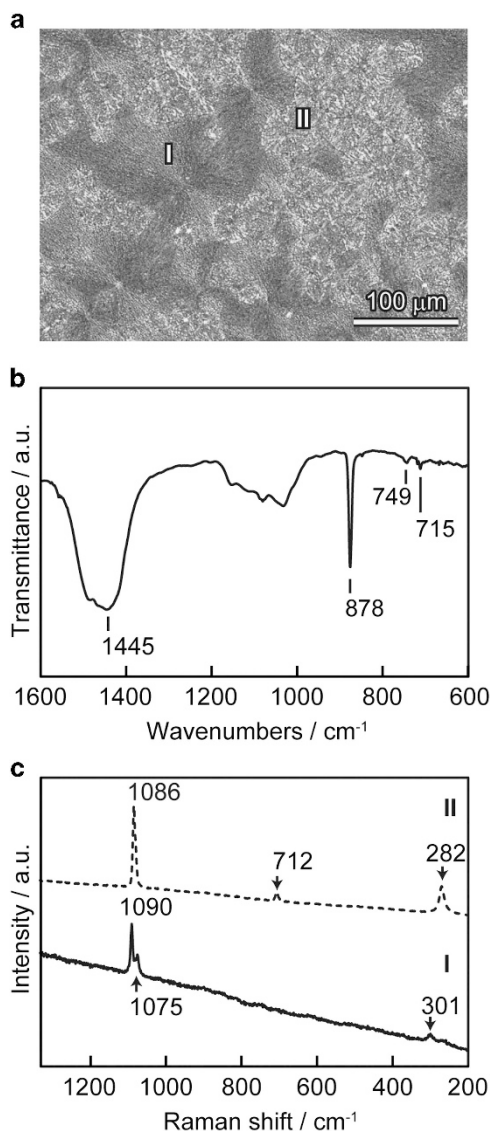
Figure 3 (a) Polarizing optical micrograph, (b) infrared spectra and (c) micro-Raman spectra of the CaCO₃ thin films formed on **poly(β-CD)** matrices in the presence of poly(acrylic acid). Numbers I and II indicate the two different types of thin films. A full color version of this figure is available at *Polymer Journal* online.

Figure 4 (a) Scanning electron microscopy images of the thin-film hybrid of CaCO₃/**poly(β-CD)** and (b) magnified image of **a**.

CaCO₃ was crystallized by immersing the **poly(CD)** matrices in a supersaturated solution of CaCO₃, which was prepared by mixing a solution of Na₂CO₃ with a solution of CaCl₂ and poly(acrylic acid). Thin-film hybrids with two types of spherulitic textures were obtained (Figure 3a). Type I films were larger with a weaker birefringence than type II films. The thin films were characterized by infrared and Raman spectra. The IR bands of CO_3^{2-} at 878 cm^{-1} (v_2, out-of-plane bending mode), 715 cm^{-1} (v_4, in-plane bending mode) and 749 cm^{-1} ($v_{4'}$) suggest that both calcite and vaterite exist in the hybrids (Figure 3b). The micro-Raman spectra (Figure 3c) show that two polymorphs are associated with the different thin-film types. Type I shows a split v_1 band between 1090 and 1076 cm^{-1}, which is indicative of vaterite formation. Type II show Raman bands at 1086 (v_1) and 282 cm^{-1} (librational lattice mode), which suggests a calcite polymorph. We also measured the powder X-ray diffraction pattern of the whole thin-film sample. As shown in Supplementary Figure S1,
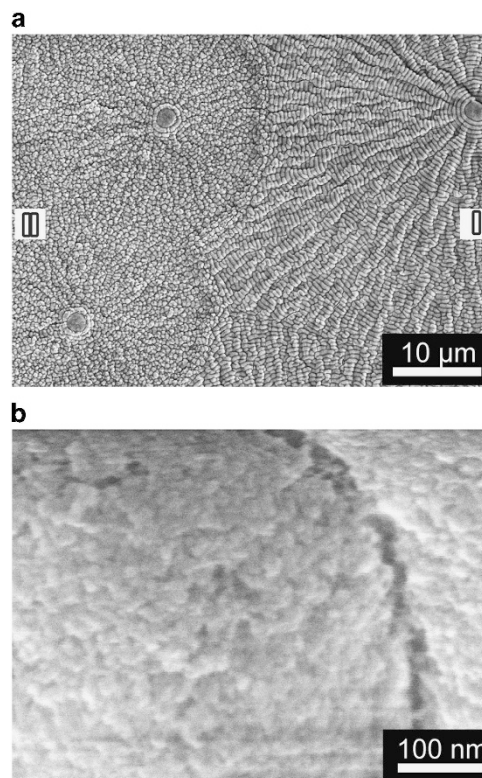
peaks corresponding to both calcite and vaterite were observed in the X-ray diffraction pattern.

The resultant thin-film hybrids of CaCO₃/**poly(β-CD)** were characterized by scanning electron microscopy. Both types of CaCO₃ thin films grew radially with spherulitic patterns (Figure 4a). The films consist of nanocrystals of ~10–20 nm in diameter (Figure 4b) with vacancies between these nanocrystals. Thus, dye molecules may access the entire hybrid film from these vacancies even after crystallization of CaCO₃.

The β-CD cavities accommodate a variety of fluorescent dyes.[57] The thin-film hybrids of CaCO₃/**poly(β-CD)** were immersed in fluorescent dye solutions to allow for their incorporation into the matrices. Figures 5a and b show the hybrid matrix with a hydrophobic fluorescent dye **D1**. The hybrid of **D1** and CaCO₃/**poly(β-CD)** is fluorescent (Figure 5a). By contrast, the CaCO₃/PVA hybrid exhibits almost no fluorescence (Figure 5b). **D1** is a fluorescent probe with fluorescent intensity that increases with the hydrophobicity of its microenvironment.[58] The fluorescence of **D1** is negligible in water. Thus, the high intensity fluorescence of the hybrid of **D1** and CaCO₃/**poly(β-CD)** is direct evidence of the successful incorporation of **D1** into the β-CD cavities.[59]

In addition to hydrophobic dyes, hydrophilic dyes with hydrophobic moieties can be incorporated into the hybrid matrices. For example, it can be seen that the CaCO₃/**poly(β-CD)** hybrid contains more **D2** than the CaCO₃/PVA hybrid (Figure 5d, right). Although both **D1** and **D2** were introduced into the hybrids after crystallization of CaCO₃ thin films, the hybrid fluorescence is generally homogeneous. This observation suggests that the CD cavities remained accessible to the fluorescent dyes after CaCO₃ crystallization. Figure 6 shows fluorescence of thin-film hybrids complexed with
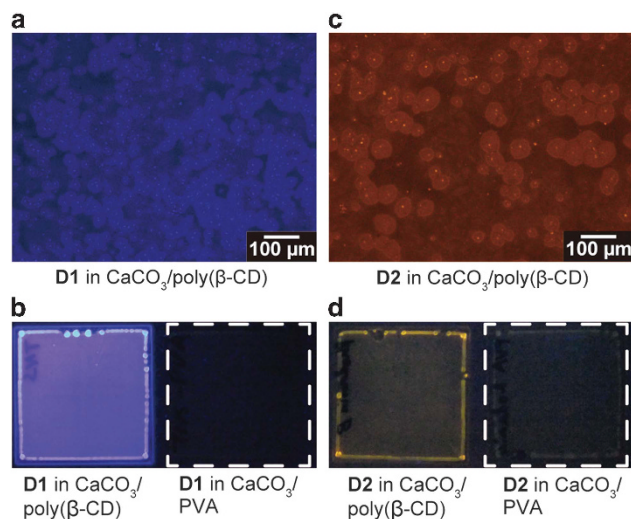
Figure 7 Chemical structure of sodium 4-ethoxy-4′-azobenzene sulfonate (**D9**).

Figure 8 (**a**) Circular dichroism spectra and (**b**) ultraviolet–visible spectra of: thin-film hybrid of CaCO₃/poly(α-CD) after incorporation of sodium 4-ethoxy-4′-azobenzene sulfonate (**D9**), thin-film hybrid of CaCO₃/poly(vinyl alcohol) after incorporation of **D9**, and aqueous solution of **D9** and poly(α-CD).

Figure 5 (**a**) Fluorescent micrograph of thin-film hybrids of CaCO₃/**poly(β-CD)** after incorporation of sodium 6-(p-toluidino)naphthalene-2-sulfonate (**D1**). (**b**) Macroscopic images comparing the fluorescence intensity of thin-film hybrids of CaCO₃/**poly(β-CD)** (I) and CaCO₃/poly(vinyl alcohol) (PVA) (II) after incorporation of **D1**. (**c**) Fluorescent micrograph of thin-film hybrids of CaCO₃/**poly(β-CD)** after incorporation of rhodamine B (**D2**). (**d**) Macroscopic images comparing the fluorescence intensity of thin-film hybrids of (I) and (II) after incorporation of **D1**.
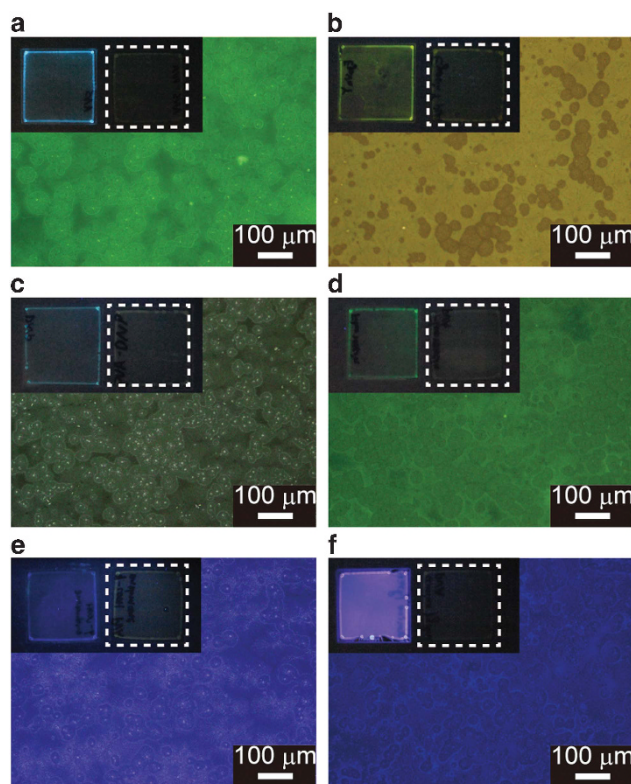

Figure 6 Microscopic images showing the fluorescence of thin-film hybrids of CaCO₃/**poly(β-CD)** after incorporation of various fluorescent dyes: (**a**) 8-anilinonaphthalene-1-sulfonate (**D3**), (**b**) eosin Y (**D4**), (**c**) dansyl-L-phenylalanine (**D5**), (**d**) fluorescein (**D6**), (**e**) anthracene-9-carboxylic acid (**D7**) and (**f**) 1-aminopyrene (**D8**). Insets are photographs comparing the fluorescence of thin-film hybrids of CaCO₃/**poly(β-CD)** (left) and CaCO₃/poly (vinyl alcohol) (right).
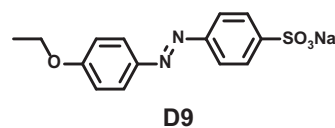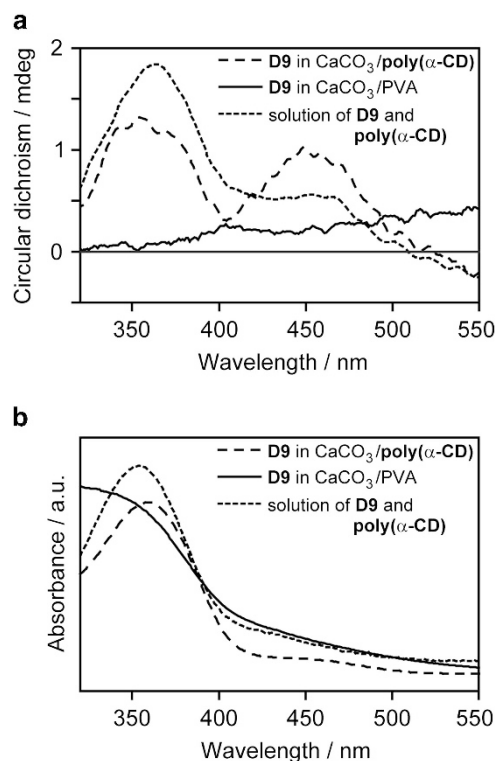
various fluorescent dyes (**D3–D8**). The fluorescence intensity of each dye in the CaCO₃/**poly(β-CD)** hybrids is higher than that of the dyes in the CaCO₃/PVA matrices. These results suggest that the dyes interact more strongly with the cavities of **poly(β-CD)** than with the PVA chains.

Azo-dyes show *cis–trans* isomerization. They have been previously incorporated into a variety of polymeric materials.[60–62] For introduction of an azo dye, **D9** (Figure 7), into the thin-film materials, a CaCO₃/**poly(α-CD)** hybrid was utilized, as *cis*-azobenzene binds more strongly to the smaller cavities of α-CD than to the cavities of β-CD.[63] The morphology of the obtained CaCO₃/**poly(α-CD)** hybrid was similar to that of the CaCO₃/**poly(β-CD)** hybrid. The hybrid was immersed into an aqueous solution of **D9** (5 mM) to allow for dye incorporation. The incorporation of **D9** into **poly(α-CD)** is evidenced by the induced circular dichroism of **D9**, as shown in Figure 8. **D9** adsorbed onto the thin-film hybrid of CaCO₃/PVA exhibits no circular dichroism, as **D9** is achiral (Figure 8a). However, for **D9** adsorbed onto the thin-film hybrid of CaCO₃/**poly(α-CD)**, two cotton bands at ~350 and 450 nm are observed (Figure 8a). These two bands correspond to the $\pi \rightarrow \pi^\star$ and $n \rightarrow \pi^\star$ transition of **D9**.[64] The induced circular dichroism suggests the presence of interactions between **D9** and **poly(α-CD)** in the hybrid. **D9** in solution of **poly(α-CD)** also
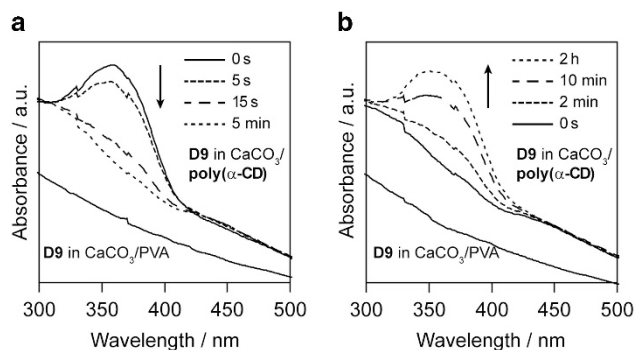
Figure 9 Time-dependent Ultraviolet–visible (UV–Vis) spectra of thin-film hybrid of CaCO₃/**poly(α-CD)** after incorporation of sodium 4-ethoxy-4′-azobenzene sulfonate (**D9**) with (**a**) irradiation of 350 nm UV light and (**b**) irradiation of visible light (>440 nm light) after 350 nm UV irradiation for 5 min. The UV–Vis spectrum of thin-film hybrids of CaCO₃/poly(vinyl alcohol) after incorporation of **D9** and subsequent washing is also displayed.

shows two cotton bands located at ~350 and 450 nm (Figure 8a). However, relative intensities of these two bands are different from those in the spectrum of the CaCO₃/**poly(α-CD)** hybrid.

The hybrids were washed and characterized by UV–Vis spectroscopy. The attachment of **D9** to the CaCO₃/PVA hybrid is relatively weak, as it is observed that no **D9** remains in the hybrid after washing (Figure 9). By contrast, because of the interaction between **D9** and **poly(α-CD)**, the absorption peak of **D9** is still distinct in the spectrum of the washed CaCO₃/**poly(α-CD)** hybrid. The photoisomerization behavior of **D9** in the CaCO₃/**poly(α-CD)** hybrid was examined (Figure 9). On irradiation with UV light, the absorption at ~350 nm ($\pi \to \pi^{\star}$) decreases (Figure 9a), suggesting that the incorporated **D9** changes conformation from *trans* to *cis*. Recovery of this conformational change is observed when the hybrid is subsequently irradiated with visible light, as shown in Figure 9b. Photoisomerization of azo dyes is generally disturbed in the solid state,[65] because such isomerization requires free volume.[66] The observed photoisomerization of **D9** in the hybrid may be facilitated by the cavities of α-CDs.[67,68]

CONCLUSIONS

In this study, we prepared thin-film CaCO₃-based hybrid materials using **poly(CD)** matrices. The resulting hybrids were easily functionalized by immersion in solutions of functional molecules. The selected functional molecules were incorporated into the thin-film organic/inorganic hybrids and dispersed throughout the molecular level with efficient function. These studies provide an option for fusion materials inspired by biomineralization. CaCO₃-based biominerals are attractive due to their environmental friendly processing and formation; however, the function of synthetic CaCO₃ is relatively limited. Here, we provide a new approach to the addition of photofunction to CaCO₃-based hybrid materials. These fusion materials take advantage of the harmonization of organic and inorganic, soft and hard and polymeric and ceramic materials with the aim of providing new functional materials.

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