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Editor's Choice

Controlled Encapsulation of Photoresponsive Macromolecules in Porous Coordination Polymer

Takashi Uemura,*[1] Gosuke Washino,[1] Nobuhiro Yanai,[1,†] and Susumu Kitagawa*[1,2]
[1]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510*
[2]*Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501*

(Received November 29, 2012; CL-121189; E-mail: uemura@sbchem.kyoto-u.ac.jp)

A photoresponsive controlled adsorption system based on a porous coordination polymer (PCP) was fabricated, using azobenzene tethered with poly(ethylene glycol) (PEG-AB) as macromolecular guests. Specific adsorption behavior of *trans*-PEG-AB into the nanochannels of a PCP was observed in an EtOH medium. When this composite was irradiated with UV light in EtOH, isomerization of PEG-AB from the trans to the cis form resulted in release of PEG-AB because of the large changes in the molecular shape and solubility of PEG-AB. Subsequent visible light irradiation induced photoisomerization of PEG-AB, which led to readsorption of PEG-AB into the nanochannels.

In recent years, controllable encapsulation–release systems using porous and capsule materials operated by external stimuli, such as heat, pH, and light, have attracted great interest in materials science.[1–4] Intelligent host–guest systems that can be reversibly switched in a controlled manner have enormous potential for innovative applications such as in energy harvesting and storage, in controlled-release delivery of drugs, and in the development of nanoscale optical and molecular electronics devices.[5–7]

Porous coordination polymers (PCPs), composed of metal ions and bridging organic ligands, have recently emerged as an important family of porous materials because of their unique structural and functional properties.[8–12] PCPs have highly regular and designable nanopores that can be used for storage, separation, and catalysis. In particular, developing new PCP-based carrier systems for controlled release is of current interest.[13,14] Because of their nontoxic nature, imaging properties, and capability for large drug loadings, PCPs are suitable candidates as drug-delivery carriers.[13,14]

Herein, we report a photoresponsive reversible encapsulation–release system using [Zn_2(terephthalate)$_2$(triethylenediamine)] (**1**)[15] and an azobenzene derivative (Figure 1). The key in this work is appropriate design of the guest azobenzene molecule, in which modification of azobenzene with poly(ethylene glycol) (PEG) at the 4,4′-position affords large differences in the shape and solubility upon cis–trans isomerization. In this system, irradiation with UV and visible light could reversibly switch the host–guest adsorption as a result of isomerization of the PEG-tethered azobenzene (PEG-AB) (Figure 1).

PEG-AB was synthesized by the reaction of 4,4′-dihydroxyazobenzene[16] with tetra(ethylene glycol) monomethyl ether tosylate.[17] We prepared various PEG-AB solutions, such as MeOH, EtOH, acetone, *n*-hexane, tetrahydrofuran, dimethylformamide, dichloromethane, toluene, diethyl ether, and 1,4-dioxane,

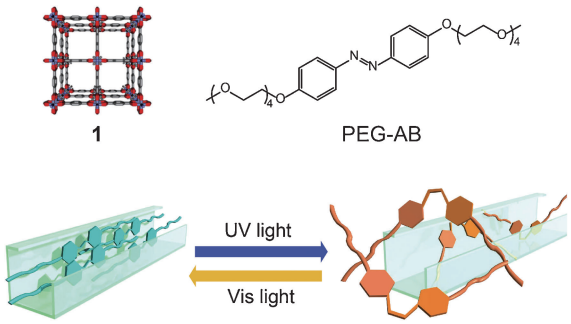

Figure 1. Schematic illustration of host **1**, PEG-AB, and photoresponsive encapsulation of PEG-AB in **1**.

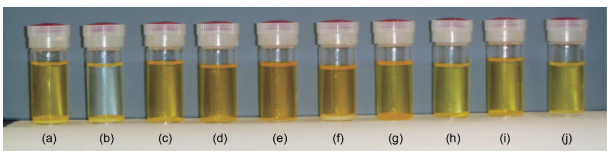

Figure 2. Incorporation of PEG-AB into **1** in various solvents, such as (a) MeOH, (b) EtOH, (c) acetone, (d) *n*-hexane, (e) tetrahydrofuran, (f) dimethylformamide, (g) dichrolomethane, (h) toluene, (i) diethyl ether, and (j) 1,4-dioxane. The experiment using EtOH only gave colorless solution, showing the quantitative adsorption of the PEG-AB molecules into **1**.

and attempted to incorporate PEG-AB into **1** via liquid-phase adsorption (Figure 2). Successful incorporation of PEG-AB was only observed in EtOH, where the yellow-colored solution of PEG-AB became colorless after mixing with **1** (Figure 2). This is probably because of the relatively low solubility of PEG-AB in EtOH compared with the other solvents. The resulting yellow precipitate was isolated by filtration, and subsequent washing with EtOH gave the inclusion composite. X-ray powder diffraction measurements of **1** showed no changes in the peak positions before and after the inclusion of PEG-AB, indicating that the host structure of **1** was maintained upon macromolecular guest inclusion (Figure S1).[21] DSC measurements of the composite did not show an appreciable peak for melting of neat PEG-AB, suggesting no excess PEG-AB existed outside the host frameworks (Figure S2).[21] To isolate the PEG-AB inside the channels, the composite was stirred in a 0.05 M aqueous solution of sodium ethylenediaminetetraacetate (Na-EDTA) for complete dissolution of the host porous framework.[18] Subsequent extraction with $CDCl_3$ allowed ^{1}H NMR measurements, which clearly show the existence of PEG-AB, indicating the inclusion of PEG-AB in the channels of **1** (Figure S2).[21]

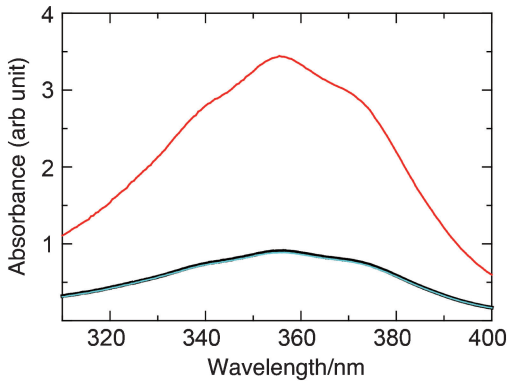

Figure 3. UV–vis absorption spectra of supernatants of **1** with PEG-AB in EtOH (black: before UV irradiation, red: after UV irradiation, and blue: left under visible light). For comparison, the spectrum of UV irradiated PEG-AB (cis form) was measured after the isomerization to the trans form left under visible light. Absorbance at 355.5 nm was used for determining the concentration of PEG-AB in EtOH.

The cis–trans photoisomerization of azobenzenes is a well-known phenomenon that is the basis of many molecular devices.[19,20] The changes in molecular shape on isomerization are predictable but not large enough to switch the encapsulation behavior in the channels of **1**. Because of the large macromolecular substitution, PEG-AB will show large differences in shape and solubility upon cis–trans photoisomerization. In fact, the solubility of *cis*-PEG-AB in EtOH at room temperature is at least 20 times higher than that of *trans*-PEG-AB (2.7×10^{-3} mol L^{-1}), which will lead to photoresponsive encapsulation and release in a controlled manner.

The photoresponsive reversible adsorption properties of PEG-AB in **1** were evaluated by detecting the concentration of PEG-AB in EtOH using UV–vis absorption measurements (Figure 3). When the host **1** (20 mg) was soaked in an EtOH solution (10 mL) of *trans*-PEG-AB (3 mg), **1** could adsorb 92% of the PEG-AB molecules dissolved in the solution. Subsequent irradiation of the composite with UV light (360 nm) for 8 h resulted in a yellowish supernatant by the release of PEG-AB from the pores of **1**, which is ascribable to the cis isomerization of PEG-AB. Although the photoisomerization reaction of PEG-AB was restricted in the narrow pores, 29% of the PEG-AB molecules were released by UV irradiation. When this system was left under visible light, PEG-AB molecules were effectively readsorbed into **1** to give the initial host–guest adduct with a similar adsorption rate of PEG-AB in **1**. This cycle was repeatable many times without decomposition of the host framework (Figure S1)[21] and deterioration of the integrity of the system (Figure 4).

In conclusion, we have demonstrated that adsorption of PEG-tethered azobenzene into **1** can be photoresponsively controlled in EtOH as a result of the large differences in molecular shape and solubility between the cis and trans forms. This interesting behavior will enable us to create a stimuli-responsive nanovalve system that can release secondary guests upon photoirradiation. We envision that this photoresponsive system using PCPs will contribute to the development of future applications of PCPs for controlled drug-delivery and sensory nanodevices.

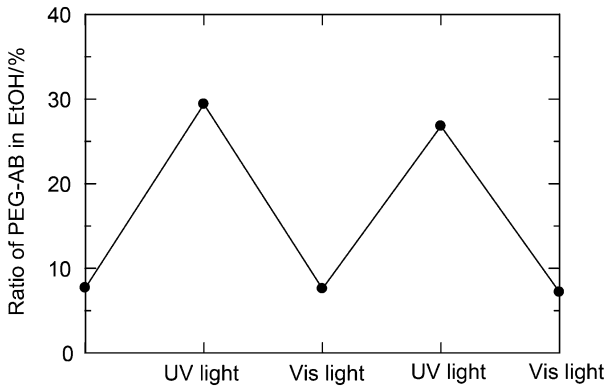

Figure 4. Repeatability of PEG-AB encapsulation and release by photoirradiation.

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† Present address: Center for Molecular Systems, Department of Chemistry and Biochemistry, Kyushu University, Nishi-ku, Fukuoka 819-0395.
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