Reversible Photoswitching Liquid-phase Adsorption on Azobenzene Derivative-grafted Mesoporous Silica

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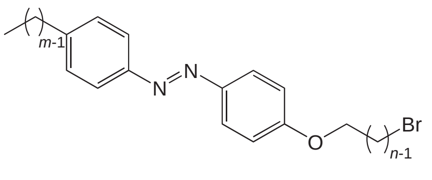
Mesoporous silica tethered with alkyl chain-headed azobenzene derivatives exhibits reversible photoswitching behavior in liquid-phase adsorption of an octabutoxyphthalocyanine (OBPc) probe molecule on alternating ultraviolet and visible light irradiation.

Reversible switching of structure and properties of nanospace on external stimuli such as photoirradiation, electronic current, magnetic field, and pH change is attracting attention for intelligent nanoporous materials.[1–7] Especially, azobenzene is one of the representative photoresponsive molecules, and there were several reports on hybrid materials with mesoporous silica.[2–6] Recently, Brinker and co-workers synthesized a mesoporous silica film including azobenzene-bonded siloxane, confirming photoisomerization of the azobenzene moiety, wherein nanoscale mass transport is assumed to be regulated on photoisomerization.[3] However, all the above photoresponsive mesoporous silica materials are based on "molecular gate" concepts, namely opening and closing of nanochannels with photoresponsive molecules. Regulation of adsorption properties in nanochannels is not possible through the molecular gates. "Command surface" concept, which has been developed by one of us (T. Seki) and co-workers,[8] also uses azobenzene derivatives bound on Langmuir–Blodgett (LB) films. In this system, a few terminal alkyl chains of azobenzene derivative (Az) moieties can control the orientation of liquid crystal molecules on the film surface by photoresponsive switching of the Az moieties. We attempted to extend this concept to control adsorption properties of nanoporous materials. In this article, we report on the first reversible photoresponsive control of liquid-phase adsorption using azobenzene derivatives-tethered mesoporous silica powder on UV and vis light irradiation.

A 2D hexagonal mesoporous silica MSU-H[9] was chosen because the pore surface is rich in reactive silanol groups and the pore size distribution is narrow. The MSU-H sample prepared at 338 K had a DH (Dollimore–Heal) pore diameter of 6.2 nm, a DH pore volume of $1.14\,\mathrm{cm^3\,g^{-1}}$, and a BET specific surface area of $732\,\mathrm{m^2\,g^{-1}}$. Aminopropylsilyl groups were grafted on the pore surface (Ap-MSU-H).[10] The azobenzene derivative bromides *m*Az*n*Br (Scheme 1),[8] where the numbers *m* and *n* denote the carbon numbers of the head alkyl groups and tail methylene chains, respectively, were tethered to the amino groups of Ap-MSU-H (*m*Az*n*-MSU-H) by refluxing in ethanol followed by washing with NaOH/H_2O–ethanol. There was a negligible change of the peak positions in SAXRD on the modification. The nitrogen adsorption isotherm of 8Az2-MSU-H degassed at 100 °C for 6 h was of type IV, confirming that mesoporosity was maintained even after the modification with Az. According to the CHN analysis data, the number of aminopropylsilyl (AP) groups per 1 $\mathrm{nm^2}$ MSU-H pore surface in Ap-MSU-H and that of 8Az2 molecules in 8Az2-MSU-H were estimated at 1.15 and 0.54 $\mathrm{nm^{-2}}$, respectively.



Scheme 1. Azobenzene derivatives denoted as *m*Az*n*Br.

In order to improve light irradiation efficiency, Az-MSU-H powder was suspended in an organic solvent of which the reflective index is relatively close to that of silica and irradiated by light under a continuous vigorous stirring. According to UV–vis spectra of a suspension of 8Az2-MSU-H powder in dichloromethane, it was confirmed that the azobenzene moieties were isomerized from the trans form to the cis form on an UV light irradiation ($\lambda = 365$ nm) at 10 °C and that the isomerization was almost saturated after irradiation for 5 min. Reversely, the cis form isomerized to the trans form on a vis light irradiation ($\lambda = 436$ nm) at 10 °C reaching saturation after 3 min. Standing in the dark at elevated temperatures also gave rise to the trans form. It was verified that most of the cis form was retained and transformation to the trans form was negligible during the standing in the dark at 0 °C for 1 h after the UV light irradiation because 85% of the cis form was retained even after standing at 0 °C for 24 h. If the adsorbed solvent molecules in the mesopores can be removed by quick degassing at 0 °C, it should be possible to obtain gas and vapor adsorption isotherms of *cis*-Az-MSU-H. Thus, Az-MSU-H powder was dispersed in diethyl ether, irradiated by UV or vis light under stirring, filtered and degassed at 0 °C for 1 h. Afterward, nitrogen gas adsorption isotherms at 77 K and carbon tetrachloride vapor isotherm at 0 °C were promptly measured. However, no significant difference was observed between the isotherms with both the isomers. Those probe molecules may be too small to discriminate slight difference in nanospace environment.

Consequently, we attempted liquid-phase adsorption experiments using 1,4,8,11,15,18,22,25-octabutoxy-29*H*,31*H*-phthalocyanine (OBPc) as a probe (ca. 2.3 nm in diameter including butoxy chains).[11] Variation of the unadsorbed OBPc concentration after each alternating irradiation of UV and vis light is shown in Figure 1. The OBPc concentration increased by UV light irradiation and decreased by vis light irradiation, indicating that the cis form adsorbed less OBPc than the trans form. The almost con-

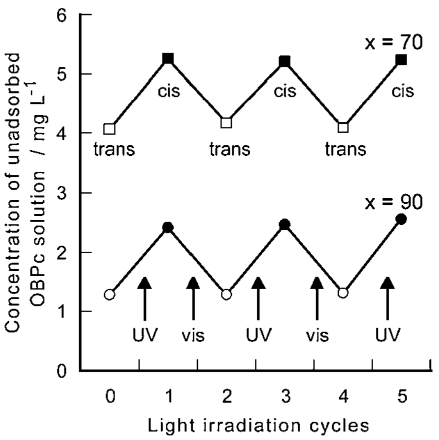


Figure 1. Variation in concentration of unadsorbed OBPc solution on photoresponsive adsorption at 0 °C when x mg of 8Az2-MSU-H was used.

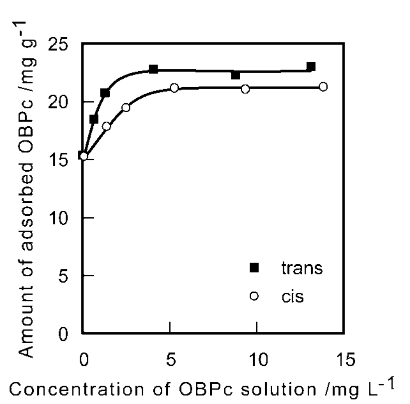


Figure 2. Liquid-phase adsorption isotherms of OBPc/hexane solution on the trans and cis forms of 8Az2-MSU-H.

stant concentration of each solution after repeated UV and vis light irradiations clearly indicates that the adsorption behavior is photoresponsive. Similarly, the adsorption isotherms (Figure 2) revealed that the difference in adsorption amount between the trans and cis forms is significant except very low concentration region. Since the head alkyl groups of the azobenzene moieties point toward the inner nanospace of the channels in the trans form, it was initially expected that *trans*-8Az2-MSU-H should have a smaller effective pore size and adsorb less OBPc than *cis*-8Az2-MSU-H. Nonetheless, the trans form adsorbed more OBPc not only for 8Az2-MSU-H but also for all the alkyl-headed Az-MSU-H samples irrespective of chain length so far as we attempted (Table 1). Such a photoswitching adsorption behavior cannot be explained by molecular gate mechanisms. Meanwhile, no significant difference was observed in the case of 0Az2-MSU-H with no head alkyl group. This suggests that orientation of the OBPc molecules surrounded by the Az groups in the channels is affected by the direction of the head alkyl chains as in the case of "command surface" on a flat surface. The diameter of the core area in the channels, where only the alkyl groups exist, was estimated at ca. 3 nm according to an idealized model of *trans*-8Az2-MSU-H. The size of OBPc should fit to the core area, and the OBPc molecules adsorbed in the area will be stabilized by van der Waals interaction between butoxy groups of OBPc and alkyl groups of Az. When the head alkyl groups of azobenzene molecules are declined on the photo-isomerization to the cis form, the stabilization should be disturbed and the OBPc molecules will be more randomly oriented. Such an orientation change of OBPc should result in a smaller adsorbed amount. Therefore, it is reasonable to conclude that variation of OBPc packing in the core area contributes to the photoresponsive adsorption behavior. However, the differences in absolute amount of adsorbed OBPc appeared to be not very large. Considering the large adsorption amount on Ap-MSU-H, this is probably because considerable amounts of OBPc are adsorbed also on the silica surface and near the aminopropyl groups where Az is less densely grafted.

Table 1. Amount of OBPc adsorbed on *trans*- and *cis*-Az-MSU-H[b]

Az	Amount of adsorbed OBPc/mg·g^{-1}	
	trans form	cis form
None (Ap-MSU-H)	47.6	
8Az2	22.8	21.3
8Az2[a]	34.4	32.6
6Az2[a]	38.3	36.5
4Az2[a]	40.1	35.9
0Az2[a]	45.9	45.8

[a] $x = 40$ for all samples. [b] MSU-H sample prepared at 363 K (pore diameter: 7.6 nm, pore volume: 1.21 cm^3 g^{-1}, BET surface area: 615 m^2 g^{-1}) was used.

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11 Liquid-phase adsorption using OBPc was typically performed as follows: OBPc (2 mg) was dissolved in 100 mL of hexane. The solution was cooled to 0 °C and x (= 40–90) mg of 8Az2-MSU-H powder was dispersed in the solution. After stirring for 12 h, 5 mL of suspension was pipetted from the well-dispersed solution, followed by an immediate and rapid filtration (within five minutes) to isolate an unadsorbed OBPc solution. The concentration of the unadsorbed OBPc solution was determined using UV–vis spectrum. The remaining suspension was exposed to the UV light for 1 h. The solution was stirred for 1 h in the dark and the concentration was similarly determined using another 5-mL suspension. Thus, vis and UV light irradiation was alternately repeated.