Photochemistry

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Improvement in Photocyclization Efficiency of Diaryl Ethenes by Adjusting the Pore Size of Mesoporous Silica**

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Photochromic compounds have attracted much attention because of their potential application in photonic devices such as optical memories and optical switches. Diaryl ethenes (DE) are known to show excellent thermal stability and resistance to fatigue,[1] and they are one of the most promising family of compounds for such applications. The two isomers, open-ring and closed-ring, undergo reversible cyclization/

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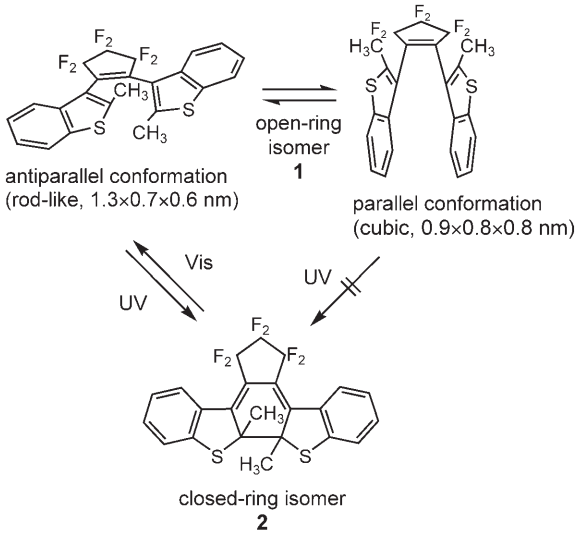
cycloreversion upon irradiation with UV and visible light (Scheme 1). There are two conformations, parallel and antiparallel, in the open-ring isomer. Since only the antiparallel conformation participates in the photocyclization, the quantum yield of photocyclization is usually lower than 0.5.[1] Effort has been made to increase the fraction of the antiparallel conformation by, for example, encapsulation of DE into the cylindrical framework of a cyclodextrin host,[2a] introduction of bulky substituents to the reactive carbon atoms of DE,[2b] incorporation of DE into the main chain of a polymer,[2c] and photochromic ractions in the crystalline phase.[2d–e]



Scheme 1. Photochromic reactions of **1**. Values for molecule size are given in nm, as in the text.

Mesoporous silica materials such as MCM-41 (M41) and FSM-16 have regular pore structures and uniform pore diameters. [3,4] The pore diameter can be adjusted by changing the carbon number—the number of carbon atoms in the backbone of the alkyl chain—of the surfactant micelles in the hydrothermal synthesis,[3,5,6] by adding swelling agents to the synthesis gels,[3] or by modifying the surface of the silica with organic silylating reagents.[3,7,8] Although the photochromism of azobenzene and spiropyran on mesoporous materials has already been studied,[9] no attention has been paid to the correlation between the pore diameter and the quantum yield of photoisomerization. This subject is dealt with here: the photocyclization rate constants were greatly dependent on the pore diameters of M41. In addition, reversible photochromism was observed in substrates with limited functional groups. Our findings establish a new technique to control photochromism by tuning the pore size.

Table 1: Properties of unmodified M41 and M41s modified with organic groups.[a]

	Unmodified M41	Ph-M41			Me-M41		
	d [nm][c]	Organic groups per nm^2	d [nm][c]	Δd [nm][d]	Organic groups per nm^2	d [nm][c]	Δd [nm][d]
M41-12	2.27	0.99	1.35[b]	0.92	2.3	1.84[b]	0.43
M41-16	3.00	0.88	1.80	1.20	2.7	2.51	0.49
M41-22	4.04	1.1	2.74	1.30	3.6	3.50	0.54

[a] The amounts of organic groups were determined by the elemental analysis and the pore diameters by the Barrett–Joiner–Halenda (BJH) method with N_2 desorption isotherms. [b] Determined by the HKSF (Horvath–Kawazoe–Saito–Foley) method with Ar desorption isotherms. [c] Pore diameter. [d] Decrements of pore diameter upon modification of the organic group.

M41 materials with different pore diameters were prepared by using surfactants with carbon numbers of 10, 12, 14, 16, and 22.[6] The M41 sample obtained with a dodecyltrimethylammonium salt, for example, is abbreviated as M41–12. Various organic groups (phenyl, methyl, 3-aminopropyl, 3-sulfanylpropyl, and 4-hydroxyphenyl) were planted on M41 and the resulting products are designated R-M41s (R = organic group). The DE 1,2-Bis[2-methyl-benzo[b]thiophen-3-yl]-3,3,4,4,5,5- hexafluoro-1-cyclopentene (**1**, Scheme 1) was used as a model photochromic compound. The diffuse-reflectance UV/Vis absorption spectrum of Ph-M41 was almost the same as that of PhSi(OEt)$_3$ itself (see Supporting Information). The observation of characteristic vibrational structures of the phenyl group reveals that there is no exciton coupling between the phenyl groups and no interaction between the phenyl groups and the silica surface; therefore, each phenyl ring is isolated on the M41 wall. The pore diameters measured by N_2 or Ar adsorption/desorption measurements are summarized in Table 1. The decrements in the pore diameters on modification were 0.9–1.3 nm on Ph-M41 and 0.4–0.5 on Me-M41; these values are very close to twice the lengths of Si–Ph (0.55 nm) and Si–Me units (0.22 nm), respectively, which indicates that each organic group is bonded upright on the surface.

Reversible and irreversible photoisomerization of **1** were observed, which were dependent on the surface states of the pore wall. The UV/Vis spectra for a typical example of the former are shown in Figure 1. The absorption bands at 358 and 525 nm, which are assignable to the closed-ring isomer **2**, increased with UV irradiation and decreased with visible-light irradiation. The diffuse-reflectance spectra are plotted in Figure 2 as a function of the alternating irradiation with UV and visible light: A reversible change in the UV/Vis bands was obtained on Ph-M41 (Figure 2a). The Me-, 3-aminopropyl-, or 3-sulfanylpropyl-modified M41 also provided this reversible, fatigue-resistant reaction (see Supporting Information). In contrast, the change that occurred on irradiating **1** loaded on unmodified M41 was irreversible (Figure 2b). After several UV/Vis irradiations, a new UV band at 388 nm emerged which could not be assigned (see Supporting

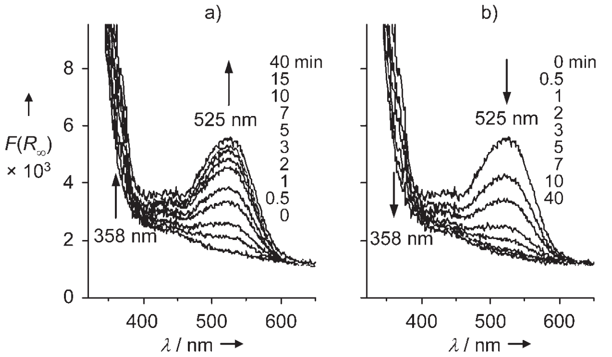


Figure 1. Changes in the diffuse-reflectance UV/Vis absorption spectra of Ph-M41-12 loaded with **1** during a) UV and b) visible-light irradiation. The amount of loaded **1** was 0.56 μmol g^{-1}. *F* is Kubelka–Munk function, R_∞ is the absolute reflectance.

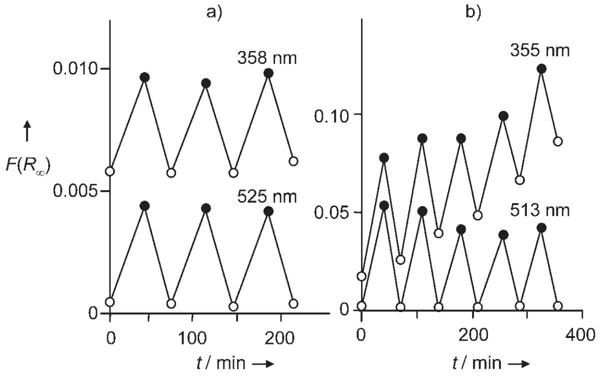


Figure 2. Changes in the intensities of diffuse-reflectance UV/Vis spectra of **1** loaded on a) Ph-M41-12 and b) M41-12 during alternate UV (●) and visible-light (○) irradiation. The amounts of **1** loaded on Ph-M41-12 and M41-12 were 0.56 and 1.57 μmol g^{-1}, respectively.

Information). A similar phenomenon was also observed on 4-hydroxyphenyl-M41. The degradation mechanism is likely to be associated with the hydroxy groups on the surface of the M41.

The dependence of the coloration rate constant (*k*) of **1** on the pore diameter was studied on Ph-M41 and Me-M41 as the quantum yield was very difficult to determined in the present solid sample system. The *k* values were calculated from the changes in UV/Vis spectra (Figure 1) on the assumption of a pseudo-first-order reversible reaction and used to compare the efficiencies of photocyclization.[10] The dependence of the value of *k* on the amount of **1** loaded onto M41 was measured (Figure 3). Note that the *k* values were calculated per mole of supported **1**. The values were remarkably dependent on the amount of **1** in the cases of Ph-M41-12 and Ph-M41-14. Too high loadings of **1** gave incorrect *k* values due to insufficient irradiation of UV light so that *k* values should be determined only for loadings of **1** below 1.5 μmol g^{-1}.

As shown in Figure 4, the *k* value depended greatly on the pore diameter of the M41 samples. Two interesting findings are revealed: 1) The *k* value was 0.4–0.5 10^3 g mol^{-1} min^{-1} for pore diameters of 2.5–3.8 nm and it increased to about 2.0 10^3 g mol^{-1} min^{-1} when the pore diameter decreased to around 2.5 to 1.2 nm. When the pore size was below 0.9 nm, no molecules of **1** could be incorporated into the pore, which is reasonable in light of the molecular size of **1** (see Scheme 1). 2) There was no difference in the *k* values on Ph-M41 and Me-M41. Clearly, the *k* value is controlled only by the pore diameter and is independent of the organic groups on the surface of M41.

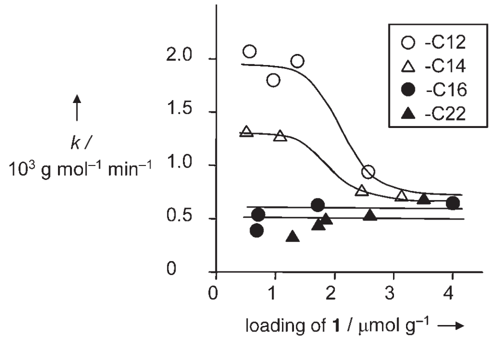


Figure 3. The *k* values for the photochromic reaction of **1** in Ph-M41 at different pore diameters and the loadings of **1**.

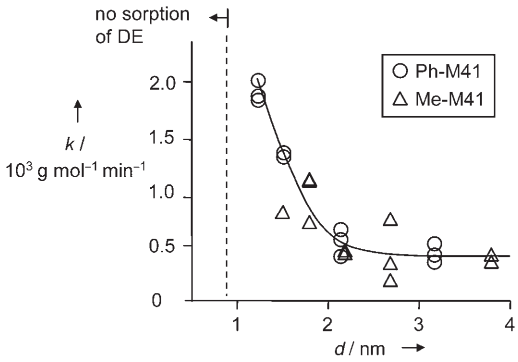


Figure 4. Dependence of *k* on the pore diameter of Ph-M41 and Me-M41.

In conclusion, reversible photochromic reaction of **1** occurred without any deactivation in the pores of M41 modified with organic groups. The efficiency of the reaction increased with shrinking pore diameter in the range 1.2–3.8 nm, which results from how well the rod-like antiparallel form fits into the pore structure. The materials described here would be useful for high-density optical memory.

Experimental Section

The parent M41s were prepared by using colloidal silica or water glass according to a previously described method.[5,6] The modification of M41 was carried out as follows: M41 (1 g) was suspended in a solution (6 mmol) of R-Si(OEt)$_3$ in *n*-heptane (20 mL) and stirred for 24 h at 353 K. The resulting samples were filtered, washed with *n*-heptane and acetone, then dried at 323 K in air. The M41 samples were simply stirred with the *n*-heptane solution (1 mM) of **1**[11] for 6 h at room temperature. After the samples were isolated by filtration and washed with *n*-heptane, they were dried at 323 K in air.[12] The amount of loaded **1** was determined by measuring the difference between the concentrations of **1** in solution before and after the loading procedure.

UV and visible light came from a superhigh-pressure Hg lamp (USHIO, 500 W) with one or two filter papers and an optical filter UV-D33S or L-39 (Asahi technoglass). Diffuse-reflectance UV/Vis spectra were measured by using a Perkin Elmer Lambda 19 spectrometer with barium sulfate as a reference. The obtained spectra were converted into absorption spectra through the Kubelka–Munk function.

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[1] a) M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985–996; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716, and references therein.

[2] a) K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura, M. Irie, *Chem. Lett.* **1999**, 63–64; b) M. Takeshita, C.-N. Choi, M. Irie, *Chem. Commun.* **1997**, 2265–2266; c) F. Stellacci, C. Bertarelli, F. Toscano, M. C. Gallazzi, G. Zotti, G. Zerbi, *Adv. Mater.* **1999**, *11*, 292–295; d) S. Kobatake, T. Yamada, M. Irie, *J. Am. Chem. Soc.* **1999**, *121*, 2380–2386; e) S. Kobatake, Y. Matsumoto, M. Irie, *Angew. Chem.* **2005**, *117*, 2186–2189; *Angew. Chem. Int. Ed.* **2005**, *44*, 2148–2151.

[3] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712; b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.

[4] a) T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988–992; b) S. Inagaki, Y. Fukushima, K. Kuroda, *J. Chem. Soc. Chem. Commun.* **1993**, 680–681.

[5] a) T. Abe, Y. Tachibana, T. Uematsu, M. Iwamoto, *J. Chem. Soc. Chem. Commun.* **1995**, 1617–1618; b) M. Iwamoto, T. Abe, Y. Tachibana, *J. Mol. Catal. A* **2000**, *155*, 143–153.

[6] S. Namba, A. Mochizuki, M. Kito, *Chem. Lett.* **1998**, 569–570.

[7] a) N. Nakajima, H. Aritani, S. Namba, M. Irie, M. Iwamoto, *Shokubai* **2000**, *42*, 160–162 (in Japanese); b) T. Kimura, S. Saeki, Y. Sugahara, K. Kuroda, *Langmuir* **1999**, *15*, 2794–2798.

[8] a) A. Stein, B. J. Medle, R. C. Schroden, *Adv. Mater.* **2000**, *12*, 1403–1419; b) A. P. Wight, M. E. Davis, *Chem. Rev.* **2002**, *102*, 3589–3613, and references therein.

[9] a) M. Ogawa, K. Kuroda, J. Mori, *Chem. Commun.* **2000**, 2441–2442; b) K. Hoffmann, U. Resch-Genger, F. Marlow, *Microporous Mesoporous Mater.* **2000**, *41*, 99–106; c) C. Schomburg, M. Wark, Y. Rohlfing, G. Schulz-Ekloff, D. Wöhrle, *J. Mater. Chem.* **2001**, *11*, 2014–2021.

[10] The k values were calculated by using the following equation.

$$\frac{x_e}{a_0}\ln\frac{x_e}{x_e-x}=k\,t$$

in which x is the $F(R_\infty)$ value of the Kubelka–Munk calculation at time t, x_e the value at the steady state under UV irradiation, and a_0 the amount of **1** loaded in M41 ($\mathrm{mol\,g^{-1}}$).

[11] Compound **1** was purchased from Tokyo Chemical Industry Co., Japan, and used without further purification. No impurity was observed by ^{1}H NMR spectroscopy.

[12] The inclusion materials obtained were stable in air during our experiments; no change in the spectra or photochromic behavior was observed.