The Effect of Layered Sodium–Magadiite on the Photochromic Reversibility of Diarylethene Immobilized on Its Surfaces

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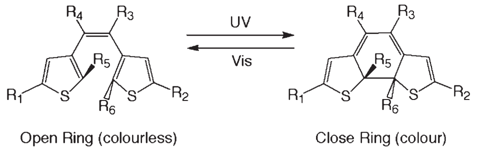
Diarylethene covalently bonded to the silanol oxygen of the layered surfaces of magadiite was seen to undergo a more improved photochromic reversibility than a corresponding silylated analog in ethanol without fixation to the magadiite.

Diarylethene derivatives are thermally stable and yet highly efficient in their photochemical interconvertibility with their closed-ring isomers, as shown in Eq 1.[1] They can, thus, be considered one of the most promising materials for applications in memory devices. For their use in the form of solid thin films, however, a number of hosts such as organic polymers[2] and inorganic layered or mesoporous materials have been used to form a complex with diarylethene.[3]



(1)

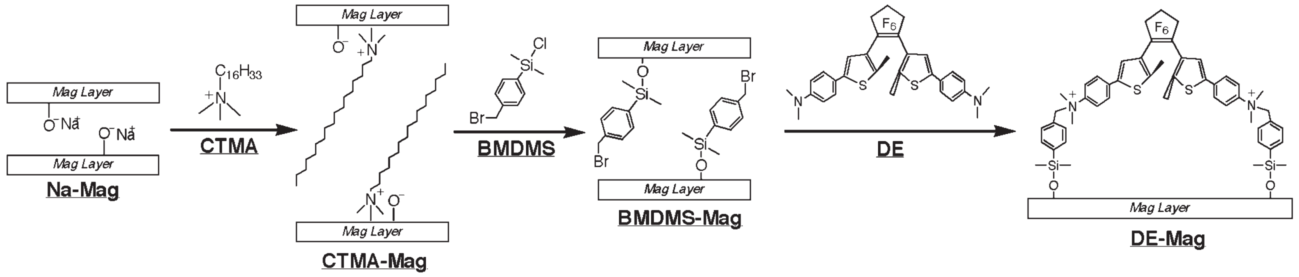
Among the hybridization methods reported thus far, clay minerals have been observed to form transparent thin films of a clay–diarylethene hybrid with geometrically anisotropic alignments of the guest ions in its interlayer spaces,[3] however, such hybrids exhibit a low photochromic reversibility attributed to the accumulation of the inert parallel form during irradiation.[4]

In the present communication, we have presented our findings on the improvement of the photochromic reversibility of diarylethene prepared by covalent bonding to the polysilicalte surfaces of magadiite, i.e., a diarylethene/magadiite (DE–Mag) hybrid. Moreover, to clarify its effect, a comparative control experiment using a corresponding diarylethene modified by silyl substituents at the terminal thiophene rings was also carried out.

The sodium–magadiite (Na–Mag) was synthesized with an adsorption of the laurylpyridinium: surface area of 710 m^2/g and a cation exchange capacity (CEC) of 2.25 meq/g, along with 1,2-bis[2-methyl-5-(4-dimethylaminophenyl)thien-3-yl] perfluorocyclopentene (DE) according to previous literature.[3,5]

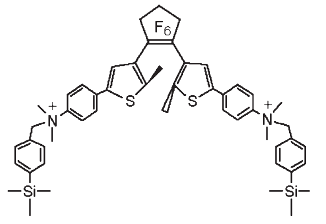
The DE–Mag hybrids were prepared in the following three steps: (1) preparation of cetyltrimethylammonium bromide (CTMA) modified Mag (CTMA–Mag) by cation exchange of the Si–ONa group of Mag with the CTMA; (2) silyl coupling with 4-(bromomethyl)phenylchlorodimethylsilane (BMDMS) for the modification of the Mag layer (BMDMS–Mag); and (3) the covalent bonding of DE to Mag (DE–Mag), as outlined in Scheme 1. In step (1), a 400-mL aqueous solution of CTMA (20 mM) was added to 4.4 g of powdered Na–Mag under stirring at 70 °C for 5 days. After the reaction and filtration of the mixture, a white precipitate was obtained as the CTMA–Mag powder, washed well with water and dried under vacuo for 1 day. In step (2), 1.11 mg of CTMA–Mag was heated under reflux with 10 mmol of BMDMS for 60 h in 30 mL of dry benzene under N_2 atmosphere, and the resulting precipitate was filtered and dried under vacuo to obtain the BMDMS–Mag. Finally, in step (3), 618 mg of BMDMS–Mag was refluxed with 1.39 mmol of DE for 60 h in 30 mL of dry benzene under N_2 atmosphere, and the resulting precipitate was filtered and dried under vacuo to yield the DE–Mag powder. DE–Mag was then analyzed by XRD and the ^{13}C cross-polarization/magic-angle spinning (CP/MAS) NMR spectra were obtained by a CMX-300 solid NMR system. The obtained DE–Mag hybrid possessed a layer distance of 21.4 Å by estimations of the $d(001)$ diffractions of its XRD profiles.

The ^{13}C NMR spectra of DE–Mag exhibits not only the resonance of the methyl groups adjacent to the Si atoms of BMDMS at δ 1.00, but also the methylene and methyl carbons of the DE molecules at δ 30.9 and δ 53.3 as relatively weak peaks. Also, aromatic carbon atoms were observed in the region of δ 100–250 as a broad resonance. The broadening of the NMR peak is noteworthy since it implies the limited mobility of the DE and BMDMS units attributed to the DE and BMDMS fixed onto Mag. A blue colored absorption could clearly be observed in the closed form of the DE molecules upon UV light irradiation of DE–Mag. XRD, ^{13}C NMR and absorption analyses showed that DE molecules are, indeed, present within the Mag layers.



Scheme 1. Outline of the preparation sequence for the diarylethene/magadiite (DE–Mag) hybrids.

However, the intercalated DE amounts could not be quantitatively estimated, although its coverage degree in Mag may not be high. Independently, 1,2-bis[2-methyl-5-{4′-[*N*-(*p*-trimethylsilylbenzyl), *N*,*N*-dimethylammonio]phenyl}thien-3-yl) perfluorocyclopentene (DE-Si) was synthesized by silylation of the DE with *p*-trimethylsilylbenzylchloride.



DE-Si

UV (250–380 nm) and visible (>500 nm) light irradiation was carried out on the DE-Mag powder in a reaction cell with a quartz window, and its diffuse reflectance absorption spectrum is shown in Figure 1. The blue coloration of the transparent starting DE–Mag hybrids became more pronounced at around 625 nm upon UV light irradiation (250–380 nm). Moreover, the resulting blue-colored closed ring species of DE–Mag then reverted to the original open form by irradiation in visible light regions (>500 nm), as shown in Figures 1a–1c. These spectral changes were confirmed to be reversible under repeated and alternate UV–vis light irradiation, as compared with an analog, the sililated diarylethene (DE–Si) without the layered magadiite (Mag).

Repeated and alternate irradiation confirmed the repetitive control of the photochromism for the DE–Mag hybrid powder which reached a photostationary state between the open and closed forms for 30 s and 30 min upon UV–vis irradiation, respectively. More than 80% of the closed form could be seen after the first run of UV and then visible light irradiation. The reversible transformation between the colorless and blue-colored form was then analyzed as a function of the irradiation cycles, as shown in Figure 2, along with control experiments using DE–Si. The relative intensity of the colored form at 625 nm was normalized by dividing it with the absorbance intensity of the photolysate after the first run, and was plotted against the horizontal axis, showing alternate UV–vis light cycles. The photochromic behavior for DE–Si gradually and monotonically decreased with light irradiation,[4] and eventually, over 80% of the photochromic activity was lost during 10 cycles of UV–visible light irradiation. In contrast, most of the DE molecules survived, i.e. 89%, in the DE–Mag hybrid even after 10 cycles of UV–vis light irradiation.

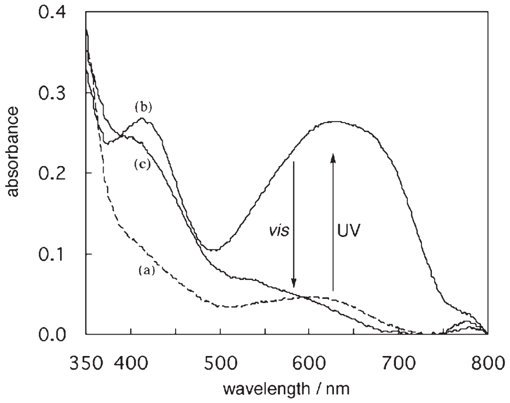


Figure 1. The diffuse reflectance absorption spectra of DE–Mag: (a) before light irradiation; (b) after UV light irradiation and; (c) visible light irradiation after run (b).

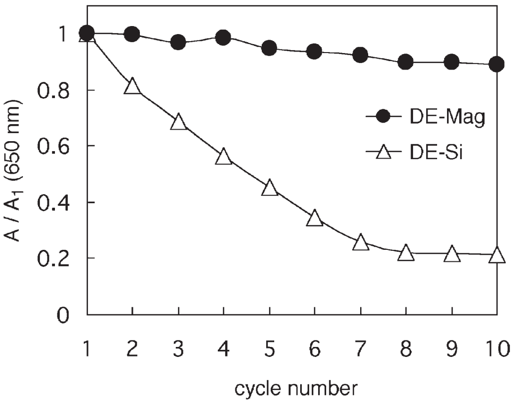


Figure 2. Successive irradiation of the DE–Mag powder by UV (250–380 nm) and visible light (>500 nm) after the first run.

For DE–Si, a new absorption band was observed at around 550 nm during alternative UV–vis light irradiation, attributed to a yet unidentified product and causing the low durability of the hybrid. In contrast, no such absorption band at around 550 nm was observed for the DE–Mag hybrid. The open form of the diarylethene (DE) compounds is known to exist as two types of rotation conformers, i.e., *anti-parallel* and *parallel*, in solution. Of these, only the *anti-parallel* isomers were able to undergo photochemical transformation into the closed form while the *parallel* form remained inert against UV irradiation.[6] With the present DE–Mag hybrids, it is thought that isomerization from *anti-parallel* to *parallel* isomers may have been suppressed due to fixation by the covalent bonding of DE onto the Mag layer surface. Such organic and inorganic hybrid materials in which the photochromic reversibility can be easily controlled is promising for applications in highly advanced photofunctional systems such as optical and memory devices.

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