A photochromic fluorescent switch in an organogel system with non-destructive readout ability†

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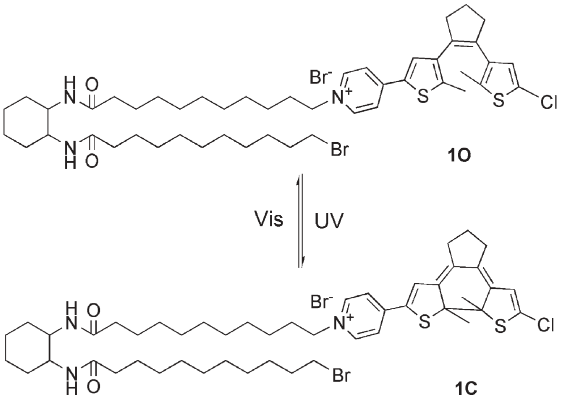
A fluorescent organogel based on photochromic dithienylethene was obtained, whose optimal excitation wavelength (470 nm) results in little structural change of both open and closed isomers of diarylethene, thus presenting the first example of a fluorescent switch with non-destructive readout ability in the gel state.

Low-molecular-weight organogels have been of increasing interest in recent years for their diverse applications in drug delivery,[1] sensors,[2] templates for synthesis of nanostructures[3] *etc.* Research into organogel systems has been focused mainly on the variety of supramolecular structures constructed in the gels, which are expected to show characteristic absorption, fluorescence spectroscopic, and structural properties arising from their difference in aggregation mode. Specially, the formation and properties of those supramolecular gels can possibly be controlled by an environmental stimulus such as light,[4] sound,[5] electrochemical,[6] or pH,[7] correspondingly giving signal outputs in fluorescence, absorption or other changes. Reversible light-responsive gels are the most desirable since they are very convenient, using only light as stimulus with no other additives. Photochromic organogels based on azo[8] and phenylenevinylene[9] chromophores have been studied most widely, since their conjugated structures facilitate organogel formation, while, generally, their fluorescent properties could not be controlled by light, and azo chromophores usually exhibited no fluorescent emission at all. Within those photochromic systems, such as diarylethene, spiro, fulgide and *etc*., diarylethene has been proved to be the most promising switchable unit for its excellent fatigue resistance and thermal stability.[10] However, their non-conjugated structure makes it difficult to form stable gels, thus there have been only a few reports on diarylethene-based organogels until now. Feringa *et al.* developed a series of photochromic diarylethenes applied in chiral organogels, which exhibited no fluorescent emission.[11] The first fluorescent diarylethene organogel was reported recently by Tian *et al.*, while the fluorescence intensity in the gel state changed little before and after UV light irradiation.[12] This prompted us to obtain photochromic diarylethene materials operating in the gel state with highly fluorescent emission and typical fluorescent switch properties. Moreover, by careful control of the supramolecular self-assembly, a non-destructive readout capability of the fluorescent signal can also be realized, which affords an essential prerequisite to the successful application of organic materials in memory devices.[10]

In our previous research, we found that the positively charged pyridine moiety emitted moderate fluorescence even in the solid state.[13] Herein we extend our research to a switchable organogel system, and report a novel fluorescent organogel (compound **1**, Scheme 1) containing a photochromic diarylethene unit, and a bis-amido cyclohexane unit (racemic) for the capacity to gelate organic solvents by intermolecular hydrogen bonding, as has been reported before.[14] The gelator exhibits strong orange fluorescence, both in solution and in gel state, for the existence of pyridinium. Moreover, the fluorescence could be switched by alternate UV and visible light irradiation both in solution and in the gel state. However, the gel formation ability is rather poor for the compound containing two diarylethene moieties (compound **2**, see Scheme S1 in ESI†), so we studied mainly the properties of compound **1**.

The gelation properties of **1O** (open form of **1**) were studied at a concentration of 20 mg ml^{-1} (2.0×10^{-2} M) in various solvents. It can form a stable gel in acetonitrile, acetone and THF; acetonitrile was the most effective solvent for gelation (Fig. S1†). The T_g of the acetonitrile gel was at about 50 °C. SEM images of the xerogel prepared from acetonitrile gel showed a three-dimensional flower-like structure with thickness of about 200 nm (Fig. 1A). The TEM images of the xerogel indicated that the flower-like structure of **1O** seemed to be formed by nanofibers with an average diameter of 7 nm (Fig. 1B). ^{1}H NMR spectra of **1O** solution (5.0×10^{-3} M in CD_3CN) at 20 °C showed well-resolved peaks (Fig. S2†), however, the peaks became broad in the gel state (2.0×10^{-2} M). With increasing temperature, from 20 to 50 °C, well-resolved peaks appeared again, with a small downfield shift (8.52 to 8.60 ppm) for protons at the α-position of the



Scheme 1 The structure and photochromic process of **1O**.

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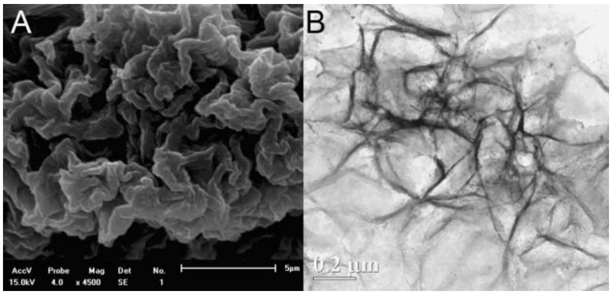

Fig. 1 (A) SEM (scale bar, 5 µm) and (B) TEM images of the xerogel obtained from acetonitrile (20 mg ml^{-1}).

pyridinium and an upfield shift (6.60 to 6.53 ppm) for the amide protons.

1O undergoes reversible photochromism in both dilute solution and the gel state. The main absorption of **1O** solution in its open form was at 377 nm (1.0×10^{-5} M in acetonitrile, molar absorption coefficient ε, 2.1×10^4 M^{-1} cm^{-1}). Irradiation of **1O** solution with 365 nm light led to a new absorption at 604 nm (Fig. 2A), which is attributed to the increased π-electron delocalization in the closed isomer (**1C**). The acetonitrile gel of **1O** (2.0×10^{-2} M) exhibited almost the same absorption property with that in dilute solution (Fig. 2C). The pale brown **1O** gel changed to blue (Fig. S1†) under irradiation of 365 nm light with the new absorption at 605 nm. As illustrated previously, pyridine-based diarylethenes usually have a high photocyclic conversion,[15] however, the effort to measure the conversion degree from open to closed isomer in the photostationary-state (PSS) failed. What interests us is the fluorescent property of **1**, since pyridinium derivatives usually emit comparatively strong fluorescence. As shown in Fig. 2B, **1O** solution exhibited obvious fluorescent emission at about 607 nm (Ex: 380 nm) with a fluorescent quantum yield of 0.023 using Rhodamine B as reference. Most of the fluorescence could be quenched by UV light irradiation (90% quenched). While the emission of **1O** in the gel state was located at 623 nm (Ex: 470 nm), 16 nm red-shifted compared with that in dilute solution (Fig. 2D). Under 365 nm light irradiation for 15 min, the fluorescence was efficiently quenched and only 4% remained. The absorption and fluorescence of the PSS in both solution and the gel state could be recovered by visible light irradiation (620 nm) to the open isomer, showing the classical switchable property of diarylethene. Certainly, it takes a much longer time (3.5 h) for the **1O** gel to revert to the open isomer from the PSS. Fortunately, the gel is, to some extent, stable to light stimuli; for example, no distinct variety of both absorbance and gel status was observed after 6 cycles of alternate irradiation with UV (365 nm, 15 min/cycle) and visible light (620 nm, 3.5 h/cycle) of the gel state (Fig. S3†).

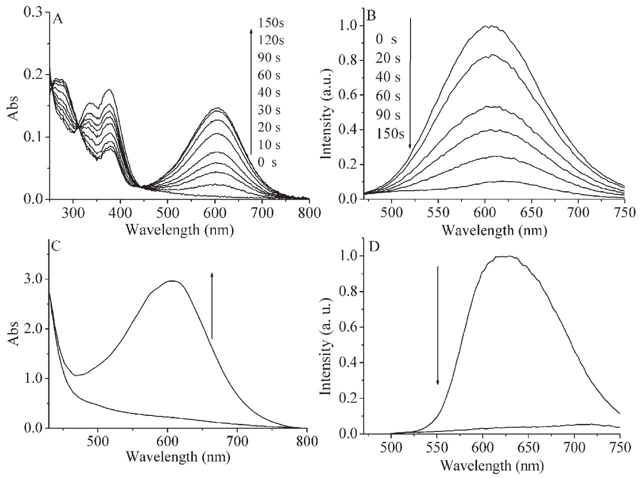

Fig. 2 (A) Absorption and (B) fluorescent changes of **1O** solution under 365 nm light irradiation (1.0×10^{-5} M in acetonitrile, Ex: 380 nm); (C) absorption and (D) fluorescent changes of **1O** gel under 365 nm light irradiation (2.0×10^{-2} M, Ex: 470 nm).

To further study the origin of the optimal excitation wavelength in **1O** gel, the concentration-dependent absorption and excitation spectra were investigated (Fig. S4† and Fig. 3A). Comparing the UV-vis absorption in dilute solution with that in gel, it can be seen that the concentration has little effect on photochromic properties expressed by absorption spectra, whereas the excitation spectra were very different (Fig. 3A) between solution and the gel, suggesting different excited states as compared to those in the ground state. In dilute acetonitrile solution (1.0×10^{-6} M), the excitation peak of **1O** was located mainly at 380 nm, consistent with absorption spectra. However, the excitation wavelength in the UV region decreased, and another excitation peak at 485 nm increased evidently, with an increase in the concentration and became a prior excitation wavelength at concentrations up to 1.0×10^{-4} M, even though there was a comparatively small absorbance at 485 nm in the absorption spectra (Fig. S4†). Consequently, the best excitation wavelength for **1O** gel (2.0×10^{-2} M) was also located at 485 nm, resembling that for the concentrated solution. Lehn and Tsivgoulis have reported a diarylethene containing protonated pyridine with an oligothiophene moiety, whose best excitation wavelength was at about 459 nm,[16] which was ascribed to the protonated pyridinyl-dithieno(thiophene) unit by comparison of the spectra with that of the isolated unit.[16,17] Therefore, we suppose that the excitation peak at 485 nm should be due mainly to the existence of pyridinium. Regretfully, the mechanism for the large shift of the excitation wavelength has still not been proved by reasonable proofs.

From concentration-dependent emission spectra (Fig. 3B), a slight red-shift and intensity enhancement were observed (from 607 to 624 nm as the concentration increased from 1.0×10^{-6} to 1.0×10^{-3} M). The corresponding life times of the emission were 1.04, 1.11 and 0.98 ns for solutions of 1.0×10^{-5}, 1.0×10^{-4} and 1.0×10^{-3} M, respectively. However, in the gel state

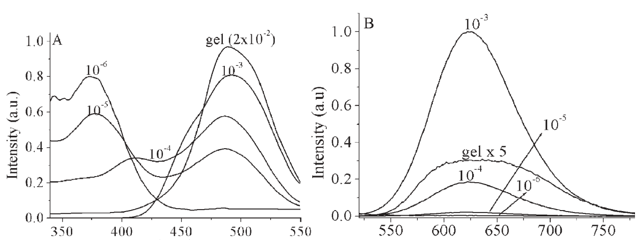

Fig. 3 (A) Concentration-dependent excitation (Em: 620 nm) (A) and emission (B) spectra of **1O** in acetonitrile at room temperature (Ex: 470 nm).

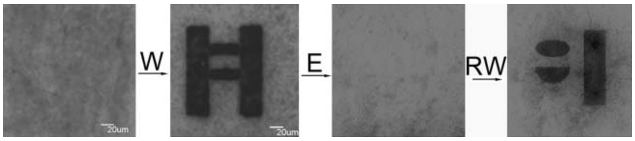

Fig. 4 Microsized erasable fluorescent images of **1O** on a gel (20 mg ml^{-1} in acetonitrile) using confocal laser scanning microscopy. (Written (W) and rewritten (RW) by a 405 nm laser for 10 min, erased (E) with 550 nm light for 1 h; fluorescence readout by a 488 nm laser. Scale bar: 20 μm).

(2.0×10^{-2} M), the emission became broad and weaker than that of 1.0×10^{-3} M solution, probably due to the inner-filter effect.[18]

For the applications of diarylethenes, information storage is one of the most attractive fields, in which non-destructive readout is a key factor. IR spectroscopy has been proved useful in achieving non-destructive readout in diarylethene systems,[19] however, fluorescent emission is considered to be a more promising signaling mode for its sensitivity and digitization of applications in optical memory as well as in fluorescent probes. In our present system, we found that the emission in high concentrated solution, as well as in the gel state, of **1O** can be excited by 470–490 nm, and that the intense irradiation of 470 nm induced little conformation conversion for both open and closed isomers. After 1 h irradiation with 470 nm light, the conversion from open to closed isomer was less than 1%; and less than 3% from PSS to open isomer (Fig. S5†). This was suitable for application in information storage, especially for high-density information storage. Here, a write–erase–rewrite cycle was realized in a gel state by using confocal laser scanning microscopy (Fig. 4).

In conclusion, we have obtained a photochromic organogel based on diarylethene, whose optimal excitation wavelength (470 nm) would not destroy the structures of both open and closed isomers of diarylethene. Therefore, this system is suitable for application in a non-destructive fluorescent readout switch for storage. Further studies on pure enantiomers of those compounds with polarizing light excitation and micro-pattern fabrication are in progress.

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