Photo-induced colour generation and colour erasing switched by the sol–gel phase transition

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The controlled colour generation and colour erasing phenomena of alkylammonium polyoxomolybdate complexes were first observed in the *trans*-(1R,2R)-1,2-bis(undecylcarbonylamino)cyclohexane organogel system using the sol–gel phase transition.

Construction of well-ordered inorganic materials under the influence of organic molecular assemblies is an important area of current research in nanochemistry and materials chemistry.[1] Since inorganic materials with well-defined sizes and shapes have many potential applications (catalysis, photochemistry, molecular devices, *etc.*), chemists working in new materials science as well as in other related fields have devoted a great deal of their research efforts toward the development of efficient and innovative fabrication methods in order to obtain these potential materials. Recently, increasing attention has been paid to low molecular-weight compounds that can efficiently gelate various organic solvents upon forming three-dimensional networks of fibrous aggregates.[2] These gels have successfully been used as organic templates for preparation of inorganic nanomaterials by sol–gel transformation.[3] More recently, a few trials to construct photo-responsive gels by photoinduced gelation have been reported for functional organogels.[4]

It is known that alkylammonium polyoxomolybdates exhibit significant photochromism which makes them suitable as nanocomposite molecular devices.[5] A photochromic material is one whose light-absorbing properties are altered upon optical excitation.[4,5] These materials are of technological interest because they behave in a reversible manner in that they return to their original state either thermally or upon irradiation with light of a frequency corresponding to the induced absorption.[4–6] Because of the low solubility and uncontrollable reversibility in both solution and solid states, these polyoxometalates exist only as basic structural motifs and have been difficult to use as real device materials. In this work, we have successfully transferred the alkylammonium polyoxomolybdate complex to an organogel system and developed a novel controllable photo-induced colour generation and colour erasing gel system.

Trans-(1R,2R)-1,2-bis(undecylcarbonylamino)cyclohexane (**1**) was synthesized according to the method described previously[7] and identified by IR, ^{1}H NMR and mass spectral evidence and elemental analysis. Compound **1** is an excellent gelator that can harden a wide variety of organic fluids such as alcohols, DMF and DMSO.[7] This gelling phenomenon has been attributed to the formation of a three-dimensional network on the basis of fibrous aggregates grown in organic fluids.[7] $[NH_2(CH_2CH_2CH_2NH_3)_2]_2 \cdot [Mo_8O_{26}(MoO_4)]$† (**A**) was obtained by the reaction of $K_6Mo_7O_{24}$ with $[NH_2(CH_2CH_2CH_2NH_3)_2](ClO_4)_3$. Since **A** could not form a stable gel by itself, the appropriate mixtures of **1** and **A** were used to gelate organic solvents.

The T_{gel} values were determined in DMSO as a function of **A** concentration with constant concentration of **1** (2% w/v). The pure sample **1** has a T_{gel} value of 85 °C, and the values are initially enhanced up to 88.5 °C with increasing **A** concentration up to 0.6% w/v, and then gradually decrease.

The visual images of the molecular aggregates prepared from the gel samples of **1** and **1 + A** (made from DMSO) were obtained using a transmission electron micrograph (TEM). The gel sample from pure **1** has a flexible fibrous structure with fibre diameters of 50–200 nm as pointed in Hanabusa's work,[7] whereas the fibrous structure in the **1 + A** gel shows a straighter crisscross structure (Fig. 1). No obvious change is observed before and after photo-irradiation on sample **1 + A**.

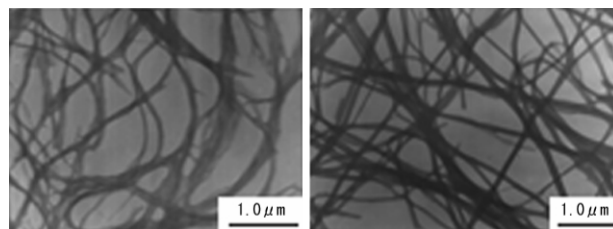**Fig. 1** TEM images of the gel **1** (left, stained by phosphotungstic acid aqueous solution (2.0 wt%)) and **1 + A** (right, not stained, [**1**] : [**A**] = 3 w/w).

Electronic absorption spectra of the solution of **A** and the gel samples of **1 + A** before and after UV irradiation were measured in DMSO at 25 °C with a 1.0 mm optical cell.‡ Both gel and solution samples result in a blue species[6] when irradiated by UV light (λ_{max}(gel) = 728 nm, λ_{max}(sol) = 732 nm; Fig. 2a) due to the photo-redox reaction of $[(Mo_8O_{26})(MoO_4)]^{6-}$. In solution, the induced absorbance has a linear relationship with concentration of **A** as expected, whereas in the gel system, the absorbance does not only depend on the concentration of **A**, it also varies with the concentration of gelling reagent. The light induced saturated absorbance is 0.63 in the gel phase, while the value obtained with the same concentration of molybdenum is only 0.19 in the solution. To compare the colouration reaction rates between the solution and the gel phase, eqn. (1) is used to determine each initial reaction rate. We thus obtained v_{0gel} = 0.0086 min^{-1} and v_{0sol} = 0.0035 min^{-1}, from which one can realize that the initial rate in the gel phase is twice as fast as that in the solution phase.

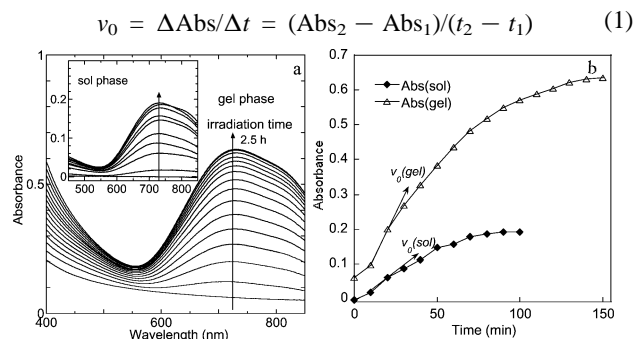$$v_0 = \Delta Abs/\Delta t = (Abs_2 - Abs_1)/(t_2 - t_1) \qquad (1)$$

Fig. 2 a: Spectral changes of the gel (**1 + A**) and solution (**A**) (inset) by photo-irradiation (scanning interval, 10 min). b: Time courses of absorption at 728 nm for the gel and 732 nm for the solution, respectively. (Conditions: gel: [**1**] = 2% w/v (4.18 × 10^{-2} mol dm^{-3}), [**A**] = 0.8% w/v (4.87 × 10^{-3} mol dm^{-3}) in DMSO, solution: [**1**] = 0%, [**A**] = 0.8% w/v in DMSO).

When the light source was removed from the system after irradiation, the coloured solution gradually faded to colourless in the dark within 5 h at room temperature, whereas the gel sample was decolourized very slowly: its colour was retained at room temperature for more than one week (Fig. 3a). The plots of ln $[(A - A_e)/(A_s - A_e)]$ for both gel and solution in Fig. 3b have a linear relationship with the relaxation time, indicating
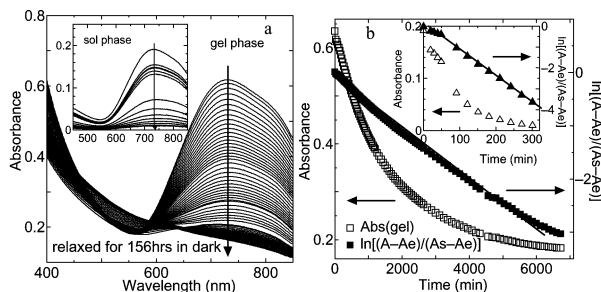
Fig. 3 a: Spectral changes of the gel ($A + 1$) and the solution (A) (inset) in the dark at 298 K after irradiation. b: Time courses of the absorptions and first-order plots of decolouration at 728 nm for the gel and 732 nm for the solution (inset) in the dark at 298 K, respectively. (For conditions see Fig. 2 caption).
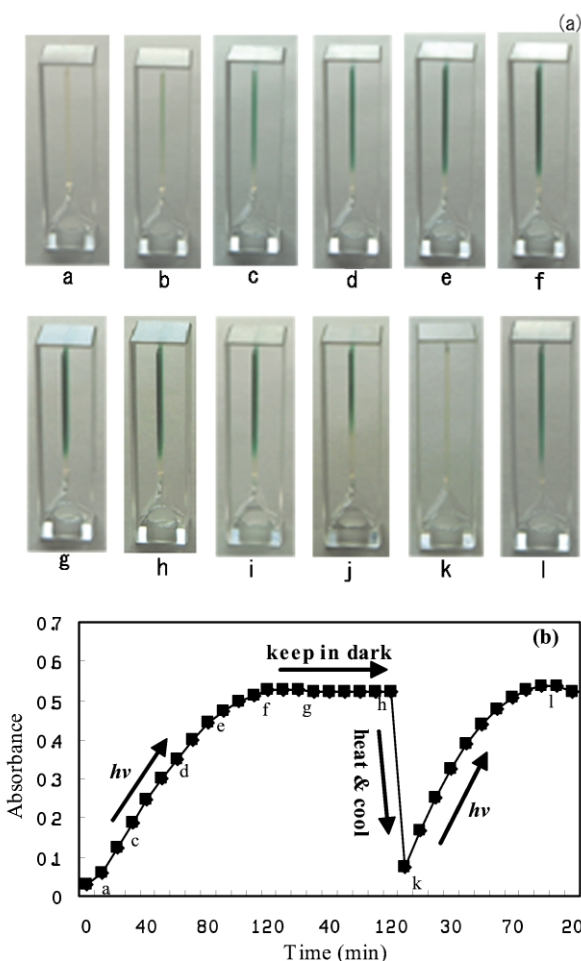
that the decolouration in the dark occurs according to a first-order reaction in both the gel and the solution. The first-order rate constants were estimated according to eqn. (2):

$$-\ln(A - A_e)/(A_s - A_e)] = kt \qquad (2)$$

where $A_s = A_{t = 0} =$ Abs(initial), $A_e =$ Abs(equilibrium). The linear fitting of the plots to eqn. (2) gives rate constants $k_{gel} = 4.6 \times 10^{-4}$ min^{-1} and $k_{sol} = 1.2 \times 10^{-2}$ min^{-1}. The results establish the decolouration in the gel phase is 26 times slower than that in the solution. The result proves that the gel acts not only a nice colour acceptor, but also as a colour depositor, because it can keep the colour for a longer time.

The most interesting observation is that the decolouration in the gel phase can be controlled by heating through a sol–gel phase transition. The coloured gel turned to the sol state by heating, where colour disappeared quickly, and then cooling to room temperature gave the original colourless gel. The colour of the gel could be regenerated by irradiation. This photochromism of the gel state is reversible (Fig. 4). We thus believe that it is worth exploring that the photochromic organogel system performs in applications as a colour storage device, in which the colour generation is 'switched ON' by irradiation and stored as memory, whereas colour erasing is 'switched OFF' by the sol–gel phase transition (Scheme 1).

Scheme 1 Schematic diagram of a colour storage media device.

Fig. 4 (a) Photo-induced colour generation and colour erasing of the gel (**1** + **A**); a–f: colouration by irradiation (a: original gel, b: 10 min, c: 30 min, d: 1 h, e: 1.5 h, f: 2 h at 298 K); g–j: decolouration in the dark at 298 K (g: 30 min, h: 2 h; i: 24 h; j: 48 h); k: decolouration by heating to the sol, followed by cooling; l: reirradiation of the colourless gel for 1 h. (b) Absorption change of the gel at 728 nm corresponding to the photos in (a).

Notes and references

1 L. A. Estroff and A. D. Hamilton, *Chem. Mater.*, 2001, **13**, 3227; R. A. Caruso and M. Antonietti, *Chem. Mater.*, 2000, **13**, 3272.
2 S. Shinkai and K. Murata, *J. Mater. Chem.*, 1998, **8**, 485; J. V. Esch, F. Schoonbeek, M. Deloos, R. Kellogg and B. L. Feringa, *Where It Is and Where It Is Going*, ed. R. Ungaro and E. Dalcanale, Kluwer, Dordrecht, 1999, p. 233; J. H. Jung, H. Kobayashi, M. Masuda, T. Shimizu and S. Shinkai, *J. Am. Chem. Soc.*, 2001, **123**, 8785.
3 J. H. Jung, Y. Ono and S. Shinkai, *Angew. Chem., Int. Ed.*, 2000, **39**, 1862; J. H. Jung, Y. Ono, K. Hanabusa and S. Shinkai, *J. Am. Chem. Soc.*, 2000, **122**, 5008; Y. Ono, K. Nakashima, M. Sano, J. Hojo and S. Shinkai, *J. Mater. Chem.*, 2001, **11**, 2412; J. H. Jung, M. Amaike and S. Shinkai, *Chem. Commun.*, 2000, 2343; K. Sugiyasu, S. Tamaru, M. Takeuchi, D. Berthier, I. Huc, R. Oda and S. Shinkai, *Chem. Commun.*, 2002, 1212; S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai and K. Hanabusa, *J. Am. Chem. Soc.*, 2002, **124**, 6550.
4 M. de Loos, J. van Esch, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2001, **40**, 613; S. van der Laan, B. L. Feringa, R. M. Kellogg and J. van Esch, *Langmuir*, 2002, **18**, 7136; L. Frkanec, M. Jokic, J. Makarevic, K. Wolsperger and M. Zinic, *J. Am. Chem. Soc.*, 2002, **124**, 9716.
5 T. Yamase, *Chem. Rev.*, 1998, **98**, 307.
6 E. Ishikawa and T. Yamase, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 641; T. Yamase and M. Sugeta, *J. Chem. Soc., Dalton Trans.*, 1993, 759; T. Yamase, *Polyhedron*, 1986, **5**, 79; T. Yamase, *J. Chem. Soc., Dalton Trans.*, 1991, 3055; Y. Ohashi, K. Yanagi, Y. Sasada and T. Yamase, *Bull. Chem. Soc. Jpn.*, 1982, 1254; T. Yamase, R. Sasaki and T. Ikawa, *J. Chem. Soc., Dalton Trans.*, 1981, 628.
7 K. Hanabusa, M. Yamada, M. Kimura and H. Shirai, *Angew. Chem., Int. Ed.*, 1996, **35**, 1949.