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Absorption and emission behavior of bis(2,2′-bipyridine)[2-(2-pyridyl)benzimidazole]ruthenium(II) doped in silica gel matrices

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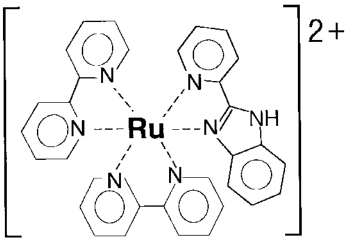
Silica gels doped with bis(2,2′-bipyridine)[2-(2-pyridyl)benzimidazole]ruthenium(II), $[Ru(bpy)_2(pbimH)]^{2+}$, which dissociates a proton from the imino group upon light irradiation, were prepared by the sol–gel method under both acidic and basic conditions. Changes in the absorption spectra of the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared under basic conditions with the transition from sols to wet gels were similar to those of $[Ru(bpy)_2(pbimH)]^{2+}$ in methanol–water solution with a change from basic to acidic conditions. Therefore, the acid–base equilibrium is shifted from the deprotonated form, $[Ru(bpy)_2(pbim)]^{+}$, to the protonated form, $[Ru(bpy)_2(pbimH)]^{2+}$, during the sol–gel transition. At the gelation point, the wavelength of the emission maximum under basic conditions was shorter than that under acidic conditions, indicating that the mobility of the Ru complex in silica gels was more strongly restricted under basic conditions than under acidic conditions.

Introduction

Organic–inorganic composites have become of great interest in recent years since they have characteristic properties of both organic and inorganic materials. The sol–gel method is one of the most promising techniques to synthesize organic–inorganic composites.[1,2] The amorphous inorganic gel can be synthesized at room temperature *via* the sol–gel process, so that organic molecules and metal complexes with low thermal stability can be incorporated into the gel matrix without thermal decomposition.[3–5] The organic molecules in the gel matrix can retain their functional properties which are only observed in liquid solutions and not in the solids themselves. Composites doped with photosensitive molecules have so far been prepared by the sol–gel method for applications as optical sensors,[6,7] dye laser,[8–10] and photoelectrodes for solar cells.[11–13]

Among the composites doped with photosensitive molecules, much attention has been paid to gels doped with tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$.[14–16] $[Ru(bpy)_3]^{2+}$-doped gels are useful as photocatalysts and solar energy conversion materials.[14–16] Complexes of the type $[Ru(bpy)_2L]^{2+}$ which contain two 2,2′-bipyridine ligands and another ligand, L, are expected to be promising as multifunctional composites.



As an example of $[Ru(bpy)_2L]^{2+}$, we were interested in bis(2,2′-bipyridine)[2-(2-pyridyl)benzimidazole]ruthenium(II), $[Ru(bpy)_2(pbimH)]^{2+}$ (ref. 17) which contains an imino group in the 2-(2-pyridyl)benzimidazole ligand which can dissociate a proton upon light irradiation.[17] As a consequence, $[Ru(bpy)_2(pbimH)]^{2+}$-doped composites are thus promising as a new type of photo-responding material to control ion transport by photons and are very useful as energy and electron transfer materials for solar cells. However, the preparation of gel composites doped with $[Ru(bpy)_2(pbimH)]^{2+}$ by the sol–gel method has not, as yet, been reported.

In the present study, we have prepared $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica gels under acidic and basic conditions since the structure of $[Ru(bpy)_2(pbimH)]^{2+}$ changes depending on the surrounding pH owing to the presence of the imino group. The present paper reports the changes in the absorption and emission spectra of $[Ru(bpy)_2(pbimH)]^{2+}$ doped in silica matrices during the transition from the sol to dry gel under both acidic and basic conditions.

Experimental

$[Ru(bpy)_2(pbimH)]Cl_2 \cdot nH_2O$ was synthesized according to a procedure reported by one of the authors.[17] A suspension of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.3 g) in EtOH–H_2O (1 : 1 v/v, 60 ml) was refluxed under nitrogen for *ca.* 1 h. 2-(2-Pyridyl)benzimidazole (Aldrich Chemicals) (0.17 g), was added to the solution and the mixed solution was refluxed at *ca.* 90 °C for a further 5 h, during which it changed from brown to red. After filtration, the filtrate was concentrated under reduced pressure to allow removal of residual ligand. Dilute hydrochloric acid was subsequently added to the filtrate to promote the protonation of the complex. The solvent was then removed by evaporation and the obtained residue was dissolved in a minimum amount of acetonitrile. Dropwise addition of diethyl ether to the solution gave a precipitate of the desired complex, which was recrystallized from the acetonitrile–diethyl ether.

Silica sols containing the Ru(II) complex were prepared under both acidic or basic conditions. Under acidic conditions, precursor sols were prepared from tetraethoxysilane, TEOS (Wako Chemicals), distilled ethanol (Wako Chemicals), and hydrochloric acid (pH 1); the mole ratio of TEOS : EtOH : water was 1 : 4 : 10. The Ru complex was dissolved in dilute hydrochloric acid (pH 1). The solution was added to TEOS and

EtOH, and the mixture was stirred to form a homogenous and transparent sol. The atomic ratio Ru : Si was fixed to 1×10^{-5}. Under basic conditions, the silica sols were prepared by mixing tetramethoxysilane, TMOS (Tokyo Kasei), distilled methanol, MeOH (Wako Chemicals) and NH_3(aq) (pH 10). The solution of the Ru complex in aqueous ammonia was added to an MeOH solution containing TMOS. The mole ratio of TMOS : MeOH : water was 1 : 4 : 10 and the atomic ratio of Ru : Si was fixed to 1×10^{-5}.

The resultant sols prepared under acidic or basic conditions were poured into polystyrene cuvettes. The cuvettes were then sealed with a silicone rubber stopper. Cuvettes containing sols prepared under acidic and basic conditions were kept at 35 °C and room temperature (*ca.* 25 °C), respectively, until gelation occurred. Both acidic and basic gels were then aged at 35 °C in sealed cuvettes. The silicone rubber stoppers were them removed from the cuvettes which were covered with aluminium foil containing a small hole and kept at 35 °C to allow slow evaporation of the solvent. Both dry gels obtained under acidic and basic conditions wree free from cracks and were transparent.

Absorption spectra of the sols and wet gels were measured on a UV spectrophotometer (JASCO Corporation V-560). Emission spectra of the sols and gels doped with Ru complexes were recorded at room temperature on a fluorescent spectrophotometer (Shimazu RF-5000). The emission spectra of the $[Ru(bpy)_2(pbimH)]^{2+}$-doped sols and gels were obtained with an excitation wavelength at 476 nm.

Results and discussion

Preparation of $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels

$[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and wet gels prepared under acidic and basic conditions were homogeneous and transparent. After slow evaporation of the solvent, transparent and crack-free dry gels were obtained under acidic conditions. The dry gels prepared under basic conditions, however, finally became translucent. All the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols, wet gels and dry gels were yellow.

Absorption spectra of $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels

Fig. 1 shows the variation of the UV–VIS absorpton spectra of the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels under acidic conditions during the sol–gel transition. An absorption band was observed in each spectrum at *ca.* 460 nm which did not change during storage and gelation; the absorbance slightly increased during gelation.

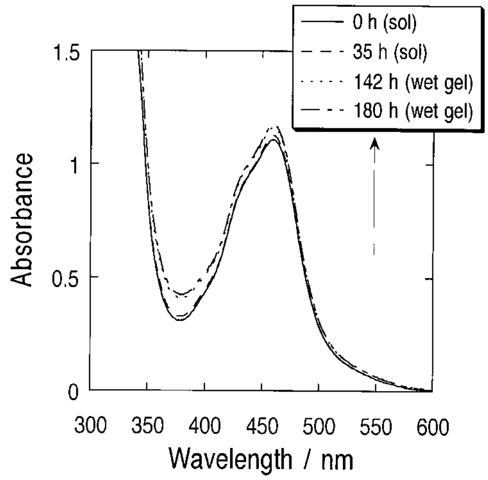


Fig. 1 Variation of UV–VIS absorption spectra of $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared from TEOS under acidic conditions during the sol–gel transition. The indicated times are the storage time and the direction of the arrow corresponds to an increase of the storage time.

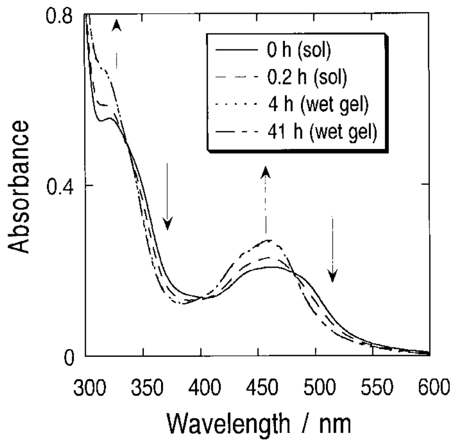


Fig. 2 Variation of UV–VIS absorption spectra of $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared from TMOS under basic conditions during the sol–gel transition. The indicated times are the storage time and the direction of the arrow corresponds to an increase of the storage time.

Fig. 2 shows the variation of the UV–VIS absorption spectra of $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels under basic conditions during the sol–gel transition. The initial absorption spectrum shows a broad absorption band at *ca.* 450–500 nm and an intense band at *ca.* 320–370 nm. With an increase of the storage time, *i.e.* transition from the sol to the wet gel, the shoulder at *ca.* 370 nm and the band at 500 nm decrease while bands at *ca.* 330 and 460 nm increase; in this spectral change three isosbestic points are observed at 337, 401 and 481 nm.

Since $[Ru(bpy)_2(pbimH)]^{2+}$ contains an imino group in pbimH, a change of UV absorption spectra should be induced by a change in pH of the solution. Fig. 3 shows the change of the UV absorption spectra of $[Ru(bpy)_2(pbimH)]^{2+}$ in MeOH–water with varying pH of solution. The complex shows an intense absorption band at *ca.* 460 nm and a shoulder at *ca.* 330 nm in solutions of low pH whereas at high pH, the complex shows an broad absorption band at *ca.* 400–500 nm and an intense band at *ca.* 330 nm. Upon increasing the pH of the solution, the absorbance of the bands at *ca.* 330 and 460 nm decrease while the bands at *ca.* 370 and 500 nm increase. Three isosbestic points are also observed at 328, 411 and 476 nm. The absorption band at *ca.* 460 nm is assigned to a metal-to-ligand

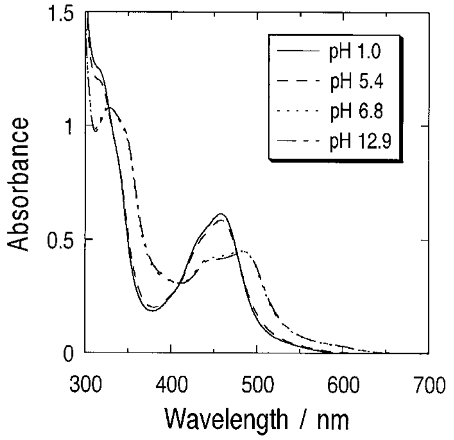


Fig. 3 UV–VIS absorption spectra of $[Ru(bpy)_2(pbimH)]^{2+}$ in MeOH–water as a function of pH. The mole ratio of MeOH to water was 2 : 5 and the concentration of $[Ru(bpy)_2(pbimH)]^{2+}$ was 5×10^{-5} mol dm^{-3}. Adjustment of pH was carried out by using HCl and NH_3(aq).

charge transfer (MLCT) transition.[17] Since isosbestic points are observed, these spectral changes indicate a process $A \rightleftharpoons B$ as expected for an acid–base equilibrium as shown in eqn. (1).

$$[\mathrm{Ru(bpy)_2(pbimH)}]^{2+} \rightleftharpoons [\mathrm{Ru(bpy)_2(pbim)}]^{+} + \mathrm{H}^{+} \qquad (1)$$

Comparing Fig. 1 and 2 with Fig. 3, the absorption spectra of the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared under acidic conditions during the transition from sols to wet gels were similar to that of $[Ru(bpy)_2(pbimH)]^{2+}$ in acidic solution. The changes in the absorption spectra of the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared under basic conditions during the transition from sols to wet gels were similar to those of $[Ru(bpy)_2(pbimH)]^{2+}$ upon changing from basic to acidic solution. In the silica sols and gels prepared under acidic conditions, it is noted that the Ru complexes with 2-(2-pyridyl)benzimidazole were retained in the protonated form, $[Ru(bpy)_2(pbimH)]^{2+}$. The change of absorption spectra under basic conditions reveals that the acid–base equilibrium (1) shifts from the deprotonated form, $[Ru(bpy)_2(pbim)]^{+}$, to the protonated form, $[Ru(bpy)_2(pbimH)]^{2+}$, during the sol–gel transition, *i.e.* the imido group in $[Ru(bpy)_2(pbim)]^{+}$ in the sols is protonated during storage and gelation.

It is clear that the complex $[Ru(bpy)_2(pbimH)]^{2+}$ acts as a pH indicator since the acid–base equilibrium of the imino group in $[Ru(bpy)_2(pbimH)]^{2+}$ is sensitive to pH changes of the system. For the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared under acidic conditions, it is presumed that the local environment of the Ru complex in both the sols and gels is acidic. On the other hand, for the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared under basic conditions, we conclude that the local environment of Ru complexes in the sols prepared under basic conditions changes from basic to acidic upon gelation.

Emission spectra of silica gels doped with Ru complexes

Fig. 4 shows changes in wavelength and intensity of the emission maximum (a) and weight loss (b) for the silica gels doped with $[Ru(bpy)_2(pbimH)]^{2+}$ under acidic conditions as a function of storage time. The emission maximum of the sol just after preparation is at 602 nm, which is very similar to that of $[Ru(bpy)_2(pbimH)]^{2+}$ in MeOH–water. The emission maximum is blue-shifted during the sol–gel transition and reaches 597 nm at the gelation point. No change is observed in the emission maximum in the aging stage (175–320 h) of the wet gel with almost no weight loss in a closed system and also in the early stage (320–500 h) of drying of the gel accompanied by a drastic weight loss by 85% in an open system. However, in the later stage ($t > 500$ h) of drying of the gel, in which weight loss of the gel is not observed, the emission maximum is again blue-shifted to 593 nm. The intensity of the emission maximum increases slightly during the sol–gel transition (0–175 h) while no change is observed in the emission intensity in the aging stage (175–320 h) of the wet gel. However, in the early stage (320–500 h) of drying of gel, the emission intensity steeply increases to reach a maximum at *ca.* 500 h and then decreases in later stages ($t > 500$ h) of drying of gel.

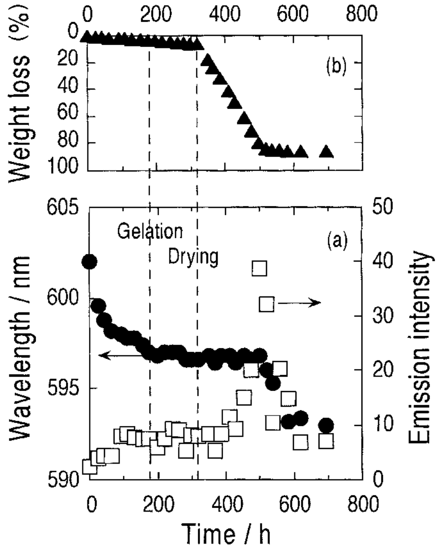


Fig. 4 Changes in wavelength and intensity of the emission maximum (a) and weight loss (b) for silica gels doped with $[Ru(bpy)_2(pbimH)]^{2+}$ as a function of storage time. The silica gel was prepared from TEOS under acidic conditions. The gelation time was 175 h and drying of the gel was commenced 320 h after storage.

The blue shift of the emission maximum can be explained on the basis of the restriction of the mobility of the complexes, and the increase in emission intensity on the basis of non-radiative transitions of the Ru complex in an excited state.[18,19] The blue shift in emission spectra during the sol–gel transition is presumably caused by an increase in the electrostatic interaction between $[Ru(bpy)_2(pbimH)]^{2+}$ and oxygen atoms in Si–OH or Si–O–Si bonds of silica polymer chains formed upon hydrolysis and condensation of TEOS. The mobility of $[Ru(bpy)_2(pbimH)]^{2+}$ in going from the sol to the gel matrix becomes gradually restricted by the silica polymer chains. Almost no change in wavelength of the emission maximum is seen in the aging and early drying stages of the gel, so that the interaction between $[Ru(bpy)_2(pbimH)]^{2+}$ and silica chains should be similar in these stages. In the later stage of drying of the gel, in which the solvent is almost completely evaporated, the emission maximum is again blue-shifted significantly, indicating that the mobility of $[Ru(bpy)_2(pbimH)]^{2+}$ is clearly restricted by the silica matrix in this stage. The maximum in emission intensity observed after 500 h storage, can be rationalized as follows: the drastic increase in the emission intensity in the early stage of drying of the gel, which corresponds to a drastic weight loss of the silica gel, is attributed to the suppression of non-radiative transitions of the Ru complex in an excited state owing to the evaporation of the solvent molecules surrounding the complex. On the other hand, the steep decrease in the emission intensity in the later stages of drying of the gel is caused by the enhancement of non-radiative transitions of the excited complex since the complex gradually becomes adsorbed to the silica gel matrix and consequently energy transfer from the excited complex to the silica gel matrix is promoted.

Fig. 5 shows changes in wavelength and intensity of the emission maximum (a) and weight loss (b) for silica gels doped with $[Ru(bpy)_2(pbimH)]^{2+}$ under basic conditions as a function of storage time. The emission maximum is blue-shifted during the sol–gel transition and reaches 594 nm at the gelation point. In the aging stage (3–140 h) of the wet gel, a slight blue shift of the emission maximum is observed. However, in the early stage (140–450 h) of drying of the gel accompanied by a large weight loss of 80% in an open system, the emission maximum is red-shifted to 594 nm. Then in the later stages ($t > 450$ h) of drying of gel, with almost no weight loss, the position of the emission maximum is again blue-shifted to 593 nm.

The gelation time under basic conditions is much shorter than that under acidic conditions, so that the wavelength of the emission maximum of $[Ru(bpy)_2(pbimH)]^{2+}$ just after the preparation of sol under basic conditions is estimated to be at *ca.* 602 nm, which is almost the same as that in MeOH–water and in the sol under acidic conditions. The blue shift of the emission maximum up to the gelation point is due to an increase in restriction of mobility of $[Ru(bpy)_2(pbimH)]^{2+}$ by the silica gel matrix. Compared with the results shown in Fig. 4, it can be seen that the wavelength of the emission maximum at the gelation point under basic conditions (594 nm) is slightly

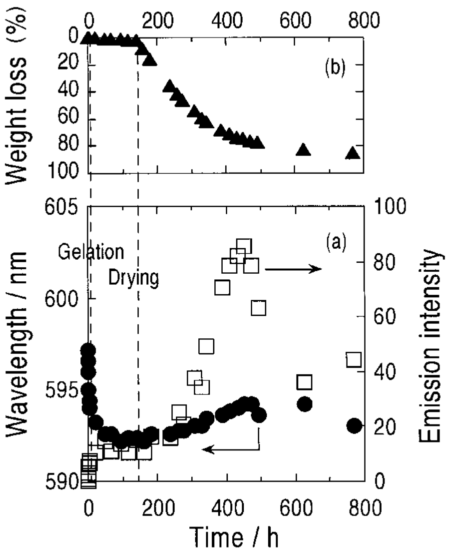


Fig. 5 Changes in wavelength and intensity of the emission maximum (a) and weight loss (b) for silica gels doped with $[Ru(bpy)_2(pbimH)]^{2+}$ as a function of storage time. The silica gel was prepared from TMOS under basic conditions. The gelation time was 3 h and drying of the gel was commenced 140 h after storage.

shorter than that under acidic conditions (597 nm). This difference in emission maximum indicates that the electrostatic interaction between $[Ru(bpy)_2(pbimH)]^{2+}$ and the gel matrix at the gelation point under basic conditions is stronger than that under acidic conditions. $[Ru(bpy)_2(pbimH)]^{2+}$ should be trapped in the gel pores in a more strongly restricted state under basic conditions since the silica gel matrix prepared under basic conditions tends to form a more three-dimensionally extended network in comparison with the matrix prepared under acidic conditions. It is expected that positively charged $[Ru(bpy)_2(pbimH)]^{2+}$ has a strong electrostatic interaction with silica particles prepared under basic conditions because of the negative surface charge of the silica particles. The red shift in the early stage of drying of gel is observed under basic conditions, but is not observed under acidic conditions. This red shift of the emission maximum under basic conditions is probably due to an energy increase of the d orbitals upon deprotonation of the imino group or a relaxation of greater restriction of mobility of $[Ru(bpy)_2(pbimH)]^{2+}$ upon evaporation of the solvent than found under acidic conditions.

Conclusions

$[Ru(bpy)_2(pbimH)]^{2+}$ has been doped into silica matrix under both acidic and basic conditions by the sol–gel method. The $[Ru(bpy)_2(pbimH)]^{2+}$-doped dry gels prepared under both acidic and basic conditions were transparent and free from cracks. Changes in the absorption spectra of the $[Ru(bpy)_2(pbimH)]^{2+}$-doped silica sols and gels prepared under basic conditions with the transition from the sol to the wet gel were similar to those of $[Ru(bpy)_2(pbimH)]^{2+}$ in solution upon changing from basic to acidic solutions. It is of note that the sol–gel transition shifts the equilibrium from the deprotonated form, $[Ru(bpy)_2(pbim)]^{+}$, to the protonated form, $[Ru(bpy)_2(pbimH)]^{2+}$.

The mobility of Ru complexes was observed to be restricted in silica gel matrices since a blue-shift of the emission maximum was observed during the sol–gel transition. At the gelation point, the wavelength of the emission maximum under basic conditions was shorter than that observed under acidic conditions. This indicates that the Ru complex was more strongly trapped in the gel pores under basic conditions than under acidic conditions.

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References

1 P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511.
2 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431.
3 D. Avnir, V. R. Kaufman and R. Reisfeld, *J. Non-Cryst. Solids*, 1985, **74**, 395.
4 J. C. Pouxviel, S. Parvaneh, E. T. Knobbe and B. Dunn, *Solid State Ionics*, 1989, **32/33**, 646.
5 M. Tatsumisago, Y. Sakai, H. Takashima and T. Minami, *J. Sol–Gel Sci. Technol.*, 1997, **10**, 13.
6 J. Samuel, M. Strinkovski, S. Shalom, M. Ottolenghi, D. Avnir and A. Lewis, *Mater. Lett.*, 1994, **21**, 431.
7 A. K. McEvoy, C. McDouagh and B. D. MacCraith, *J. Sol–Gel Sci. Technol.*, 1997, **8**, 1121.
8 D. Avnir, D. Levy and R. Reisfeld, *J. Phys. Chem.*, 1984, **88**, 5956.
9 R. Gvishi and R. Reisfeld, *J. Non-Cryst. Solids*, 1991, **128**, 69.
10 R. Reisfeld, R. Gvishi and Z. Bushtein, *J. Sol–Gel Sci. Technol.*, 1995, **4**, 49.
11 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.
12 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
13 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
14 F. N. Castellano, T. A. Heimer, M. T. Tandhasetti and G. J. Meyer, *Chem. Mater.*, 1994, **6**, 1041.
15 K. Matsui, K. Asaki and N. Takahashi, *Langmuir*, 1991, **7**, 2866.
16 P. Innocenzi, H. Kozuka and T. Yoko, *J. Phys. Chem.*, 1997, **101**, 2285.
17 M. Haga, *Inorg. Chim. Acta*, 1983, **75**, 29.
18 J. Mckiernan, J. C. Pouxviel, B. Dunn and J. I. Zink, *J. Phys. Chem.*, 1989, **93**, 2129.
19 S. D. Hanna, B. Dunn and J. I. Zink, *J. Non-Cryst. Solids*, 1994, **167**, 239.

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