

## ORIGINAL ARTICLE

# Enhancement of dye dispersibility in silica hybrids through local heating induced by the Imidazolium group under microwave irradiation

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We prepared imidazolium-containing silica hybrid films by sol–gel reactions of 1-(trimethoxysilylpropyl)-3-methylimidazolium chloride under microwave irradiation. Furthermore, we incorporated hydrophobic dyes such as pyrene and 1-pyrenecarboxaldehyde into the silica hybrids, and we investigated the dispersion behaviors of these dyes in the matrices. The local heating of the imidazolium groups under microwave irradiation was suggested to contribute to the enhancement of reaction rates in the sol–gel process. Finally, we achieved the incorporation of higher dye concentrations in the silica hybrids compared with those achieved with conventional heating.

*Polymer Journal* (2014) 46, 195–199; doi:10.1038/pj.2013.81; published online 25 September 2013

**Keywords:** hybrid; microwave; imidazolium; pyrene; sol–gel

## INTRODUCTION

Dye-doped silica or glass materials and organic-inorganic hybrids have attracted significant attention in the fields of light-emitting diodes (LEDs),<sup>1,2</sup> photochromic materials,<sup>3</sup> optical sensors,<sup>4</sup> biomaterials<sup>5–9</sup> and solid-state dye laser oscillators.<sup>10</sup> If organic dyes can be dispersed homogeneously and embedded in the matrices, then the luminescent properties of the dyes should be highly preserved. In particular, because the matrices restrict the molecular motion of the dyes and restrict the access of water and oxygen active species, the photostability of the dyes can be significantly enhanced.<sup>11–13</sup> Interactions between the guest molecules and matrices have been found to have an important role in the immobilization of the dyes in the matrices and in the improvement of the photostability of the dyes.<sup>11–13</sup> However, more effective approaches are still needed for immobilization of dye molecules because critical molecular motions of the dyes in the matrices could exist and cause dye degradation.<sup>11,12,14</sup>

Ionic liquids, which are air-stable molten salts and are in the liquid state below 100 °C, have received much attention in the field of chemistry as a 'green' recyclable alternative to traditional organic solvents. Various combinations and modifications of cations and anions allow the properties of ionic liquids to be tuned. Recently, microwave-assisted organic, inorganic and polymer syntheses with ionic liquids have been explored.<sup>15</sup> Ionic liquids can absorb microwaves effectively because of their high polarity, and the ionic conduction induced by microwave irradiation can generate extremely large amounts of heat. Therefore, the combination of ionic liquids and microwave irradiation provides significant advantages such as the acceleration of reaction rates.

Often, by increasing the temperatures in a sol–gel reaction, the reaction time can be decreased. However, porous products are often obtained because of the rapid evaporation of the solvent. We expect that the incorporation of ionic compounds into the preparation of silica gels allows for the increase of localized heating under microwave irradiation and results in the rapid and homogeneous formation of silica materials. Here we prepared an imidazolium-containing alkoxy-silane, 1-(trimethoxysilylpropyl)-3-methylimidazolium chloride (**1**, shown in Scheme 1), and the sol–gel reaction of **1** was performed under microwave irradiation to prepare imidazolium-containing silica hybrid films. Furthermore, we investigated the dispersion behaviors of the dyes in the imidazolium-containing hybrid matrices with pyrene and 1-pyrenecarboxaldehyde. The local heating caused by the imidazolium ions under microwave irradiation was found to allow the rapid formation of silica gel containing the alkoxy-silane and to allow increases in the dye content without the loss of the optical properties in the silica matrices.

## EXPERIMENTAL PROCEDURE

### Materials

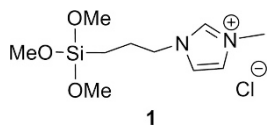
All reagents were purchased from commercial sources and were used as received without further purification.

### Measurements

The <sup>1</sup>H (400 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer (Jeol, Tokyo, Japan), and tetramethylsilane (TMS) was used as an internal standard in CDCl<sub>3</sub>. Scanning electron microscopy (SEM) measurements were conducted with a JEOL JSM-5600 system (Jeol). The luminescent spectra of the obtained hybrids were measured with a HORIBA JOBIN YVON FluoroMax-4

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Received 27 June 2013; revised 5 August 2013; accepted 6 August 2013; published online 25 September 2013



**Scheme 1** Chemical structure of 1-(trimethoxysilylpropyl)-3-methylimidazolium chloride **1**.

fluorescence spectrometer (Horiba, Kyoto, Japan). Thermogravimetric analysis (TGA) was performed on a SEIKO TG/DTA 6200 (SEIKO, Tokyo, Japan) at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in air. Fourier transform-infrared (FT-IR) spectra were recorded on a Perkin-Elmer 1600 infrared spectrometer (Perkin-Elmer, Waltham, MA, USA). Pyrene was dissolved in methanol and was cast on a glass plate to measure the optical properties of pyrene in the solid state.

### Synthesis of 1-(Trimethoxysilylpropyl)-3-methylimidazolium Chloride (**1**)

A mixture of 1-methylimidazole (11.3 g, 0.137 mol) and 3-chloropropyltrimethoxysilane (27.3 g, 0.137 mol) was stirred at  $95\text{ }^{\circ}\text{C}$  for 24 h under nitrogen in a round-bottomed flask equipped with a reflux condenser.<sup>16</sup> The mixture was washed with  $\text{Et}_2\text{O}$  (40 ml  $\times$  5) and was dried at  $90\text{ }^{\circ}\text{C}$  under vacuum. Yield: 96%.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.58$  (s, 1H, Ar-H), 7.65 (t, 1H,  $J = 1.5$  Hz, Ar-H), 7.43 (t, 1H,  $J = 1.5$  Hz, Ar-H), 4.34 (t, 2H,  $J = 7.3$  Hz, Ar- $\text{CH}_2$ -), 4.14 (s, 3H, N- $\text{CH}_3$ ), 3.57 (s, 9H,  $-\text{OCH}_3$ ), 2.02 (quint, 2H,  $J = 7.3$ , 8.1 Hz,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 0.64 (t, 2H,  $J = 8.1$  Hz, Si- $\text{CH}_2-$ ) p.p.m.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 137.3$ , 123.6, 121.6, 51.3, 50.3, 36.1, 23.8, 5.6 p.p.m.

### Preparation of imidazolium-containing silica matrices doped with pyrene and 1-pyrenecarboxaldehyde

The typical preparation procedure is shown here: 1-(Trimethoxysilylpropyl)-3-methylimidazolium chloride (**1**, 0.40 g) and methyltrimethoxysilane (MeTMOS, 0.60 g) were dissolved in methanol (10 ml), and 0.1 N aqueous hydrochloric acid (1.0 ml) was added. MeTMOS was used to improve the formability of the films of the silica matrices. After stirring for 1 h, 2.0 ml of a 20 mM solution of pyrene in methanol was added to the reaction solution. The resulting solution was poured into a polypropylene vessel and was heated in a microwave apparatus (Milestone General MicroSYNTH). The microwave irradiation conditions were 400 W for 10 min, followed by 800 W for 20 min. For conventional heating, the solution was heated in an oven at  $60\text{ }^{\circ}\text{C}$  for 24 h. The internal reaction temperature of the reaction solution under microwave irradiation was monitored with an optical fiber temperature sensor. When 1-pyrenecarboxaldehyde was used instead of pyrene, 2.0 ml of 10 mM 1-pyrenecarboxaldehyde in methanol was added.

## RESULTS AND DISCUSSION

The imidazolium-containing hybrids were prepared by the sol-gel reaction of 1-(trimethoxysilylpropyl)-3-methylimidazolium chloride (**1**) and methyltrimethoxysilane (MeTMOS) under microwave irradiation and conventional heating. Table 1 summarizes the results from both preparation methods for the films. We used MeTMOS to improve the formability of the films of the silica matrices. In both methods, transparent films were obtained when the weight ratios of **1** to MeTMOS were 1/4 (run 2) and 2/3 (run 3). When only **1** was used (Table 1, run 6), sponge-like silica gels were obtained under microwave irradiation. In contrast, the materials prepared under conventional heating were viscous sols. It has been suggested that Species **1** absorbs microwaves efficiently, and the sol-gel reaction of **1** proceeded rapidly. When the sol-gel reaction of MeTMOS occurred in the presence of 1-butyl-3-methylimidazolium chloride (molar ratio of 1-butyl-3-methylimidazolium chloride to MeTMOS was 2/3), a transparent film was not obtained, and a viscous sol was formed. This result indicates that the covalent bond between the imidazolium group and the trimethoxysilyl group has an important role in the formation of homogeneous films.

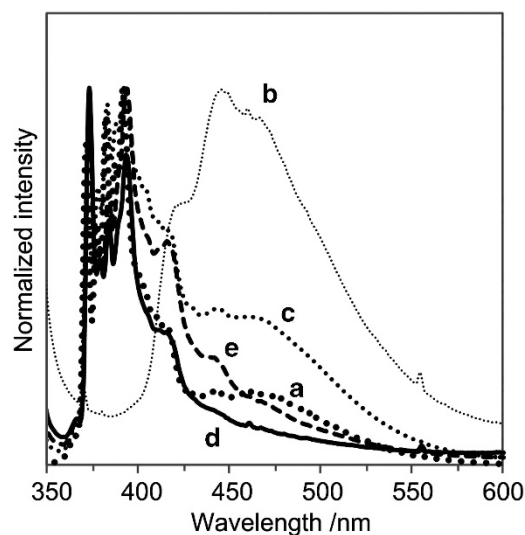
**Table 1** Preparation of imidazolium-containing hybrids

Run	<b>1</b> (g)	MeTMOS (g)	Appearance	
			Microwave <sup>a</sup>	Conventional <sup>b</sup>
1	0	1.0	Turbid film	Turbid film
2	0.20	0.80	Transparent film	Transparent film
3	0.40	0.60	Transparent film	Transparent film
4	0.60	0.40	Viscous gel	Viscous gel
5	0.80	0.20	Sponge-like solid	Sol
6	1.0	0	Sponge-like solid	Sol

Solvent, methanol 10 ml; catalyst, 0.10 N hydrochloric acid aqueous solution 1.0 ml.

<sup>a</sup>Microwave irradiation condition was 400 W for 10 min and 800 W for 20 min.

<sup>b</sup>Reaction was carried out in an oven at  $60\text{ }^{\circ}\text{C}$  for 24 h.



**Figure 1** The photoluminescence spectra of pyrene in solution, in the solid state, and doped in imidazolium-containing hybrids. (a)  $1.0 \times 10^{-3}$  M solution in methanol, (b) in the solid state, (c) in a hybrid prepared under microwave irradiation (run 1), (d) in an imidazolium-containing hybrid prepared under microwave irradiation (run 3), (e) in an imidazolium-containing hybrid prepared under conventional heating (run 3). The amount of pyrene dopant in the hybrids was  $40\text{ }\mu\text{mol}$ .

Next, pyrene was incorporated into the imidazolium-containing hybrids prepared with both methods. Figure 1 shows the photoluminescence spectra of a  $1.0 \times 10^{-3}$  M solution of pyrene in methanol, pyrene in the solid state and the pyrene-doped hybrids. The amount of pyrene dopant in the hybrid matrix was  $40\text{ }\mu\text{mol}$ . The pyrene exhibited excimer emission with a peak at  $\sim 470$  nm in methanol solution and showed an emission peak at  $\sim 440$  nm in the solid state. When the MeTMOS-based hybrids prepared under microwave irradiation (run 1) were doped with pyrene, a broad emission peak in the region from 420 nm to 500 nm was observed and could be attributed to the emission of pyrene aggregates. In contrast, the imidazolium-containing hybrid, which was obtained from 0.60 g of MeTMOS and 0.40 g of **1** (Table 1, run 3) and was prepared under microwave irradiation doped with pyrene, showed no emission derived from pyrene excimers or aggregates. These results suggest that the presence of imidazolium groups improved the dispersion of pyrene in the silica matrices. When the pyrene-doped hybrid was prepared under conventional heating, emission from pyrene aggregates was observed, and this emission indicates that pyrene molecules

were dispersed more homogeneously in the hybrids prepared under microwave irradiation.

SEM images of the obtained hybrids doped with 40  $\mu\text{mol}$  of pyrene are shown in Figure 2. In the SEM image of the hybrid prepared under microwave irradiation (Figure 2a), a few aggregates of pyrene were observed. In contrast, an inhomogeneous structure was observed in the film prepared under conventional heating. The aggregation of pyrene induced the critical phase separation in the film (Figure 2b).

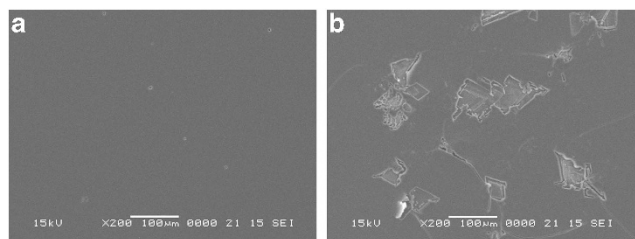
The TGA profiles and FT-IR spectra of the obtained pyrene-doped hybrids prepared under microwave irradiation and conventional heating are shown in Figures 3 and 4, respectively. In Figure 3, the hybrids prepared under both methods showed almost the same behaviors upon pyrolysis. As shown in Figure 4, the FT-IR spectra of the hybrids prepared under both methods are similar. These results indicate that the heating methods should less significantly affect the degree of condensation of the alkoxy silanes and the structures of the obtained hybrids.

To explain the role of the imidazolium groups, the change in the internal temperatures during the microwave-assisted synthesis of the hybrids was monitored. The temperature profiles are shown in Figure 5. When only MeTMOS was used to enhance the dispersibility of the pyrene in the hybrid formation (Table 1, run 1), the temperature during the reaction was constant after it reached at 66  $^{\circ}\text{C}$ . In contrast, for run 3, the reaction temperature reached 85  $^{\circ}\text{C}$  after 180 s. Subsequently, the temperature decreased gradually because

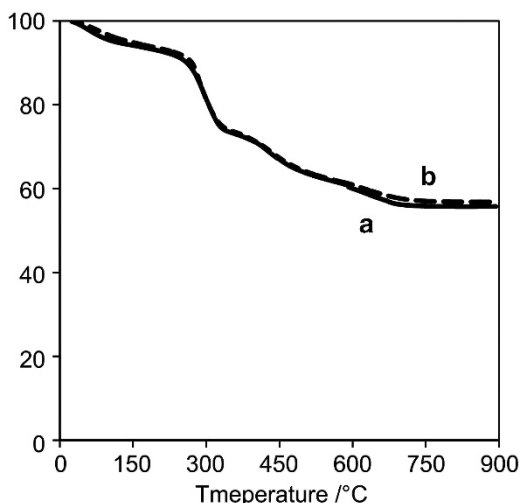
of solvent evaporation. The imidazolium groups of **1** were found to absorb microwaves and convert the microwaves to heat.

The proposed mechanism for the enhancement of the dispersibility of pyrene in the hybrid under microwave irradiation is illustrated in Scheme 2. The solubility of the pyrene increased because of the local heating around the imidazolium groups induced by the microwave irradiation. Moreover, the sol-gel reaction of **1** and MeTMOS should have been enhanced by microwave heating. Consequently, the homogeneous dispersion of pyrene was improved in the hybrid matrices prepared under microwave irradiation relative to the dispersion in those matrices prepared under conventional heating.

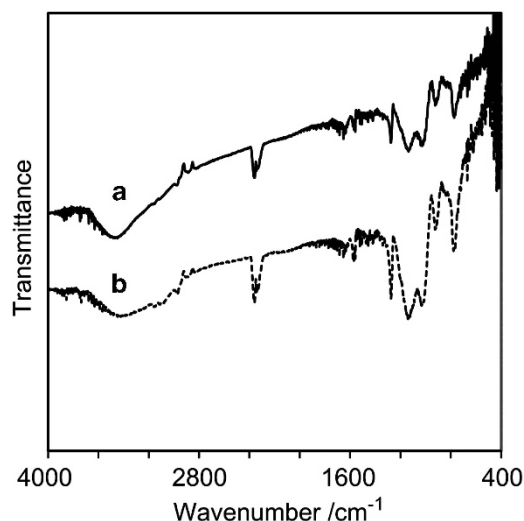
Furthermore, the polarity of the environments surrounding the pyrene in the hybrid matrices was investigated. The relative intensity of emission bands 1 ( $I_1$ ) and 3 ( $I_3$ ) of pyrene ( $I_1/I_3$ ) is known to be correlated with the solvent polarity.<sup>17–19</sup> The relative intensity increased as the environmental polarity increased around the pyrene molecule. When 40  $\mu\text{mol}$  of pyrene dopant was used, the relative intensities  $I_1/I_3$  of the hybrids prepared under



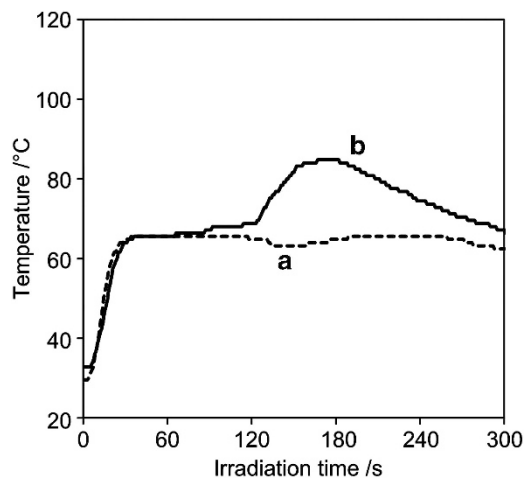
**Figure 2** SEM images of pyrene-doped hybrids prepared under (a) microwave and (b) conventional heating. The amount of pyrene dopant in the hybrids was 40  $\mu\text{mol}$ .



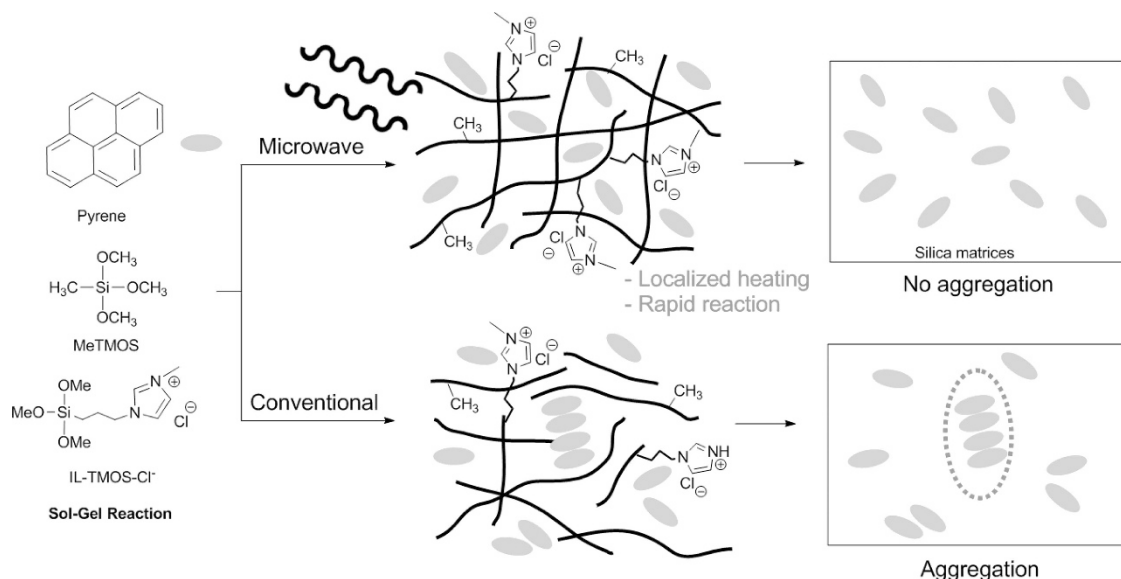
**Figure 3** TGA profiles of pyrene-doped imidazolium-containing hybrids prepared under (a) microwave and (b) conventional heating. The amount of pyrene dopant in the hybrids was 40  $\mu\text{mol}$ .



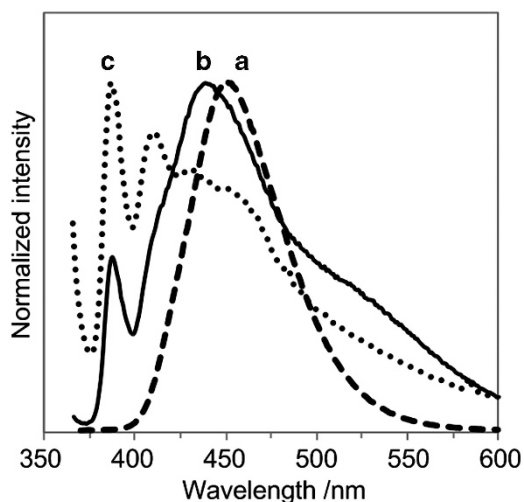
**Figure 4** FT-IR spectra of pyrene-doped imidazolium-containing hybrids prepared under (a) microwave and (b) conventional heating. The amount of pyrene dopant in the hybrids was 40  $\mu\text{mol}$ .



**Figure 5** Temperature profiles for the reaction solution of (a) run 1 and (b) run 3 under microwave irradiation.



**Scheme 2** Proposed mechanism for the homogeneous dispersion of pyrene in imidazolium-containing hybrids prepared under microwave irradiation. A full color version of this scheme is available at *Polymer Journal* online.



**Figure 6** PL spectra of 1-pyrenecarboxaldehyde in (a) methanol ( $1.0 \times 10^{-5}$  M), (b) imidazolium-containing hybrid prepared under microwave irradiation and (c) imidazolium-containing hybrid prepared under conventional heating.

microwave irradiation and conventional heating were 1.55 and 1.30, respectively. This result indicates that the surroundings of the pyrene molecule are considerably polar. In addition, pyrene molecules in the hybrids prepared under microwave irradiation were located in more polar environments than the molecules prepared under conventional heating. For the MeTMOS-based hybrids, the relative intensities  $I_1/I_3$  of the hybrids prepared under microwave irradiation and conventional heating were 0.88 and 0.70. These results suggest that the hydrophobic pyrene molecules could be dispersed even in the hydrophilic environment of the hybrid matrices prepared under microwave irradiation.

1-Pyrenecarboxaldehyde is widely used as a probe for solvent polarity in various isotropic and complex solubilizing media. The

fluorescence maxima of 1-pyrenecarboxaldehyde are known to redshift as the dielectric constant of the surrounding milieu increases.<sup>20</sup> We incorporated 1-pyrenecarboxaldehyde into the hybrids in the same manner as pyrene was incorporated. Figure 6 shows the PL spectra of 1-pyrenecarboxaldehyde in solution and in the hybrids prepared under microwave irradiation and conventional heating. The peak of 1-pyrenecarboxaldehyde in methanol was at 451 nm. In contrast, the peak of the imidazolium-containing hybrid prepared under microwave irradiation was at 438 nm, which was a slight blueshift. The PL spectrum of 1-pyrenecarboxaldehyde in the hybrid prepared under conventional heating was measured, and the observed spectrum was similar to that in cyclohexane.<sup>20</sup> The peak of the emission band from 1-pyrenecarboxaldehyde in the hybrid prepared under conventional heating was at 387 nm. These results suggest that the polarity of the hybrid prepared under microwave irradiation was higher than that prepared under conventional heating, similar to pyrene. Isolation of the dyes might occur in the film prepared under microwave irradiation.

## CONCLUSIONS

We demonstrated the microwave-assisted preparation of imidazolium-containing hybrids and effective incorporation of hydrophobic dyes, such as pyrene and 1-pyrenecarboxaldehyde, into the hybrid matrices. Compared with conventional heating, microwave irradiation allowed the incorporation of a higher concentration of hydrophobic dyes in the hybrid matrices. In addition, local heating of imidazolium groups under microwave irradiation and acceleration of the sol-gel reaction led to the incorporation of hydrophobic dyes in more polar environments. This method will be applicable to various types of hydrophobic molecules and will lead to the design of optical materials with excellent luminescent properties.

## ACKNOWLEDGEMENTS

This work was partially supported by the Kansai Research Foundation for the promotion of technology.

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