

Fluorescent Probes of the Molecular Environment within Mesostructured Silica/Surfactant Composites under High Pressure

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ABSTRACT

The molecular environment of the organic component of periodic silica/surfactant composites under elevated pressure is studied using a rigidochromic Re complex as a molecular probe. This amphiphilic organometallic complex is incorporated into the organic component of the silica/surfactant composite during synthesis. Shifts in the luminescence peak position of the Re complex indicate changes in the rigidity or viscosity of the surrounding matrix. In the experiment, under elevated pressure, the luminescence from the complex provides a measure of the changing molecular environment inside the mesophase. The results confirm conclusions from earlier experiments on the mechanical properties of silica/surfactant composites under high pressure: Although an increase in viscosity is observed with increasing pressure, the molecular environment does not become fully rigid until pressures as high as 10 GPa have been reached. This pressure is significantly higher than the solidification point of most pure organic phases and suggests that the mechanical strength of the silica framework provides a protected molecular environment for organic molecules situated within the silica nanopores.

1. Introduction. Cellular materials are widely used in modern engineering applications because of their desirable combination of light weight and good mechanical properties. These mechanical properties are confirmed by both high-pressure experiments and modeling of cellular solids.¹ Of the cellular structures, ordered cellular materials such as the hexagonal honeycomb structure show better mechanical properties than disordered materials. Specifically, the periodic, honeycomb-like hexagonal microstructure is one of the known microstructures that can lead to the highest possible values of the bulk modulus.²

Ordered hexagonal surfactant templated silicas (MCM-41 type materials)³ provide the unique opportunity to extend the length scale of honeycomb-based materials down to a much smaller size than the cellular materials mentioned above. In such composites, hexagonally packed surfactant domains are surrounded by a cross-linked, amorphous silica network, forming a continuous inorganic framework with two-dimensional hexagonal symmetry. The repeat distance of the composites is readily tunable from 20 to 300 Å.^{3,4} The structural similarity with the cellular materials described above suggests that some of the favorable mechanical properties found in bulk materials, such as high bulk modulus, may carry over to these nanoscale materials.

In recent work, we have studied the compressibility of periodic, hexagonal surfactant-templated silica under high pressures.⁵ We found that under optimized conditions, the mesoscopic order of the composite can be retained up to about 12 GPa. More importantly, the measured bulk modulus of the best composites (35 ± 2 GPa)⁵ was basically equal to that of bulk vitreous silica (32 GPa).⁶ Rigidity and elasticity in composites with such small amounts of inorganic material (<40 vol %) and wall thicknesses of only about 10 Å are unexpected. Because the compressibility of the organic surfactant is much lower than the silica matrix,⁷ it seems likely that the silica framework works as a scaffold to withstand the compressive forces. In such a case, the full compressive load would not be transmitted to the surfactant template until the silica pores distort or collapse. In other words, our past high-pressure results⁵ suggest that the interior of the mesopore is likely to be protected from the applied compressive forces by the rigidity of the silica framework. The goal of this paper is, thus, to examine the environment in the organic component of these composites under pressure.

A wide variety of molecules have been incorporated into the nanopores of the silica/surfactant composites. For example, ordered porous silicas have been used as hosts for conductive polymers,⁸ graphitic carbon,⁹ and a wide range of organic and organometallic molecules.^{10,11,12,13,14} Generally, there are two ways to incorporate guest molecules into the

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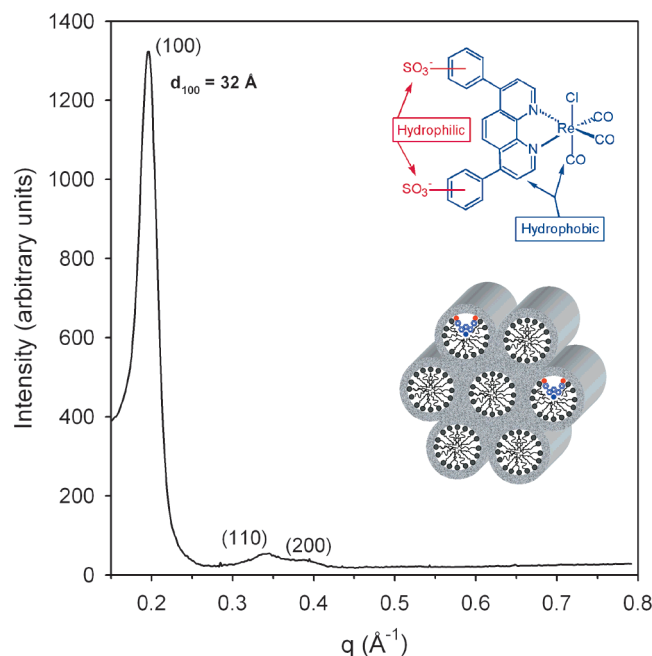


Figure 1. X-ray diffraction pattern of a rhenium complex doped silica/surfactant composite. The peaks can be indexed to a hexagonal $P6mm$ structure. Top insert—the molecular structure of the rhenium complex. Bottom insert—schematic of the Re complex incorporated into a hexagonally ordered silica/surfactant composite.

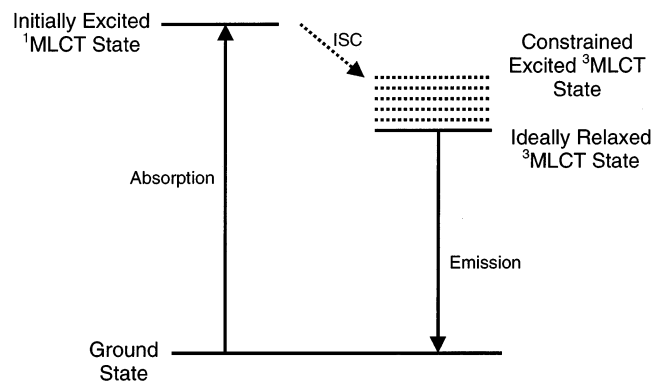


Figure 2. Proposed energy level diagram for absorption and emission processes in the Re(I) complex. ISC refers to intersystem crossing. The dotted lines represent energy levels for the unrelaxed $^3\text{MLCT}$ states.

nanopores. One is by co-dissolving the guest molecule with the surfactant during the synthesis step.^{10,11} The other is to graft the guest molecule onto the silica wall after removing the surfactant template.^{12,13,14} In this letter, we will show that by choosing an appropriate fluorescent guest probe molecule, we can partition the molecule into the surfactant component of our inorganic/organic composites. We can then obtain insight into the molecular environment within the pores under elevated pressures.

The probe molecule we use is $\text{ClRe(I)(CO)}_3(\text{Bathophenanthroline disulfonic acid, disodium salt})$; the molecular structure is shown in the top insert of Figure 1 and henceforth will be described as Re complex.¹⁵ As shown in Figure 2, when such a complex is excited by a photon with the appropriate energy, it is promoted to the first excited $^1\text{MLCT}$ state. By fast intersystem crossing, the excited molecule can

convert to a triplet state ($^3\text{MLCT}$). The ideal molecular conformation of the triplet state differs significantly from that of the singlet state, and thus, molecular motion can lower the energy of the long-lived $^3\text{MLCT}$ state. The $^3\text{MLCT}$ state typically gives rise to a strong luminescence band.¹⁶ Because of the $^3\text{MLCT}$ state relaxation, these complexes display rigidochromism, i.e., the emission maximum shifts depending on the environmental rigidity, yielding red-orange luminescence in fluid media and yellow-green luminescence in rigid media when the complex is trapped in a higher energy conformation because molecular motion is hindered. Luminescence rigidochromism of Re(I) complexes has been widely used as a spectroscopic probe to monitor the change in rigidity of many systems, such as polymerization in thin films,¹⁷ gelation and densification of sol-gel glasses,¹⁸ and the effect of pressure and freezing.¹⁹

2. Experimental Section. 2.1. Preparation of Rhenium Complex Doped Samples. The rhenium complex was synthesized according to the method outlined in Ref 15. To make the composites, a small amount of the rhenium complex was dissolved into an aqueous solution of cetyltrimethylammonium bromide (CTMABr). The mole ratio of the reagents used in the synthesis was SiO_2 : CTMABr: NaOH: H_2O = 4.4:1:0.5:147; the rhenium complex was incorporated at a mole ratio of complex: CTMABr = 1:390. After the addition of base (NaOH) and tetraethoxysilane (TEOS), the reaction solution was stirred in a sealed container for 30 min and subsequently filtered under house vacuum overnight. Tetrahydrofuran (THF) and methanol were then used to rinse the yellow product exhaustively to remove any residual rhenium complex located on the outer surface until the filtrate showed no indication of the characteristic luminescence from the complex.

The nanoscale order of the sample was characterized using a Rigaku rotating anode X-ray generator with a Roper Scientific X-ray CCD detector. The X-ray diffraction pattern is indicative of a two-dimensional hexagonal structure (Figure 1). Three diffraction peaks can be indexed according to $P6mm$ symmetry, which shows that the doping of the complex molecules does not disrupt the nanoscale order of the composite. The molecular structure of the rhenium complex is shown in the top insert of Figure 1. Due to the amphiphilic nature of the molecule, when it is mixed with CTMABr in an aqueous solution, it is likely to preferentially reside close to or inside the surfactant micelles. The negative charges on the aromatic ligand may drive the complex molecule close to the palisade region of the surfactant micelles. As a result, when the silica/surfactant composite is formed, some of the Re complex will be incorporated with the surfactant template into the channels of the composite. In the bottom insert of Figure 1 is a schematic of the doped silica/surfactant composite. The hexagonally packed organic surfactant arrays are surrounded by cross-linked, amorphous silica walls.

Several solutions of this complex and one polymer film doped with the complex were prepared as well. Typically, 1 mg of the rhenium complex was dissolved into 1 mL of different liquid media, such as 4:1 MeOH/EtOH, glycerol,

and poly(ethylene glycol) (MW = 400). Polymer films were prepared by dissolving 1 mg of complex in 1 mL of poly(acrylic acid), (average $M_w \sim 240\,000$, 25 wt. % solution in water). The doped polymer solution was then drop cast onto pre-cleaned glass slides. The film was dried in a vacuum (~ 0.4 mTorr) at around 60 °C for 12 h to remove residual water.

2.2. Measurements of Excitation and Emission Spectra at Ambient and Elevated Pressures. A Fluorolog, Jobin Yvon – Spex fluorometer was used to obtain the excitation and emission spectra of the rhenium complex doped solutions and film samples. In the luminescence excitation experiments, the exciting wavelength was scanned from 300 to 500 nm, while the emission line was monitored at 600 nm. In the emission experiments at atmospheric pressures, the excitation wavelength was at 400 nm, and luminescence was collected from 500 to 700 nm. In the high-pressure fluorescence experiments, both ambient pressure and high-pressure emission spectra were obtained by exciting the samples at 363.8 nm using a Coherent I90 Ar⁺ laser. Luminescence was collected using a SPEX-1702 single monochromator with a photo multiplier tube and a Stanford Research System SR400 photon counter. In the high-pressure experiments, a Holzapfel style diamond anvil cell²⁰ was used to generate pressure. The as-synthesized composite was dried in a vacuum (~ 0.4 mTorr) for 12 h before it was loaded into the high-pressure cell. Liquid Ar was used as the pressure medium because of its excellent hydrostatic properties.²¹ Solutions of the rhenium complex dissolved in glycerol and poly(ethylene glycol) (MW = 400) were also subjected to high pressures in the Holzapfel cell. Ruby fluorescence was used to determine the pressure inside the high-pressure cell.²²

3. Results and Discussion. **3.1. Excitation and Emission Spectra of the Rhenium Complex in Rigid and Nonrigid Environments at Atmospheric Pressure.** The room-temperature excitation and emission spectra of the rhenium complex in a poly(acrylic acid) film and a 4:1 MeOH/EtOH solution are shown in Figure 3. When the molecule is dissolved in the alcohol solution, there is no space confinement, and it is free to move. The excited ³MLCT state can fully relax to the lower energy conformation, and the maximum of the red emission is located at about 605 nm. When the molecule resides in a rigid environment such as the polymer film, the maximum of the luminescence blue shifts to about 555 nm.

As discussed above, the origin of the luminescence blue shift occurring in rigid materials is the inability of the complex molecule to rearrange itself to accommodate the optimal conformation of the excited ³MLCT state. In a fluid environment, the conformation of the excited ³MLCT state can fully relax to the lowest energy state (Figure 2). To facilitate this relaxation, the surrounding matrix molecules must be able to easily reorient or translate. If the viscosity of the medium substantially increases (which is the case for molecules confined in rigid polymer matrix or when the solvent passes through the glass transition point), the complex in the excited state will be restrained from reaching the ideal conformation. The blue shift observed in the polymer film thus indicates that the complex molecules are confined in a

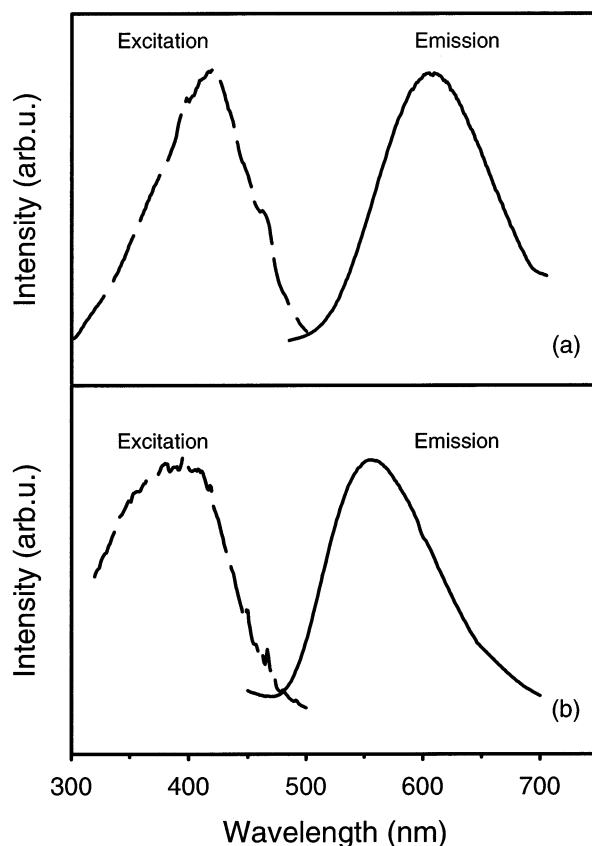


Figure 3. Excitation and emission spectra of the rhenium complex in different environments. (a) Re complex in a 4:1 MeOH/EtOH. The maximum of the luminescence peak is at 605 nm, indicating a fluid environment. (b) Re complex in a poly(acrylic acid) film. The maximum of the luminescence peak is at 555 nm, indicating a rigid environment.

rigid polymer matrix. We note that although solvent properties such as viscosity have a dramatic effect on the luminescence energy, there is less polarity based solvent shift to the luminescence.¹⁶ This suggests that the rigidochromic effect is due largely to changes (or lack thereof) in the geometry of the Re complex and not to changes in solvation. As a result, luminescence shifts can be meaningfully compared across environments with very different polarity.

3.2. Emission Spectra from the Rhenium Complex under Pressure. When the solution of rhenium complex dissolved in poly(ethylene glycol) (MW = 400) is subjected to high pressure (up to 10 GPa), the emission spectra shifts as pressure increases (Figure 4a). As soon as the polymer matrix becomes rigid (<1.5 GPa), the maximum of the luminescence peak shifts blue and does not change significantly as the pressure is increased further. This indicates that by 1.5 GPa the complex molecules are already in the confined environment of a rigid glassy matrix. As in the rigid poly(acrylic acid) film, the peak maximum in the rigid state is around 550 nm. Small red shifts with further increases in pressure are probably the intrinsic pressure effect of the complex caused by the changing metal–ligand bond lengths. On the contrary, in Figure 4b, for the rhenium doped surfactant/silica composite, the blue shift in the luminescence peak maximum increases gradually as pressure increases. The blue

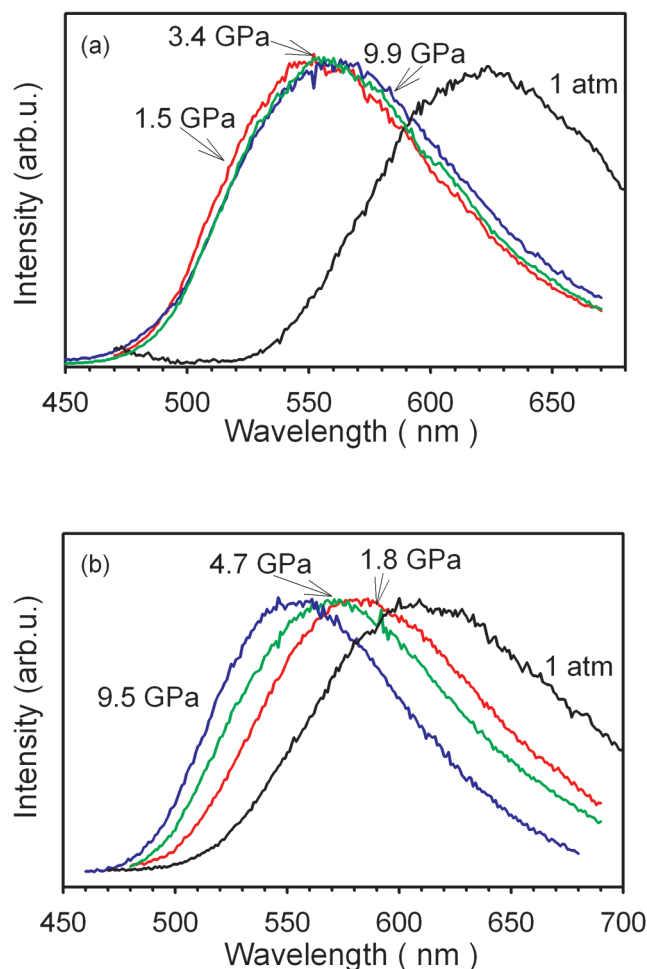


Figure 4. High-pressure luminescence spectra of Re complex doped samples. (a) poly(ethylene glycol) (MW = 400) solution containing the Re complex. (b) hexagonal silica/surfactant composite doped with the Re complex.

shift does not reach its maximum until the pressure is near 10 GPa, suggesting slow freezing of the molecular environment within the composite at high pressure.

Because of small solvent effects and possible differences in spectral calibration, the simplest way to compare the data shown in Figure 4 is to plot the relative blue shift of the luminescence peak. The blue shift of the luminescence peak maximum relative to its atmospheric pressure value for the Re complex in a range of environments is thus presented in Figure 5. The Re complex in poly(ethylene glycol) reaches its maximum blue shift at only 1.5 GPa. In glycerol, by contrast, the luminescence peak maximum shifts gradually up to 4 GPa as the solvent fluid environment becomes more viscous and rigid with pressure. Fundamentally, the pressure at which the luminescence indicates rigidity should correspond to the point where the solvent environment no longer allows for molecular motion within the luminescence lifetime. For the Re complex confined in rigid PAA polymer matrix we measure this luminescence lifetime to be $38 \mu\text{s}$.²³ High-pressure viscosity measurements on glycerol indicate that the relaxation time of the glycerol is near $38 \mu\text{s}$ at a pressure of 2.7 GPa.²⁴ In our experiment, the blue shift of the Re complex in the glycerol solution indicates that the

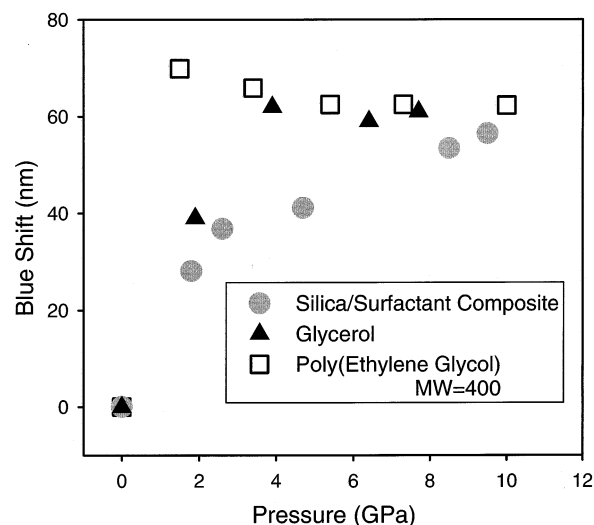


Figure 5. Blue shift in the luminescence peak maxima as a function of pressure for the Re complex in different media. The meanings of the symbols are indicated in the figure caption. The poly(ethylene glycol) (MW = 400) is observed to become rigid at the lowest pressure, followed by the glycerol, and finally the organic domains of the silica/surfactant composite.

Re molecule become fully rigid between 2 and 4 GPa, a range which is in excellent agreement with a pressure of 2.7 GPa calculated from the luminescence lifetime. We note that 2.7 GPa is slightly lower than the reported glass transition pressure (4–5 GPa^{25,26}) because the glass transition point corresponds to the pressure where the solvent relaxation time reach minutes or longer.

The blue shift of the complex molecules in the meso-structured composite, on the other hand, increases more slowly with pressure. At around 10 GPa the shift eventually reaches the level at which the matrix is fully rigid according to the results from both the poly(ethylene glycol) and glycerol. In other words, the rhenium complexes in the composites are in a much more fluid environment under pressure; the surfactant templates in the mesopores are able to rearrange to some degree on the $40 \mu\text{s}$ time scale up to pressures as high as 10 GPa.

The observed luminescent properties of the complex incorporated into the silica/surfactant composites under high pressure can be well correlated to the mechanical properties of the silica framework. From our previous study on the mechanical properties of silica/surfactant composites under high pressure, it was found that composite synthesized under similar conditions has a bulk modulus of about 16 GPa.⁵ Although this bulk modulus is much higher than that of typical organics, it is still low enough that significant volume changes occur upon compression. On the basis of our diffraction data, the volume compression can be as high as 20% at pressures approaching 8 GPa.⁵ As a result, the space within the nanopores will decrease with increasing pressure, and the packing density of the surfactant will increase accordingly, resulting in a more rigid environment for the Re complex molecules. Unlike the poly(ethylene glycol) or glycerol matrixes, however, which were chosen for their high pressure liquidity but which still become fully

rigid at fairly modest pressures, the luminescence peak of the complex incorporated in the silica/surfactant composite blue shifts gradually. This indicates some freedom of motion in the environment, despite a steady increase in rigidity and viscosity.

At the highest pressures, in-situ X-ray diffraction shows that the nanometer scale periodicity of the silica/surfactant composite starts to distort as evidenced by decreases in the intensity of the X-ray diffraction patterns of the composite.⁵ This distortion may lead to the partial collapse of the silica framework and the eventual compression of the organic domains of the composite. If molecules residing in the organic domains of the composites are viewed as protected by the rigid silica framework from the compressive stress applied, then collapse of the structure would mark the point when this protection is no longer effective. Accordingly, the luminescence of the Re complex in the silica/surfactant composites at pressures greater than 10 GPa shows a completely rigid molecular environment.

The results presented here lead to the conclusion that the internal pressure in these materials (that is, the pressure felt by the Re complex) is lower than the external pressure (that is, the applied pressure in the diamond cell). This would not be the case, however, if the Ar pressure medium was able to penetrate the surfactant filled pores and thus equalize the internal and external pressure. For example, when zeolites are compressed, the behavior of the system is dramatically altered when the molecules of the pressure medium can penetrate the pores and equalize the pressure, compared to the case where the molecules are too large to fit within the zeolitic pores.²⁷ In our case, the unequal pressure is probably rooted in the insolubility of liquid Ar at cryogenic temperature and of solid Ar at room temperature and high pressure in the hydrocarbon surfactant.²⁸ As a result, the pressure cannot equalize, and the surfactant and the Re complex experience a pressure that is less than that applied to the silica framework.

4. Conclusion. The molecular environment inside of MCM-41 type silica/surfactant composites was probed by incorporating a rhenium(I) complex, $\text{ClRe(I)(CO)}_3(\text{Bathophenanthrolinedisulfonic acid, disodium salt})$, into the organic domains in the nanochannels of the composites during synthesis. The luminescence rigidochromic property of the rhenium complex under high pressure suggests that the molecular environment of the organic surfactant template retains some fluidity up to about 10 GPa. The result indicates that the cross-linked, amorphous silica framework is working as a rigid matrix under high pressure, providing protection to the molecules incorporated inside the nanometer-sized pores.

These results suggest that silica/surfactant composites, and by extension mesoporous silica, can be used as host materials to provide mechanical protection for guest molecules such as catalysts. This may be useful for HPLC or catalytic reactions that require extreme conditions. It may also provide a route to the incorporation of stable organic functionality into inorganic materials designed for structural applications.

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