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Silica–polyoxazoline hybrid with nanosized hollow enclosing porphyrin in hybrid walls†

Ren-Hua Jin

Synthetic Chemistry Lab, Kawamura Institute of Chemical Research, 631 Sakado, Sakura, Chiba 285-0078, Japa. E-mail: jin@kicr.or.jp; Fax: (+81)43-498-2202

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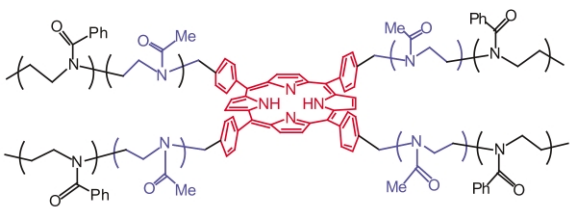
A silica–polyoxazoline hybrid with nanosized hollows and porphyrin moieties was fabricated *via* an emulsion templated sol–gel route.

Poly(methyloxazoline) (PMO) has strong compatibility with organic and inorganic materials.[1] This property was applied in the fabrication of an inorganic–organic hybrid nano composite *via* a sol–gel reaction in the presence of PMO.[2] Our aim is to construct a shaped silica–polyoxazoline hybrid enclosing porphyrin in the hybrid walls with help of an emulsion template sol–gel reaction.[3] Much recent work established that encapsulation of bio-functional molecules such as cytochrome *c*[4] and porphyrins[5] in sol–gel glasses is considerably effective in the development of bio-catalysts and bio-sensors. However, shaped sol–gel materials with a porphyrin moiety are scarce.

We synthesised‡ porphyrin centred star polyoxazoline Por(M–P)$_4$ (Scheme 1).[6] Because of the star copolymer molar composition of 73% MO (water soluble) and 27% PO (water insoluble) units, the polymer exhibited a good hydrophilic/hydrophobic balance, soluble in organic solvents and in water. We found that Por(M–P)$_4$ induces very stable opaque emulsions in normal (O/W) or reversed (W/O) fashion§ in a water–chloroform mixture. Such emulsions would be useful in templating engineering for fabrication of hybrid materials *via* sol–gel because the backbone of PMO, which is likely *N*,*N*-dimethylacetoamide in structure, can composite with silica by hydrogen bonding and dipole–dipole interactions.[2]

We performed silica-polymer hybridisation from sol–gel reaction of TEOS (tetraethoxy silane) in W/O and O/W emulsions.¶ Opaque reverse emulsion (W/O) containing 0.025 g of Por(M–P)$_4$, 0.2 mL of TEOS, 1 mL of chloroform and 0.1 mL of 1 M HCl solution was aged without stirring at room temperature for 2 days. This produced a green precipitate (due to protonated porphyrin). After washing the precipitate thoroughly by acetone and methanol with repeated sonication, centrifugation and decantation to remove free TEOS, Por(M–P)$_4$ and HCl(aq), brownish-red (free base porphyrin) particles (H-1) were obtained. In a similar manner, we performed the sol–gel reaction of TEOS in the normal emulsion (O/W) containing 0.2 mL of chloroform, 0.042 g TEOS, 0.7 mL 1M HCl, 0.3 mL H_2O and 0.025 g Por(M–P)$_4$. This opaque mixture was also aged 2 days at room temperature and the green precipitate produced changed to brownish-red particles (H-2) after work-up as described above. H-1 and H-2 were placed in methanol and both dispersions were used in casting and/or depositing for characterisation. Fig. 1 shows the images obtained by optical and fluorescent microscopy of the particles on glass slides. It is clear that H-1 from W/O routes produced micron spheres below 6 μm in diameter but H-2 from O/W route yielded irregular monolith-like particles. Both H-1 and H-2 emitted nicely red luminescence under fluorescent microscopy arising from porphyrin moieties , indicating that the particles are embedded with porphyrin moieties due to hybridisation of silica and Por(M–P)$_4$. We measured absorption (UV-vis with an integration spherical attachment), emission and excitation spectra of the particles for clarifying the state of the porphyrin on the particles. As shown in Fig.1(e–f), the spectra for Por(M–P)$_4$ in three states, hybrid spheres H-2, as cast film on glass-slide and as solution in $CHCl_3$, were similar. This means that the existent state of the porphyrin sites in the solid is similar to that in solution where the porphyrin sites exist without stacking. Thus, we expect that the porphyrin sites embedded on silica–polymer hybrid exist as an isolated state. We also confirmed that the porphyrin embedded on the hybrid materials could be transformed easily to the metalloporphyrin such as zinc type.

Fig. 2 shows the images of H-1 on TEM. They are smooth spheres with diameter from 50 to 5000 nm. The interest is in the internal structure of the spheres. Fig. 2(b) and (c) show a thin-sectioned slice of a spherical particle of H-1 and a local enlarged image of the slice, respectively. In Fig. 2(c), it is clearly observable that white circles in the range of diameter 22–25 nm are interspersed in the grain section. These white circles, which arise from electron transparency, indicate strongly that hollow cells exist inside the sphere. In the thin-sectioned slice of a group of spheres, Fig. 2(d), it can be seen that the larger the sphere the more white circles inside and that the white circles are nearly the same in diameter (*ca.* 25 nm) either for the larger



Scheme 1

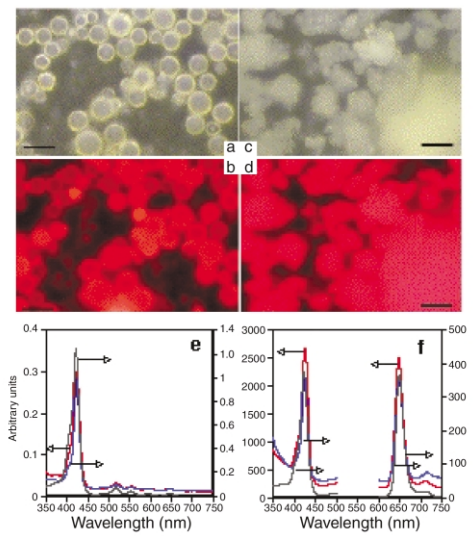


Fig. 1 Micrographs of optical (a,c) and fluorescent (b,d) microscope for H-1 (a,b) and H-2 (c,d), scale bar: 10 μm. Absorption (e), excitation, em = 650 nm (f) and emission, ex = 420 nm (f) spectra for Por(M–P)$_4$ in spheres H-2 (red), as casting film (blue) and as solution (grain) in $CHCl_3$.

† Electronic supplementary information (ESI) available: Figs. 1S–4S. See http://www.rsc.org/suppdata/cc/b1/b108763k/

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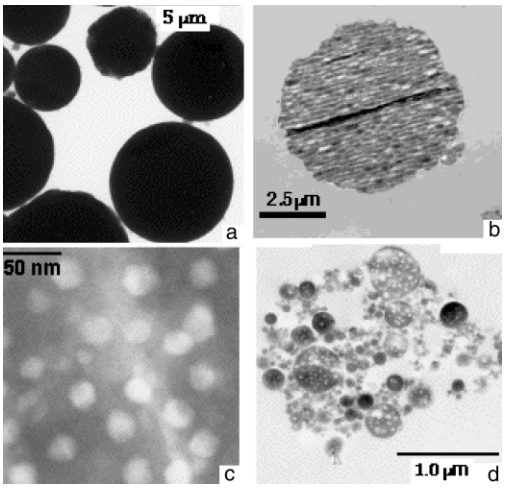

Fig. 2 TEM images for (a) the spheres H-1; (b) thin-sectioned slice for one sphere; (c) locally enlarged view of an area in (b); d) thin-sectioned slice for a group of spheres.

or for the smaller spheres. These results indicate that the size of the hollows is nearly monodisperse in the spherical particles H-1, although the size distribution of the spherical particles seems extremely wide. Apparently different from the H-1 particles, those of H-2 had irregular shape under optical microscopy and appear as a two-dimensional sheet with honeycomb-like structure in long range order, Fig. 3(a). In the locally enlarged image, Fig. 3(b), it is evident that cells having dark framework and slightly bright centre are connected together in an almost hexagonal pattern. At the edge of the sheet (dashed zone in Fig. 3(b)), we can observe a very thick wall due to disruption of the spherical cells. We further measured a thin-sectioned slice from the sheet, Fig. 3(c). The image of white rings surrounded by the broken dark frames demonstrate that the original cells in the sheet have a closed hollow structure. Therefore, we conclude that spherical hollow cells constructed the sheet-like particles H-2. The diameters of the larger and the smaller hollows are about 120 and 50 nm, respectively. The thickness of the dark framework, which is an image of hollow walls, is regular and less than 10 nm. Those spheres (H-1) and sheets (H-2) are quite novel because they have embedded porphyrin residues in shaped hollow walls. Moreover, it should be noted that the spheres and sheets were not cracked in the cutting of their thin-sections. Such high toughness may be attributed to the hybrid formed from silica and the star polymer.

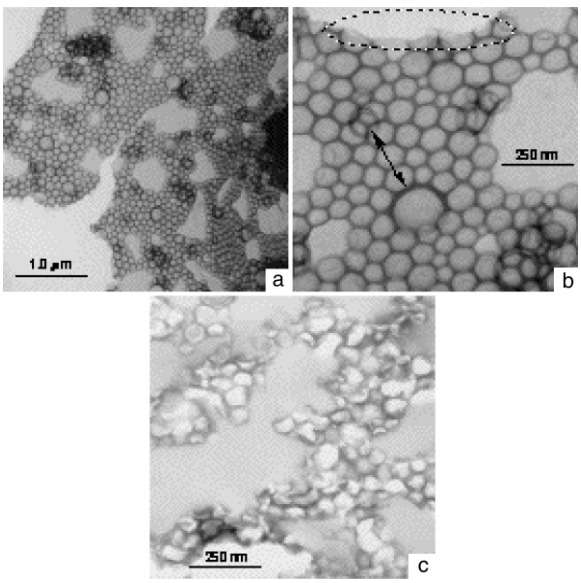

Fig. 3 TEM images for (a) H-2; (b) locally enlarged view of an area in (a); (c) thin-sectioned slice of H-2.

By placing a drop of sol–gel reaction liquid in the cavity of a microscope slide and covering it with a glass slip, we were able to follow the image changes under an optical microscope. In the W/O ($H_2O/CHCl_3$) sol–gel system, we observed that isolated spherical images existed from sol through to gel. In contrast, the initial spherical images of emulsion droplets became foam-like with time in the O/W ($CHCl_3/H_2O$) sol–gel system. It is reasonably conceivable that TEOS dissolved in $CHCl_3$ hydrolyses on the interface between water and chloroform and gelation of Si–OH occurs on the water rich side. Although the reasons for the formation of such small hollows and such different shapes in W/O and O/W sol–gel systems are not clear at present,‖ we speculate that the hollow director would be the same, *i.e.*, chloroform droplets either for $CHCl_3/H_2O$ or for $H_2O/CHCl_3$ sol–gel systems. Particularly, formation of ($CHCl_3/H_2O$)/$CHCl_3$ type emulsion in $H_2O/CHCl_3$ sol–gel route is possible owing to miscibility of chloroform in water. Thus, *many small chloroform droplets* (microemulsion) would be dispersed in *an emulsion droplet* (microemulsion-in-emulsion) and such chloroform droplets that are also stabilised by the star polymer induce very small hollows (*ca*. 25 nm) with formation of a gel of sphere H-1.

The silica–polyoxazoline hybrid with porphyrin moiety and nanosize hollow would be potentially applicable in biotechnology as bio-catalysts[4] and bio-sensors.[5] We also synthesised several porphyrin centred star block copolymers, and found that they are utilisable in the fabrication of shaped nanomaterials. Work on this aspect is in progress.

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Notes and references

‡ The mixture containing tetra-(4-iodomethylphenyl)porphyrin (0.0176 g, 0.0015 mmol), 2-methyl-2-oxazoline (MO, 1.06 mL, 12 mmol), 2-phenyl-2-oxazoline (PO, 1.81 mL,12 mmol) and phenylacetonitrile (2.0 mL) was stirred at 100 °C under nitrogen atmosphere for 24 h. After cooling, the mixture was poured into ethyl acetate to precipitate the polymer. The solid fraction was dissolved in small amount of methanol and the polymer reprecipitated in ethyl acetate. The solvents were filtered off and the polymer, violet in colour, was dried under vacuum. Yield 83.5%. The mole composition of the star copolymer evaluated by ^{1}H NMR was 73% in MO and 27% in PO, indicating at least that the attached monomer units near to the core porphyrin would be MO but not PO. Number average molecular weight (M_n) was 19400 with molecular weight distributions (M_w/M_n) 1.44 (determined by GPC relative to poly(ethyleneoxide) standard; RI detector; DMF as eluent).

§ The W/O (H_2O-in-$CHCl_3$) and O/W ($CHCl_3$-in-H_2O) emulsions were estimated by ^{1}H NMR and optical microscopy.

¶ Sol–gel reactions were performed by adding HCl(aq) to the solution containing Por(M–P)$_4$ and TEOS in chloroform or by addition of TEOS in chloroform into acidic aqueous solution containing Por(M–P)$_4$.

‖ Ethanol produced from the hydrolysis of TEOS would also influence the emulsions and hollow formations.

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