membrane lipid/water systems.\(^7\) It has been suggested that two lipid bilayers transform through an inverted micellar intermediate to a cubic mesophase.\(^8\) We propose that the 3-dH film is derived from the parent cubic film by constrained one-dimensional shrinkage between the two mesophases allowing seamless transitions between ordered domains and cause cubic and 3-dH domains to be essentially indistinguishable in plan-view (Fig. 4c).

A surface acoustic wave technique\(^9\) was used to determine pore accessibility of supported films. Figure 5 compares nitrogen sorption isotherms of the incipient 1-dH and cubic 3-dH films. Despite the substantially different degrees of ordering, the isotherms are qualitatively similar. The lack of hysteresis and absence of any appreciable adsorption at relative pressures above 0.3 is consistent with a unimodal porosity with no interparticle meso- or macroporosity.\(^10\) The surface areas calculated for the cubic 3-dH and incipient 1-dH films are 734 and 648 m\(^2\) g\(^{-1}\), respectively, demonstrating the accessibility of the mesophase porosity. In addition, the trans-film flux of cubic 3-dH films prepared as supported membranes increased by over 1,000\(^*\) upon calcination, establishing through-thickness pore connectivity (A. Tsai, unpublished results).

We have demonstrated a rapid, continuous process, enabling the practical utilization of mesostructures in thin-film form. The uniform three-dimensional pore channel systems of cubic 3-dH films and the absence of granularity suggest applications in molecular separation, catalysis and sensors. The dip-coating procedure combined with the optical probe technique enables us to follow the progressive evolution of the mesostructured films and should provide insight into the synthesis of complex, self-organized organic/inorganic assemblies in general.\(^11\)

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**Figure 5**

Figure 5: N\(_2\) sorption isotherms obtained at 77 K for a 400-nm-thick incipient 1-dH film prepared with C\(_2\) = 0.06 M (adsorption, white circles; desorption, black circles) and a 250-nm-thick cubic 3-dH film prepared with C\(_2\) = 0.10 M (adsorption, white squares; desorption, black squares). The films were applied to ~1 cm\(^2\) area of a piezoelectric ST-cut quartz substrate with interdigital gold transducers operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy.

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**Extraction of a hydrophilic compound from water into liquid CO\(_2\) using dendritic surfactants**


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Dendrimers are well defined, highly branched polymers\(^1-5\) that adopt a roughly spherical, globular shape in solution. Their cores are relatively loosely packed and can trap guest molecules\(^1-7\) and by appropriate functionalization of the branch tips the macro-molecules can act as unimolecular micelle-like entities.\(^7\) Here we show that dendrimers with a fluorinated shell are soluble in liquid carbon dioxide and can transport CO\(_2\)-insoluble molecules into this solvent within their cores. Specifically, we demonstrate the extraction of a polar ionic dye, methyl orange, from contaminated water, the extraction of pharmaceutical products from fermentation vessels, the selective encapsulation of drugs for targeted delivery\(^8\) and the transport of reagents for chemical...
reactions (such as polymerization\textsuperscript{8–11}) in liquid and supercritical CO\textsubscript{2} solvents.

Although CO\textsubscript{2} is a good solvent for many small molecules, only two classes of polymers have shown significant solubility (>10%) in CO\textsubscript{2} under practicable conditions (<100°C and <350 bar); amorphous (and low-melting) fluoropolymers\textsuperscript{8,12} and polysiloxanes\textsuperscript{8,13}. As a result, there has been considerable effort to design fluorinated and siloxane-based surfactants that can stabilize dispersions of otherwise insoluble polymeric materials in carbon dioxide\textsuperscript{10,13,14}. Small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) studies have shown that partially fluorinated amphiphilic surfactants can aggregate into micelles in carbon dioxide solution, the precise number of polymer chains per micelle being influenced by the CO\textsubscript{2} density\textsuperscript{15–17}.

The micelle-like structure investigated here is quite different. By extending methods developed by Meijer\textsuperscript{8}, a fourth-generation hydrophilic dendrimer\textsuperscript{14}, DAB-\textsubscript{dendr}-(NH\textsubscript{2})\textsubscript{32}, I, was functionalized with a 'CO\textsubscript{2}philic' shell, derived from a heptamer acid fluoride of hexafluoropropylene oxide

\[ 2 \text{ CF}_3\text{CF}_2\text{CF}_2(\text{OCF}(\text{CF}_3)\text{CF}_2)_{5}(\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{F}) \text{OF} \]

thus generating what may be considered as a well-defined, CO\textsubscript{2}soluble, unimolecular dendritic micelle, 3 (compounds 1, 2 and 3 are shown in Fig. 1). Characterization data agreed with a structure where, on average, 90% of the peripheral amine groups of 1 had been functionalized with perfluoropolyether chains. NMR spectroscopy showed that the NHCO proton signal for 3 (8.70 p.p.m.) was shifted significantly downfield from the corresponding signal at 7.75 p.p.m. for the single-chain model compound, \( P_3 \text{CF}_3\text{CF}-\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2)_{5}(\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{N})\text{CH}_2\text{CH}_2\text{CH}_3 \). This is consistent with strong intramolecular hydrogen bonding between amide groups in the closely packed dendritic structure of 3, as described previously for analogous systems\textsuperscript{8}. We found the functionalized dendrimer 3 to be insoluble in water (<10 p.p.m.) and most common organic solvents (methanol, ethanol, chloroform, hexane, chloroform and acetone), but to be soluble at room temperature in liquid CO\textsubscript{2}, at pressures above 76 atm (1,110 pounds per square inch). Dendrimer 1 was insoluble in CO\textsubscript{2} under the same conditions.

As many highly polar molecules are insoluble in carbon dioxide, we decided to investigate the potential of 3 as a host system for polar guests in CO\textsubscript{2}. It has been demonstrated previously that guest molecules can be trapped in a permeable dendritic core in situ by constructing a dense shell around the impregnated core and generating a 'dendritic box'\textsuperscript{19–21}. Alternatively, the dendritic core of a pre-formed, micelle-like host can be loaded with guest molecules in a homogeneous solution of both host and guest\textsuperscript{8}. By contrast, we have concentrated on the micelle-assisted transfer of guest molecules between two immiscible phases. Quite surprisingly, we have
found that the dendritic micelle 3 can transfer methyl orange (5), a 
CO_2-insoluble ionic dye^2, from aqueous solution into carbon 
dioxide (Fig. 2). A small quantity of 3 was weighed onto one of 
the CaF_2 windows of a 2.5-ml high-pressure cell, the cell assembled, 
and an aqueous solution of 5 (3.30 \times 10^{-3} \text{ mol l}^{-1}) was added such 
that it did not come into contact with 3. On addition of CO_2, 
the dendritic micelle dissolved rapidly, forming a colourless CO_2 phase 
(Fig. 2a). With time and in the absence of agitation, the colour in the 
aqueous phase decreased in intensity and a gradual colouring of the 
CO_2 layer was observed (Fig. 2b, c). After 150 min, it appeared that 
no dye remained in the aqueous phase (Fig. 2d). When the cell was 
depressurized, the dye-loaded micelle was deposited on the interior 
of the cell as a yellow film.

Spectroscopic analysis detected no dye in the residual aqueous 
phase, which suggests that under these conditions (a large excess of 
3) it was possible to extract this dye completely from the aqueous 
layer. No coloration of the CO_2 phase was observed in the absence of 
3. The wavelength of the ultraviolet absorption for 5 in the dendritic 
core of 3/CO_2 (Fig. 3a) was found to be significantly shifted from the 
absorption of 5 in aqueous solution (425–430 nm compared to 
464 nm), and also from the wavelength observed for 5 dissolved in a 
water-in-CO_2 microemulsion^23.24. This wavelength shift is also 
evident from the difference in colour of the aqueous and CO_2 
phases in Fig. 2. To calculate the maximum number of dye 
molecules that could occupy the dendritic core, experiments were 
conducted with varying molar ratios of 5 and 3 in the aqueous/CO_2 
phases (Fig. 3b). In all cases, the growth of the ultraviolet absorption 
of 5 was monitored as a function of time until the absorbance 
reached a constant value, usually after 25–35 h at room temperature 
without stirring. The maximum integral absorbance was related to 
the concentration of the dye in the CO_2 phase, which was then used 
to calculate the number of dye molecules per micelle core. At low 
ratios of dye to micelle (for example, 1 : 1), it was possible to extract 
extensively all of the dye from the aqueous layer and, indeed, 
an average value of about two dye molecules per dendritic core was 
determined spectroscopically. This is important because it suggests 
that the extinction coefficient of the dye absorption does not change 
significantly in the dendrimer core, and also that our quantification 
methods are valid^4. As the molar ratio of 5 to 3 was increased, 
the average dye loading increased accordingly, up to a maximum of 
around 12 dye molecules per dendritic core. Equivalent experiments 
were conducted with the dye rose bengal, 6 (Fig. 3b). The maximum 
number of dye molecules per dendritic core (around seven) was 
consistent with the somewhat larger size of this guest molecule 
(relative molecular mass, M_5 of 5, 327.37; M_6 of 6, 1017.65), and was 
also comparable with Meijer’s observations for alkyl modified 
dendrimers^6.

The precise mechanism by which the dyes migrate from the 
aqueous phase into the dendritic core in CO_2 is not yet known. As 
dyes 5 and 6 are essentially insoluble in the CO_2 phase and 3 is 
especially insoluble in water, it seems conceivable that the highly 
plasticized dendritic micelle might adopt a distorted conformation 
at the water–CO_2 interface, such that the hydrophilic core comes in 
close proximity to the aqueous layer. Preliminary experiments using 
Reichert’s dye^25 as a solvatochromic probe for the effective polarity 
of the dendritic micelle interior^26 suggest that the diffusion of 
significant amounts of water into the micelle core may accompany 
the phase transfer of both 5 and 6.

Small angle X-ray scattering measurements^16,27, using a high-
pressure cell similar to that described previously^8, were used to 
estimate the radius of gyration and the relative molecular mass of 
the fluorescent dendrimer. Standard corrections were applied and 
the data were normalized to units of absolute differential scattering 
cross-section^9, d\Sigma/d\Omega (Q) (\text{cm}^{-1}) where \Sigma denotes the total 
scattering cross-section, d\Omega is the solid angle and Q is the scattering 
vector. Scattering data were collected at 340 atm and 25°C for a 
number of concentrations of 3 in CO_2. Data were fitted to a variable 
arm number star model (an ‘f-arm star model’) over the whole 
range of Q, and linear fits were also obtained for [d\Sigma/d\Omega (Q)]^{-1} 
versus Q^2, in the range 0.01 \lesssim Q \lesssim 0.05 \text{ Å}^{-1}. The radius of 
gyration, R_g derived from the f-arm star fits for 3 in CO_2 was 
30.0 \pm 1.0 \text{ Å}. The value of R_g did not vary significantly with 
concentration, which suggests that no particle aggregation 
ocurred in the CO_2 solution under these conditions. A plot of

\begin{align*}
\text{Figure 3 a.} & \quad \text{Ultra-violet-visible spectra illustrating the} 
\text{diffusion of methyl orange (5) from an aqueous phase} 
\text{into a unimolecular dendritic micelle (3) in liquid CO}_2 
\text{(24.9°C, 340 atm). Spectra taken every 30 min. The high-} 
\text{pressure cell was arranged so that the ultra-violet beam} 
\text{passed only through the CO}_2 \text{ phase. Molar ratio of} 
\text{5} : \text{3} = 60 : 1. 
\text{b. Maximum number of guest molecules per micelle core} 
\text{(p}_{\text{max}}) \text{ for methyl orange (trace labelled '5')} 
\text{and rose bengal (trace labelled '6')} \text{ versus the initial} 
\text{molar ratio (p}_0 \text{) of 5 : 6.} 
\end{align*}

\begin{align*}
\text{Figure 4 Plot of} K_c [\Sigma (d\Omega/dQ)^{-1}] \text{ versus concentration (c) for the dendritic micelle (3)} 
\text{in liquid CO}_2 \text{ (23.7°C, 340 atm); see text.} 
K_c = (\rho_0 - \rho_1)^2 A_0 V_s (d\Sigma/d\Omega)(0), \text{ where} \rho_0 \text{ and} \rho_1 \text{ are} 
\text{the scattering length densities of particle and solvent, A}_0 \text{ is Avogadro’s} 
\text{number and} V_s \text{ is the estimated particle volume.} 
\end{align*}
\[ K_c (\frac{\partial \Sigma}{\partial \Omega}(0)) \] versus concentration of 3 is shown in Fig. 4, based on the \[ \frac{\partial \Sigma}{\partial \Omega}(0) \] values derived from f-star fits. (Here \( K_c \) is the SAXS contrast factor and \( c \) is the concentration.) The intercept at zero concentration gives the weight average relative molecular mass for 3 to be 33.5 (\pm 3.0) \times 10^3 which is consistent with values obtained by \( ^1 \)H NMR and elemental microanalysis (36.4 (\pm 1.0) \times 10^3). The \( M_w \) value derived from linear (Zimm) fits was within 0.3% of the value derived from the f-star fit.

These experiments demonstrate that surfactant-modified CO\(_2\) can be used to enhance dramatically the applicability of supercritical-fluid extraction applications using environmentally benign CO\(_2\) to replace some of the billions of pounds of organic solvents used every year in extraction and cleaning applications.

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