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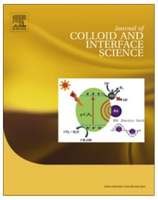


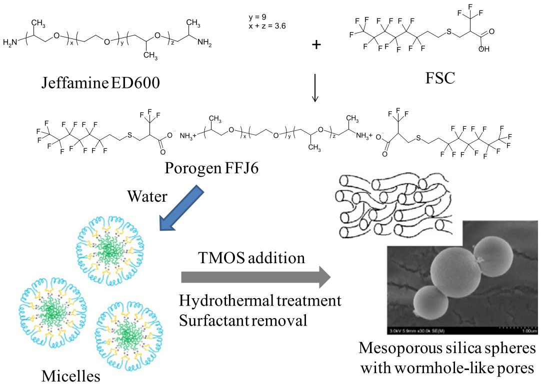
Regular Article

Investigation of a novel fluorinated surfactant-based system for the design of spherical wormhole-like mesoporous silica

Philippe Riachy [a], Gérald Lopez [b], Mélanie Emo [a], Marie-José Stébé [a], Jean-Luc Blin [a,*], Bruno Ameduri [b,*]

[a] *Université de Lorraine/CNRS, SRSMC, UMR 7565, F-54506 Vandoeuvre-lès-Nancy Cedex, France*
[b] *Engineering and Macromolecular Architectures, Institut Charles Gerhardt UMR (CNRS) 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue Ecole Normale, F-34296 Montpellier Cedex 5, France*

GRAPHICAL ABSTRACT



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ABSTRACT

In contrast to hydrogenated based systems that led to many studies, fluorinated surfactants have been little reported. Thanks to their high chemical and thermal stability, these compounds are considered as suitable candidates for the synthesis of porous materials with an enhanced hydrothermal stability. This study reports the synthesis of a new fluorinated surfactant, 2-trifluoromethyl-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-thia-1-dodecanoic acid (FSC) obtained from the thiol-ene radical addition of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol onto 2-trifluoromethyl acrylic acid in 85% yield. In the aim of achieving micelles in water to design mesoporous materials according to the cooperative templating mechanism, FSC was modified with water-soluble telechelic diamine (Jeffamine) ED-600. The modified surfactant was deeply characterized by spectroscopic methods and the FSC-Jeffamine ED-600 micellar system was used as porogen to prepare mesoporous materials *via* the cooperative templating mechanism. Spherical wormhole-like mesostructured silica materials of high specific surface area (850 m^2/g) and homogeneous pore size distribution (ca. 3.4 nm) were obtained by conveniently adjusting the porogen/silica molar ratio and the hydrothermal conditions.

1. Introduction

Thanks to the presence of fluorine atoms, fluorinated surfactants have unique properties [1] and have been involved in more than 200 applications [2] under severe conditions that would be

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* Corresponding authors at: Université de Lorraine, SRSMC, UMR 7565, Faculté des Sciences et Technologies, BP 70239, F-54506 Vandoeuvre-lès-Nancy Cedex, France (J.L. Blin).

E-mail addresses: Jean-Luc.Blin@univ-lorraine.fr (J.L. Blin), bruno.ameduri@enscm.fr (B. Ameduri).

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too harsh for their hydrocarbon counterparts. For example, fluorosurfactants can lower the surface tension of water down to a value half of what can be reached by using hydrocarbon surfactants. Moreover, they allow cosolubilization of water and perfluorocarbons [3,4] and the specific property of fluorocarbons to dissolve high quantities of oxygen and carbon dioxide makes them very attractive for biomedical applications such as oxygen vectorization [5,6]. More recently, fluorosurfactants have been used for the synthesis of mesoporous materials [7–9]. These compounds are obtained by the addition of a silica precursor to surfactant-based systems. They have tuneable pore sizes (from 2 to 30 nm), high specific surface areas (>800 m^2/g) and high pore volumes (>0.7 cm^3/g) [10,11]. These characteristics are of particular interest for various applications such as adsorbents, catalysts, host matrixes for electronic and photonic devices, drug delivery, and sensors [12–15]. Mesoporous materials are prepared from ionic or nonionic templates [10,11,16–18]. Among them, fluorinated surfactants are very attractive since they allow a high temperature hydrothermal treatment. Hence, thanks to a better condensation of silica [19], materials with a high hydrothermal stability are obtained. For instance, we synthesized mesoporous materials with a hexagonal channel array *via* a cooperative templating mechanism using nonionic fluorinated polyoxyethylene alkyl ethers [7]. In addition, Rankin et al. [8] reported a cationic fluorinated surfactant used as template to obtain ordered porous ceramic materials with a 2D hexagonal structure, a specific surface area of 982 m^2/g and a pore diameter of 2.6 nm. Furthermore, Esquena et al. [9] prepared mesostructured silica using $CF_3(CF_2)_7SO_2\text{-}[CH_3(CH_2)_2]N\text{-}(C_2H_4O)_nH$ as the templating surfactant. Mesoporous silica with a hexagonal channel array were formed for n = 10 while other n values lead to disordered structures. Nevertheless, fluorinated surfactants are scarce and few are commercially available. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most known but they are considered as toxic, persistent and bioaccumulative [2,20,21], because of the stable C_7F_{15} or C_8F_{17} groups. Consequently, their productions were banned last year. This limits the investigations to better understand the relation between the characteristics of the surfactant-based systems (such as structural parameters, phase behavior...) and the properties of the mesoporous materials (mesopore ordering, mesopore diameter...). Therefore, there is a need to synthesize new fluorosurfactants with shorter perfluorinated groups, as an alternative to PFOA and PFOS. However, fluorinated surfactants are known to be poorly soluble in water. To overcome this drawback, an attractive way consists in coupling them to water-soluble entities through covalent or ionic interactions. This way was recently used to synthesize a series of novel surfactants from fatty acids and homoditopic polyetheramine [22], employed for the preparation of mesoporous materials [22–24]. The objective of the present work was the synthesis of a novel fluorosulfonylcarboxylate surfactant (FSC) and its modification with water-soluble telechelic diamine (Jeffamine) ED-600 to afford a new porogen, further employed as template for the design of mesoporous materials. It should be outlined that when used alone, neither FSC nor Jeffamine ED-600 led to mesostructured silica.

2. Materials and methods

All reagents were used as received unless stated otherwise. 2-Trifluoromethyl acrylic acid (MAF) was kindly offered by Tosoh F-Tech Company (Shunan, Japan). 2,2′-Azobis (isobutyronitrile) (AIBN, Merck) was recrystallized from methanol. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanethiol ($CF_3(CF_2)_5CH_2CH_2SH$) was kindly supplied by Elf Atochem (Pierre Benite, France). 1,1,1,3,3-Pentafluorobutane (PFB) was kindly offered by Solvay S.A. (Tavaux, France, and Brussels, Belgium). Acetonitrile of analytical grade (Aldrich), was distilled over calcium hydride prior to use. Deuterated chloroform used for NMR spectroscopy was purchased from Euroiso-top (purity >99.8%). O,O′-bis(2-aminopropyl) polypropyleneglycol-*block*-polyethylene glycol-*block*-polypropylene glycol, $H_2N\text{-}(PO)_x(EO)_y(PO)_zNH_2$, where x + z = 3.6 and y = 9 (trade name Jeffamine ED-600) was supplied by Huntsman Corporation (St Mihiel, France). Tetramethoxysilane (TMOS), used as the silica source, was purchased from Sigma-Aldrich. Deionized water was obtained using a Milli-Q water purification system.

2.1. Materials

2.1.1. Synthesis of 2-trifluoromethyl-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-thia-1-dodecanoic acid, labeled as FSC

Fluorinated surfactant was obtained from the radical addition of $CF_3(CF_2)_5CH_2CH_2SH$ onto MAF (Scheme 1). The fluorinated thiol (5.00 g, 13.2 mmol, 1 eq.), 2-(trifluoromethyl)acrylic acid (1.84 g, 13.2 mmol, 1 eq.), and AIBN (0.11 g, 0.7 mmol, 0.05 eq.) were refluxed in 20 mL acetonitrile for 16 h. The reaction mixture was concentrated *in vacuo*, diluted with PFB (50 mL) and washed with water (6 × 50 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure to afford the desired product [FSC] in 85% yield (colorless oil).

The resulting FSC was completely insoluble in water. To be used as template it has been coupled with Jeffamine ED-600, which has complete water solubility. It should be noted that when used alone, Jeffamine ED-600 does not form any aggregates in water. Thus, no micelle was obtained and, as a consequence, no templated material can be obtained after the addition of the silica precursor.

2.1.2. Modification of FSC with Jeffamine ED-600, labeled as FFJ6

The ionic coupling between FSC and Jeffamine ED-600 was achieved as described in Scheme 2. A stoichiometric amount of Jeffamine ED-600 and FSC (1:2) was vortexed for 90 s then stirred for 48 h at room temperature.

2.1.3. Mesoporous materials preparation

Surfactant micellar solutions were prepared (from 1 to 5 wt.% of FFJ6). The solution pH was kept to 7. TMOS, used as the silica source, was added dropwise to the surfactant solution at room temperature under stirring. The surfactant/silica molar ratio (R) was varied from 0.01 to 0.50. Then, the mixture was transferred into sealed Teflon autoclaves for the hydrothermal treatment that proceeded for 1 day at 80 °C, 2 days at 50 °C or 9 days at room temperature. After the hydrothermal treatment, the material was transferred into cellulose extraction cartridges and left for 48 h under Soxhlet ethanol extraction to remove the template. Finally, the material was left to air-dry.

2.2. Characterization

2.2.1. Characterization of FSC

After reaction and purification, the resulting fluorosurfactant was characterized by ^1H and ^{19}F NMR spectroscopy. ^1H and ^{19}F NMR spectra were recorded on a Bruker AC 400 Spectrometer (400 MHz for ^1H and 376 MHz for ^{19}F) using $CDCl_3$ as the solvent. The coupling constants and the chemical shifts are given in Hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording ^1H [or ^{19}F] NMR spectra were as follows: flip angle 90° [or 30°], acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 5 s], number of scans 32 [or 64], and a pulse width of 5 μs for ^{19}F NMR.

^1H NMR ($CDCl_3$), δ (ppm) (Fig. SI1, ^1H NMR spectrum of product 1 recorded in $CDCl_3$): 2.30 (m, 2H, $C_6F_{13}\text{-}CH_2\text{-}$); 2.80 (m, 4H, $C_6F_{13}\text{-}CH_2\text{-}CH_2\text{-}S$ & $S\text{-}CH_2\text{-}CH(CF_3)\text{-}$); 3.40 (m, 1H, $S\text{-}CH_2\text{-}CH(CF_3)\text{-}$); 10.25 (br. s, 1H, -COOH).