Photoluminescent Surfactants: Mesostructured Organosilica Nanocomposites via Evaporation-induced Self Assembly (EISA)

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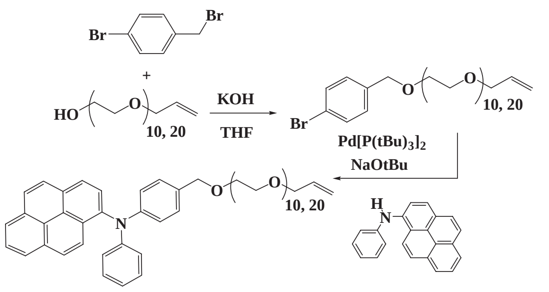
Two new photoluminescent (PL) surfactants consisting of hydrophobic/PL diphenylpyreneamine chromophores and hydrophilic oligo(ethylene glycol) segments have been synthesized and characterized. The PL surfactants induce the molecular self-assembly of hydrolyzed 1,2-bis(triethoxysilyl)ethane (BTSE) via evaporation induced self assembly (EISA) under mildly acidic conditions into PL mesostructured nanocomposites. The mesostructure forming capability for both PL surfactants were confirmed by XRD. PL spectra of the final functionalized nanocomposites suggest that the PL surfactants are confined within the nanometer regime of the rigid organosilica matrix.

Surfactant molecules have been recently used for the preparation of a wide range of nanostructured materials for various applications such as catalysts, sorbents, hosts, separation, and opto-electronic devices.[1–16] In most cases, the surfactant is a sacrificial material that is used to promote a desired nanostructure and is then removed by washing or calcination. Filling the empty pore network with an active material is generally achieved by a post-treatment process.[1–9] However, this process may not provide complete filling of the torturous nanochannel network. Thus, new strategies are required for the synthesis of well-defined mesostructured nanocomposites with complete pore-filling.[1–9] Our interest in these types of materials arises in that the emission and charge-transport properties of an active organic material could be greatly affected by their confinement within the nanochannels. Such nanocomposite materials may have application in organic-light emitting diodes (OLEDs), solar cells, and thin-film transistors.

We report here the synthesis of two photoluminescent surfactants (PLS10 and PLS20) and their use to promote mesostructured nanocomposites via evaporation-induced self-assembly (EISA).[1–6] PLS10 and PLS20 were designed and synthesized (Scheme 1) to have PL/conjugated diphenylpyreneamine-based hydrophobic groups covalently linked to hydrophilic oligo(ethylene glycol) segments.[17] As the surfactants act as the structure formation material, the pore network is filled with the active material. The synthesis is straightforward and provides the active surfactants in two high yield steps from readily available starting materials. In this study, we use 1,2-bis(triethoxysilyl)ethane (BTSE) as the matrix material as BTSE allows us to prepare defect-free thin films more consistently than when using tetraethoxysilane (TEOS). MALDI (Figure 1) and NMR confirm the formation of the desired surfactants. MALDI of the starting polyethylene glycol monoallyl ether materials (Polyglycol A 500 and Polyglycol A 1100) shows a distribution ranging from 6–20 and 11–34 ethylene glycol segments respectively, similar to the distribution of the final surfactants, demonstrating no chemical breakdown occurred during the course of the reaction.



Scheme 1. Synthesis of photoluminescent surfactants, PLS10 and PLS20.

XRD (Figure 2) of thin films deposited by spin coating show intense peaks for the PLS-based nanocomposites with respect to the (100) reflection, indicating the formation of mesostructured materials. The resulting mesophase dimension could be controlled by changing the length of the ethylene glycol segments. For example, *d*-spacings of 6.04 and 6.40 nm respectively were observed for PLS10 and PLS20. The obtained XRD results are consistent with TEM images (not shown here) and previously reported surfactant-based mesoporous silicas.[1–12,18–23] Additionally, similar XRD and TEM results were obtained for powders prepared from an EISA process.

Photoluminescent (PL) spectroscopy was used to investigate the effect of chain length on the formation of PLS-based nanocomposites. Both PLS-functionalized nanocomposite films (Figure 2) show blue shifted PL of 5–6 and 7–9 nm for PLS10 and PLS20 respectively versus that of pure PLS,[7] suggesting that PLS molecules are confined in the nanometer scale regime with-

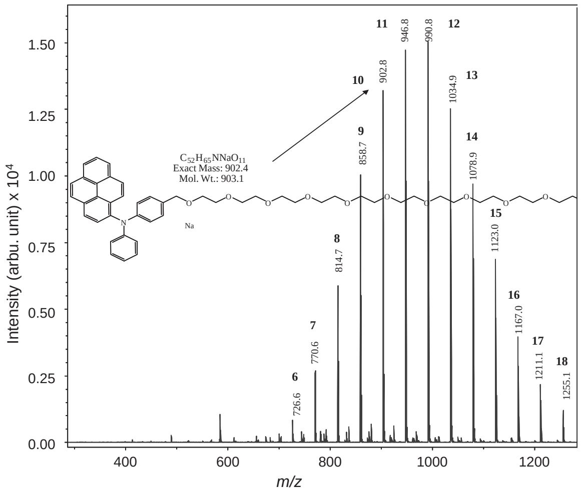


Figure 1. MALDI spectrum of PLS10. The distribution of ethyleneglycol segments closely follows that of the starting polyethyleneglycol monoallylether.

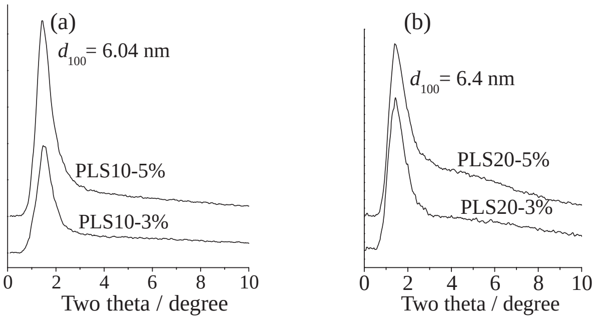


Figure 2. XRD patterns of the PL surfactant-based mesoporous organosilica nanocomposites: (a) PLS10 and (b) PLS20. Percentages (3 and 5%) refer to the amount of PL surfactants in the initial solutions.

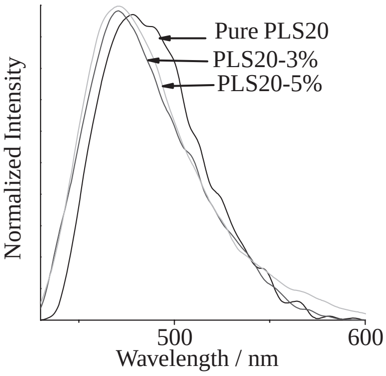


Figure 3. Emission spectra of PL mesostructured nanocomposites: PLS20 (upon excitation at 407 nm).

in the rigid organosilica matrix.

In conclusion, we have demonstrated the design, synthesis and self-assembly of new photoluminescent (PL) surfactants that form mesostructured nanocomposites with controlled architecture via EISA. The chemistry used to prepare the PL surfactants is straightforward and forms the desired materials in two high yield steps. Further studies to use these materials as active components in organic light emitting diodes, solar cells and thin-film transistors are in progress.

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17 General experimental procedure for the preparation of PLS10 surfactant. Potassium hydroxide (1.45 g of 85% KOH, 22.0 mmol) and Polyglycol A 500 (polyethyleneglycol mono-allyl ether MW 500 g/mol, 9.5 mL, 20.5 mmol) were added to a 25 mL Schlenk flask followed by three vacuum/argon refill cycles. Dry THF (10 mL) was added and the mixture was stirred at 65 °C for 1 h at which point 4-bromobenzyl bromide (5 g, 20.0 mmol) in 5 mL of dry THF was added. The reaction was complete after stirring at 75 °C for 20 h. The crude product [polyethyleneglycol (α-monoallyl-ω-4-bromophenyl) ether] was obtained as a light brown viscous liquid in quantitative yield after filtration and solvent removal. Characterization by MALDI-TOF indicated the material was sufficiently pure for use in the next step. Polyethyleneglycol (α-monoallyl-ω-4-bromophenyl) ether (2.00 g, 2.77 mmol), *N*-phenylpyreneamine (0.81 g, 2.77 mmol), sodium *t*-butoxide, (0.40 g, 4.16 mmol) and bis(tri-*t*-butylphosphine)palladium(0) (28 mg, 2 mol %) were added to a 50 mL Schlenk flask followed by three vacuum/argon refill cycles. Dry toluene (20 mL) was added and the reaction was stirred at 80 °C for 24 h. The product was obtained as a viscous dark brown liquid in quantitative yield after filtration and solvent removal. Characterization by MALDI-TOF indicated the material was sufficiently pure for use in the EISA process.

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