The Bergman cyclopolymerization of polymerizable surfactant monomer was carried out within the hexagonal channels of functional hybrid nanocomposite formed by co-assembly with silica.

Ordered periodic mesoscopic materials allow the construction of composites with many guest types like organic molecules or polymers. Inclusion of dye molecules such as Coumarin 40, Rhodamine BE50, Oxazine 1 inside the nanopores has been demonstrated.\textsuperscript{1–3} Nanocomposites that contain conjugated polymers confined within a silica matrix show enhanced conductivity, mechanical strength, processability, environmental stability, and other unique properties\textsuperscript{4} that allow for potential use in light emitting diodes, information storage devices, optical signal processors, and sensors. To name a few, nanocomposite formation of polymers such as poly(phenylene vinylene),\textsuperscript{5} polyalanine,\textsuperscript{6} polydiacetylene,\textsuperscript{7} poly(2,5-thiénylene ethynylene),\textsuperscript{4} polythiophene, polypyrrole, and polyanilines\textsuperscript{8,9} have been reported. Several synthetic efforts to obtain such nanocomposites used mainly slow procedures like monomer or polymer infiltration of inorganic nanostructures\textsuperscript{5,10–13} or sequential deposition.\textsuperscript{14,15} Such nanocomposites are heterogeneous, exhibiting two distinct conjugated polymer environments, that is, polymers inside and outside the hexagonally arranged pore channels of the silica particles. However, self-assembly, one of the few practical strategies for making ensembles of nanostructures provides one solution to the fabrication of ordered aggregates from components with sizes from nanometers to micrometers.\textsuperscript{16} It typically employs asymmetric molecules that are pre-programmed to organize into well-defined supramolecular assemblies.

The use of polymerizable surfactants as both structure-directing agents and monomers in various evaporation-driven self-assembly schemes represents a general, efficient route to the formation of robust and functional nanocomposites.\textsuperscript{7} In this research we utilize this self-assembly\textsuperscript{4} route to form mesostructured polynaphthalene/silica nanocomposites. One of the many approaches to form the polynaphthalenes (PN) is through Bergman cycloaromatization,\textsuperscript{17,18} a remarkable isomerization in which an endyne forms an arene 1,4-di-radical. Here, we make use of this approach with a

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**Chart 1** Chemical structure of amphiphilic surfactant monomer.

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and photoluminescence spectroscopy. UV-vis spectroscopy has been used previously to relate the degree of polymerization and absorbance. Fig. 2A shows the absorption spectra of the nanocomposite before and after the polymerization. Monomer nanocomposite showed maximum absorbance at about 285 nm, whereas polymer nanocomposite showed absorbance between 345 to 390 nm tailing up to 450 nm, indicating extensive conjugation of the polymer backbone. Direct molecular weight determination of such type of polymer/nanocomposite films is difficult. Monomer nanocomposite showed photoluminescence (PL) in UV-blue region with maximum peak at 353 nm. After polymerization, the photoluminescence was red-shifted with a maximum peak at 415 nm and a shoulder at around 483 nm.

Bergman cyclopolymerization of the monomers with terminal acetylene groups, as in the present case, generally gives insoluble polymers, making their characterization difficult. Monomer nanocomposite showed photoluminescence (PL) in UV-blue region with maximum peak at 353 nm. After polymerization, the photoluminescence was red-shifted with a maximum peak at 415 nm and a shoulder at around 483 nm.

Bergman cyclopolymerization of the monomers with terminal acetylene groups, as in the present case, generally gives insoluble polymers, making their characterization difficult. We carried out the polymerization of surfactant monomer dissolved in benzene as described in literature. Heating the monomer at about 140 °C for one day indeed afforded insoluble red brown solid. Monomer and polymer were characterized by infra-red (IR) spectra for comparison, as shown in Fig. 3. The characteristic alkyne triple bond C–H and C≡C stretching bands at 3280 and 2107 cm\(^{-1}\), respectively, present in the monomer disappeared after the polymerization. A new broad and strong band at 1625 cm\(^{-1}\), due to C–C stretching was observed, indicating formation of polymer with extensive conjugation. The degree of polymerization in thin film and in bulk might be different as these are two different environments and should affect the extent of conjugation. There are controversies regarding the structure of the polymer formed by Bergman cyclization of monomer with terminal triple bonds, as presence of five-membered ring and terminal triple bonds has been reported recently. However, from the IR spectra shown above, the possibility of presence of terminal triple bonds in the final product is ruled out in this case. Enhanced topochemistry due to the self-assembly and orientation of the surfactant monomers within the inorganic framework limits the formation of unidentified polymeric by-products, thereby giving small chain polynaphthalenes or their oligomers. We envisage formation of low molecular weight PN obtained by Bergman cyclization of polymerizable surfactant monomer within the hybrid nanocomposites formed by evaporative self-assembly. The polymers thus obtained could be soluble and be applied in opto-electronic devices. This route to polynaphthalenes (or polyphenylenes) and their derivatives is most attractive since it requires no exogenous chemical catalysts or reagents for the polymerization.

In summary, we have demonstrated Bergman cyclopolymerization of polymerizable surfactant monomer within the hexagonal channels of functional hybrid nanocomposite formed by evaporative self-assembly. Such a technique allows the patterned polymerization of the polymer precursor material directly onto a surface, thus avoiding solubility related problems that may be encountered when attempting to directly coat the pristine polymeric material, which is often insoluble, thereby facilitating its use in device fabrication.

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Notes and references