Synthesis and Characterization of Luminescent Conjugated Polymer−Silica Composite Spheres

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A novel poly(*p*-phenylene) derivative (**C_{12}PPPC_{11}OH**) was synthesized and used as a template for silica polymerization under ambient conditions in the absence of added catalysts. A few polymers of analogous molecular structures were also simultaneously used in control experiments to derive a molecular mechanism for the observed catalytic activity of **C_{12}PPPC_{11}OH**. Silica spheres can be dispersed in both hydrophobic and hydrophilic solvents. The optical spectra of the solution-dispersed polymer−silica composite spheres indicated the presence of polymers incorporated in the silica matrix. The UV spectra of the silica−**C_{12}PPPC_{11}OH** composite dispersed in THF solution was similar to those of the polymer in THF, indicating no significant effect of solvent on the electronic structure of **C_{12}PPPC_{11}OH** in the composite. Moreover, confocal micrographs of the blue fluorescent spheres of the composites were also taken to show the presence of polymers in the composite. It is anticipated that, by appropriate modifications of the conjugated polymers, we may able to develop homogeneous semiconducting polymer−silica particles with tunable electrical and optical properties.

Introduction

The exploration of novel electronic and optical properties of organic molecules, especially conjugated polymers, has opened many new avenues in the design and fabrication of optoelectronic devices.[1−4] Devices fabricated using conjugated polymers include field-effect transistors,[5−7] solar cells,[8] solid-state lasers,[9,10] waveguides,[11,12] light-emitting diodes (LEDs),[13,14] and chemical and biomolecular sensors.[15−21] Controlling interchain interactions, orientation, and conformation of the polymers on a larger scale would be useful for the fabrication and optimization of optical displays and optoelectronic devices with enhanced optical and electronic properties.[22−29] The incorporation of conjugated polymers into an inorganic matrix and the development of organic−inorganic hybrid materials is an efficient method to fine-tune the optical and electronic properties as well as to improve the environmental stability.[30−35] There has been a

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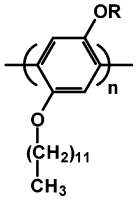
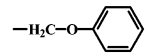
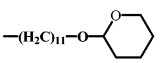
great interest in the incorporation of conjugated polymers into silica; however, its preparation is severely limited by the incompatibility of the two components. Several laboratories have used the sol−gel method to prepare such composites.[36−40] Among this, poly(1,4-phenylenevinylene)/silica composites have been successfully prepared using water/alcohol-soluble sulfonium salt precursors.[37−40] Recently, Kubo et al.[41] reported another approach by introducing polar functional groups into conjugated polymers in order to improve the compatibility between polymer and silica. Luminescent, nanostructured composite material was prepared by Clark et al. using an amphiphilic semiconducting polymer, 4-octyloxy-1-(2-trimethylammoniumethoxy)-2,5-poly(phenylene ethynylene) chloride in the presence of CTAB as a structure-directing agent in silica condensation.[42] In both cases, acid or base was used as a catalyst for the polycondensation of tetraethoxysilane (TEOS) in the presence of these polymers to give homogeneous composite with silica.

In another area of research for the preparation of organic−inorganic hybrid materials, novel methods were adopted from Nature's "bottom-up" strategy in which biomacromolecules were employed to control the size, shape, and function of inorganic materials with controlled dimensions. The adoption and manipulation of the synthesis of inorganic materials using artificial or natural templates created interesting nanostructured inorganic materials.[43−53] The elegant demonstration of silica condensation using silicatein enzyme or bifunctional small molecules as silicatein mimics for the biomimetic synthesis of silica by Morse and co-workers illustrated the potential of such pathways for the development of interesting novel materials.[54−57] The formation mechanisms seen in biogenic systems can be extended to the synthesis of conducting polymer−silica nanocomposites where the conducting polymer acts as both catalyst and template for the polymerization of silica.

Scheme 1. Chemical Structures of the PPPs Used for Silica Polymerization

	R =	Symbol
	H	C_{12}PPPOH
		C_{12}PPPOBZn
		C_{12}PPPC_{11}OTHP
		C_{12}PPPC_{11}OH

The present paper delineates the formation of polyparaphenylene (PPP)−silica nanocomposites by exploring the structure-directing and catalytic properties of functionalized PPPs.[58,59] A few polymers were designed and their molecular structures are given in Scheme 1. Even though both **C_{12}PPPOH** and **C_{12}PPPC_{11}OH** possess hydroxyl groups for silica polymerization, it is important to note the difference in their structures. The hydroxyl groups in **C_{12}PPPOH** are attached directly to the benzene ring on the polymer backbone (i.e., phenolic) whereas in **C_{12}PPPC_{11}OH** a long spacer [$-(CH_2)_{11}-$] was used to separate the hydroxyl groups from the polymer backbone. Such structural variations were expected to cause significant differences in their reactivities and aggregation behavior in solution. It is also interesting to see if the polymers with blue emission properties would be incorporated into the silica particles during silica polymerization, thus leading to composite particles with interesting emission properties. Our synthetic strategy involves a relatively simple, one-step route method which gives easy access to conjugated polymer−silica composites with light-emitting and nonlinear optical properties. In addition, such luminescent silica nanoparticles are of great importance in biology, biomedical sciences, and biotechnology as fluorescent biological labels.[60−62]

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Materials and Methods

Reagents were purchased from Aldrich, Fluka, and Merck and used without further purification, unless otherwise stated. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone under nitrogen atmosphere. Tetraethyl orthosilicate (TEOS) was purchased from Merck.

Synthesis of Polymers. The synthesis and characterization of dibromohydroquinone, 2,5-dibromo-4-dodecyloxyphenol, and polymers **C_{12}PPPOBZn** and **C_{12}PPPOH** have been reported earlier.[58] The details of the synthesis of polymers, **C_{12}PPPOC_{11}OTHP** and **C_{12}PPPOC_{11}OH**, and the monomers are summarized below.

*2,5-Dibromo-1-(ω-hydroxyundecyloxy)-4-dodecyloxybenzene (**3**).* The monoalkylated dibromohydroquinone **2** (11.25 g, 0.025 mol) was dissolved in 300 mL of absolute alcohol under nitrogen atmosphere. Potassium carbonate (8.91 g, 0.064 mol) was added to the reaction mixture and warmed to 70 °C. 11-Bromo-1-undecanol (9.73 g, 0.038 mol) dissolved in 50 mL of absolute alcohol was added dropwise to the above reaction mixture, stirred for 10 h, cooled to room temperature, filtered, and concentrated under reduced pressure. Distilled water (500 mL) was added to the residue and the mixture was acidified with concentrated HCl. It was stirred for 2 h and filtered. The crude product was precipitated from a mixture of chloroform and methanol (1:4) under 0 °C. The white precipitate obtained was filtered off and dried. Yield = 50% (7.82 g). ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.08 (s, 2H, aromatic C−H), 3.94 (t, 4H, OCH_2), 3.63 (t, 2H, CH_2OH), 1.77 (q, 4H, OCH_2CH_2), 1.26 (m, 34H, CH_2), 0.86 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 73.4 MHz, δ ppm): 150, 118.4, 111, 70.2, 63, 32.7, 31.8, 29.5, 29.3, 29.1, 25.8, 25.6, 22.5, 13.96. MS-ESI: *m*/*z*, 606 (M^+). Elemental analysis calculated (%) for $C_{29}H_{50}Br_2O_3$: C, 57.43; H, 8.31. Found: C, 57.38; H, 8.32. FT-IR (KBr, cm^{-1}): 3290, 2916, 2850, 1498, 1467, 1388, 1365, 1269, 1219, 1064, 1017, 990, 854, 790, 719.

*2-[(2,5-Dibromo-1-(ω-tetrahydropyranoxy undecyloxy)-4-dodecyloxy)]benzene (**4**).* Compound **3** (9.76 g, 0.016 mol) was dissolved in 50 mL of anhydrous tetrahydrofuran under nitrogen atmosphere. A catalytic amount of *p*-toluene sulfonic acid was added at 0 °C. Dihydropyran (2.5 mL, 0.04 mol) was added to the above reaction mixture and stirred at 0 °C for 2 h and at RT overnight. Solvent was removed and the crude product was purified using column chromatography with a solvent mixture of hexane:ethyl acetate (9:1) to get the pure product in 95% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.08 (s, 2H, ArC−H), 4.5 (s, 1H, OCHO), 3.96 (t, 4H, $ArOCH_2$), 3.71 (t, 2H, OCH_2), 3.57 (q, 2H, CH_2O), 3.37 (q, 4H, OCH_2CH), 1.77 (m, 6H, CH_2), 1.26 (m, 34H, CH_2), 0.86 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$: 73.4 MHz, δ ppm): 155.8, 120.3, 108.2, 100.7, 71.6, 64, 63.6, 33.00, 32.5, 31.2, 30.5, 30.3, 26.6, 23.1, 13.9. MS-ESI: *m*/*z*, 691 (M^+). Elemental analysis calculated (%) for $C_{34}H_{58}Br_2O_4$: C, 59.13; H, 8.46. Found: C, 59.32; H, 8.49. FT-IR (KBr, cm^{-1}): 2920, 2850, 1494, 1463, 1392, 1361, 1265, 1211, 1120, 1064, 1027, 807, 722.

*1-(Dodecyloxy)-4-(ω-tetrahydropyranoxy undecyloxy)-2,5-bis-(boronic acid)Benzene (**5**).* Two molar solution of butyllithium in hexane (70 mL, 0.141 mol) was added slowly to a solution of dibromide **4** (24.3 g, 0.035 mol) in THF (150 mL) under nitrogen atmosphere at −78 °C. The solution was warmed to RT and then cooled to −78 °C, followed by the dropwise addition of triisopropylborate (51 mL) during a 2 h period. After complete addition, the mixture was again warmed to RT, stirred overnight, and mixed with 2 L of deionized water. The crystalline precipitate obtained was collected and recrystallized from acetone in 60% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.77 (m, 4H, BOH), 7.18 (s, 2H, ArC−H), 4.51 (s, 1H, OCHO), 3.96 (t, 4H, $ArOCH_2$), 3.71 (t, 2H, OCH_2), 3.57 (q, 2H, CH_2O), 3.4 (q, 4H, OCH_2CH_2), 1.77 (m, 6H, CH_2), 1.26 (m, 34H, CH_2), 0.86 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 73.4 MHz, δ ppm): 156.8, 117.9, 97.80, 68.2, 66.5, 61.1, 31.2, 30.2, 29.1, 28.8, 28.7, 28.6, 25.6, 25.3, 24.9, 22, 19.1, 13.8. MS-ESI: *m*/*z*, 621 (M^+). Elemental analysis calculated (%) for $C_{34}H_{62}B_2O_8$: C, 65.81; H, 10.07. Found: C, 65.49; H, 10.23. FT-IR (KBr, cm^{-1}): 3479, 3358, 2920, 2851, 1495, 1465, 1415, 1389, 1288, 1195, 1047, 1132, 1047, 881, 817, 721, 640.

*Poly(1-dodecyloxy-4-(ω-tetrahydropyranoxy undecyloxy)-2,5-phenylene) (**6**).* Diboronic acid **5** (13.42 g, 0.023 mol) and dibromo compound **4** (15.75 g, 0.023 mol) were mixed in 200 mL of dry toluene under nitrogen atmosphere. A 400 mL aliquot of K_2CO_3 solution (2 M) was added to this mixture followed by tetrakis-(triphenylphosphino)palladium (1.5 mol % with respect to monomer **5**) as catalyst. The mixture was stirred at 80 °C for 72 h and precipitated twice from methanol to yield a yellowish polymer, which was filtered and dried under reduced pressure. Yield: 20 g. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.08 (b, ArC−H), 4.56 (b, OCHO), 3.85 (b, $ArOCH_2$), 3.69 (b, OCH_2), 3.46 (b, CH_2O), 3.37 (b, OCH_2CH_2), 1.66 (b, CH_2), 1.24 (b, CH_2), 0.87 (b, CH_3). ^{13}C NMR ($CDCl_3$, 73.4 MHz, δ ppm): 150, 117.1, 98.6, 69.5, 67.5, 62.1, 31.8, 30.6, 29.6, 29.4, 29.2, 26.1, 26, 25.4, 22.6, 19.5, 14. Elemental analysis calculated (%) for **C_{12}PPPC_{11}OTHP**: C, 76.97; H, 11.02. Found: C, 76.71; H, 11.14. FT-IR (KBr, cm^{-1}): 2921, 2851, 1609, 1471, 1350, 1212, 1066, 1031, 865, 789, 720.

*Poly(1-dodecylxy-4-(ω-hydroxy undecyloxy)-2,5-phenylene) (**7**).* Precursor polymer **6** (10 g) was dissolved in dry THF (100 mL). Concentrated hydrochloric acid (10 mL) was added to the solution and the reaction mixture stirred at 60 °C overnight. The polymer was precipitated by adding methanol. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.08 (b, ArCH), 3.88 (b, OCH_2), 3.6 (b, CH_2OH), 1.60 (b, CH_2), 1.22 (b, CH_2), 0.84 (b, CH_3). ^{13}C NMR ($CDCl_3$, 73.4 MHz, δ ppm): 149.9, 127.4, 117.2, 69.5, 62.8, 32.7, 31.8, 30.7, 29.6, 29.2, 26, 25.6, 22.5, 13.9. Elemental analysis calculated (%) for **C_{12}PPPC_{11}OH**: C, 78.02; H 11.29. Found: C, 78.12; H, 11.18. FT-IR (KBr, cm^{-1}): 3317, 2919, 2852, 1600, 1471, 1350, 1212, 1057, 848, 786, 720.

Synthetic routes for the polymers **C_{12}PPPOC_{11}OTHP** and **C_{12}PPPOC_{11}OH** are shown in Scheme 2. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) with reference to polystyrene standards using chloroform as eluent. **C_{12}PPPOBZn** (M_n = 5776, M_w = 12443, M_w/M_n = 2.1), **C_{12}PPPC_{11}OTHP** (M_n = 5543, M_w = 7248, M_w/M_n = 1.3).

Thermogravimetric Analysis. The PPP polymers studied in this paper are stable at room temperature. The thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under nitrogen.

Synthesis and Characterization of the Polymer−Silica Composites. Stock solution of the polymers (100 mg/mL) in dry THF was diluted to different concentrations. One milliliter of TEOS was mixed with 1 mL polymer solutions of varying concentrations (100, 50, 25, and 10 mg/mL, respectively), stirred thoroughly for 1 min at room temperature, and kept under static conditions until gelation had occurred. The mixture was centrifuged for 15 min (RT, 12000 rpm) and the supernatant liquid removed. The resulting silica composite was thoroughly washed with THF to remove any excess polymer and TEOS. The polymer−silica composite was dried under vacuum and analyzed using UV−Vis (Shimadzu SPD-10A) and FTIR (Bio-Rad FTS 165 FTIR) spectroscopy. Fluorescence emission of the polymer and the dispersed polymer−silica composites were collected on a Shimadzu RF-5301PC spectrofluorometer, with the emission spectra and excitation band-passes set at 1.5 nm. The morphology of the silica particles was checked using a JEOL 2010

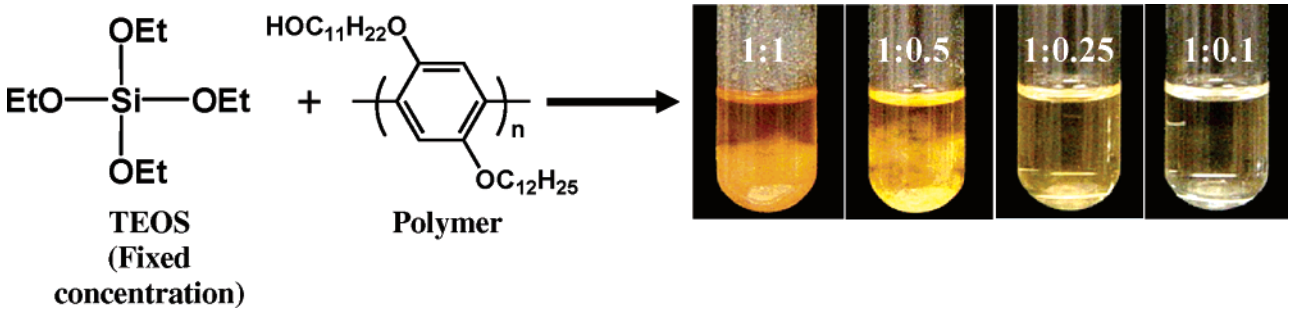
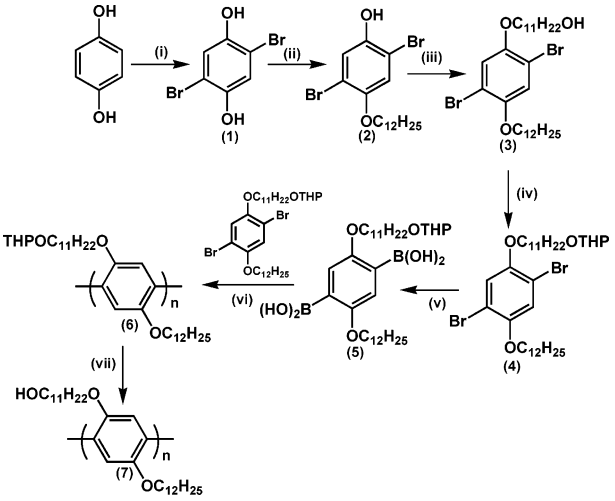


Figure 1. Photograph of the gels obtained after mixing the **C_{12}PPPC_{11}OH** solutions with TEOS. The ratios of TEOS−polymer solutions are given on the figure.

Scheme 2. Synthesis of C_{12}PPPC_{11}OH and C_{12}PPPC_{11}OTHP[a]



[a] (i) Br_2 in glacial AcOH, 85%; (ii) NaOH in absolute EtOH, $C_{12}H_{25}Br$, 60 °C for 10 h, 60%; (iii) K_2CO_3 in absolute EtOH, $BrC_{11}H_{22}OH$, 60 °C for 10 h, 80%; (iv) *p*-toluene sulfonic acid/DHP in THF, 0 °C, 90%; (v) BuLi in cyclohexane (2 M solution), THF at −78 °C, $B(OiPr)_3$, water-stirred at RT for 10 h, 75%; (vi) 2 M K_2CO_3 solution, toluene, 1−1.5 mol % $Pd(PPh_3)$, reflux for 3 days; (vii) HCl/THF at 60 °C.

TEM instrument at an accelerating voltage of 200 kV. The calcination of the composites was carried out in a programmable furnace at 600 °C for 2 h in air. For the fluorescence imaging, the polymer−silica particles were dispersed in THF and evaporated on a glass slide. The images were taken using a Carl Zeiss LSM 510 laser scanning microscope with a UV excitation wavelength of 365 ± 12 nm at 40× magnification. For AFM measurements, the polymer aggregates were prepared on a mica substrate from **C_{12}PPPC_{11}OH** polymer solution (250 μg/mL) in THF. The imaging was done in air using a Nanoacope III AFM (Digital Instruments Inc.) in the tapping mode using silicon cantilevers. A Brookhaven BI2005M goniometer system equipped with a 522 channel BI9000AT digital multiple τ correlator was used for the light-scattering experiments.

Results and Discussion

Synthesis of the Polymer−Silica Composites. Two amphiphilic PPPs were synthesized and used for the precipitation of organo-silica hybrid materials. The polymers, **C_{12}PPPOH** and **C_{12}PPPC_{11}OH**, were obtained using the Suzuki polycondenstation method reported earlier.[39,40] Stock solutions (100 mg/mL) of polymers in tetrahydrofuran (THF) were prepared and diluted to the appropriate concentrations. Tetraethoxysilane (TEOS) was used as the silica source. Polymerization of TEOS was carried out in the presence of the polymer by mixing TEOS and polymer solutions in THF at a TEOS:polymer ratio (v/v) of 1:1, 1:0.5, 1:0.25, and 1:0.1, respectively. As seen from the ratio, the concentration of the polymer was varied systematically and TEOS concentration was kept constant. The solutions were stirred for 1 min and kept under static conditions at RT. Gelation was observed in the case of the polymer, **C_{12}PPPC_{11}OH**, without the addition of an external catalyst. An interesting relationship between polymer concentration and silica polymerization was observed; i.e., an increase in polymer concentration led to a decrease in gelation time (Table 1, Supporting Information). Figure 1 presents photographs of gels obtained after mixing the **C_{12}PPPC_{11}OH** in THF with TEOS solutions for 25 min. The analogous precursor polymers, **C_{12}PPPOBZn** and **C_{12}PPPOC_{11}OTHP**, did not yield silica precipitation in the absence of a catalyst. Similarly, the monomer, 2,5-dibromo-1−11-undecyloxy-4-dodecyloxybenzene (**3**), did not precipitate silica even after several days.

In the case of the **C_{12}PPPOH** polymer, no gelation was observed in the absence of an added catalyst even after 2 days, which indicates that either the polymer does not form a well-ordered structure in solution or the phenolic −OH groups on the polymer backbone do not catalyze the polymerization of TEOS. After the addition of 2 drops of ammonia, polymerization followed by gelation was observed. All the above control experiments indicate that both the structure and functional groups of the polymer are important factors in silica polymerization.

Full characterization of the structure, optical properties, and chemical composition of the thoroughly washed silica−polymer composites were obtained using UV, FTIR, fluorescence spectroscopy, fluorescence imaging, and TEM analysis. The polymer **C_{12}PPPC_{11}OH** showed an absorption maximum at λ_{max} = 335 nm and an emission maximum of 395 nm in tetrahydrofuran. The polymer is not water-soluble. The UV spectra of the silica−**C_{12}PPPC_{11}OH** composite dispersed in THF solution are similar to those of the polymer, indicating no significant effect on the electronic structure of **C_{12}PPPC_{11}OH** incorporated into the composite. The absorption maxima of the composites showed a small blue shift ($\Delta\lambda_{max}$ = 2 nm) and an increase in intensity in absorption with an increase in polymer concentration (from 1:0.25 to 1:1) (Figure 2i (**I**)). This correlates with the thermogravimetric analysis, where the percentage weight loss for the 1:1 silica−**C_{12}PPPC_{11}OH** composite was ca. 69% and 60% for 1:0.5 silica−**C_{12}PPPC_{11}OH** composite (see Supporting

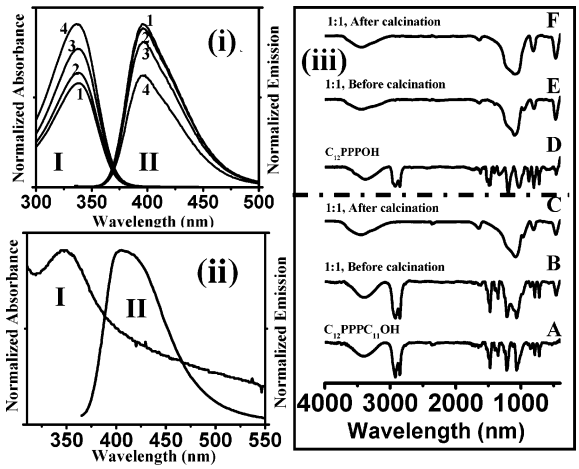


Figure 2. (i) Absorption (I) and emission spectra (II) of the polymer **C_{12}PPPC_{11}OH** (1) and polymer−silica composites (in THF) obtained from TEOS:polymer ratios of 1:0.25 (2), 1:0.5 (3), and 1:1 (4) in solution. (ii) Absorption (I) and emission (II) spectra of **C_{12}PPPC_{11}OH**-incorporated silica particles dispersed in water. Note that the pure polymer is not water-soluble. (iii) IR spectra of **C_{12}PPPC_{11}OH** (A), **C_{12}PPPOH** (D), and the polymer−silica composites before (B, E) and after (C, F) calcinations. The ratios of TEOS:polymer are given in the figure.

Information 2), which indicates that more polymer was incorporated into 1:1 silica−**C_{12}PPPC_{11}OH** composite. In THF, the particle showed an emission maximum (λ_{emiss}) at 397 nm. The fluorescence emission intensity of the silica−**C_{12}PPPC_{11}OH** composite (Figure 2i (**II**)) decreased as the concentration of the polymer increased in the composite preparation. Quenching of the fluorescence emission also indicates the incorporation of more polymer aggregates in the 1:1 polymer composite as compared to the other samples. A similar fluorescence quenching was observed in the case of higher concentrations of polymer in THF. The observed similarities between the UV−Vis and emission spectrum in THF solution and that of silica composites indicate that **C_{12}PPPC_{11}OH** was successfully incorporated while retaining its π-conjugated structure. The absorbance and fluorescence spectra in water were recorded (Figure 2 (ii)) using the particles dispersed in water. The absorption and emission maxima of the particles in water were red-shifted to 345 and 407 nm, respectively. Such solvatochromic behavior has been reported for other conducting polymers, especially in organic solvents.[58]

Infrared spectra of the polymers, **C_{12}PPPC_{11}OH** and **C_{12}PPPOH**, and polymer−silica composites before and after calcination are given in Figure 2 (iii). In the **C_{12}PPPC_{11}OH**−silica composite the observed peaks at 3403, 2848, 2913, 1608, 1460, 1053, 793, and 723 cm^{-1} correspond to **C_{12}PPPC_{11}OH** (Figure 2 (iii)-A,B) whereas the peaks around 963 and 457 cm^{-1} correspond to Si−O stretching vibrations. After calcination of the **C_{12}PPPC_{11}OH**−silica composite, the peaks due to the polymer were absent in the FTIR spectrum (Figure 2(iii)-C). The FTIR spectra of the silica particles prepared in the presence of the second polymer, **C_{12}PPPOH**, and ammonia did not show any characteristic peak due to **C_{12}PPPOH** polymer before or after calcination (Figure 2(iii)-E,F). This indicates that ammonia initiated the polymerization of TEOS and the polymer **C_{12}PPPOH** was not involved or incorporated in the process.

The morphologies of the silica−polymer composites were characterized using TEM. The silica−**C_{12}PPPC_{11}OH** composites showed a spherical morphology with sizes ranging from 500 to 900 nm (Figure 3). Fluorescence images of the particles under UV light were recorded using the confocal laser scanning microscope LSM 510. The observed blue color of the particles confirmed the incorporation of blue light-emitting **C_{12}PPPC_{11}OH** in the composites and formation of highly luminescent polymer−silica particles (Figure 3). It is interesting to note that no absorption or emission was observed with silica precipitates obtained in the presence of the polymer **C_{12}PPPOH**.

Mechanism of Silica Polymerization. Inspired by the natural silicification mechanism, environmentally benign synthesis of spherical silica particles at neutral pH has been studied in the presence of synthetic templates such as catalytic polypeptides[54−56] and bifunctional small molecules.[57] In the proposed mechanism, the nucleophilic groups (−OH, −SH) or hydrogen bond donor groups (−NH_2, imidazole, etc.) act as catalytic sites. Owing to the formation of −O---H hydrogen bonds among the −OH groups of the aggregated polymer, the nucleophilicity of the oxygen atom increases, thereby enhancing the efficiency of the SN_2-type nucleophilic attack on the alkoxy silane precursor. A similar mechanism is expected to be active in the case of the polymer **C_{12}PPPC_{11}OH**, which shows aggregation behavior in solution. The inactivity of the nonaggregating monomer, 2,5-dibromo-1,11-undecanoloxy-4-dodecyloxybenzene and the weakly aggregating precursor polymers, **C_{12}PPPOC_{11}OTHP**, **C_{12}PPPOH**, and **C_{12}PPPOBZn** with no free −OH groups, in the silica polymerization supports such a mechanism. Aggregation behavior of the polymers was studied both in

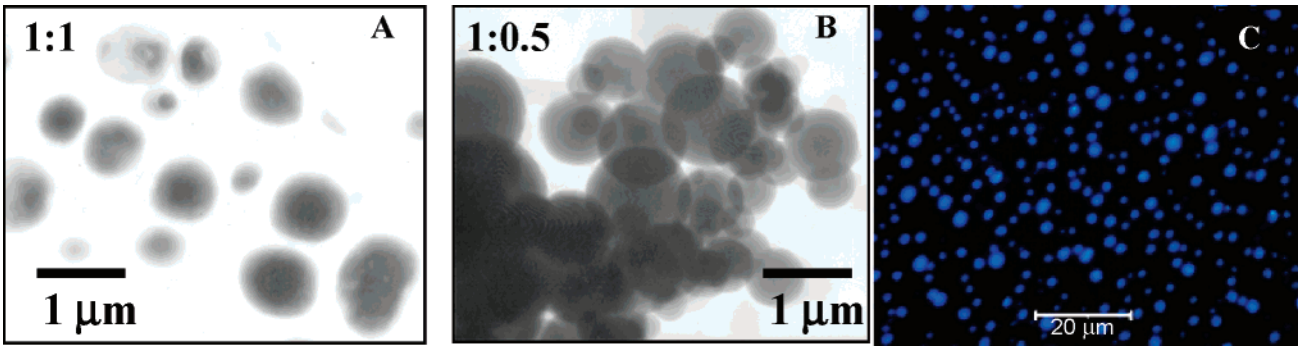


Figure 3. TEM images of the polymer−silica composites. TEOS:**C_{12}PPPC_{11}OH** concentration ratio of 1:1 (A) and 1:0.5 (B). Fluorescence image (C) of the particles shown in micrograph B.

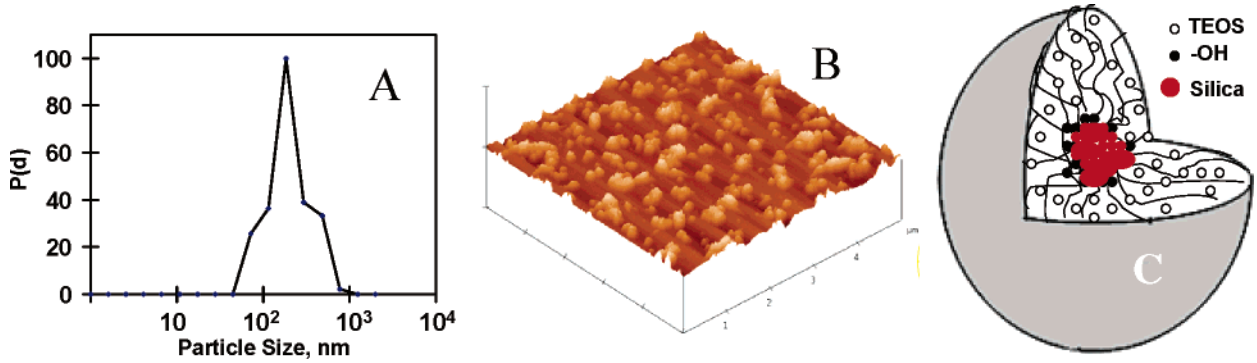


Figure 4. Dynamic light scattering data of $C_{12}PPPC_{11}OH$ in THF (10 mg/mL) (A). AFM height image of self-assembled spherical aggregates (B) from the solution (250 μg/mL) of $C_{12}PPPC_{11}OH$ on a mica substrate. Cartoon representation of the possible shape of $C_{12}PPPC_{11}OH$ polymer aggregate and polymerization of TEOS inside the aggregate (C).

solution and on a mica substrate. Dynamic light scattering studies were performed to investigate the aggregation behavior of **$C_{12}PPPC_{11}OH$**, **$C_{12}PPPOC_{11}OTHP$**, **$C_{12}PPPOH$**, and **$C_{12}PPPOBZn$** in solution. Particles with a mean hydrodynamic radius of ca. Rh = 185 nm from **$C_{12}PPPC_{11}OH$** in THF solution (10 mg/mL) were observed (Figures 4A). The polymer, **$C_{12}PPPOH$**, shows similar aggregation behavior in THF solution (ca. Rh = 145 nm). However, the precursor polymers, **$C_{12}PPPOC_{11}OTHP$** and **$C_{12}PPPOBZn$**, showed weak aggregation behavior with a mean hydrodynamic radius of ca. Rh = 35 and 45 nm, respectively (see the Supporting Information S1). Nevertheless, the unavailability of the free −OH groups and poor nucleophilicity of the phenolic groups limit the nucleation of silica polymerization in both former and latter cases. However, reaction of the side-chain OH groups in **$C_{12}PPPOC_{11}OH$** with TEOS occurs much more readily and leads to SiO_2 gelation.

The large aggregate formation of **$C_{12}PPPC_{11}OH$** in solution was further confirmed using atomic force microscopy (AFM) investigations. A few drops of the polymer solution (250 μg/mL) in THF were placed on a mica substrate and allowed to evaporate slowly at ambient conditions. The obtained structures were imaged using an AFM. The observed average aggregate size of ca. d = 250 nm indicated the ability of the polymer to form aggregates even at low polymer concentrations (Figure 4B). It is conceivable that the amphiphilic polymer, **$C_{12}PPPC_{11}OH$**, forms spherical aggregates in solution (Figure 4C). The observed difference in size of the polymerized polymer−silica composite particles and the pure polymer particle implies that there is a considerable volume change during silica polymerization. Moreover, the dispersability of the polymerized particles in water also indicates that the silica particle surfaces are exposed to the outside or water can diffuse into the composite particle.

Conclusion

In conclusion, we incorporated blue light-emitting conjugated polymers into silica particles through an ambient solution-synthesis route. The silica particles were obtained without an additional catalyst, only in the presence of **$C_{12}PPPC_{11}OH$**, which implies that the polymer plays a key role as both template and catalyst in this silicification process. Structurally similar control polymers such as **$C_{12}PPPOH$** and **$C_{12}PPPC_{11}OTHP$** and monomers did not induce silica polymerization. Full characterization of the polymer−silica composite is given and a mechanism proposed. Control experiments were done to establish the activity and mechanism of the observed catalytic activity. The luminescent spherical silica particles are dispersable in water and organic solvents. On comparison of the UV−Vis and emission studies of the polymers in THF and polymer-incorporated composite dispersed in THF, no significant shift in the absorption and emission maxima was observed. The obtained composite material is homogeneous and there is no influence on the structure, i.e., conjugation length of the polymer. Further studies of luminescent conjugated polymer−silica particles such as photostability, size tuning, optoelectronic properties, and functionalization and tagging of biomolecules for use as fluorescent biological labels are underway and will be published at a later stage.

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Supporting Information Available: One table and two figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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