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Fluorescence Properties of π-Conjugated Polymers in Porous Silica

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ABSTRACT: The fluorescence properties of poly(2,6-(4-phenylquinoline)) (PPQ) and poly(ethylene glycol)-*b*-poly(*p*-phenylene ethynylene)-*b*-poly(ethylene glycol) (triblock) within porous glass were investigated. Emission was shifted to different wavelengths by varying the pore size. The emission shift is attributed to the unique aggregation state at each pore size. At small pore sizes (~8 nm), the polymers emit lights as the monomer-like states (490 nm for PPQ and 420 nm for triblock when excited at 365 nm). The emission shifts to the red region as the pore size increases until it reaches 30 nm at which PPQ emits light at 545 nm and triblock at 500 nm. As the pore size continues to increase, there is sufficient space for the relatively smaller PPQ to orient in different directions, reducing the interchain interaction and causing the emission to be blue-shifted to ~500 nm. The bulky triblock, however, prevents the polymer from orienting randomly, obliging the chains to align in a relatively planar geometry and retaining a strong interchain interaction.

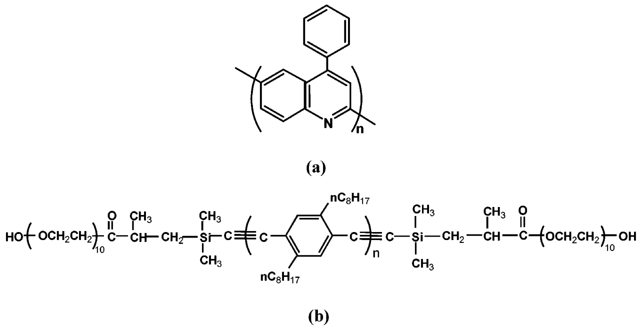
Introduction

π-Conjugated rigid polymers have been extensively investigated as photoconductive, photoluminescent, and nonlinear polymeric materials.[1−8] It is a well-known fact that there are strong interchain interactions between conjugated polymer chains to form nonemissive aggregates, resulting in a reduction of quantum efficiency.[1] Thus, it is common to avoid using high-concentration conjugated polymers or to employ chemical or physical approaches to maintain a distance between the conjugated polymer chains.[9−14] For the past decade, the method of constructing organic−inorganic nanocomposites has drawn a lot of attention, especially for the preparation of molecular photonic and electronic devices. Cavities in porous silica or anodized aluminum oxide with an average channel size of less than 50 nm were utilized to impregnate the dye molecules.[12,13] The molecular assemblies of rhodamine dyes similar to those of the mostly monomer-like states in nanopores were successfully achieved with high quantum efficiency. This is an appealing approach since it is possible to retain the spectacular fluorescent properties of dye materials, while the inorganic matrices provide superior optical properties and thermal/chemical stability.

Previously we have reported a series of studies on integrating conjugated polymers into sol−gel silica.[8] Through a sol−gel process, we demonstrated a full color display with its spectrum covering the entire visible range by incorporating different amounts of polyquinoline into the silica. In this report, we will demonstrate the ability of color tunability by using controlled pore-size porous glass.

Experimental Section

The conjugated polymers used in this report are poly(2,6-(4-phenylquinoline)) (PPQ) and poly(ethylene glycol)-*b*-poly(*p*-phenylene ethynylene)-*b*-poly(ethylene glycol) (triblock), as shown in Figure 1. The polymers were synthesized as reported previously.[15−17] The number-average degree of polymerization is estimated to be 10 and 40, respectively. PPQ is soluble in acidic solvents such as formic and dichloroacetic acids. Triblock dissolves in common organic solvents like THF and dioxane. The solutions are prepared from a stock solution of 10 g/L for each chemical. The stocks solutions were held under constant stirring at room temperature. The controlled pore glass (CPG) powders were purchased from CPG, Inc., Lincoln Park, NJ. The pore sizes used are in the range 8−97 nm.



(a)

(b)

Figure 1. Chemical structures of (a) poly(2,6-(4-phenylquinoline)), PPQ, and (b) poly(ethylene glycol)-*b*-poly(*p*-phenylene ethynylene)-*b*-poly(ethylene glycol), triblock.

The polymers are driven into the pores by capillary effects. Vacuum was employed to facilitate the process. Generally, the CPG powders were placed in a vacuum-connected glass tube filled with a polymer solution. The solution containing CPG was vacuumed and then was allowed to stand over 1 day at room temperature. The treated CPG were then washed with a large excess of solvent to remove the polymer attached to the powder surface. The washed CPG were dried in an oven at 140 °C for 2 days before fluorescence measurements. The fluorescence measurements were taken with a Perkin-Elmer LS-50B luminescence spectrophotometer with the powder samples sandwiched between two quartz plates. The measurements were performed in the 30°/60° geometry.

The fluorescence lifetime τ was measured on a sandwich of polymer−CPG between quartz plates at room temperature. The measurements were taken with a time-resolved fluorometer FL900 CDT (Edinburgh Analytical Instrument, UK) using the time-correlated single photon counting (TCSPC) method.[18,19] Least-squares analysis of the observed time-resolved decay,

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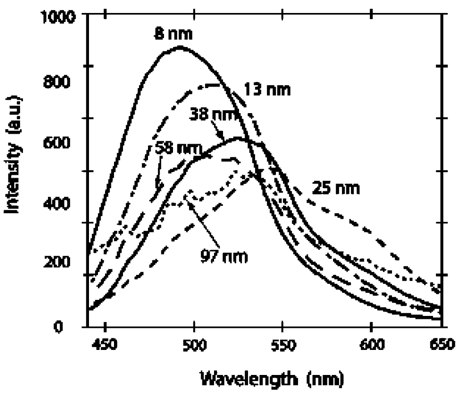

Figure 2. Emission spectra of different sizes of controlled-pore-size glass treated with 1 g/L PPQ/formic acid solution. The pore size is indicated adjacent to each spectrum.

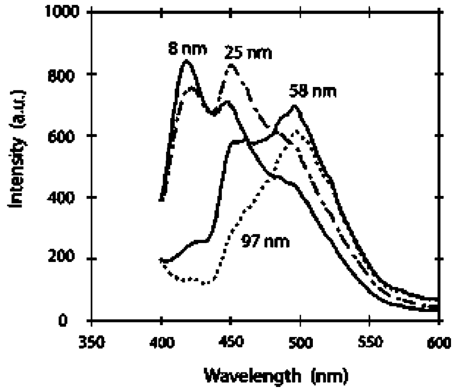

Figure 3. Emission spectra of different sizes of controlled-pore-size glass treated with 1 g/L triblock/THF solution. The pore size is indicated adjacent to each spectrum.

$R(t)$, was used for estimation of the impulse response function, $F(t)$. The goodness-of-fit parameter, χ^2, was calculated from eq 1.

$$\chi^2 = \sum_i \frac{[R(t) - R_c(t)]^2}{R(t)} = \sum_i \left[\frac{R(t) - R_c(t)}{\sigma(t)}\right]^2 = \sum_i u^2(t) \quad (1)$$

where $R_c(t)$ is the calculated decay of fluorescence, $\sigma(t)$ the standard deviation of each data point, and $u(t)$ the weighted residuals. From Poisson statistics, the standard deviation is known to be the square root of the number of photon counts, $\sigma(t) = [R(t)]^{1/2}$. The value of χ^2 to be less than 1.7 is typically a good fit.

Results and Discussion

Figure 2 shows the emission spectra of different pore sizes of CPG treated with 1 g/L PPQ/formic acid solution. The emission peak of 1 g/L PPQ/formic acid solution is at 450 nm. Variable pore sizes of CPG were treated with the PPQ acidic solution. The position of the emission peak shifts from 490 to 545 nm as the pore size increases from 8 to 25 nm, and the color shown under UV radiation at 365 nm is blue, green to yellow. The emission starts to shift back as the pore size continues to increase. When the pore size is larger than 50 nm, the spectrum shows a broad, multiple peak emission between 490 and 525 nm. One thing noteworthy is that the treated CPG with the size of 97 nm shows a whitish color under UV radiation at 365 nm.

Figure 3 shows the emission spectra using different pore sizes of CPG treated with 1 g/L triblock/THF solution. The emission of the triblock/THF solution is around 420 nm. With the pore size of 8 nm, the polymer emits light at two peaks: a large one at 420 nm and a small one at 450 nm. As the pore size increases, the peak at 450 nm becomes larger. With 58 nm pores, the emission are red-shifted to 465 and 500 nm, and the latter becomes dominant as the pore size increases to 97 nm. The color of CPG under UV radiation at 365 nm changes from blue to yellow-green as the pore size increases.

Various concentrations of the polymer solutions within the range 0.1−1 g/L were used to carry out the measurements. All of them show consistently that the emission is red-shifted as the pore size increases.

π-Conjugated aromatic rigid polymers such as PPQ and triblock often exhibit sharp, well-resolved vibronic emission spectra when dilute solutions ($\sim 10^{-6}$ M) are excited by UV radiation.[6,7] The time-resolved fluorescence dynamics of the dilute solutions also show a single-exponential decay.[1] These observations indicate that polymers exist as a nearly isolated single polymer chain. When the concentration increases, however, the emission is shifted to longer wavelengths and shows a broad and structureless spectrum. These phenomena were accounted for assuming polymer chain aggregation/excimer formation.[1,6,7] The proposed mechanism is described in the following equations:

$$\mathrm{R} \xrightarrow{h\nu} \mathrm{R}^*$$

$$\mathrm{R}^* + \mathrm{R} \rightarrow (\mathrm{RR})^*$$

$$(\mathrm{RR})^* + n\mathrm{R} \rightarrow \mathrm{R}_{n+2}^* \quad (n = 1, 2, 3, ...)$$

$$\mathrm{R}_{n+2}^* \xrightarrow{\text{decay}} \mathrm{R}_{n+2}$$

where R is a polymer chain, R* an excited polymer chain, (RR)* an excimer, and R_{n+2}^* a multiple excimer.

The formation of excimers and multiple excimers results in the shift of emission peaks progressively to longer wavelengths. It is reasonable to expect the extent of the red shift to depend largely on the degree of aggregation. In the previous sol−gel study, the color tunability is controlled by varying the concentration of the embedded PPQ in silica.[8]

At high concentrations, the polymer-embedded glass emits red light, indicating that the conjugated polymer forms aggregates consisting of many chains in the channels within the silica network. At low concentrations, the glass emits blue light, suggesting that the polymer chains are isolated and trapped individually in the silica channels. For intermediate concentrations, the glasses show emission of green, yellow, and orange colors, resulting from different extensive chain interactions.

In the CPG system, the spatial confinement allows the polymer to slide into the porous channels by capillary forces. When the pore is small, small numbers of polymer chains are able to enter the pores, resulting in a relatively more isolated state of polymer chains with the corresponding emission peak at short wavelength (490 nm for PPQ and 420 nm for triblock). When the pore is reasonably large, multiple chains are able to get into the pore; however, the pore is only large enough to allow the chains to align in the relatively planar geometry. This leads to a higher degree of aggregation with more interplanar interactions and emission at longer wavelengths (545 nm for PPQ and 500 nm for

Table 1. Fluorescence Lifetimes in Double-Exponential Fits for PPQ and Triblock Polymers in Porous Silica with Different Pore Sizes

pore size (nm)	emission peak (nm)	fluorecense lifetime (ns) double-exponential fit τ_1	τ_2	χ^2
PPQ (Excited at 370 nm)				
8	500	0.97 [86%]	3.35 [14%]	0.936
15	510	1.04 [84%]	4.06 [16%]	1.879
34	510	1.17 [80%]	4.46 [20%]	1.238
58	490	0.96 [80%]	2.83 [20%]	1.620
Triblock (Excited at 360 nm)				
8	410	0.18 [57%]	0.69 [43%]	1.017
15	410	0.20 [47%]	0.78 [53%]	1.229
34	480	0.36 [64%]	1.39 [36%]	1.509
58	490	0.90 [87%]	4.09 [13%]	1.721

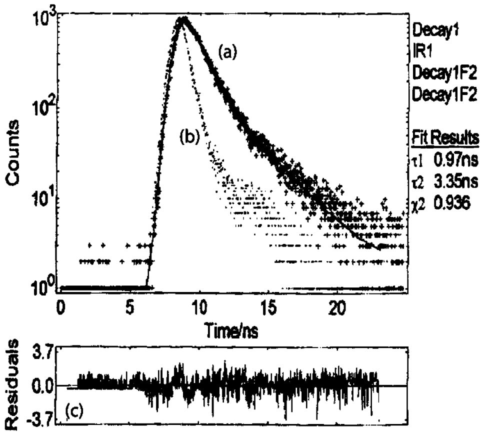

Figure 4. Fluorescence decay at 500 nm (excited at 370 nm) of PPQ in porous glass with a pore size of 8 nm: (a) the calculated fluorescence decay, $R_c(t)$, from experimental data; (b) the measured lamp pulse; and (c) the standard deviation.

triblock). In the case of PPQ, when the pore size continues increasing, the larger pores are sufficiently spacious to allow the conjugated structure to orient in different directions, reducing the interstructure interactions and resulting in the shift back to shorter wavelengths of the emission peak. However, the triblock polymer is much bulkier than PPQ. Thus, even in the largest pore size of 97 nm, there is limited space for triblock chains to flip or move, resulting in the retention of strong $\pi-\pi$ interchain interactions and the emission at 500 nm.

The fluorescence lifetime of the fluorophores is known to be longer for an excimer than a single fluorophore.[19] To test the formation of multiple excimers in a glass pore, fluorescence decay dynamics of the polymer−CPG systems were investigated. The excitation and emission wavelengths and the measured fluorescence lifetimes are summarized in Table 1. Typical decay curves are shown in Figures 4 and 5. As shown in the figures, the decay curves are nonexponentials even in the smallest pore (8 nm) for both polymers. The decay curves are best described by a biexponential with lifetimes of 0.97 and 3.35 ns for PPQ and 0.18 and 0.69 ns for triblock in 8 nm pores. The multiexponential decay dynamics of these samples may be a result of complex kinetics that includes various species of R*, RR*, and R_{n+2}*. For PPQ, the lifetimes are slightly increased until the pore size reaches 38 nm and then decreased as the pore size increases to 58 nm. This observation is consistent with the fluorescence emission in the preceding paragraphs.

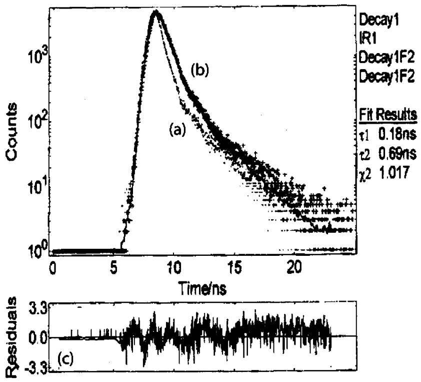

Figure 5. Fluorescence decay at 410 nm (excited at 370 nm) of triblock in porous glass with a pore size of 8 nm: (a) the measured lamp pulse; (b) the calculated fluorescence decay, $R_c(t)$, from experimental data; and (c) the standard deviation.

For the bulkier polymer, triblock, however, the lifetime progressively increases with the pore size. The data indicate that the polymer exists as different types of excimer complexes in glass pores. In small pores, few excimers are formed. With increasing pore size, polymers form multiple excimers, resulting in the emission to be shifted to longer wavelengths. The emission depends on the nature of the excimer structures in different pore sizes.

In conclusion, we demonstrate the ability of controlling the emission of π-conjugated polymers by treating controlled pore size glass with pore sizes in the range from 8 to 97 nm with two rigid polymers, poly(2,6-(4-phenylquinoline)) and poly(ethylene glycol)-*b*-poly(*p*-phenylene ethynylene)-*b*-poly(ethylene glycol). Consistent results were obtained where emission spectra covering more than half of the visible range were established by varying the pore size. The different emission from each pore size is ascribed to the unique degree of aggregation of polymer within the pore. Generally, the emission is red-shifted with an increase in the pore size. In large pores, there is sufficient space for PPQ to orient in different directions, resulting in a blue shift of the emission. The bulkiness of the triblock polymer impedes the chains from arranging randomly within large glass channels, forcing the interchain interactions and the red shift of the emission.

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