

Simultaneous blue, green, and red emission from diblock copolymer micellar films: a new approach to white-light emission†

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White-light emission is achieved from a single layer of diblock copolymer micelles containing green- and red-light-emitting dyes in the separate micellar cores and blue-light-emitting polymer around their periphery, in which fluorescence resonance energy transfer between fluorophores is inhibited due to micelle isolation, resulting in simultaneous emission of these three species.

White-light emitting organic molecules and polymers have attracted great attention due to their promising applications in full color and flexible displays, backlights, and lighting sources. To realize white light, the emission spectrum must be wide enough to span the entire visible region, containing the three primary colors blue, green, and red or at least two complementary colors. It has been achieved with a multilayer structure by consecutive evaporation, where each layer emits a primary color.^{1,2} Unfortunately, this approach is somewhat costly in the fabrication process. An alternative is to use a single-layer polymer blend system, which offers a promising low-cost technique for large-area display applications.^{3,4} However, undesired Förster-type energy transfer between fluorophores is involved in such systems. One particularly promising approach that overcomes the above problems is to develop a single-component white-light-emitting polymer.^{5,6} A drawback with this method is that the synthetic process is quite complicated and time consuming. It is therefore desirable to suggest simpler, cost-effective strategies to obtain white-light emission.

In recent years, numerous efforts have been devoted to fabricate various functional nanostructures by means of block copolymer templates.^{7,8} Diblock copolymers consisting of two different polymers can self-assemble into periodic nanostructures, with typical dimensions of 10–100 nm.⁹ In a solvent selective for one block of the diblock copolymers, micelles consisting of a soluble corona and an insoluble core are formed. In the core of copolymer micelles, for example, it has been possible to synthesize ordered arrays of metallic, inorganic, and semiconductor nanoparticles in a controlled manner.^{10,11} Recently, fluorescent dyes have also been encapsulated in diblock copolymer micelles.^{12,13} Depending

whether the two dyes were loaded in the same micellar core or in separate micellar cores, this enabled or restricted fluorescence resonance energy transfer (FRET) between the dyes, and single or simultaneous light emission have been realized. In our previous work, we demonstrated simultaneous light emission from a single layer of diblock copolymer micelles incorporated with a fluorescent dye (Rhodamine B) and a conjugated polymer (polyfluorene).¹⁴ The fluorescent dyes remained in the cores of micelles and the conjugated polymer was arranged around their periphery. The sufficient gap between the cores could isolate the dyes from the conjugated polymers, thereby effectively inhibiting energy transfer between them and enabling their simultaneous emission.

In this communication, we develop the method of micelle-isolated fluorescent species to realize pure white-light emission from a single-layer system, which consists of blue-, green-, and red-light-emitting species and diblock copolymer micelles as templates. Green- and red-light-emitting dyes are encapsulated in the separate cores of the micelles, whereas a blue-light-emitting polymer is arranged around their periphery. The diblock copolymer micelles isolate the light-emitting species from each other, which inhibits their FRET and enables simultaneous blue-, green-, and red-light emission. By simply adjusting the amounts of fluorescent species, the relative intensities of these three emissions can be varied and further combined to form pure white light. It is believed that this is the first strategy to use micelle-isolated fluorescent species in a single layer to obtain white-light emission, which has potential applications in white-light nanodevices. The overall scheme adopted in this study is schematically depicted in Fig. 1.

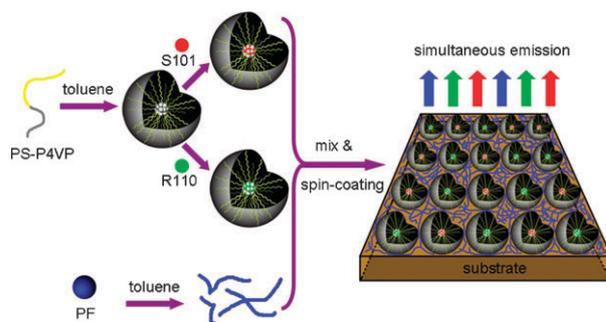


Fig. 1 Schematic illustration to achieve white-light emission from a single layer of diblock copolymer micelles containing **R110** and **S101** in the separate **P4VP** cores and **PF** around the periphery of the micelles. The diblock copolymer micelles isolate the light-emitting species from each other, which inhibits their FRET and enables simultaneous blue-, green-, and red-light emission.

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In a typical experiment, poly(styrene-*block*-4-vinyl pyridine) (**PS-*b*-P4VP**, $M_{n,PS} = 47\,600\text{ g mol}^{-1}$, $M_{n,P4VP} = 20\,900\text{ g mol}^{-1}$) was dissolved in toluene with a concentration of 2 wt%. Because toluene is a selective solvent for the **PS** block, spherical micelles that consist of a soluble **PS** corona and an insoluble **P4VP** core are formed. Polyfluorene (**PF**) was selected as the blue-light-emitting polymer due to its pure blue emission and high photoluminescence (PL) quantum yield,¹⁵ with Rhodamine 110 chloride (**R110**) and sulforhodamine 101 (**S101**) as the green- and red-light-emitting fluorescent dyes, respectively. The chemical structures of the used conjugated polymer and fluorescent dyes are shown in Fig. S1.† There are appropriate spectral overlaps between their emission and absorption (Fig. S2.†), implying that FRET can occur between them. To prepare fluorescent dye-loaded micellar solutions, each fluorescent dye was added to a separate **PS-*b*-P4VP** micellar solution with prolonged stirring (~3 days) to ensure complete loading of the dye molecules into the **P4VP** cores (see ESI for detailed experimental†). Since **R110** and **S101** were not soluble and remained as powders in toluene without micelles, formation of homogeneous solutions of fluorescent dyes with the micelles indicated effective encapsulation of the dye molecules into the **P4VP** cores. The molar ratios of **R110** and **S101** to **4VP** units were 0.008 and 0.010, respectively, where a reasonably distinct fluorescence was observed. For simultaneous emission, **PF** toluene solution, **R110**-loaded micellar solution (**PS-*b*-P4VP/R110**), and **S101**-loaded micellar solution (**PS-*b*-P4VP/S101**) were mixed and the blended solution was spin-coated or solvent-cast onto quartz or silicon substrates. For comparison, thin films of neat **PS-*b*-P4VP**, **PS-*b*-P4VP/R110**, and **PS-*b*-P4VP/S101** were also prepared. The micellar films were examined by atomic force microscopy (AFM). It can be seen that the as-cast neat **PS-*b*-P4VP** thin films exhibited micellar morphology with an average core size of $25.8 \pm 2.8\text{ nm}$, an interval of $19.2 \pm 3.1\text{ nm}$, and a height of $2.4 \pm 0.4\text{ nm}$ (Fig. S3a.†). After incorporation of **R110** or **S101** into **P4VP** cores and mixing with **PF** solution, micellar structures of all films were still observed (Fig. S3.† and Fig. 2). A core with the size, interval, and a height of 29.3 ± 2.3 , 17.6 ± 2.6 , and $3.7 \pm 0.6\text{ nm}$, respectively was ascertained from Fig. 2, indicating the slightly increased size of the cores after incorporation of the dyes. Since no macrophase separation was observed between **PF** and **PS-*b*-P4VP/R110** or **S101** micelles, **PF** could be physically arrested between the micellar cores.

Fig. 3a shows PL spectra of three individual emissive species (**PF**, **PS-*b*-P4VP/R110**, and **PS-*b*-P4VP/S101**) in solution.

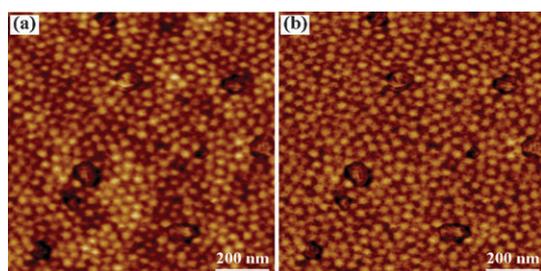


Fig. 2 (a) AFM height image and (b) the corresponding phase image of a **PS-*b*-P4VP/PF/R110/S101** hybrid film.

PF exhibited an emission maximum at 417 nm with a resolved vibronic shoulder at 440 nm, which were assigned to the 0–0 and 0–1 intrachain singlet transitions, respectively.¹⁶ The PL intensity maxima of **PS-*b*-P4VP/R110** and **PS-*b*-P4VP/S101** were located at 553 and 600 nm, respectively. The emission spectra of the dyes in **PS-*b*-P4VP** micelles were almost identical to those of the dyes in ethanol (Fig. S2.†), indicating that the dyes were effectively loaded into the micelles and their optical characteristics were retained in the micelles. After mixing the three emissive species together, the blended solution exhibited simultaneous blue-, green-, and red-light emission due to the large distances between each molecule, which resulted in a weak intermolecular interaction in this dispersed system. Most importantly, after spin-coating or solvent-casting the blended solution, the formed blended film (**PS-*b*-P4VP/PF/R110/S101**) also exhibited simultaneous blue-, green-, and red-light emission. In this case, the three simultaneous emissions were obviously due to the sufficient isolation of light-emitting species in the presence of micelles, which inhibited their FRET between each other. The Förster radii of **PF-R110**, **R110-S101**, and **PF-S101** were estimated to be 3.4, 4.0, and 2.8 nm, respectively,¹⁷ which were much shorter than the **PS** gap (19.2 nm), proving that FRET between light-emitting species was effectively suppressed. In order to keep the blue–green–red emission balance to obtain pure white light, the relative intensities of these three emissions have been tuned by simply adjusting the relative amounts of the corresponding species. When the **PF** toluene solution, **R110**-loaded micellar solution, and **S101**-loaded micellar solution were mixed with the optimized weight ratio of 3:8:4, pure white-light emission from both solution (Fig. 3b) and solid state (Fig. 3c) were obtained.

As shown in Fig. 3b, the PL spectrum of the white-light-emitting solution was wide, covering the whole visible range

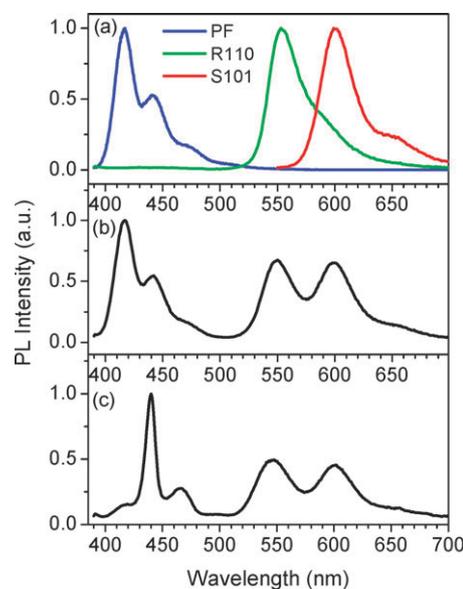


Fig. 3 (a) The normalized PL spectra of **PF** toluene solution (blue line), **PS-*b*-P4VP/R110** micellar solution (green line), and **PS-*b*-P4VP/S101** micellar solution (red line). (b) PL spectra of white-light-emitting solution and (c) white-light-emitting solid film of **PS-*b*-P4VP/PF/R110/S101**. The excitation wavelength was 380 nm.

from 400 to 700 nm with four resolved peaks located at around 417, 440, 550, and 600 nm. The peaks at 417 and 440 nm were attributed to the emission of **PF**, the peaks at 550 and 600 nm originated from **R110** and **S101**, respectively. Compared with the white-light-emitting solution, the corresponding white-light-emitting solid film showed a similar PL spectrum except that the peaks of **PF** were somewhat different from those of the solution (Fig. 3c). In the blue region, the peak positions remained the same while the shape of the **PF** peaks changed. This phenomenon is attributed to self-absorption of the emitting material.¹⁸ Due to the overlap of the 0–0 transition emission band and the absorption band, self-absorption occurred, resulting in the decreased relative intensity of the 0–0 transition band at 417 nm and the increased relative intensity of the 0–1 and 0–2 transition emission bands at 440 and 466 nm, respectively. For comparison, the PL spectrum of the individual **PF** film was also investigated and a similar phenomenon of self-absorption was observed (Fig. S4†). The white-light emission was further confirmed by the Commission Internationale de l'Éclairage (CIE) (1931) chromaticity coordinates, which were calculated from the emission spectra of Fig. 3b and c and are plotted on the diagram in Fig. 4. The

CIE coordinates of the white-light-emitting solution and solid film were (0.367, 0.326) and (0.342, 0.320), respectively, which are very close to the coordinates of standard white light (0.333, 0.333). The photographs of blue-, green-, red-, and white-light-emitting species in both solution and solid film under UV excitation are shown in Fig. 4.

In summary, we have reported an unprecedented strategy to realize pure white-light emission from a single layer of diblock copolymer micelles which contained green- and red-light-emitting dyes in the separate cores of the micelles and a blue-light-emitting polymer around their periphery. The micellar nanostructure not only inhibited the FRET between the fluorescent species effectively and enabled simultaneous blue, green, and red emission, but also made it convenient and accurate to control the relative intensities of these three emissions by simply adjusting their relative amounts. The optimized amounts of the three emitting species resulted in pure white light from a single layer system with CIE coordinates of (0.342, 0.320). It is believed that this simple strategy is the first report to use block copolymer micelles to isolate fluorophores, suppress FRET, and achieve white light, which expands the application of block copolymers and suggests a new strategy to obtain white light.

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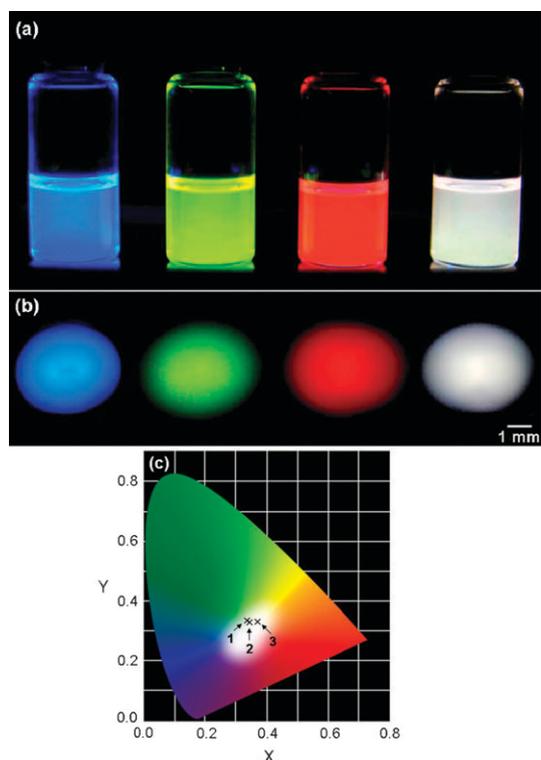


Fig. 4 (a) Photograph of **PF** toluene solution, **PS-*b*-P4VP/R110** micellar solution, **PS-*b*-P4VP/S101** micellar solution, and the blended **PS-*b*-P4VP/PF/R110/S101** solution under UV excitation. (b) Photograph of thin films of the corresponding four solutions under UV excitation. (c) CIE chromaticity diagram showing the ordinates of standard white light (point 1), white-light-emitting film of **PS-*b*-P4VP/PF/R110/S101** (point 2), and white-light-emitting solution of **PS-*b*-P4VP/PF/R110/S101** (point 3).