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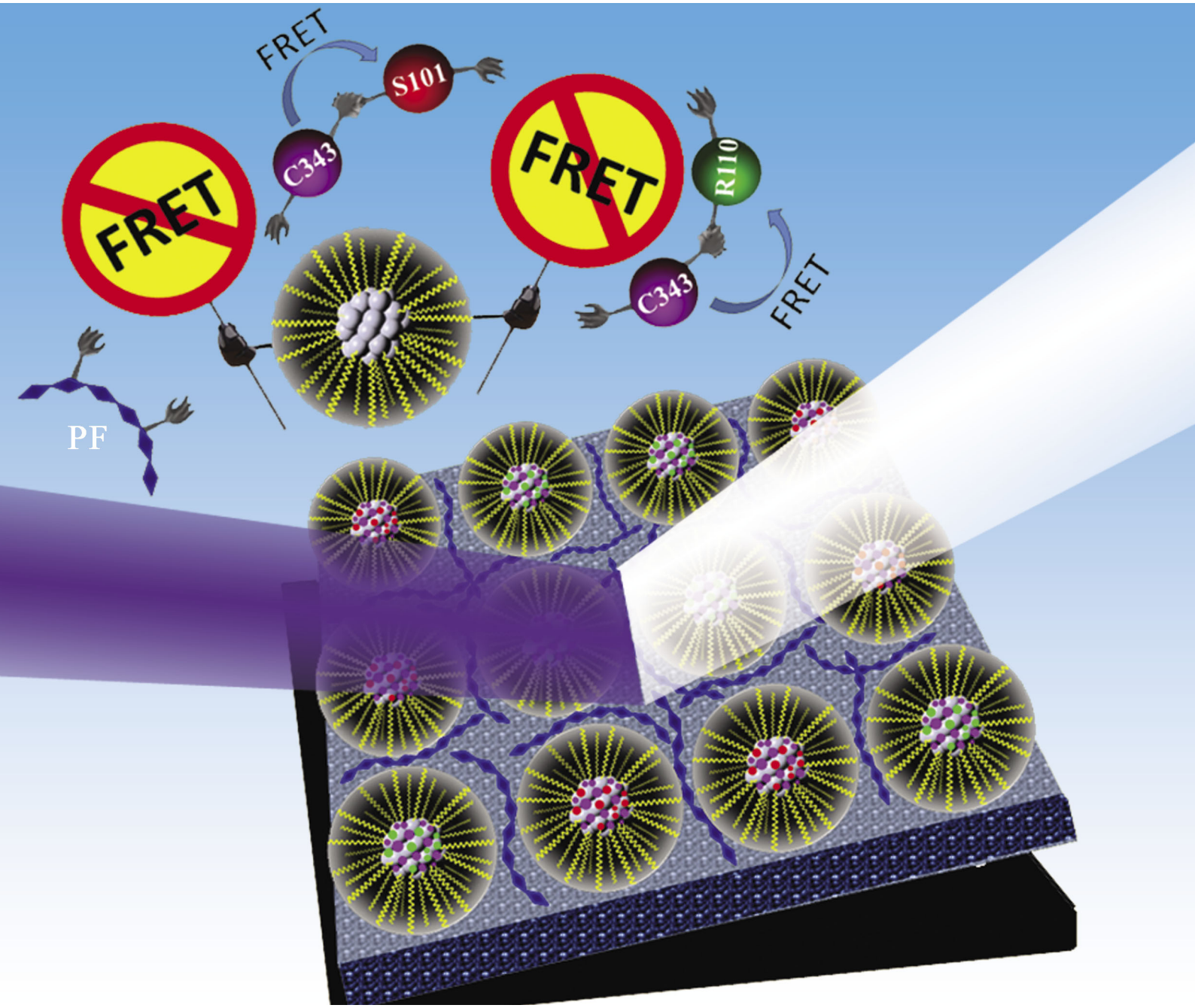

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COMMUNICATION

Enhanced white-light emission from multiple fluorophores encapsulated in a single layer of diblock copolymer micelles†

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Enhanced white-light emission was achieved by loading green- and red-light-emitting donor–acceptor pairs in the separate micellar cores and blue-light-emitting polymers around their periphery. Fluorescence resonance energy transfer was enabled between a donor and an acceptor in cores, but was suppressed among these three light-emitting species by micellar coronas, which resulted in their enhanced simultaneous emissions.

In recent years, various functional nanostructures have been fabricated by means of block copolymer (BCP) templates,[1–6] which leads to the emergence of BCPs as a promising class of materials for understanding and controlling processes associated with luminescent material and light emitting devices.[7] Recently, researches on the site-isolation of multiple fluorophores by utilizing copolymer micelles as the template have been attracting increasing attention.[8,9] For example, copolymer micelles can inhibit the fluorescence resonance energy transfer (FRET) between conjugated polymer and fluorescent dyes, which enable their simultaneous emission.[8] Copolymer micelles can also be utilized to meet the paradoxical requirement of enabling FRET from donors to acceptors and inhibiting FRET between light-emitting acceptors by loading donor–acceptor pairs in separate micellar cores.[9] As structure directors, block copolymers have great potential in optoelectronic applications.

White-light emission from organic molecules and polymers has received great attention because they offer low-cost and large-area alternatives as backlights for full-color flat-panel displays and have good potential for lighting applications.[10,11] In our recent work, we developed a novel strategy to obtain pure white-light emission by site-isolation of fluorophores in a diblock copolymer template.[12] White-light emission was achieved from a single layer of diblock copolymer micelles containing green- and red-light-emitting dyes in the separate micellar cores and a blue-light-emitting polymer around their periphery, in which the FRET between fluorophores was inhibited due to the micelle isolation, resulting in simultaneous emission of these three species.

However, it is found that the intensity of the white-light emission cannot be largely increased since the amount of fluorescent dyes encapsulated in the micellar core is limited. In the work we report here, we develop a new method to realize enhanced white-light emission through utilizing controlled FRET and micellar nanostructures to increase RGB intensities and enable their simultaneous emission. By introducing a light-collecting molecule into the cores of micelles containing green- or red-light-emitting dyes, green- or red-light-emitting donor–acceptor pairs were established in separate micellar cores and effective FRET inside a single donor–acceptor pair was permitted, leading to great enhancement of green or red light, while the intensity of blue light could be easily enhanced by increasing the content of the blue-light-emitting polymer located around the micellar periphery. Micellar coronas inhibited FRET among these three light-emitting species and enabled their simultaneous emissions, which were combined to form enhanced white light. For comparison, unenhanced white light without the introduction of the light-collecting molecule was also prepared as in our previous work.[12] The overall scheme adopted in this study is depicted in Fig. 1.

In a typical experiment, poly(styrene-*block*-4-vinyl pyridine) (**PS-*b*-P4VP**, $M_{n,PS}$ = 47 600 g mol^{-1}, $M_{n,P4VP}$ = 20 900 g mol^{-1}) was dissolved in toluene with a concentration of 2 wt%. Since toluene is a selective solvent for the **PS** block, spherical

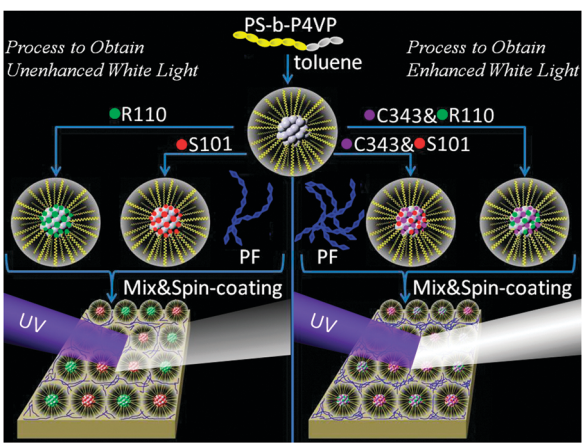

Fig. 1 Schematic illustration to achieve unenhanced (left) and enhanced (right) white light from a single layer of diblock copolymer micelles.

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micelles that consist of a soluble **PS** corona and an insoluble **P4VP** core are formed. Polyfluorene (**PF**), rhodamine 110 chloride (**R110**) and sulforhodamine 101 (**S101**) were selected as blue-, green- and red-light-emitting species, respectively. Coumarin 343 (**C343**) was utilized as the light-collecting donor which could be encapsulated in the micellar cores together with the light-emitting acceptor **R110** or **S101**, because the emission spectrum of **C343** overlaps well with the absorption spectra of **R110** and **S101** (Fig. S1, ESI†). The chemical structures of the used conjugated polymer and fluorescent dyes are shown in Fig. S2 (ESI†).

To obtain enhanced green-light emission, **R110** and **C343** were added to the **PS-*b*-P4VP** micellar solution together followed by prolonged stirring (~3 days) to form **C343–R110**-loaded micellar solution. Enhanced red-light emission was obtained in the same way by incorporating **C343** and **S101** into the same **P4VP** core. The molar ratios of **C343**, **R110** and **S101** to **P4VP** units were controlled at 0.020, 0.008 and 0.010, respectively. For simultaneous emission, **PF** toluene solution, **C343–R110**-loaded micellar solution, and **C343–S101**-loaded micellar solution were mixed and the blended solution was spin-coated onto quartz or silicon substrates. For comparison, **PF** toluene solution with lower concentration, **R110**-loaded and **S101**-loaded micellar solutions without **C343** were also mixed and thin films were obtained by spin-coating (see ESI† for detailed experimental).

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 25.6 ± 2.2 nm, an interval of 19.5 ± 1.5 nm, and a height of 2.8 ± 0.2 nm (Fig. S3a and b, ESI†). After incorporation of **R110** or **S101** into **P4VP** cores and mixing with **PF** solution, the micelles slightly expanded to a core with the size, interval, and height of 30.5 ± 2.7, 17.4 ± 1.9, and 3.7 ± 0.3 nm (Fig. S3c and d, ESI†), respectively. After introducing **C343** besides **R110** or **S101** into **P4VP** cores and mixing with **PF** solution, the micelles further expanded to a core with the size, interval, and height of 37.4 ± 2.5, 15.0 ± 2.5, and 4.3 ± 0.3 nm (Fig. S3e and f, ESI†), respectively. Since no macrophase separation was observed between **PF** and fluorescent dyes-loaded micelles, **PF** could be physically arrested between the micellar cores.

Next, we demonstrate how the green- and red-light emissions were enhanced by locating **C343** and **R110** or **S101** in the same micellar cores. Fig. 2a showed PL spectra of thin films of **PS-*b*-P4VP/C343** (blue dotted line), **PS-*b*-P4VP/R110** (green dotted line) and **PS-*b*-P4VP/C343–R110** (green solid line). It clearly showed that the introduction of **C343** enabled a 13-fold enhancement of **R110** at 545 nm and a dramatical quenching of **C343** at 490 nm, which indicated that the energy was effectively transferred to **R110** through FRET. The change in the intensities of fluorescent dyes can be explained by calculation of the FRET efficiency.[13] The efficiency of FRET (E) is the fraction of photons absorbed by the donor which are transferred to the acceptor and it can be calculated from the equation $E = R_0^6/(R_0^6 + r^6)$, in which R_0 is the Förster radius and r is the distance between the donor and acceptor, respectively.[13] Assuming that dye molecules were evenly distributed in the spherical core of 37.4 nm in diameter, the **C343–R110** distance was estimated to be 2.22 nm, which was shorter than the Förster radius of **C343–R110** (~3.52 nm).[13] By calculation, $E_{\mathbf{C343\text{–}R110}}$ was estimated to be 0.94, which means 94% of the photons absorbed by **C343** were transferred to **R110**.

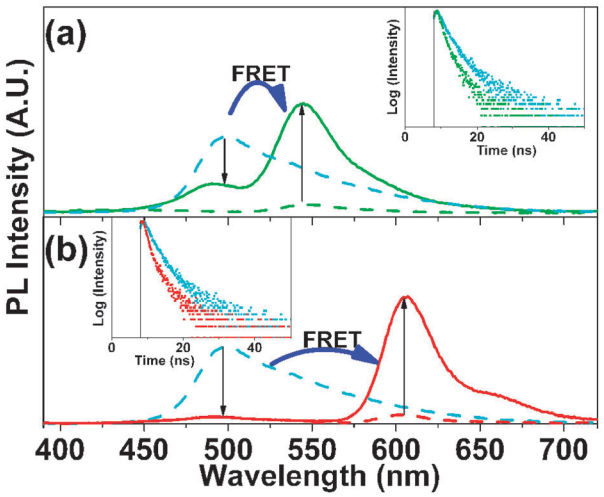

Fig. 2 PL spectra of (a) **C343–R110** (green solid line), **C343** (blue dotted line) and **R110** (green dotted line) loaded in a **PS-*b*-P4VP** micellar thin film. The inset shows the normalized TRF of **C343** in the micellar film at 490 nm. **C343** alone (blue) and **C343** with **R110** (green). (b) **C343–S101** (red solid line), **C343** (blue dotted line) and **S101** (red dotted line) loaded in the **PS-*b*-P4VP** micellar thin film. The inset shows the normalized TRF of **C343** in the micellar film at 490 nm. **C343** alone (blue) and **C343** with **S101** (red). The thickness of thin films was about 135 nm and the excitation wavelength was 380 nm in all cases.

However, due to the fact that **C343** and **R110** cannot be perfectly evenly mixed in micellar cores[9] and there existed a complex donor–acceptor spatial distribution function,[13–16] the FRET efficiency was presumably lower than 0.94, which means more than 6% of photons absorbed by **C343** were not transferred to **R110**. This part of photons could lead to the weak emission of **C343** at 490 nm in Fig. 2a. The energy transferring process from **C343** to **R110** through FRET was further confirmed by time-resolved fluorescence (TRF) of **C343** at 490 nm in the absence or presence of **R110**, which was shown in the inset of Fig. 2a. The TRF of thin films of **PS-*b*-P4VP/C343** showed a single exponential decay with a lifetime of 2.6 ns. However, when **C343** was encapsulated with **R110** in the same **P4VP** core, by fitting with a multiexponential equation,[13] the average lifetime of **C343** decreased to 1.3 ns, with two decay times of 780 ps (70%) and 2.6 ns (30%). The short decay time belongs to the quenched part of **C343** which leads to the enhancement of **R110**, while the long decay time is corresponding to the unquenched part of **C343** due to complex donor–acceptor spatial distribution.

In the case of red-light emission, Fig. 2b showed that FRET inside each **C343–S101** pair in P4VP cores enabled 14-fold enhancement of red-light emission of **S101** at 600 nm and the dramatical quenching of **C343** at 490 nm. Under the ideal assumption as above, the Förster radii of **C343–S101** were estimated to be 3.48 nm,[13] which exceeded the average distance between **C343** and **S101** in the core (~2.16 nm). $E_{\mathbf{C343\text{–}S101}}$ was estimated to be 0.95. Moreover, similar result of TRF was obtained as shown in the inset of Fig. 2b. When **C343** was encapsulated with **S101** in the same core, the average lifetime of **C343** was 1.1 ns, with a short decay time of 620 ps (75%) corresponding to the quenching of **C343** at 490 nm and a long decay time of 2.6 ns (25%) corresponding to the weak emission from the unquenched part of **C343**. Thus, it is concluded that

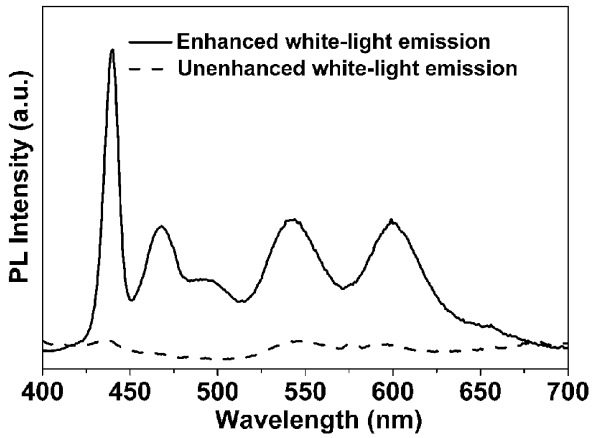

Fig. 3 The spectra of both enhanced white-light-emitting thin film **PS-*b*-P4VP/PF/C343–R110/C343–S101** (black solid line) and unenhanced white-light-emitting thin film **PS-*b*-P4VP/PF/R110/S101** (black dotted line) under the same excitation light of 380 nm. The thickness of both thin films was about 135 nm.

efficient FRET was enabled between **C343** and **R110** (or **S101**) in micellar cores and contributed to the enhancement of green- and red-light emission.

As shown above, green- and red-light emissions were greatly enhanced by locating **C343** and **R110** or **S101** in the same **P4VP** core, in which FRET was permitted due to the dye-to-dye distance being shorter than their Förster radii. Next, we showed that blue-, green-, and red-light-emitting species were isolated from each other by utilizing the micellar corona to inhibit their FRET and enabled their simultaneous emissions. For enhanced white-light emission, **PF** toluene solution, **C343–R110**-loaded micellar solution and **C343–S101**-loaded micellar solution were mixed at an optimized weight ratio of 5 : 12 : 7 and spin-coated (Fig. 3). For comparison, an unenhanced white-light-emitting film without the introduction of **C343** was also prepared in the same way. According to the PL spectra of **PF**, **R110**-loaded and **S101**-loaded micellar films (Fig. S4, ESI†), it can be found that both the enhanced and unenhanced white-light-emitting films exhibited simultaneous emission of the three emissive species (**PF**, **R110** and **S101**). The peaks at 440 and 466 nm were attributed to the emission of **PF**, and the peaks at 545 and 600 nm originated from **R110** and **S101**, respectively. Compared with the white-light-emitting film without **C343**, the intensity of white-light emission was greatly enhanced up to 13-fold as shown in Fig. 3. By calculation, the Förster radii of **PF–R110**, **R110–S101**, and **PF–S101** were estimated to be 3.4, 4.0 and 2.8 nm, respectively,[14] which were much shorter than the **PS** gap of the **PS-*b*-P4VP/PF/R110/S101** thin film (~17.4 nm) and **PS-*b*-P4VP/PF/C343–R110/C343–S101** thin film (~15.0 nm), proving that the FRET between blue-, green-, and red-light-emitting species was effectively suppressed. The Commission Internationale de l'Eclairage (CIE) (1931) coordinates of the enhanced and unenhanced white-light emission were (0.317, 0.320) and (0.372, 0.345), respectively, which were very close to the coordinates of standard white light (0.333, 0.333) (Fig. S5, ESI†). The photographs of thin films of unenhanced and enhanced blue-, green-, red- and white-light-emitting species under UV excitation were shown in Fig. 4.

In summary, we have reported a novel method to realize white light with enhanced intensity. In the cores of micelles, FRET was

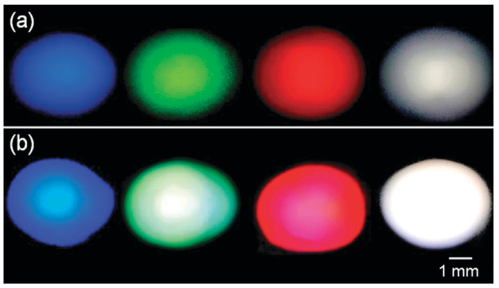

Fig. 4 (a) Photographs of **PF** (from dilute **PF** toluene solution), **PS-*b*-P4VP/R110**, **PS-*b*-P4VP/S101** and **PS-*b*-P4VP/PF/R110/S101** thin films under UV excitation. (b) Photographs of **PF** (from concentrated **PF** toluene solution), **PS-*b*-P4VP/C343–R110**, **PS-*b*-P4VP/C343–S101** and **PS-*b*-P4VP/PF/C343–R110/C343–S101** thin films under UV excitation.

permitted by placing **C343** and **R110** (or **S101**) closely within their Förster radii. **C343** could transfer energy to **R110** or **S101** through FRET upon excitation, leading to the enhanced intensities of green- or red-light emission. On the other hand, **C343–R110** pair and **C343–S101** pair were located in the separate micellar cores and PF around the periphery of micelles. These three light-emitting species were separated beyond their Förster radii by the **PS** corona, leading to the inhibition of FRET among them and enabling their simultaneous emission. The optimized contents of the three emitting species resulted in pure white light from a single layer system with the CIE coordinates of (0.317, 0.320) and the intensity of white-light emission was enhanced up to 13-fold compared with the case in the absence of **C343**. Our exploitative study demonstrated an effective way to control FRET among four different kinds of fluorophores and endow them with different functions when realizing an enhanced white-light-emitting system, which facilitated their ongoing exploration in optoelectronic application.

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