Simultaneous light emissions from two different types of fluorophores in diblock copolymer micellar films

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We report a simple strategy to realize simultaneous light emissions from a single layer of poly(styrene-*block*-2-vinyl pyridine) (PS-b-P2VP) copolymer micelles incorporated with a fluorescent dye in the P2VP core and a conjugated polymer in the PS corona. The fluorescence resonance energy transfer between the dye and the conjugated polymer is effectively inhibited due to the isolation of micelles. This study may offer an effective way to facilitate the ongoing exploration of white light emission in optics and optoelectronics. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3000605]

Multiple light emissions from fluorescent molecules have received considerable attention because they are essential to achieve white light emitting diodes (LEDs), which play an important role in full-color display and flat screens.[1] Various strategies have been proposed to realize multiple light emissions including (1) multilayer systems by thermal deposition, where each layer emits separately;[2] (2) single-layer polymer blend systems, where all the emitting components are mixed in one layer;[3] and (3) single-polymer systems with simultaneous different light-emitting units.[4] In the case of the multilayer system, a multiple fabrication process is unavoidable, which increases fabrication costs. While a spin-coated single layer of polymer blend system offers a promising low-cost technique for large-area display applications, undesired energy transfer between fluorophores is involved. These problems seem avoidable if a single polymer composed of different light-emitting units can be used as the emitting species; however, the synthetic process is complex and time consuming. Thus, more efforts have been devoted to suggest simpler, cost-effective means to obtain multiple light emissions.

Diblock copolymers consisting of two chemically distinct polymers linked covalently at the chain end can self-assemble into ordered, periodic nanostructures with typical dimensions of 10–100 nm.[5,6] In a selective solvent for one of the constituent blocks of diblock copolymers, spherical micelles are spontaneously formed consisting of an insoluble core and a soluble corona, which can be used as an effective nanostructured template to synthesize nanoparticles or a lithographic mask to fabricate nanopatterns in a controlled manner.[7–10]

Recently, Sohn and co-workers[10] reported on controlled light emission combining diblock copolymer micelles with two fluorescent dyes, where the emitting colors can be tuned depending on the spatial location of two dyes loaded in the same micellar cores or different ones. When one of the fluorescent dyes was substituted by quantum dots (QDs), the fluorescent dyes remained in the cores of micelles and QDs were arranged around their periphery.[11] The degree of fluorescence resonance energy transfer (FRET) can be controlled by tuning the size of micellar coronas. In this letter, we demonstrate simultaneous light emissions from a monolayer of diblock copolymer micelles incorporated with a fluorescent dye and a conjugated polymer. The fluorescent dye and the conjugated polymer are encapsulated in the micellar core and distributed between the micellar cores, respectively. The sufficient gap between the cores can isolate the dyes from the conjugated polymers, thereby effectively inhibiting energy transfer between them and enabling their simultaneous emissions. This strategy may open a simple route to achieve multiple light emissions from a single polymer layer and their ongoing applications in LED devices.

In a typical experiment, poly(styrene-block-2-vinyl pyridine) (PS-b-P2VP, $M_{n,\text{PS}}$=54 900 g/mol, $M_{n,\text{P2VP}}$=18 600 g/mol, M_w/M_n=1.06, Polymer Source, Inc.) was dissolved in toluene with a concentration of 1.5 wt %. Because toluene is a selective solvent for the PS block, spherical micelles that consist of a soluble PS corona and an insoluble P2VP core are formed. In this study, we selected Rhodamine B (RB) and polyfluorene (PF) as two light-emitting model compounds whose chemical structures are depicted:

PF   RB
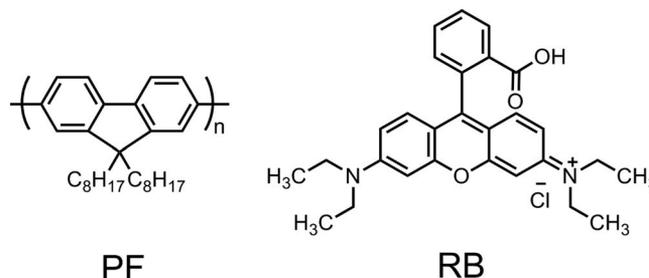
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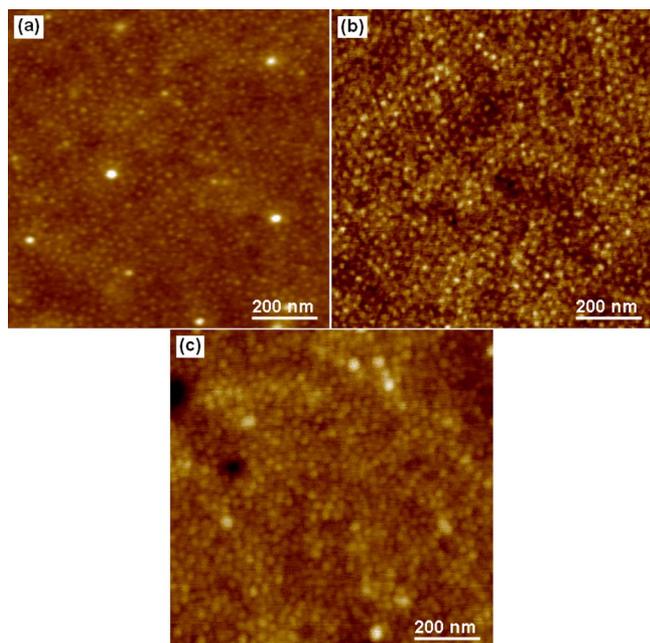b)Author to whom correspondence should be addressed. Electronic mail: dhkim@ewha.ac.kr.

FIG. 1. (Color online) Height-contrast AFM images of (a) a neat PS-b-P2VP micellar thin film, (b) a PS-b-P2VP/RB hybrid film, and (c) a PS-b-P2VP/RB/PF hybrid film.
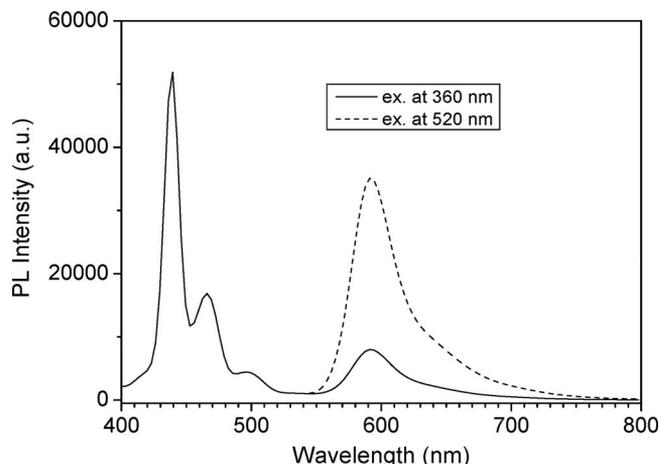

FIG. 2. PL spectra of spin-coated PS-b-P2VP/RB/PF hybrid film. Simultaneous two emission bands in the blue and red regions were ascribed to the emission from PF (peaks at 439, 466, and 498 nm) and RB (peak at 591 nm), respectively. The excitation wavelengths were 360 nm (solid line) and 520 nm (dashed line), respectively.

RB is a well known red light-emitting dye and PF is one of the most popular and promising emitting materials due to their pure blue emission, high photoluminescence (PL) quantum yield, high thermal and chemical stability, as well as facile modification. The absorption spectrum of RB overlaps with the emission spectrum of PF, implying FRET from PF donor to RB acceptor can occur. The UV-visible absorption spectra and PL spectra of RB in ethanol and PF in toluene solution are given in the supporting information.[12]

When PS-b-P2VP micellar solution is mixed with a certain amount of RB, P2VP can encapsulate polar RB, which is insoluble in toluene. The molar ratio of RB molecules to 2VP units was adjusted to 0.05, where a reasonably distinct PL intensity is observed. Prolonged stirring (~3 days) was necessary to ensure complete loading of the dye molecules into the P2VP cores. Then, a certain amount of PF toluene solution (0.05 wt %) was added to the RB-loaded micellar solution with the weight ratio of PS-b-P2VP/RB/PF of 100:6.2:2.5. The blended solution was then spin coated onto quartz or silicon substrates with a thickness of ~31 nm determined by a surface profiler (Tencor P-10, KLA Tencor). The morphology of the neat PS-b-P2VP thin film and that of PS-b-P2VP/RB/PF blended thin film was examined by atomic force microscopy (AFM) (Fig. 1). The as-cast neat PS-b-P2VP thin films exhibited micellar morphology with a short-range hexagonal order with an average core size of ~17.6 nm, an interval of ~15.5 nm, and a height of ~0.9 nm [Fig. 1(a)]. After incorporation of RB into P2VP cores, the micellar structures remain unchanged [Fig. 1(b)]. When PS-b-P2VP/RB solution is mixed with PF, micellar structure is still observed [Fig. 1(c)]. Since no macrophase separation was observed between the PF and PS-b-P2VP/RB micelles, the PF can be physically arrested between the micellar cores.

PL studies have been performed on the ternary PS-b-P2VP/RB/PF blended films with an excitation wavelength at 360 nm. As shown in Fig. 2, the PS-b-P2VP/RB/PF blended film showed simultaneous two major emission bands in the blue and red regions, which are ascribed to the emission from PF and RB, respectively. In the blue region, a well-resolved emission profile with multiple peaks at 439, 466, and 498 nm was observed, which was assigned to the 0–0, 0–1, and 0–2 intrachain singlet transitions of PF, respectively. In the red region a single emission band was observed with a peak maximum at 591 nm, which showed hypsochromic shift by 14 nm compared with the PL maximum of RB in ethanol. This phenomenon can be interpreted as a result of the binding between the pyridine unit in P2VP and the carboxylic group in RB, which weakens the interaction between the carboxylic group and amino group in RB and leads to hypsochromic-shifted charge transfer emission. As the absorption spectrum of RB overlaps the emission of PF, it is expected that the FRET from PF to RB should be possible. However, the simultaneous PL emissions observed in the PS-b-P2VP/RB/PF blended films indicate that the FRET from PF to RB is effectively inhibited due to the isolation of PS-b-P2VP micelles. The proposed mechanism of isolation-inhibited energy transfer was further supported by confirming that no measurable fluorescence was observed (not shown here) from the layer obtained from spin coating *N*,*N*-dimethylformamide solutions of RB and PF in the absence of PS-b-P2VP micelles. In this case, the blue emission of PF disappeared due to efficient energy transfer from the blue PF to red RB and subsequent aggregation of RB, which led to luminescence quenching. We note that PF yielded higher PL intensity than RB (the PL intensity ratio of the emission bands at 436 and 591 nm was around 6:1 and the integrated area ratio of the two emission bands was calculated to be around 3:1). The weaker fluorescence of RB was originated from the unsuitable excitation at 360 nm. When the blended film was excited at 520 nm, which was the maximum excitation wavelength for RB, a much more intense red emission peak was observed. The ratio of the integrated areas between the original blue emission and the red emission was calculated to be 1:1.4, indicating that excellent fluorescence efficiency was achieved and the system was considered to be favorable in the application in LED device. The PL efficiency can also be modified by tuning the concentration of
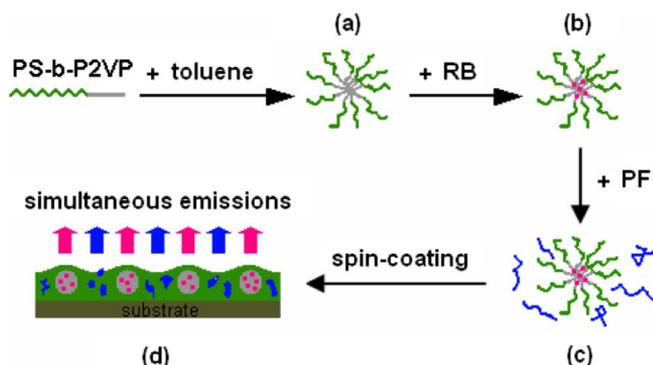
FIG. 3. (Color online) Schematic illustration to achieve simultaneous light emissions from a single layer generated by one-step spin coating from diblock copolymer micelles solution mixed with a fluorescent dye (RB) and a conjugated polymer (PF). (a) Formation of micellar solution of PS-b-P2VP copolymer in toluene. (b) Incorporation of RB into the P2VP domains. (c) The PS-b-P2VP/RB micellar solution is mixed with the desired amount of PF; the PF chains are distributed outside the P2VP cores. (d) Formation of PS-P2VP/RB/PF hybrid film by spin coating and simultaneous light emissions are induced due to the isolated location of RB and PF.

the fluorophores and the color purity can be adjusted by selecting different dyes.

On the basis of the experimental observation and mechanism of isolation-inhibited energy transfer discussed above, the overall scheme adopted in this study is depicted in Fig. 3. Compared with previous reported systems, there are several advantages in utilizing fluorescent conjugated polymers to fabricate such a simultaneous light emitting layer. First of all, the addition of conducting conjugated polymers may endow the film conductive property and facilitate its application in optoelectronic devices. Moreover, the introduction of fluorescent conjugated polymers enlarges the candidates for multiple light emissions, especially for white light emission.

In conclusion, simultaneous light emissions from a single layer have been achieved by mixing a fluorescent dye (RB) and a conjugated polymer (PF) with PS-b-P2VP diblock copolymer micelles as templates. The RB is encapsulated in the micellar cores and the PF is distributed be-

tween micellar cores. The gap between the cores and shells effectively inhibited the FRET between RB and PF and enabled simultaneous emissions. Without complex synthesis and multiple fabrication process, we herewith provide an alternative way to achieve simultaneous emissions from a single layer system. The incorporation of other fluorescent molecules into a single layer concurrent with the integration into light emitting devices is a key element for future research topics.

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[12] See EPAPS Document No. E-APPLAB-93-013842 for normalized UV-visible and PL spectra of PF in toluene solution and RB in ethanol solution. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.