

# Fluorescence Response of Conjugated Polyelectrolyte in an Immiscible Two-Phase System via Nonelectrostatic Interaction with Surfactants

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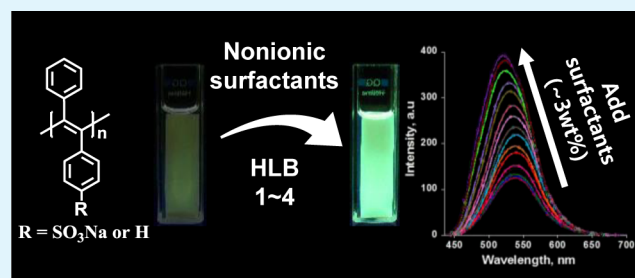
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## S Supporting Information

**ABSTRACT:** This paper reports a unique fluorescence (FL) response and diverse applications of conjugated polyelectrolyte (CPE) through nonelectrostatic interaction with appropriate (bio)surfactants in an immiscible two-phase system. A sulfonated microporous conjugated polymer (SMCP) with a conformation-variable intramolecular stacked structure was used as the CPE film. Despite the extremely high hydrophilicity, the SMCP film responded significantly to the hydrophobic circumstances, either physicochemically or electronically, in the presence of water-in-oil (w/o)-type nonionic surfactants with appropriate hydrophile–lipophile balance (HLB) values. The polymer film became fully wet with hydrophobic solvents due to the addition of small amounts of (bio)surfactant to reveal remarkable FL emission enhancement and chromism. Microcontact and inkjet printing using the SMCP film (or SMCP-adsorbed paper) and the surfactant solution as substrate and ink, respectively, provided high-resolution FL images due to the distinctive surfactant-induced FL change (SIFC) characteristic. Moreover, the additional electrostatic interaction of SMCP film with oppositely charged surfactants further enhanced the FL emission. Our findings will help comprehensive understanding of the nonelectrostatic SIFC mechanism of CPEs and development of novel SIFC-active materials.

**KEYWORDS:** conjugated polyelectrolyte, fluorescence, nonelectrostatic interaction, surfactant, printing ink



## INTRODUCTION

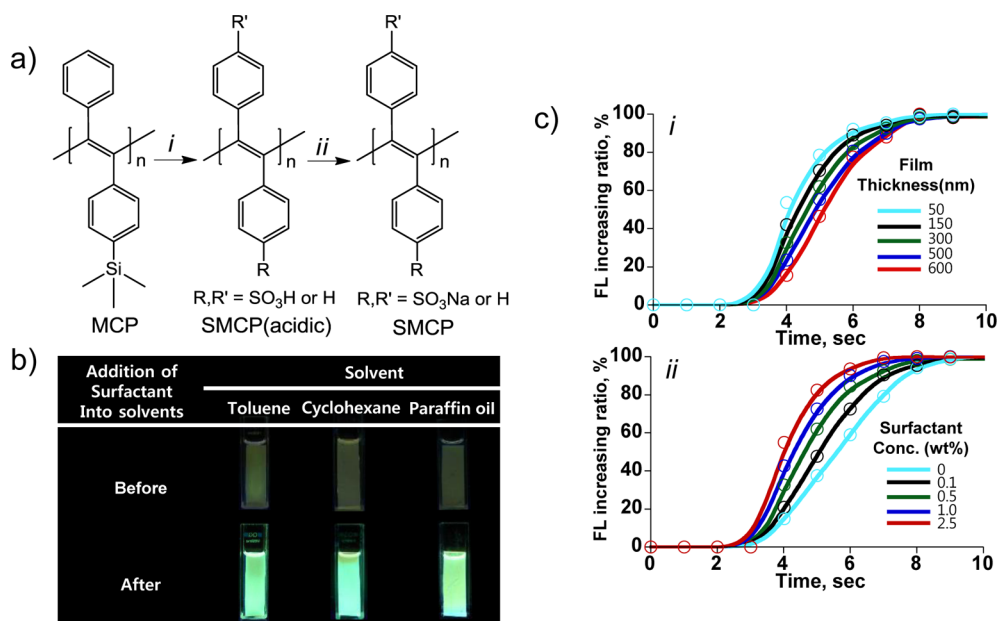
Conjugated polyelectrolytes (CPEs) have recently emerged as a key material for optoelectronic devices, biological sensors, and bioimaging probes because of their enhanced water solubility, coupled with excellent optical and electrical properties.<sup>1–6</sup> In particular, when an oppositely charged ionic surfactant was added to an aqueous CPE solution, a strong electrostatic interaction occurred between the polymer and the surfactant, causing a significant change in the chain conformation and packing structure within the CPE–surfactant aggregates.<sup>7–12</sup> These CPE–surfactant complexes obtained from electrostatic self-assembly (ESA) have been used in many advanced applications.<sup>13–15</sup> Significant changes in the color and intensity of fluorescence (FL) emissions are often observed during the ESA process, which can be referred to as a surfactant-induced FL change (SIFC).<sup>16–21</sup> These significant optical changes should be very unique and fascinating events in surfactant chemistry and can be used to increase the range of applications of CPEs.

Usually, SIFCs have been revealed exclusively in one-phase systems consisting of an aqueous CPE solution, except for one case<sup>21</sup> of in situ ESA in a film.<sup>7–12,16–21</sup> Because the ESA process can lead to a change in the water-solubility of CPEs that causes sudden precipitation of the polymer in water, a nonelectrostatic interaction between two immiscible phases may be found universally in fundamental studies on the intrinsic physicochemical properties of CPEs and is important for their advanced applications. In our previous study, a significant enhancement in the FL emission of a hydrophobic microporous conjugated polymer (MCP, poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene], in Figure 1a) film with an extremely high fractional free volume (FFV) was revealed in water in response to oil-in-water (o/w)-type nonionic surfactants.<sup>22</sup> When the surface tension of water was reduced by the addition of surfactants with appropriate hydrophile–

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**Figure 1.** (a) Chemical structures and reactions of MCP to form SMCP ((i)  $(\text{CH}_3\text{CO})_2\text{O}$  and  $\text{H}_2\text{SO}_4$  in  $\text{CHCl}_3$ ; (ii)  $\text{NaOH}$  in water). (b) Photographs of the SMCP film in various organic solvents before and after addition of 1 wt % Span 80 (film thickness 300 nm, spin-coated on PET film, excited at  $>365$  nm). (c) Time-course FL intensity of SMCP films in toluene according to (i) the film thickness after addition of Span 80 (concentration 1 wt % Span 80, excited at 365 nm, scanning rate 10 dots/s) and (ii) the amount of Span 80 added (film thickness 300 nm, excited at 365 nm, scanning rate 10 dots/s).

lipophile balance (HLB) values, water promptly penetrated the hydrophobic MCP film via the many microvoids and wetted it entirely to induce a conformational relaxation in the intramolecular stack structure, resulting in FL emission enhancement. This was a first-time demonstration of a SIFC in an immiscible two-phase system consisting of a hydrophobic polymer film and water via nonelectrostatic interaction. Inspired by this unique FL response behavior in surfactant chemistry, we have recently focused our attention on identifying the reverse case that reveals the nonelectrostatic SIFC between a hydrophilic polymer film and a hydrophobic solvent.

In this study, we examined the SIFC of the CPE film under hydrophobic surroundings to find new functions and applications. Sulfonated MCP (SMCP, sulfonated polydiphenylacetylene, in Figure 1a), as an ionic CPE, was synthesized by a polymer reaction according to a previously reported method.<sup>5,21</sup> The degree of sulfonation was estimated as  $\sim 1.6$  using titration. The SMCP dissolved completely in water owing to the hydrophilic sulfonate groups, whereas it neither dissolved nor swelled in hydrophobic solvents such as toluene, cyclohexane, and paraffin oils. Previously, the SMCP underwent ESAs with oppositely charged proteins in aqueous solution<sup>5</sup> and with cationic surfactants in situ in the film<sup>21</sup> to exhibit dramatic enhancements in FL intensity, which are defined as “turn-on”-type FL responses in potential sensor applications. Surprisingly, in this study, the SMCP film exhibited remarkable SIFC without ESA in the presence of appropriate water-in-oil (w/o)-type nonionic surfactants. The SMCP film readily became wet with the hydrophobic solvents with the aid of the surfactants to reveal a significant enhancement and blue shift in the FL emission. In addition, the SMCP was adsorbed onto various papers strongly and uniformly to produce highly featured fluorescent papers. The nonelectrostatic SIFC of SMCP found many advanced applications of FL image

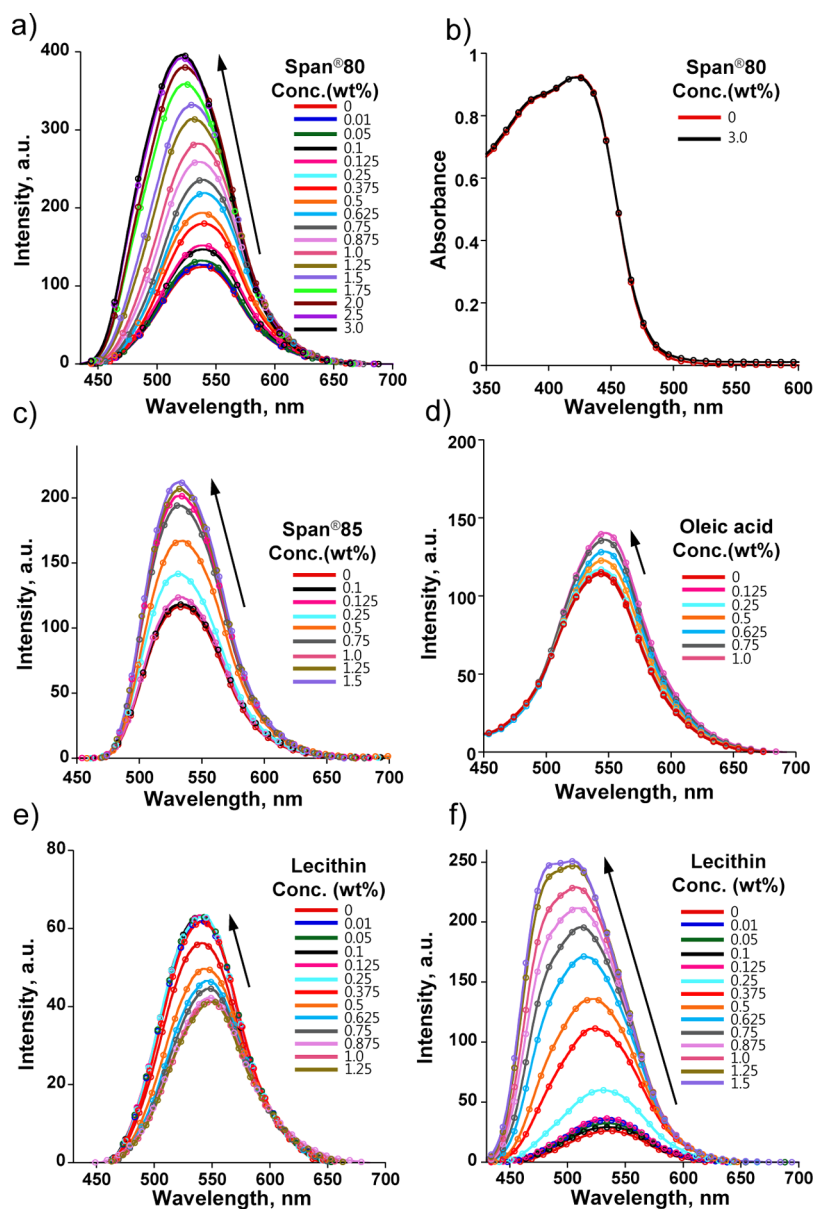
patterning, fingerprinting, and inkjet printing on films and papers. Herein we describe the details of the SIFC mechanism and applications of SMCP based on spectroscopic and microscopic analyses.

## EXPERIMENTAL SECTION

**Materials.** The MCP was donated by NOF Co. Ltd., Japan, and was used as received. The synthetic method was already described in the literature.<sup>23</sup> The MCP used in this study has a high weight-average molecular weight ( $M_w$ ) of  $1.23 \times 10^6$  g mol<sup>-1</sup> and a polydispersity index ( $\text{PDI} = M_w/M_n$ ) of 2.1. Span 80, Span 85, Oleic acid, lecithin ( $1$ - $\alpha$ -phosphatidylcholine; biological source, egg yolk; purity,  $>99\%$  TLC), and decyltrimethylammonium bromide were purchased from Sigma-Aldrich. Commercial pad material was purchased from Maepyo Chemistry Co., Ltd. Korea. A4 business paper, cotton paper, and filter paper were purchased from Duple A Public Co., Ltd., Neenah Paper, Inc., and Advantec MFS, Inc., respectively.

**Preparation of SMCP and Its Films.** Sulfonation of MCP was conducted according to the literature method.<sup>24</sup> Acetyl sulfate was prepared by a reaction of acetic anhydride and sulfuric acid in  $\text{CHCl}_3$ . MCP was dissolved in  $\text{CHCl}_3$ . To obtain a water-soluble sulfonated MCP, a 40-fold equimolar amount of acetyl sulfate was added slowly to the MCP solution with stirring. The reaction was terminated by precipitation in a large amount of THF after 1 h. The precipitate was washed several times with THF and dried in desiccator under vacuum at room temperature for 1 h. The degree of sulfonation was calculated by chemical titration: SMCP (0.05 g) was dissolved in methanol (100 mL) and the solution was titrated with 0.05 mol L<sup>-1</sup> ethanolic potassium hydroxide or mol L<sup>-1</sup> aqueous potassium hydroxide using phenolphthalein and a pH meter (YK-2001PH, LUTRON Electronics Inc.) as indicators. The sulfonic acid at the side chain of the product was converted to sodium sulfonate by a potentiometric titration with 0.1 M NaOH. The excess NaOH was removed by dialysis. The final product, SMCP, was obtained by lyophilization. The polymers were dissolved in water (concentration 1 wt %), and SMCP films of appropriate thickness were prepared on oxygen plasma treated PET films by a spin-coating method (spinning rates 500–2400 rpm).

**Measurements.** The  $M_w$  and  $M_n$  values of the polymers were determined using gel permeation chromatography [Shimadzu A10



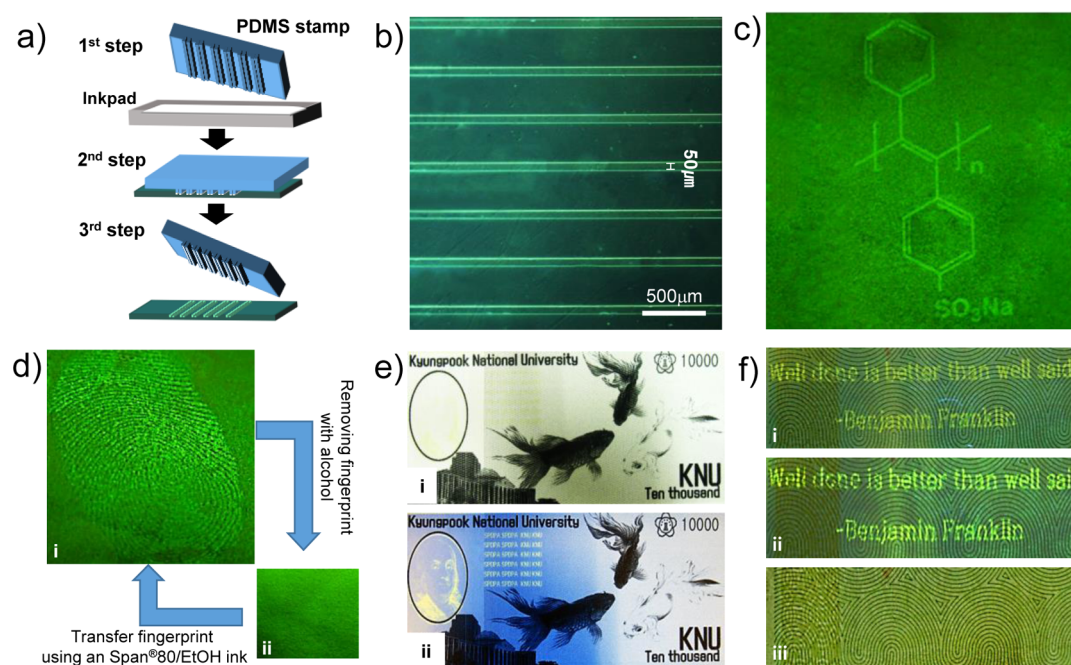
**Figure 2.** (a) Steady state FL emission (excited at 420 nm) and (b) UV-vis absorption spectra of SMCP film (film thickness 300 nm) in toluene at FL enhancing equilibrium state upon addition of Span 80. Steady state FL emission spectra of SMCP film in toluene at FL enhancing equilibrium state upon addition of (c) Span 85 and (d) oleic acid, respectively (film thickness 300 nm, excited at 420 nm). Steady state FL emission spectra of (e) SMCP and (f) acidic SMCP films in toluene at the FL enhancing equilibrium state upon addition of lecithin (film thickness 300 nm, excited at 420 nm).

chromatograph, Polymer Laboratories, PLgel Mixed-B (300 mm in length) column, and HPLC-grade THF as eluent at 40 °C], calibrated with polystyrene standards. The UV-vis absorption spectra were obtained using a JASCO V-650 spectrophotometer, and the FL emission spectra were recorded using a JASCO FP-6500 spectrofluorometer. The polymer films were immersed in toluene and front-face FL spectroscopy was conducted with adding the surfactants. The excitation and emission slits were set in a range from 1–3 nm. The time-course integral fluorescence intensity was recorded at an excitation wavelength of 365 nm and a scanning rate of 10 dots  $s^{-1}$  at room temperature using an Ocean Optics HR4000 high-resolution spectrofluorometer attached to a Nikon Eclipse E400 fluorescence microscope equipped with a superhigh-pressure 100 W Hg lamp (OSRAM, HBO103W/2). The fluorescence intensities were collected at 520 nm. The fluorescence CCD images were also recorded on the same fluorescence microscope equipped with a Nikon DS-Fi1 digital camera. The quantum yields of polymer films were obtained relative to

9,10-diphenylanthracene in a poly(methyl methacrylate) matrix ( $\Phi_{re} = 0.83$ ). The film thickness was monitored using an  $\alpha$ -step surface profiler (Veeco, Dektak150). The image patterns were designed using Photoshop CSS.1 (Adobe) and printed on filter paper with a printer (Hewlett-Packard, Model HP Deskjet F4480) with a resolution of 400 dpi.

## RESULTS AND DISCUSSION

The ultimate aim of this study was to reveal the SIFC of the CPE film in an immiscible two-phase system through nonelectrostatic interaction. SMCP (the neutralized form in Figure 1a) was used as the CPE. Several commercial surfactants were tested to identify the most suitable surfactant for wetting the SMCP film under hydrophobic circumstances. Span 80 and 85 are typical w/o-type nonionic surfactants with HLB values of 4.3 and 1.8, respectively. These surfactants disperse very well in



**Figure 3.** (a)  $\mu$ CP procedure: first step, the PDMS stamp was exposed to the 1 wt % Span 80-in-paraffin oil ink; second step, after inking, the stamp was brought into contact with the surface of the SMCP film; third step, the ink component diffused into the polymer film in a depth direction, but significant lateral diffusion was not observed. (b) Representative FL image pattern obtained from the  $\mu$ CP procedure (excited at  $>365$  nm). (c) FL image of the SMCP-adsorbed paper inkjet printed using 1 wt % Span 80-in-ethanol as an ink (excited at  $>365$  nm). (d) Fingerprinting on the SMCP-adsorbed paper using 1 wt % Span 80-in-paraffin oil as an ink in the process of (i) writing and (ii) erasing (excited at  $>365$  nm). (e) Photographs of the watermarks-printed mockup paper money using a mixture solution containing 1 wt % SMCP and 1 wt % Span 80 in ethanol as an ink ((i) under room light, (ii) under UV lamp with an excitation  $>365$  nm). (f) Photographs of Korean paper money inkjet printed using the same mixture solution ((i) excited at  $>365$  nm) and then multiple-pass printed using an 1 wt % DTMAB aqueous solution ((ii) excited at  $>365$  nm, (iii) under room light).

hydrophobic solvents such as toluene, cyclohexane, and paraffin oil, to produce completely clear solutions in the visible region.

When the SMCP film was immersed in the hydrophobic solvents, no change in FL emission occurred. On the other hand, the polymer film enhanced the FL emission quickly when a small amount of Span 80 was added to the solvents (Figure 1b). Simultaneously, the emission color changed slightly, resulting in chromism in the FL emission. Consequently, an SIFC was revealed in the immiscible two-phase system of the SMCP film and hydrophobic solvent. This is quite surprising because SMCP is intrinsically hydrophilic and basically oil-repelling. To our knowledge, this is the first observation of an SIFC between two different phases of hydrophilic solid and hydrophobic liquid.

We also determined the FL response rate by time-resolved FL spectroscopy on a millisecond time scale. Figure 1c plots the integral FL intensity of the SMCP film at the emission maximum wavelength as a function of the time course when Span 80 was added to the toluene. The FL intensity increased rapidly to reach an enhancing equilibrium within several seconds. The FL response rate was somewhat different depending on the thickness of the SMCP film and the concentration of the surfactant. The FL response rate increased with decreasing polymer film thickness (Figure 1ci). Also, the FL intensity increased more rapidly in Span 80 solution with a higher concentration (Figure 1cii).

To investigate the SIFC in more detail, we measured the changes in the steady state FL emission of SMCP film at the enhancing equilibrium state upon the addition of various surfactants. As shown in Figure 2a, this polymer film in toluene

even responded to an extremely low concentration of 0.01 wt % Span 80. The FL intensity increased with increasing amount of surfactant, to reach a maximum (emission quantum yield,  $\Phi_{em} = 5.02\%$ ) at approximately 2.5 wt % Span 80, which was more than 3.3 times that ( $\Phi_{em} = 1.53\%$ ) found before the addition of the surfactant. Simultaneously, the FL emission band shifted to a shorter wavelength by 20 nm. It is expected that the emission enhancement and the chromic FL can be attributed entirely to the wetting of the SMCP film with toluene. That is to say, the solvent molecules should penetrate the hydrophilic polymer film due to an increased degree of continuity between the polymer and the solvent due to the presence of the surfactant. Simultaneously, the solvent molecules should relax the stack structure of the side phenyl rings efficiently, resulting in a significant degeneration of the nonradiative emission decay channel in the electronic transition, ultimately enhancing the FL emission and changing the FL color. Similar FL response behavior using MCP film in water has already been reported and the mechanism has been well established by our research group.<sup>22,25–30</sup> On the other hand, the SMCP film did not show any change in the UV–vis absorption spectra, even with the addition of an excess amount of Span 80, indicating that the present polymer does not have an unexpected heterogeneous phase in the film (Figure 2b). Similarly, the SIFC behavior was also observed by the addition of Span 85 (Figure 2c). However, the degree of FL increase in response to Span 85 was much less than that found in the case of Span 80. This is probably because Span 85 has a much lower HLB value and thus the molecular affinity is weighted toward toluene. This may reduce its ability to introduce a degree of continuity between the SMCP film and

toluene. Ultimately, oleic acid (that has an extremely low HLB value of 1.0) was almost unable to reveal an SIFC due to its higher affinity toward toluene (Figure 2d). This suggests that the HLB value of surfactants is of critical importance to achieve an effective SIFC.

Lecithins are one of the most important biosurfactants. They have recently emerged as commercially important compounds with expanding applications in the food, cosmetics, and pharmaceutical fields.<sup>31</sup> Such biochemical compounds are characterized by their low toxicity, biocompatibility, biodegradability, and wide range of biological activities. Lecithins are also w/o-type surfactants having HLB values in the wide range of ~4.0–8.0, depending on the natural sources.<sup>32</sup> The values are close to those of nonionic Span series surfactants although lecithins are amphoteric but not nonionic surfactants. Therefore, we tested a lecithin for SIFC to compare with the Span series. L- $\alpha$ -Phosphatidylcholine (biological source, egg yolk; purity, >99% TLC) was chosen as the lecithin in this study. Unexpectedly, the SMCP film did not show a significant SIFC, even with the addition of an excess amount of lecithin (Figure 2e). However, the acidic SMCP before neutralization (Figure 1a) responded significantly to lecithin in toluene (Figure 2f). The FL intensity increased with an increasing amount of lecithin to reach an enhancing equilibrium with an approximately 10-fold increase at 1.5 wt % lecithin, indicating a remarkable SIFC activity. The significant difference in FL response between the neutralized and acidic SMCPs indicates that, in the case of amphoteric surfactants such as lecithin, the contribution to the SIFC revelation is much greater for the direct electrostatic interaction between the polymer and surfactant than for the physicochemical assistance provided by increasing the degree of continuity between the polymer film and toluene. The broader FL band (the 475 nm shoulder) at the higher concentration of lecithin in Figure 2f should be because of the kink structure of polymer chain due to the enhanced solubility of a newly formed SMCP–lecithin complex in toluene.<sup>27–30</sup>

To make more diverse use of this SIFC behavior, the Span 80 in toluene solution was used as an ink for printing patterns. The microcontact printing ( $\mu$ CP) method was utilized for FL image patterning (Figure 3a). A polydimethylsiloxane (PDMS) elastomer stamp was prepared routinely. Commercial pad material was used as a virgin pad for stamping. The ink pad was prepared by moistening the virgin one with the surfactant solution. The  $\mu$ CP process was carried out on an SMCP film to give an FL image pattern at high resolution (Figure 3b). The SMCP adsorbed into various types of papers very well. The pristine papers were immersed in aqueous SMCP solution and then dried in air to produce well-featured fluorescent papers (Figure S1 of the Supporting Information). Once the SMCP was adsorbed onto the paper, the polymer was hardly extracted by water, indicating a good resistance to washing. This fluorescent paper was used as a printing paper for inkjet printing. An ethanolic solution of Span 80 was used as an ink. The surfactant solution was injected into an empty cartridge. Very strong FL images appeared on the paper under a UV lamp when the solution was deposited on the paper by using a commercial inkjet printer (Figure 3c). The fluorescent paper was also used as a fingerprinting paper for potential application in creating secret documents. A solution of Span 80 in paraffin oil solution was used as the ink in this case because the paraffin oil is harmless to human skin. When the ink was deposited onto the paper by fingerprinting, a high-resolution FL fingerprint

image was obtained (Figure 3d). Moreover, the FL image was readily erased by washing with alcohols to remove the paraffin oil from the paper whereas the image was resistant to water. The writing and erasing was reversible and reproducible several times.

Since the history of paper money began several tens of centuries ago, many advanced manufacturing technologies have been developed up to now. This paper money is now used worldwide. However, the existence of counterfeit bills has always been a serious problem.<sup>33</sup> The core technology for prevention of production of fake paper money should be developed using highly advanced materials for inimitable printing techniques. Advanced embedded figures in paper money will be one of the most promising techniques available to the manufacturers. In this respect, the present inkjet printing technique using our SMCP was very useful. In fact, using the mixture of SMCP and Span 80 in ethanol as an ink, we deposited some embedded images and characters, which appeared clearly only under UV light, onto mockup or real paper money (Figure 3e,f). Additionally, when a cationic surfactant (DTMAB: decyltrimethylammonium bromide) was multideposited onto the same part, the FL images became brighter owing to the strong electrostatic interaction between the anionic SMCP and DTMAB and then were not removable by washing with water, as already described in a previous study.<sup>21</sup>

## CONCLUSIONS

We demonstrated for the first time an SIFC revelation and the diverse applications of CPE film through nonelectrostatic interaction in an immiscible two-phase system. The SMCP with a microporous structure and an intramolecular stack structure was used as the CPE film for the examination of SIFC activity. This polymer was hydrophilic and water-soluble. Surprisingly, however, this polymer film responded significantly to the hydrophobic circumstances, either physicochemically or electronically, in the presence of w/o-type nonionic surfactants. The polymer film became completely wet with hydrophobic solvents by the addition of small amounts of a (bio)surfactant to reveal a significant FL emission enhancement and chromism. Utilizing  $\mu$ CP and inkjet printing techniques, high-resolution FL imaging could be achieved using the SMCP film and SMCP-adsorbed paper with the distinctive SIFC characteristic. Our findings should be helpful in fundamentally understanding the nonelectrostatic SIFC revelation mechanism of CPEs as well as the already-well-known ESA-based SIFC mechanism and developing new SIFC-active materials. The unique FL emission behaviors in response to various (bio)surfactants in immiscible two-phase system may find further advanced (bio)applications in the future.

## ASSOCIATED CONTENT

### Supporting Information

Photographs of various types of paper adsorbed with SMCP solution. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03717.

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## Notes

The authors declare no competing financial interest.

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