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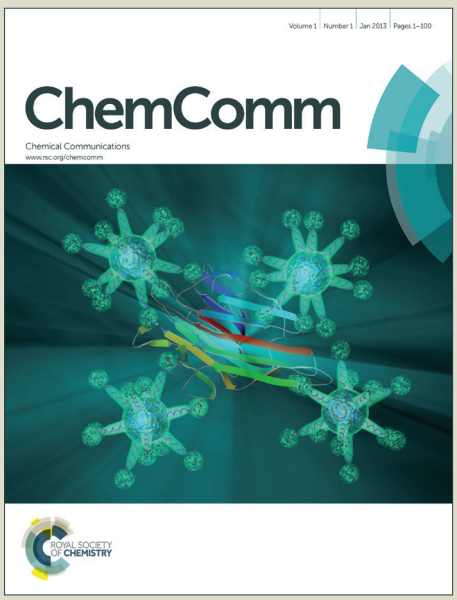

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Surfactant Chemistry for Fluorescence Imaging of Latent Fingerprints Using Conjugated Polyelectrolyte Nanoparticles

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When aqueous conjugated-polyelectrolyte colloidal solutions containing an adequate amount of surfactant with an appropriate hydrophile–lipophile balance were sprayed onto latent fingerprints (LFPs), the polymer nanoparticles were readily transferred to the LFPs to reveal highly distinguishable fluorescent images, while the LFPs themselves remained intact.

Latent fingerprints (LFPs) at the scene of a crime are one of the most important clues in modern criminal investigations.[1] However, LFPs are usually invisible under ambient light. In forensic science, many methods and sequences, including powder dusting, chemical staining, and spectroscopic techniques, have been explored for the visualization of LFPs under specific circumstances.[2] Particularly, the detection of LFPs using chemical reagents is of particular importance for their high visualization. Some reagents, such as ninhydrin (NH), 1,8-diazafluoren-9-one (DFO), and cyanoacrylate (CA), have been commercialized, leading to many advantages in their utilities.[3] In spite of their extensive uses, however, these reagents still have several drawbacks. First, it takes a relatively long working time to develop LFP images because the high visualization requires a heating process for NH and DFO and a fuming process for CA. Second, NH and CA are not fluorescent dyes in themselves, and hence, they often require bothersome post-treatments such as luminescent-stain spraying for higher visualization of the LFPs. Third, NH and DFO react exclusively with amino acids in an LFP so as to reveal a colored species. Hence, if the LFP is exposed to water or humidity for a long period of time, the amino acid components are readily washed out of the LFP, and the colored species cannot be formed. Therefore, there is still a strong demand for universal probe materials and simple and convenient techniques for fingerprint detection.

The oil on the surface of human skin is a complex mixture of sebum, lipids, sweat, etc. Human sebum is comprised mainly of triglycerides, wax esters, and squalene with some cholesterol and cholesterol esters.[3,4] Owing to common human behaviors of touching the face and hair unconsciously, these oily components are always present in LFPs despite the individual variations. Therefore, if a certain fluorescent reagent can diffuse into the oily components without wiping the LFP out with the substrates, it could be a highly universal probe for the fluorescence (FL) imaging of LFPs. To make this idea feasible, it will be key for the fluorophores to have a high affinity for these oily components. The simplest method that could achieve this purpose may well be the use of a surfactant as a phase-transfer agent. Surfactant molecules dissolve in both aqueous and oily phases owing to their amphiphilic characteristics. These molecules tend to locate at the interface of the two different phases, leading to a degree of continuity. Therefore, many useful functions, such as wetting, emulsification, detergency, solubilization, foaming, lubrication, etc., can be revealed in surfactant chemistry.[5] Particularly, surfactants are often used as phase-transfer agents in immiscible two-phase systems to transfer the hydrophilic solutes from the aqueous phase to the oil phase. This strategy is commonly utilized in organic chemistry for alkylation and polymerization reactions.[6] A more precisely controlled surfactant reaction may be needed for the visualization of LFPs, because the surfactant should transfer the hydrophilic fluorophore from the aqueous solution to the oily components while the LFP remains intact.

This new approach utilizing surfactant chemistry may render many kinds of water-dispersed small particles useful for the FL imaging of LFPs. A wide range of fluorescent nanoparticles, such as inorganic semiconductor quantum dots (QDs),[7] conjugated-polymer dots (CPDs),[8] conjugated-polyelectrolyte dots (CPEDs),[9] and carbon dots (CDs),[10] have been extensively developed for various advanced applications. Particularly,

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CPEDs have been considered recently as bioimaging probes because of their potential benefits, including good biocompatibility, low cytotoxicity, and excellent FL brightness.[9a] CPEDs are commonly prepared from water-soluble conjugated polyelectrolytes (CPEs) in water, forming an aqueous colloidal solution. Although the water solubility of CPEDs is significantly enhanced by their polar side chains, CPEDs usually exist as nano-sized particles in water, because the polymer chains tend to aggregate within aqueous environments due to the intrinsic hydrophobicity and structural rigidity of the main chains.[11] If the amphiphilic characteristics of CPEDs can be adjusted precisely with the aid of surfactants with appropriate hydrophile–lipophile-balance (HLB) values, the fluorescent nanoparticles may be transferred to the oily phase of an LFP efficiently while the LFP remains intact.

In this study, several CPEDs were investigated to assess their utility as FL-imaging probes for LFPs. The aqueous CPED colloidal solutions could not stain the LFPs by themselves. However, when an appropriate surfactant was added to the aqueous solutions and then sprayed onto the LFPs, the CPED nanoparticles were readily transferred to the LFPs to reveal highly distinguishable FL images. Moreover, when a cationic-surfactant solution was additionally sprayed onto the LFPs, the FL images were further enhanced and became brighter. We herein describe the surfactant chemistry for the FL imaging of LFPs using CPEDs. This approach provides a very simple, convenient, and universal technique that is applicable to most water-dispersible fluorescent particles and could possibly be further extended to water-soluble dyes.

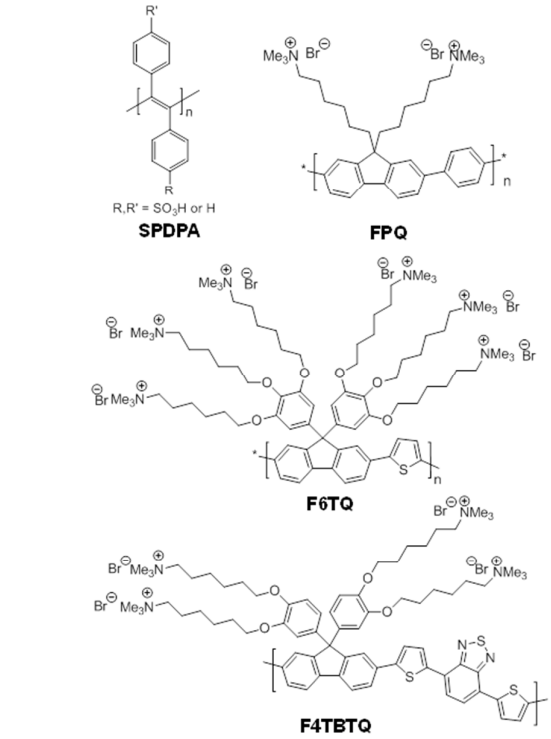

Chart 1 Chemical structures of the CPEDs used in this study

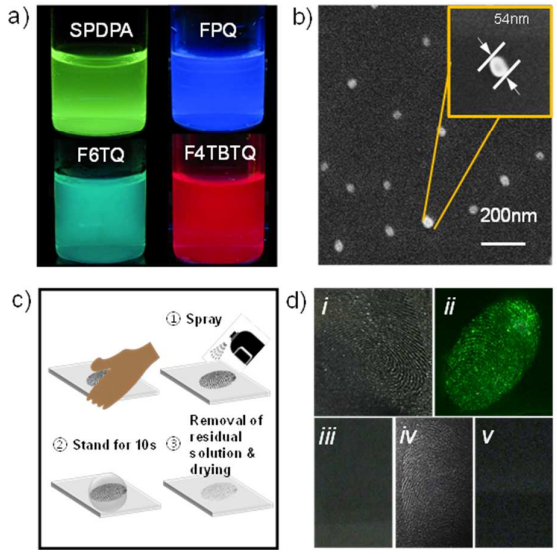

Fig. 1 (a) Features of aqueous CPED colloidal solutions (1×10^{-5} M, excited at >365 nm under a UV lamp). (b) SEM image of SPDPA nanoparticles in the dry state. (c) Scheme of the LFP-detection process. (d) Features of LFPs on glass slides when stained using 0.5 wt% aq. SPDPA colloidal solutions containing (*i*) no surfactant, (*ii*) 0.25 wt% Tween85, (*iii*) 0.25 wt% SDS, (*iv*) 0.25 wt% Tween80, and (*v*) 0.25 wt% Span80.

A solution-based, spray-type agent would be a convenient medium for criminal investigators, as commercial chemical reagents are already commonly used in such a manner.[2a,2b,4] An aqueous solution is desirable because water is not toxic and does not dissolve the oily LFP components. Four different types of CPEDs were tested to examine their applicability to the FL imaging of LFPs. The chemical structures of CPEDs (SPDPA, F4TBPQ, F6TQ, and FPQ) used in this study are shown in **Chart 1**. They dissolved in water, affording highly fluorescent colloidal solutions under ambient conditions (**Fig. 1a**). Their FL-emission and physical properties are summarized in **Table 1**. The measured average hydrodynamic diameter ($D_{ave,aq}$) of a particle of SPDPA in its colloidal solution was 50 nm. Moreover, the dispersed aqueous colloidal solution was highly stable for a period of several months because of the large value of its negative zeta potential (ζ, –14.3 mV). Scanning-electron-microscopy (SEM) images clearly showed the nanoparticles in their dry state (**Fig. 1b**). Notably, the particle sizes of the dried sample (observed via SEM) were similar to the $D_{ave,aq}$ value of the wet particles, measured via dynamic

Table 1 FL-emission properties and physical features of CPEDs

CPEDs	Properties			
	$\lambda_{max,FL}$ (nm)[a]	Φ_{FL} (%)	$D_{ave,aq}$ (nm)[b]	ζ (mV)[b]
SPDPA	523	4.31	50	-14.3
FPQ	420	14.9	19	7.24
F6TQ	475	49.5	53	16.1
F4TBTQ	642	0.12	127	8.19

[a] Excited at each maximum absorption wavelength in an aqueous solution with a concentration of 1.0×10^{-5} M. [b] Determined via DLS.

light scattering (DLS). The other CPEDs (F4TBPQ, F6TQ, and FPQ) had $D_{ave,aq}$ values in the range of 19~127 nm and were also highly stable in dispersions for several months, owing to their large, positive ζ values. The maximum FL-emission wavelengths ($\lambda_{max,FL}$) of the CPEDs in aqueous colloidal solutions were determined to be 523 nm (green) for SPDPA, 420 nm (blue) for FPQ, 475 nm (bluish green) for F6TQ, and 642 nm (red) for F4TBTQ (**Fig. S1, ESI†**). Their FL quantum yields (Φ_{FL}) widely ranged from 0.12 to 49.5%, depending on their individual molecular and electronic structures.

One donor deposited LFPs on the surface of glass slides after rubbing his thumb on the oily part of his face three times. The aqueous colloidal solution of SPDPA was sprayed onto the LFPs and left to sit for a while before shaking the residual solution off and subsequently drying the LFPs in air (**Fig. 1c**). However, no FL images were left behind [(*i*) in **Fig. 1d**], indicating that the nanoparticles were preferentially located in the water phase. Namely, the nanoparticles still had a molecular affinity weighted toward the water phase, so they did not transfer to the oily LFP phase by themselves. The hydrophilicity of the SPDPA nanoparticles was fine-tuned via the addition of a surfactant with an appropriate HLB value. The various types of surfactants with different HLB values (**Table S1, Fig. S2, ESI†**) were thus tested as phase-transfer agents. Among them, Tween85 (HLB = 10) was very effective in conjunction with the SPDPA CPEDs. A 0.5 wt% aqueous SPDPA solution containing 0.25 wt% Tween85 was prepared by adding the surfactant to the aqueous colloidal solution of SPDPA. When this SPDPA–Tween85 solution was sprayed onto an LFP, according to the same procedure described in **Fig. 1c**, a clearly distinguishable FL image was obtained [(*ii*) in **Fig. 1d**]. The success or failure of the FL imaging of the LFPs was greatly dependent on the concentration of Tween85 (**Table S2, ESI†**). On the other hand, when an anionic surfactant, sodium dodecyl sulfate (SDS), with an extremely high HLB value of 40 was used as the surfactant, the LFP collapsed completely, leaving no images despite the use of an extremely small amount of SDS (**Table S2, ESI†**) because of the high detergency of this compound [(*iii*) in **Fig. 1d**]. Although Tween80 with an HLB of 15 did not collapse the LFP, the LFP FL image was not clear, suggesting an inefficient phase transfer of the CPED particles to the oily phase [(*iv*) in **Fig. 1d**]. Span80 with its extremely low HLB value of 4 was also ineffective for the phase transfer [(*v*) in **Fig. 1d**]. Consequently, the water-to-LFP phase transfer of the SPDPA nanoparticles could be fine-tuned via the selection of a surfactant with an appropriate HLB value and concentration to achieve high-resolution FL imaging of LFPs. The CPEDs clearly showed great potential as an FL-imaging agent of LFPs with a combination of surfactants. Using the SPDPA–Tween85 solution, we were also able to detect extremely thin LFPs which oily component were thoroughly wiped off or unrecharged in a consecutive deposition. (Fig. S3 and S4, ESI†)

Noticeably, strongly luminescent spots were observed in the FL images [(*ii*) in **Fig. 1d**] that were probably due to the existence of charged particulates within the LFP that might have reacted with the ionic SPDPA via electrostatic interactions, increasing the local concentration of the CPEDs in the LFP. The charged species, such as proteins, amino acids, dust, etc., on the surface were readily removed from the LFP by washing it with water. When an LFP was lightly rinsed with water before spraying the aqueous colloidal solution, the luminescent spots no longer appeared, and the ridge pattern of the LFP was more distinctive (**Fig. S5, ESI†**). As should be expected, on the other hand, the water-exposed LFPs were not detected with commercial reagents such as NH and DFO because these reagents react with amino-acid components of LFPs to form colored and emissive species. Consequently, our surfactant-chemistry approach was especially effective for the FL imaging of water-exposed LFPs.

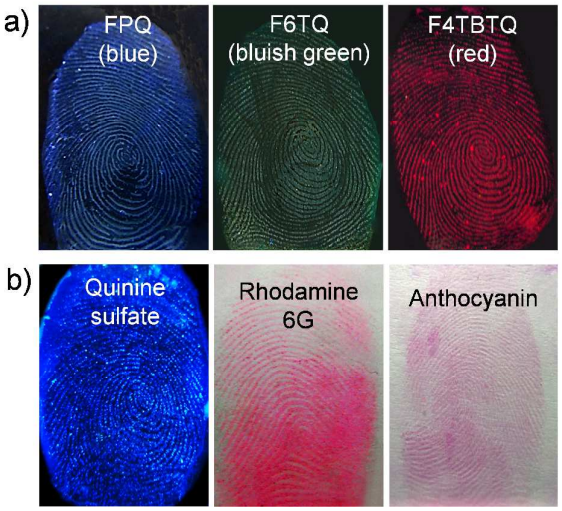

Fig. 2 Photographs of LFPs stained with (a) other CPEDs and (b) common water-soluble dyes: (FPQ, F6TQ, F4TBTQ, and quinine sulfate: on glass slides under UV irradiation) (Rhodamine 6G and anthocyanin: on papers under room light).

Other CPEDs (F4TBPQ, F6TQ, and FPQ in **Chart 1**) were also effective for FL imaging when an appropriate amount of surfactant (with an appropriate HLB value) was added to the aqueous solution. Similar to the case of SPDPA, the non-ionic Tween-series surfactants with HLB values of 10~15 were the most effective as phase-transfer agents of these CPEDs (**Tables S3-S5, ESI†**). The FL images of the LFPs obtained with these CPEDs are shown in **Fig. 2a**. Because each CPED has a different FL-emission wavelength, various, colored FL images could be obtained. This variety may allow for the choice of the best FL color of a probe material so as to provide an optimized contrast with the background color of the substrate where an LFP was left. This FL color variety should be very useful for better discriminating LFPs from colored substrates. This LFP-imaging strategy using surfactants could also be extended to commonly used dyes. Common, organic, water-soluble dyes, such as quinine sulfate (QS), Rhodamine 6G, and anthocyanine, were also tested for the detection of LFPs. They all yielded distinguishable LFP images with the aid of a surfactant (**Fig. 2b, Table S6 in ESI†**).

The electrostatic self-assembly (ESA) reaction may be another important aspect of surfactant chemistry that could be utilized in conjunction with CPEDs for LFP detection. When

an oppositely charged surfactant was added to an aqueous CPED solution, a strong electrostatic interaction occurred between the polymer and surfactant, leading to significant changes in the chain conformation and packing structure within the polymer–surfactant aggregate.[12] These ESA reactions often led to significant changes in the color and intensity of FL emissions, potentially further enhancing the FL imaging of the LFPs.[13] When a dilute aqueous solution of cationic surfactant [octadecyltrimethylammonium bromide (C_{18}TAB) in both **Table S1** and **Figure S2, ESI†**] was additionally sprayed onto the LFPs after staining with an SPDPA–Tween85 solution, the FL emission was remarkably enhanced (**Fig. S6, ESI†**). The ESA reaction of SPDPA with a cationic surfactant in situ on film elucidates this phenomenon very well.[14] According to our previous study, when the C_{18}TAB solution was sprayed onto an SPDPA film, the polymer–surfactant complex formed immediately, showing significantly enhanced FL emissions of about 50 times those of the virgin films. This FL-emission enhancement occurred because the long hydrophobic tails of C_{18}TAB within the complex acted as plasticizers, loosening the intramolecular stacked structure of the side phenyl rings of SPDPA.[15]

In summary, we examined the utilities of various surfactants as phase-transfer agents and CPEDs as FL-imaging probes for the detection of LFPs. The aqueous CPED colloidal solutions could not stain the LFPs by themselves. When an adequate amount of a surfactant with an appropriate HLB value was added to an aqueous CPED solution, the polymer nanoparticles readily transferred to the LFPs, resulting in highly distinguishable FL images of different colors, according to the CPEDs used. This approach was also applicable to common water-soluble dyes. When a cationic surfactant solution was additionally sprayed onto the LFPs stained with CPEDs, the FL image was further enhanced. This surfactant-chemistry approach using fluorescent nanoparticles is expected to be a very simple, convenient, and universal technique for the high visualization of LFPs.

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