Electronic Supplementary Information

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

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Experimental Methods

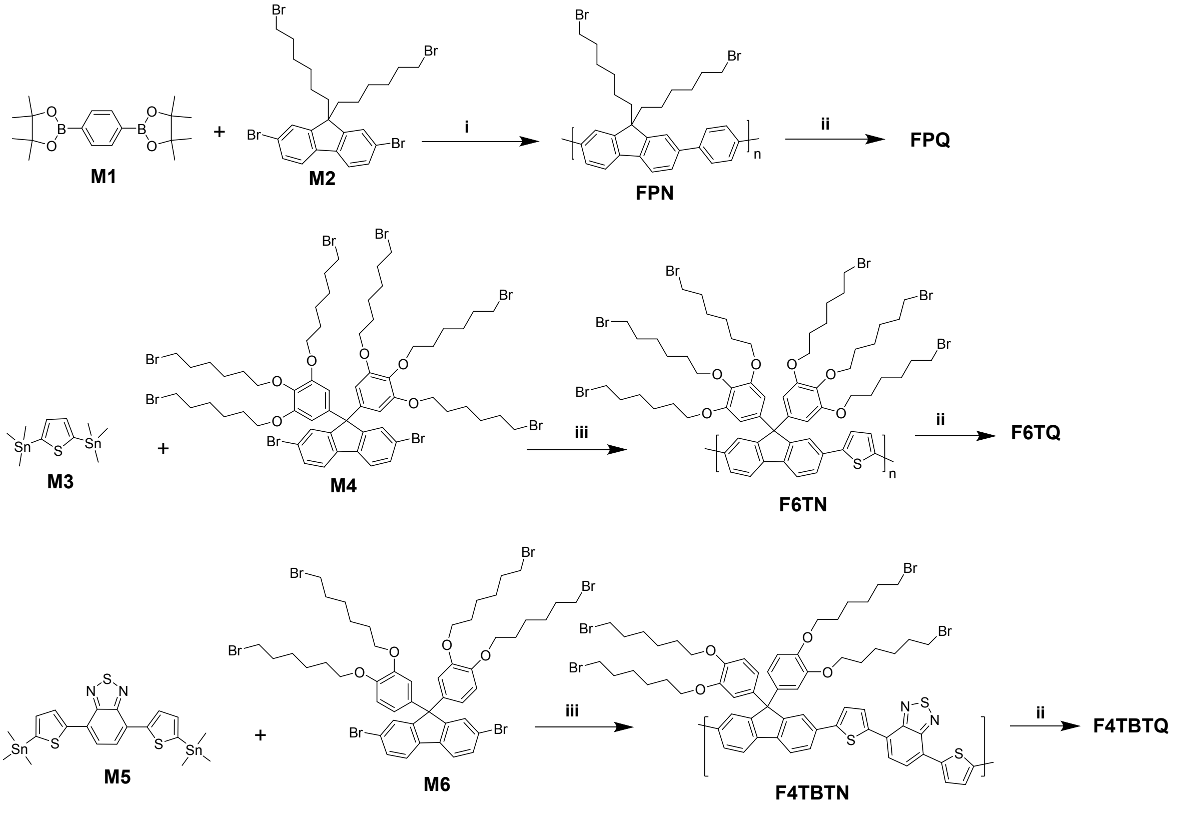
(1) Materials

All chemical reagents were purchased from either Sigma-Aldrich (St. Louis, MO) or Tokyo Chemical Industry and used without further purification. 1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (M1), 2,7-dibromo-9,9-bis(6′-bromohexyl)fluorene (M2), and 2,5-bis(trimethylstannyl)thiophene (M3) were purchased from Tokyo Chemical Industry. 2,7-Dibromo-9,9-bis(3,4,5-tris(6-bromohexyloxy)phenyl)fluorene (M4), 4,7-bis(5-trimethylstannylthiophen-2-yl)-2,1,3-benzothiadiazole (M5), and 2,7-dibromo-9,9-bis(3,4-bis(6-bromohexyloxy)phenyl)fluorene (M6) were prepared according to the procedures reported in the literature.[1,2]

(2) Synthesis

1) SPDPA

The PTMSDPA was donated by NOF Co. Ltd., Japan, and was used as received. The synthetic method has already been described in the literature.[3] The PTMSDPA used in this study had a high average molecular weight (M_w) of 1.23 × 10^6 g/mol and a polydispersity index (PDI = M_w/M_n) of 2.1. SPDPA was prepared via the sulfonation of PTMSDPA by means of a polymer reaction. This process was conducted according to the method reported in the literature.[4]



Scheme S1 Synthetic routes to three cationic conjugated polymers. Reagents and conditions: (i) $(PPh_3)_4Pd(0)$, toluene, 2 M aqueous K_2CO_3, and Aliquat 336; (ii) trimethylamine, THF/MeOH; and (iii) $Pd_2(dba)_3$, tris(*o*-tolyl)phosphine, toluene.

2) FPQ

FPQ was synthesized by modifying the previously reported procedures.[5,6] The number-average molecular weight (M_n) and polydispersity index (PDI) of FPQ were 10,400 g/mol and 2.39, respectively.

3) F6TQ

(i)Poly[(9,9-bis(3,4,5-tris(6-bromohexyloxy)phenyl)fluorene-2,7-diyl)-alt-2,5-thiophene] (F6TN in **Scheme S1**)

In a glove box, 2,5-bis(trimethylstannyl)thiophene (150 mg, 0.366 mmol), 2,7-dibromo-9,9-bis(3,4,5-tris(6-bromohexyloxy)phenyl)fluorene (568 mg, 0.366 mmol), tris(dibenzylideneacetone)dipalladium(0) (3 mol%), and tri(*o*-tolyl)phosphine (8 mol%) were added to a 5 mL microwave vial. The vial was sealed, and 3.5 mL toluene was added. The polymerization reaction was carried out in a microwave reactor: 10 min at 80 °C, 10 min at 100 °C, and 40 min at 140 °C. The polymer was end-capped via the addition of 0.1 equivalents of 2-(tributylstannyl)thiophene and reacted further at 140 °C for 20 min. The polymer solution was cooled down, 0.2 equivalents of 2-bromothiophene were added by syringe, and the reaction solution was further reacted at 140 °C for 20 min. The crude polymer was precipitated in a mixture of methanol and HCl (350 mL : 10 mL) and purified via a Soxhlet extraction with acetone and tetrahydrofuran (THF). The dissolved portion in THF was concentrated under reduced pressure and precipitated in cold methanol. The polymer was dried under vacuum for 24 h. Yield: 80%. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80-7.50 (br, 8H), 6.40 (br, 4H), 3.89-3.76 (br, 12H), 3.38-3.22 (br, 12H), 1.86-1.68 (br, 24H), 1.47-1.23 (br, 24H). Number-average molecular weight (GPC, *o*-dichlorobenzene): M_n = 6,700 g/mol (PDI = 1.72).

(ii)Poly[(9,9-bis(3,4,5-tris(6-N,N,N-trimethylammoniumhexyloxy)phenyl)fluorene-2,7-diyl)-alt-2,5-thiophene] hexabromide (F6TQ)

Condensed trimethylamine (3-5 mL) was added dropwise to a solution of the neutral precursor polymer F6TN (100 mg) in 5 mL THF at −78 °C. The mixture was allowed to warm up to room temperature overnight. The precipitate was redissolved by the addition of excess methanol, and an additional 2 mL trimethylamine was added at −78 °C. The resulting mixture was further stirred for another 24 h at room temperature. After the removal of the solvents and excess trimethylamine under reduced pressure, the polymer was dissolved in methanol and precipitated in cold diethyl ether. The precipitated polymer was collected via filtration and dried under vacuum for 24 h. Yield: 98%. ^1H NMR (300 MHz, DMSO-d_6): δ

(ppm) 8.20-7.50 (br, 8H), 6.50-6.35 (br, 4H), 3.80 (br, 12H), 3.15-2.90 (br, 66H), 1.80-1.50 (br, 24H), 1.50-1.20 (br, 24H).

4) F4TBTQ

(i)Poly[(9,9-bis(3,4-bis(6-bromohexyloxy)phenyl)fluorene-2,7-diyl)-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (F4TBTN in **Scheme S1**).

In a glove box, 4,7-bis(5-trimethylstannylthiophen-2-yl)-2,1,3-benzothiadiazole (180 mg, 0.288 mmol), 2,7-dibromo-9,9-bis(3,4-bis(6-bromohexyloxy)phenyl)fluorene (343 mg, 0.288 mmol), tris(dibenzylideneacetone)dipalladium(0) (3 mol%), and tri(o-tolyl)phosphine (8 mol%) were added to a 5 mL microwave vial. The vial was sealed, and 3.5 mL toluene was added. F4TBTN was prepared similarly to F6TN. Yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.00-7.40 (br, 12H), 7.20-6.50 (br, 6H), 3.94 (br, 8H), 3.40-3.10 (br, 8H), 2.00-1.60 (br, 16H), 1.50-1.20 (br, 16H). Number-average molecular weight (GPC, *o*-dichlorobenzene): M_n = 13,500 g/mol (PDI = 2.46).

(ii)Poly[(9,9-bis(3,4-bis(6-N,N,N-trimethylammoniumhexyloxy)phenyl)fluorene-2,7-diyl)-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] tetrabromide (F4TBTQ)

F4TBTQ was prepared similarly to F6TQ. Yield: 96%. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 8.20-7.50 (br, 12H), 7.10-6.70 (br, 6H), 3.95 (br, 8H), 3.20-2.90 (br, 44H), 2.00-1.50 (br, 16H), 1.50-1.20 (br, 16H).

(3) Measurements

The M_w and M_n values of the polymers were determined using gel-permeation chromatography [Shimadzu A10 chromatograph, Polymer Laboratories, PLgel Mixed-B (300 mm in length) column with HPLC-grade THF as the 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. Fluorescence images were recorded with a digital camera (Cannon Power Shot A2000 IS) under UV irradiation at an excitation wavelength of >365 nm. The sizes of the nanoparticles were determined via DLS (Zetasizer Nano-ZS90, Malvern) and field-emission SEM (Hitachi S-4800) at an accelerating voltage of 5.0 kV. TEM imaging was performed using a Hitachi H-7600 instrument operated at 100 kV. The zeta potential was determined using the DLS equipment. The quantum yields of the aqueous colloidal solutions were obtained relative to the quinine-sulfate solution in 1 N H_2SO_4 (Φ_{re} = 0.546).

References

(1) B. H. Lee, I. H. Jung, H. Y. Woo, H. K. Shim, G. Kim and K. Lee, *Adv. Funct. Mater.*, 2014, **24**, 1100-1108.
(2) T. L. Nguyen, H. Choi, S. J. Ko, M. A. Uddin, B. Walker, S. Yum, J. E. Jeong, M. H. Yun, T. J. Shin, S. Hwang, J. Y. Kim and H. Y. Woo, *Energy Environ. Sci.*, 2014, **7**, 3040-3051.
(3) T. Sakaguchi, K. Yumoto, M. Shiotsuki, F. Sanda, M. Yoshikawa and T. Masuda, *Macromolecules*, 2005, **38**, 2704-2709.
(4) T. Sakaguchi, K. Kameoka and T. J. Hashimoto, *Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6463-6471.
(5) B. R. Lee, W. Lee, T. L. Nguyen, J. S. Park, J. S. Kim, J. Y. Kim, H. Y. Woo and M. H. Song, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5690-5695.
(6) C. V. Hoven, A. Garcia, G. C. Bazan, T. Q. Nguyen, *Adv. Mater.*, 2008, **20**, 3793-3810.

Fig. S1 The UV-Vis absorption (blue) and FL-emission (red) spectra of the CPEDs in aqueous solution.

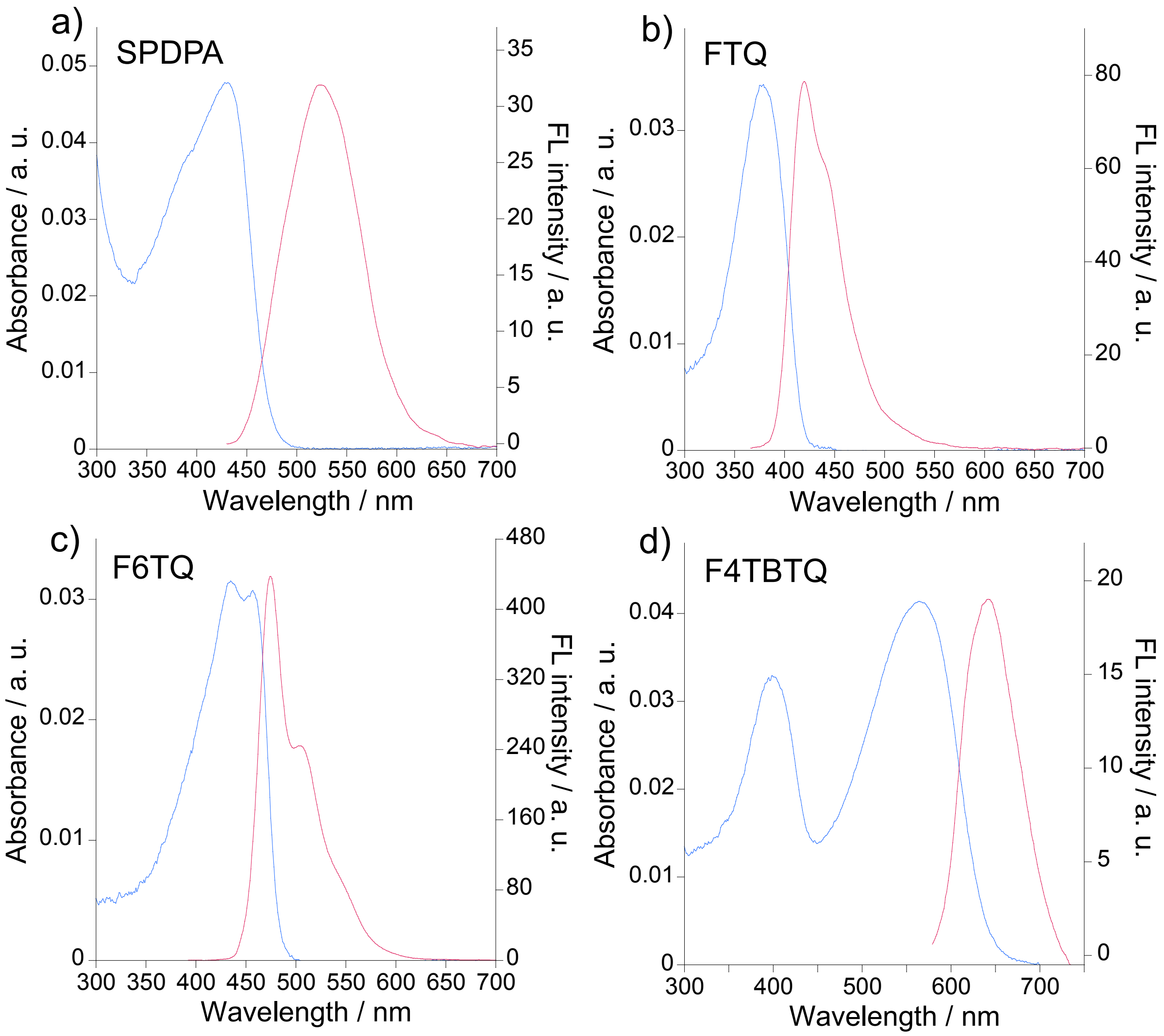


Table S1 Types and HLB values of the surfactants tested in this study

Surfactant Type	Non-ionic					Anionic		Cationic
Surfactant	Tween80	Tween85	Span20	Span80	Span85	SDS	Niaproof	C18TAB
HLB Value	15.6	10	8	4	1	40	20	7.85

Fig. S2 Chemical structures of the surfactants used in this study.

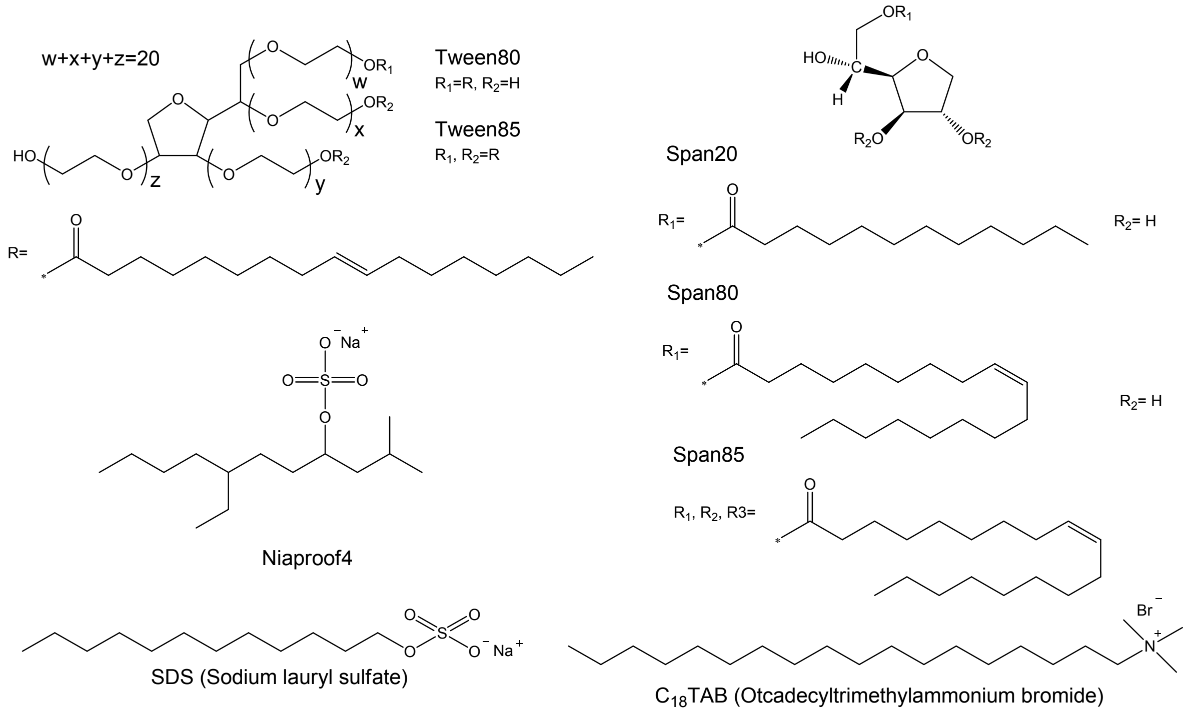


Table S2 Appearance of the FL images of the LFPs, stained with 0.5 wt% aqueous SPDPA under different conditions

Conditions	Appearance of the FL image of an LFP[a]						
Surfactant (HLB) Conc. (wt%)	SDS (40)	Niaproof4 (20)	Tween80 (15.6)	Tween85 (10)	Span20 (8)	Span80[b] (4)	Span85[b] (1)
0	△	△	△	△	△	△	△
0.001	△	○	△	△	△	△	△
0.01	△	◎	△	○	○	△	△
0.1	X	○	△	◎	○	△	△
0.25	X	△	△	◎	◎	X	X
0.5	X	X	△	◎	◎	X	X
0.75	X	X	△	△	○	X	X
1	X	X	X	X	X	X	X
1.25	X	X	X	X	X	X	X
1.5	X	X	X	X	X	X	X
1.75	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X

[a] Judged by the naked eye through 10 rounds of experiments; ◎: very good, ○: good, △: bad, X: no appearance. [b] Diluted with a small amount of methanol before being added to water.

Fig. S3 The FL images of LFPs (stained with the 0.5 wt% SPDPA-0.25wt% Tween85 solution) which were deposited onto the surface of slide glass without recharging the finger with an oily component.

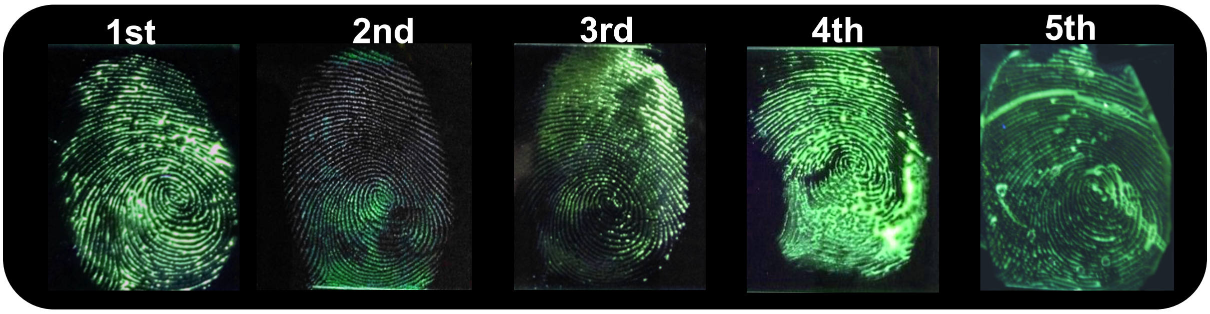
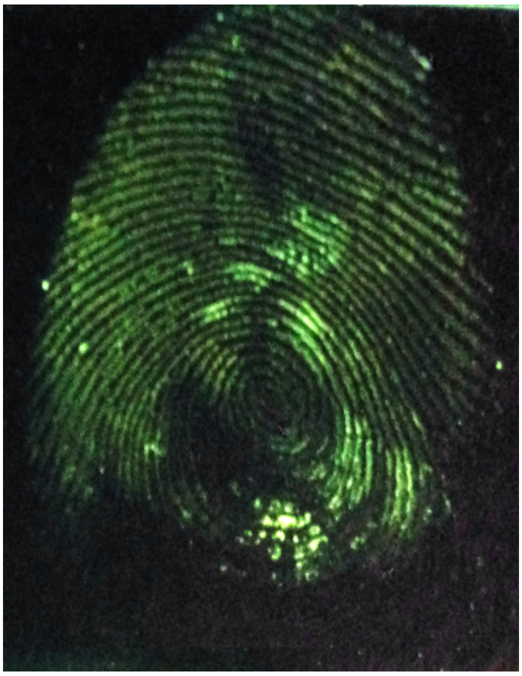


Fig. S4 The FL images of LFP which was deposited onto the surface of slide glass after thoroughly wiping off the oily component of the finger with Kimwipes by the SPDPA-Tween85 solution.



A consecutive set of LFPs was deposited onto glass side without recharging the finger with an oily component in order to produce LFPs with varying amounts of secretion. A same amount of SPDPA-Tween85 (0.5-0.25 wt%) solution was sprayed onto the LFPs in order to compare the contrast ratios in FL images (**Figure S3**). Eventually, all the FL images of LFPs were clearly visible. We were also able to detect an extremely thin LFP, which was deposited onto the surface of slide glass after thoroughly wiping off the oily component of the finger with Kimwipes, by the SPDPA-Tween85 solution (**Figure S4**).

Fig. S5 FL image of an LFP rinsed with water before staining with the aqueous SPDPA–Tween85 solution.

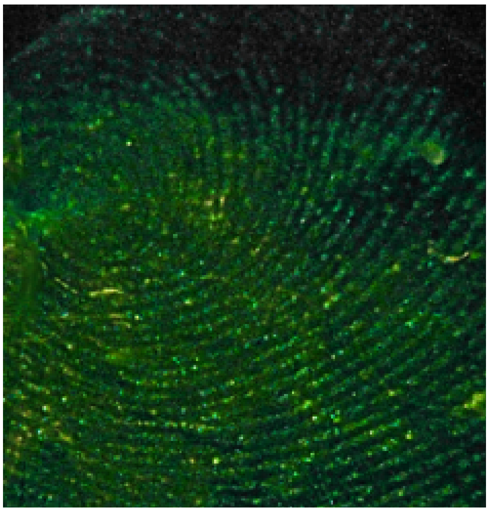


Table S3 Appearance of the FL images of the LFPs, stained with 0.5 wt% aqueous FPQ under different conditions

Conditions	Appearance of the FL image of an LFP[a]						
Surfactant (HLB) / Conc. (wt%)	SDS (40)	Niaproof (20)	Tween80 (15.6)	Tween85 (10)	Span20 (8)	Span80[b] (4)	Span85[b] (1)
0	△	△	△	△	△	△	△
0.001	○	○	○	○	○	○	○
0.01	○	○	○	○	○	○	○
0.1	○	○	○	○	○	△	△
0.25	△	△	○	○	○	△	△
0.5	△	△	○	○	○	△	△
0.75	X	△	○	○	○	△	△
1	X	X	○	○	○	X	X
1.25	X	X	△	△	△	X	X
1.5	X	X	△	△	△	X	X
1.75	X	X	△	△	△	X	X
2	X	X	△	△	△	X	X

[a] Judged by the naked eye through 10 rounds of experiments; ◎: very good, ○: good, △: bad, X: no appearance. [b] Diluted with a small amount of methanol before being added to water.

Table S4 Appearance of the FL images of the LFPs, stained with 0.5 wt% aqueous F6TQ under different conditions

Conditions	Appearance of the FL image of an LFP[a]						
Surfactant (HLB) / Conc. (wt%)	SDS (40)	Niaproof (20)	Tween80 (15.6)	Tween85 (10)	Span20 (8)	Span80[b] (4)	Span85[b] (1)
0	○	○	○	○	○	○	○
0.001	○	○	○	○	○	○	○
0.01	◎	◎	◎	◎	◎	◎	◎
0.1	○	○	◎	◎	◎	△	△
0.25	○	○	◎	◎	◎	△	△
0.5	△	△	◎	◎	◎	△	△
0.75	X	△	◎	◎	◎	△	△
1	X	X	◎	◎	◎	X	X
1.25	X	X	◎	○	○	X	X
1.5	X	X	○	○	△	X	X
1.75	X	X	○	○	△	X	X
2	X	X	○	△	△	X	X

[a] Judged by the naked eye through 10 rounds of experiments; ◎: very good, ○: good, △: bad, X: no appearance. [b] Diluted with a small amount of methanol before being added to water.

Table S5. Appearance of the FL images of the LFPs, stained with 0.5 wt% aqueous F4TBTQ under different conditions

Conditions	Appearance of the FL image of an LFP[a]						
Surfactant (HLB) / Conc. (wt%)	SDS (40)	Niaproof (20)	Tween80 (15.6)	Tween85 (10)	Span20 (8)	Span80[b] (4)	Span85[b] (1)
0	○	○	○	○	○	○	○
0.001	○	○	○	○	○	○	○
0.01	◎	◎	◎	◎	◎	◎	◎
0.1	○	○	◎	◎	◎	△	△
0.25	○	○	◎	◎	◎	△	△
0.5	△	△	◎	◎	◎	△	△
0.75	X	△	◎	◎	◎	△	△
1	X	X	◎	◎	◎	X	X
1.25	X	X	◎	○	○	X	X
1.5	X	X	○	○	△	X	X
1.75	X	X	○	○	△	X	X
2	X	X	○	△	△	X	X

[a] Judged by the naked eye through 10 rounds of experiments; ◎: very good, ○: good, △: bad, X: no appearance. [b] Diluted with a small amount of methanol before being added to water.

Table S6 Appearance of the FL images of the LFPs, stained with 0.5 wt% aqueous Rhodamine 6G under different conditions

Conditions	Appearance of the FL image of an LFP[a]						
Surfactant (HLB) Conc. (wt%)	SDS (40)	Niaproof (20)	Tween80 (15.6)	Tween85 (10)	Span20 (8)	Span80[b] (4)	Span85[b] (1)
0	○	○	○	○	○	○	○
0.001	◎	◎	◎	◎	◎	◎	◎
0.01	◎	◎	◎	◎	◎	◎	◎
0.1	◎	◎	◎	◎	◎	◎	◎
0.25	○	◎	◎	◎	◎	○	△
0.5	△	◎	◎	◎	◎	○	△
0.75	X	○	◎	◎	◎	○	△
1	X	X	◎	◎	◎	X	X
1.25	X	X	◎	◎	◎	X	X
1.5	X	X	◎	◎	◎	X	X
1.75	X	X	◎	◎	○	X	X
2	X	X	◎	◎	○	X	X

[a] Judged by the naked eye through 10 rounds of experiments; ◎: very good, ○: good, △: bad, X: no appearance. [b] Diluted with a small amount of methanol before being added to water.

Fig. S6 The FL images of an LFP stained with SPDPA–Tween85 solution before and after treatment with dilute aqueous 0.1 wt% C_{18}TAB solution.