Supporting Information

Self-assembly of Amphiphilic BODIPY Derivatives on Micropatterned Ionic Liquid Surfaces for Fluorescent Films with Excellent Stability and Sensing Performance

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1. Synthesis of amphiphilic BODIPY derivatives (1-3)

1.1 Synthesis of amphiphilic BODIPY derivatives

a) Synthesis of compound 1b

4-(5, 5-Dimethyl-1, 3, 2-dioxaborinan-2-yl) phenol (0.68 g, 3.3 mmol) was dissolved in anhydrous acetonitrile (30 mL) and stirred under N_2 atmosphere. Compound **1a** (0.95 g, 3.0 mmol), prepared by the literature method (*T. D. James et al., Chem. Sci., 2012, 3, 1049-1061)*, and K_2CO_3 (1.25 g, 9.00 mmol) were added successively to the above solution. The mixture was then refluxed for 12 hours. The organic solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (30 mL×3). The organic phase was dried with anhydrous Na_2SO_4 and evaporated to dryness. The obtained oil was purified by a silica gel column eluting with ethyl acetate/petroleum ether (1:1, *v*/*v*) to give **1b** as colorless oil (0.93 g, yield 81%). MS (*m*/*z*, ESI^+): calculated for $C_{20}H_{33}BO_7$, 419.2217 ($[M+Na]^+$), found: 419.2212; IR (KBr, ν_{max}/cm^{-1}): 3046 (C=CH), 2930, 2881 (C-H), 1601 (C=C), 1322 (C-O); ^1H NMR δ_H (600 MHz, $CDCl_3$, Me_4Si): 7.71 (2H, benzene ring), 6.89 (2H, benzene ring), 4.14 (2H, CH_2), 3.84 (2H, CH_2), 3.74 (6H, CH_2), 3.68 (8H, CH_2), 3.52 (2H, CH_2), 3.36 (3H, CH_3), 1.01 (6H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 160.97 (1C, C=<u>C</u>-O), 135.48 (2C, benzene ring), 129.37 (1C, C=<u>C</u>-B), 113.80 (2C, benzene ring), 72.24 (2C, CH_2), 71.94 (1C, CH_2), 70.84 (1C, CH_2), 70.63 (1C, CH_2), 70.61 (1C, CH_2), 70.51 (2C, CH_2), 69.71 (1C, CH_2), 67.18 (1C, CH_2), 58.99 (1C, CH_3), 31.79 (1C, $(CH_2)_2\underline{C}(CH_3)_2$), 22.03 (2C, CH_3).

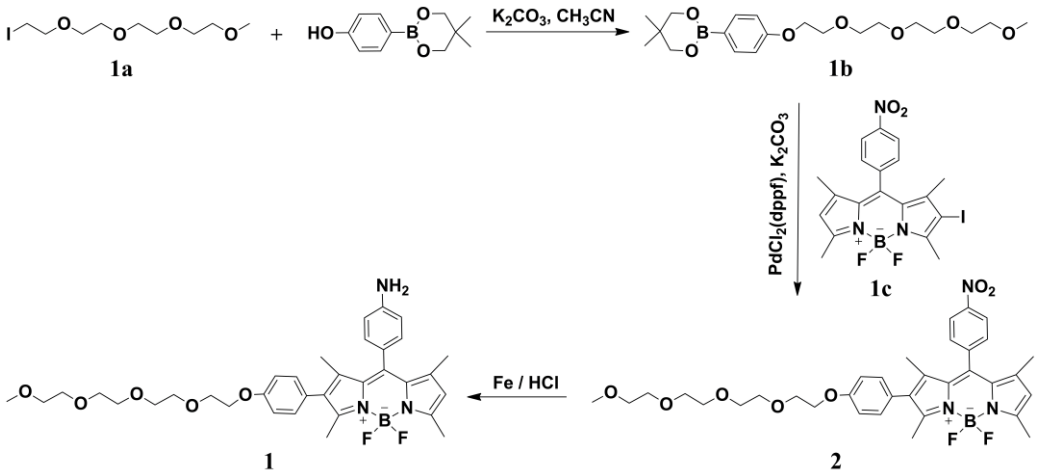

Figure S1 Synthesis of compound **1** and **2**.

b) Synthesis of compound 2

Compound **1b** (238 mg, 0.60 mmol) was dissolved in anhydrous dioxane (16 mL) and stirred under N_2 atmosphere. Compound **1c** (248 mg, 0.5 mmol), which was prepared by the literature method (*T. D. James et al., Chem. Sci., 2012, 3, 1049-1061*), K_2CO_3 (166 mg, 1.2 mmol), ultrapure water (0.8 mL), and $PdCl_2$(dppf) (122 mg, 0.15 mmol) were added successively to the above solution. The resulting mixture was then refluxed for 10 hours. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (30 mL×3) and brine (30 mL×3), respectively. The organic phase was dried with anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by silica gel column eluting with ethyl acetate to give **2** as red solids (198 mg, yield 61%). M.p.: 88.5~89.2 °C; MS (*m*/*z*, ESI$^+$): calculated for $C_{34}H_{40}BF_2N_3O_7$, 674.2825 ([M+Na]$^+$), found: 674.2801; IR (KBr, ν_{max}/cm^{-1}): 3078 (C=CH), 2875 (C-H), 1607 (C=N), 1546 (C=C), 1521(NO_2), 1074 (C-O); ^{1}H NMR δ_H (600 MHz, $CDCl_3$, Me_4Si): 8.39 (2H, benzene ring), 7.58 (2H, benzene ring), 7.04 (2H, benzene ring), 6.96 (2H, benzene ring), 6.03 (1H, pyrrole ring), 4.13 (2H, CH_2), 3.88 (2H, CH_2), 3.74 (2H, CH_2), 3.67 (8H, CH_2), 3.54 (2H, CH_2), 3.37 (3H, CH_3), 2.58 (3H, CH_3), 2.51 (3H, CH_3), 1.37 (3H, CH_3), 1.26 (3H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 158.16 (1C, benzene ring), 156.43 (1C, pyrrole ring), 155.91 (1C, pyrrole ring), 148.39 (1C, pyrrole ring), 142.27 (1C, pyrrole ring), 138.55 (1C, pyrrole ring), 138.35 (1C, benzene ring), 134.20 (1C, benzene ring), 131.12 (2C, benzene ring), 130.76 (1C, pyrrole ring), 130.36 (1C, benzene ring), 129.76 (2C, benzene ring), 125.45 (1C, C=$\underline{C}C_2$), 124.39 (1C, pyrrole ring), 121.83 (1C, pyrrole ring), 114.63 (4C, benzene ring), 71.97 (1C, CH_2), 70.87 (1C, CH_2), 70.68 (1C, CH_2), 70.66 (2C, CH_2), 70.55 (1C, CH_2), 69.74 (1C, CH_2), 67.49 (1C, CH_2), 59.04 (1C, CH_3), 14.74 (1C, CH_3), 14.67 (1C, CH_3),13.47 (1C, CH_3), 13.06 (1C, CH_3). Elemental analysis (%): calculated for $C_{34}H_{40}BF_2N_3O_7$ (651.2927): C 62.68, H 6.19, N 6.45, found: C 62.72, H 5.81, N 6.25.

c) Synthesis of compound 1

Compound **2** (130 mg, 0.2 mmol) was dissolved in anhydrous methanol (10 mL). Ultrapure water (4 mL) and reduced Fe powder (300 mg, 5.4 mmol) were added successively to the above solution. The above mixture was heated to reflux. Then, the methanol solution of hydrochloric acid (4 mL, 0.5 mol/L) was added dropwise. The reaction mixture was refluxed for 2 h until TLC monitoring indicated the complete consumption of the starting material. The mixture was filtered and the solvent was removed under reduced pressure. The residue was

purified by silica gel column eluting with ethyl acetate/petroleum ether (6:1, *v*/*v*) to give **1** crude product as red oil. The red oil was recrystallized from methanol to give **1** as red crystals (60 mg, yield 50%). M.p.: 77.0~78.1 °C; MS (*m*/*z*, ESI^+): calculated for $C_{34}H_{42}BF_2N_3O_5$, 644.3083 ($[M+Na]^+$), found: 644.3074; IR (KBr, ν_{max}/cm^{-1}): 3414, 3352 (NH_2), 3042 (C=CH), 2871 (C-H), 1607 (C=N), 1522(C=C), 1072 (C-O); ^1H NMR δ_H (600 MHz, DMSO, Me_4Si): 7.13 (2H, benzene ring), 6.96 (4H, benzene ring), 6.70 (2H, benzene ring), 6.17 (1H, pyrrole ring), 5.44 (2H, NH_2), 4.11 (2H, CH_2), 3.74 (2H, CH_2), 3.58 (2H, CH_2), 3.50 (8H, CH_2), 3.42 (2H, CH_2), 3.37 (3H, CH_3), 2.45 (3H, CH_3), 2.38 (3H, CH_3), 1.51 (3H, CH_3), 1.42 (3H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 157.84 (1C, benzene ring), 154.82 (1C, pyrrole ring), 153.88 (1C, benzene ring), 147.07 (1C, pyrrole ring), 143.05 (1C, pyrrole ring), 142.74 (1C, pyrrole ring), 139.32 (1C, pyrrole ring), 133.13 (1C, pyrrole ring), 132.22 (2C, benzene ring), 131.65 (2C, benzene ring), 131.22 (1C, benzene ring), 129.00 (1C, C=$\underline{C}C_2$), 126.25 (1C, pyrrole ring), 124.92 (1C, benzene ring), 120.95 (1C, pyrrole ring), 115.51 (2C, benzene ring), 114.45 (2C, benzene ring), 71.94 (1C, CH_2), 70.83 (1C, CH_2), 70.65 (1C, CH_2), 70.63 (1C, CH_2), 70.61 (1C, CH_2), 70.51 (1C, CH_2), 69.75 (1C, CH_2), 67.44 (1C, CH_2), 59.01 (1C, CH_3), 14.71 (1C, CH_3), 14.57 (1C, CH_3), 13.29 (1C, CH_3), 12.99 (1C, CH_3). Elemental analysis (%): calculated for $C_{34}H_{42}BF_2N_3O_5$ (621.3186): C 65.70, H 6.81, N 6.76, found: C 65.06, H 6.64, N 6.45.

1.2 Synthesis of BODIPY derivatives

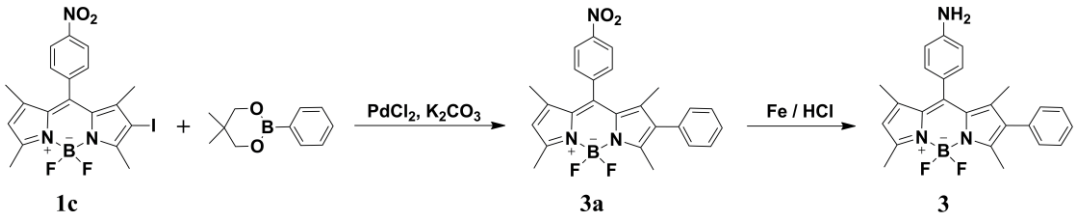

Figure S2 Synthesis of compound **3**.

a) Synthesis of compound 3a

Compound **1c** (148 mg, 0.3 mmol) was dissolved in anhydrous dioxane (16 mL) and stirred under N_2 atmosphere. 5, 5-Dimethyl-2-phenyl-1, 3, 2-dioxaborinane (57 mg, 0.3 mmol), K_2CO_3 (85 mg, 0.6 mmol), ultrapure water (0.8 mL) and $PdCl_2$(dppf) (122 mg, 0.15 mmol) were added successively to the above solution. The resulting mixture was then refluxed for 10 h. The solvent was removed under reduced pressure. The residue was

dissolved in CH_2Cl_2 (50 mL) and washed with water (30 mL×3) and brine (30 mL×3), respectively. The organic phase was dried with anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by silica gel column eluting with dichloromethane/petroleum ether (2:1, *v*/*v*) to give **3a** as red solids (110 mg, yield 82 %). M.p.: 235.8-236.2 °C; MS (*m*/*z*, ESI^+): calculated for $C_{25}H_{22}BF_2N_3O_2$, 468.1671 ($[M+Na]^+$), found: 468.1685; IR (KBr, ν_{max}/cm^{-1}): 3065 (C=CH), 2968, 2923 (C-H), 1604 (C=N), 1538 (C=C), 1469 (NO_2), 1165 (C-O); ^1H NMR δ_H (600 MHz, $CDCl_3$, Me_4Si): 8.38 (2H, benzene ring), 7.60 (2H, benzene ring), 7.06 (3H, benzene ring), 7.12 (2H, benzene ring), 6.04 (1H, pyrrole ring), 2.59 (3H, CH_3), 2.53 (3H, CH_3), 1.38 (3H, CH_3), 1.28 (3H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 156.81 (1C, pyrrole ring), 155.43 (1C, pyrrole ring), 148.38 (1C, pyrrole ring), 142.49 (1C, benzene ring), 142.20 (1C, pyrrole ring), 138.50 (1C, pyrrole ring), 134.45 (1C, benzene ring), 133.09 (1C, benzene ring), 130.89 (1C, benzene ring), 130.28 (1C, pyrrole ring), 130.05 (2C, pyrrole ring and C=<u>C</u>C_2), 129.72 (2C, benzene ring), 128.49 (3C, benzene ring), 127.38 (1C, pyrrole ring), 124.42 (2C, benzene ring), 121.91 (1C, benzene ring), 14.81 (1C, CH_3), 14.71 (1C, CH_3),13.46 (1C, CH_3), 13.03 (1C, CH_3).

b) Synthesis of compound 3

Compound **3a** (89 mg, 0.2 mmol) was dissolved in anhydrous methanol (10 mL). Ultrapure water (4 mL) and reduced Fe powder (300 mg, 5.4 mmol) were added successively to the above solution. The mixture was heated to reflux. Then, the methanol solution of hydrochloric acid (4 mL, 0.5 mol/L) was added dropwise. The reaction mixture was stirred at reflux for 2 h. The mixture was filtrated and concentrated at reduced pressure. The crude product was purified by silica gel column eluting with dichloromethane/petroleum ether (2:1, *v*/*v*) to give **3** as red solids (62 mg, yield 75%). M.p.: 234.6-235.2 °C; MS (*m*/*z*, ESI^+): calculated for $C_{25}H_{24}BF_2N_3$, 438.1928 ($[M+Na]^+$), found: 438.1946; IR (KBr, ν_{max}/cm^{-1}): 3497, 3413 (NH_2), 3044 (C=CH), 2934 (C-H), 1628 (C=N), 1544 (C=C), 1185 (C-O); ^1H NMR δ_H (600 MHz, $CDCl_3$, Me_4Si): 7.38 (3H, benzene ring), 7.14 (2H, benzene ring), 7.03 (42H, benzene ring), 6.80 (2H, benzene ring), 5.99 (1H, pyrrole ring), 3.88 (2H, NH_2), 2.57 (3H, CH_3), 2.51 (3H, CH_3), 1.51 (3H, CH_3), 1.42 (3H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 155.18 (1C, pyrrole ring), 153.55 (1C, pyrrole ring), 146.94 (1C, pyrrole ring), 143.31 (1C, benzene ring), 142.85 (1C, pyrrole ring), 139.23 (1C, pyrrole ring), 133.80 (1C, benzene ring), 133.36 (1C, benzene ring), 132.38 (1C, benzene ring), 131.65 (1C, pyrrole

ring), 130.19 (2C, pyrrole ring and C=<u>C</u>C_2), 129.00 (2C, benzene ring), 128.26 (2C, benzene ring), 126.94 (1C, benzene ring), 124.92 (1C, pyrrole ring), 121.11 (1C, benzene ring), 115.54 (2C, benzene ring), 14.74 (1C, CH_3), 14.61 (1C, CH_3), 13.29 (1C, CH_3), 12.98 (1C, CH_3).

2. Synthesis of other amphiphilic fluorescent molecules (4-6)

2.1 Synthesis of compound 4

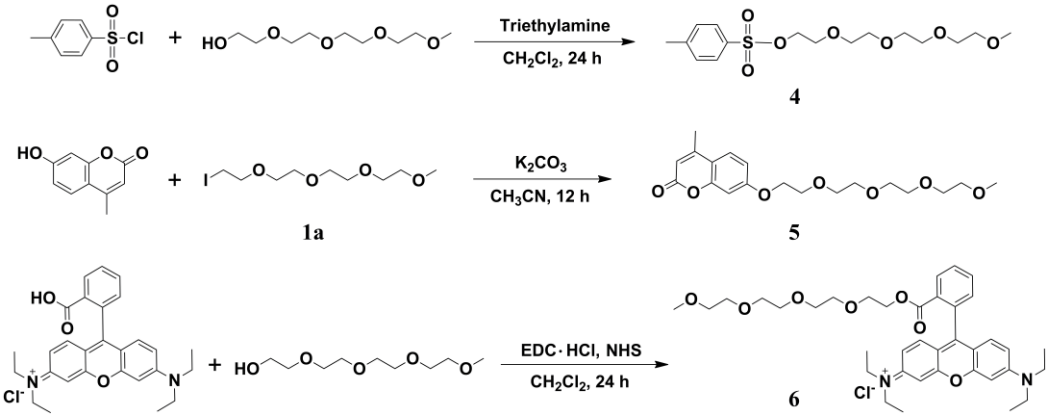

Figure S3 Synthesis of amphiphilic fluorophores.

Compound **4** was prepared by a literature method (*T. D. James et al., Chem. Sci., 2012, 3, 1049-1061)*. MS (*m*/*z*, ESI^+): calculated for $C_{16}H_{26}O_7S$, 385.1297 ($[M+Na]^+$), found: 385.1292; IR (KBr, ν_{max}/cm^{-1}): 3063 (C=CH), 2881 (C-H), 1354 (O=S=O), 1108 (C-O), 1032 (S=O); ^1H NMR δ_H (600 MHz, $CDCl_3$, Me_4Si): 7.79 (2H, benzene ring), 7.34 (2H, benzene ring), 4.15 (2H, CH_2), 3.73-3.51 (14H, CH_2), 3.36 (3H, CH_3), 2.45 (3H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 145.01 (1C, CH=<u>C</u>-CH_3), 133.06 (1C, CH=<u>C</u>-SO_2), 129.83 (2C, <u>C</u>H=C-CH_3), 127.81(2C, <u>C</u>H=C-SO_2), 71.92 (1C, CH_2), 70.71 (1C, CH_2), 70.58 (1C, CH_2), 70.56 (1C, CH_2), 70.51 (1C, CH_2), 70.47 (1C, CH_2), 69.28 (1C, CH_2), 68.66 (1C, CH_2), 58.97 (1C, CH_3), 21.47 (1C, CH=C-<u>C</u>H_3).

2.2 Synthesis of compound 5

7-Hydroxy-4-methylcoumarin (176 mg, 1.1 mmol) was dissolved in anhydrous acetonitrile (30 mL) and stirred under N_2 atmosphere. Compound **1a** (318 mg, 1.0 mmol) and K_2CO_3 (0.42 g, 3.0 mmol) were added successively to the above solution. The mixture was then refluxed1 for 12 h. The organic solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (30 mL×3). The organic phase was dried with anhydrous Na_2SO_4 and evaporated to dryness. The obtained oil was

purified by a silica gel column eluting with ethyl acetate to give **5** as colorless oil (238 mg, yield 65%). MS (*m*/*z*, ESI^+): calculated for $C_{19}H_{26}O_7$, 389.1576 ($[M+Na]^+$), found: 389.1573; IR (KBr, ν_{max}/cm^{-1}): 3080 (C=CH), 2878 (C-H), 1728 (C=O), 1619(C=C), 1140 (C-O); ^1H NMR δ_H (600 MHz, $CDCl_3$, Me_4Si): 7.45 (1H, coumarin ring), 6.80 (2H, coumarin ring), 6.07 (1H, coumarin ring), 4.15 (2H, CH_2), 3.87 (2H, CH_2), 3.57 (12H, CH_2), 3.33 (3H, CH_3), 2.35 (3H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 161.82 (1C, C=O), 161.18 (1C, CH=C-O), 155.11 (1C, C=C), 152.53 (1C, CH_3C=CH), 125.51 (1C, CH=CH), 113.62 (1C, C=C), 112.57 (1C, CH=CH), 111.87 (1C, CH_3C=CH), 101.54 (1C, CH=C-O), 71.88 (1C, CH_2), 70.83 (1C, CH_2), 70.51 (4C, CH_2), 69.37 (1C, CH_2), 67.95 (1C, CH_2), 58.93 (1C, CH_3), 18.59 (1C, CH_3C=CH).

2.3 Synthesis of compound 6

Rhodamine B (479 mg, 1.0 mmol) and methyl tetraglycol (229 mg, 1.1 mmol) were dissolved in 50 mL CH_2Cl_2 and stirred at 0 °C. EDC•HCl (288 mg, 1.5 mmol) and NHS (173 mg, 1.5 mmol) were added successively to the stirred solution. After the mixture was stirred at 0 °C for 30 minutes, the system was allowed to react for another 24 hours at room temperature. After that, the mixture was washed with water (30 mL×3). The organic phase was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by a silica gel column eluting with CH_2Cl_2/MeOH (6:1, *v:v*) to give **6** as red oil (448 mg, yield 67%). MS (*m*/*z*, ESI^+): calculated for $C_{37}H_{49}ClN_2O_7$, 633.3534 ($[M-Cl]^+$), found: 633.3546; IR (KBr, ν_{max}/cm^{-1}): 3060 (C=CH), 2987, 2926 (C-H), 1725 (C=O),1585(C=C), 1083 (C-O); ^1H NMR δ_H (600 MHz, $CDCl_3$, Me_4Si): 8.30 (1H, rhodamine B ring), 7.76 (2H, rhodamine B ring), 7.26 (1H, rhodamine B ring), 7.04 (2H, rhodamine B ring), 6.81 (4H, rhodamine B ring), 4.12 (2H, CH_2), 3.60-3.52 (22H, CH_2), 3.32 (3H, CH_3), 1.25 (12H, CH_3); ^{13}C NMR δ_C (600 MHz, $CDCl_3$, Me_4Si): 164.90 (1C, C=O), 158.87 (1C, C=C-N(CH_2CH_3)$_2$), 157.77 (1C, C=C-O), 155.55 (1C, C=C-O), 133.67 (1C, C=C), 133.15 (1C, C=CH), 131.51 (1C, CH=C), 131.33 (1C, CH=C), 130.37 (2C, CH=C), 130.19 (2C, CH=C), 129.74 (2C, CH=CH), 114.26 (2C, C=CH), 113.57 (2C, CH=CH), 96.30 (2C, CH=C), 71.89 (1C, CH_2), 70.53 (1C, CH_2), 70.47 (2C, CH_2), 70.45 (2C, CH_2), 68.67 (1C, CH_2), 64.64 (1C, CH_2), 58.98 (1C, CH_3), 46.15 (2C, CH_2), 29.65 (2C, CH_2), 12.66 (4C, CH_3).

3. Frontier molecular orbitals computation

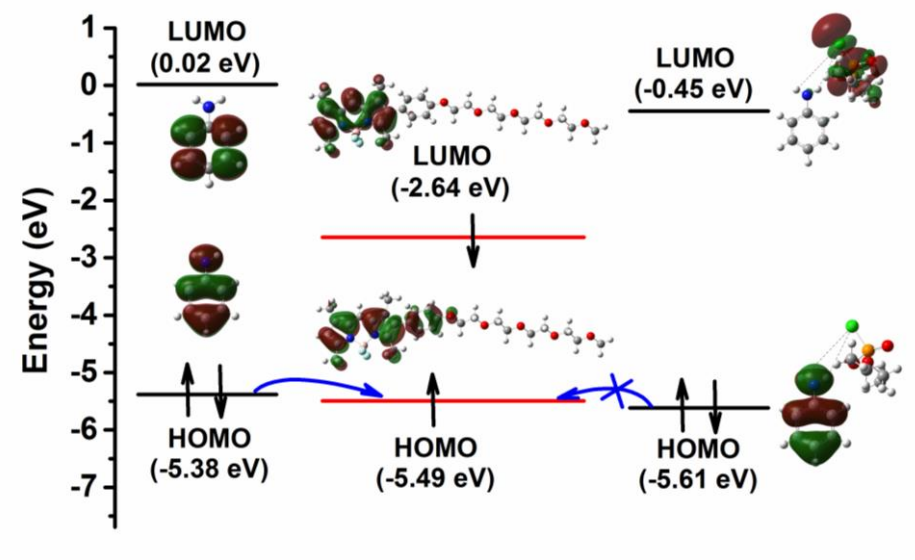

Figure S4 Computed frontier molecular orbitals (isovalue = 0.02) and their corresponding energy levels of aniline group, BODIPY skeleton and aniline-DCP complex, calculated at B3LYP/6-311G(d,p) level.

4. Characterization of 1/ILs microarrays

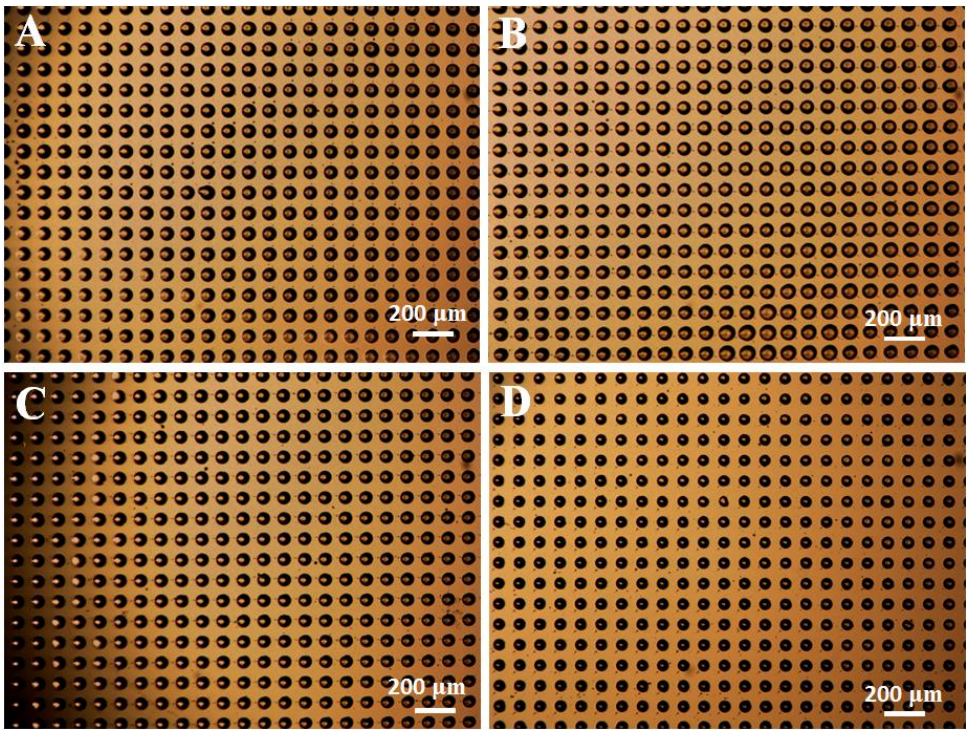

Figure S5 Optical micrographs of **1**/ILs (A EMIM]BF_4, B [OMIM]BF_4, C [BMIM]PF_6) and **1**/PEG200 (D) microarrays. The concentration of **1** is 80 μM.

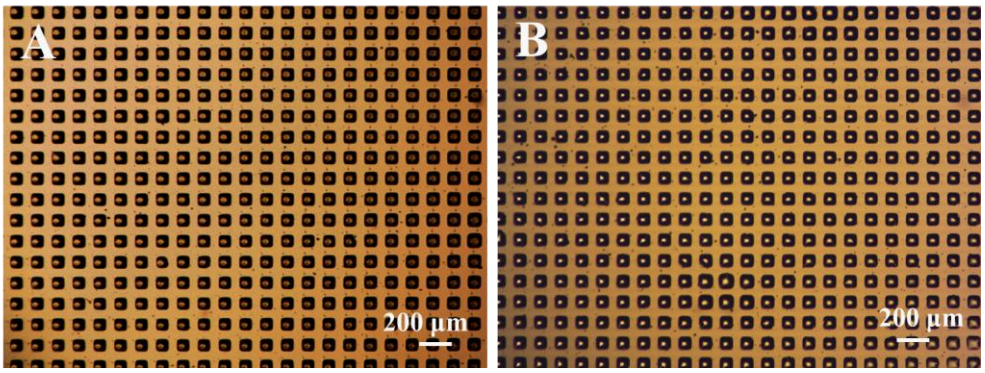

Figure S6 Optical micrographs of newly prepared **1**/[BMIM]BF_4 microarray (A) and the one being left for 6 months (B). The concentration of **1** is 80 μM.

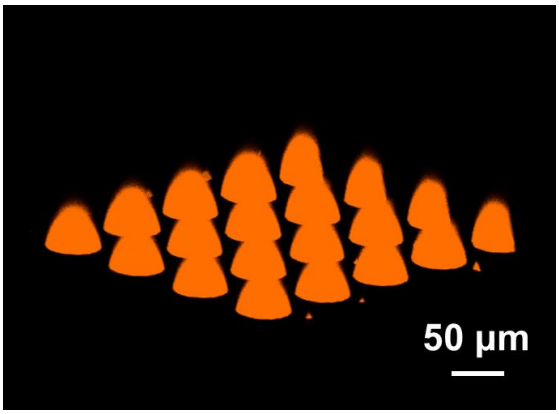

Figure S7 Three-dimensional reconstructed confocal images of **1** containing IL microdroplets.

5. Surface tension and surface pressure-area isotherm measurements

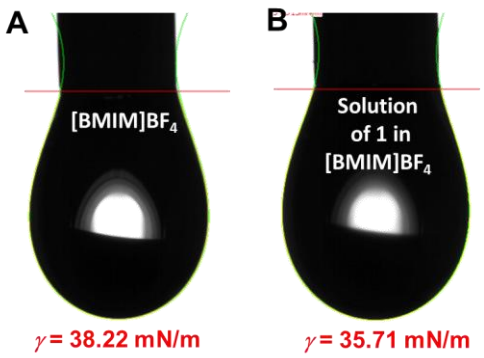

Figure S8 Pendant droplets of [BMIM]BF_4 (A) and solution of **1** in [BMIM]BF_4 (B) in the surface tension measurement.

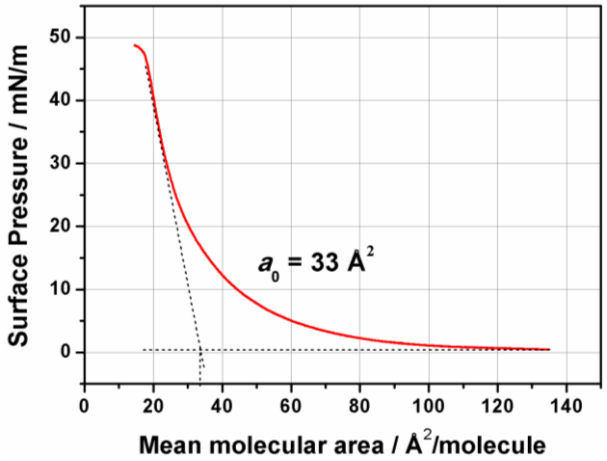

Figure S9 Surface pressure-area (*Π*-*A*) isotherms of **1** at air-water interface.

6. Photochemical stability studies of compound 1 in different films

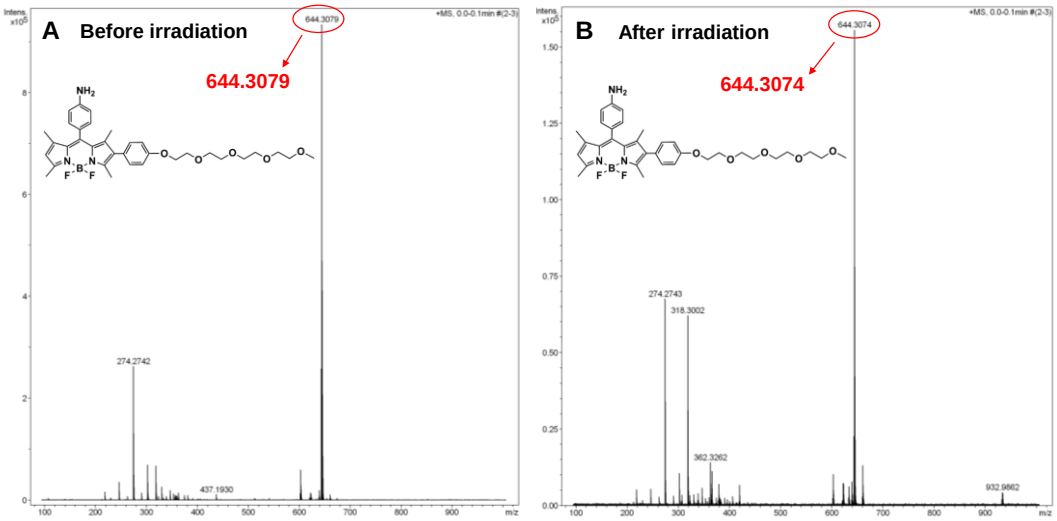

Figure S10 MS spectra (*m*/*z*, ESI$^+$) of compound **1** in monolayer film before (A) and after (B) 30 mins of irradiation with a 450 W xenon lamp.

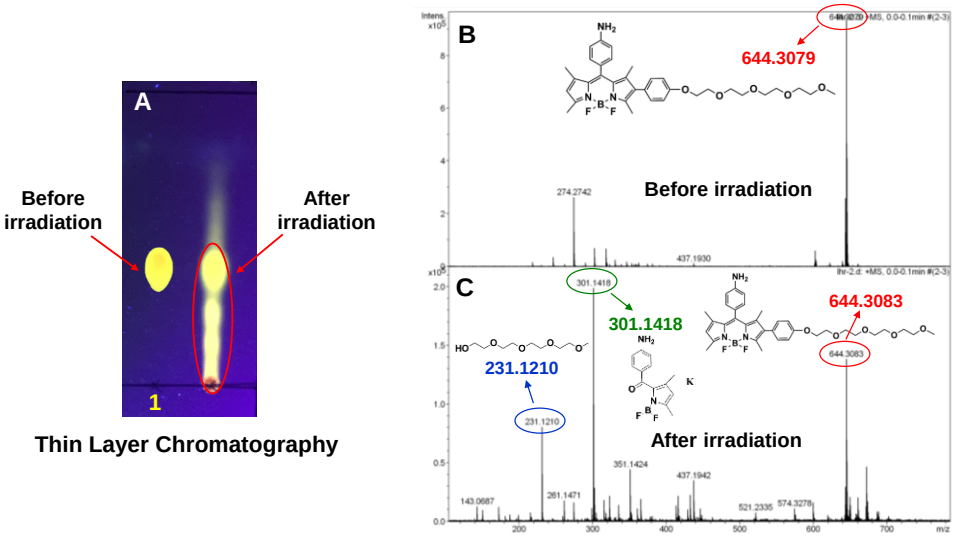

Figure S11 Thin layer chromatography (A) and MS spectra (*m*/*z*, ESI$^+$) of compound **1** in solid-state film before (B) and after (C) 30 mins of irradiation with a 450 W xenon lamp.

7. Characterization of the photochemical stability of amphiphilic fluorophores in different films

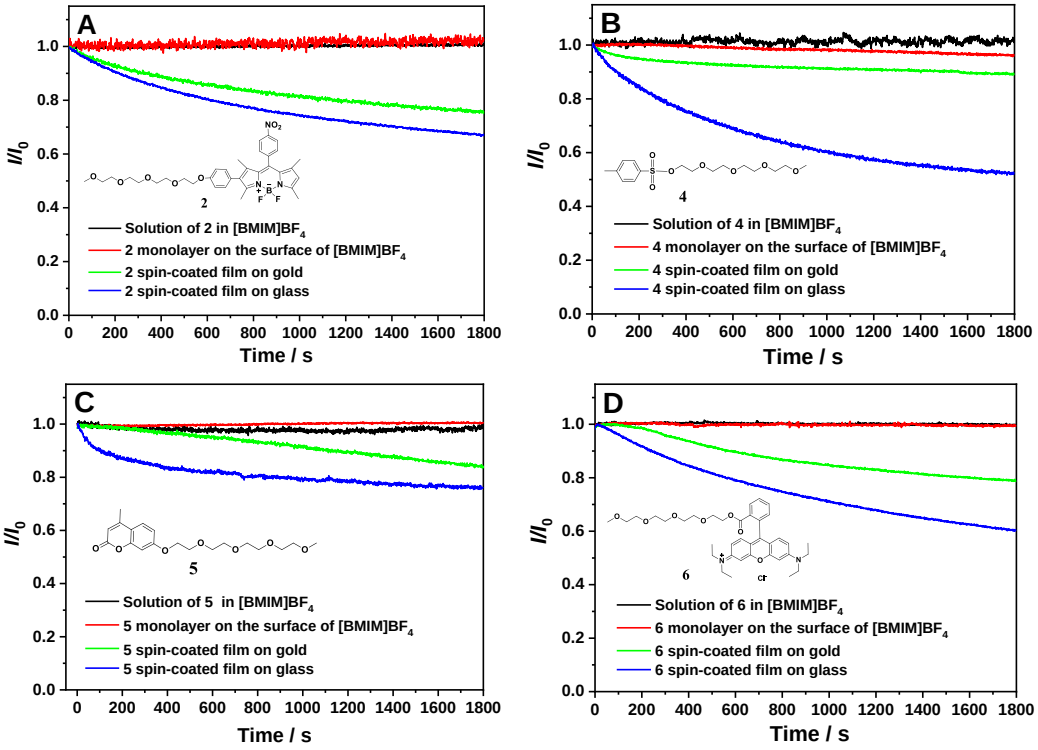

Figure S12 Evolution of the normalized fluorescence intensity (I/I_0) as a function of illumination time for **2**, **4**, **5**, **6** in different microenvironments. A 450 W xenon lamp was used as a light source. The fluorescence intensity was monitored at the peak value for this analysis. The concentration of all compounds was 80 μM.

8. Schematic illustration of the home-made sensing platform

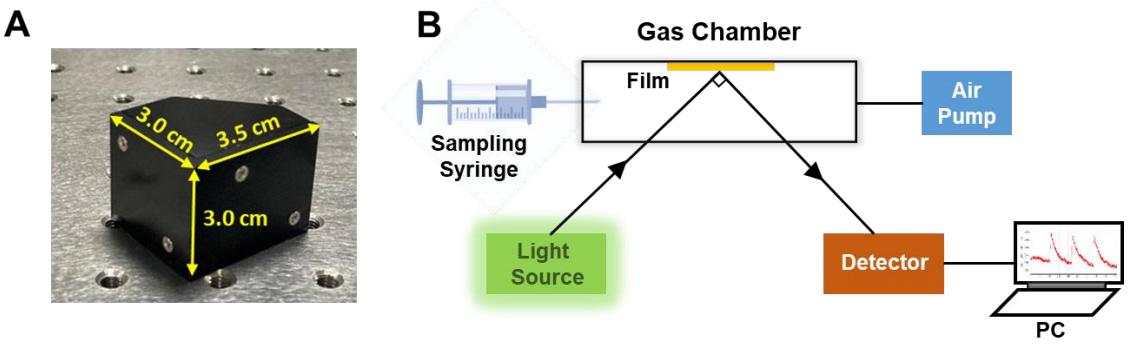

Figure S13 (A) Picture of the fluorescent sensor. (B) Schematic illustration of the home-made sensing platform for the fluorescent film tests.

9. Fluorescent property studies of 3 in [BMIM]BF_4

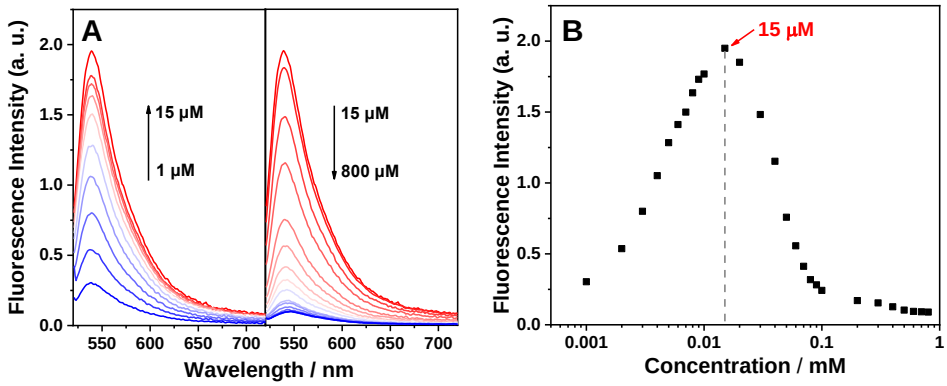

Figure S14 (A) Fluorescence emission spectra of **3** in [BMIM]BF_4 with various concentrations. (B) Plots of the fluorescence emission intensity against the concentration of **3**. The fluorescence intensity at 540 nm was selected for analysis, λ_{ex} = 518 nm.

10. Sensing performance of 3/[BMIM]BF_4 microarray to DCP

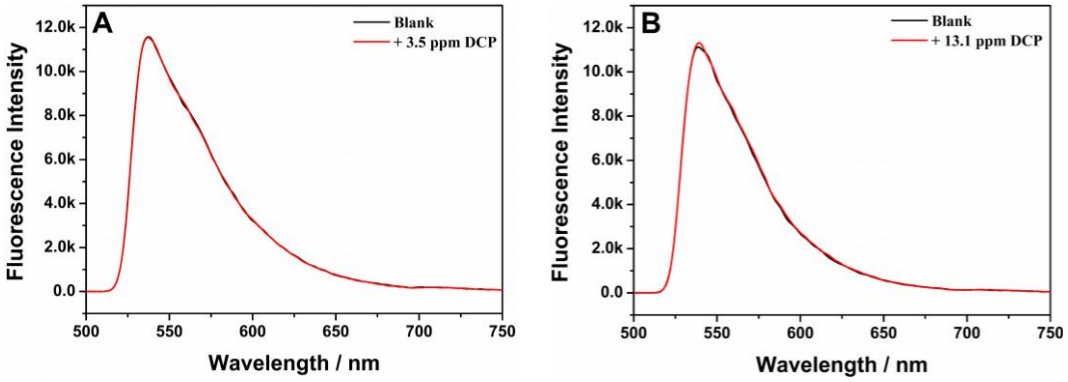

Figure S15 Fluorescence emission spectra of **3**/[BMIM]BF_4 microarray before and after adding DCP vapor with different concentrations.

11. Sensing mechanism studies

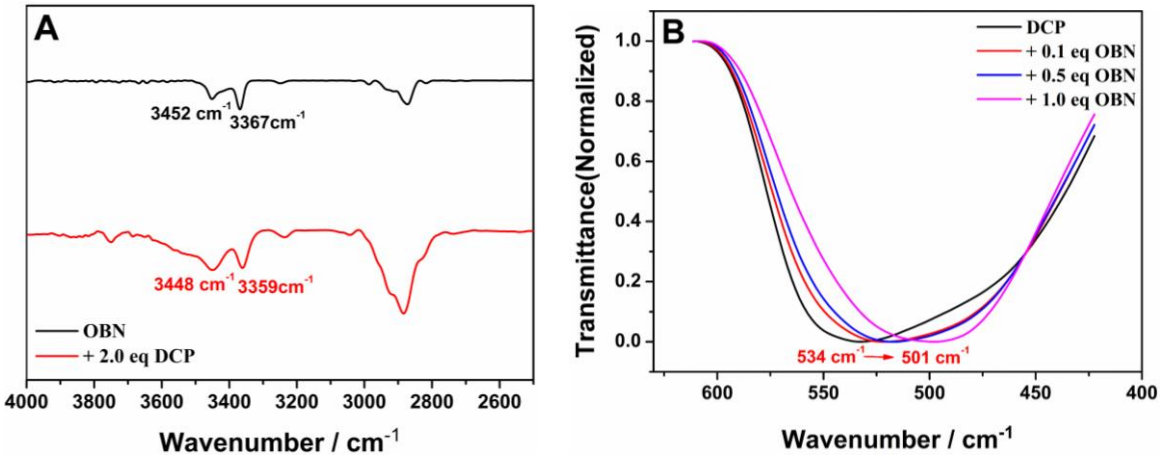

Figure S16 (A) FT-IR spectra of compound **1** before and after adding DCP vapor; (B) FT-IR spectra of DCP upon adding different mole ratios of compound **1**.

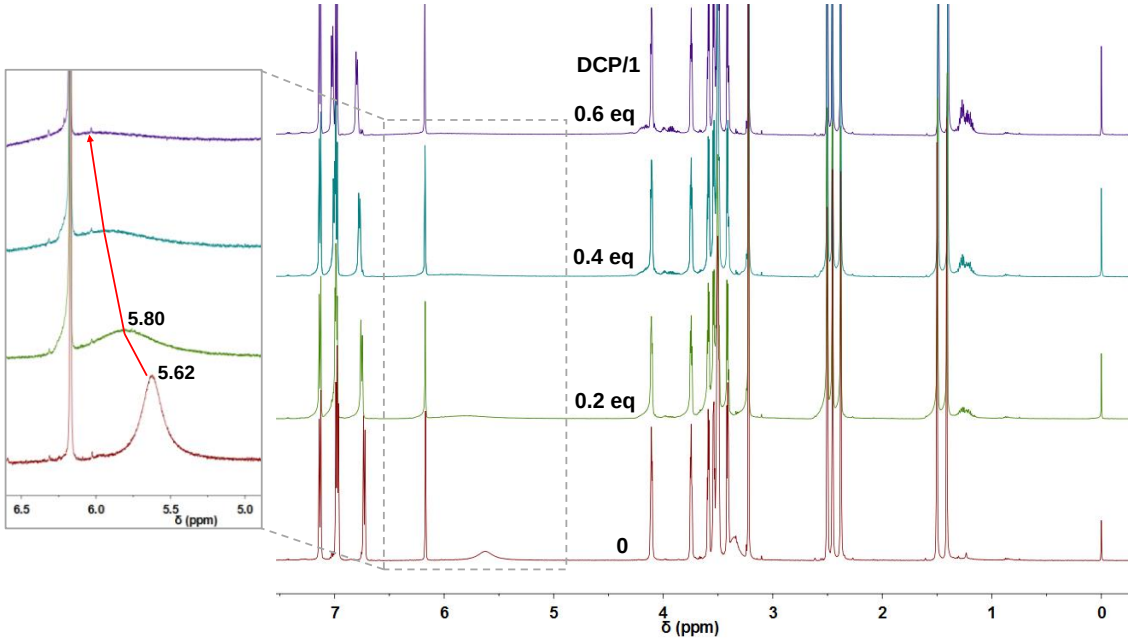

Figure S17 ^{1}H NMR spectra of compound **1** upon adding different mole ratios of DCP in DMSO-d6. The concentration of compound **1** is 20 mmol/L.