

Electronic Supplementary Information

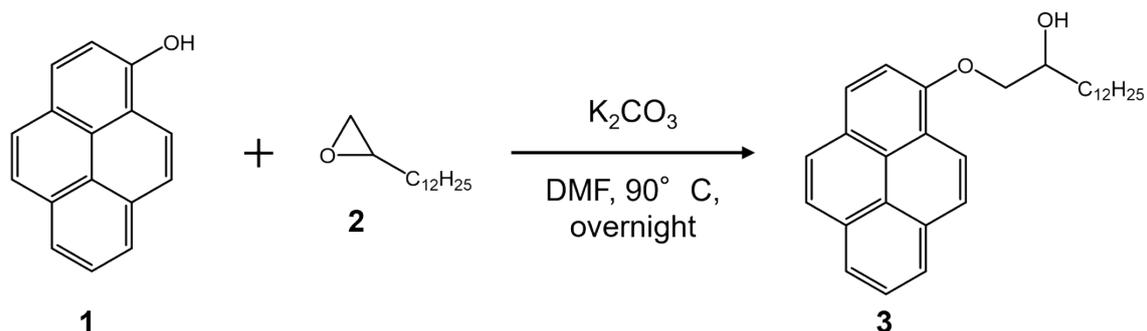
Förster Resonance Energy Transfer-Based Anion Responsive Nanoemulsion Optodes: Importance of Fluorescent Dye Liquid Lipophilicity and Ionophore-dye Interaction for Stable and Background-free Anion Response

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Scheme S1: 1st step for Synthesis of [P₆₆₆₁₄][HPES].

Synthesis of Compound (3)

1-Hydroxypyrene (**1**) (2.01 g, 9.19 mmol) was dissolved in DMF (20 mL), followed by the addition of K₂CO₃ (1.29 g, 9.32 mmol). The mixture was stirred for 1 hour at room temperature.

Subsequently, 1,2-epoxytetradecane (**2**) (1.95 g, 9.20 mmol), pre-dissolved in DMF (15 mL), was added, and the reaction mixture was heated to 90 °C and stirred overnight. After cooling, the reaction mixture was subjected to liquid–liquid extraction using a mixture of hexane and ethyl acetate (4:1) and 1 M HCl. The organic layer was washed twice with deionized water and concentrated under reduced pressure using a rotary evaporator. The crude product was purified by normal-phase silica gel column chromatography (eluent: hexane/chloroform = 1:9) to afford compound (**3**) as a purified product (0.956 g, 24% yield).

¹H-NMR (400 MHz, CDCl₃) δ (ppm) 0.876 (t, 3H), 1.247-1.671 (m, 22H), 4.086-4.213 (m, 3H), 7.395 (d, 1H), 7.847-8.056 (m, 7H), 8.347 (d, 1H)

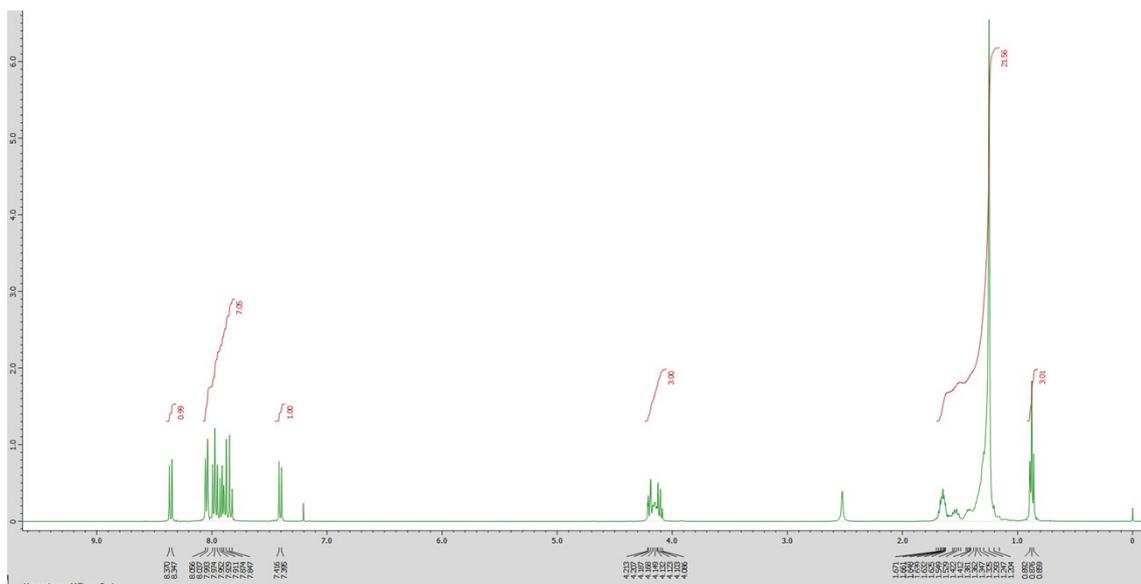
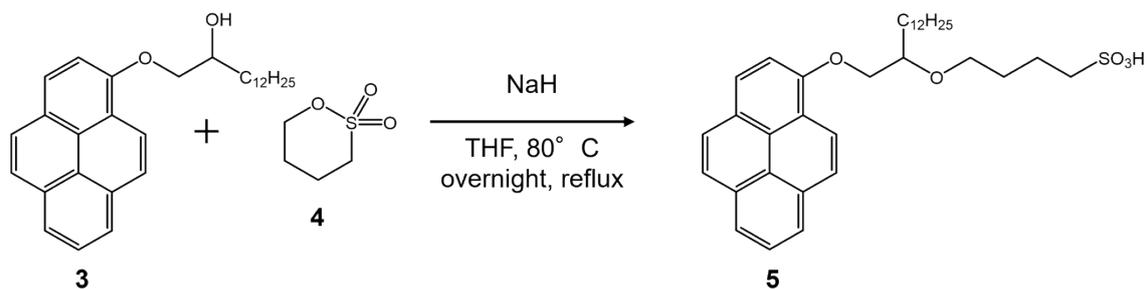


Fig. S1: ¹H-NMR spectrum of compound **3**.



Scheme S2: 2nd step for Synthesis of [P₆₆₆₁₄][HPES].

Synthesis of Compound (5):

Compound (3) (546 mg, 1.27 mmol) was dissolved in THF (20 mL), and NaH (94.2 mg, 3.77 mmol) was added. The mixture was heated and stirred at 80 °C. After 1 hour, 1,4-butanedithione (4) (190 mg, 1.40 mmol), pre-dissolved in THF (20 mL), was added, and the reaction mixture was refluxed overnight at 80 °C. The reaction mixture was subjected to liquid–liquid extraction using a mixture of hexane and ethyl acetate (4:1) and 1 M HCl. The organic layer was collected, and the aqueous layer was further extracted with water and chloroform. The combined organic layers were concentrated under reduced pressure using a rotary evaporator to afford the crude product. Purification was performed by normal-phase silica gel column chromatography (eluent: methanol/chloroform = 2:8 → 2.5:7.5), yielding compound (5) as a purified product (151 mg, 21% yield).

¹H-NMR (400 MHz, DMSO-*d*₆) δ (ppm) 0.829 (t, 3H), 1.176-1.675 (m, 26H), 2.446 (t, 2H), 3.569 (m, 1H), 3.692-3.818 (m, 2H), 4.344 (t, 2H), 7.780 (d, 1H), 7.960-8.258 (m, 7H) 8.363 (d, 1H)

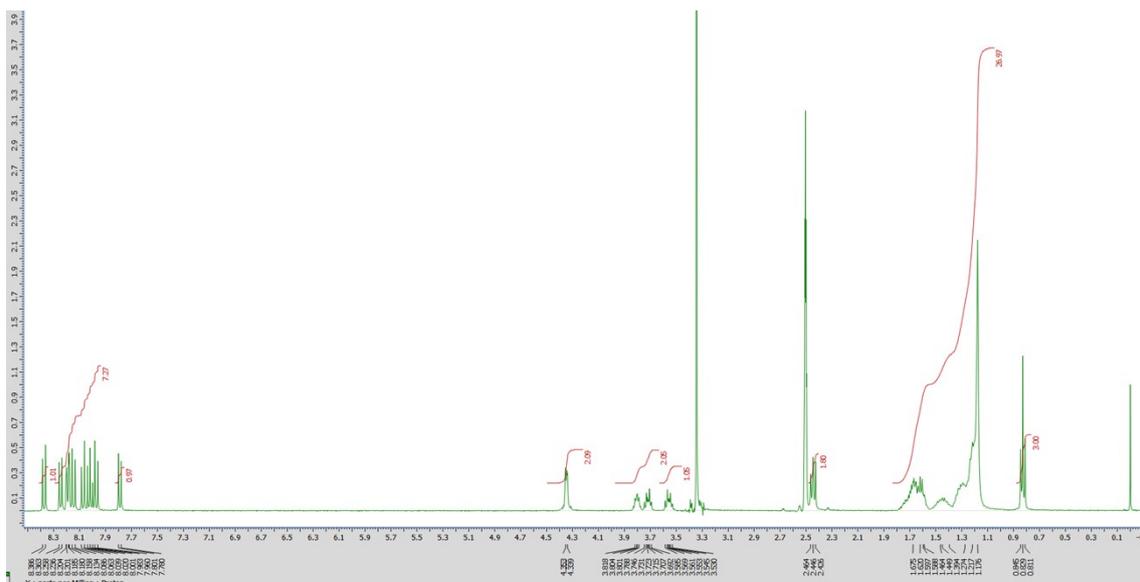
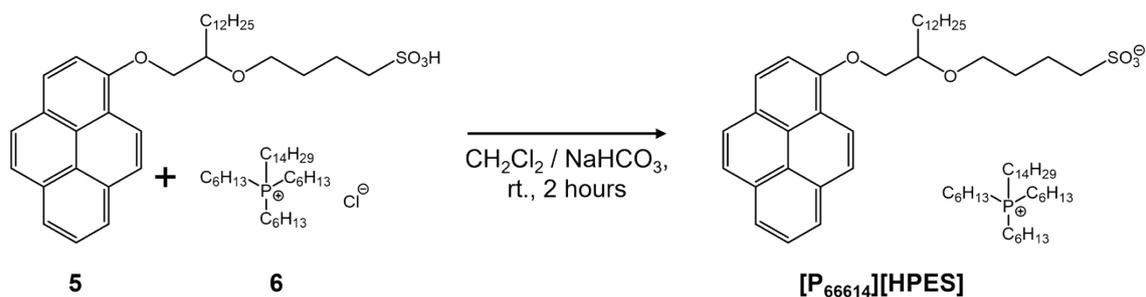


Fig. S2: ¹H-NMR spectrum of compound 5.



Scheme S3: 3rd step for Synthesis of [P₆₆₆₁₄][HPES].

Synthesis of [P₆₆₆₁₄][HPES]:

Compound (**5**) (151 mg, 0.266 mmol) and [P₆₆₆₁₄][Cl] (**6**) (133 mg, 0.257 mmol) were dissolved in CH₂Cl₂ (40 mL), followed by the addition of saturated aqueous NaHCO₃ (10 mL). The mixture was stirred at room temperature for 2 hours. The organic layer was separated, washed twice with water, dried over Na₂SO₄, and concentrated under reduced pressure using a rotary evaporator. The product, [P₆₆₆₁₄][HPES], was obtained as a brown liquid (278 mg, >99% yield).

¹H-NMR (400 MHz, CDCl₃) δ (ppm) 0.849-0.889 (m, 15H), 1.232-1.575 (m, 76H), 2.223-2.295 (m, 8H), 2.863 (t, 2H), 3.627-3.843 (m, 3H), 4.233-4.351 (m, 2H), 7.534 (d, 1H), 7.858-8.105 (m, 7H), 8.431 (d, 1H)

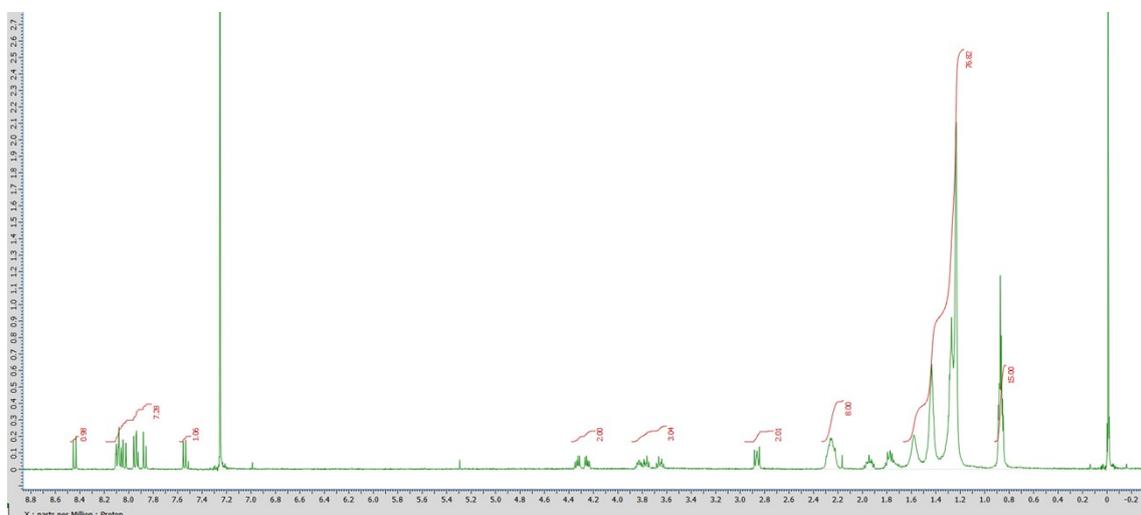


Fig. S3: ¹H-NMR spectrum of [P₆₆₆₁₄][HPES].

ESI-TOF-MS (m/z) $C_{32}H_{68}P^+$ ($[M]^+$): 483.5

(JMS-T100LP AccuTOF LC-plus 4G (JEOL), JMS-700 Mstation (JEOL))

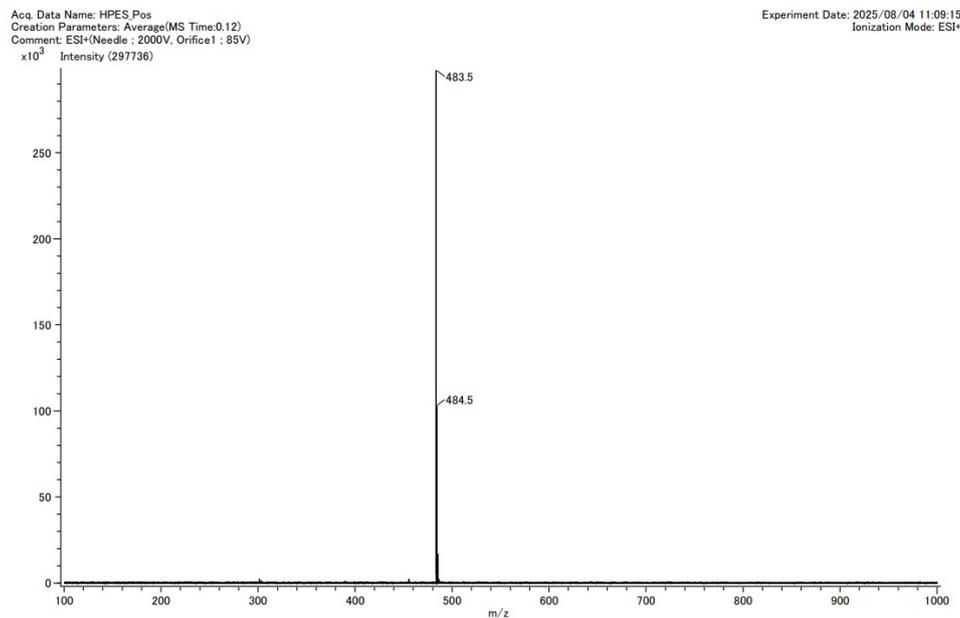


Fig. S4: mass spectrum of $[P_{66614}][HPES]$ (positive mode).

ESI-TOF-MS (m/z) $C_{34}H_{45}O_5S^-$ ($[M]^-$): 565.4

(JMS-T100LP AccuTOF LC-plus 4G (JEOL), JMS-700 Mstation (JEOL))

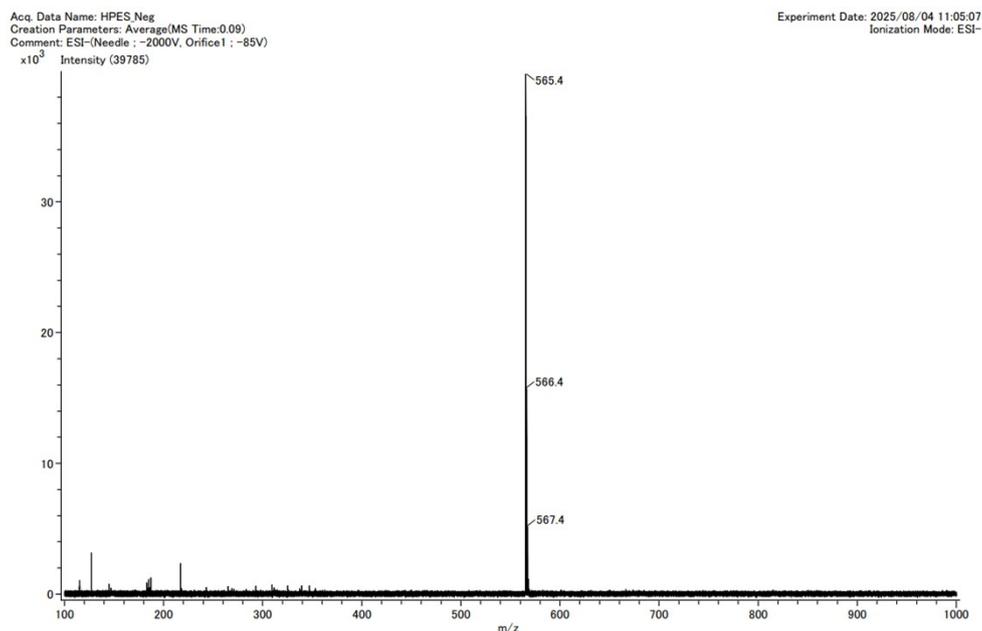


Fig. S5: mass spectrum of $[P_{66614}][HPES]$ (negative mode).

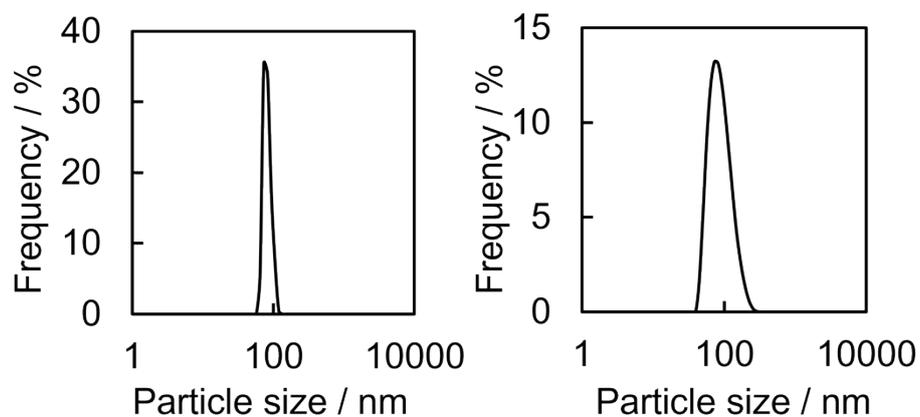


Fig. S6: Particle size distribution of each FRET-NE without TTU-1 (left) and with TTU-1 (right).
without TTU-1 : 72.5 nm, 0.302 (PDI), with TTU-1 : 79.2 nm, 0.222 (PDI).

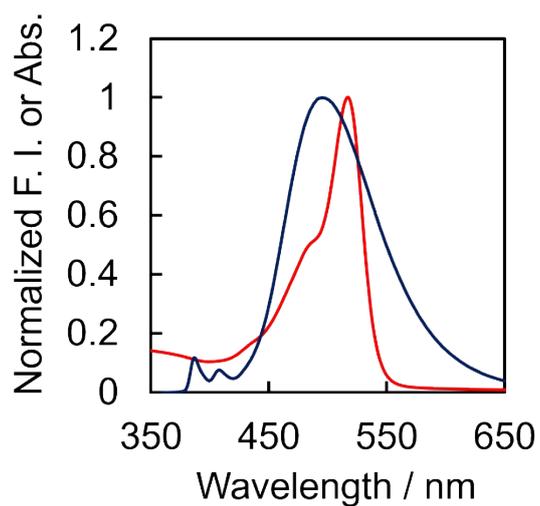


Fig. S7: Normalized fluorescence spectrum of NE prepared by donor dye liquid [P₆₆₆₁₄][HPES] (blue) and absorption spectrum of NE prepared by acceptor dye [P₆₆₆₁₄][12-FL] and bis(2-ethylhexyl) sebacate (DOS) (red).

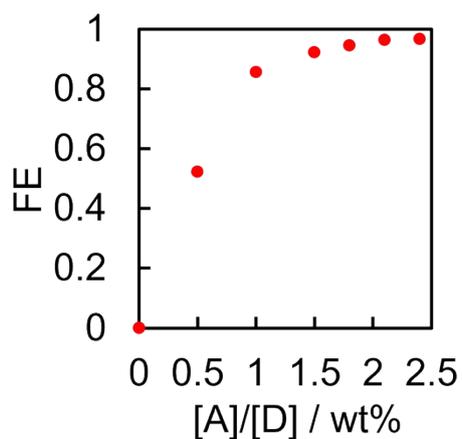


Fig. S8: FRET efficiency at various amount of acceptor dye doping
 FE was calculated based on the fluorescence intensity of the FRET-NE system under NaOH conditions.

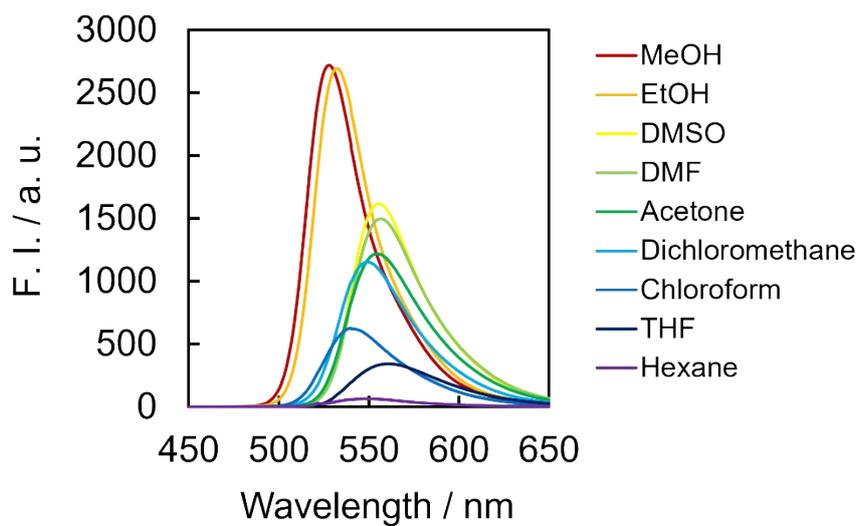


Fig.S9: Fluorescence spectra of $[P_{66614}][12\text{-FL}]$ in various solvents (5×10^{-6} M).

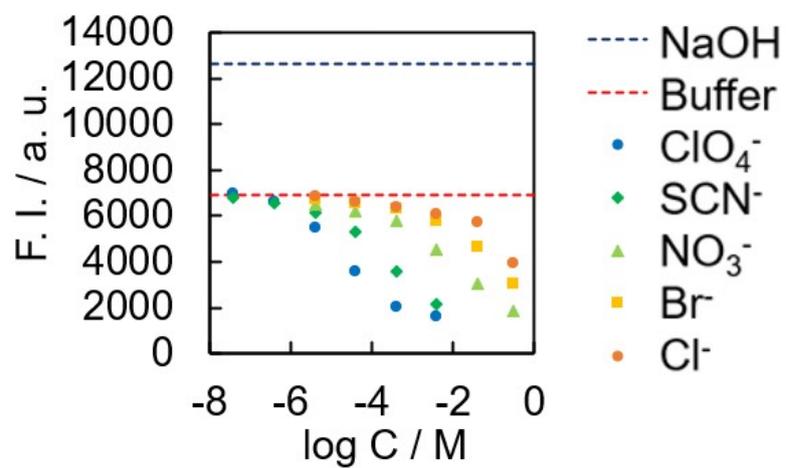


Fig. S10: Fluorescence intensity of the FRET-NE without TTU-1 for various anions (excitation wavelength: 348 nm)