Electronic Supplementary Information

Multiple emissions from indenofluorenedione in solution and polymer films

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**Experimental section**

**Materials.** All chemicals were purchased from Sigma-Aldrich, Kanto Chemical, Tokyo Chemical Industry, or Wako Pure Chemical Industries and used as received. Anhydrous DMF, anhydrous THF, p-xylene and methylcyclohexene (MCH) spectroscopic grade (Wako Pure Chemical Industries) were used for analysis. Polysulfone (PSF) \( M_w \) is 60 kDa and polystyrene (PS) \( M_w \) is 350 kDa were used as host polymer matrices. Fluorenone derivatives (IFO and FO) were synthesized according to the literature procedures shown below (Scheme S1).

**General method.** \( ^1H \) NMR and \( ^{13}C \) NMR spectra were recorded on a JEOL ECS-400; chemical shifts were recorded in ppm relative to TMS (0 ppm for \( ^1H \) NMR as an internal standard). UV-Vis absorption and fluorescence spectra were obtained on a Hitachi U-2900 spectrophotometer and a Hitachi F-7000 spectrophotometer, respectively. Fluorescence quantum yields were obtained on a Hamamatsu Photonics, Absolute PL Quantum Yield Measurement System, C9920-02G. Fluorescence lifetimes were measured using an IBH (FluoroCube) time correlated picosecond single photon counting (TCSPC) system. Samples were excited using a pulsed diode laser (NanoLED-11, <100 ps pulse duration) at a wavelength of 375 nm with a repetition rate of 1 MHz.
**Scheme S1. Synthetic routes to IFO and FO.**

(a) C₈H₁₇Br, CH₃CN, K₂CO₃, reflux, 2 days; (b) n-BuLi, THF, –78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, –78 °C to r.t.; (c) Pd(PPh₃)₄, Na₂CO₃, toluene, H₂O, EtOH, reflux, overnight.

**Synthesis of 1.** 4-Bromocatechol (5 g, 26.45 mmol) and K₂CO₃ (22 g, 158.7 mmol) were dissolved in acetonitrile (100 mL) and the mixture was heated to reflux for 1 hour. Then 1-bromoctanoate (12.77 g, 66.13 mmol) was added and the mixture was kept refluxed for 2 days with vigorous stirring. After cooling, the mixture was poured into water and extracted with Et₂O for three times. The combined organic layers were washed with 2 M NaOH, dried over anhydrous MgSO₄ and concentrated to give pale brown solids. The crude products were freed from the residual 1-bromoctanoate by distillation and purified by column chromatography (silica gel) with hexane:DCM (2:1) as the eluent, affording the pure product as a white solid. (10.1 g, 93% yield). ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ 0.84-0.95 (m, 6H), 1.29-1.34 (m, 20H), 1.74-1.85 (m, 4H), 3.91-4.0 (m, 4H), 6.72-6.75 (d, 1H, J = 6.6 Hz), 6.97-7.01 (m, 2H) ppm. ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ 14.09, 22.66, 25.97, 29.13, 29.25, 29.33, 29.35, 31.81, 69.37, 69.53, 112.77, 115.14, 116.91, 123.41, 148.36, 150.03. MALDI/TOF-MS: m/z = 413.44 (calc. = 413.56).
Synthesis of 2. Compound 1 (5 g, 12.1 mmol) was dissolved in anhydrous THF (65 mL) by stirring under argon. The reaction temperature was reduced to −78 °C by using a slush bath (ethyl acetate/liq. N₂) and continued stirring for 10 minutes. 2.65 M n-BuLi solution in hexane (5.5 mL) was added dropwise and the mixture was stirred at −78 °C for 1 h. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.75 g, 36.3 mmol) was added rapidly to the reaction mixture, and the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel) with hexane:CHCl₃ = 2:1 as eluent to provide the pure product as liquid. (3.93 g, 71% yield). 1H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ 0.86-0.90 (m, 6H), 1.25-1.29 (m, 16H), 1.31 (s, 12H), 1.33-1.37 (m, 4H), 1.78-1.85 (m, 4H), 3.97-4.04 (m, 4H), 6.86-6.88 (d, 1H, J = 8 Hz), 7.29 (s, 1H), 7.37-7.39 (d, 1H, J = 7.8 Hz) ppm. 13C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ 14.09, 22.66, 24.84, 25.98, 26.04, 29.17, 29.26, 29.28, 29.38, 31.83, 68.84, 69.20, 83.54, 112.64, 119.34, 128.58, 148.47, 151.91. MALDI/TOF-MS: m/z = 460.51 (calc. = 460.67).

Synthesis of IFO. A 50 mL two-necked round bottom flask was charged with 2,8-dibromoindeno[1,2-b]fluorene-6,12-dioneS1 (856 mg, 1.95 mmol) and compound 2 (1.97 g, 4.28 mmol), sodium carbonate (1.24 g, 11.67 mmol), and evacuated and back-filled with Ar gas three times. Then 9.0 mL of dry toluene, 3.0 mL EtOH and 3.0 mL water which were already deaerated for 30 min were added under Ar. The mixture was stirred vigorously and refluxed at 90°C, tetrakis(triphenylphosphine)palladium (225 mg, 0.2 mmol) was then added to the reaction mixture. After the stirring was continued for 24 hours, the mixture was then allowed to cool to room temperature and the solvent was evaporated by reduced pressure. Water was poured into the reaction mixture and extracted by DCM for three times, the combined organic layer was washed by brine and dried over anhydrous MgSO₄. The crude product was purified by column chromatography (silica gel) with hexane:CHCl₃ (1:1) as the eluent, affording the pure
product as a dark blue solid (736 mg, 45%). $^1$H NMR (CDCl$_3$, 400 MHz, TMS, 298 K):
$\delta$ 0.87-0.91 (m, 12H), 1.30-1.35 (m, 40H), 1.82-1.88 (m, 8H), 4.03-4.10 (m, 8H), 6.95-6.97 (d, 2H, $J = 8$ Hz), 7.15-7.17 (m, 4H), 7.58-7.60 (d, 2H, $J = 7.6$ Hz), 7.73-7.76 (d, 2H, $J = 8$ Hz), 7.83 (s, 2H), 7.89 (s, 2H), ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS, 298 K): $\delta$ 14.10, 22.67, 26.05, 29.29, 29.39, 31.83, 69.31, 69.52, 112.44, 113.89, 115.93, 119.37, 120.89, 122.72, 132.34, 133.29, 134.65, 139.63, 141.68, 142.60, 145.66, 149.47, 149.51, 193.04. MALDI/TOF-MS: $m/z = 947.91$ (calc. = 947.35). Anal. Calcd for C$_{64}$H$_{82}$O$_6$•H$_2$O: C, 79.63; H, 8.77. Found: C, 80.02; H, 8.65.

**Synthesis of FO.** A 50 mL two-necked round bottom flask was charged with 2,7-dibromo-9-fluorenone (400 mg, 1.17 mmol) and compound 2 (1.18 g, 2.58 mmol), sodium carbonate (0.74 g, 7 mmol), and evacuated then back-filled with Ar gas three times. Then 12.0 mL of dry toluene, 3.0 mL EtOH and 3.0 mL water which were already deaerated for 30 min were added under Ar. The mixture was stirred vigorously and refluxed at 90 °C, tetrakis(triphenylphosphine)palladium (40.6 mg, 0.1 mmol) was then added to the reaction mixture. After the stirring was continued for 24 hours, the mixture was then allowed to cool to room temperature and the solvent was evaporated by reduced pressure. Water was poured into the reaction mixture and extracted by DCM for three times, the combined organic layer was washed by brine and dried over anhydrous MgSO$_4$. The crude product was purified by column chromatography (silica gel) with hexane:CHCl$_3$ (2:1) as the eluent, affording the pure product as orange powder (681 mg, 69% yield). $^1$H NMR (CDCl$_3$, 400 MHz, TMS, 298 K): $\delta$ 0.87-0.91 (m, 12H), 1.25-1.34 (m, 32H), 1.81-1.88 (m, 8H), 4.03-4.10 (m, 8H), 6.95-6.97 (d, 2H, $J = 8$ Hz), 7.15-7.17 (m, 4H), 7.55-7.57 (d, 2H, $J = 7.6$ Hz), 7.68-7.69 (d, 2H, $J = 7.2$ Hz), 7.87 (s, 2H), ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS, 298 K): $\delta$ 14.20, 22.77, 26.15, 29.39, 29.49, 31.92, 69.42, 69.60, 112.58, 114.04, 119.40, 120.68, 122.71, 132.82, 132.93, 135.24, 142.07, 142.07, 149.43, 149.55, 194.27. MALDI/TOF-MS: $m/z = 845.41$ (calc. = 845.26). Anal. Calcd for C$_{57}$H$_{80}$O$_5$•H$_2$O: C, 79.31; H, 9.57. Found: C, 79.56; H, 9.45.
Preparation of IFO-doped and FO-doped films.
Polysulfone or polystyrene (200 mg) and IFO (2 mg) or FO (2 mg) and were dissolved in 2 mL of CHCl₃, and the solution was drop-casted onto the surface of quartz cell. The transparent polysulfone or polystyrene films of the IFO or FO were obtained by slow evaporation of CHCl₃.

Acetonitrile detection by the IFO-doped PS film.
The IFO doped PS film was fabricated by drop casting from a CHCl₃ solution containing IFO (1 wt%) onto the surface of quartz cells until complete evaporation of CHCl₃. Pipette drops (ca. 80 µL) of organic solvents (MCH, DCM, CHCl₃, THF and toluene, acetonitrile, ethyl acetate and methanol) were placed onto the IFO-embedded PS film and resulting luminescent color change was monitored after 10 min.

References:
Scheme S2. Plausible deactivation mechanism for our designed system in polar and non-polar media.
Fig. S1 Absorption spectra of IFO (20 µM) in MCH (orange), p-xylene (red), THF (black), DMF (blue) at 298K.
Fig. S2 The absorbance at 369 nm as a function of concentration of IFO in (a) DCM, (b) THF, (c) p-xylene and (d) DMF.
Fig. S3 (a) Concentration dependence of fluorescence spectra of IFO in $p$-xylene in the range of 5 to 40 µM (from black to red line); (b) fluorescent intensity as a function of IFO concentration.
Fig. S4 Excitation spectra of IFO (19 µM) measured in (a) MCH ($\lambda_{\text{moni}} = 586$ nm), (b) $p$-xylene ($\lambda_{\text{moni}} = 610$ nm), (c) THF (green $\lambda_{\text{moni}} = 555$ nm, red $\lambda_{\text{moni}} = 618$ nm) and (d) in DMF ($\lambda_{\text{moni}} = 437$ nm) dash lines are the corresponding absorption spectra.
Fig. S5 Fluorescence lifetime decay profiles of IFO measured in (a) MCH ($\lambda_{\text{moni}} = 585$ nm), (b) $p$-xylene ($\lambda_{\text{moni}} = 610$ nm), (c) THF (blue $\lambda_{\text{moni}} = 420$ nm, red $\lambda_{\text{moni}} = 619$ nm) and (d) DMF ($\lambda_{\text{moni}} = 435$ nm) at 298K. Excitation wavelengths are 375 nm. IRF: Instrumental Response Function.
Fig. S6 (a) Absorption and (b) emission spectra of FO (15 μM) measured in DMF (blue), MCH (green), p-xylene (orange) and THF (black) at 298K. Excitation wavelengths are 345 nm. The intensities were normalized at the emission maximum. Inset: photographs under irradiation with 365 nm UV-lamp.
**Fig. S7** Fluorescence lifetime decay profiles of FO measured in (a) MCH (\(\lambda_{\text{moni}} = 523\) nm), (b) \(p\)-xylene (\(\lambda_{\text{moni}} = 546\) nm), (c) THF (\(\lambda_{\text{moni}} = 557\) nm) and (d) DMF (blue \(\lambda_{\text{moni}} = 420\) nm, red \(\lambda_{\text{moni}} = 570\) nm) at 298K. Excitation wavelengths are 375 nm. IRF: Instrumental Response Function.
Fig. S8  Excitation spectra of FO (15 μM) measured in (a) MCH (black, $\lambda_{\text{moni}} = 520$ nm), p-xylene (blue $\lambda_{\text{moni}} = 547$ nm), THF (green $\lambda_{\text{moni}} = 557$ nm) and (b) DMF (blue $\lambda_{\text{moni}} = 422$ nm, red $\lambda_{\text{moni}} = 570$ nm) dash lines are the corresponding absorption spectra.
Fig. S9 Excitation spectra of IFO film doped in (a) polystyrene ($\lambda_{\text{moni}} = 598$ nm) and (b) polysulfone ($\lambda_{\text{moni}} = 393$ nm) as host matrixes containing 1 wt% IFO. The dash lines are the corresponding absorption spectra.
Fig. S10 Fluorescent spectra of FO film doped in polystyrene (orange) and polysulfone (blue) as host matrixes fabricated by drop casting of CHCl$_3$ solution containing 1 wt% FO. Excitation wavelengths are 345 nm. Inset: corresponding photograph under irradiation with 365 nm UV-lamp.
Fig. S11 Excitation spectra of FO film doped in (a) polystyrene (λ_{moni} = 545 nm) and (b) polysulfone (blue λ_{moni} = 385 nm, orange λ_{moni} = 550 nm) as host matrixes containing 1 wt% FO. The dash lines are the corresponding absorption spectra.
$^1$H NMR of IFO (400 MHz, in CDCl$_3$)

$^{13}$C NMR of IFO (100 MHz, in CDCl$_3$)
$^1$H NMR of FO (400 MHz, in CDCl$_3$)

$^{13}$C NMR of FO (100 MHz, in CDCl$_3$)