Electronic Supplementary Information

Multiple emissions from indenofluorenedione in solution and polymer films

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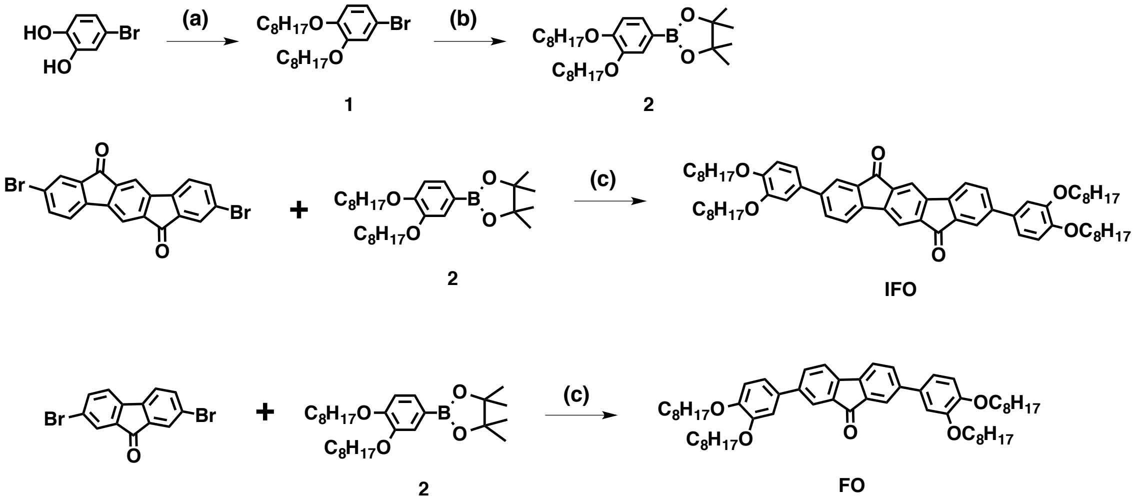
Experimental section

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 matrixes. Fluorenone derivatives (**IFO** and **FO**) were synthesized according to the literature procedures shown below (Scheme S1).[S1]

General method. ^{1}H 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 ^{1}H 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) $C_8H_{17}Br$, CH_3CN, K_2CO_3, 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) $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O, EtOH, reflux, overnight.

Synthesis of 1. 4-Bromocatechol (5 g, 26.45 mmol) and K_2CO_3 (22 g, 158.7 mmol) were dissolved in acetonitrile (100 mL) and the mixture was heated to reflux for 1 hour. Then 1-bromooctane (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 Et_2O for three times. The combined organic layers were washed with 2 M NaOH, dried over anhydrous $MgSO_4$ and concentrated to give pale brown solids. The crude products were freed from the residual 1-bromooctane 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 ($CDCl_3$, 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. ^{13}C NMR ($CDCl_3$, 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. N_2) 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 $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel) with hexane:$CHCl_3$ = 2:1 as eluent to provide the pure product as liquid. (3.93 g, 71% yield). ^{1}H NMR ($CDCl_3$, 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. ^{13}C NMR ($CDCl_3$, 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-dione[S1] (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 $MgSO_4$. The crude product was purified by column chromatography (silica gel) with hexane:$CHCl_3$ (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): δ 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): δ 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 $C_{64}H_{82}O_6{\bullet}H_2O$: 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): δ 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): δ 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, 142.70, 149.43, 149.55, 194.27. MALDI/TOF-MS: m/z = 845.41 (calc. = 845.26). Anal. Calcd for $C_{57}H_{80}O_5{\bullet}H_2O$: 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 $CHCl_3$, 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 $CHCl_3$.

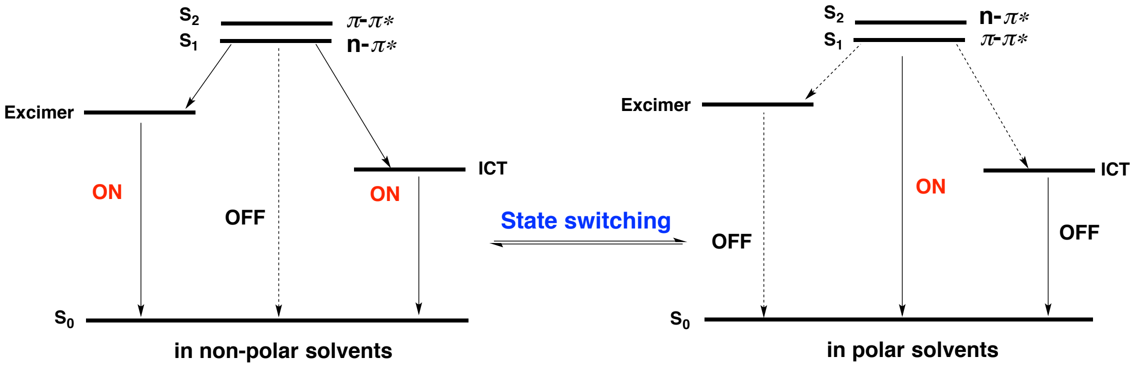
Acetonitrile detection by the IFO-doped PS film.

The **IFO** doped **PS** film was fabricated by drop casting from a $CHCl_3$ solution containing **IFO** (1 wt%) onto the surface of quartz cells until complete evaporation of $CHCl_3$. Pipette drops (*ca.* 80 μL) of organic solvents (MCH, DCM, $CHCl_3$, 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:

(S1) H. Usta, C. Risko, Z. Wang, H. Huang, M. K. Deliomeroglu, A. Zhukhovitskiy, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, **2009**, *131*, 5586.

Scheme S2. **Plausible deactivation mechanism for our designed system in polar and non-polar media.**



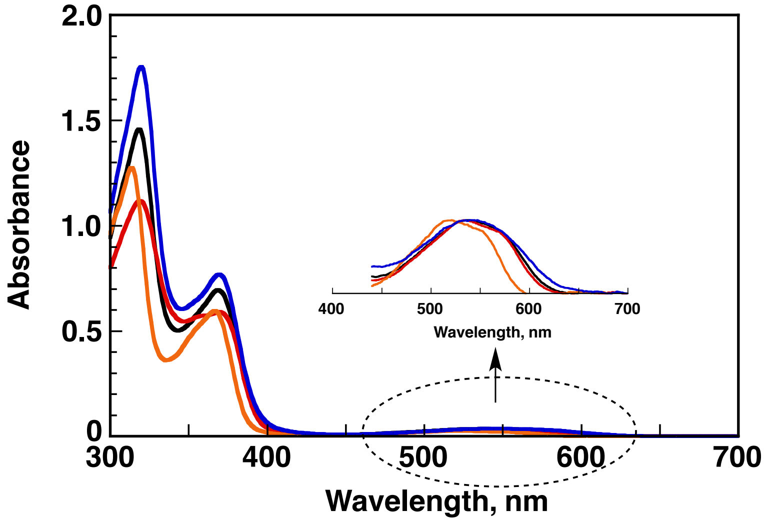


Fig. S1 Absorption spectra of **IFO** (20 μM) in MCH (orange), *p*-xylene (red), THF (black), DMF (blue) at 298K.

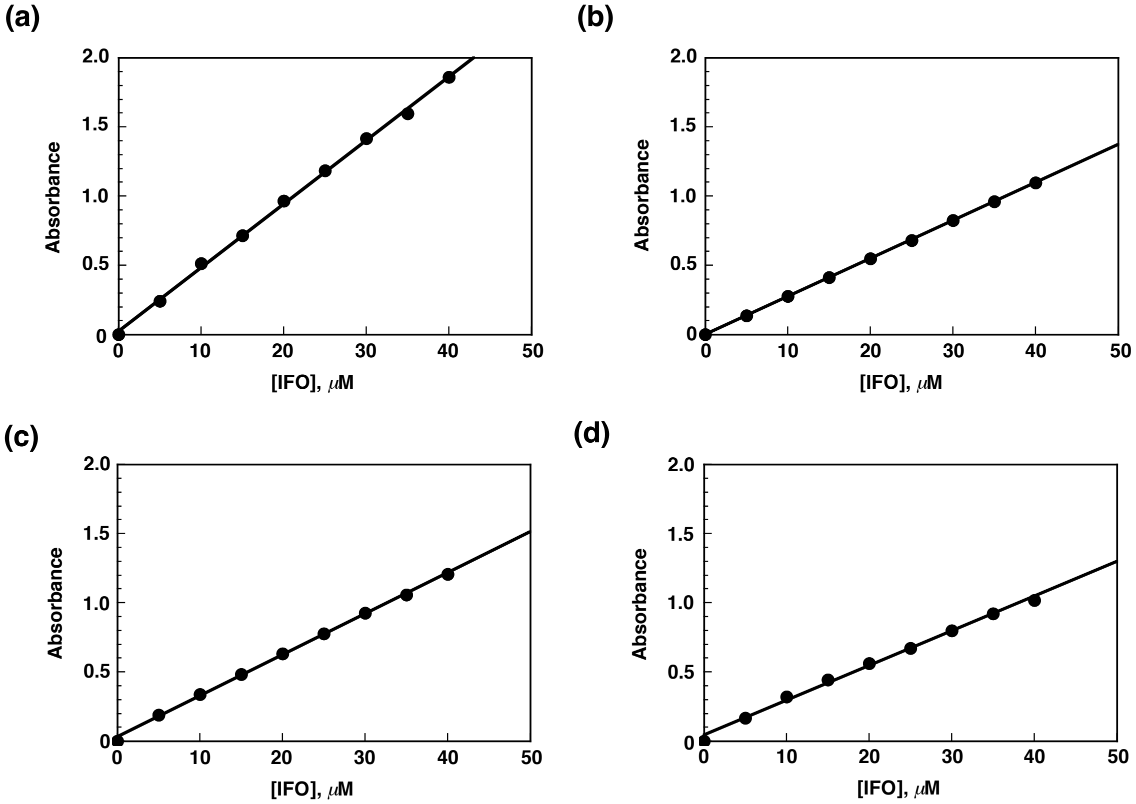


Fig. S2 The absorbance at 369 nm as a function of concentration of **IFO** in (a) DCM, (b) THF, (c) *p*-xylene and (d) DMF.

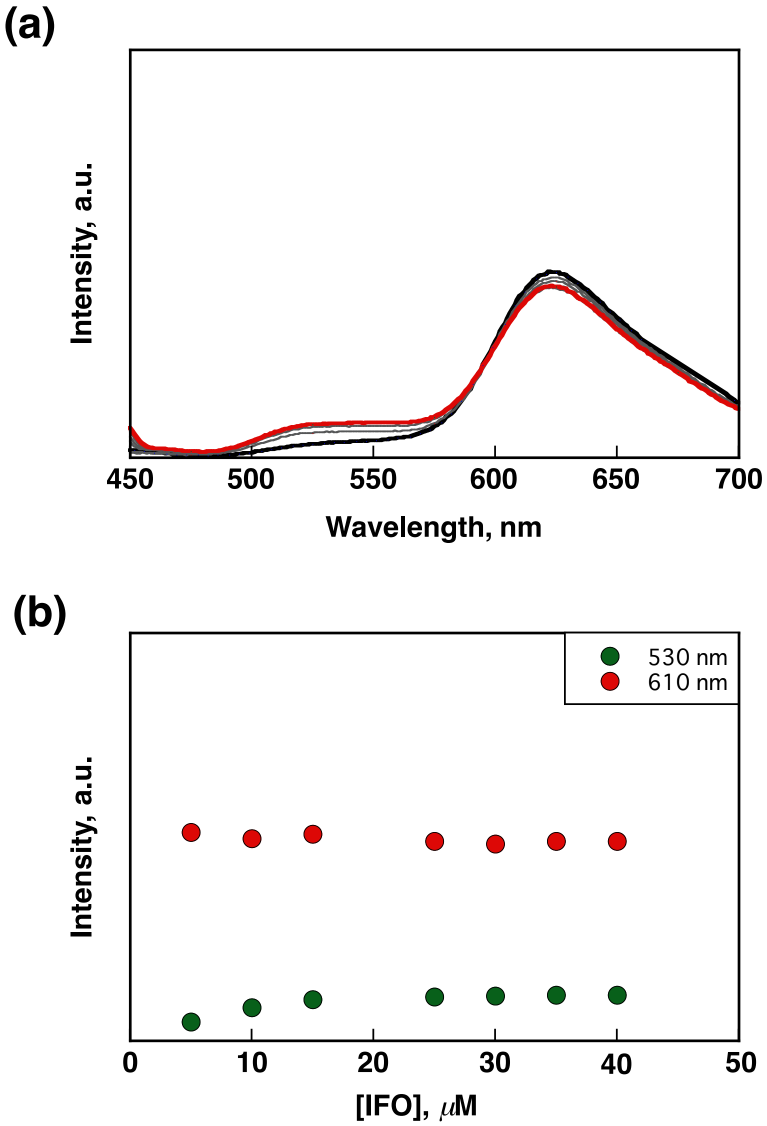


Fig. S3 (a) Concentration dependence of fluorescence spectra of **IFO** in *p*-xylene in the range of 5 to 40 μM (from black to red line); (b) fluorescent intensity as a function of **IFO** concentration.

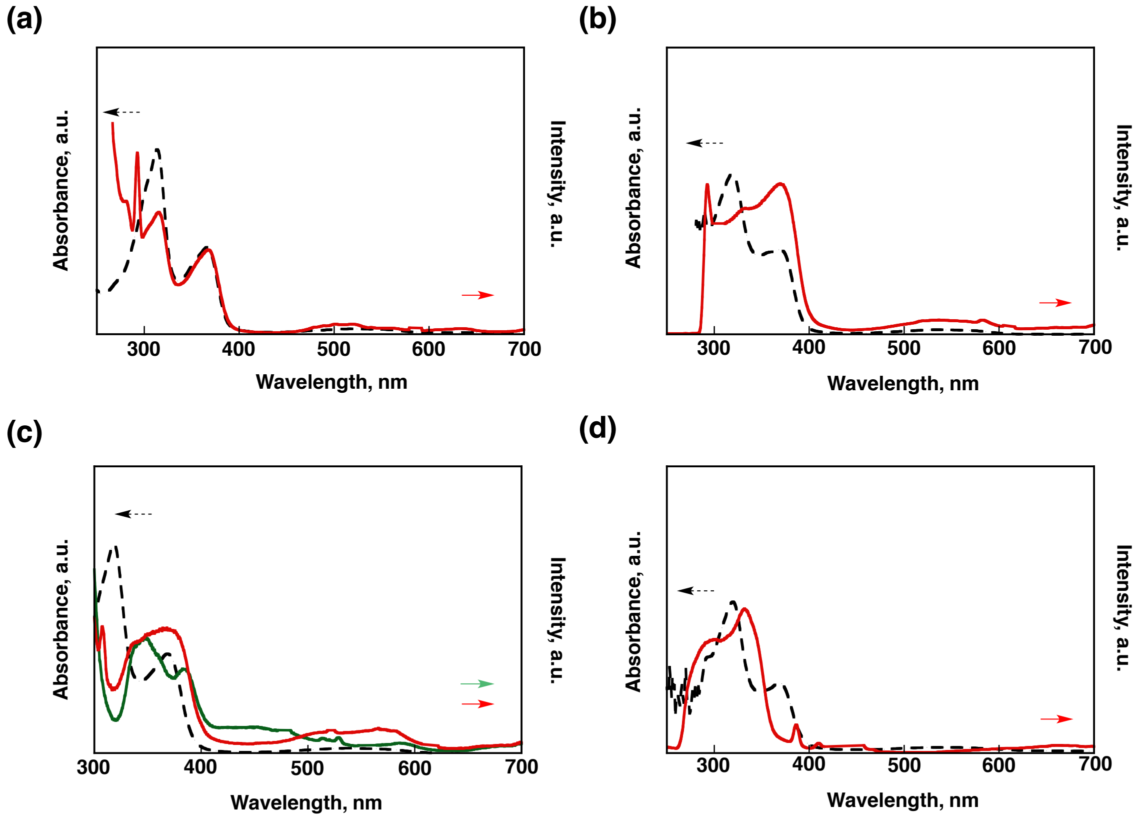


Fig. S4 Exciation spectra of **IFO** (19 μM) measured in (a) MCH (λ_{moni} = 586 nm), (b) *p*-xylene (λ_{moni} = 610 nm), (c) THF (green λ_{moni} = 555 nm, red λ_{moni} = 618 nm) and (d) in DMF (λ_{moni} = 437 nm) dash lines are the corresponding absorption spectra.

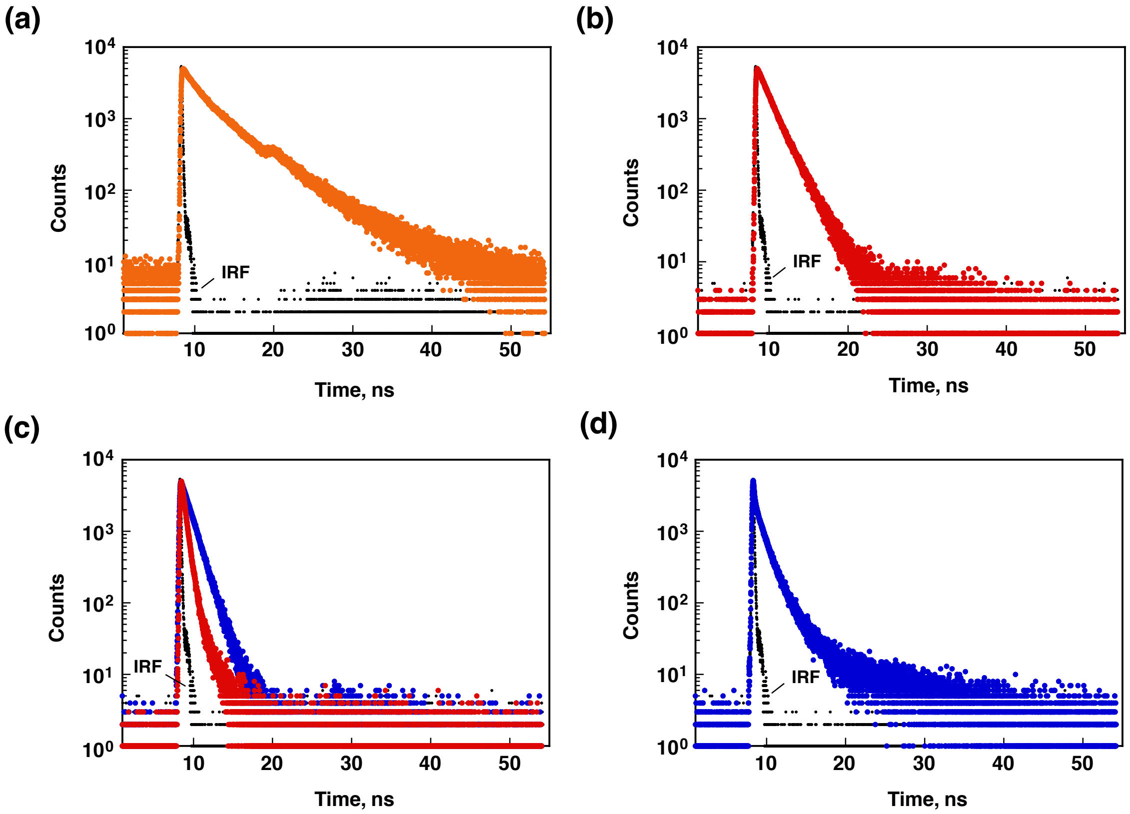


Fig. S5 Fluorescence lifetime decay profiles of **IFO** measured in (a) MCH (λ_{moni} = 585 nm), (b) *p*-xylene (λ_{moni} = 610 nm), (c) THF (blue λ_{moni} = 420 nm, red λ_{moni} = 619 nm) and (d) DMF (λ_{moni} = 435 nm) at 298K. Excitation wavelengths are 375 nm. IRF: Instrumental Response Function.

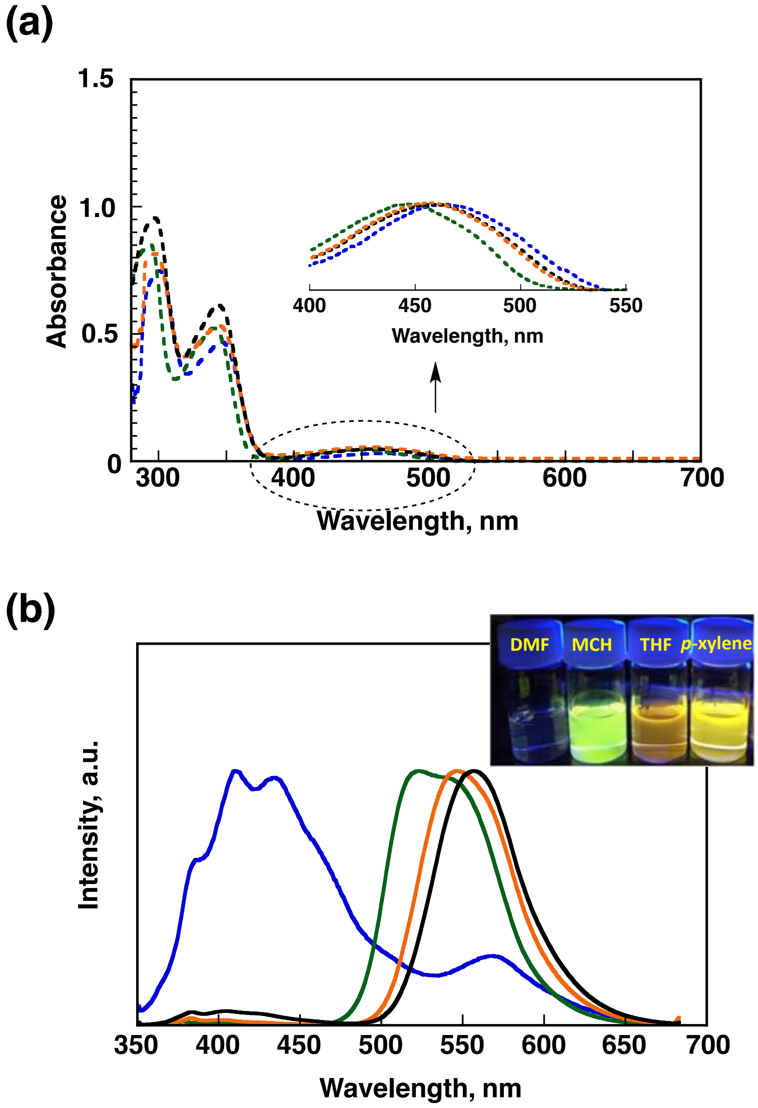


Fig. S6 (a) Absorption and (b) emission spectra of **FO** (15 μM) measured in DMF (blue), MCH (green), *p*-xylene (orange) and THF (black) at 298K. Excitation wavelengths are 345 nm. The intensities were normalized at the emission maximum. Inset: photographs under irradiation with 365 nm UV-lamp.

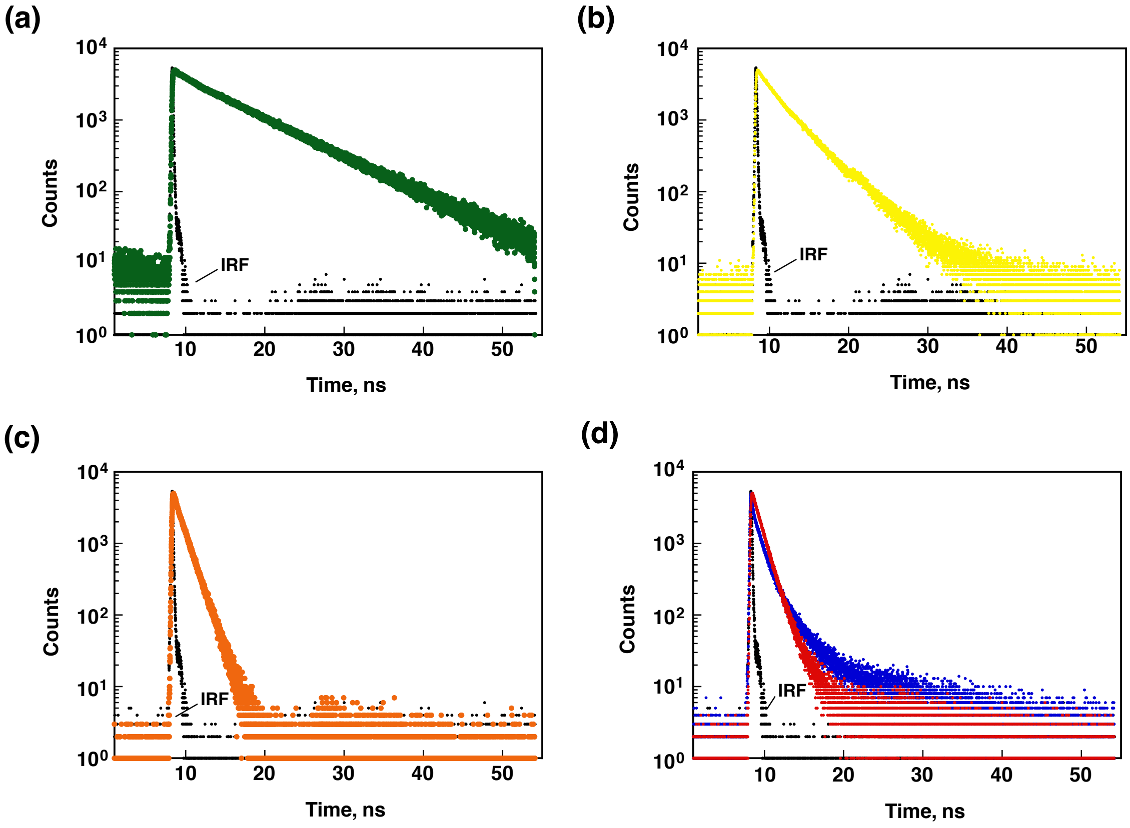
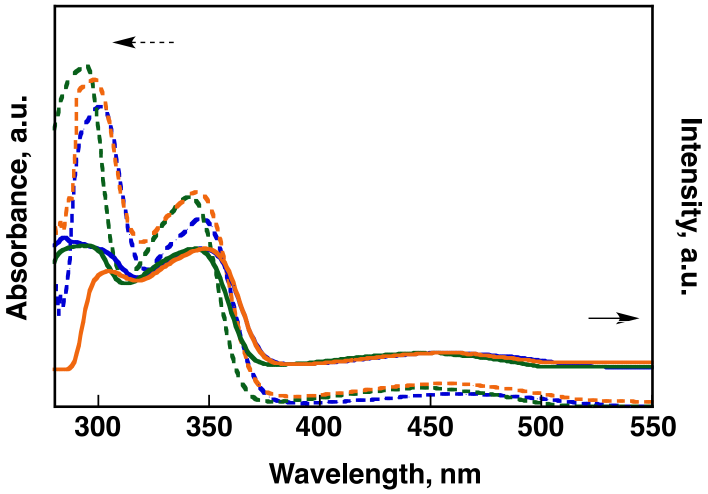


Fig. S7 Fluorescen lifetime decay profiles of **FO** measured in (a) MCH (λ_{moni} = 523 nm), (b) *p*-xylene (λ_{moni} = 546 nm), (c) THF (λ_{moni} = 557 nm) and (d) DMF (blue λ_{moni} = 420 nm, red λ_{moni} = 570 nm) at 298K. Excitation wavelengths are 375 nm. IRF: Instrumental Response Function.

(a)



(b)

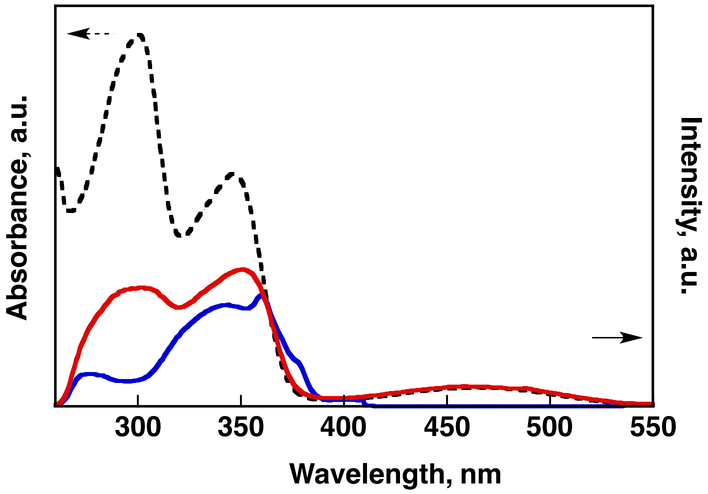


Fig. S8 Exciation spectra of **FO** (15 μM) measured in (a) MCH (black, λ_{moni} = 520 nm), *p*-xylene (blue λ_{moni} = 547 nm), THF (green λ_{moni} = 557 nm) and (b) DMF (blue λ_{moni} = 422 nm, red λ_{moni} = 570 nm) dash lines are the corresponding absorption spectra.

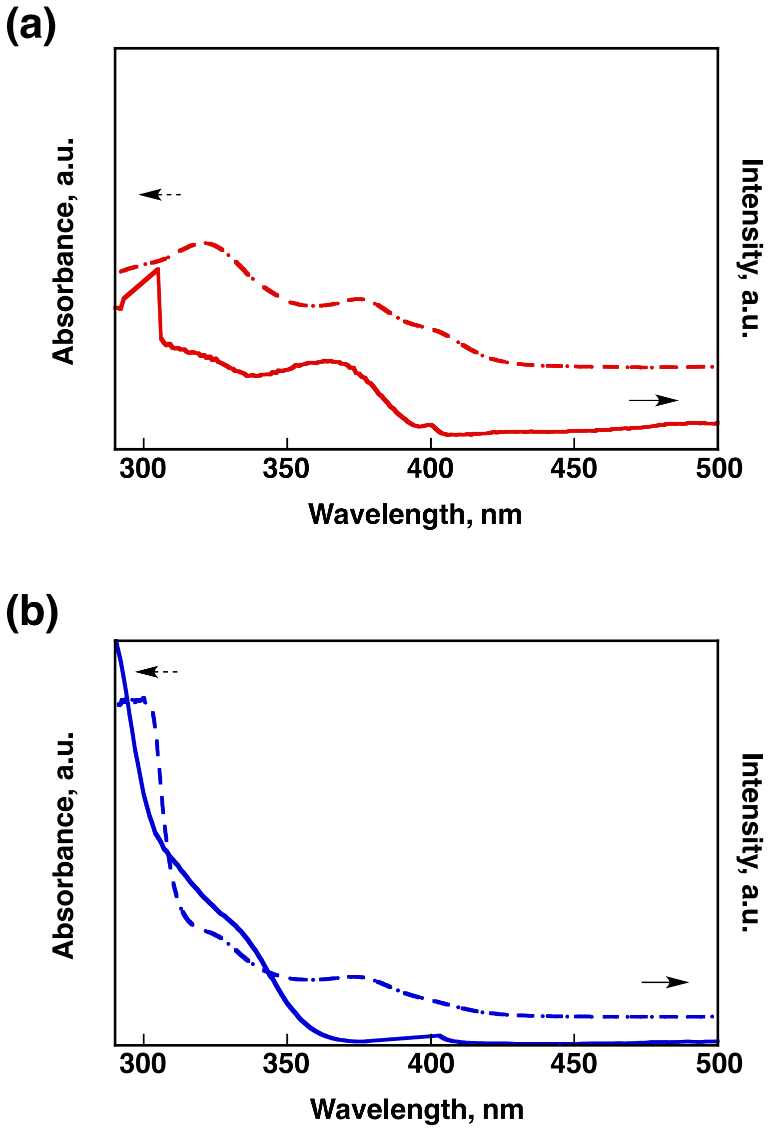


Fig. S9 Exciation spectra of **IFO** film doped in (a) polystyrene (λ_{moni} = 598 nm) and (b) polysulfone (λ_{moni} = 393 nm) as host matrixes containing 1 wt% **IFO**. The dash lines are the corresponding absorption spectra.

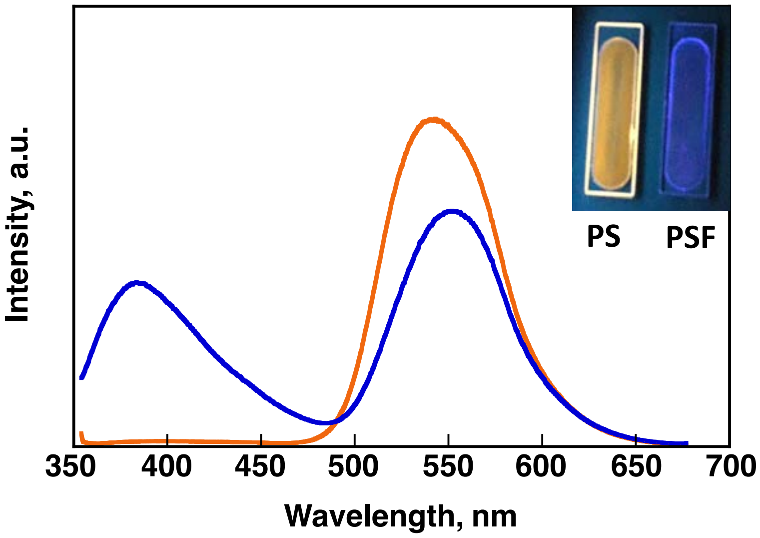


Fig. S10 Fluorescent spectra of **FO** film doped in polystyrene (orange) and polysulfone (blue) as host matrixes fabricated by drop casting of $CHCl_3$ solution containing 1 wt% **FO**. Excitation wavelengths are 345 nm. Inset: corresponding photograph under irradiation with 365 nm UV-lamp.

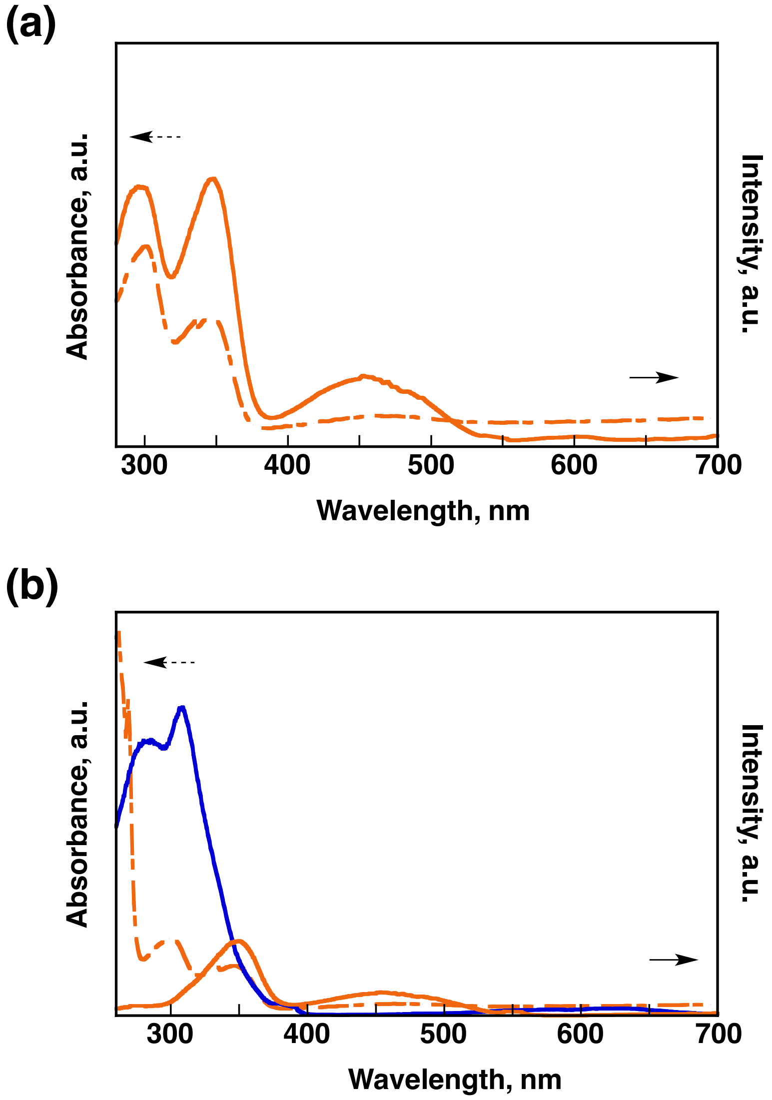
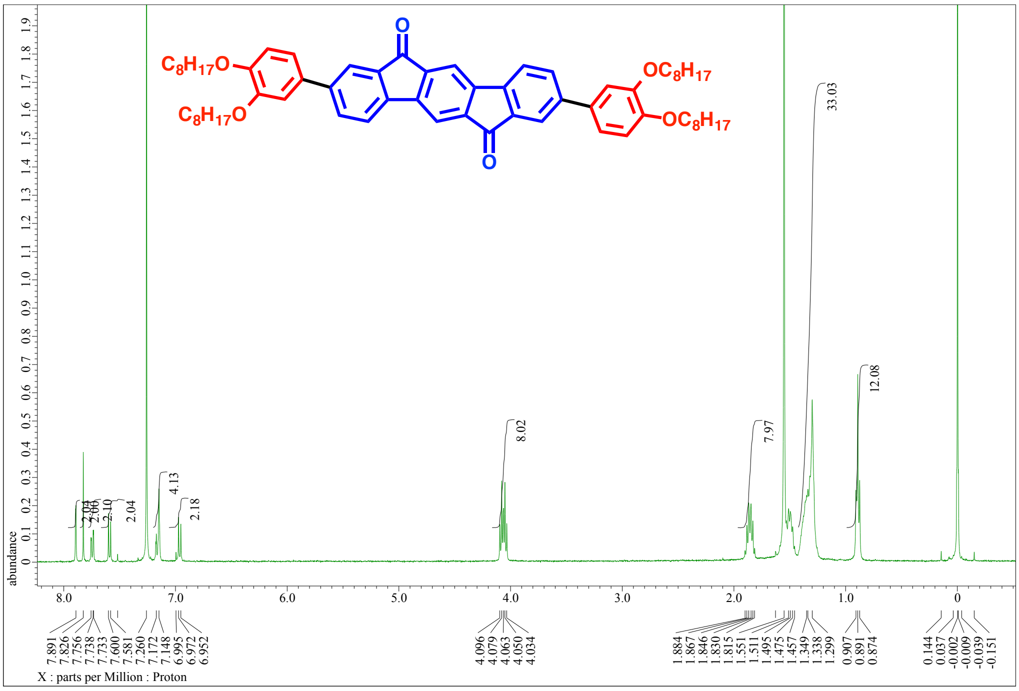
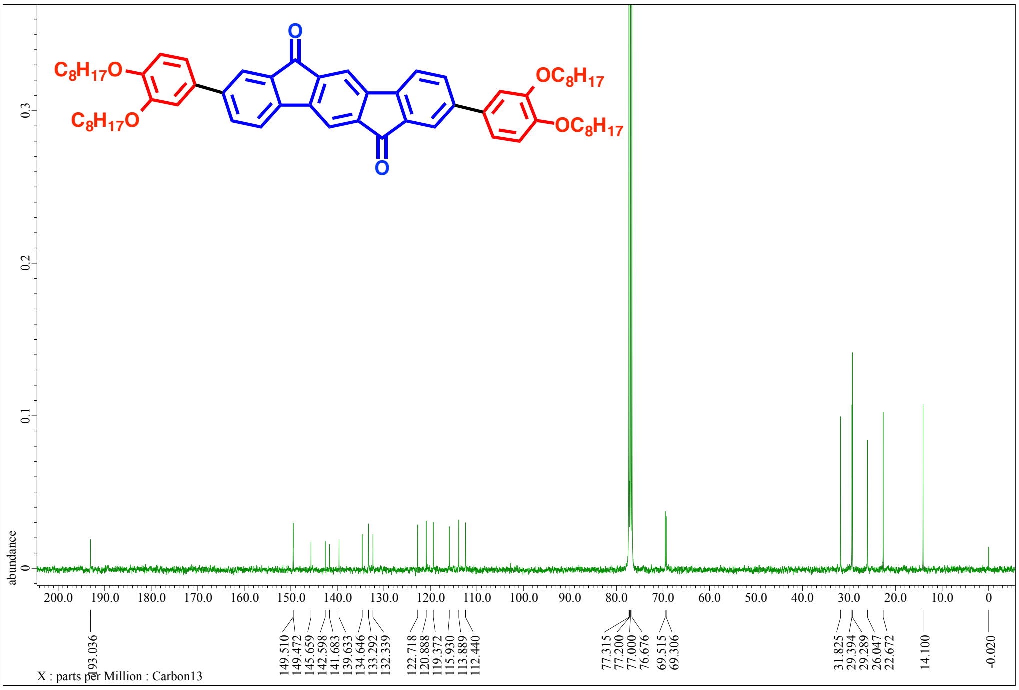


Fig. S11 Exciation spectra of **FO** film doped in (a) polystyrene (λ_{moni} = 545 nm) and (b) polysulfone (blue λ_{moni} = 385 nm, orange λ_{moni} = 550 nm) as host matrixes containing 1 wt% **FO**. The dash lines are the corresponding absorption spectra.

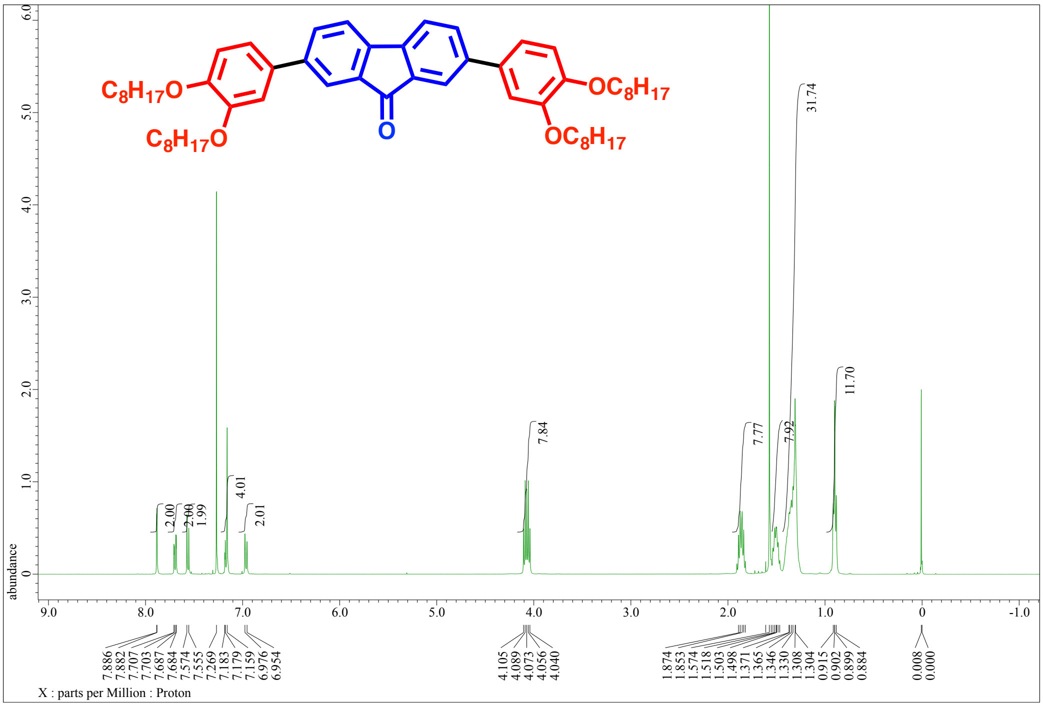
^{1}H NMR of **IFO** (400 MHz, in $CDCl_3$)



^{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 $CDCl_3$)