

Supplementary Information

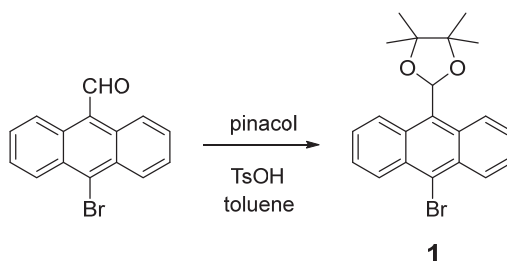
Fluorescence sensors for detection of water based on tetraphenylethene–anthracene possessing both solvatochromic properties and aggregation-induced emission (AIE) characteristics

Yuta Mise, Keiichi Imato, Takashi Ogi, Nao Tsunoji and Yousuke Ooyama*

*Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University,
Higashi-Hiroshima, 739-8527, Japan.*

Fax: +81 82 424 5494; Tel: +81 82 424 7689; E-mail:yooyama@hiroshima-u.ac.jp

2-(10-Bromoanthracen-9-yl)-4,4,5,5-tetramethyl-1,3-dioxolane (1): A solution of 10-bromoanthracene-9-carbaldehyde (1.88 g, 6.58 mmol), pinacol (3.98 g, 33.69 mmol), and *p*-toluenesulfonic acid monohydrated (0.14 g, 0.81 mmol) in toluene (100 mL) was stirred for 1.5 h at 120 °C with Dean-Stark apparatus in the dark. The reaction mixture was cooled to room temperature. NaHCO₃, water, and brine were added in turn to the reaction mixture, and the aqueous layer was extracted with toluene. The toluene extract was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was chromatographed on alumina (dichloromethane : hexane = 1 : 9 as eluent) to give **1** (0.68 g, yield 27%) as a yellow solid; m.p. 158–159 °C; FT-IR (ATR): $\tilde{\nu}$ = 2974, 1442, 1147, 1104 cm⁻¹; ¹H NMR (400 MHz, acetone-*d*₆): δ = 1.45 (s, 6H), 1.52 (s, 6H), 7.34 (s, 1H), 7.59–7.70 (m, 4H), 8.60 (d, *J* = 8.8 Hz, 2H), 9.13 (d, *J* = 8.8 Hz, 2H) ppm; ¹³C NMR (100 MHz, acetone-*d*₆): δ = 23.24, 25.24, 83.52, 98.54, 125.72, 126.75, 126.98, 127.89, 128.72, 129.66, 131.07, 131.90 ppm; HRMS (APCI): *m/z* (%): [M+H⁺] calcd for C₂₁H₂₂BrO₂, 385.07977; found 385.08038.



Scheme S1 Synthesis of **1**.

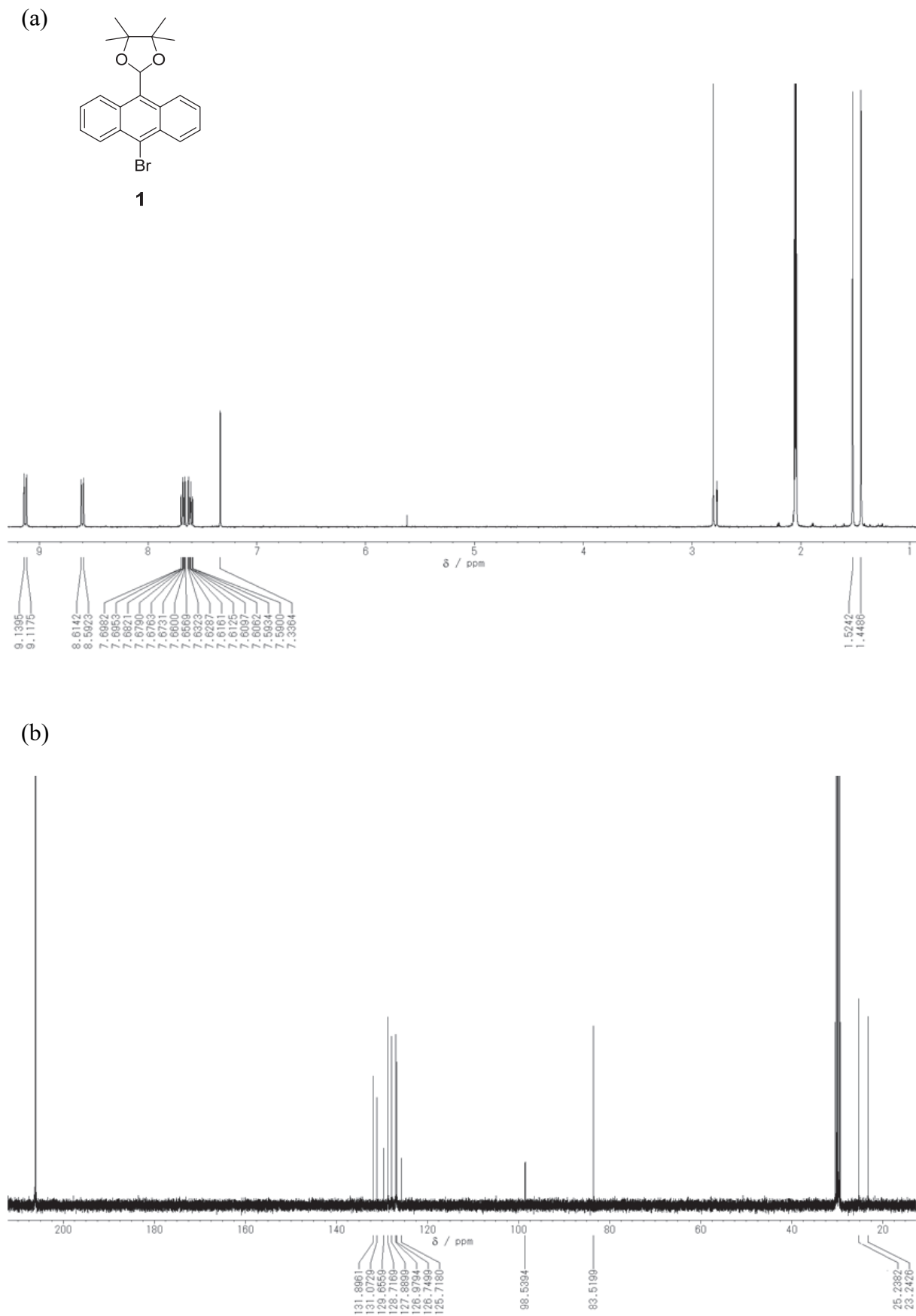


Fig. S1 (a) ^1H NMR (400 MHz) and (b) ^{13}C NMR (100 MHz) spectra of **1** in acetone- d_6 .

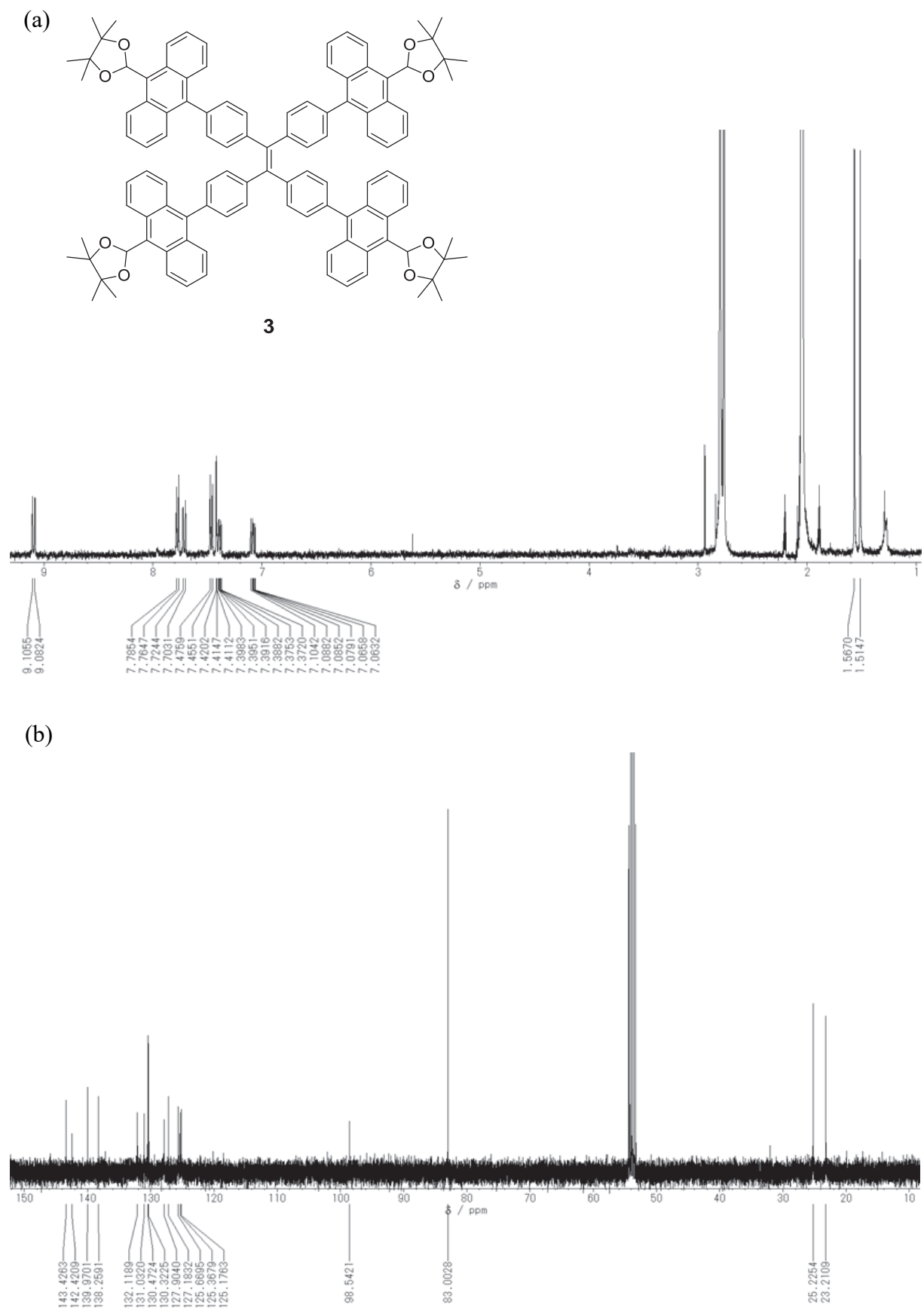


Fig. S2 (a) ^1H NMR (400 MHz) spectrum of **3** in acetone- d_6 . (b) ^{13}C NMR (100 MHz) spectrum of **3** in CD_2Cl_2 .

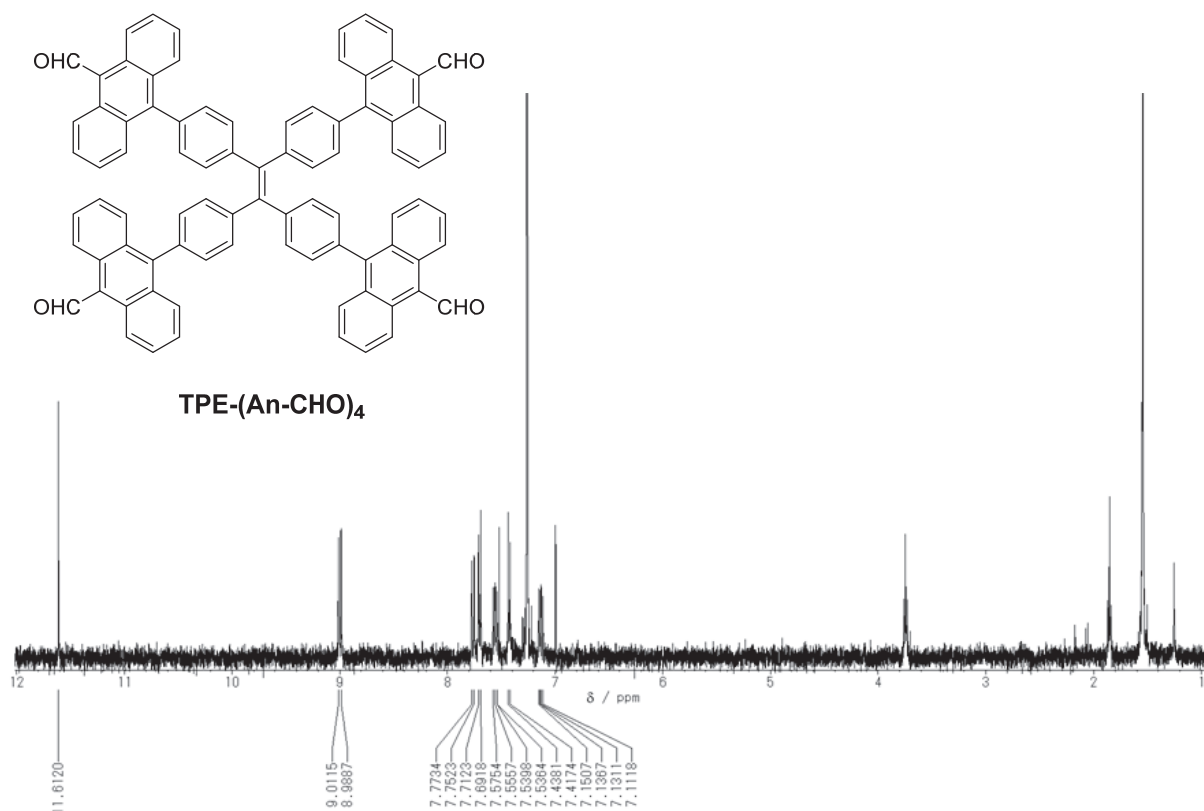


Fig. S3 ^1H NMR (400 MHz) spectrum of **TPE-(An-CHO)₄** in CDCl_3 .

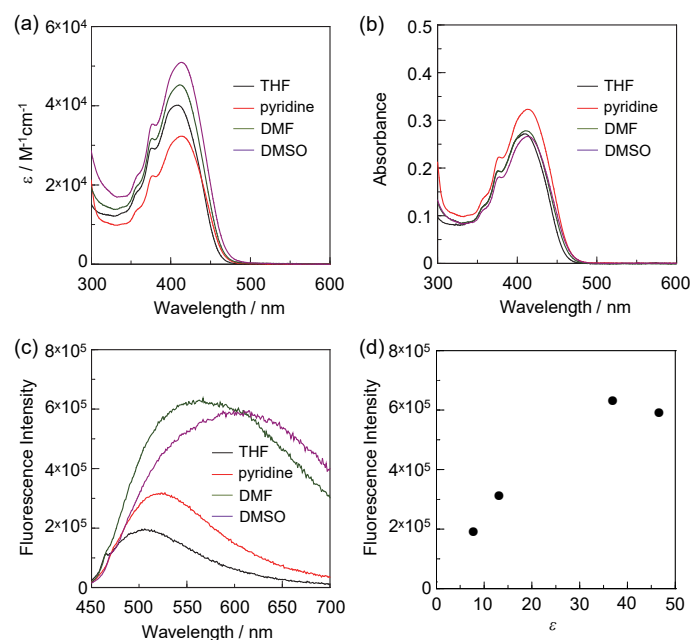


Fig. S4 (a) Photoabsorption spectra (molar extinction coefficient (ϵ_{max})-wavelength) of **TPE-(An-CHO)₄** in various solvents. (b) Photoabsorption (absorbance-wavelength) and (c) the corresponding fluorescence ($\lambda^{\text{ex}} = 409\text{--}413\text{ nm}$) spectra of **TPE-(An-CHO)₄** in various solvents; for photoabsorption spectra, each absorbance at around 410 nm was adjusted to ca. 0.3. (d) Plot of fluorescence peak intensity corresponding to fluorescence spectra of (c) versus the static dielectric constant (ϵ) of solvent.

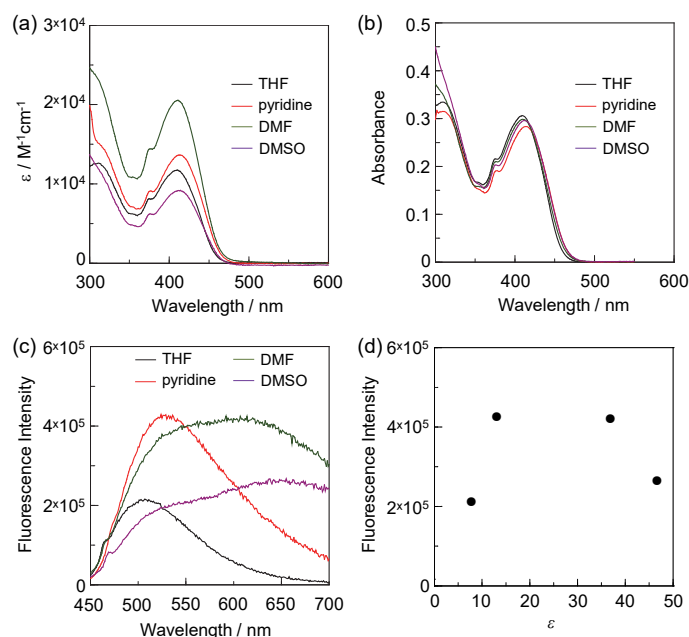


Fig. S5 (a) Photoabsorption spectra (molar extinction coefficient (ϵ_{max})-wavelength) of **TPE-(An-CHO)** in various solvents. (b) Photoabsorption (absorbance-wavelength) and (c) the corresponding fluorescence ($\lambda^{\text{ex}} = 409\text{--}413$ nm) spectra of **TPE-(An-CHO)** in various solvents; for photoabsorption spectra, each absorbance at around 410 nm was adjusted to ca. 0.3. (d) Plot of fluorescence peak intensity corresponding to fluorescence spectra of (c) versus the static dielectric constant (ϵ) of solvent.

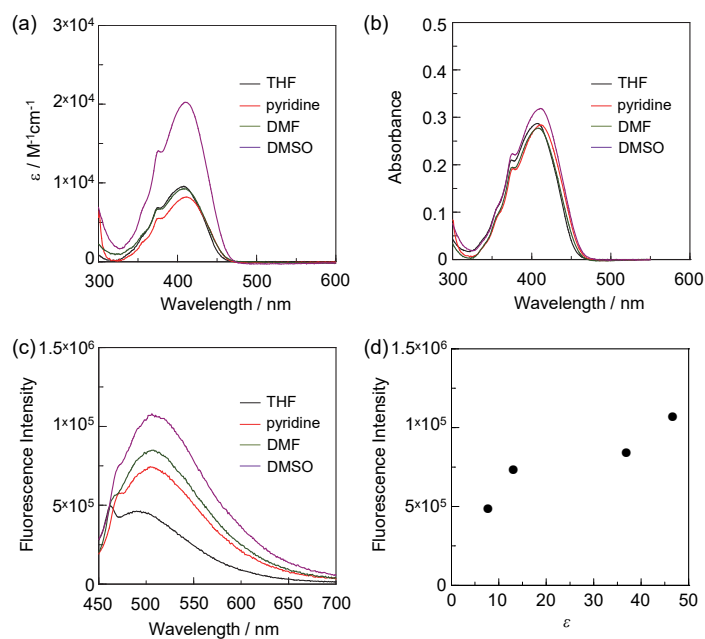


Fig. S6 (a) Photoabsorption spectra (molar extinction coefficient (ϵ_{max})-wavelength) of **Ph-(An-CHO)** in various solvents. (b) Photoabsorption (absorbance-wavelength) and (c) the corresponding fluorescence ($\lambda^{\text{ex}} = 407\text{--}411$ nm) spectra of **Ph-(An-CHO)** in various solvents; for photoabsorption spectra, each absorbance at around 410 nm was adjusted to ca. 0.3. (d) Plot of fluorescence peak intensity corresponding to fluorescence spectra of (c) versus the static dielectric constant (ϵ) of solvent.

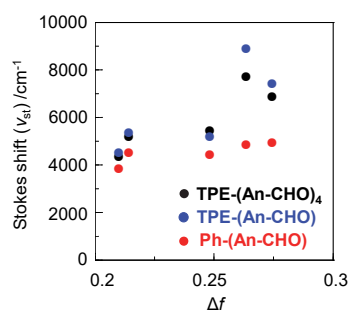


Fig. S7 Correlation of the Stokes shift (ν_{st}) and the Lippert-Mataga polarity parameter (Δf) according to eqn (1) and (2), respectively, for **TPE-(An-CHO)₄**, **TPE-(An-CHO)**, and **Ph-(An-CHO)**; Solvent (static dielectric constant (ϵ), refractive index (n), Δf): THF (7.58, 1.4072, 0.2096), THF-water (10 wt%) mixture (12.9, 1.4033, 0.2478), pyridine (12.91, 1.5102, 0.2138), DMF (36.71, 1.4305, 0.274), and DMSO (46.65, 1.4793, 0.2631).

Lippert–Mataga equation [eqn (1)]:

$$\nu_{st} = \frac{1}{4\pi\epsilon_0} \cdot \frac{2\Delta\mu^2}{hca^3} \Delta f + \text{Const.} \quad (1)$$

where

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

In the above equations, ν_{st} is the Stokes shift, ϵ_0 is the vacuum permittivity, h is Planck's constant, c is the velocity of light, a is the Onsager radius of dye molecule, $\Delta\mu = \mu_e - \mu_g$ is the difference in the dipole moment of dye between the excited (μ_e) and the ground (μ_g) states, ϵ and n are the static dielectric constant and the refractive index of the solvent, respectively, and Δf is the orientation polarizability.