

Supporting Information for

Stereoelectronics of the Hydrogen Bond-Induced Fluorescence Quenching of 3-Aminofluorenones with Alcohols

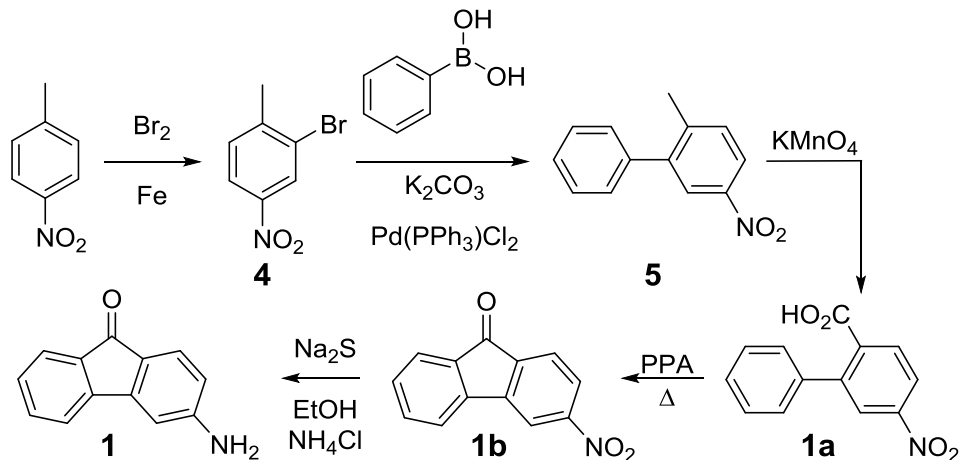
*Isaac G. Alty and Christopher J. Abelt**

Department of Chemistry, College of William and Mary, Williamsburg, VA 23185

General Information. NMR spectra were obtained with an Agilent DD2-400 or Varian Mercury VX-400 spectrometer. High resolution ESI-MS were acquired with a Bruker Apex-Qe instrument. All solvents were spectrophotometric grade except for tetrahydrofuran and ethylene glycol which were distilled from Na⁰ under N₂. Reagents were obtained from Acros Organics or Sigma-Aldrich unless otherwise indicated. Fluorescence emission data were collected using a fiber optic system with a 366 nm LED light source and an Ocean Optics Maya CCD detector. Solution cells were thermostated at 23°C. Absorption spectra were obtained with a miniature deuterium/tungsten light source with the same fiber optic system.

Syntheses.

Preparation of 3-amino-9-fluorenone (1).¹



A mixture of 4-nitrotoluene (13.7 g, 100 mmol) and Fe powder (0.20 g, 3.6 mmol) was heated to 80°C at which point bromine (6.1 mL, 120 mmol) was added slowly over 10 min. The mixture was stirred for 1.5 h at 80°C and then poured into aq. NaOH (150 mL, 10%). The resulting precipitate was collected by vacuum filtration and dissolved in CH_2Cl_2 (150 mL). The solution was washed twice with aq. HCl (50 mL ea, 10%), once with aq. NaOH (50 mL, 5%), then dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude cream-colored product was recrystallized from EtOH to yield pale yellow crystals of 2-bromo-4-nitrotoluene (**4**, 14.23 g, 66%).² ^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1 H), 8.09 (d, 2 H), 7.41 (d, 2 H), 2.72 (s, 3 H).

A solution of H_2O (20 mL) and ethylene glycol dimethyl ether (25 mL) was degassed with N_2 for 5 min, after which were added K_2CO_3 (10.40 g, 75.3 mmol), phenylboronic acid (3.15 g, 25.8 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (830 mg, 1.9 mmol) and 2-bromo-4-nitrotoluene (**4**, 5.08 g, 23.5 mmol). The

¹ Ray, F. E.; Barrick, J. G. 3-Nitrofluorenone. *J. Am. Chem. Soc.* **1948**, *70*, 1492-1494.

² Bunnett, J.F.; Rauhut, M. M.; 2-Bromo-3-Methylbenzoic Acid. *Organic Syntheses* **1958**, *38*, 11-12.

mixture was heated at reflux with stirring for 18 h. The mixture was allowed to cool, diluted with H₂O (100 mL) and extracted three times with EtOAc (50mL ea). The combined organic extracts were dried over Na₂CO₃, filtered, and concentrated *in vacuo*. The product oil was triturated with H₂O, and the resulting crystals were recrystallized from MeOH (30mL), collected by vacuum filtration and washed with H₂O to yield gray-brown crystals of 4-nitro-2-phenyltoluene (**5**, 4.53 g, 90%).³ ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1 H), 8.11 (d, 1 H), 7.38–7.51 (m, 4 H), 7.32 (d, 2 H), 2.37 (s, 3 H). A mixture of 4-nitro-2-phenyltoluene (**5**, 7.05 g, 33.1 mmol), in pyridine (33 mL) and H₂O (66 mL) was heated to 80°C at which point KMnO₄ (31.35 g, 198 mmol) was added in portions, and the mixture was subsequently heated at 135°C for 2 h. The reaction mixture was filtered and acidified with aq. HCl (100 mL, 6M), and the resulting precipitate was collected by vacuum filtration. The crude product was dissolved in CH₂Cl₂ (200 mL) and extracted twice with aq. NaOH (100 mL ea, 10%). The combined aqueous layers were acidified with conc. HCl to cloudiness. The suspension was cooled, and the precipitate was collected by vacuum filtration and washed with ice-cold H₂O to yield yellow-white crystals of 4-nitro-2-phenylbenzoic acid (**1a**, 4.26 g, 53%).⁴ ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, 2 H), 8.27 (s, 1 H), 8.07 (d, 1 H), 7.40–7.45 (m, 3 H), 7.35 (d, 2 H).

4-Nitro-2-phenylbenzoic acid (**1a**, 4.26 g, 17.5 mmol) was covered with polyphosphoric acid (64.33 g), and the mixture was heated to 160°C with stirring under N₂ for 5 h. The mixture was allowed to cool below 100°C, after which H₂O (200 mL) was added. The mixture was stirred for

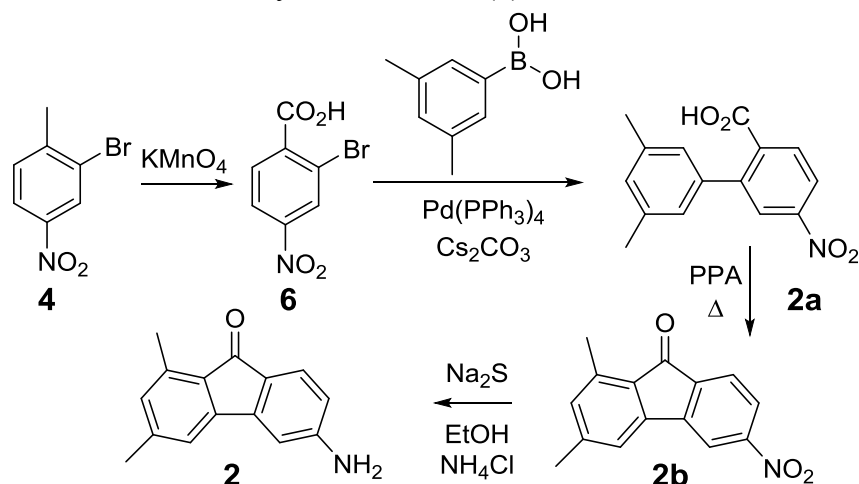
³ Sams, A.; Larsen, M.; Mikkelsen, G. *N*-thiazol-2-yl-benzamide derivatives. U.S. Patent Application 11/312,661. 2005 Dec 20.

⁴ Sebti, S.; Hamilton, A. and Seong, C. M. Inhibition of farnesyltransferase. U.S. Patent No. 5,856,310. 5 Jan. 1999.

30 min then cooled in an ice bath. The resulting solid was collected by vacuum filtration to yield yellow crystals of 3-nitrofluoren-9-one (**1b**, 3.79 g; 96%).⁵ ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1 H), 8.20 (d, 1 H), 7.82 (d, 1 H), 7.75 (d, 1 H), 7.67 (d, 1 H), 7.62 (t, 1 H), 7.43 (t, 1 H).

A mixture of 3-nitro-9-fluorenone (**1b**, 1.00 g, 4.4 mmol) and NH₄Cl (2.00 g, 37.4 mmol) in EtOH (100 mL) was to reflux, Na₂S (5.00 g, 64.1 mmol) was added in portions over 2 h and reflux was continued for an additional hour. The reaction was allowed to cool, H₂O (100 mL) was added and the solution was extracted three times with Et₂O (75 mL ea). The combined organic layers were extracted twice with aq. HCl (150 mL ea, 10%), and the combined acid layers were neutralized with aq. NaOH. The resulting solid was collected by vacuum filtration to yield yellow crystals of 3-aminofluoren-9-one (**1**, 470 mg; 54%).¹ ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, 1 H), 7.51 (d, 1 H), 7.42 (t, 1 H), 7.41 (d, 1 H), 7.29 (t, 1 H), 6.77 (s, 1 H), 6.45 (d, 1 H), 4.28 (s, 2 H, NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 192.26, 152.86, 147.37, 143.21, 135.95, 133.59, 129.10, 126.75, 124.63, 123.55, 119.77, 113.34, 106.28. This material was sublimed under vacuum before use.

Preparation of 6-amino-1,3-dimethylfluoren-9-one (**2**)



⁵ Iihama, T.; Bourguignon, M.; Snieckus, V. Regiospecific syntheses of all isomeric nitrofluorenones and nitrofluorenes by transition metal catalyzed cross-coupling reactions. *Synthesis* **1989**, 184-188.

A mixture of 2-bromo-4-nitrotoluene (**4**, 5.00g, 23.1 mmol) in pyridine (23 mL) and H₂O (46 mL) was heated to 60°C at which point KMnO₄ (18.29 g, 116 mmol) was added in portions with stirring. After addition was complete the mixture was heated to reflux overnight. The reaction mixture was allowed to cool, filtered, acidified with conc. HCl (5 mL) and extracted three times with EtOAc (50 mL ea). The organic extracts were combined, dried with Na₂SO₄, filtered, and concentrated *in vacuo* to yield orange-brown crystals of 2-bromo-4-nitrobenzoic acid (**6**, 3.04 g, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.50 (s, 1 H), 8.20 (d, 1 H), 7.97 (d, 1 H).

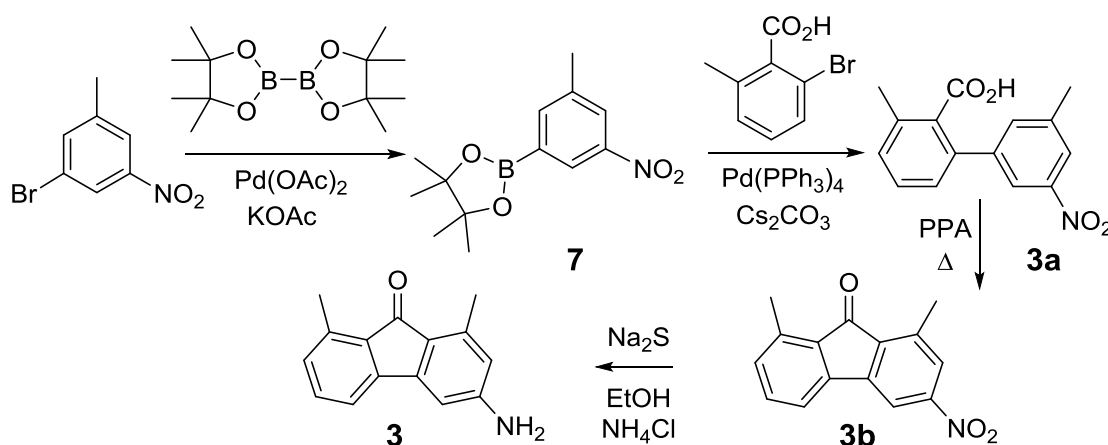
A mixture of 2-bromo-4-nitrobenzoic acid (**6**, 500 mg, 2.0 mmol), 3,5-dimethylphenylboronic acid (340 mg, 2.3 mmol), Cs₂CO₃ (1.66 g, 5.1 mmol) and Pd(PPh₃)₄ (120 mg, 0.10 mmol) in DMF (25 mL) was heated to 100°C overnight. The reaction mixture was allowed to cool and poured into 50mL 10% aq. HCl (50 mL, 10%). The mixture was extracted three times with Et₂O (50 mL ea) and the combined organic extracts were dried over MgSO₄, filtered, concentrated *in vacuo* to yield a brown oil. Silica gel column chromatography (10%EtOAc in hexanes) provided yellow crystals of 2-(3,5-dimethylphenyl)-4-nitrobenzoic acid (**2a**, 170 mg, 31%). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1 H), 8.24 (d, 1 H), 8.02 (d, 1 H), 7.07 (s, 1 H), 6.98 (s, 2 H), 2.37 (s, 6 H).

2-(3,5-Dimethylphenyl)-4-nitrobenzoic acid (**2a**, 1.45 g, 5.3 mmol) was covered with polyphosphoric acid (19.6 g) and heated to 160°C under N₂ with stirring for 5 h. The mixture was allowed to cool to below 100°C, after which H₂O (70 mL) was added. The mixture was stirred for 30 min then cooled in an ice-bath. The solid product was collected by vacuum filtration and sublimed at 175°C to yield yellow crystals of 1,3-dimethyl-6-nitrofluoren-9-one (**2b**, 550 mg, 41%). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1 H), 8.18 (d, 1 H), 7.68 (d, 1 H), 7.31 (s, 1 H), 6.99 (s, 1 H), 2.60 (s, 3 H), 2.41 (s, 3 H).

A mixture of 1,3-dimethyl-6-nitrofluoren-9-one (**2b**, 550 mg, 2.2 mmol) and NH_4Cl (1.10 g, 2.1 mmol) in EtOH (55 mL) was heated to reflux at which point and 2.75g Na_2S (2.75 g, 2.8 mmol) was added in portions over 2 h. Reflux was continued for 1 hr. The mixture was allowed to cool, diluted with H_2O (50 mL) and extracted three times with Et_2O (50 mL ea). The combined organic layers were extracted three times with aq. HCl (50 mL ea, 10%). The combined aqueous layers were neutralized with aq. NaOH (25%) solution and cooled in an ice-bath giving a yellow solid. The solid was collected by vacuum filtration and sublimed at $200^\circ\text{C}/0.5$ Torr to yield bright yellow crystals of 6-amino-1,3-dimethylfluoren-9-one (**2**, 90 mg, 20%), m.p. $260\text{--}261^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, 1 H), 7.09 (s, 1 H), 6.83 (s, 1 H), 6.75 (s, 1 H), 6.43 (d, 1 H), 4.18 (s, 2 H, NH_2), 2.57 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.34, 152.38, 146.52, 143.67, 138.40, 132.32, 125.96, 118.43, 117.28, 113.23, 105.89, 104.92, 21.80, 17.47.

HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{13}\text{NONa}^+ [\text{M}+\text{Na}]^+$ 246.08894; found 246.08905.

Preparation of 3-amino-1,8-dimethylfluoren-9-one (**3**)



A mixture of 3-bromo-5-nitrotoluene (Combi-Blocks, 1.17 g, 5.4 mmol), bis(pinacolato)diboron (1.38 g, 5.4 mmol), KOAc (1.59 g, 16.2 mmol) in DMF (25 mL) was degassed under vacuum for

15 min after which Pd(OAc)₂ (61 mg, 0.27 mmol) was added and the mixture was heated to 90°C with stirring for 2 h under N₂. The mixture was allowed to cool, poured into CH₂Cl₂ (150 mL) and washed six times with H₂O (100 mL ea). The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo* to yield a dark brown oil. Silica gel column chromatography (12% EtOAc in hexanes) gave pale yellow powdery crystals of 4,4,5,5-tetramethyl-2-(3-methyl-5-nitrophenyl)-1,3,2-dioxaborolane (**7**, 620 mg, 44%). ¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 1 H), 8.11 (s, 1 H), 7.92 (s, 1 H), 2.46 (s, 3 H), 1.35 (s, 12 H).

A mixture of 2-bromo-6-methylbenzoic acid (Matrix Scientific, 460 mg, 2.1 mmol) and 4,4,5,5-tetramethyl-2-(3-methyl-5-nitrophenyl)-1,3,2-dioxaborolane (**7**, 600 mg, 2.3 mmol) in DMF (25 mL) was degassed under vacuum for 15 min after which were added CsCO₃ (1.66 g, 5.1 mmol) and 0.12 g Pd(PPh₃)₄ (120 mg, 0.10 mmol). The mixture was heated to 100°C for 24 h under N₂. The reaction was allowed to cool then poured into aq. HCl (50 mL, 10%) and extracted three times with Et₂O (50 mL ea). The combined organic extracts were dried with MgSO₄, filtered and concentrated *in vacuo* to yield a cloudy light brown oil. Silica gel column chromatography (20% EtOAc in hexanes) gave orange crystals of 3,3'-dimethyl-5'-nitro-[1,1'-biphenyl]-2-carboxylic acid (**3a**, 300 mg, 52%). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 1 H), 8.01 (s, 1 H), 7.52 (s, 1 H), 7.41 (t, 1 H), 7.29 (d, 1 H), 7.20 (d, 1 H), 2.46 (s, 6 H).

3,3'-Dimethyl-5'-nitro-[1,1'-biphenyl]-2-carboxylic acid (**3a**, 430 mg, 1.6 mmol) was covered with polyphosphoric acid (5.82 g) and the mixture was heated to 150°C under N₂ with stirring for 5 h. The mixture was allowed to cool to below 100°C, after which H₂O (30 mL) was added and stirred for 30 min. The mixture was poured into H₂O (150 mL) and extracted three times with CH₂Cl₂ (50 mL ea). The combined organic extracts were dried with MgSO₄, filtered and concentrated *in vacuo* to yield yellow crystals of 1,8-dimethyl-3-nitrofluoren-9-one (**3b**, 160 mg,

40%). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1 H), 7.95 (s, 1 H), 7.47 (d, 1 H), 7.44 (t, 1 H), 7.16 (d, 1 H), 2.76 (s, 3 H), 2.64 (s, 3 H).

A mixture of 1,8-dimethyl-3-nitrofluoren-9-one (**3b**, 160 mg, 0.63 mmol) and NH_4Cl (320 mg, 6.0 mmol) in EtOH (16 mL) was heated to reflux at which point Na_2S (800 mg, 10 mmol) was added in portions over 2 h. The reaction was allowed to reflux for an additional hour. The mixture was allowed to cool, diluted with H_2O (15 mL) and extracted three times with Et_2O (25 mL ea). The combined organic layers were dried with MgSO_4 , filtered, and concentrated to a volume of 20 mL. The organic layer was extracted three times with aq. HCl (20 mL ea, 10%) and the combined aqueous layers were neutralized with aq. NaOH (25%) and extracted three times with CH_2Cl_2 (50 mL ea). The combined organic extracts were dried with MgSO_4 , filtered and concentrated *in vacuo* to yield yellow crystals of 3-amino-1,8-dimethylfluoren-9-one (**3**, 30 mg, 21%), m.p. 205-207 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.27 (t, 1 H), 7.02 (d, 1 H), 6.63 (s, 1 H), 6.22 (s, 1 H), 4.13 (s, 2 H, NH_2), 2.62 (s, 3 H), 2.54 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 226.18, 157.09, 152.76, 146.94, 143.05, 141.16, 137.54, 132.44, 132.36, 131.63, 117.03, 114.98, 103.97, 17.97, 17.36.

HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{14}\text{NO}^+$ $[\text{M}+\text{H}]^+$ 224.10699; found 224.10691.

Absorption Data. Two solutions of identical concentrations of **1** - **3** in the aprotic and protic solvents were made by diluting a fixed volume (~50 μL) of a stock solution of **1** - **3** (~5 mg /10 mL toluene) to 5 mL. Two sets of data were acquired for each solvent pair. In the first set 2.0 mL of the aprotic solution was sequentially spiked with four aliquots of the protic solution. The solution was stirred for thirty seconds before recording the transmission intensity. In the second set, 2.0 mL of the protic solution was spiked with two aliquots of the aprotic solution. The best-fit third-order polynomial to the plot of normalized absorption vs. mole fraction of the protic

solvent was used to calculate the relative molar absorptivities at 366 nm for the solutions used in the fluorescence titrations below.

Fluorescence Data. Two solutions of identical concentrations of **1** - **3** in the aprotic and protic solvents were made by diluting a fixed volume (~25 μ L) of a stock solution of **1** - **3** (~5 mg /10 mL toluene) to 5 mL. Two sets of emission data were acquired for each solvent pair. In the first set 2.0 mL of the toluene solution was sequentially spiked with twenty aliquots of the alcohol solution. In the second set, 2.0 mL of the alcohol solution was spiked with four aliquots of the aprotic solution. The solution was stirred for thirty seconds before recording the emission of each sample. The electronic noise was subtracted from the raw emission intensity. The wavelength scale was converted to wavenumbers, and the net intensity was multiplied by $\lambda^2/\lambda_{\text{max}}^2$ to account for the effect of the abscissa-scale conversion.⁶ The resulting intensity was divided by the spectral response of the Hamamatsu S10420 CCD.

Calculation of spectral values (Y). The relative quantum yield, Q_{rel} , and the product of the fluorescence center-of-mass and the relative quantum yield, $\tilde{\nu}_{\text{CM}} \cdot Q_{\text{rel}}$, were determined for each fluorescence spectrum.⁷ These quantities are the spectral values (Y) used in equation S3. The relative quantum yields were calculated using equation S1. This equation adjusts the integrated fluorescence intensities (I_{int}) to account for changes in the relative molar absorptivities (ϵ) at 366 nm and refractive indices (η) in the various solvent mixtures. The refractive indices of

⁶ Lakowicz, J., *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum Publishers: New York, 1999; Vol. 2.

⁷ Zurawsky, W.P; Scarlata, S.F. Preferential Solvation of 6-Propionyl (*N,N*-Dimethylamino) Naphthalene in Binary, Polar Solvent Mixtures. *J. Phys. Chem.* **1992**, 96, 6012-6016.

toluene/ethanol mixtures have been reported.⁸ The refractive indices of the toluene/isopropanol and tetrahydrofuran/ethylene glycol mixtures were calculated using the Gladstone-Dale equation.⁹ The required excess molar volume data were obtained from the literature for toluene/isopropanol¹⁰ and tetrahydrofuran/ethylene glycol mixtures.¹¹ The fluorescence center-of-mass ($\tilde{\nu}_{\text{CM}}$) values were calculated using equation S2. Fractional changes (I) in the spectral values (Y) were determined from equation S3 where Y_0 is the value in the aprotic solvent and Y_2 is the value in the protic solvent.

$$Q_{rel} = I_{\text{adj}} / (I_{\text{adj}})_{\text{max}} \quad \text{where } I_{\text{adj}} = I_{\text{int}} \cdot \frac{\varepsilon_{\text{max}}}{\varepsilon} \cdot \frac{\eta^2}{\eta_{\text{min}}^2} \quad (\text{S1})$$

$$\tilde{\nu}_{\text{CM}} = \frac{\int I(\tilde{\nu}) \cdot \tilde{\nu} \, d\tilde{\nu}}{\int I(\tilde{\nu}) \, d\tilde{\nu}} = \frac{\int I(\tilde{\nu}) \cdot \tilde{\nu} \, d\tilde{\nu}}{I_{\text{int}}} \quad (\text{S2})$$

$$\Gamma = \frac{Y_0 - Y}{Y_0 - Y_2} \quad (\text{S3})$$

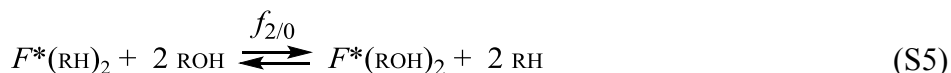
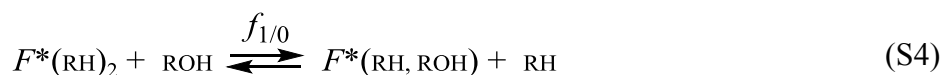
⁸ Atik, Z. Experimental and Predicted Volumetric and Refractive Index Properties of Ternary Mixtures of Iodoethane with Toluene and Alcohols at Temperature 298.15 K and Pressure 101 kPa. *J. Chem. Thermodyn.* **2006**, 38, 201-208.

⁹ Herráez, J.V.; Belda, R. Refractive Indices, Densities and Excess Molar Volumes of Monoalcohols + Water. *J. Solution Chem.* **2006**, 35, 1315-1328.

¹⁰ Singh, K.; Kalra, K.; Maken, S.; Yadav, B. Excess Volumes of 1-Propanol and 2-Propanol with Aromatic Hydrocarbons at 298.15 K. *J. Chem. Eng. Data* **1994**, 39, 241-244.

¹¹ Chawla, B; Suri, S. K. Thermodynamic Studies of Some Binary Mixtures Containing a Self-Associated Component. II. Excess Volumes of Some Mixtures of Tetrahydrofuran with Alcohols. *Thermochem. Acta* **1980**, 41, 147-151.

Preferential Solvation Model. A two-step exchange process formulated by Rosés and Bosch¹² is used to model formation of the singly H-bonded and doubly H-bonded excited states (equations S4 and S5). The three excited states (F^*) each contain two aprotic (RH), two hydroxylic (ROH) or a mixture of the two in their solvation sphere. The equilibrium constants $f_{1/0}$ and $f_{2/0}$ are for single solvent exchange and double exchange, respectively.



The fractional changes in the spectral values (Γ , equation S3) are related to the equilibrium constants and the mole fraction of the hydroxylic solvent (x) through equation S6. The value of r is defined as $(Y_0 - Y_1)/(Y_0 - Y_2)$. It will ultimately determine the spectral values for the singly H-bonded species.

$$\Gamma = \frac{f_{2/0}x^2 + f_{1/0}r x (1-x)}{(1-x)^2 + f_{2/0}x^2 + f_{1/0}x(1-x)} \quad (\text{S6})$$

The second order term in the numerator can be eliminated by taking the difference between the two spectral values ($\tilde{\nu}_{\text{CM}} \bullet Q_{\text{rel}}$ and Q_{rel}) (equation S7):

¹² Rosés, M.; Rafols, C.; Ortega, J; Bosch, E. Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 1. A comparison of several preferential solvation models for describing ET (30) polarity of bipolar hydrogen bond acceptor-cosolvent mixtures. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1607-1615.

$$\Gamma_{\text{CM}\bullet\text{Q}} - \Gamma_{\text{Q}} = \frac{f_{1/0} \Delta r x (1-x)}{(1-x)^2 + f_{2/0} x^2 + f_{1/0} x (1-x)} \quad \text{where } \Delta r = r_{\text{CM}\bullet\text{Q}} - r_{\text{Q}} \quad (\text{S7})$$

The derivative of S7 with respect to x gives a quadratic term in the numerator (S8).

$$\frac{d(\Gamma_{\text{CM}\bullet\text{Q}} - \Gamma_{\text{Q}})}{dx} = \frac{(x^2(1-f_{2/1}) - 2x + 1) \times (f_{12/1} \Delta r)}{((1-x)^2 + f_{2/1} x^2 + f_{12/1} x (1-x))^2} \quad (\text{S8})$$

The difference function $\Gamma_{\text{Q}} - \Gamma_{\text{CM}\bullet\text{Q}}$ has an extreme value when its first derivative is zero; hence when the quadratic term is zero. The mole fraction where the maximum occurs is determined by fitting six points ($[\Gamma_{\text{Q}} - \Gamma_{\text{CM}\bullet\text{Q}}]$ vs. x) around the maximum to a third-order polynomial function, taking the first derivative, and solving the quadratic equation. This mole fraction determines the value for $f_{2/0}$ (equation S9).

$$f_{2/1} = \frac{1}{x^2} - \frac{2}{x} + 1 \quad (\text{S9})$$

The remaining parameters $f_{2/0}$ and r in equation S6 are determined through non-linear least squares fitting for both plots of $\Gamma_{\text{CM}\bullet\text{Q}}$ and Γ_{Q} vs. mole fraction. The r -values are used to determine the spectral values for the singly H-bonded species.

Determination of ground-state association constants with alcohols. The effects of alcohols on the absorption spectra of **1** – **3** were modeled using equation S10. Association constants (K) for the formation of ground-state complexes of **1** – **3** with the three alcohols were determined through non-linear least squares fitting of equation S11 using the absorption values (A and A_0) at 374 and 423 nm in Figures S1-S9. The f -term in S11 corresponds to the ratio of the molar absorptivity values (ϵ) of the complex ($F * ROH$) and the free fluorenone derivative (F), and it is also calculated in the non-linear least squares fitting.



$$A - A_0 = \frac{K(f - 1)[ROH]}{1 + K[ROH]} \quad (S11)$$

Absorption spectra

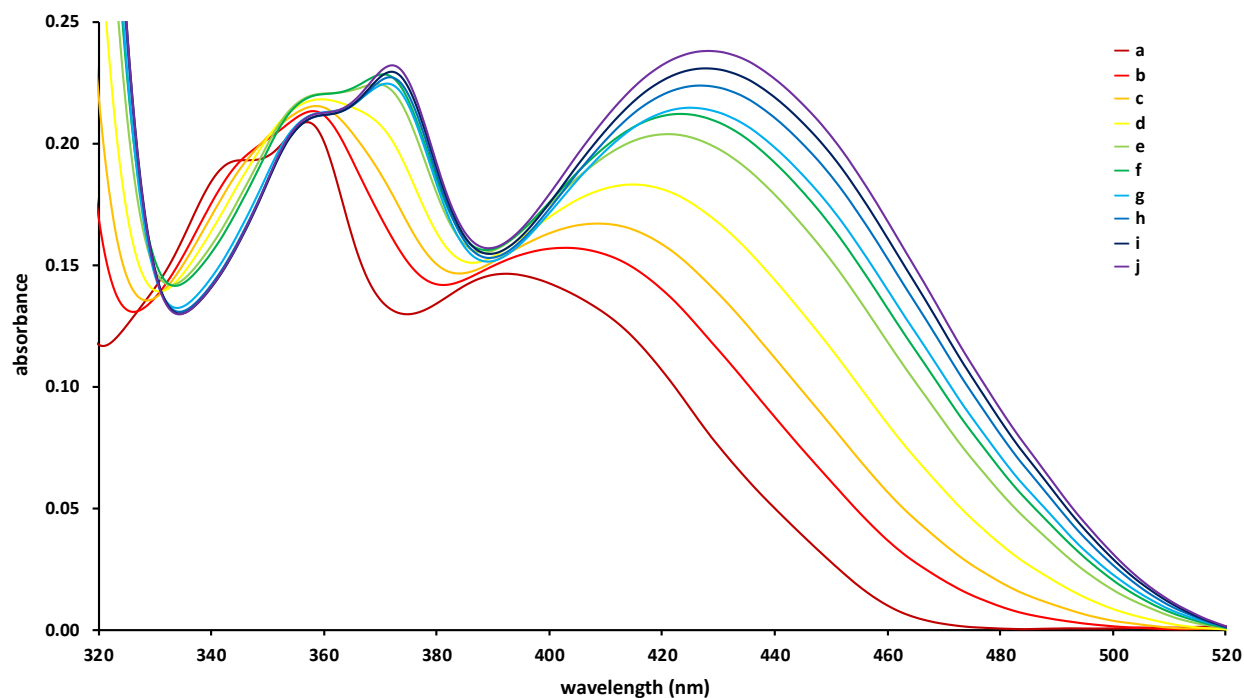


Figure S1. Absorption spectra of 48 μ M solutions of **1** in toluene/isopropanol mixtures. [i PrOH] (mole %, a-j): 0, 5, 10, 20, 40, 53, 64, 80, 90, 100.

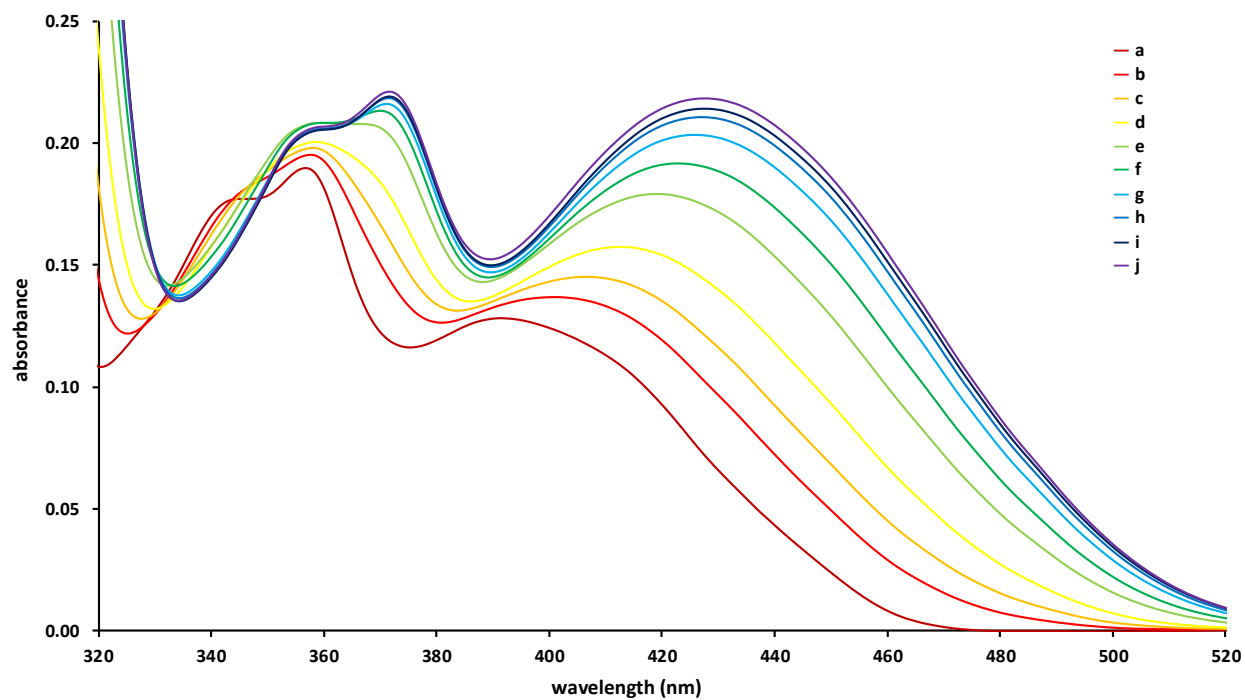


Figure S2. Absorption spectra of 48 μM solutions of **1** in toluene/ethanol mixtures. [EtOH] (mole %, a-j): 0, 3, 6, 12, 27, 44, 69, 83, 91, 100.

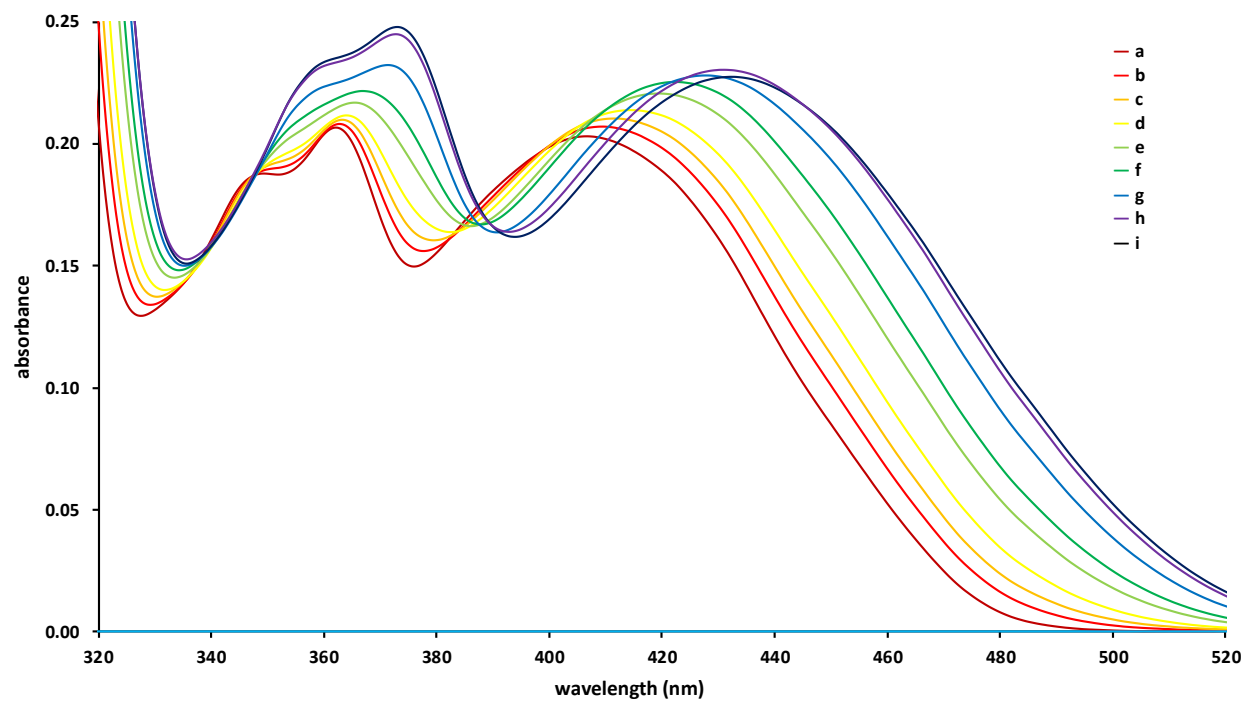


Figure S3. Absorption spectra of 48 μM solutions of **1** in tetrahydrofuran/ethylene glycol mixtures. [EG] (mole %, a-i): 0, 5, 10, 20, 39, 54, 79, 94, 100.

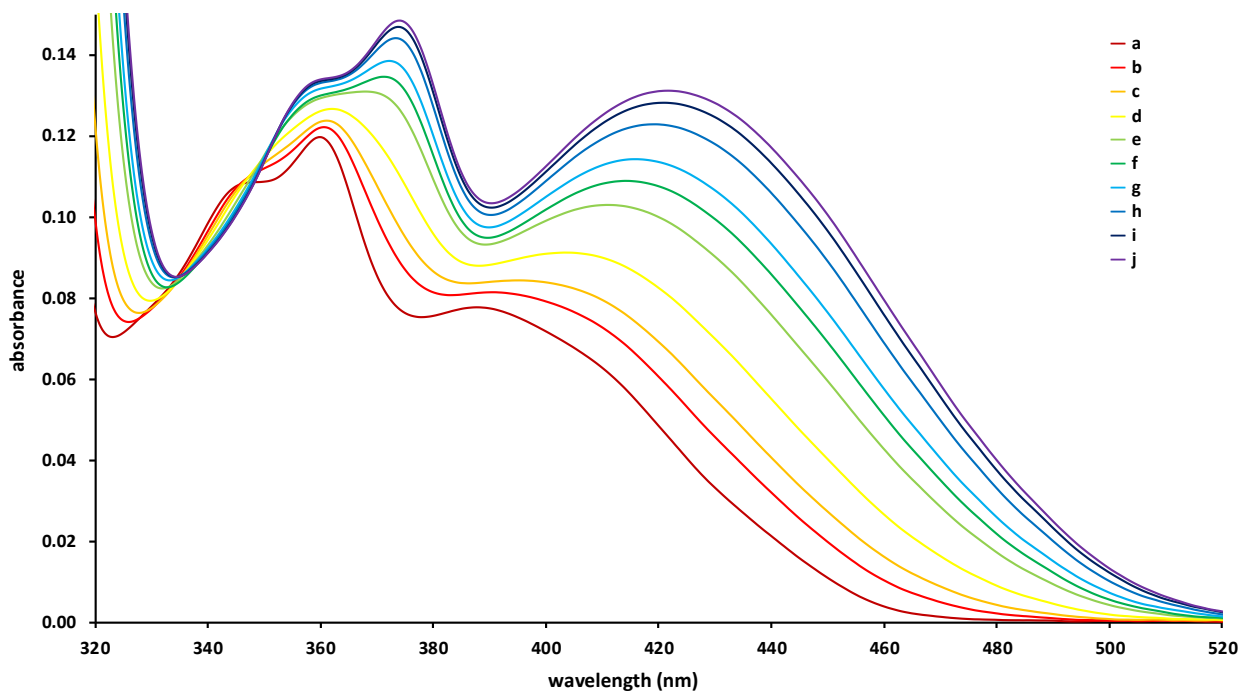


Figure S4. Absorption spectra of 46 μM solutions of **2** in toluene/isopropanol mixtures. [*i*PrOH] (mole %, a-j): 0, 5, 10, 20, 40, 53, 64, 80, 90, 95, 100.

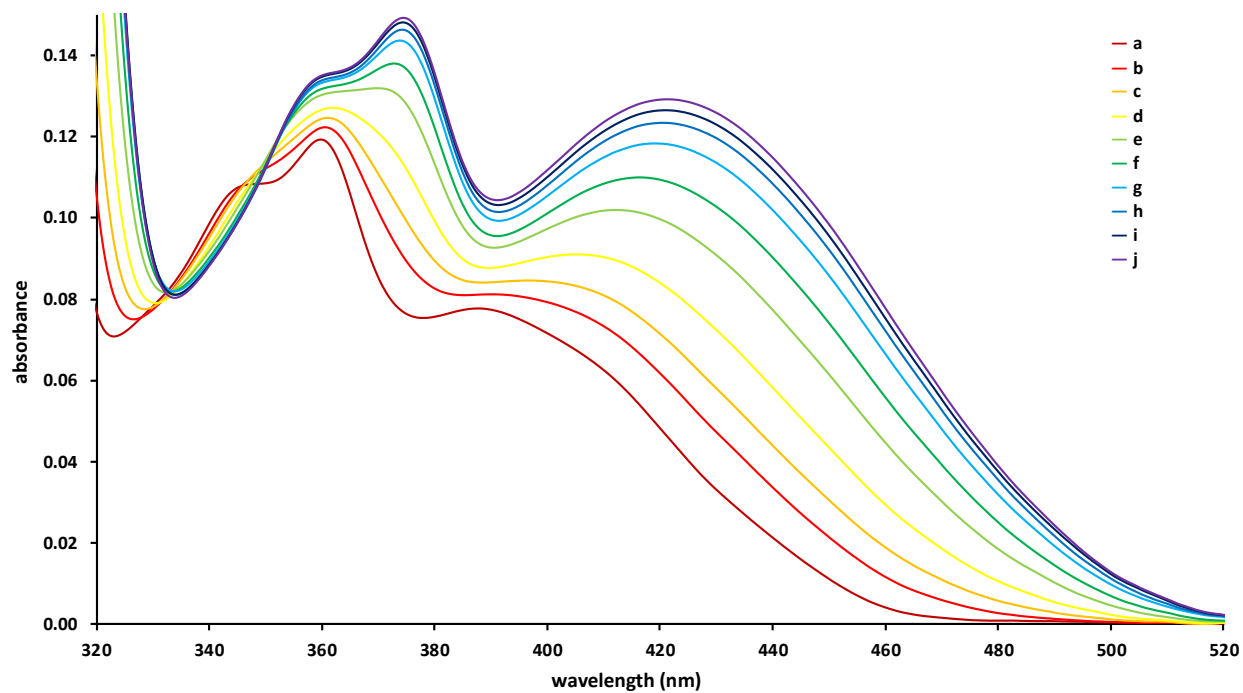


Figure S5. Absorption spectra of 46 μM solutions of **2** in toluene/ethanol mixtures. [EtOH] (mole %, a-j): 0, 5, 10, 20, 41, 59, 80, 90, 95, 100.

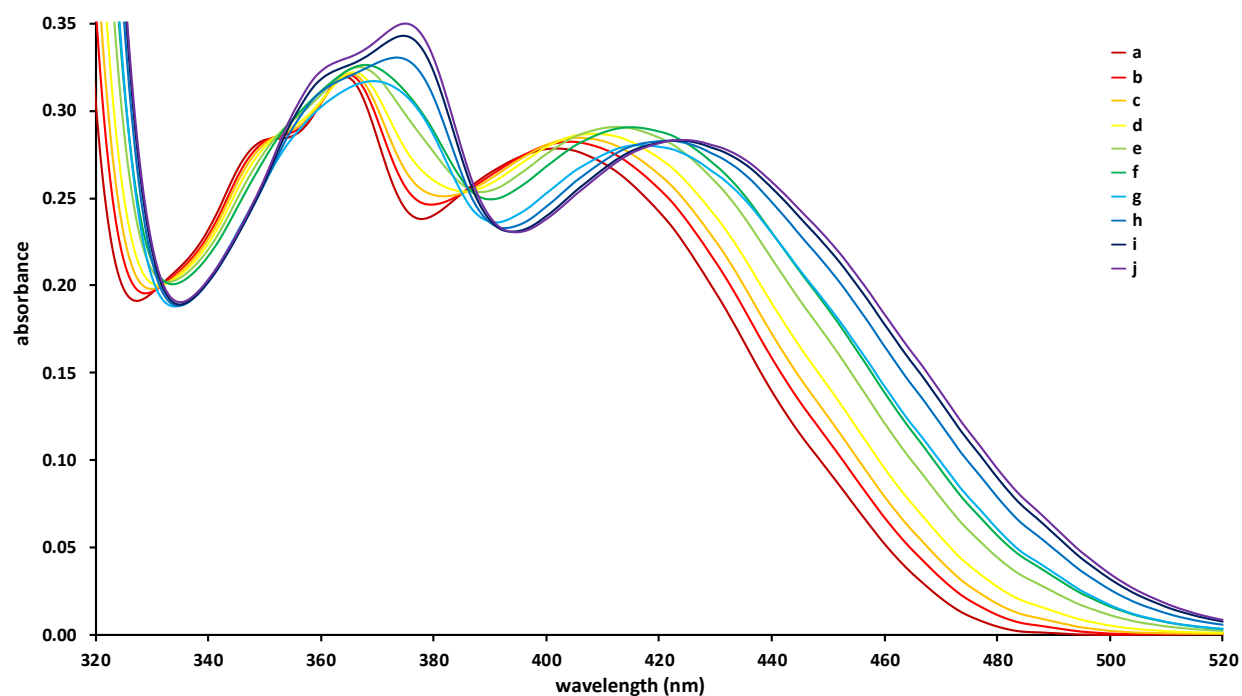


Figure S6. Absorption spectra of 92 μM solutions of **2** in tetrahydrofuran/ethylene glycol mixtures. [EG] (mole %, a-j): 0, 5, 10, 20, 39, 54, 64, 79, 89, 94, 100.

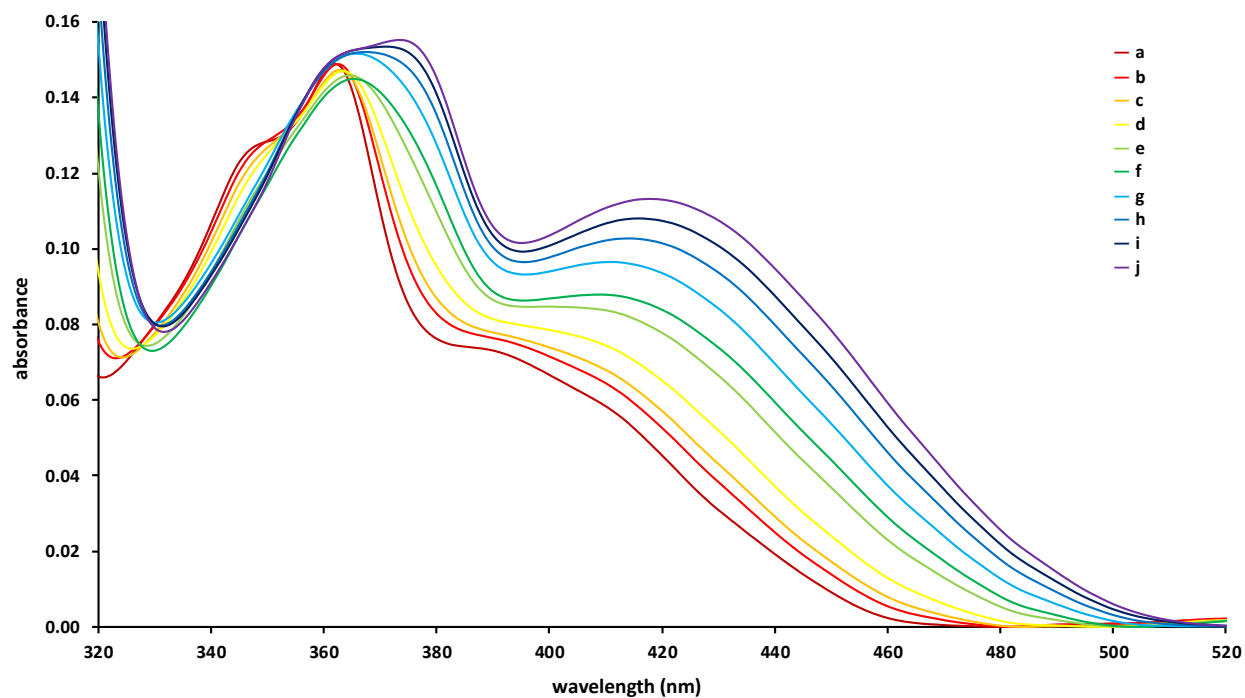


Figure S7. Absorption spectra of 48 μM solutions of **3** in toluene/isopropanol mixtures. [iPrOH] (mole %, a-j): 0, 5, 10, 20, 40, 53, 64, 80, 90, 100.

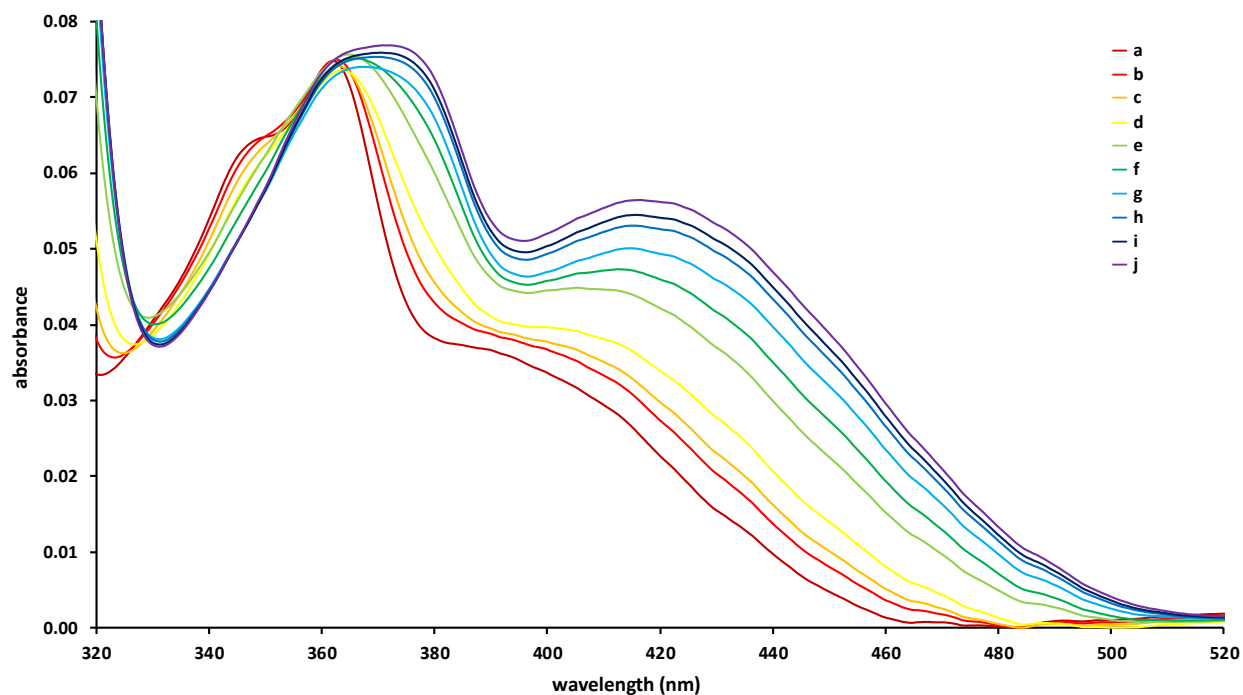


Figure S8. Absorption spectra of 24 μM solutions of **3** in toluene/ethanol mixtures. [EtOH] (mole %, a-j): 0, 3, 6, 12, 27, 44, 69, 83, 91, 100.

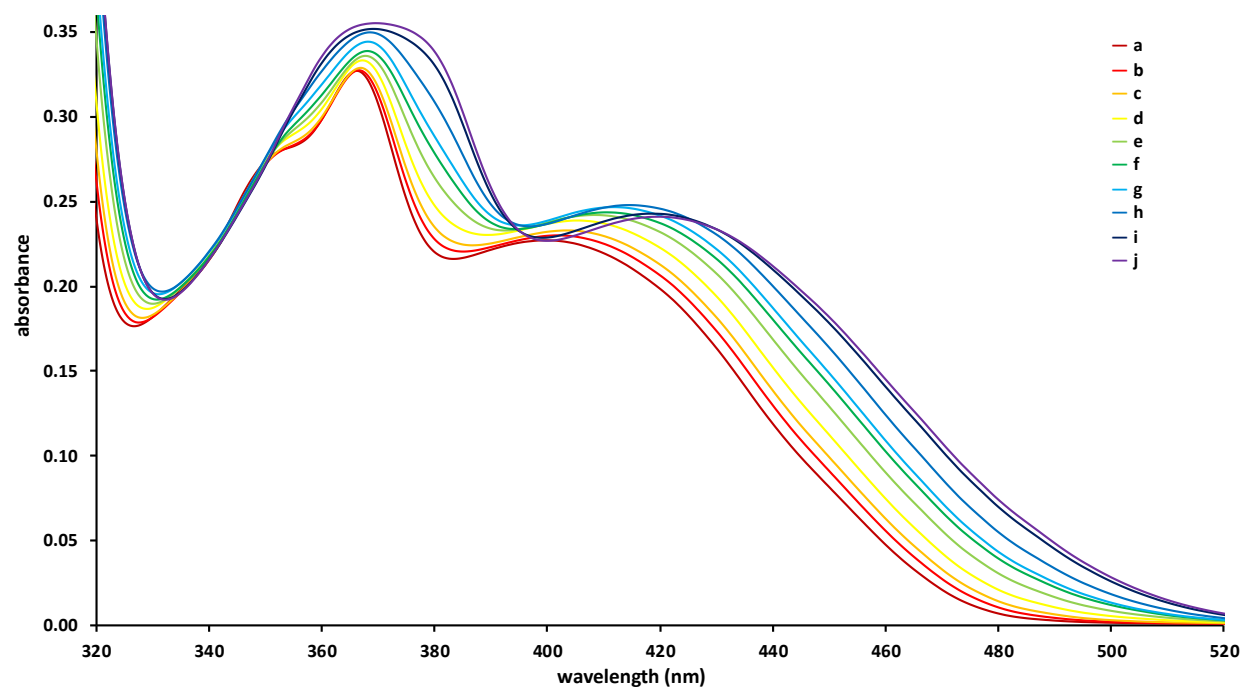


Figure S9. Absorption spectra of 97 μM solutions of **3** in tetrahydrofuran/ethylene glycol mixtures. [EG] (mole %, a-j): 0, 5, 10, 20, 39, 54, 62, 76, 94, 100.

Fluorescence Titrations

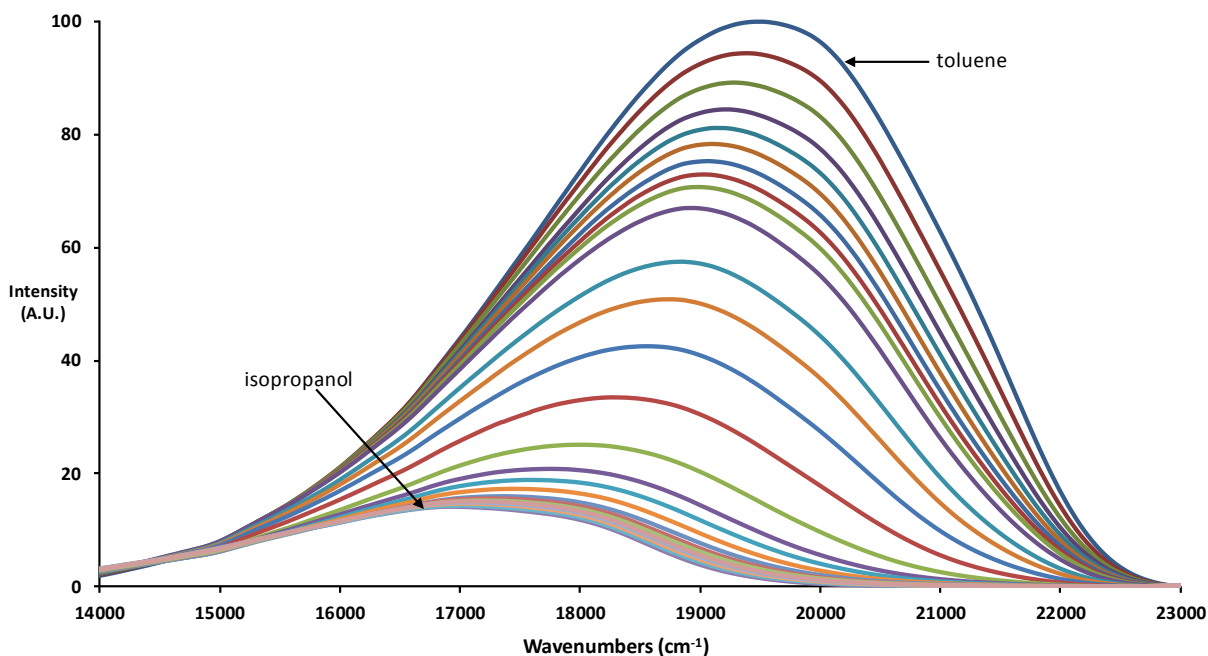


Figure S10. Fluorescence spectra of 24 μM solutions of **1** in toluene/isopropanol mixtures. [iPrOH] (mole %): 0, 0.07, 0.14, 0.21, 0.28, 0.35, 0.42, 0.49, 0.55, 0.69, 1.0, 1.4, 2.0, 3.4, 6.5, 12, 17, 26, 36, 46, 53, 64, 70, 78, 87, 100. $\lambda_{\text{ex}} = 366 \text{ nm}$.

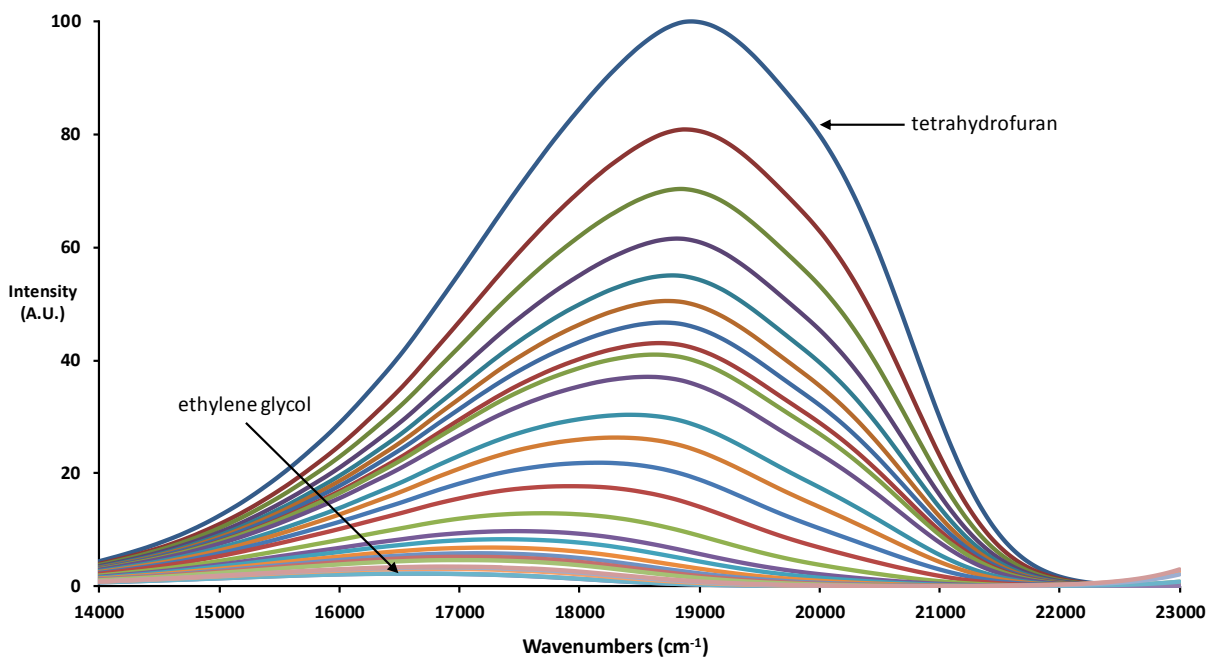


Figure S11. Fluorescence spectra of 19 μM solutions of **1** in tetrahydrofuran/ethylene glycol mixtures. [EG] (mole %): 0, 0.07, 0.14, 0.22, 0.29, 0.36, 0.43, 0.51, 0.58, 0.72, 1.1, 1.4, 2.1, 3.5, 6.8, 13, 18, 27, 37, 46, 54, 64, 71, 78, 88, 100. $\lambda_{\text{ex}} = 366 \text{ nm}$.

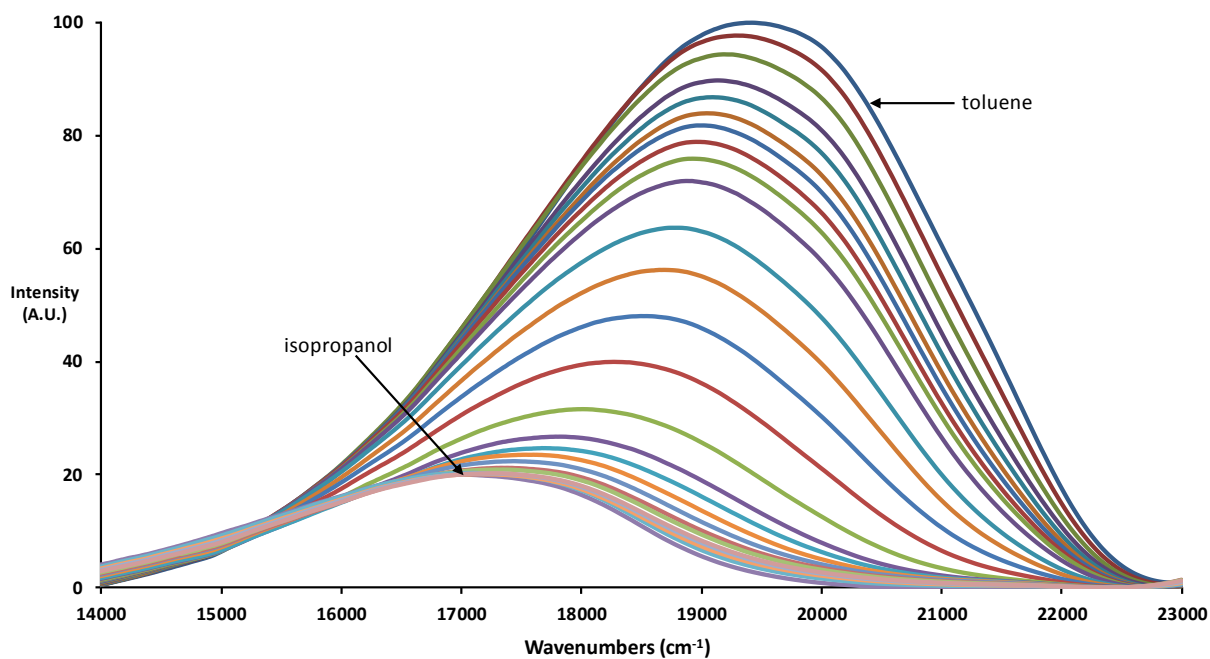


Figure S12. Fluorescence spectra of 23 μM solutions of **2** in toluene/isopropanol mixtures. $[\text{iPrOH}]$ (mole %): 0, 0.07, 0.14, 0.21, 0.28, 0.35, 0.42, 0.49, 0.55, 0.69, 1.0, 1.4, 2.0, 3.4, 6.5, 12, 17, 26, 36, 46, 53, 64, 70, 78, 87, 100. $\lambda_{\text{ex}} = 366 \text{ nm}$.

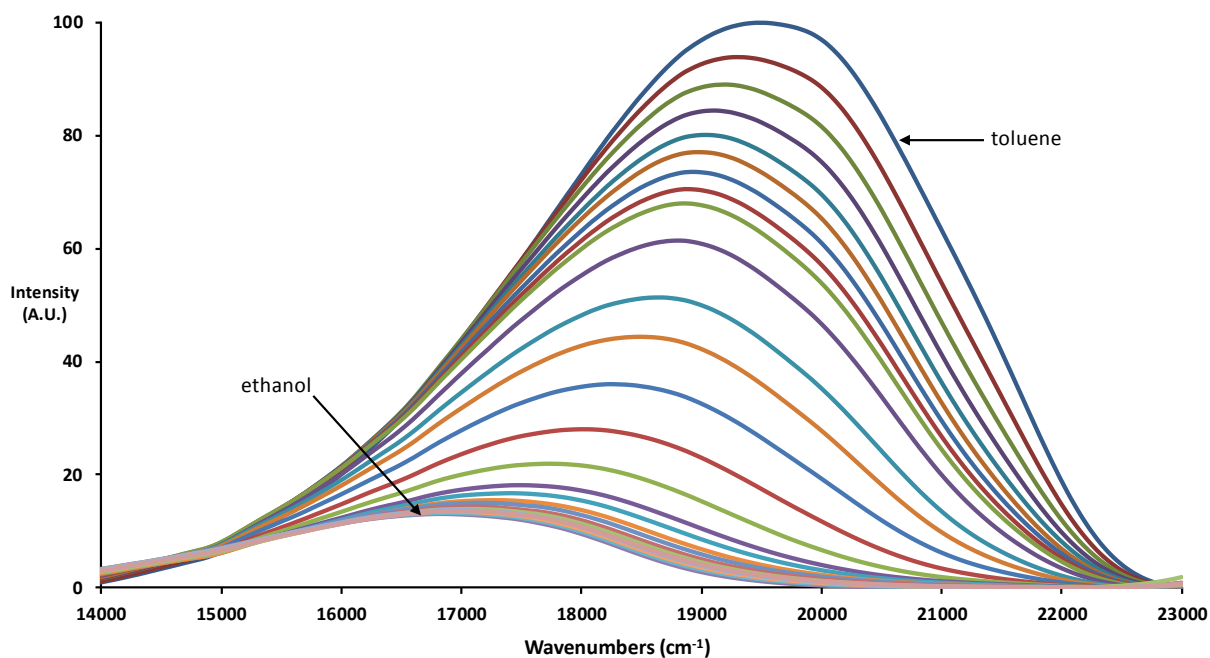


Figure S13. Fluorescence spectra of 23 μM solutions of **2** in toluene/ethanol mixtures. $[\text{EtOH}]$ (mole %): 0, 0.09, 0.18, 0.27, 0.36, 0.45, 0.54, 0.63, 0.72, 0.90, 1.3, 1.8, 2.7, 4.4, 8.4, 15, 21, 31, 42, 52, 59, 70, 75, 82, 90, 100. $\lambda_{\text{ex}} = 366 \text{ nm}$.

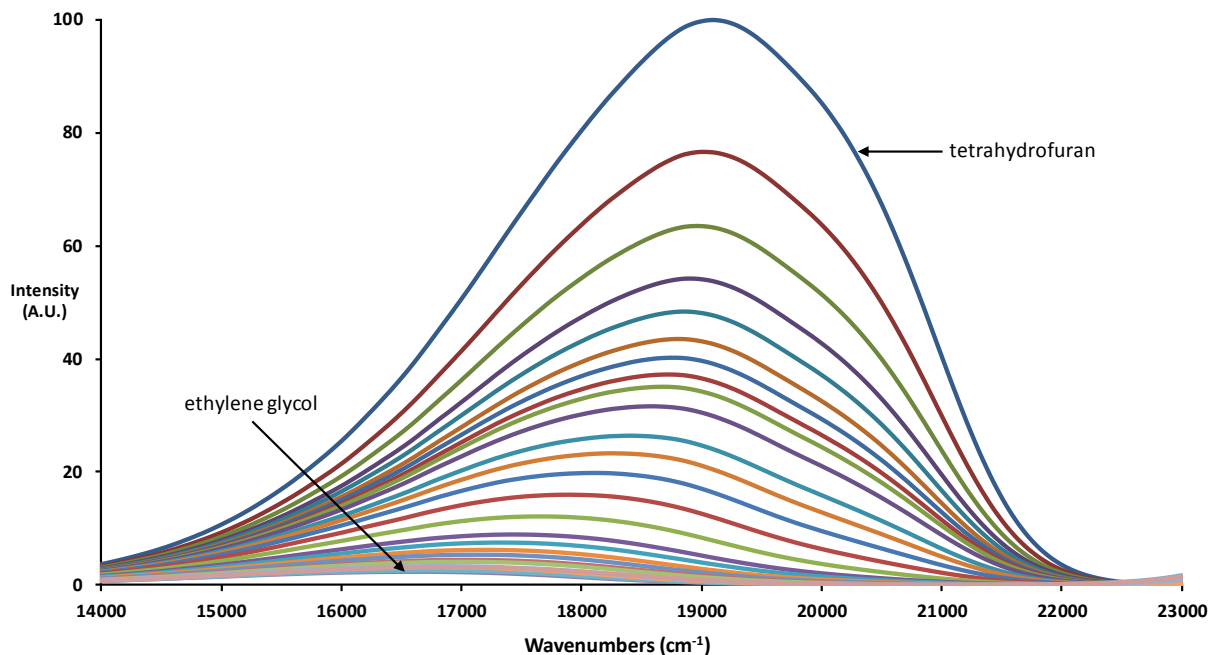


Figure S14. Fluorescence spectra of 23 μM solutions of **2** in tetrahydrofuran/ethylene glycol mixtures. [EG] (mole %): 0, 0.07, 0.14, 0.22, 0.29, 0.36, 0.43, 0.51, 0.58, 0.72, 1.1, 1.4, 2.1, 3.5, 6.8, 13, 18, 27, 37, 47, 54, 64, 71, 78, 88, 100. $\lambda_{\text{ex}} = 366 \text{ nm}$.

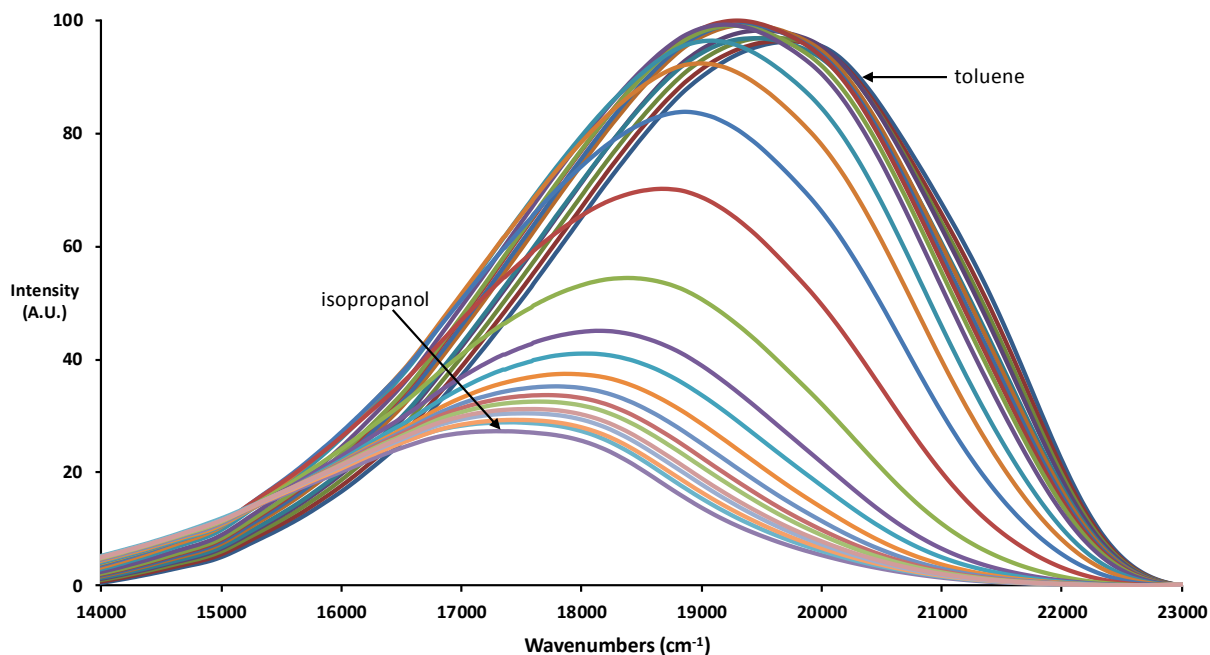


Figure S15. Fluorescence spectra of 48 μM solutions of **3** in toluene/isopropanol mixtures. [*i*PrOH] (mole %): 0, 0.07, 0.14, 0.21, 0.28, 0.35, 0.42, 0.49, 0.55, 0.69, 1.0, 1.4, 2.0, 3.4, 6.5, 12, 17, 26, 36, 46, 53, 64, 70, 78, 87, 100. $\lambda_{\text{ex}} = 366 \text{ nm}$.

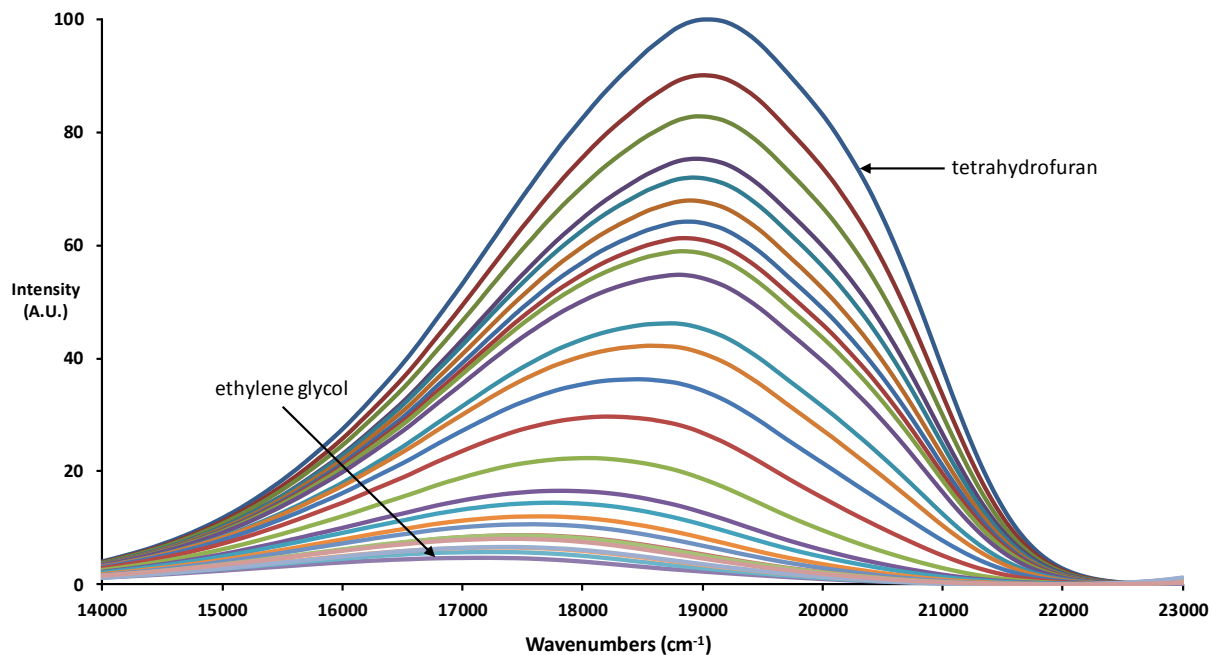


Figure S16. Fluorescence spectra of 48 μM solutions of **3** in tetrahydrofuran/ethylene glycol mixtures. [EG] (mole %): 0, 0.07, 0.14, 0.22, 0.29, 0.36, 0.43, 0.51, 0.58, 0.72, 1.1, 1.4, 2.1, 3.5, 6.8, 13, 18, 27, 37, 47, 54, 64, 71, 78, 88, 100. $\lambda_{\text{ex}} = 366 \text{ nm}$.