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Supplementary Information

Chain-Dependent Emission Color Codes of Extended Tetraphenylethylene Derivatives: Discrimination between Water and Methanol

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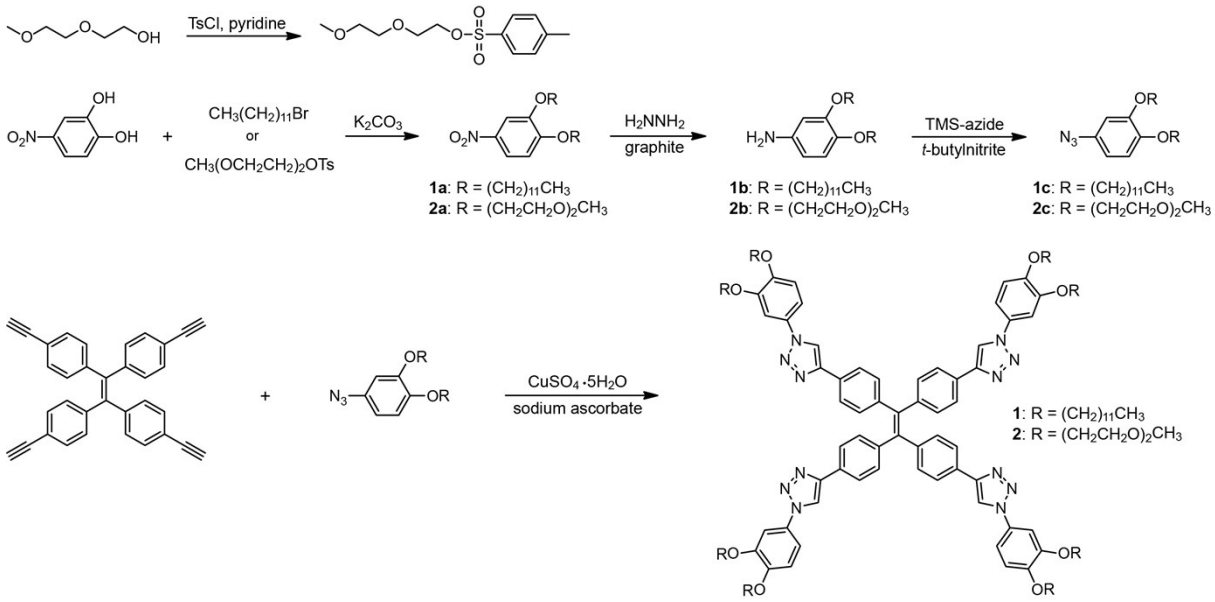
Experimental Details

Materials. Nitrocatechol, 1-bromododecane, trimethylsilyl azide (TMS-azide), trimethylsilyl acetylene, diethylene glycol monomethyl ether, diphenylmethane, molecular iodine, copper(I) iodide, triphenylphosphine, bis(triphenylphosphine)palladium(II) dichloride, piperidine, zinc powder, titanium(IV) chloride, tetrabutylammonium fluoride (in 75wt% water solution), copper sulfate pentahydrate, *t*-butylnitrite, sodium ascorbate were purchased from Sigma-Aldrich Chemical. Hydrazine monohydrate (min. 99%) was purchased from Tokyo Chemical Industry. *p*-Toluenesulfonyl chloride was purchased from Junsei Chemical Co., Ltd. Graphite powder, anhydrous potassium carbonate (min. 99%), anhydrous $MgSO_4$ (min. 99%) were purchased from Duksan Pure Chemical, Korea. Pyridine, nitric acid, sulfuric acid, acetic acid, cellite, silica gel were purchased Samchun Chemical. *N,N*-Dimethylformamide (DMF) was distilled under vacuum and stored over a type 4 Å molecular sieve. Tetrahydrofuran (THF) was dried by distillation from sodium metal and stored over a type 4 Å molecular sieve. Dichloromethane (DCM) was dried by distillation from calcium hydride (CaH_2). Acetonitrile (ACN) was dried by distillation from P_2O_5.

Methods. ^{1}H-, and ^{13}C-NMR spectra of the intermediate and final compounds were recorded from a $CDCl_3$ solution using Varian 200 and Bruker AM 400 spectrometers. The ^{1}H-NMR studies of the chloroform/poor solvent mixtures were carried out using Bruker AM 400 spectrometer. Each NMR sample was prepared by adding an appropriate amount of poor solvent to the chloroform stock solution. The concentrations of all NMR solutions were set to be 1.0 mM, because the solution concentration of 10 μM employed in the fluorescence experiments was too dilute to be proper for the ^{1}H-NMR study. By keeping the solution concentration (1 mM), the volume fraction of the poor solvents was varied. From the obtained NMR spectra, the relative integrals of the aromatic signals were determined. By doing so, we could assign which aromatic parts were conformationally restricted upon adding the poor solvents. Above the maximum volume fraction of the poor solvent in each NMR study, the compounds began to precipitate, by which the NMR signals were not measured. Gel permeation chromatography (GPC) measurements were performed in THF and *N,N'*-dimethylacetamide (98:2 volume ratio) using a Waters 401 instrument equipped with KF-802, KF-803, AT-G and AT-804S Shodex columns at a flow rate of 1.0 mL/min. The morphologies of samples were observed with a field-emission scanning electron microscope (FE-SEM) using a FE-SEM, Hitachi S4300, Hitachi Inc. The purity of the compounds was checked by thin-layer chromatography (TLC; Merck, a gel 60). The compounds were purified by column chromatography (silica gel) and prep-HPLC (Japan Analytical Instrument). Element analyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center, Sogang University, Korea. The UV-vis absorption spectra were obtained using Perkin Elmer Lambda 950 UV/Vis/NIR spectrometer. The luminescence spectra were obtained using Hitachi F-7000 fluorescence spectrophotometer. The UV handy lamp used for the emission photos was a Spectroline ENF-240C/FE 6 W 254 nm/365 nm. Life-time measurements were performed using a MicroTime-200 instrument at the National Center for Inter-University Research Facilities (Korea). For the fluorescence quantum yields (Φ_F) of the chloroform/methanol solutions of **1** were determined using quinine sulfate as a standard reference (0.1 M, $\Phi_F = 0.54$).

Synthesis. The synthetic procedure is outlined in Scheme 1. The synthesis of **1** and **2** was accomplished by click chemistry using $CuSO_4 \cdot 5H_2O$ and sodium ascorbate as catalysts. Compound **1** was prepared as described previously, and the synthetic details of **1a-c** and **1** were reported in the previous publication.[S1] The synthetic details of **2** with the hydrophilic OEG peripheries are described as below. The experimental data are in good agreement with the designed molecular structures.

Synthesis of 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate. Diethylene glycol monomethyl ether (15.0 g, 124 mmol), *p*-toluenesulfonyl chloride (26.2 g, 137 mmol) and pyridine (10.9 g, 137 mmol) were dissolved in dried dichloromethane, and the mixture was stirred at reflux for 12 h. After removing the solvent, the mixture was extracted using dichloromethane and water, and dried over anhydrous magnesium sulfate. After removing dichloromethane by a rotary evaporator, the resulting mixture was purified by column chromatography (silica gel) using ethyl acetate:dichloromethane = 1:8 as the eluent, to yield 32.0 g (93.4%) of a colorless solid as the product. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.80 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.34 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 4.16 (t, 2H, *J* = 4.8 Hz, Ar-SO_3-CH_2-), 3.68 (t, 2H, *J* = 5.2 Hz, Ar-SO_3-CH_2CH_2-), 3.56 (t, 2H, *J* = 4.4 Hz, Ar-SO_3-CH_2CH_2-O-CH_2-), 3.48 (t, 2H, *J* = 4.8 Hz, Ar-SO_3-CH_2CH_2-O-CH_2CH_2-), 3.34 (s, 3H, -OCH_3), 2.44 (s, 3H, Ar-CH_3).



Scheme S1. Synthetic procedures of **1** and **2**.

Synthesis of 1,2-bis(2-(2-methoxyethoxy)ethoxy)-4-nitrobenzene (2a). Nitrocatechol (3.00 g, 19.3 mmol), 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (12.7 g, 46.4 mmol) and potassium carbonate (6.42 g, 46.4 mmol) were dissolved in dried DMF, and the mixture was heated at reflux for 12 h. After removing the solvent, the mixture was extracted using dichloromethane and water, and dried over anhydrous magnesium sulfate. After removing dichloromethane by a rotary evaporator, the resulting mixture was purified by column chromatography (silica gel) using ethyl acetate:dichloromethane = 1:20 as the eluent, to yield 6.00 g (86.3%) of a yellowish liquid as the product. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.88 (d, 1H,

J = 6.4 Hz, Ar-*H*), 7.80 (s, 1H, Ar-*H*), 6.94 (d, 1H, *J* = 9.2 Hz, Ar-*H*), 4.24-4.21 (m, 4H, Ar-OC*H*$_2$-), 3.90-3.88 (m, 4H, Ar-OCH$_2$C*H*$_2$-), 3.36 (s, 6H, -OC*H*$_3$).

Synthesis of 4-azido-1,2-bis(2-(2-methoxyethoxy)ethoxy)benzene (2c). 1,2-Bis(2-(2-methoxyethoxy)ethoxy)-4-nitrobenzene (**2a**) (6.00 g, 16.7 mmol), hydrazine (7.78 ml, 25.0 mmol) and graphite (2.66 g) were dissolved in ethanol (150 ml), and the mixture was heated at reflux for 24 h under nitrogen atmosphere. After removing the solvent, the mixture was extracted using dichloromethane and water. The organic layer was washed several times with distilled water, and dried over anhydrous magnesium sulfate. After removing dichloromethane by a rotary evaporator, 4.30 g of a yellowish liquid (**2b**) was obtained. Without further purification, the obtained compound (**2b**) was used for the next reaction. The resulting compound (**2b**) (4.30 g, 13.1 mmol) was dissolved in dried acetonitrile (20 ml). The solution was cooled to 0 ^{o}C, and *t*-butylnitrite (2.34 g, 14.4 mmol) was then added dropwise to the solution. After trimethylsilyl azide (TMS-azide, 1.65 g, 14.4 mmol) was added, the mixture solution was stirred for 12 h at room temperature. After removing dichloromethane by a rotary evaporator, the resulting mixture was purified by column chromatography (silica gel) using ethyl acetate:dichloromethane = 1:20 as the eluent, to yield 3.80 g (81.9%) of a yellowish liquid as the product. ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.89 (d, 1H, *J* = 9.4 Hz, Ar-*H*), 6.60-6.57 (m, 2H, Ar-*H*), 4.19 (t, 4H, Ar-O-C*H*$_2$), 3.88-3.81 (m, 4H, Ar-O-CH$_2$C*H*$_2$-), 3.74-3.70 (m, 4H, Ar-OCH$_2$CH$_2$OC*H*$_2$-), 3.58-3.54 (m, 4H, Ar-OCH$_2$CH$_2$OCH$_2$C*H*$_2$-), 3.38 (s, 6H, -OC*H*$_3$).

Synthesis of 2. 1,1,2,2-Tetrakis(4-ethynylphenyl)ethane (0.150 g, 0.350 mmol), 4-azido-1,2-bis(2-(2-methoxyethoxy)ethoxy)benzene (**2c**) (0.750 g, 2.10 mmol), sodium ascorbate (277 mg, 1.40 mmol) and $CuSO_4 \cdot 5H_2O$ (175 mg, 0.700 mmol) were dissolved in dichloromethane (8 ml) and distilled water (0.3 ml). The reaction mixture was stirred for 12 h at room temperature under nitrogen atmosphere. It was then extracted with dichloromethane and water, and the organic layer was dried over anhydrous magnesium sulfate. After removing dichloromethane by a rotary evaporator, the resulting mixture was purified by column chromatography (silica gel) using methanol:dichloromethane = 1:10 as the eluent. A further purification using a HPLC yielded 0.420 g (64.9%) of a yellowish solid as the product. ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 8.07 (s, 4H, triazole-*H*), 7.68 (d, 8H, *J* = 8.0 Hz, Ar-*H*), 7.41 (s, 4H, Ar-*H*), 7.23-7.19 (m, 12H, Ar-*H*), 7.00 (d, 4H, *J* = 8.8 Hz, Ar-*H*), 4.26-4.21 (m, 16H, Ar-O-C*H*$_2$-), 3.90-3.88 (m, 16H, -O-CH$_2$-C*H*$_2$-O-), 3.74-3.73 (m, 16H, -O-C*H*$_2$-C*H*$_2$-), 3.58-3.56 (m, 16H, -CH$_2$-C*H*$_2$-O-), 3.37 (s, 24H, -C*H*$_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): 149.71, 149.30, 148.06, 143.59, 140.86, 132.13, 131.08, 128.80, 125.46, 117.99, 114.61, 113.18, 107.74, 72.06, 70.92, 69.75, 69.26, 59.18. M_w/M_n = 1.01 (GPC). Anal. Calcd for $C_{98}H_{120}N_{12}O_{24}$: C, 63.62; H, 6.54; N, 9.09. Found: C, 63.66; H, 6.62; N, 9.00.

Reference

(S1) J. Kim, S. Cho and B.-K. Cho, *Chem. Eur. J.*, 2014, **20**, 12734-12739.

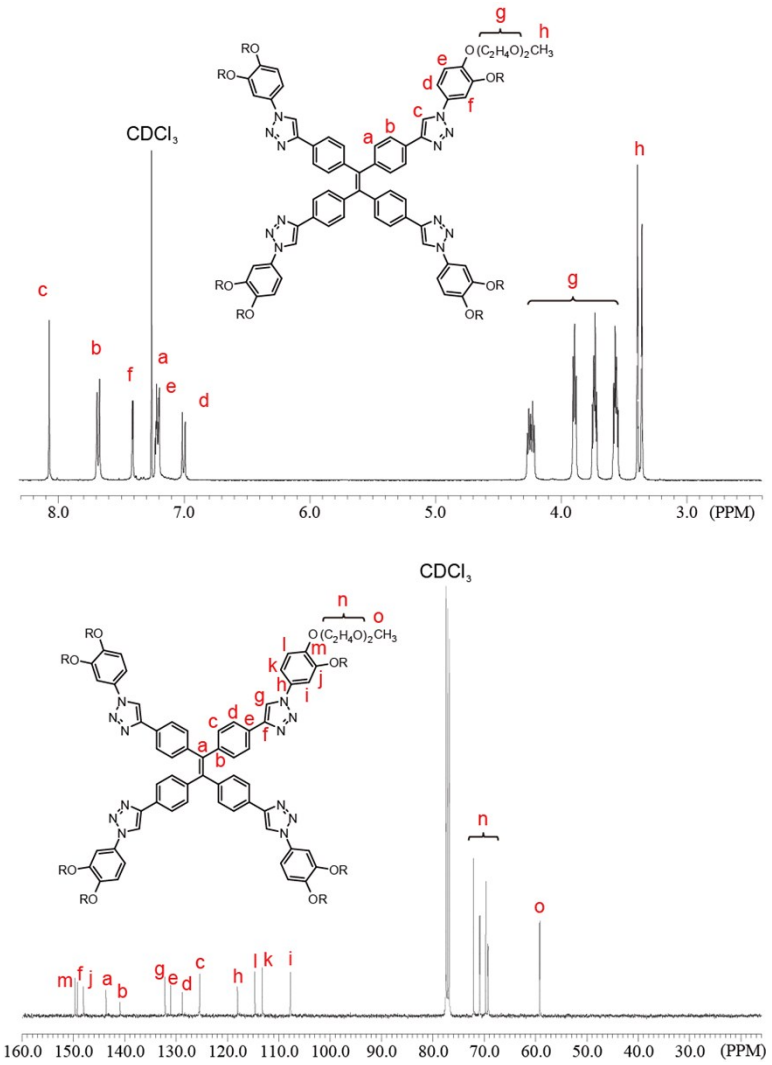


Fig. S1 ^{1}H- and ^{13}C-NMR spectra of compound **2**.

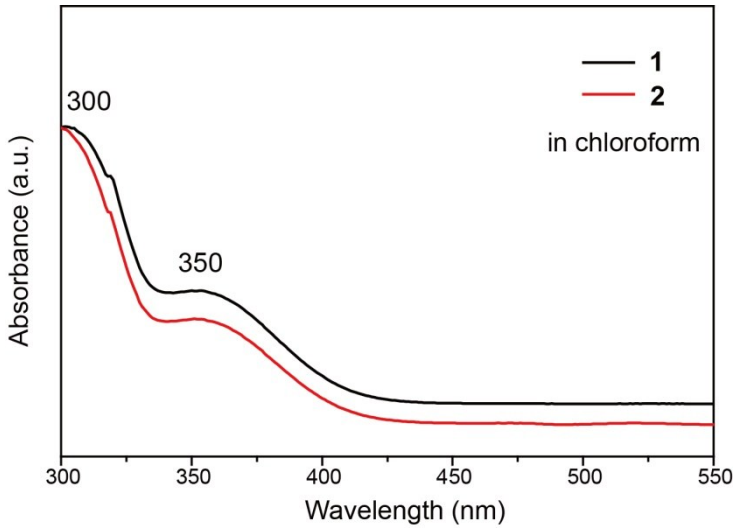


Fig. S1 UV absorption spectra of **1** and **2** in chloroform.

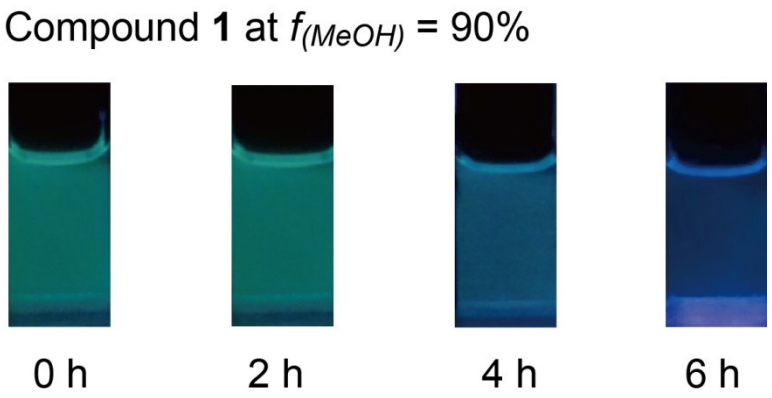


Fig. S3 Emission color change of **1** at $f_{(MeOH)}$ = 90% as a function of time.

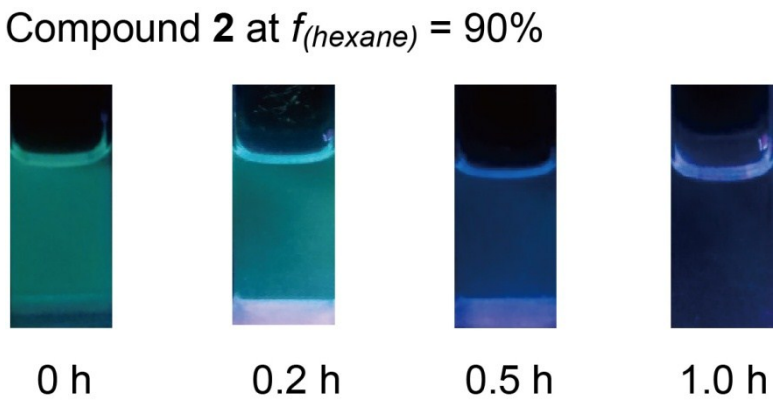


Fig. S4 Emission color change of **2** at $f_{(hexane)}$ = 90% as a function of time.

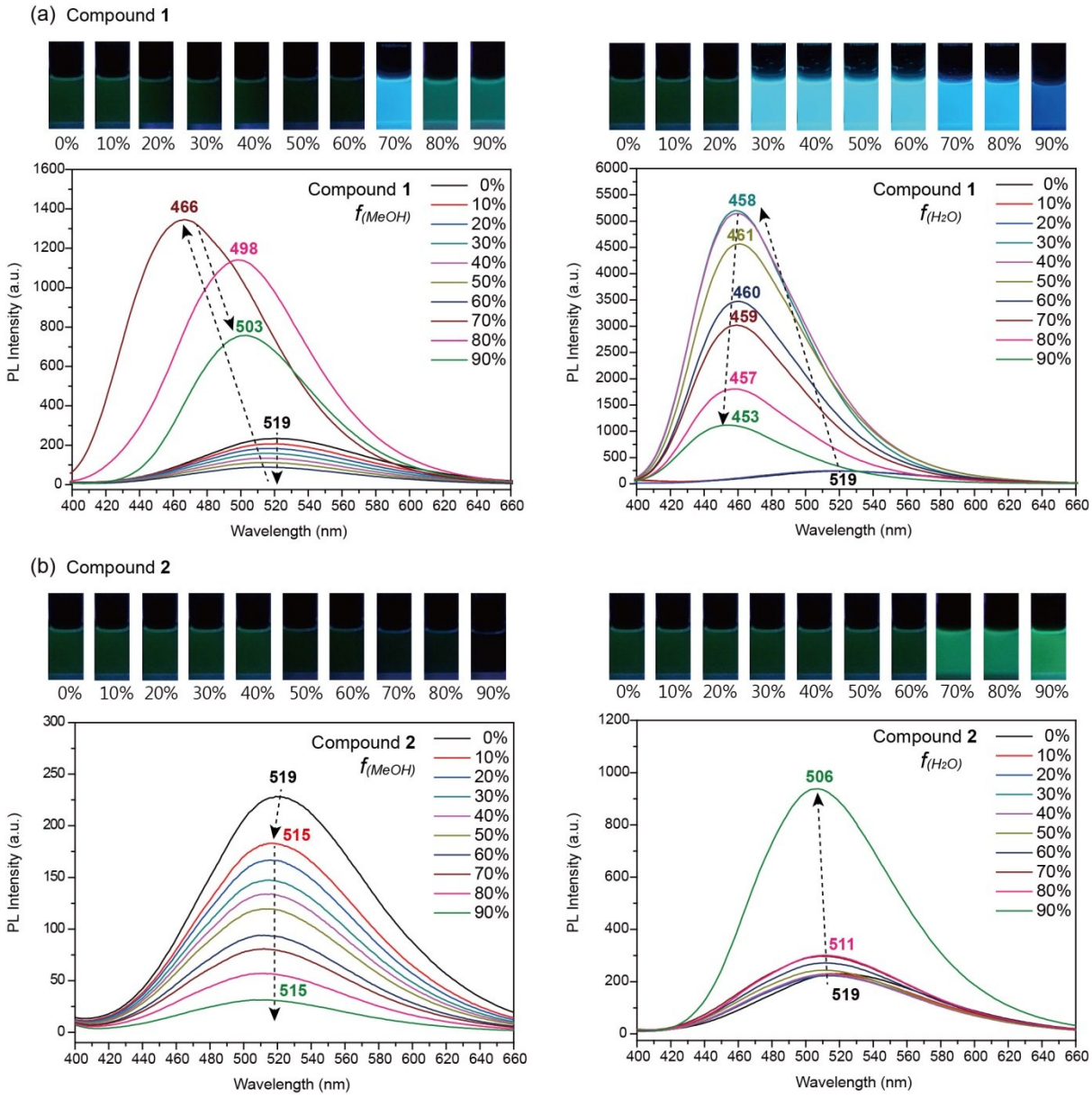


Fig. S5 Emission photos and spectra of the THF/methanol (or Water) solutions of **1** and **2** as a function of the poor solvent volume fraction (*f*). The photos were taken under UV illumination at 365 nm. The excitation wavelength of the emission spectra is 350 nm.