Supplementary Information

Aggregation Induced Blue Shift of Emission and Self-Assembly Naonoparticles from a Novel Amphiphilic Oligofluorene

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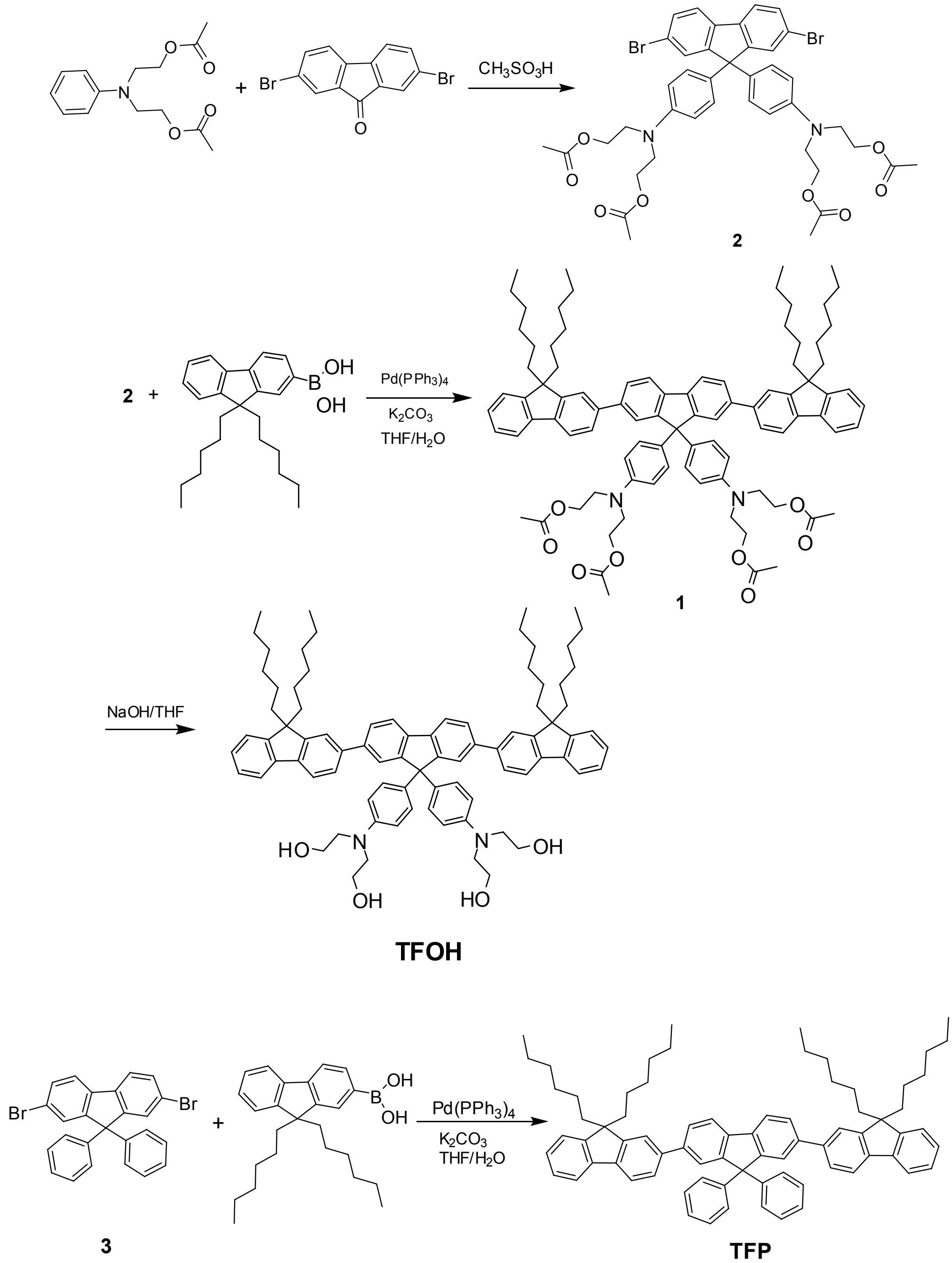
1. General Information

The 2,7-dibromofluorenone,[1] *N*,*N*-bis(2-acetoxyethyl)aniline,[2] 9,9-di-*n*-hexylfluorenyl-2-boronic acid,[3] and the compound **3** (2,7-Dibromo-9,9-dipheneyl fluorene)[4] were prepared according to the literature procedures. Tetrakis-(triphenylphosphine)palladium was purchased from Acros. Other materials were used directly without further purification unless otherwise stated.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a MECUYRVX300 spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. MALDI TOF was measured on a Voyager-DE STR MALDI TOF instrument, using α-cyano-4-hydroxyclinnamic acid (CHCA) as a matrix. EI Mass was recorded on a Finnigan TRACE Mass Spectrometer. UV-Vis absorption spectra were recorded on Shimadzu 160A recording spectrophotometer. PL spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured from the trifluorenes solution (ca. 10^{-6} mol/L) by an absolute method using the Edinburgh Instruments (FLS920) integrating sphere excited with Xe lamp. The concentration of **TFP** and **TFOH** in UV-vis absorption and fluorescence emission tests are 5×10^{-6} M. DLS (Dynamic Light Scattering) experiments were measured on a NANO-ZS Instruments. The aggregation behavior of **TFOH** in THF/H_2O mixtures was studied by FE-SEM and TEM images. SEM images were taken by using a field emission scanning electron microscope (FEI Sirion FEG) operated at a voltage of 15 kV. Water was added into **TFOH** in THF solution (at a concentration of 5.0×10^{-4} M). After the mixture was allowed to equilibrate over a period, one drop of this mixed solution was transferred onto a quartz substrate. TEM images were taken by using a JEOL JEM 2010 FEF. A carbon grid was dipped into 5.0×10^{-6} M **TFOH** in THF solution.

2. Synthesis and Characterization of the compounds

Scheme 1. Synthetic routes for the trimeric fluorenes **TFP** and **TFOH**.



Synthesis of compound 2

A mixture of 2,7-dibromofluorone (1.00 g, 3.0 mmol), *N*,*N*-bis(2-acetoxyethyl)aniline (13.2 g, 54.8 mmol) and CH_3SO_3H (0.23 mL, 3.5 mmol) in 5 mL CCl_4 were heated at 80 ˚C for 40 h. Then the reactant was extracted with $CHCl_3$, the compound **2** was gained as white solid after column chromatography using EA/PE (1:4, V/V) as eluent. Yield: 1.84 g, 78 %.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.48 (d, J = 6 Hz, 2H, aromatic H of fluorene), 7.37 (s, 2H, aromatic H of fluorene), 7.36 (d, J = 6 Hz, 2H, aromatic H of fluorene), 6.93 (d, J = 9 Hz, 4H, phenyl ring), 6.55 (d, J = 9 Hz, 4H, phenyl ring), 4.13 (t, J = 6 Hz, 8H, $-CH_2O-$), 3.50 (t, J = 6 Hz, 8H, $-NCH_2$). 1.95 (s, 12H, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 171.24 (carbonyl C), 154.33, 146.24, 138.07, 132.87, 130.76, 129.43, 129.32, 121.95, 121.70, 112.11, 64.20 (fluorene C9), 61.67 (CH_2O), 50.00 (NCH_2), 21.14 (CH_3). Anal. Calcd. for $C_{41}H_{42}Br_2N_2O_8$ (%): C, 57.89; H, 4.98; N, 3.29; Found: C 57.71, H 5.18, N 3.29. EI-MS: *m/z* 848.6 (M^+). FT-IR: 2959 (C-H stretching), 1740 (C=O stretching), 1610, 1517, 1448 (aromatic), 1247 (C-O stretching).

Synthesis of compound 1

A mixture of compound **2** (300 mg, 0.37 mmol), 2-(boronic acid-2-yl)-9,9'-dihexylfluorene (310 mg, 0.82 mmol), $Pd(PPh_3)_4$ (34 mg, 0.74 mmol), and 2 M K_2CO_3 aqueous solution (4 mL) in THF (12 mL) were stirred at 75 ℃ for 24 h. After reaction, the organic layer was extracted by $CHCl_3$, and was washed with saturated brine, then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the compound **1** was gained as a white solid after column chromatography using EA/PE (1:4, V/V) as eluent. Yield: 0.32 g, 67 %.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.85 (d, J = 6 Hz, 2H, aromatic H of fluorene), 7.73-7.65 (m, 8H, aromatic H of fluorene), 7.55 (d, J = 6 Hz, 2H, aromatic H of fluorene), 7.53 (s, 2H, aromatic H of fluorene), 7.24 (d, *J* = 9 Hz, 4H, phenyl ring), 6.67 (d, *J* = 9 Hz, 4H, phenyl ring), 4.21 (t, *J* = 6 Hz, 8H, $-CH_2O-$), 3.58 (t, *J* = 6 Hz, 8H, $-NCH_2$), 2.00 (t, *J* = 6 Hz, 8H, $-CCH_2-$), 1.98 (s, 12H, $-COCH_3$), 1.14-1.06 (m, 24 H, alkyl H), 0.78-0.66 (m, 20H, alkyl H).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 171.15 (carbonyl C), 153.47, 151.57, 151.22, 146.05, 141.29, 141.02, 140.53, 139.02, 129.65, 127.19, 126.99, 126.74, 126.34, 124.81, 123.12, 121.50, 120.57, 120.06, 112.15, 61.76 (central fluorene C9), 55.38, 50.11, 40.63 (side fluorene C9), 31.71, 29.93, 23.99, 22.82, 21.08 ($COCH_3$), 14.24 (alkyl CH_3). Anal. Calcd. for $C_{91}H_{108}N_2O_8$ (%): C, 80.49; H, 8.02; N, 2.06; Found: C 80.38, H 7.86, N 2.08. MALDI-TOF-MS: *m/z* 1357.3 (M^+). FT-IR: 2928 (C-H stretching), 1742 (C=O stretching), 1609, 1515, 1450 (aromatic), 1229 (C-O stretching).

Synthesis of TFOH

Compound **1** (220 mg, 0.16 mmol) and NaOH (256 mg, 6.4 mmol) were dissolved into a mixture of THF/H_2O (V:V/1:1). The solution was heated at 50 ℃ overnight. After reaction, the organic layer was extracted with ether, and washed with brine for 3 times, then dried over anhydrous Na_2SO_4. Pure **TFOH** was obtained as white powder by recrystallization in $CHCl_3$/hexane mixture. Yield: 0.18 g, 96 %.

^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.84 (d, *J* = 6 Hz, 2H, aromatic H of fluorene), 7.71-7.64 (m, 8H, aromatic H of fluorene), 7.53 (s, 4H, aromatic H of fluorene), 7.35-7.31 (m, 4H, aromatic H of fluorene), 7.24 (d, *J* = 9 Hz, 4H, phenyl ring), 6.64 (d, *J* = 9 Hz, 4H, phenyl ring), 3.82 (t, *J* = 6 Hz, 8H, $-CH_2O-$), 3.53 (t, *J* = 6 Hz, 8H, $-NCH_2$), 1.98 (t, *J* = 6 Hz, 8H, $-CCH_2-$), 1.11-1.05 (m, 24 H, alkyl H), 0.77-0.65 (m, 20H, alkyl H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 153.48, 151.56, 151.16, 146.67, 141.21, 140.92, 140.53, 140.35, 138.96, 129.47, 127.22, 126.98, 126.70, 126.28, 124.77, 123.10, 121.45, 120.57, 120.02, 119.91, 112.42, 61.16 (central fluorene C9), 55.72, 55.35, 40.60 (side fluorene C9), 31.70, 31.19, 29.92, 23.97, 22.81, 14.25 (alkyl CH3). Anal. Calcd. for $C_{83}H_{100}N_2O_4$ (%): C, 83.70; H, 8.18; N, 2.47; Found: C 83.63, H 8.46, N 2.47. MALDI-TOF-MS: *m/z* 1189.3 (M^+). FT-IR: 3306 (H-O···H), 2927 (C-H stretching), 1609, 1514, 1465, 1450 (aromatic).

Synthesis of TFP

A mixture of compound **3** (120 mg, 0.25 mmol), 2-(boronic acid-2-yl)-9,9’-dihexylfluorene (378 mg, 0.56 mmol), $Pd(PPh_3)_4$ (23 mg, 0.5 mmol), and 2 M KOH aqueous solution (3 mL) in THF (9 mL) were stirred at 75 ℃ for 24 h. After reaction, the organic layer was extracted by $CHCl_3$, and washed with saturated brine, then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the compound **TFP** was gained as a white solid after column chromatography using EA/PE (1:15, V/V) as eluent. Yield: 0.15 g, 59 %.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.88 (d, *J* = 6 Hz, 2H, aromatic H), 7.70 (br, 8H, aromatic H), 7.54 (s, 2H, aromatic H), 7.51 (s, 2H, aromatic H), 7.38-7.25 (m, 12H, aromatic H), 1.97 (t, *J* = 9 Hz, 8H, $-CCH_2-$), 1.13-1.04 (m, 24H, alkyl H), 0.76-0.71 (m, 8H, alkyl H), 0.65 (br, 8H, alkyl H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 152.3, 151.6, 151.2, 146.2, 141.5, 140.9, 140.6, 140.2, 139.2, 128.6, 128.5, 127.2, 127.1, 126.9, 126.3, 125.1, 123.1, 121.5, 120.6, 120.0, 119.9, 66.0 (central fluorene C9), 55.3 (side fluorene C9), 40.5, 31.7, 29.9, 24.0, 22.8, 14.2 (alkyl CH_3). Anal. Calcd. for $C_{75}H_{82}$ (%): C, 91.60; H, 8.40; Found: C 91.88, H 9.08. MALDI-TOF-MS: *m/z* 982.65 (M^+).

3. *Photophysical Properties*

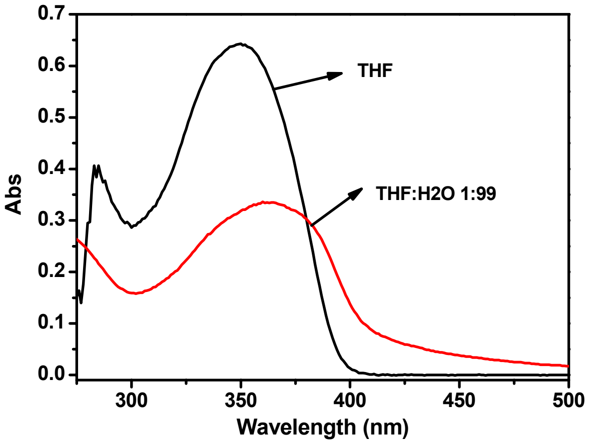


Figure S1. UV-vis spectra of **TFOH** in THF solution and THF:H_2O (V:V/1:99) mixture.

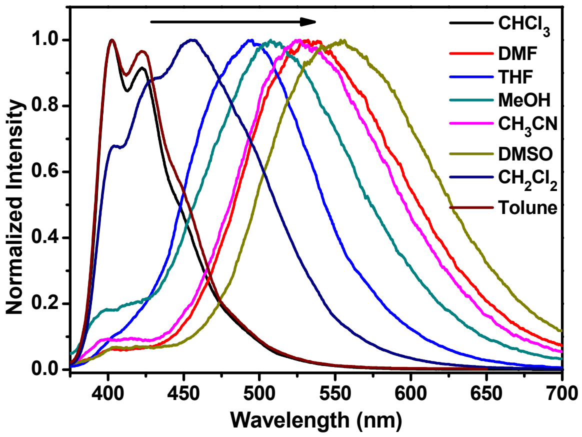


Figure S2. Normalized fluorescence emission spectra of **TFOH** in different solvents.

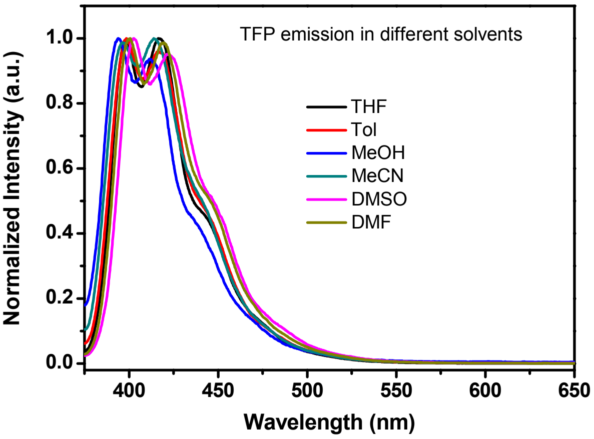


Figure S3. Normalized fluorescence emission spectra of **TFP** in different solvents.

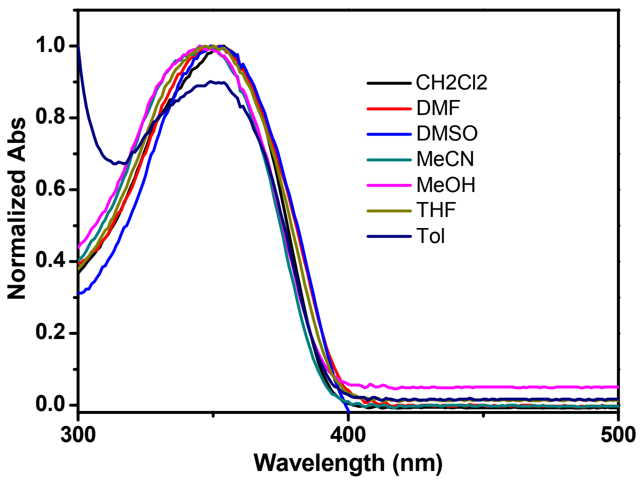


Figure S4. Normalized UV-Vis absorption spectrum of **TFOH** in different solvents.

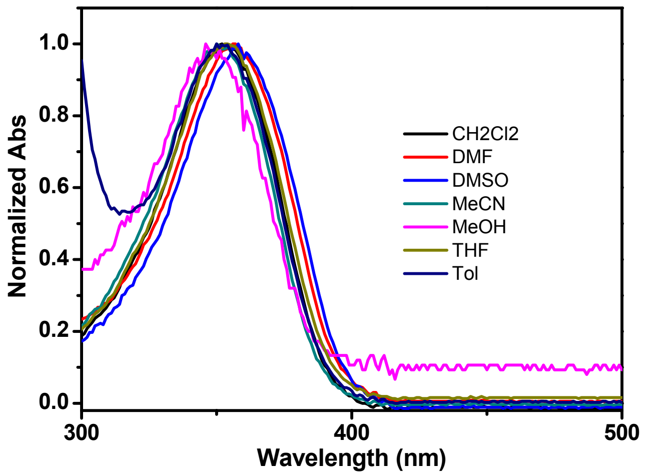


Figure S5. Normalized UV-Vis absorption spectrum of **TFP** in different solvents.

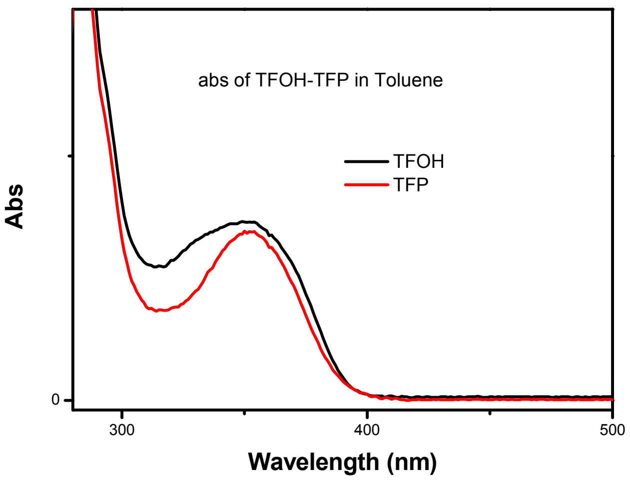


Figure S6. UV-Vis absorption spectra of **TFP** and **TFOH** in toluene.

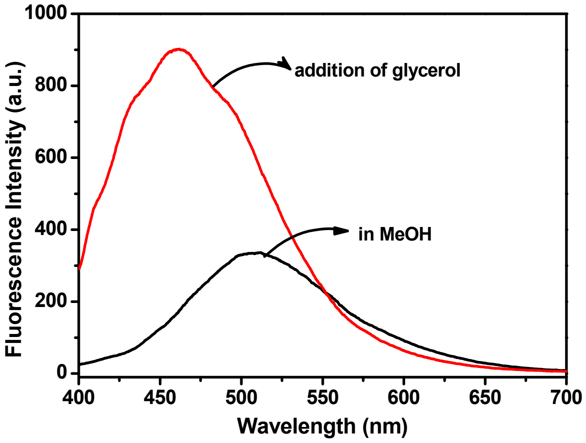


Figure S7. Viscosity effect by addition of glycerol into the solution of **TFOH** in MeOH.

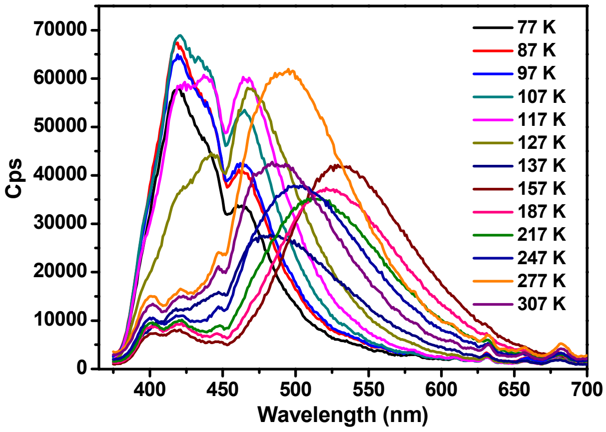


Figure S8. Fluorescence spectra of **TFOH** in THF solution at different temperatures.

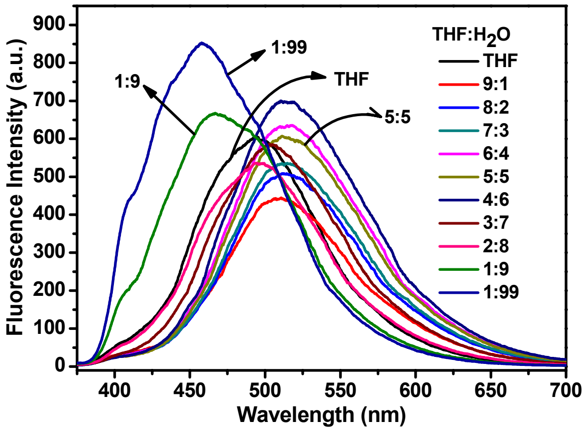


Figure S9. Fluorescence spectra of **TFOH** in THF/H_2O mixtures with different ratios.

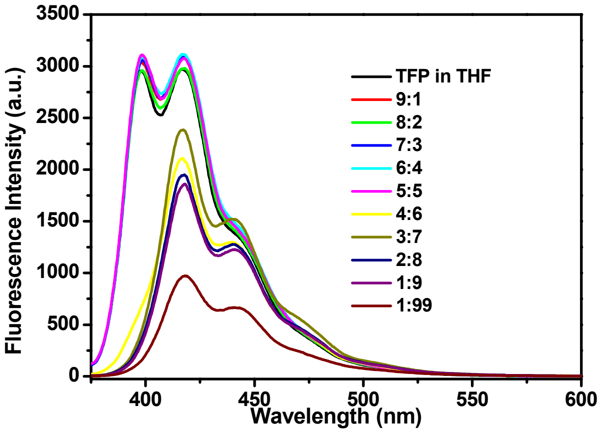


Figure S10. Fluorescence emission of **TFP** in THF/H_2O mixtures with different ratios.

4. SEM Images

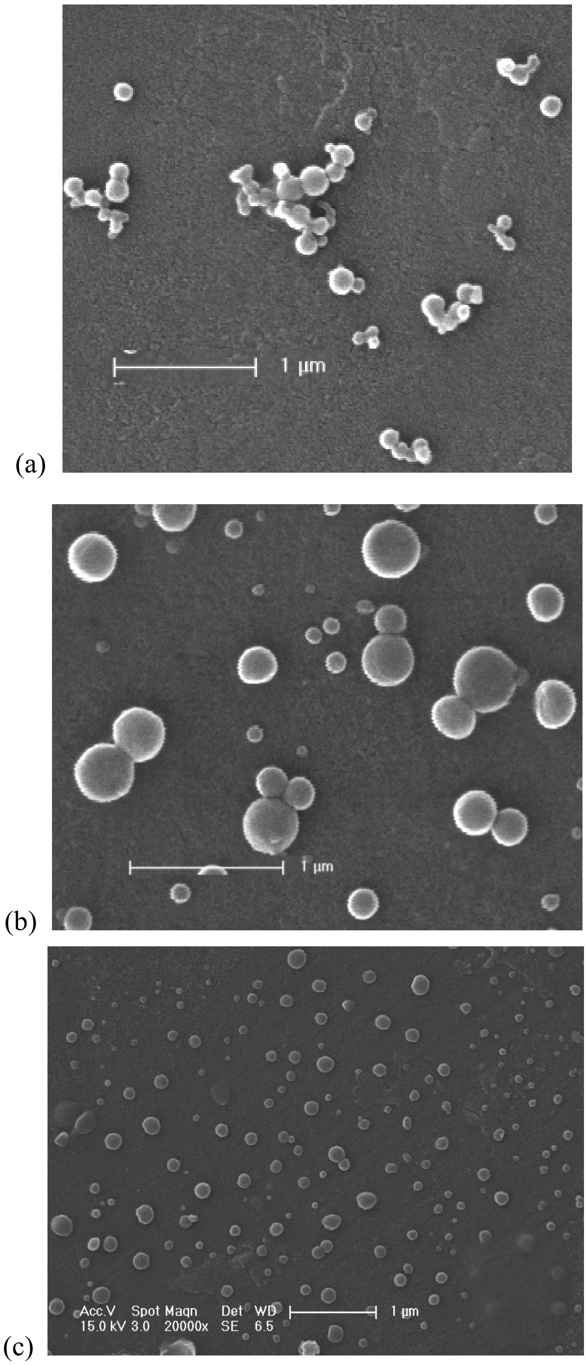


Figure S11. FE-SEM images of **TFOH** (at a concentration of 5 µM) (a) THF:H_2O 1:99; (b) THF:H_2O 5:5. (c) THF:H_2O 4:6 (as THF ratio increases, the morphologies are more irregular, and difficult to be observed).

References:

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