Supporting Information

Synthesis and Self-Assembly of Propeller-shaped Amphiphilic Molecules

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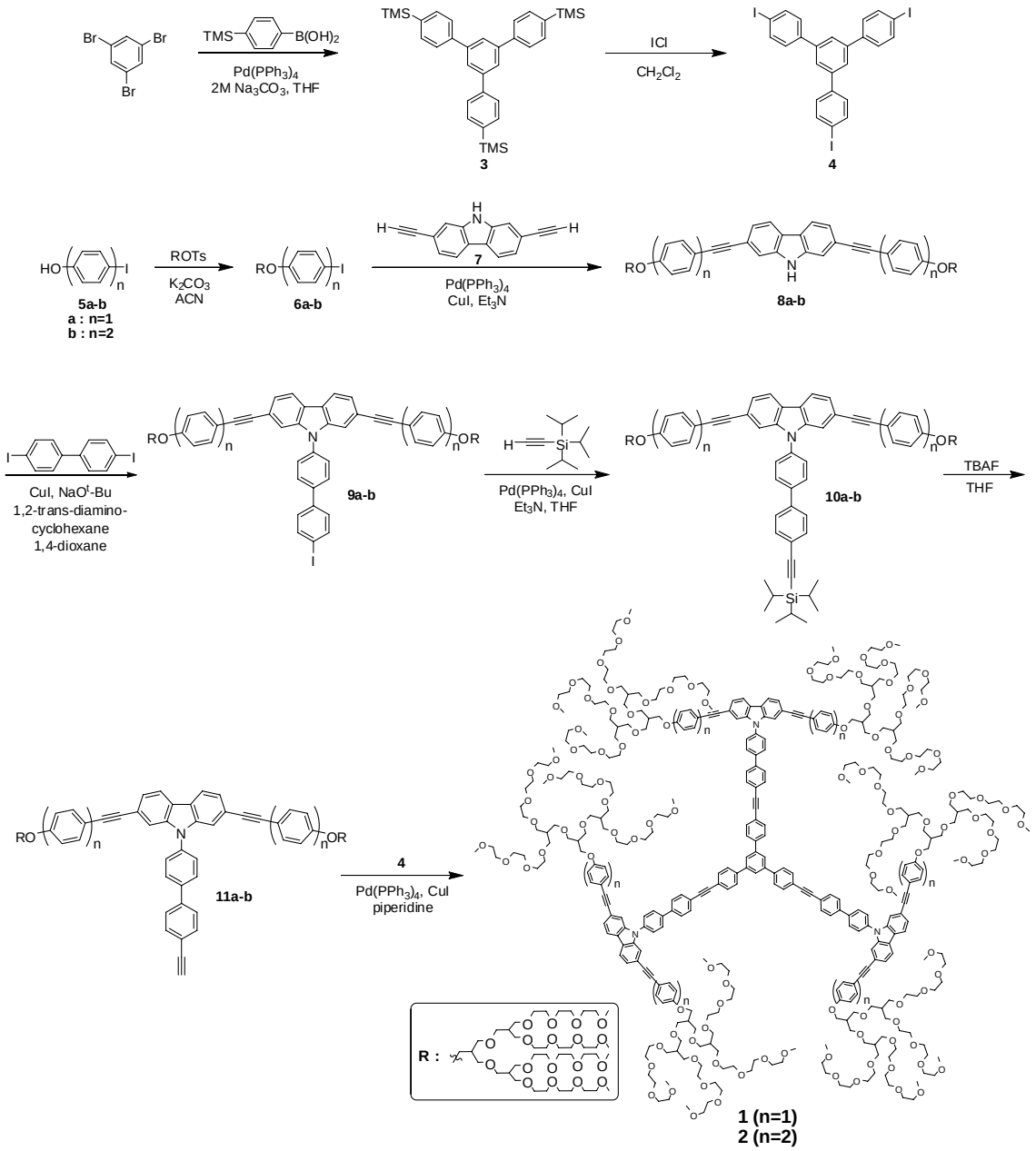
Experimental Section

Materials. *p*-Toluenesulfonyl chloride (98%), 4-bromo-4'-hydroxybiphenyl (99%) and tetrakis(triphenylphosphine) palladium (0) (99%) from TCI and Tokyo Kasei were used as received. 4, 4'-dibromobiphenyl (99%) from Acros and 4, 4'-diiodobiphenyl (90%), 1,3,5-tribromobenzene (98%), 4-(trimethylsilyl)phenylboronic acid, tri(ethylene glycol) monomethyl ether (95%), *n*-butyllithium (1.6 M solution in *n*-hexane), borane-THF complex (1.0 M solution in THF) and triisopropyl borate (98+%), iodine monochloride (1.0 M solution in dichloromethane) from Aldrich were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, etc.) and were used without purification. Visualization was accomplished with UV light, iodine vapor. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. Dry triethylamine was obtained by vacuum transfer from calcium hydride. Dry THF was obtained by vacuum

transfer from sodium and benzophenone.

Techniques. ^{1}H- and ^{13}C-NMR spectra were recorded from $CDCl_3$ and DMSO solutions on a Bruker AM 250 spectrometer and Bruker AVANCE 400 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at Organic Chemistry Research Center, Sogang university. MALDI TOF-MS was performed on a Perceptive Biosystems Voyager-DE STR using a 2, 5-dihydroxy benzoic acid matrix. Preparative high performance liquid chromatography (prep. HPLC) was performed at room temperature using a 20 mm × 600 mm polystyrene column on a Japan Analytical Industry Model LC-908 recycling prep. HPLC system, equipped with UV detector 310 and RI detector RI-5. Dynamic light scattering (DLS) measurements were performed using an ALV / CGS-3 Compact Goniometer System. The steady-state fluorescence spectra were obtained from a Hitachi F-4500 fluorescence spectrophotometer. The transmission electron microscopy (TEM) was performed at 120kV using JEOL 1020.

Synthesis



Scheme S1. Synthesis of compounds **1** and **2**.

Synthesis of compound 3

1, 3, 5-Tribromobenzene (463 mg, 1.47 mmol) and 4-trimethylsilylphenyl boronic acid (1000 mg, 5.15 mmol) were dissolved in degassed THF (80 mL). Degassed 2M aqueous

Na_2CO_3 (60 mL) was added to the solution and then tetrakis(triphenylphosphine) palladium (0) (45 mg, 0.036 mmol) was added. The mixture was heated at reflux for 27 hours with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with dichloromethane. The combined organic layer were dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using hexane : dichloromethane (9:1 v/v) as eluent to yield 748 mg (97 %). ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 7.79 (s, 3Ar-*H*), 7.70-7.60 (m, 12Ar-*H*), 0.33 (s, 27H, *trimethyl*silyl).

Synthesis of compound 4

To a solution of compound **3** (300 mg, 0.57 mmol) in dichloromethane (300 ml) at 0 °C was dropped 1.0 M solution of ICl in dichloromethane (2.85 ml, 2.85 mmol). The reaction mixture was stirred for 1 hour under nitrogen. 1 M aqueous $Na_2S_2O_5$ solution (150 ml) was added and stirred over 1 hour. The layers were separated, the aqueous layer was washed twice with dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude products was purified by column chromatography (silica gel) using hexane : ethyl acetate (9:1 v/v) as eluent to yield 389 mg (97%). ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 7.84 (d, 6Ar-*H*, *J* = 8.9 Hz), 7.68 (s, 3Ar-*H*), 7.38 (d, 6Ar-*H*, *J* = 8.9 Hz).

Synthesis of compound 5b

The synthesis of a compound **5b** was performed according to the procedures reported

previously.[S1]

^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 7.75 (d, 2Ar-*H*, *J* = 7.5 Hz), 7.47 (d, 2Ar-*H*, *J* = 7.5 Hz), 7.30 (d, 2Ar-*H*, *J* = 7.5 Hz), 6.92 (d, 2Ar-*H*, *J* = 7.5 Hz).

Synthesis of compounds 6a-b

The synthesis of a compounds **6a-b** were performed according to the procedures reported previously.[S1]

6a : Yield : 72% ; ^{1}H-NMR (250MHz, $CDCl_3$, ppm): δ = 7.52 (d, 2Ar-*H*, *J* = 8.9 Hz), 6.67 (d, 2Ar-*H*, *J* = 8.9 Hz), 3.94 (d, 2H; Ar-OC*H*$_2$, *J* = 5.5Hz), 3.65-3.42 (m, 64H; OC*H*$_2$), 3.36 (s, 12H; OC*H*$_3$), 2.34-2.15 (m, 3H; C*H*$(OCH_2)_2$).

6b : Yield : 84% ; ^{1}H-NMR (250MHz, $CDCl_3$, ppm): δ = 7.74 (d, 2Ar-*H*, *J* = 7.5 Hz), 7.52 (d, 2Ar-*H*, *J* = 7.5 Hz), 7.31 (d, 2Ar-*H*, *J* = 7.5 Hz), 6.97 (d, 2Ar-*H*, *J* = 7.5 Hz), 4.04 (d, 2H; Ar-OC*H*$_2$, *J* = 5.5Hz), 3.65-3.45 (m, 64H; OC*H*$_2$), 3.37 (s, 12H; OC*H*$_3$), 2.34-2.15 (m, 3H; C*H*$(OCH_2)_2$).

Synthesis of compound 7

The synthesis of a compound **7** was performed according to the procedures reported previously.[S1]

^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 8.06 (s, 1H; carbazole amine), 8.00 (d, 2Ar-*H*, *J* = 8.1 Hz), 7.58 (s, 2Ar-*H*), 7.40 (d, 2Ar-*H*, *J* = 8.1 Hz), 3.14 (s, 2H; acetylene).

Synthesis of compounds 8a-b

The synthesis of a compounds **8a-b** were performed according to the procedures

reported previously.[S1]

8a : Yield 70% ; ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 8.84 (s, 1H; carbazole amine), 8.00 (d, 2Ar-*H*, *J* = 8.1 Hz), 7.63 (s, 2Ar-*H*), 7.49 (d, 4Ar-*H*, *J* = 8.7 Hz), 7.39 (d, 2Ar-*H*, *J* = 8.1 Hz), 6.90 (d, 4Ar-*H*, *J* = 8.7 Hz), 4.04 (d, 4H; Ar-OCH_2, *J* = 5.5Hz), 3.64-3.44 (m, 128H; OCH_2), 3.37 (s, 24H; OCH_3), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$).

8b : Yield 62% ; ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 8.39 (s, 1H; carbazole amine), 8.05 (d, 2Ar-*H*, *J* = 8.1 Hz), 7.67-7.42 (m, 16Ar-*H*), 6.99 (d, 4Ar-*H*, *J* = 8.7 Hz), 4.05 (d, 4H; Ar-OCH_2, *J* = 5.5Hz), 3.71-3.46 (m, 128H; OCH_2), 3.37 (s, 24H; OCH_3), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$).

Synthesis of compounds 9a-b

The synthesis of a compounds **9a-b** were performed according to the procedures reported previously.[S1]

9a : Yield 80% ; ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 8.09 (d, 2Ar-*H*, *J* = 8.0 Hz), 7.86 (d, 2Ar-*H*, *J* = 6.0 Hz), 7.83 (d, 2Ar-*H*, *J* = 5.9 Hz), 7.70-7.38 (m, 12Ar-*H*), 6.94 (d, 4Ar-*H*, *J* = 8.8 Hz), 4.02 (d, 4H; Ar-OCH_2, *J* = 5.5Hz), 3.64-3.42 (m, 128H; OCH_2), 3.36 (s, 24H; OCH_3), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$).

9b : Yield 78% ; ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 8.12 (d, 2Ar-*H*, *J* = 8.1 Hz), 7.87-7.82 (dd, 4Ar-*H*, *J* = 8.5 Hz, 5.5 Hz), 7.70-7.44 (m, 20Ar-*H*), 6.99 (d, 4Ar-*H*, *J* = 8.7 Hz), 4.05 (d, 4H; Ar-OCH_2, *J* = 5.5Hz), 3.64-3.44 (m, 128H; OCH_2), 3.37 (s, 24H; OCH_3), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$).

Synthesis of compounds 10a-b

Compounds were synthesized using the same procedure. A representative example is described for **10a**. Compound **9a** (900 mg, 0.39 mmol) and triisopropylsilyl acetylene(356 mg, 1.95 mmol) were placed into a dry 100 mL RBF. Degassed dry Et_3N (30 mL) and THF (15 mL) were added and then tetrakis(triphenylphosphine) palladium (0) (45 mg, 0.036 mmol) and copper iodide (10 mg, 0.053 mmol) were added. The resulting solution was stirred at 50 °C for 12 hours. The solvent was removed in a rotary evaporator, the resulting mixture was extracted with EtOAc (2 x 100 mL), dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate : methanol (10:1 v/v) as eluent and then further purified by prep-HPLC to yield 692 mg (73%). ^{1}H-NMR (250MHz, $CDCl_3$, ppm): δ = 8.09 (d, 2Ar-*H*, *J* = 8.1 Hz), 7.88 (d, 2Ar-*H*, *J* = 8.5 Hz), 7.64-7.44 (m, 14Ar-*H*), 6.89 (d, 4Ar-*H*, *J* = 8.8 Hz), 4.03 (d, 2H; Ar-OC*H*$_2$, *J* = 5.5Hz), 3.64-3.45 (m, 128H; OC*H*$_2$), 3.37 (s, 24H; OC*H*$_3$), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$), 1.17 (s, 21H; *triisopropyl*silyl).

10b : Yield 82% ; ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 8.13 (d, 2Ar-*H*, *J* = 8.0 Hz), 7.89 (d, 2Ar-*H*, *J* = 8.5 Hz), 7.86-7.49 (m, 22Ar-*H*), 6.99 (d, 4Ar-*H*, *J* = 8.9 Hz), 4.06 (d, 4H; Ar-OC*H*$_2$, *J* = 5.5Hz), 3.65-3.45 (m, 128H; OC*H*$_2$), 3.37 (s, 24H; OC*H*$_3$), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$), 1.13 (s, 21H; *triisopropyl*silyl).

Synthesis of compounds 11a-b

Compounds were synthesized using the same procedure. A representative example is described for **11a**. Compound **10a** (454 mg, 0.19 mmol) was placed into a dry 100 mL

RBF. Dry THF was added and then tetrabutylammonium fluoride 1M solution in THF (1 mL, 1.0 mmol) was added. The resulting solution was stirred at room temperature for 1 hour. The solvent was removed in a rotary evaporator, the resulting mixture was extracted with EtOAc (2 x 100 mL), dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate : methanol (10:1 v/v) as eluent to yield 390 mg (90%). ^{1}H-NMR (250MHz, $CDCl_3$, ppm): δ = 8.09 (d, 2Ar-*H*, *J* = 8.2 Hz), 7.88 (d, 2Ar-*H*, *J* = 8.5 Hz), 7.69-7.43 (m, 14Ar-*H*), 6.88 (d, 4Ar-*H*, *J* = 8.8 Hz), 4.02 (d, 2H; Ar-OC*H*$_2$, *J* = 5.5Hz), 3.64-3.44 (m, 128H; OC*H*$_2$), 3.36 (s, 24H; OC*H*$_3$), 3.17 (s, 1H; acetylene-*H*), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$).

11b : Yield : 92% ; ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): δ = 8.13 (d, 2Ar-*H*, *J* = 8.1 Hz), 7.89 (d, 2Ar-*H*, *J* = 8.6 Hz), 7.71-7.49 (m, 22Ar-*H*), 6.99 (d, 4Ar-*H*, *J* = 8.8 Hz), 4.06 (d, 2H; Ar-OC*H*$_2$, *J* = 5.5Hz), 3.64-3.46 (m, 128H; OC*H*$_2$), 3.17 (s, 1H; OC*H*$_3$), 3.17 (s, 1H; acetylene-*H*), 2.34-2.15 (m, 6H; C*H*$(OCH_2)_2$).

Synthesis of compounds 1 and 2

Compounds were synthesized using the same procedure. A representative example is described for **1**. Compound **11a** (380 mg, 0.17 mmol) and compound **4** (24 mg, 0.035 mmol) were placed into a dry 100 mL RBF. Degassed dry piperidine (20 mL) was added and then tetrakis(triphenylphosphine) palladium (0) (23 mg, 0.018 mmol) and copper iodide (10 mg, 0.053 mmol) were added. The resulting solution was stirred at 50 °C for 20 hours. The solvent was removed in a rotary evaporator, the resulting mixture was extracted with EtOAc (2 x 100 mL), dried over anhydrous magnesium sulfate and

filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using dichloromethane : methanol (3:1 v/v) as eluent and then further purified by prep-HPLC to yield 85 mg (34%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.10 (d, 6Ar-*H*, *J* = 8.1 Hz), 7.92-7.87 (m, 6Ar-*H*), 7.79-7.68 (m, 31Ar-*H*), 7.61 (s, 6Ar-*H*), 7.47-7.44 (m, 18Ar-*H*), 6.89 (d, 12Ar-*H*, *J* = 8.9 Hz), 4.03 (d, 12H; Ar-OCH_2, *J* = 5.5Hz), 3.64-3.44 (m, 384H; OCH_2), 3.36 (s, 72H; OCH_3), 2.34-2.15 (m, 18H; C*H*$(OCH_2)_2$). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 159.0, 141.3, 140.6, 140.4, 132.4, 132.3, 128.9, 127.6, 127.4, 126.5, 121.5, 121.1, 120.5, 114.9, 91.1, 89.4, 70.20, 69.7, 69.6, 69.5, 66.4, 59.1, 39.9; Anal. Calcd. for $C_{390}H_{567}N_3O_{114}$: C, 65.77; H, 8.02; N, 0.59. Found C, 65.79; H, 8.02; N, 0.57. MALDI-TOF-MS m/z 7139.86 ($[M+Na]^+$), Calcd 7139.10.

2 : Yield : 49% ; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.14 (d, 6Ar-*H*, *J* = 8.1 Hz), 7.94-7.87 (t, 10Ar-*H*, *J* = 8.4 Hz), 7.74-7.52 (m, 77Ar-*H*), 6.99 (d, 12Ar-*H*, *J* = 8.8 Hz), 4.06 (d, 12H; Ar-OCH_2, *J* = 5.5Hz), 3.63-3.45 (m, 384H; OCH_2), 3.36 (s, 72H; OCH_3), 2.34-2.15 (m, 18H; C*H*$(OCH_2)_2$). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ = 159.5, 141.5, 140.1, 132.4, 132.3, 132.1, 128.1, 127.4, 127.2, 126.6, 122.9, 121.2, 115.0, 91.1, 89.4, 69.8, 69.6, 69.4, 66.4, 58.8, 40.3; Anal. Calcd. for $C_{426}H_{591}N_3O_{114}$: C, 67.52; H, 7.86; N, 0.55. Found C, 67.45; H, 7.84; N, 0.62. MALDI-TOF-MS m/z 7601.05 ($[M+Na]^+$), Calcd 7601.06.

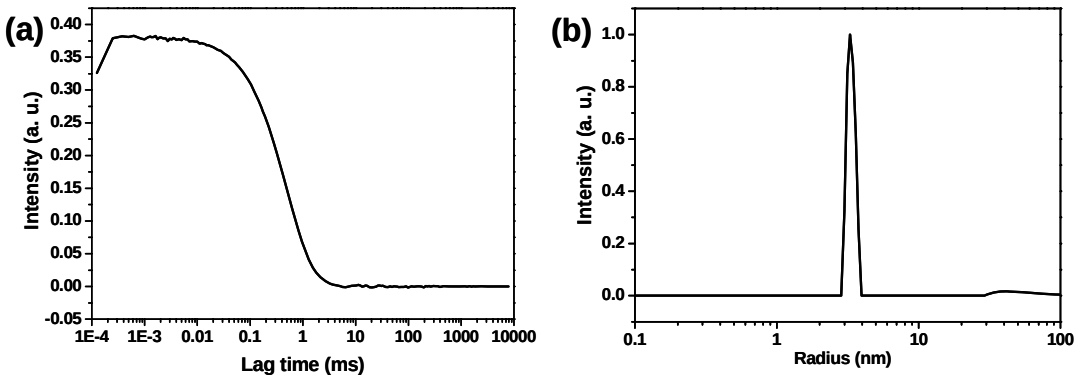


Figure S1. (a) Autocorrelation function of 0.01wt% of **2** in water/THF (9 : 1) solution at a scattering angle 90°. (b) Mass weighted hydrodynamic radius distribution of 0.01wt% of **2** in water/THF (9 : 1) solution.

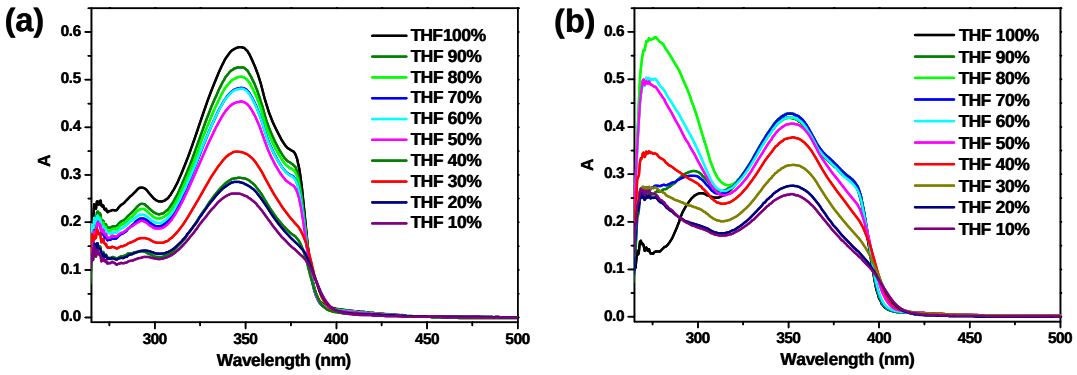


Figure S2. (a) Changes in the absorption spectra of 0.01 wt% of **1** in different water/THF solvent ratio. (b) Changes in the absorption spectra of 0.01 wt% of **1** in different water/THF solvent ratio.

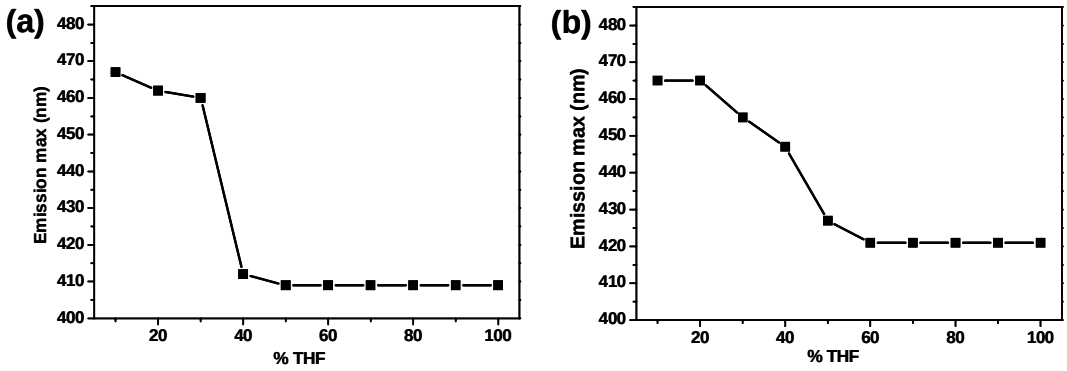


Figure S3. Changes in λ_{em} maxima of (a) **1** and (b) **2** in water/THF mixed solution with increasing THF ratio.

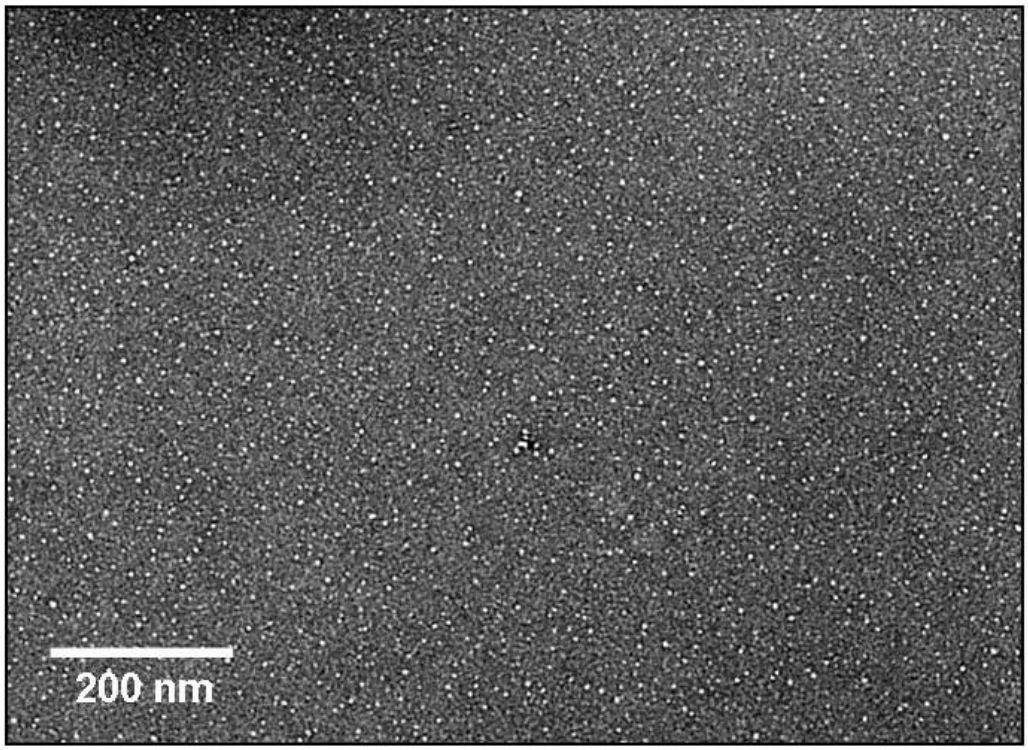


Figure S4. TEM image of compound **1** in water/THF (9 : 1) solution with magnification.

Supporting Reference

S1. K.-S. Moon, H.-J. Kim, E. Lee and M. Lee, *Angew. Chem. Int. Ed.*, 2007, **46**, 6807.