Electronic Supplementary Information (ESI)

Fluorescence Enhancements of Benzene-Cored Luminophors by Restricted Intramolecular Rotations: AIE and AIEE Effects

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Materials and Instrumentations

THF was dried over, and distilled from, K-Na alloy under nitrogen. 1-Bromo-4-butoxybenzene (S**10**) was prepared by the reaction of 4-bromophenol with 1-bromobutane in acetone in the presence of potassium carbonate. 3-Bromocarbazole (S**7**) was prepared according to our previously published synthetic procedures.[1]

^{1}H and ^{13}C NMR spectroscopy studies were conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. Fourier-transfer infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1} on KBr pellets. UV-vis spectra were obtained using a Shimadzu 160A spectrometer. FAB-MS spectra were recorded with a VJ-ZAB-3F mass spectrometer. The apparatus for measuring the melting point was uncorrected. Particle sizes of the polyarylated benzene nanoaggregates in the water/acetone mixtures were measured on a Bechman Coulter Delas 440SX Zeta potential analyzer.

Synthesis and Characterization

The mono-, di- and triarylated benzene derivatives (**1**–**6**) were prepared according to the synthetic routes given in Schemes S1 and S2.

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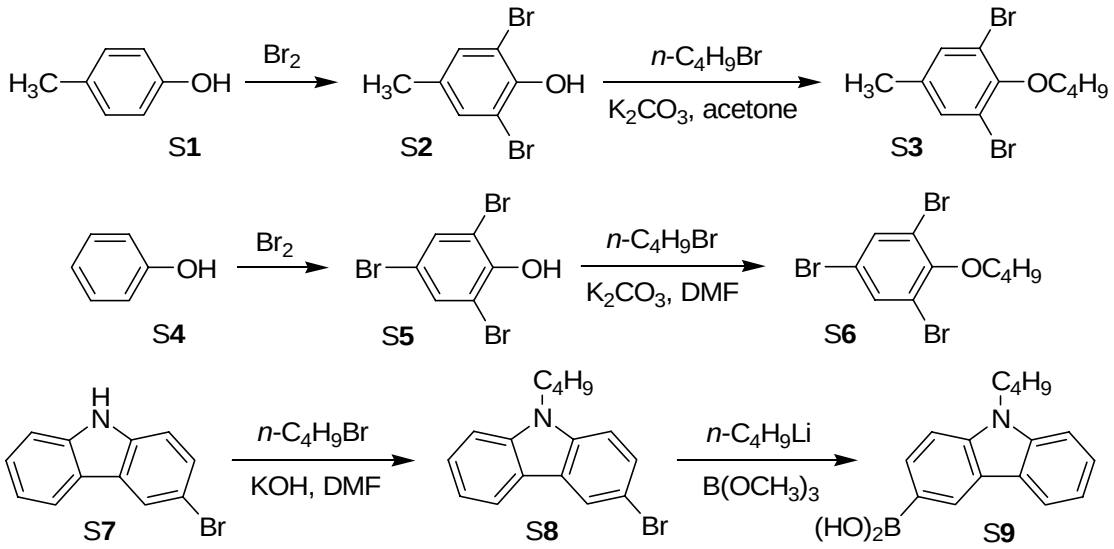
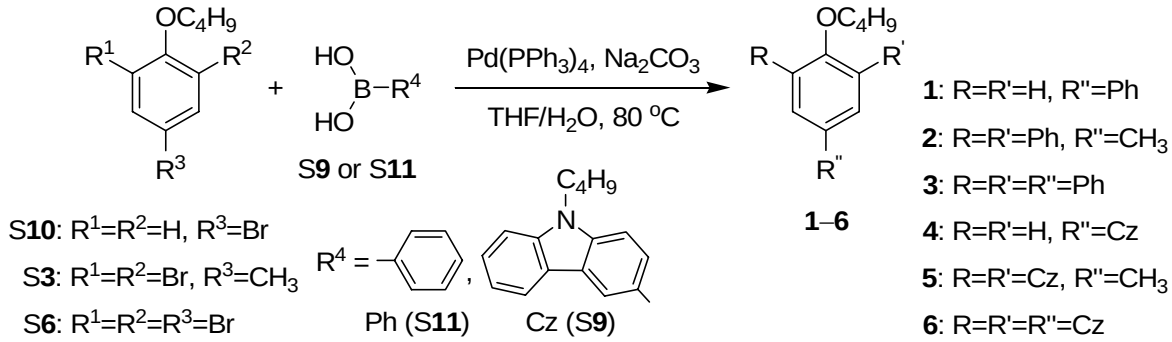
[1] Z. Li, C. Di, Z. Zhu, Q. Li, Q. Zeng, K. Zhang, Y. Liu, C. Ye and J. Qin, *Macromolecules*, 2006, **39**, 6951.

Scheme S1



Scheme S2



*Preparation of 2,6-Dibromo-4-methylphenol (S**2**)*

p-Cresol (S**1**; 0.43 g, 4.0 mmol) was dissolved in chloroform (15 mL) in a flask, into which 1.4 g of bromine (8.8 mmol) was added dropwise. After stirring for 1.5 h at room temperature, the reaction mixture was washed with saturated aqueous solution of sodium hydrogen sulfite. The organic layer was separated and dried over sodium sulfate and then evaporated to dryness. The crude product was purified by recrystallization from ethanol to afford a white solid in 85.5% yield (0.91 g). ^{1}H NMR ($CDCl_3$), δ (ppm): 2.17 (s, 3H, –CH_3), 7.17 (s, 2H, Ar–H).

*Preparation of 1, 3-Dibromo-2-butoxy-5-methylbenzene (S**3**)*

A mixture of S**2** (0.46 g, 1.7 mmol) and potassium carbonate (0.95 g, 6.9 mmol) in acetone (15 mL) was stirred at room temperature. After 10 min, 1-bromobutane (0.52 g, 3.8 mmol) was added. After refluxing for 2 days, the mixture was cooled to room temperature and concentrated. The resultant

product was extracted with chloroform and washed with distilled water for three times. The organic layer was dried over sodium sulfate and evaporated to dryness to afford a pale-yellow oil in 78.5% yield (0.43 g). ^{1}H NMR ($CDCl_3$), δ (ppm): 0.91 (t, J = 6.6 Hz, 3H, –CH_3), 1.50 (m, 2H, –CH_2–), 1.76 (m, 2H, –CH_2–), 2.19 (s, 3H, –CH_3), 3.89 (t, J = 4.8 Hz, 2H, –O–CH_2–), 7.22 (s, 2H, Ar–H).

*Preparation of 2,4,6-Tribromophenol (S**5**)*

Phenol (S**4**; 7.86 g, 83.5 mmol) was dissolved in 100 mL water in a flask, into which bromine (40.85 g, 256 mmol) was added dropwise. The reaction mixture was stirred at room temperature until a lot of yellow precipitate appeared. The precipitate was filtered and washed with saturated aqueous solution of sodium hydrogen sulfite for three times. The crude product was recrystallized from ethanol to afford a white solid in 94.0% yield (25.96 g). Mp: 93–94 ^{o}C. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.53 (s, 2H, Ar–H).

*Preparation of 1-Butoxy-2,4,6-tribromobenzene (S**6**)*

The procedure was similar to that for the preparation of S**3** except for that the solution was changed to DMF and S**5** (1.50 g, 4.5 mmol) was used as the starting material. A pale-yellow oil was obtained in 97.1% (1.69 g). ^{1}H NMR ($CDCl_3$), δ (ppm): 0.92 (t, J = 7.2 Hz, 3H, –CH_3), 1.48 (m, 2H, –CH_2–), 1.77 (m, 2H, –CH_2–), 3.90 (t, J = 6.0 Hz, 2H, –O–CH_2–), 7.55 (s, 2H, Ar–H).

*Preparation of 9-Butyl-3-bromocarbazole (S**8**)*

3-Bromocarbazole (S**7**; 4.00 g, 16.3 mmol) was dissolved in DMF (35 ml) in a flask, into which powdered potassium hydroxide (3.74 g, 66.7 mmol) was added. After the mixture was stirred for 1 h, a solution of 1-bromobutane (2.80 g, 20.4 mmol) was added slowly. After stirred for 20 h at room temperature, the mixture was poured into ice water (300 mL), extracted with chloroform, and washed with water. The organic layer was dried over sodium sulfate. The crude product was purified with column chromatography on silica gel using chloroform/hexane (1/2) to afford a colorless oil in 76.5% yield (3.77 g). ^{1}H NMR ($CDCl_3$), δ (ppm): 0.96 (t, J = 7.2 Hz, 3H, –CH_3), 1.40 (m, 2H, –CH_2–), 1.85(m, 2H, –CH_2–), 4.27 (t, J = 8.1 Hz, 2H, –N–CH_2–), 7.26 (m, 2H, Ar–H), 7.40–7.56 (m, 3H, Ar–H), 8.06 (d, J = 7.8 Hz, 1H, Ar–H), 8.22 (s, 1H, Ar–H).

*Preparation of 9-Butyl-3-carbazolylboronic Acid (S**9**)*

A solution of S**8** (1.82 g, 6.0 mmol) in THF (10 mL) was added dropwise to a solution of *n*-BuLi

(3.3 mL, 6.6 mmol, 2.0 M in *n*-hexane) in THF (10 mL) at –78 °C under nitrogen. The mixture was stirred for 1 h and then trimethyl borate (1.30 g, 12.5 mmol) was added dropwise. The mixture was stirred for another hour at –78 °C and then stirred overnight at room temperature. Hydrochloric acid (2 M, 15 mL) was then added into the mixture and the resultant mixture was stirred for 30 min. The reaction mixture was extracted with diethyl ether and washed with distilled water for three times. The organic layer was dried over sodium sulfate and then evaporated to dryness. The crude product was dissolved in diethyl ether and dropped into *n*-hexane (40 mL). The precipitate was filtered and washed with *n*-hexane to afford a white solid in 56.2% yield (0.90 g). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.01 (t, J = 7.2 Hz, 3H, $–CH_3$), 1.45 (m, 2H, $–CH_2–$), 1.93 (m, 2H, $–CH_2–$), 4.41 (t, J = 7.5 Hz, 2H, $–N–CH_2–$), 7.35 (m, 1H, Ar–H), 7.4–7.6 (m, 3H, Ar–H), 8.37 (d, J = 7.8 Hz, 1H, Ar–H), 8.50 (d, J = 8.4 Hz, 1H, Ar–H), 9.13 (s, 1H, Ar–H).

*General Procedures for the Syntheses of **1**–**6** through Suzuki Reaction*[2]

To a mixture of S**10**, S**3** or S**6** (1.00 equiv), boronic acid S**11** or S**9** (for **1** and **4**, 1.05 equiv; for **2** and **5**, 2.10 equiv; for **3** and **6**, 3.15 equiv), sodium carbonate (for **1** and **4**, 10 equiv; for **2** and **5**, 20 equiv; for **3** and **6**, 30 equiv), and tetrakis(triphenylphosphine)palladium $Pd(PPh_3)_4$ (3–5 mol %) were added a degassed mixture of THF and water (3:1 in volume) under nitrogen. The concentration of S**10**, S**3** or S**6** was ca. 0.03 M. The mixture was stirred at 80 °C for 30 h. After the mixture was cooled to room temperature, the organic layer was separated, dried over sodium sulfate, and evaporated to dryness. The crude product was purified by recrystallization or column chromatography.

1: 0.3 g of S**10** (1.32 mmol) and 0.17 g of S**11** (1.39 mmol) were used in the reaction. Purification of the crude product by column chromatography on silica gel with chloroform/hexane (1:3) as eluate gave a white powder of **1** in 87.0% yield (0.26 g). Mp: 68–69 °C. IR (thin film), υ (cm^{-1}): 1607 (–C=C–), 1256, 1071 (C–O–C). ^{1}H NMR ($CDCl_3$), δ (ppm): 0.92 (t, J = 7.2 Hz, 3H, $–CH_3$), 1.46 (m, 2H, $–CH_2–$), 1.72 (m, 2H, $–CH_2–$), 3.94 (t, J = 6.6 Hz, 2H, $–O–CH_2–$), 6.90 (d, J = 8.7 Hz, 2H, Ar–H), 7.22 (m,1H, Ar–H), 7.34 (t, J = 7.8 Hz, 2H, Ar–H), 7.46 (m, 4H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 12.8, 18.2, 30.3, 66.6, 113.5, 125.3, 125.4, 126.8, 127.4, 132.2, 139.6, 157.4. MS (EI), *m/z*: 226.0 ([M^+], calcd. 226.1).

2: 0.15 g of S**3** (0.47 mmol) and 0.12 g of S**11** (0.98 mmol) were used. Purification by column

[2] A. Suzuki and N. Miyaura, *Chem. Rev.*, 1995, **95**, 2457.

chromatography on silica gel with chloroform/hexane (1:3) as eluate gave colorless, viscous syrup of **2** in 80.7% yield (0.12 g). IR (thin film), υ (cm^{-1}): 1600, 1497 (–C=C–), 1217, 1069 (C–O–C). ^1H NMR ($CDCl_3$), δ (ppm): 0.47 (t, J = 7.2 Hz, 3H, $–CH_3$), 0.86 (m, 2H, $–CH_2–$), 1.05 (m, 2H, $–CH_2–$), 2.32 (s, 3H, $–CH_3$), 3.10 (t, J = 6.3 Hz, 2H, $–O–CH_2–$), 7.08 (s, 2H, Ar–H), 7.25–7.36 (m, 6H, Ar–H), 7.53 (d, J = 7.5 Hz, 4H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 13.7, 19.0, 21.1, 32.1, 73.1, 127.2, 128.2, 129.8, 131.0, 133.6, 136.1, 139.3, 152.2. MS (EI), *m/z*: 316.0 ([M^+], calcd. 316.2).

3: 0.51 g of S**6** (1.3 mmol) and 0.50 g of S**11** (4.1 mmol) were used. Purification by column chromatography on silica gel with hexane as eluate gave colorless, viscous syrup of **3** in 95.6% yield (0.47 g). IR (thin film), υ (cm^{-1}): 1598, 1495 (–C=C–), 1218, 1073 (C–O–C). ^1H NMR ($CDCl_3$), δ (ppm): 0.59 (t, J = 7.2 Hz, 3H, $–CH_3$), 1.00 (m, 2H, $–CH_2–$), 1.18 (m, 2H, $–CH_2–$), 3.26 (t, J = 6.0 Hz, 2H, $–O–CH_2–$), 7.33–7.48 (m, 9H, Ar–H), 7.59 (s, 2H, Ar–H), 7.68 (m, 6H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 13.9, 19.2, 30.1, 32.2, 73.3, 127.4, 127.5, 128.4, 129.1, 129.3, 130.0, 136.9, 137.4, 139.3, 140.9, 154.2. MS (EI), *m/z*: 378.0 ([M^+], calcd. 378.2).

4: 0.065 g of S**10** (0.28 mmol) and 0.080 g of S**9** (0.30 mmol) were used. Purification by column chromatography on silica gel with chloroform/hexane (1:4) as eluate gave pale-yellow, viscous syrup of **4** in 86.5% yield (0.090 g). IR (thin film), υ (cm^{-1}): 1607, 1517 (–C=C–), 1242, 1071 (C–O–C). ^1H NMR ($CDCl_3$), δ (ppm): 0.91 (m, 6H, $–CH_3$), 1.35 (m, 2H, $–CH_2–$), 1.46 (m, 2H, $–CH_2–$), 1.69–1.86 (m, 4H, $–CH_2–CH_2–$), 3.96 (t, J = 6.6 Hz, 2H, $–O–CH_2–$), 4.25 (t, J = 7.2 Hz, 2H, $–N–CH_2–$), 6.93 (d, J = 7.5 Hz, 2H, Ar–H), 7.15 (m, 1H, Ar–H), 7.32–7.44 (m, 3H, Ar–H), 7.53–7.60 (m, 3H, Ar–H), 8.05 (d, J = 7.8 Hz, 1H, Ar–H), 8.18 (s, 1H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 12.9, 18.3, 19.5, 30.1, 30.4, 41.8, 66.8, 107.7, 107.8, 113.8, 117.3, 117.7, 119.3, 121.9, 122.3, 123.8, 124.6, 127.2, 131.0, 133.6, 138.6, 139.9, 157.1. MS (EI), *m/z*: 371.3 ([M^+], calcd. 371.2).

5: 0.10 g of S**3** (0.31 mmol) and 0.18 g of S**9** (0.67 mmol) were used. Purification by column chromatography on silica gel with chloroform/hexane (1:3) as eluate gave a pale-yellow powder of **5** in 63.8% yield (0.12 g). Mp: 70–72 ^oC. IR (thin film), υ (cm^{-1}): 1600, 1490 (–C=C–), 1244, 1069 (C–O–C). ^1H NMR ($CDCl_3$), δ (ppm): 0.27 (t, J = 7.5 Hz, 3H, $–CH_3$), 0.80 (m, 2H, $–CH_2–$), 0.90 (t, J = 7.5, 6H, $–CH_3$), 1.00 (m, 2H, $–CH_2–$), 1.37 (m, 4H, $–CH_2–$), 1.83 (m, 4H, $–CH_2–$), 2.39 (s, 3H, $–CH_3$), 3.15 (t, J = 6.3 Hz, 2H, $–O–CH_2–$), 4.28 (t, J = 7.5 Hz, 4H, $–N–CH_2–$), 7.15–7.22 (m, 4H, Ar–H), 7.34–7.42 (m, 6H, Ar–H), 7.71–7.74 (m, 2H, Ar–H), 8.08(d, J = 8.1 Hz, 2H, Ar–H), 8.32 (s, 2H, Ar–H).

^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 13.8, 14.3, 19.2, 21.0, 21.4, 30.1, 31.6, 32.2, 43.3, 72.6, 108.3, 108.9, 118.9, 120.6, 121.5, 122.9, 123.3, 125.7, 127.9, 130.0, 130.8, 133.5, 136.7, 139.9, 140.9, 152.4. MS (EI), *m/z*: 606.8 ([M^+], calcd. 606.4).

6: 0.19 g of S**6** (0.49 mmol) and 0.42 g of S**9** (1.6 mmol) were used. Purification by column chromatography on silica gel with chloroform/hexane (1:5) as eluate gave a white powder of **6** in 65.2% yield (0.26 g). Mp: 112–114 °C. IR (thin film), υ (cm^{-1}): 1600 (–C=C–), 1213, 1076 (C–O–C). ^{1}H NMR ($CDCl_3$), δ (ppm): 0.31 (t, J = 7.5 Hz, 3H, $–CH_3$), 0.79 – 0.93 (m, 11H, $–CH_3$), 1.05 (m, 2H, $–CH_2–$), 1.37 (m, 6H, $–CH_2–$), 1.84 (m, 6H, $–CH_2–$), 3.27 (t, J = 6.0 Hz, 2H, $–O–CH_2–$), 4.28 (m, 6H, $–N–CH_2–$), 7.15 – 7.21 (m, 3H, Ar–H), 7.33 – 7.44 (m, 9H, Ar–H), 7.76–7.85 (m, 5H, Ar–H), 8.10 (t, J = 9.3 Hz, 3H, Ar–H), 8.37 (s, 1H, Ar–H) , 8.43 (s, 2H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 14.2, 14.7, 19.6, 21.4, 32.0, 32.6, 43.7, 73.2, 108.8, 109.4, 109.5, 119.4, 121.0, 122.0, 123.4, 123.6, 123.7, 124.0, 125.8, 126.1, 126.3, 128.3, 129.4, 130.5, 132.6, 137.6, 138.4, 140.3, 140.4, 141.3, 141.5, 153.9. MS (EI), *m/z*: 814.1 ([M^+], calcd. 813.5).

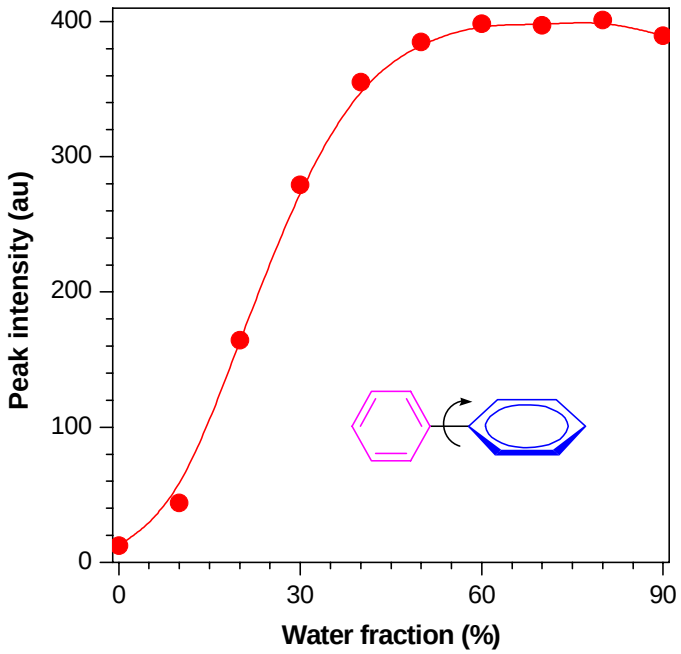


Figure S1 Changes in the PL peak intensity of biphenyl in the water/DMF mixtures with different water contents. Biphenyl concentration: 20 μM. Excitation wavelength: 263 nm.

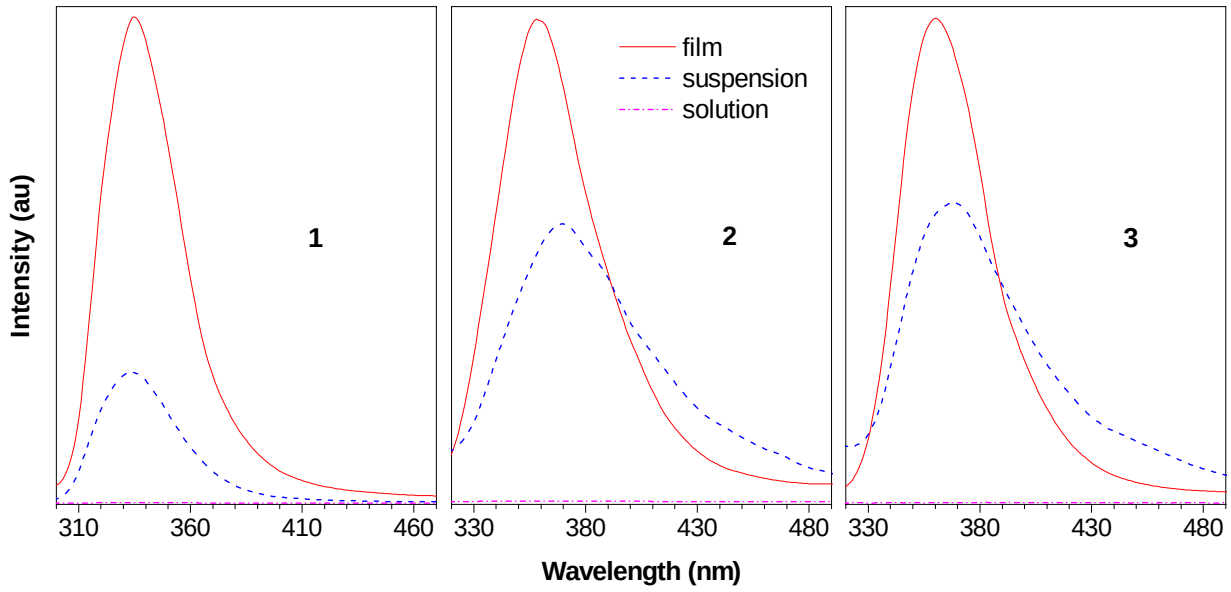


Figure S2 PL spectra of **1**, **2** and **3** in dilute acetone solutions (20 μM), as nanoparticle suspensions in the water/acetone mixtures with 90 vol % water contents, and in PMMA films (30 wt %).

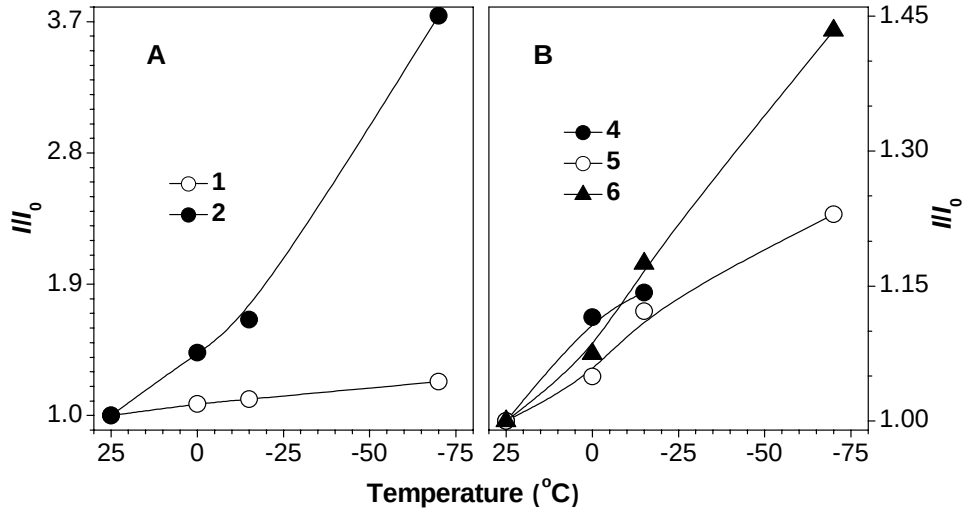


Figure S3 Effect of temperature on the PL peak intensities of dilute solutions of **1**–**6** (40 μM) in THF.

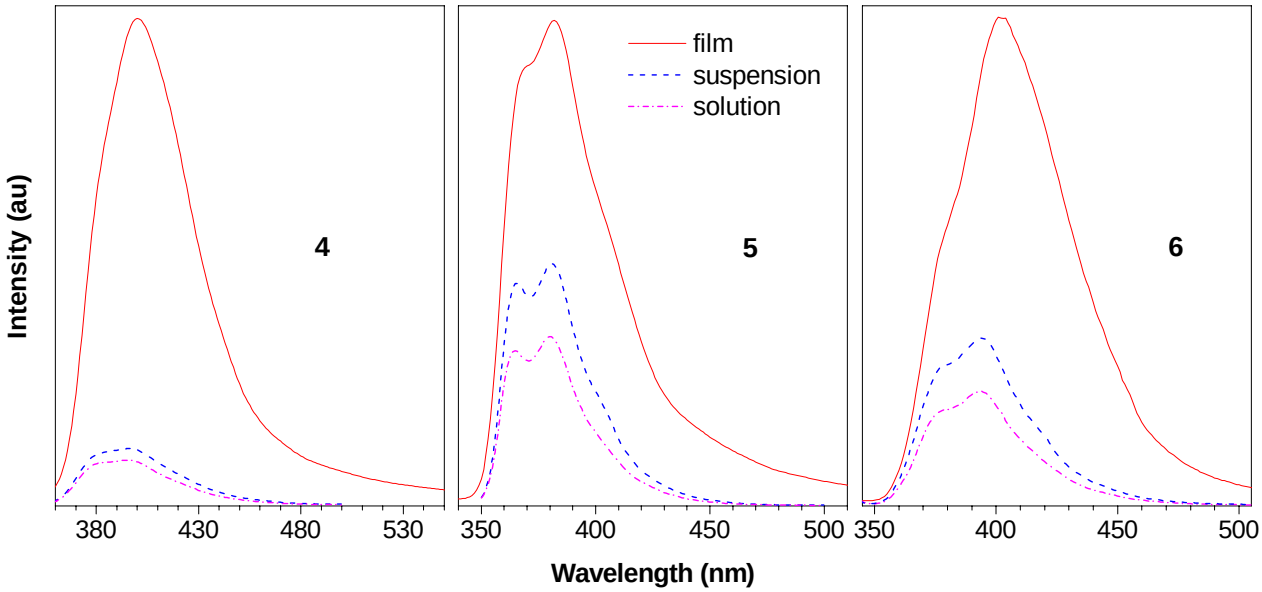


Figure S4 PL spectra of **4**, **5** and **6** in dilute acetone solutions (20 μM), as nanoparticle suspensions in the water/acetone mixtures with 70 vol % water contents, and in PMMA films (30 wt %).

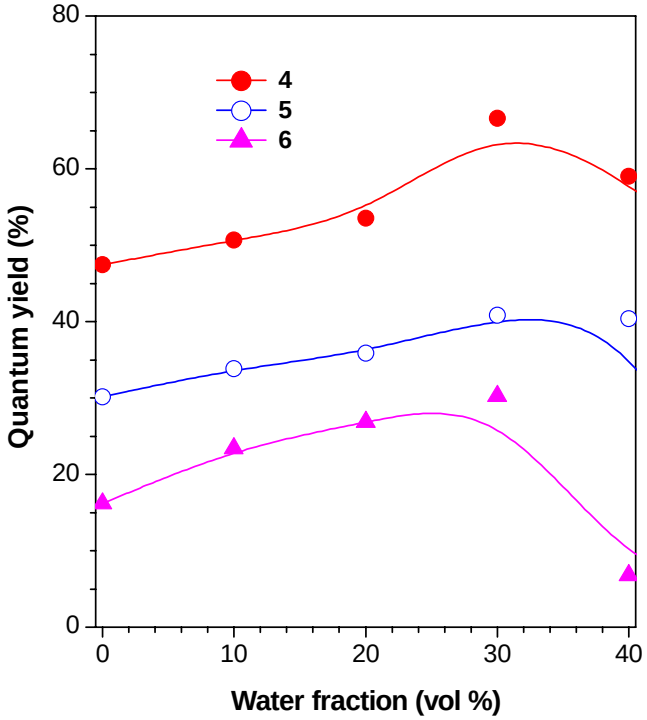


Figure S5 Dependence of the fluorescence quantum yields of solutions of **4–6** (20 μM) on the water fractions in water/acetone mixtures.