Supporting Information for

Multicolour Self-Assembled Particles from Fluorene Based Bolaamphiphiles

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Materials and Instruments

All chemicals were purchased from Acros, Belgium unless stated otherwise. Concentrated hydrochloric acid was delivered by VWR International, Belgium. Na_2SO_4 was obtained from Merck, Germany, silicagel (40 – 63 µm, 60 Å) from Screening Devices, the Netherlands and Fluka, Germany. Gelatine was purchased from Dr. Oetker. Non-deuterated solvents were purchased from Biosolve, the Netherlands. All solvents and chemicals were used as received. Deuterated solvents were bought from Cambridge Isotope Laboratories, United States.

NMR spectra were recorded using a Varian Mercury NMR Spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C or on a Varian Gemini NMR Spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C. IR, UV-vis, CD and PL spectra were measured on a Perkin Elmer 1600 FT-IR, a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer, a JASCO J-815 CD Spectrometer and an Edinburgh Instruments FS920 spectrophotometer, respectively. Elemental analysis was performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer. MALDI-TOF-MS spectra were measured on a Perseptive DE Voyager Mass Spectrometer with a-cyano-4-hydroxycinnamic acid as a matrix. Analytical Size Exclusion chromatography was done on an apparatus consisting of a Shimadzu SIL-10AD VP Auto Injector, a Shimadzu LC-10AD VP Liquid Chromatograph, a PLgel 3 µm 100 Å column set, and a SPD-M10A VP Diode Array Detector, using HPLC grade THF as the eluent. For recycling GPC, an apparatus consisting of a Shimadzu LC-10AD VP Liquid Chromatograph, a Shimadzu SPD-10AV VP UV-vis detector, and two JAIGEL columns (2.5 H and 2 H) from Japan Analytical Industry was used with HPLC grade THF as the eluent. Samples for fluorescence microscopy were prepared by injection of 10 µl of a THF stock solution (total chromophore concentration 3 mM) into 1 ml of a freshly prepared gelatine (30 g/l) solution, transferred to a glass slide and covered with a cover slip. Gelation took place overnight at a temperature of 7 °C. The images were taken on a Zeiss LSM 510 META fluorescence microscope with a Plan-Apochromat 63x objective using immersion oil. The samples were excited with laser light of 458 nm or 543 nm.

Synthesis

The synthesis of the aromatic diamines by Suzuki coupling is described elsewhere.[1,2]

General procedure for the synthesis of **1 – 5**:
3,4,5-tris(methyltetraethyleneoxy)benzoic acid chloride was prepared according to a literature procedure from its corresponding acid and oxalyl chloride.[3] Aromatic diamine and triethyl amine were dissolved in dry chloroform and an excess of acid chloride was added as a solution in dry chloroform. After stirring at room temperature for several hours, water was added to the reaction mixture and the aqueous layer was extracted several times with chloroform. The combined organic layers were washed with water and dried over Na_2SO_4. After evaporation, the crude products were purified by column chromatography and preparative recycling GPC.

Bis(9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)naphthalene-2,7'-bis(3,4,5-tris(tetraethylene glycol)benzoic)amide (**1**)

3,4,5-tris(methyltetraethyleneoxy)benzoic acid (630 mg, 0.85 mmol, 4.06 eq.), (9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)naphthalene-2,7'-diamine[2] (220 mg, 0.21 mmol, 1.00 eq.). Beige waxy solid, yield 435 mg (0.175 mmol, 83 %). ^{1}H-NMR ($CDCl_3$): δ 8.52 (s, 2 H), 8.04 (dd, 3.5 Hz, 6.5 Hz, 2 H), 7.85 – 7.80 (m, 4 H), 7.75 (d, 8.0 Hz, 2 H), 7.65 (dd, 8.0 Hz, 1.5 Hz, 2 H), 7.57 (s, 2 H), 7.53 – 7.51 (m, 4 H), 7.42 (dd, 6.5 Hz, 3.5 Hz, 2 H), 7.31 (s, 4 H), 4.30 – 4.24 (m, 12 H), 3.88 (tr, 5.0 Hz, 8 H), 3.82 (tr, 5.0 Hz, 4 H), 3.76 – 3.59 (m, 60 H), 3.59 – 3.50 (m, 12 H), 3.38 (s, 6 H), 3.34 (s, 12 H), 2.12 – 1.96 (m, 8 H), 1.47 – 1.36 (m, 4 H), 1.22 – 0.97 (m, 24 H), 0.96 – 0.54 (m, 48 H). ^{13}C-NMR ($CDCl_3$) δ 165.22, 152.58, 152.05, 150.57, 141.92, 140.30, 140.15, 139.08, 137.81, 137.20, 132.24, 130.34, 128.76, 126.57, 126.46, 125.74, 124.90, 120.05, 119.21, 119.10, 114.93, 107.01, 72.42, 71.95, 71.91, 70.69 – 70.49 (mult. C), 69.83, 69.27, 59.03, 58.98, 55.19, 39.22, 37.00, 36.78, 33.14, 33.01, 27.89, 24.76, 22.69 (mult. C), 22.58, 22.55, 19.75, 19.42. MALDI TOF MS: calc. [M$^+$] 2491.58, found 2316.37, 2404.43 (fragmentation), 2491.55, 2414.44 (M-Na$^+$), 2530.43 (M-K$^+$). IR (cm^{-1}): ν = 3522 (w), 3303 (w), 2924 (s), 2868 (s), 1640 (m), 1580 (m), 1538 (s), 1501 (s), 1472 (s), 1455 (s), 1427 (m), 1349 (s), 1329 (s), 1244 (m), 1213 (m), 1104 (vs), 1031 (m), 946 (m), 888 (w), 852 (m), 821 (s), 764 (m), 714 (w). UV-vis ($CHCl_3$) λ_{max} (logε) 343 nm (5.00). PL$_{max}$ ($CHCl_3$) 421 nm, ϕ 7 % (quinine bisulfate). EA calc. for $C_{144}H_{222}N_2O_{32}$: 69.4 % C, 9.0 % H, 1.1 % N; found 69.0 % C, 8.9 % H, 0.8 % N.

Bis(9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)quinoxaline-2,7'-bis(3,4,5-tris(tetraethylene glycol)benzoic)amide (**2**)

3,4,5-tris(methyltetraethyleneoxy)benzoic acid (770 mg, 1.04 mmol, 4.12 eq.), (9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)quinoxaline-2,7'-diamine[2] (265 mg, 0.25 mmol, 1.00 eq.). Yellow-green waxy solid, yield 475 mg (0.19 mmol, 76 %). ^{1}H-NMR ($CDCl_3$): δ 8.88 (s, 2 H), 8.50 (br s, 2 H), 7.95 (s, 2 H), 7.84 (d, 1.5 Hz, 2 H), 7.81 (d, 8.0 Hz, 2 H), 7.76 – 7.73 (m, 4 H), 7.67 (s, 2 H), 7.63 (dd, 8.5 Hz, 2.0 Hz, 2 H), 7.30 (s, 4 H), 4.31 – 4.23 (m, 12 H), 3.88 (tr, 5.0 Hz, 8 H), 3.82 (tr, 5.0 Hz, 4 H), 3.76 – 3.61 (m, 60 H), 3.58 – 3.51 (m, 12 H), 3.38 (s, 6 H), 3.34 (s, 12 H), 2.16 – 1.93 (m, 8 H), 1.45 – 1.33 (m, 4 H), 1.27 – 0.96 (m, 24 H), 0.96 – 0.60 (48 H). ^{13}C-NMR ($CDCl_3$) δ 165.22, 152.58, 152.33, 150.42, 144.06, 141.91, 141.46, 140.80, 140.49, 137.77, 137.19, 136.74, 130.36, 130.02, 129.55, 125.50, 120.14, 119.10, 118.89, 114.97, 107.88, 72.41, 71.95, 71.91, 70.68, 70.61 – 70.50 (mult, C), 69.83, 69.27, 59.03, 58.98, 55.16, 39.24, 39.23, 37.60, 36.96, 36.63, 33.10, 33.05, 30.93, 30.87, 27.91 (mult. C), 24.81, 24.66, 22.68, 22.57, 22.54, 19.71, 19.41. MALDI TOF MS: calc. [M^+], 2493.57, found 2405.47 (fragmentation), 2493.55, 2518.50 ($M-Na^+$), 2532,47 ($M-K^+$). IR (cm^{-1}): ν = 3522 (w), 3304 (w), 2950 (m), 2924 (s), 2868 (s), 1641 (m), 1580 (m), 1538 (s), 1500 (s), 1465 (s), 1427 (m), 1347 (s), 1329 (s), 1245 (m), 1219 (m), 1103 (vs), 1031 (w), 945 (m), 889 (m), 853 (s), 818 (s), 756 (w), 716 (w). UV-vis ($CHCl_3$) λ_{max} (logε) 333 nm (4.86), 386 nm (4.45). PL_{max} ($CHCl_3$) 519 nm, ϕ 50 % (quinine bisulfate). EA calc. for $C_{142}H_{220}N_4O_{32}$: 68.4 % C, 8.9 % H, 2.2 % N; found 68.0 % C, 8.8 % H, 2.0 % N.

Bis(9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)benzothiadiazole-2,7'-bis(3,4,5-tris(tetraethylene glycol)benzoic)amide (**3**)

3,4,5-tris(methyltetraethyleneoxy)benzoic acid (720 mg, 0.97 mmol, 4.23 eq.), (9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)benzothiadiazole-2,7'-diamine[2] (245 mg, 0.23 mmol, 1.00 eq.). Yellow-orange waxy solid, yield 525 mg (0.21 mmol, 92 %). ^{1}H-NMR ($CDCl_3$): δ 8.46 (br s, 2 H), 8.03 (dd, 1.5 Hz, 8.0 Hz, 2 H), 7.93 (d, 1.5 Hz, 2 H), 7.86 – 7.82 (m, 4 H), 7.75 (d, 8.5 Hz, 2 H), 7.64 (dd, 8.0 Hz, 1.5 Hz, 2 H), 7.30 (s, 4 H), 4.32 – 4.22 (m, 12 H), 3.91 – 3.80 (m, 12 H), 3.76 – 3.60 (m, 60 H), 3.58 – 3.50 (m, 12 H), 3.38 (s, 6 H), 3.34 (s, 12 H), 2.20 – 1.98 (m, 8 H), 1.45 – 1.33 (m, 4 H), 1.25 – 0.96 (m, 24 H), 0.96 – 0.57 (m, 48 H). ^{13}C-NMR ($CDCl_3$) δ 165.21, 154.39, 152.60, 152.68, 150.97, 141.96, 141.14, 137.93, 137.01, 135.77, 133.59, 130.30, 128.20, 127.77, 123.84, 120.26, 119.31, 119.10, 114.90, 107.90, 72.49, 71.96, 71.92, 70.70 – 70.52 (mult. C), 69.82, 69.30, 59.03, 58.98, 55.26, 39.25, 37.80, 37.60, 36.87, 36.62, 33.07, 32.98, 30.80, 27.91, 27.90, 24.80, 24.61, 22.67, 22.66, 22.57, 22.54, 19.71, 19.42. MALDI TOF MS: calc. [M^+] 2499.53, found 2499.57, 2522.50 ($M-Na^+$), 2538.48 ($M-K^+$). IR (cm^{-1}): ν = 3522 (w), 3304 (w), 2950 (m), 2924 (s), 2868 (s), 1641 (m), 1580 (m), 1538 (s), 1500 (s), 1465 (s), 1427 (m), 1347 (s), 1329 (s), 1245 (w), 1219 (w), 1003 (vs), 1031 (w), 945 (m), 889 (m), 853 (m), 818 (s), 756 (w), 716 (w). UV-vis ($CHCl_3$) λ_{max} (logε) 339 nm (4.94), 428 nm (4.54). PL_{max} ($CHCl_3$) 569 nm, ϕ 80 % (N,N'-pentylhexyl perylene bisimide). EA calc. for $C_{140}H_{218}N_4O_{32}S$: 67.2 % C, 8.8 % H, 2.2 % N; found 66.8 % C, 8.7 % H, 2.0 % N.

Bis(9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)thienopyrazine-2,7'-bis(3,4,5-tris(tetraethylene glycol)benzoic)amide (**4**)

3,4,5-tris(methyltetraethyleneoxy)benzoic acid (510 mg, 0.69 mmol, 4.30 eq.), (9,9,9',9'-tetra((S)-3,7-dimethyloctyl)fluorenyl)thienopyrazine-2,7'-diamine[2] (173 mg, 0.16 mmol, 1.00 eq.). Viscous dark purple oil, yield 256 mg (0.10 mmol, 64 %). ^{1}H-NMR ($CDCl_3$): δ 8.55 (s, 2 H), 8.41 (br s, 2 H), 8.22 (dd, 8.0 Hz, 1.0 Hz, 2 H), 8.10 (s, 2 H), 7.82 (s, 2 H), 7.76 (d, 8.0 Hz, 2 H), 7.72 (d, 0.5 Hz, 2 H), 7.63 (dd, 8.5 Hz, 1.0 Hz, 2 H), 7.23 (s, 4 H), 4.31 – 4.23 (m, 12 H), 3.88 (tr, 5.0 Hz, 8 H), 3.82 (tr, 5.0 Hz, 4 H), 3.77 – 3.60 (m, 60 H), 3.58 – 3.50 (m, 12 H), 3.38 (s, 6 H), 3.34 (s, 12 H), 2.22 – 1.96 (m, 8 H), 1.44 – 1.32 (m, 4 H), 1.24 – 0.96 (m, 24 H), 0.96 – 0.84 (m, 4 H), 0.84 – 0.67 (m, 40 H), 0.67 – 0.54 (m, 4 H). ^{13}C-NMR ($CDCl_3$) δ.165.17, 152.60, 152.25, 151.33, 143.97, 141.96, 140.90, 140.27, 137.92, 137.01, 132.78, 131.46, 130.31, 127.17, 122.52, 120.22, 119.70, 119.09, 114.84, 107.91, 71.96, 71.93, 70.69 – 70.52 (mult. C), 69.83, 69.32, 59.04, 58.99, 55.31, 39.22, 37.84, 37.61, 36.80, 36.59, 33.01, 32.94, 30.74, 27.90, 24.76, 24.54, 22.66, 22.56, 22.54, 19.62, 19.42. MALDI TOF MS: calc. [M^+] 2499.53, found 2324.31, 2413.35, 2457.44 (fragmentation), 2499.46, 2522.40 (M-Na^+), 2538.37 (M-K^+). IR (cm^{-1}): ν = 3522 (w), 3304 (w), 2924 (s), 2868 (s), 1641 (m), 1580 (m), 1538 (s), 1500 (m), 1466 (s), 1428 (m), 1348 (s), 1329 (s), 1305 (w), 1245 (w), 1209 (w), 1102 (vs), 1029 (w), 947 (m), 854 (m), 817 (s), 755 (m), 668 (w). UV-vis ($CHCl_3$) λ_{max} (logε) 366 nm (4.88), 520 nm (3.31). PL_{max} ($CHCl_3$) 679 nm, ϕ 10 % (Rhodamine 101). EA calc. for $C_{140}H_{218}N_4O_{32}S$: 67.2 % C, 8.8 % H, 2.2 % N; found 66.3 % C, 8.7 % H, 2.0 % N.

9,9,9',9',9'',9''-hexa((S)-3,7-dimethyloctyl)fluorene-2,7''-bis(3,4,5-tris(tetraethylene glycol)benzoic)amide (**5**)

3,4,5-tris(methyltetraethyleneoxy)benzoic acid (375 mg, 0.51 mmol, 6.92 eq.), 9,9,9'9',9'',9''-hexa((S)-3,7-dimethyloctyl)terfluorene-2,7''-diamine[1] (100 mg, 0.073 mmol, 1.00 eq.). Yield 92 mg of a yellow solid (45 %). ^{1}H-NMR (THF-d_8, 50 °C): δ 9.09 (s, 2 H), 7.82 (s, 2 H), 7.71 (d, 7.5 Hz, 2 H), 7.74 – 7.53 (m, 14 H), 7.23 (s, 4 H), 4.14 – 4.09 (m, 12 H), 3.74 (tr, 5.0 Hz, 8 H), 3.67 (tr, 5.0 Hz, 4 H), 3.58 – 3.43 (m, 60 H), 3.36 – 3.32 (m, 12 H), 3.18 (s, 6 H), 3.17 (s, 12 H), 2.13 – 1.92 (m, 12 H), 1.39 – 1.27 (m, 6 H), 1.16 – 0.91 (m, 36 H), 0.91 – 0.78 (m, 6 H), 0.76 – 0.48 (m, 66 H). ^{13}C-NMR (THF-d_8, 50 °C) δ 164.32, 152.46, 151.28, 151.19, 150.93, 141.75, 140.54, 140.46, 140.06, 139.62, 139.24, 136.22, 130.37, 125.81 (mult. C), 120.91, 120.82, 119.69, 119.49, 119.09, 118.57, 114.33, 107.50, 72.28, 71.88, 70.62 – 70.31 (mult. C), 69.59, 57.89, 54.85, 39.13, 39.10, 37.70, 37.60, 37.38, 36.71, 36.59, 36.56, 32.99, 32.92, 32.88, 30.60, 27.78, 24.79, 24.65, 24.61, 24.58, 24.52, 24.46, 24.26, 24.06, 23.86, 22.04, 21.94, 21.92, 18.99, 18.94, 18.83. MALDI TOF MS: calc. [M^+] 2809.91, found 2810.01, 2832.98 (M-Na^+). IR (cm^{-1}): ν = 3503 (w), 3322 (w), 2951 (m), 2925 (s), 2868 (s), 1670 (w), 1647 (w), 1583 (m), 1537 (m), 1491 (m), 1459 (s), 1429 (s), 1330 (s), 1302 (m), 1246 (m), 1209 (m), 1101 (vs), 946 (m), 852 (m), 816 (s), 754 (s), 665 (w). UV-vis ($CHCl_3$) λ_{max} (logε) 365 nm (5.17). PL_{max} ($CHCl_3$) 405 nm, 425 nm, ϕ 5 % (quinine bisulfate). EA calc. for $C_{167}H_{264}N_2O_{32}$: 71.3 % C, 9.5 % H, 1.0 % N; found 71.0 % C, 9.4 % H, 0.6 % N.

Supplementary measurements

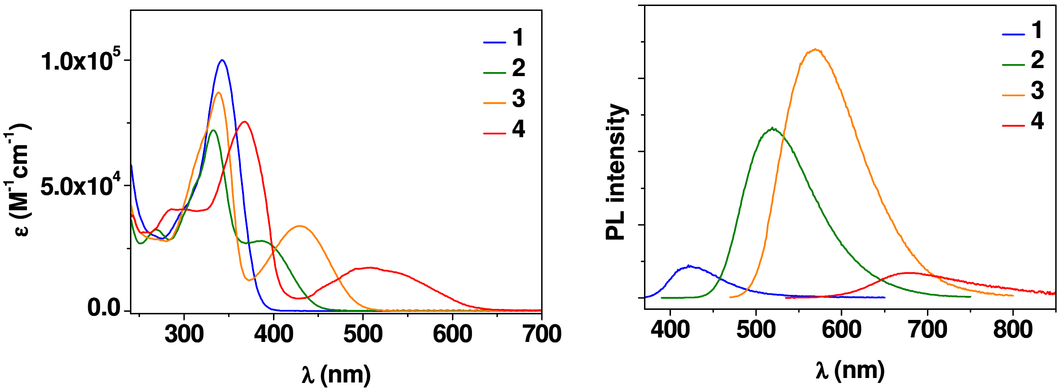

Fig. S1 UV-vis absorption and fluorescence spectra of **1 – 4** in chloroform. Fluorescence samples have been diluted to an OD below 0.1 prior to the measurements. The fluorescence spectra are weighted according to the respective quantum yields. Excitation at the absorption maximum.

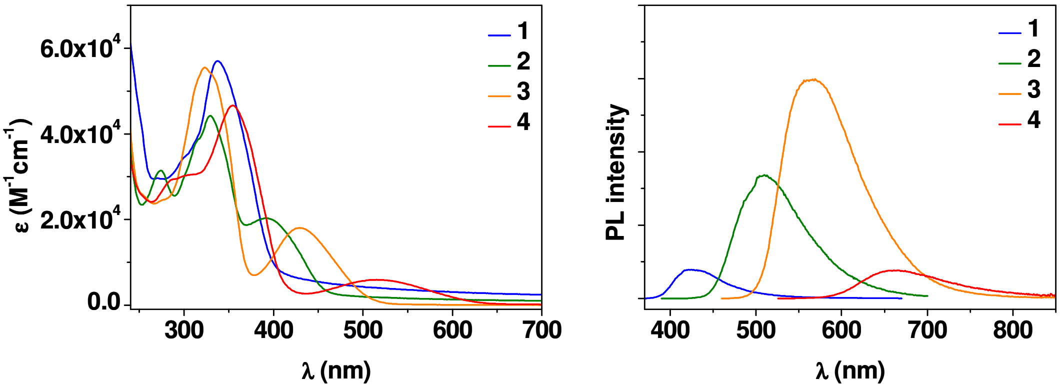

Fig. S2 UV-vis absorption and fluorescence spectra of **1 – 4** in water. Injected as 3 mM THF stock solution. Fluorescence samples have been diluted to an OD below 0.1 prior to the measurements. The fluorescence spectra are weighted according to the respective quantum yields. Excitation at the absorption maximum.

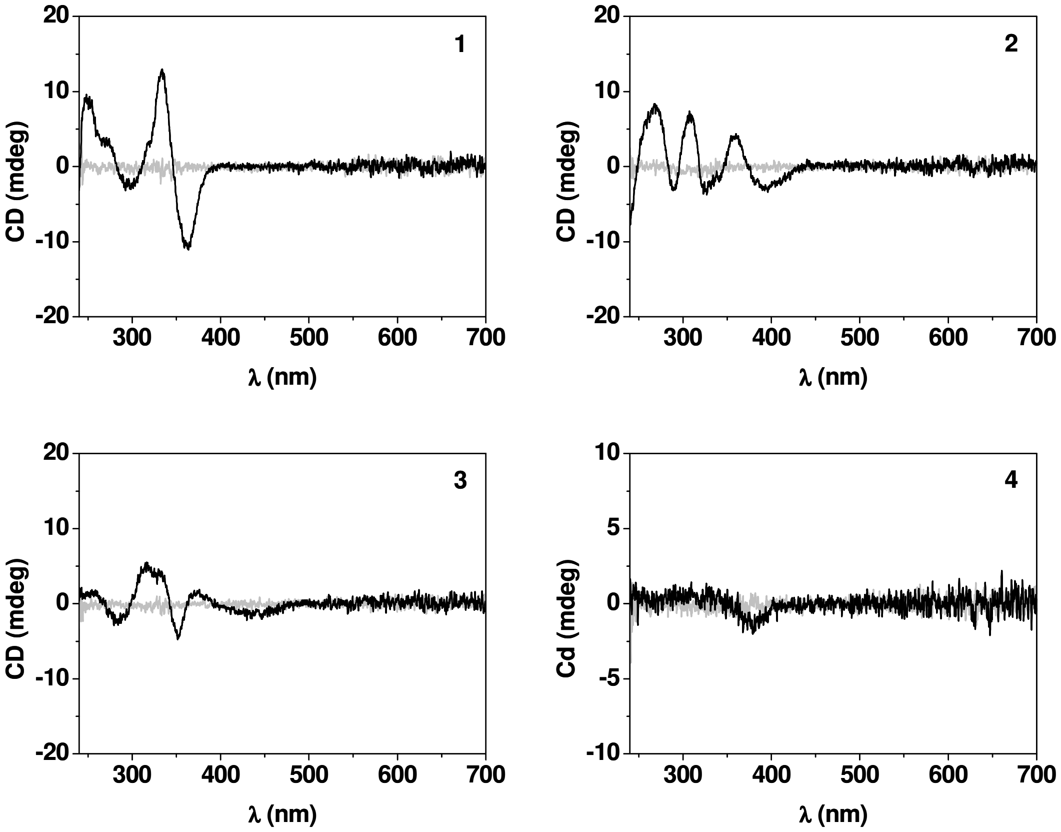

Fig. S3 CD spectra of **1 – 4** in chloroform (grey) and in water (black). Concentration 15 μM. Injected as 3 mM THF stock solution.

Tab. S1 UV-vis and PL characteristics of two aqueous solutions of **1**, prepared by injection of concentrated (3 mM) and diluted (0.2 mM) THF stock solutions into water.

	UV-vis absorption		photoluminescence	
	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{max} (nm)	ϕ_{PL}* (%)
stock sol. 0.2 mM	342	53000	421	38
stock sol. 3 mM	332	52000	431	6

* Reference compound: quinine bisulfate in 1 N H_2SO_4

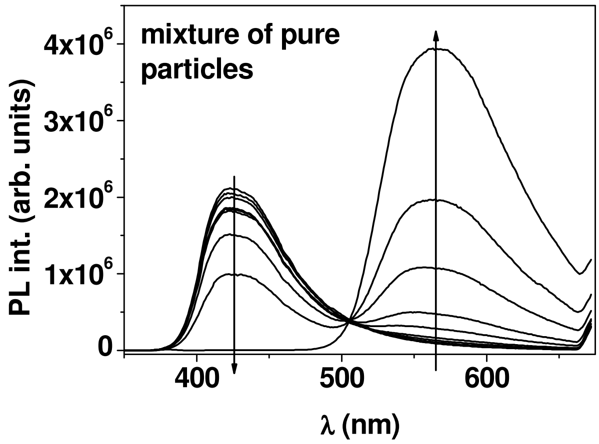

Fig. S4 PL spectra of mixtures of pure nanoparticles of **1** and **3** in aqueous solution. Arrows indicate spectral changes with decreasing donor to acceptor ratio from 100 : 0 to 0 : 100. Excitation wavelength λ_{exc} = 342 nm. Total chromophore concentration $1.5 \cdot 10^{-6}$ M.

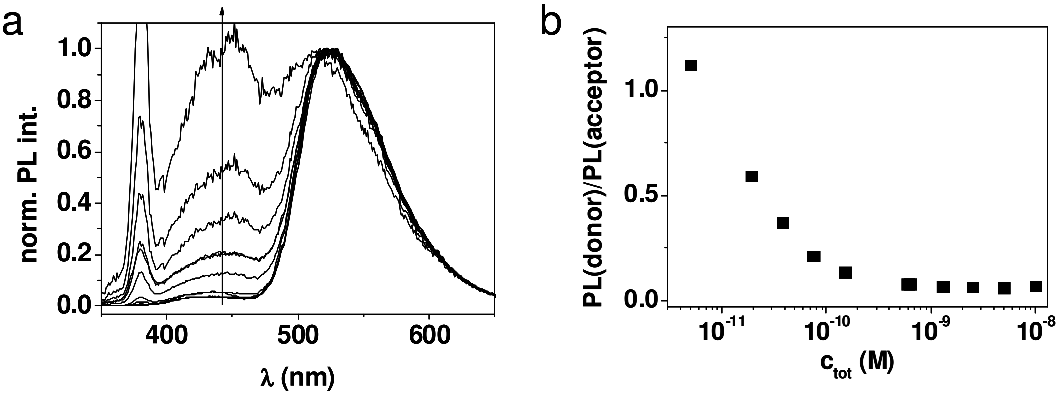

Fig. S5 (a) Concentration dependent fluorescence spectra of mixed aggregates of **1** and **3** with a composition of 95 : 5 in water, normalised to the acceptor concentration. The arrow indicates spectral changes upon dilution. The sharp peak at 380 nm is due to Raman scattering of the solvent. Excitation wavelength λ_{exc} = 340 nm. (b) Concentration dependence of the ratio of donor to acceptor emission in these mixed aggregates.

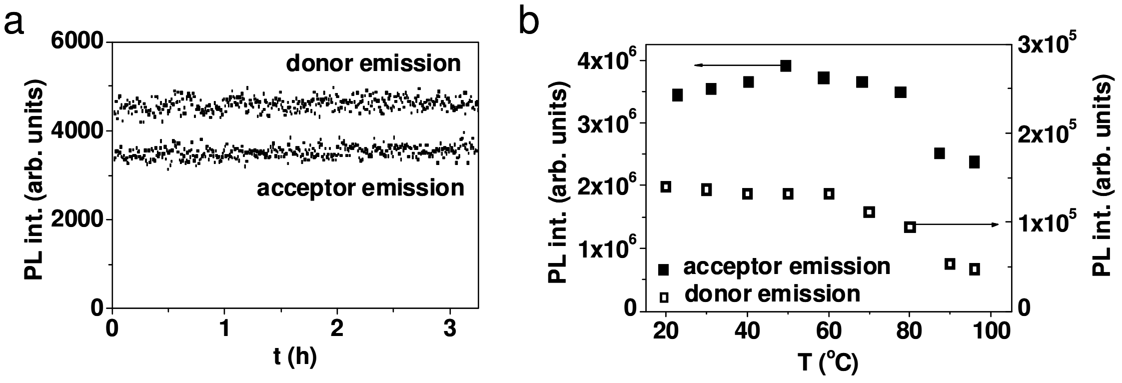

Fig. S6 Stability of aggregates of 1 and **3** in aqueous solution. (a) Time dependence of a 75 : 25 mixture of separate aggregates at 25 °C, followed at 423 nm (donor emission) and 563 nm (acceptor emission). (b) Temperature dependence of the PL emission maxima of mixed aggregates of **1** and **3** with a composition of 95 : 5. Total chromophore concentration $1.5 \cdot 10^{-6}$ M. Excitation wavelength λ_{exc} = 340 nm.

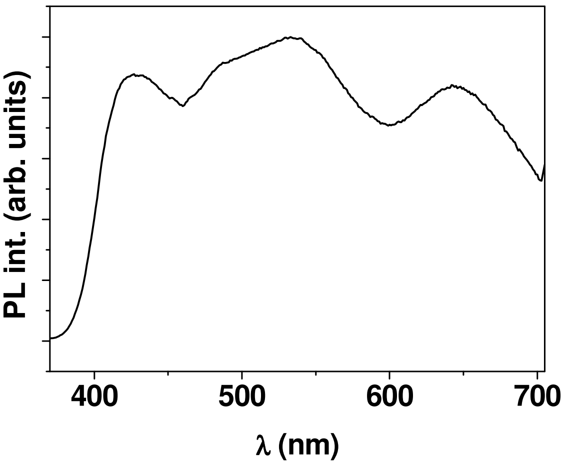

Fig. S8 Simultaneous emission of **1** – **4** in a mixture of pure nanoparticles. Excitation wavelength λ_{exc} = 360 nm. Molar ratio of **1** : **2** : **3** : **4** = 34 : 7.9 : 6.7 : 51.4. Total chromophore concentration $1.5 \cdot 10^{-6}$ M.

References

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