

Supporting Information

Side Chains Control Dynamics and Self-Sorting in Fluorescent Organic Nanoparticles

Adrien Kaeser, Irén Fischer, Robert Abbel, Pol Besenius, Debarshi Dasgupta, Martijn A. J.

*Gillissen, Giuseppe Portale, Amy L. Stevens, Laura M. Herz, Albertus P.H. J. Schenning**

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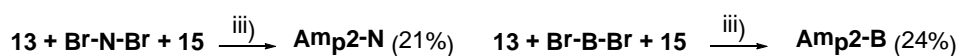
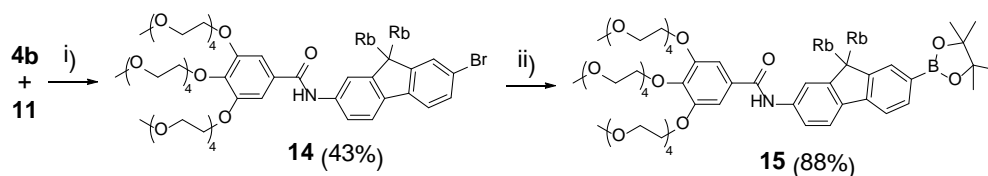
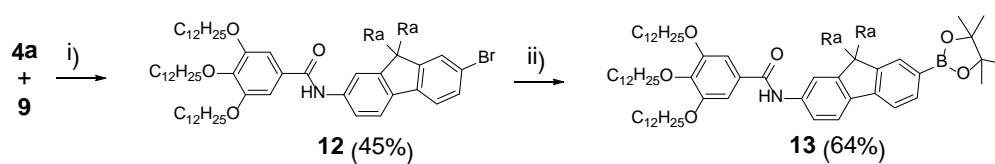
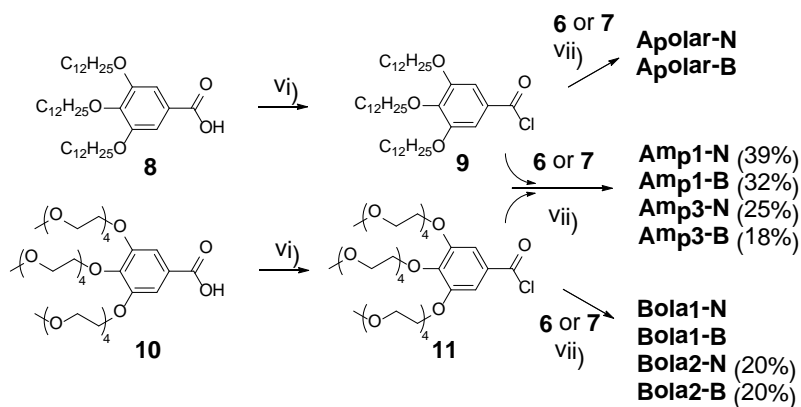
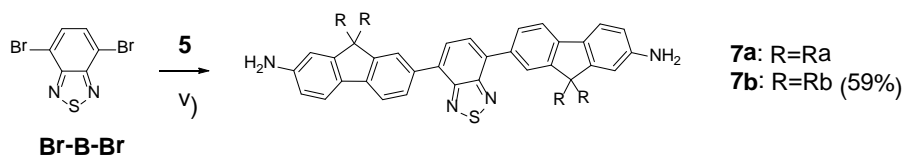
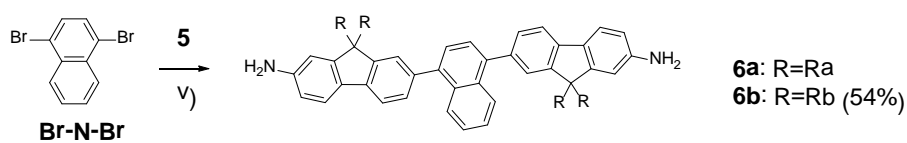
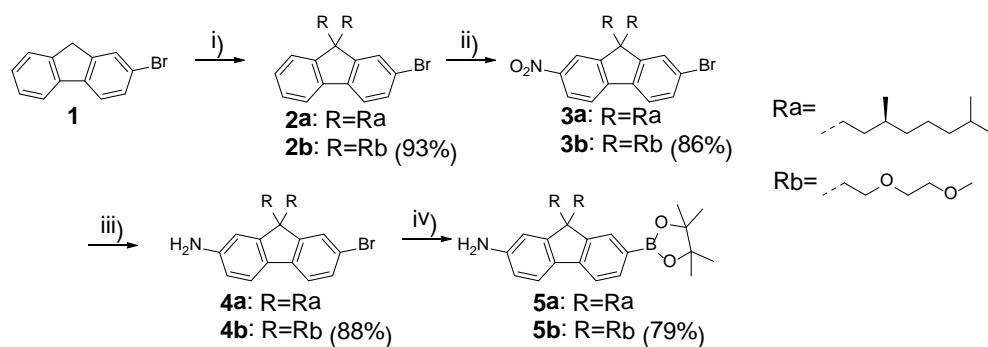
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General Methods

All solvents and chemicals were used as received. Water was demineralized prior to use. Dry dichloromethane (DCM) and tetrahydrofuran (THF) were obtained from distillation over Merck molecular sieves (4 Å). Analytical thin layer chromatography (TLC) was carried out using Merck pre-coated silica gel plates (60F-254) using ultraviolet light irradiation at 254 or 365 nm. Manual column chromatography was carried out using Merck 60 Å pore size silica gel (particle size: 63-200 µm). Flash chromatography was performed using Biotage SP1 equipped with Biotage SNAP FLASH purification silica cartridges (particles size: 50 µm). General LC-MS analysis: samples were analyzed using a Shimadzu SCL-10 AD VP series HPLC coupled to a diode array detector (Finnigan Surveyor PDA Plus detector, Thermo Electron Corporation) and an Ion-Trap (LCQ Fleet, Thermo Scientific). Analyses were performed using a reversed phase HPLC column (GraceSmart PP18, 50 mm x 2.1 mm, 3µm), using an injection volume of 1-4 µL, a flow rate of 0.20 mL/min and a typically a gradient (5% to 100% in 10 min, held at 100% for 1 more minute) of acetonitrile in water (both containing 0.1% formic acid) at 298K. Reversed phase high-pressure liquid chromatography (RP-HPLC) was performed on a Shimadzu LC-8A HPLC system by using a Gemini 5u C18 column. A gradient of water in acetonitrile, both containing 0.1% formic acid was used to elute products. Detection was performed by a Shimadzu SPD-10AV UV-detector ($\lambda = 240$ nm). Preparative recycling GPC was performed using a Shimadzu system equipped with a Shimadzu LC-10ADvp pump, a Jai-Gel 2.5 H and a Jai-Gel 2 H column in series and a Shimadzu SPD-10AVvp UV/Vis detection system performing detection at 254 nm and 340 nm. HPLC grade chloroform was used as the eluent (with a flow of 3.5 ml/min and manual injection was performed with a volume of 2 ml. One cycle through the system took 1 hour.) Matrix assisted laser desorption/ionization time of flight mass spectra (MALDI-TOF-MS) were measured on a PerSeptive Biosystems Voyager-DE PRO spectrometer with a Biospectrometry workstation using 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as matrix material. M/z values are given in gram/mol. ^1H and ^{13}C NMR spectra were recorded using a Varian Mercury Vx 400 MHz (100 MHz for ^{13}C) NMR spectrometer at 298 K. Chemical shifts are given in parts per million (ppm) and the spectra are calibrated to residual solvent signals of CDCl_3 (7.26 ppm (^1H) and 77.0 ppm (^{13}C)). Splitting patterns are labeled as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet and br stands for broad. Fluorescence spectra for the energy transfer studies of nanoparticles self-assembled of two chromophores were recorded on a Varian Cary Eclipse

fluorescence spectrophotometer equipped with a Perkin–Elmer PTP-1 Peltier temperature control system.

Synthesis



Scheme S1. Synthesis pathway for the twelve oligofluorene derivatives with two different aromatic cores (N for naphthalene derivatives, B for benzothiadiazole derivatives, **a** for chiral alkyl tails and **b** for ethylene glycol tails). Reagents and conditions: i) (a) for **2a**: dimethyl sulfoxide, aqueous NaOH, benzyltriethylammonium bromide, (S)-1-bromo-3,7-dimethyloctane, room temperature, overnight; (b) for **2b**: toluene, aqueous NaOH, tetrabutylammonium bromide, 1-bromo-2-(2-methoxyethoxy)ethane, 60 °C, overnight; ii) CH₂Cl₂, SiO₂/H₂SO₄, HNO₃, room temperature, 2 h; iii) ethanol/ethylacetate, SnCl₄, reflux, overnight; iv) bis(pinacolato)diboron, potassium acetate, Pd[dppf]Cl₂, reflux, overnight; v) dioxane/H₂O, Na₂CO₃, Pd[PPh₃]₄, reflux, overnight; vi) CH₂Cl₂, oxalyl chloride, room temperature, overnight, product used in situ; vii) CH₂Cl₂, triethyl amine, room temperature, overnight.

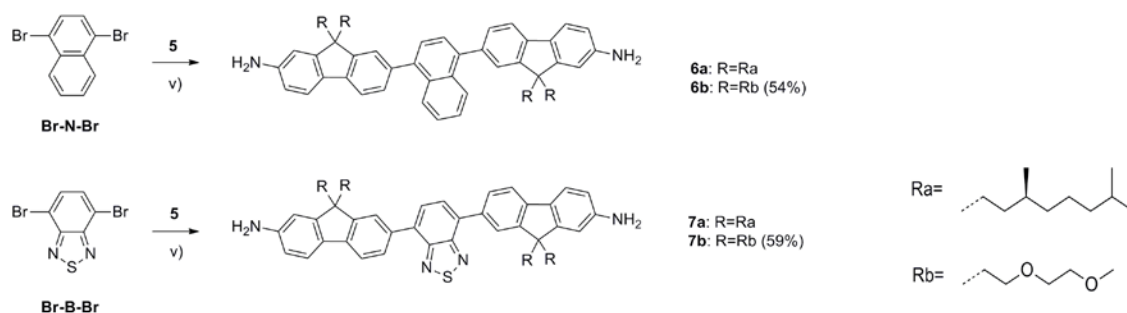
The synthesis of **2a**,^{S1} **3a**, **4a**, **5a**,^{S2} **8a**, **Apolar-N**, **Apolar-B**,^{S3} **Bola-N** and **Bola-B**^{S4} have already been described elsewhere.

General procedure for the synthesis of boronic ester (5b, 13, 14):



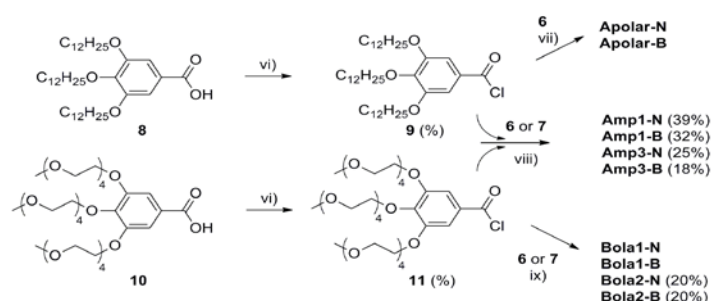
Bromofluorene derivatives were mixed to bis(pinacolato)diboron (1.5 eq.), KOAc (4 eq.), Pd(dppf)Cl₂ (cat.) in dioxane (10 ml) and refluxed overnight. The reaction was further poured into cold water (100 ml), and taken up in CHCl₃ (40 ml) and extracted several time. The organic extracts were dried over Na₂SO₄, condensed, and purified by column chromatography.

General procedure for Suzuki Couplings (8b, 9b, Amp2-N, Amp2-B):

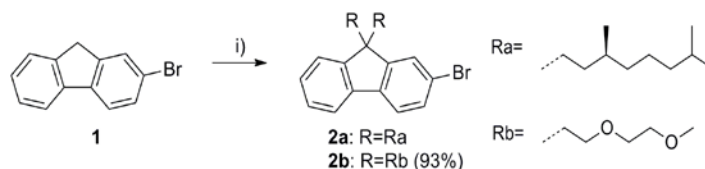


Aryl dibromide **Br-N-Br** or **Br-B-Br**, aminofluorene boronic ester, Na_2CO_3 were charged in a two necked flask under an atmosphere of Argon. $\text{Pd}(\text{PPh}_3)_4$ and subsequently a degassed mixture of dioxane and water (2:1) were added. The reaction mixture was refluxed overnight, then poured into water and extracted with CHCl_3 several times. The organic extracts were washed with brine, dried over Na_2SO_4 , and condensed. Pure compounds were obtained after column chromatography.

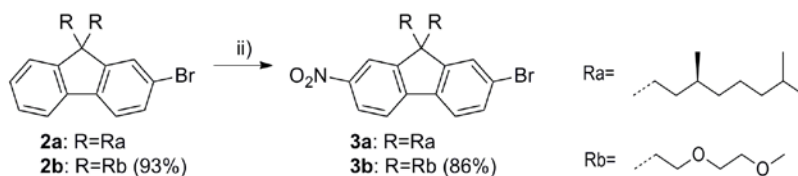
General procedure for reactions with acid chloride derivatives (12, 14, Amp1-N, Amp1-B, Amp3-N, Amp3-B, Amp2-N, Amp2-B)



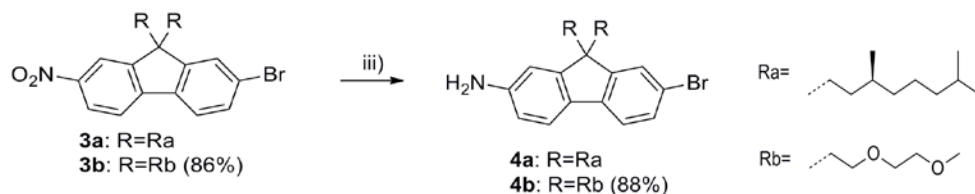
Acid chloride derivatives **10** and **11** were prepared in situ according to a literature procedure from its corresponding acid and oxalyl chloride.^{S5} Aromatic amine derivatives and triethyl amine were dissolved in dry chloroform, and the acid chloride was added as a solution in dry chloroform. After stirring at room temperature overnight, the mixture was evaporated, and the product directly purified by column chromatography.



2b. 2-Bromofluorene (3.5 g, 14 mmol, 1 eq.) and 1-bromo-2-(2-methoxyethoxy)ethane (7.9 g, 41 mmol, 3 eq.) and tetrabutylammonium bromide (2.3 g, 7 mmol, 0.5 eq.) were stirred in a mixture of toluene (100 ml) and aqueous NaOH (50 weight %, 30 ml) at 60°C overnight. The reaction was then cool down at room temperature and taken back in ethyl acetate. The organic extracts was successively washed with diluted HCl solution and brine (3 times), dried over MgSO₄, and condensed. Column chromatography (SNAP 25, AcOEt 0% to 80% in heptane) gave **2b** (5.998 g, 13 mmol, 93 %) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.67 (m, 1H), 7.56 (d, ⁴J = 1.6 Hz, 1H), 7.53 (d, ³J = 8.0 Hz, 1H), 7.46 (dd, ³J = 8.0 Hz, ⁴J = 1.6 Hz, 1H), 7.37-7.42 (m, 1H), 7.30-7.36 (m, 2H), 3.28-3.31 (m, 10H), 3.14-3.22 (m, 4H), 2.70-2.79 (m, 4H), 2.33-2.43 (m, 4H) ; ¹³C NMR (100 MHz, CDCl₃) δ 151.12, 148.52, 139.44, 139.40, 130.41, 127.80, 127.47, 126.65, 123.20, 121.20, 121.09, 119.87, 71.72, 69.91, 66.90, 58.99, 51.47, 39.57; MALDI-TOF MS: calc. [M]⁺ 448.12, found 448.02.



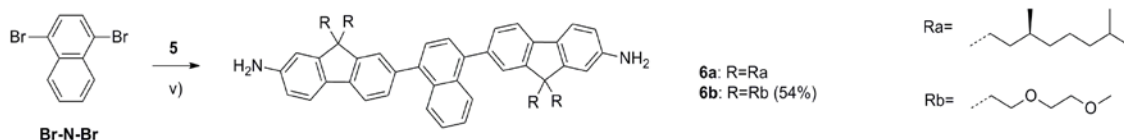
3b. **2b** (5.998 g, 13 mmol, 1eq.) was dissolved in CH₂Cl₂ (80 ml), in presence of a supported catalyst of SiO₂/H₂SO₄ (6 g) prepared according to literature procedure.^{S5} HNO₃ (0.55 ml, 13 mmol, 1 eq.) was added, and the heterogeneous mixture is stirred at room temperature for 2 hours. The solution was then filtered and condensed. After column chromatography (SNAP 100, AcOEt 0% to 50% in heptane) **3b** is obtained as yellow crystalline solid (5.698 g, 12 mmol, 86 %). ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.29 (m, 2H), 7.76 (dd, ³J = 8.2 Hz, ⁴J = 0.5 Hz, 1H), 7.62-7.64 (m, 2H), 7.54 (dd, ³J = 8.2 Hz, ⁴J = 1.6 Hz, 1H), 3.32-3.25 (m, 10H), 3.13-3.16 (m, 4H), 2.76-2.88 (m, 4H), 2.35-2.50 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 152.83, 150.25, 147.37, 145.71, 137.13, 131.12, 127.24, 123.71, 123.64, 122.44, 119.96, 119.09, 71.65, 69.95, 66.73, 58.97, 52.34, 39.19; MALDI TOF MS: calc. [M]⁺ 493.11, found 493.00.



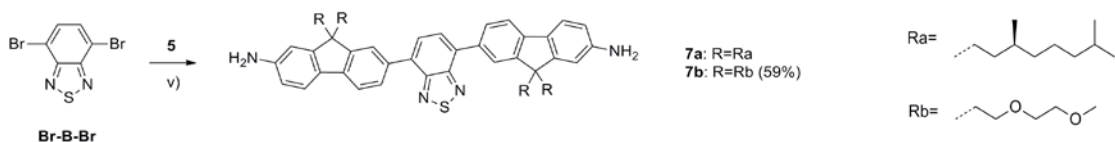
4b. A 1:1 mixture of EtOH and AcOEt (100 ml) containing **3b** (5.697 mg, 12 mmol, 1 eq.) and tin chloride (17.2 g, 101 mmol, 8.8 eq.) was refluxed overnight, then neutralized with a 1M NaOH solution (20 ml). The solution is filtered over Buchner, washed with brine, dried over MgSO_4 and then condensed. **4b** was obtained as pale solid (3.915 g, 8 mg, 88 %). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 7.36 (d, $^3J = 8.1$ Hz, 1H), 7.30-7.33 (m, 2H), 6.64 (d, $^4J = 2$ Hz, 1H), 6.58 (dd, $^3J = 8.1$ Hz, $^4J = 2$ Hz, 1H), 3.82 (br, 2H), 3.27 (t, $^3J = 4.6$ Hz, 4H), 3.23 (s, 6H), 3.12-3.20 (m, 4H), 2.67-2.79 (m, 4H), 2.20-2.33 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.16, 149.84, 146.70, 139.74, 129.92, 129.80, 125.94, 118.81, 114.12, 109.24, 71.43, 69.59, 66.64, 58.66, 50.78, 39.50; MALDI TOF MS: calc. $[\text{M}^+]$ 463.14, found 463.24.



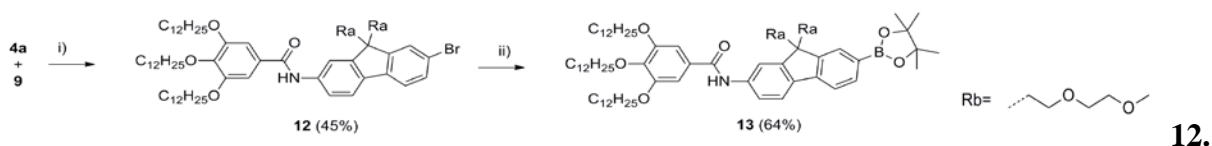
5b. **4b** (500 mg, 1 mmol) yielded **5b** (438 mg, 0.9 mmol, 79 %) as a yellow oil, purified on column (SNAP 25, AcOEt 30% to 100% in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.74 (d, $^3J = 7.6$ Hz, 1H), 7.51 (d, $^3J = 7.6$ Hz, 1H), 7.46 (d, $^3J = 8.1$ Hz, 1H), 6.74 (d, $^4J = 2.1$ Hz, 1H), 6.65 (dd, $^3J = 8.1$ Hz, $^4J = 2.1$ Hz, 1H), 3.80 (br, 2H), 3.31-3.33 (m, 4H), 3.28 (s, 6H), 3.18-3.20 (m, 4H), 2.69-2.73 (m, 4H), 2.40-2.47 (m, 2H), 2.27-2.34 (m, 2H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.38, 146.87, 146.81, 143.93, 134.10, 131.26, 128.91, 121.16, 117.74, 114.27, 109.72, 83.65, 71.76, 69.86, 67.02, 58.96, 50.66, 39.85, 24.94; MALDI TOF MS: calc. $[\text{M}^+]$ 511.31, found 511.18.



6b. **5b** (426 mg, 0.8 mmol, 2.07 eq.) reacted with **Br-N-Br** (115 mg, 0.4 mmol, 1 eq.), yielding **6b** (197 mg, 0.2 mg, 54 %) as a fluorescent yellow product, purified by column chromatography (SNAP 10, MeOH 0% to 5% in CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.99-8.03 (m, 2H), 7.66 (d, ³J = 7.7 Hz, 2H), 7.52-7.54 (m, 6H), 7.47 (dd, ³J = 7.7 Hz, ⁴J = 1.5 Hz, 2H), 7.41-7.45 (m, 2H), 6.79 (d, ⁴J = 2.1 Hz, 2H), 6.71 (dd, ³J = 8.0 Hz, ⁴J = 2.1 Hz, 2H), 3.82 (s, 4H), 3.36-3.37 (m, 8H), 3.27-3.30 (m, 20H), 2.90-2.94 (m, 8H), 2.32-2.47 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 150.84, 147.83, 146.44, 139.97, 139.84, 137.93, 131.97, 130.86, 129.10, 126.32, 126.23, 125.58, 124.47, 120.60, 118.04, 114.20, 109.60, 71.56, 69.69, 67.10, 58.74, 50.75, 39.67; MALDI TOF MS: calc. [M⁺] 894.48, found 894.43.



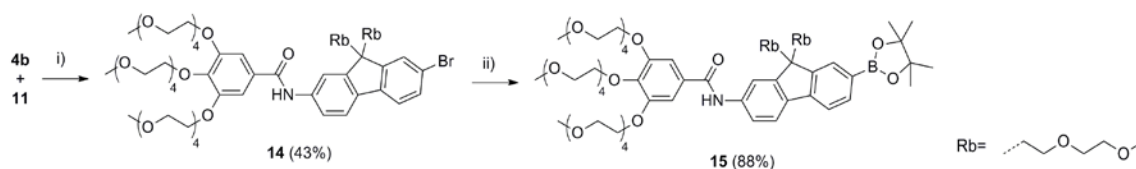
7b. **5b** (672 mg, 1.3 mmol, 2.07 eq.) reacted with **Br-B-Br** (187 mg, 0.6 mmol, 1eq), yielding **7b** (343 mg, 0.4 mmol, 59 %) as a fluorescent red solid, purified by column chromatography (SNAP 25, MeOH 0% to 5% in CH₂Cl₂) ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, ³J = 7.9 Hz, ⁴J = 1.6 Hz, 2H), 7.97 (d, ⁴J = 1.3 Hz, 2H), 7.86 (s, 2H), 7.70 (d, ³J = 7.9 Hz, 2H), 7.53 (d, ³J = 8.0 Hz, 2H), 6.79 (d, ⁴J = 2.0 Hz, 2H), 6.70 (dd, ³J = 8.0 Hz, ⁴J = 2.0 Hz, 2H), 3.84 (br, 4H), 3.31-3.35 (m, 8H), 3.25-3.27 (m, 20H), 2.86-2.95 (m, 8H), 2.47-2.54 (m, 4H), 2.34-2.42 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 154.29, 151.32, 148.25, 146.62, 141.15, 134.86, 133.19, 131.08, 128.65, 127.71, 123.64, 121.01, 118.47, 114.43, 109.85, 71.76, 69.90, 67.21, 58.97, 51.00, 39.94; MALDI TOF MS: calc. [M⁺] 902.43, found 902.39.



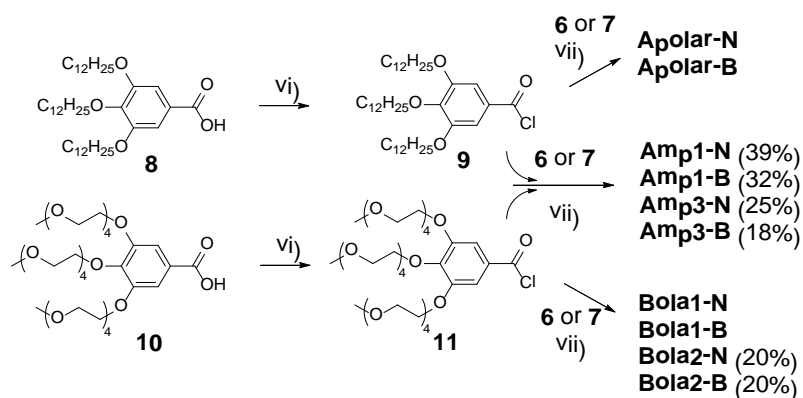
4a (250 mg, 1 mmol, 1 eq.) reacted with **9** (1.32 g, 1.9 mmol, 2 eq.), yielding **12** (527 mg, 0.4 mmol, 45 %) as a white solid, purified by column chromatography (SNAP 25, CH₂Cl₂ 25% to 60% in Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 1H), 7.73 (d, ⁴J = 1.8 Hz, 1H), 7.63 (d, ³J = 8.1 Hz, 1H), 7.49-7.52 (m, 2H), 7.43-7.45 (m, 2H), 7.08 (s, 2H), 4.01-4.07 (m, 6H), 1.88-2.04 (m, 4H), 1.79-1.86 (m, 4H), 1.72-1.77 (m, 2H), 1.41-1.50 (m, 8H), 1.263-1.39 (m, 50H), 1.00-1.14 (m, 12H), 0.86-0.89 (m, 12H), 0.78-0.81 (m, 12H), 0.65-0.70 (m, 6H), 0.53-0.65 (m, 2H), 0.41-0.52 (m, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 165.50, 153.15, 153.04, 152.76, 151.47, 141.42, 139.77, 137.78, 136.42, 129.87, 125.97, 120.54, 120.06, 118.81, 114.55, 105.78, 73.48, 69.37, 55.36, 39.13, 36.57, 36.54, 32.85, 32.78, 31.90, 30.43, 30.31, 29.72, 29.71, 29.68, 29.63, 29.56, 29.39, 29.35, 27.88, 26.06, 24.61, 24.49, 22.66, 22.54, 19.48, 19.36, 14.07; MALDI TOF MS: calc. [M⁺] 1197.89, found 1197.79.

13. **12** (502 mg, 0.4 mmol) yielded **13** (336 mg, 0.3 mmol, 64 %) as a white solid, purified on column (SNAP 25, CH₂Cl₂ 25% to 80% in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, ³J = 7.6 Hz, 1H), 7.77 (s, 1H), 7.73 (s, 1H), 7.71 (d, ⁴J = 1.5 Hz, 1H), 7.70 (d, ³J = 8.4 Hz, 1H), 7.65 (d, ³J = 7.6 Hz, 1H), 7.53 (dd, ³J = 8.4 Hz, ⁴J = 1.5 Hz, 1H), 7.08 (s, 2H), 4.01-4.07 (m, 6H), 1.91-2.08 (m, 4H), 1.72-1.87 (m, 6H), 1.22-1.57 (m, 66H), 0.96-1.16 (m, 12H), 0.86-0.89 (m, 10H), 0.78 (d, ³J = 6.5 Hz, 12H), 0.67 (d, ³J = 6.4 Hz, 6H), 0.40-0.63 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 165.53, 153.08, 152.40, 149.66, 141.25, 137.34, 133.76, 128.71, 120.37, 118.65, 118.51, 114.62, 105.72, 83.52, 73.41, 69.27, 55.06, 39.10, 37.60, 37.40, 36.56, 32.86, 32.81, 31.88, 30.47, 30.41, 30.29, 29.70, 29.68, 29.66, 29.65, 29.62, 29.60, 29.54, 29.37, 29.34, 29.32, 27.83, 26.04, 24.83, 24.59, 24.47, 22.63, 22.53, 22.51, 19.49, 19.38, 14.05; MALDI TOF MS: calc. [M⁺] 1245.07, found 1245.04.

14. **4b** (400 mg, 0.9 mmol, 1 eq.) reacted with **11** (1.025 g, 1.3 mmol, 1.6 eq.), yielding **14** (443 mg, 0.4 mmol, 43 %) as a white solid, purified by column chromatography (SNAP 25, MeOH 0% to 4% in CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 8.41 (br, 1H), 7.77 (dd, ³J = 8.3 Hz, ⁴J = 1.6 Hz, 1H), 7.70 (d, ⁴J = 1.3 Hz, 1H), 7.63 (d, ³J = 8.3 Hz, 1H), 7.54 (d, ⁴J = 1.4 Hz, 1H), 7.49 (d, ³J = 8.0 Hz, 1H), 7.45 (dd, ³J = 8.0 Hz, ⁴J = 1.4 Hz, 1H), 4.23-4.28 (m, 6H), 3.87 (t, ³J = 4.6 Hz, 4H), 3.81 (t, ³J = 5.0 Hz, 2H), 3.60-3.73 (m, 30H), 3.50-3.56 (m, 6H), 3.37 (s, 3H), 3.27-3.33 (m, 15H), 3.15-3.24 (m, 4H), 2.74-2.85 (m, 4H), 2.38 (t, ³J = 7.6 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 165.21, 152.32, 150.90, 149.28, 141.57, 138.71, 138.29, 135.27, 130.23, 129.81, 126.41, 120.54, 120.46, 120.10, 119.66, 115.07, 107.42, 72.19, 71.71, 71.67, 71.51, 70.45, 70.43, 70.38, 70.34, 70.31, 70.27, 70.24, 69.66, 68.93, 66.70, 58.79, 58.73, 51.38, 39.40; MALDI TOF MS: calc. [M+] 1187.51, found 1187.47, 1210.46 [M-Na+].



15. **14** (398 mg, 0.3 mmol) yielded **15** (366 mg, 0.3 mmol, 88 %) as a white solid, purified on column (SNAP 25, MeOH 0% to 7% in CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.79-7.82 (m, 2H), 7.76 (dd, ³J = 7.6 Hz, ⁴J = 0.7 Hz, 1H), 7.64-7.66 (m, 2H), 7.60 (d, ³J = 7.6 Hz, 1H), 7.24 (s, 2H), 4.24 (m, 6H), 3.82-3.85 (m, 4H), 3.77-3.79 (m, 2H), 3.66-3.70 (m, 6H), 3.57-3.66 (m, 24H), 3.47-3.53 (m, 6H), 3.34 (s, 3H), 3.30 (s, 6H), 3.26-2.28 (m, 4H), 3.23 (s, 6H), 3.13-3.16 (m, 4H), 2.67-2.76 (m, 4H), 2.32-2.46 (m, 4H), 1.35 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 165.10, 151.97, 149.85, 147.35, 142.62, 141.01, 138.26, 135.79, 133.71, 129.60, 128.72, 126.76, 120.17, 119.44, 118.30, 114.92, 106.95, 83.29, 71.92, 71.43, 71.39, 71.27, 70.20, 70.16, 70.14, 70.10, 70.07, 70.03, 69.99, 69.96, 69.33, 69.25, 68.53, 66.51, 58.47, 58.43, 58.40, 53.18, 53.18, 50.62, 39.21, 24.51; MALDI TOF MS: calc. [M+] 1233.68, found 1233.66, 1256.66 [M-Na+].



Amp1-N. **6a** (150 mg, 0.14 mmol, 1 eq.) reacted with **9** (198 mg, 0.28 mmol, 2 eq.) and **11** (217 mg, 0.28 mmol, 2 eq.), yielding **Amp1-N** (112 mg, 0.05 mmol, 32 %) as a colorless solid, purified by column chromatography (SNAP 25, MeOH 0% to 5% in CH₂Cl₂) and preparative recycling GPC. ¹H NMR (400 MHz, THF-d₈) δ 8.02-8.04 (m, 2H), 7.75-7.84 (m, 6H), 7.51-7.56 (m, 7H), 7.41-7.43 (m, 3H), 7.11 (s, 2H), 4.28 (br, 6H), 4.02-4.08 (m, 6H), 3.54-3.89 (m, 36H), 3.35-3.40 (m, 8H), 1.96-2.10 (m, 8H), 1.67-1.87 (m, 14H), 1.03-1.51 (m, 84H), 0.86-0.90 (m, 14H), 0.58-0.82 (m, 44H); ¹³C NMR (100 MHz, CDCl₃) δ 165.52, 165.19, 162.45, 162.27, 153.13, 153.11, 152.68, 152.48, 152.43, 152.09, 151.90, 150.46, 150.44, 144.13, 143.97, 141.71, 141.37, 140.21, 140.08, 139.94, 139.07, 138.94, 137.84, 137.42, 137.26, 137.02, 132.13, 132.12, 130.22, 129.99, 128.68, 128.64, 126.45, 126.34, 125.63, 124.80, 123.35, 122.93, 120.01, 119.91, 119.16, 119.10, 118.86, 114.91, 114.72, 110.06, 108.97, 107.73, 105.85, 73.46, 72.31, 71.84, 71.82, 71.80, 70.72, 70.48, 70.44, 70.42, 70.40, 70.38, 69.71, 69.39, 69.26, 69.09, 68.97, 58.90, 58.85, 55.11, 55.08, 39.12, 39.11, 37.66, 36.91, 36.86, 36.69, 36.64, 33.05, 32.99, 32.90, 31.86, 31.84, 30.26, 29.65, 29.63, 29.62, 29.57, 29.54, 29.52, 29.34, 29.32, 29.31, 29.29, 27.79, 26.03, 24.68, 24.66, 24.63, 22.60, 22.59, 22.49, 22.46, 19.67, 19.66, 19.35, 19.32, 14.04; MALDI TOF MS: calc. [M+] 2426.79, found 2426.59.

Amp1-B. **7a** (200 mg, 0.2 mmol, 1 eq.) reacted with **9** (304 mg, 0.4 mmol, 2 eq.) and **11** (334 mg, 0.4 mmol, 2 eq.), yielding **Amp1-B** (112 mg, 0.05 mmol, 32 %) as a yellow solid, purified by column chromatography (SNAP 25, MeOH 0% to 5% in CH₂Cl₂) and preparative recycling GPC. ¹H NMR (400 MHz, CDCl₃) δ 8.44 (br, 1H), 8.03 (d, ³J = 7.89 Hz, 2H), 7.93 (s, 2H), 7.80-7.86 (m, 7H), 7.74 (dd, ³J = 8.1 Hz, ⁴J = 2.0 Hz, 2H), 7.63 (d, ³J = 7.6 Hz, 1H), 7.56 (dd, ³J = 8.2 Hz, ⁴J = 1.6 Hz, 1H), 7.29 (s, 2H), 7.11 (s, 2H), 7.23-7.27 (m, 6H), 4.02-4.08 (m, 6H), 3.87 (t, ³J = 4.5 Hz, 4H), 3.81 (t, ³J = 4.8 Hz, 2H), 3.61-3.74 (m, 30H),

3.51-3.56 (m, 6H), 3.38 (s, 3H), 3.33 (s, 6H), 1.97-2.16 (m, 8H), 1.73-1.87 (m, 9H), 1.45-1.53 (m, 6H), 1.27-1.41 (m, 52H), 0.97-1.21 (m, 24H), 0.86-0.92 (m, 12H), 0.59-0.79 (m, 42H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.43, 165.17, 154.35, 153.26, 152.57, 152.54, 152.34, 150.94, 141.94, 141.57, 141.12, 140.97, 137.90, 137.51, 137.20, 136.97, 135.84, 135.72, 133.60, 133.52, 130.27, 130.06, 128.19, 128.17, 127.75, 127.73, 123.82, 120.31, 120.23, 119.33, 119.28, 119.06, 118.80, 114.87, 114.67, 107.88, 105.90, 73.56, 72.40, 71.93, 71.89, 70.67, 70.66, 70.60, 70.57, 70.54, 70.49, 70.48, 69.81, 69.53, 69.28, 59.01, 58.96, 55.28, 55.23, 39.22, 39.20, 39.20, 36.85, 36.79, 36.59, 36.54, 33.05, 32.99, 32.96, 32.94, 31.93, 31.91, 30.77, 30.70, 30.68, 29.74, 29.74, 29.72, 29.69, 29.65, 29.64, 29.58, 29.40, 29.38, 29.35, 27.89, 27.88, 26.08, 24.78, 24.70, 24.61, 24.59, 22.69, 22.68, 22.65, 22.63, 22.54, 22.51, 19.69, 19.67, 19.43, 19.39, 14.10; MALDI TOF MS: calc. $[\text{M}^+]$ 2434.73, found 2434.57, 2457.55 $[\text{M}-\text{Na}^+]$, 2472.54 $[\text{M}-\text{K}^+]$.

Amp2-N. A statistical reaction between **13** (100 mg, 0.08 mmol, 1.05 eq.), **15** (100 mg, 0.08 mmol, 1.05 eq.) and **Br-N-Br** (22 mg, 0.08 mmol, 1 eq.) yielded the formation of **Amp2-N**, **Apolar-N** and **Bola2-N**. **Amp2-N** was purified by column chromatography (SNAP 25, MeOH 0% to 9% in CH_2Cl_2) and recycling GPC, and obtained as a clear waxy solid (40 mg, 0.02, 21 %). ^1H NMR (400 MHz, CDCl_3) δ 8.50 (s, 1H), 8.02 (td, $^3\text{J} = 7.6$ Hz, $^4\text{J} = 1.4$ Hz, 2H), 7.91 (s, 1H), 7.73-7.86 (m, 7H), 7.51-7.58 (m, 7H), 7.40-7.47 (m, 2H), 7.29 (s, 2H), 7.11 (s, 2H), 4.24-4.29 (m, 6H), 4.01-4.07 (m, 6H), 3.88 (t, $^3\text{J} = 4.8$ Hz, 4H), 3.82 (t, $^3\text{J} = 4.9$ Hz, 2H), 3.71-3.74 (m, 6H), 3.61-3.69 (m, 24H), 3.51-3.56 (m, 6H), 3.38 (s, 3H), 3.31-3.38 (m, 10H), 3.25-3.28 (m, 10H), 2.90-2.98 (m, 4H), 2.39-2.49 (m, 4H), 1.93-2.11 (m, 6H), 1.73-1.87 (m, 6H), 1.44-1.52 (m, 6H), 0.99-1.42 (m, 66H), 0.86-0.93 (m, 12H), 0.71-0.78 (m, 20), 0.56-0.67 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.45, 165.25, 153.22, 152.59, 152.19, 150.50, 150.13, 149.06, 141.84, 141.51, 140.38, 163.99, 139.78, 139.50, 139.29, 139.07, 137.97, 137.37, 137.36, 136.40, 132.18, 132.06, 130.10, 130.05, 129.39, 128.78, 126.55, 126.38, 125.86, 125.75, 124.91, 124.83, 120.30, 120.11, 119.69, 119.29, 119.23, 118.80, 115.25, 114.68, 107.56, 105.88, 73.53, 72.39, 71.91, 71.87, 71.73, 70.67, 70.64, 70.60, 70.58, 70.54, 70.52, 70.47, 70.45, 69.85, 69.75, 69.50, 69.19, 67.23, 58.98, 58.94, 58.89, 55.19, 53.39, 51.42, 39.69, 39.16, 39.14, 36.91, 36.68, 33.02, 32.95, 31.91, 31.89, 30.31, 29.72, 29.72, 29.70, 29.67, 29.63, 29.62, 29.56, 29.39, 29.36, 29.33, 27.85, 26.07, 24.73, 24.65, 22.66, 22.63, 22.54, 22.51, 19.69, 19.42, 14.08; MALDI TOF MS: calc. $[\text{M}^+]$ 2350.61, found 2350.16.

Amp2-B. A statistical reaction between **13** (100 mg, 0.08 mmol, 1.05 eq.), **15** (100 mg, 0.08 mmol, 1.05 eq.) and **7** (23 mg, 0.08 mmol, 1 eq.) yielded the formation of **Amp2-B**, **Apolar-B** and **Bola2-B**. **Amp2-B** was purified by column chromatography (SNAP 25, MeOH 0% to 15% in CH₂Cl₂) and recycling GPC, and obtained as a yellow waxy solid (45 mg, 0.02 mmol, 24 %). ¹H NMR (400 MHz, CDCl₃) δ 8.60 (br, 1H), 8.06 (d, ³J = 8.0 Hz, 1H), 8.00-8.02 (m, 2H), 7.96 (s, 1H), 7.85-7.90 (m, 4H), 7.81-7.84 (m, 2H), 7.79 (s, 1H), 7.75 (d, ³J = 8.0 Hz, 2H), 7.56 (d, ³J = 7.9 Hz, 1H), 7.30 (br, 2H), 7.10 (s, 2H), 4.25 (m, 6H), 4.01-4.07 (m, 6H), 3.88 (br, 4H), 3.82 (br, 2H), 3.61-3.74 (m, 30H), 3.51-3.56 (m, 6H), 3.38 (s, 3H), 3.34 (s, 6H), 3.31 (br, 4H), 3.25 (s, 9H), 2.93 (m, 4H), 2.50 (m, 4H), 1.96-2.18 (m, 4H), 1.73-1.87 (m, 12H), 1.45-1.52 (m, 6H), 1.26-1.42 (m, 50H), 1.12 (br, 4H), 1.02 (br, 6H), 0.86-0.93 (m, 12H), 0.63-0.79 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 165.43, 165.29, 153.23, 152.54, 150.92, 150.33, 149.29, 141.00, 137.49, 136.12, 133.02, 128.71, 127.73, 123.89, 118.79, 115.37, 114.67, 107.75, 105.89, 71.87, 70.57, 70.54, 70.48, 70.45, 69.84, 69.51, 69.19, 67.17, 58.97, 58.90, 55.27, 51.48, 39.17, 37.57, 36.53, 31.89, 29.56, 27.87, 22.63, 22.52, 14.08; MALDI TOF MS: calc. [M⁺] 2358.56, found 2358.49, 2381.49 [M-Na⁺], 2397.46 [M-K⁺].

Amp3-N. 6b (97 mg, 0.1 mmol, 1 eq.) reacted with **9** (146 mg, 0.2 mg, 2 eq.) and **11** (161 mg, 0.2 mmol, 2 eq.), yielding **Amp3-B** (61 mg, 0.03 mmol, 25 %) as a colorless solid, purified by column chromatography (SNAP 25, MeOH 0% to 5% in CH₂Cl₂) and preparative recycling GPC. ¹H NMR (400 MHz, THF-d₈) δ 8.51 (br, 1H), 7.98-8.03 (m, 3H), 7.92 (dd, ³J = 8.3 Hz, ⁴J = 1.6 Hz, 1H), 8.84 (dd, 3J = 8.2 Hz, ⁴J = 1.4 Hz, 1H), 7.73-7.80 (m, 5H), 7.58-7.60 (m, 3H), 7.52-7.55 (m, 4H), 7.43-7.47 (m, 2H), 7.29 (s, 2H), 7.13 (s, 2H), 4.24-4.29 (m, 6H), 3.97-4.09 (m, 6H), 3.87-3.89 (m, 4H), 3.80-3.83 (m, 2H), 3.61-3.74 (m, 32H), 3.51-3.56 (m, 6H), 3.32-3.38 (m, 18H), 3.26-3.28 (m, 18H), 2.89-3.00 (m, 8H), 2.39-2.50 (m, 8H), 1.70-1.88 (m, 8H), 1.43-1.53 (m, 8H), 1.21-1.38 (m, 62H), 0.86-0.89 (m, 12H); ¹³C NMR (100 MHz, THF-d₈) δ 166.26, 166.05, 154.56, 154.15, 151.86, 151.04, 151.01, 143.25, 142.99, 141.74, 141.36, 141.34, 141.04, 140.80, 137.27, 133.88, 132.03, 131.99, 130.60, 127.88, 127.19, 126.66, 121.46, 121.42, 120.92, 120.82, 120.64, 116.46, 116.33, 109.21, 107.98, 103.54, 74.32, 73.86, 73.75, 73.32, 73.29, 72.58, 72.41, 72.33, 72.20, 71.73, 71.46, 71.42, 71.03, 70.61, 68.65, 68.61, 68.39, 60.00, 59.92, 59.58, 59.49, 53.04, 41.40, 33.53, 33.51, 32.03, 31.41, 31.37, 31.30, 31.27, 31.27, 31.22, 31.15, 31.07, 30.99, 30.96, 27.79,

24.20, 15.08; MALDI TOF MS: calc. [M+] 2274.43, found 2274.24, 2297.22 [M-Na+], 2312.20 [M-K+].

Amp3-B. 7b (75 mg, 0.09 mmol, 1 eq.) reacted with **9** (135 mg, 0.2 mg, 2 eq.) and **11** (148 mg, 0.2 mmol, 2 eq.), yielding **Amp3-B** (43 mg, 0.02 mmol, 18 %) as a colorless solid, purified by column chromatography (SNAP 25, MeOH 0% to 5% in CH₂Cl₂) and preparative recycling GPC. ¹H NMR (400 MHz, THF-d₈) δ 8.45 (br, 1H), 8.07 (d, ³J = 7.9 Hz, 2H), 8.03 (s, 2H), 7.90-7.92 (m, 4H), 7.83 (d, ³J = 7.9 Hz, 2H), 7.76 (d, ³J = 8.1 Hz, 2H), 7.67-7.86 (br, 1H), 7.61 (s, 1H), 7.31 (br, 2H), 7.11 (s, 2H), 4.21-4.36 (m, 6H), 4.09 (t, ³J = 6.5 Hz, 4H), 4.04 (t, ³J = 6.6 Hz, 2H), 3.54-3.91 (m, 40H), 3.26-3.38 (m, 36H), 2.87-3.01 (m, 8H), 2.44-2.58 (m, 8H), 1.82-1.89 (m, 4H), 1.74-1.81 (m, 2H), 1.47-1.52 (m, 6H), 1.24-1.41 (m, 46H), 0.86-0.90 (m, 8H); ¹³C NMR (100 MHz, THF-d₈) δ 165.49, 165.45, 165.26, 165.23, 154.19, 153.24, 152.58, 150.42, 150.37, 150.09, 150.03, 149.55, 149.49, 149.27, 149.20, 141.84, 141.82, 141.42, 141.38, 140.32, 140.25, 140.10, 139.99, 139.35, 139.29, 138.13, 137.80, 137.54, 136.43, 136.33, 136.21, 136.11, 136.02, 133.25, 133.17, 130.10, 130.08, 129.82, 129.79, 128.80, 128.77, 127.89, 126.63, 126.58, 121.45, 121.37, 120.61, 120.54, 120.37, 120.30, 119.81, 119.75, 119.56, 119.49, 115.11, 107.69, 107.67, 105.63, 105.61, 73.52, 72.43, 71.93, 71.88, 71.72, 70.69, 70.66, 70.62, 70.59, 70.56, 70.49, 70.47, 69.85, 69.38, 69.23, 67.14, 67.07, 59.03, 58.97, 58.91, 58.89, 51.49, 51.39, 51.37, 39.86, 39.74, 31.90, 31.88, 30.31, 29.71, 29.69, 29.67, 29.66, 29.62, 29.61, 29.56, 29.39, 29.35, 29.32, 26.08, 26.06, 22.64, 14.07; MALDI TOF MS: calc. [M+] 2282.38, found 2282.30, 2305.28 [M-Na+], 2321.26 [M-K+].

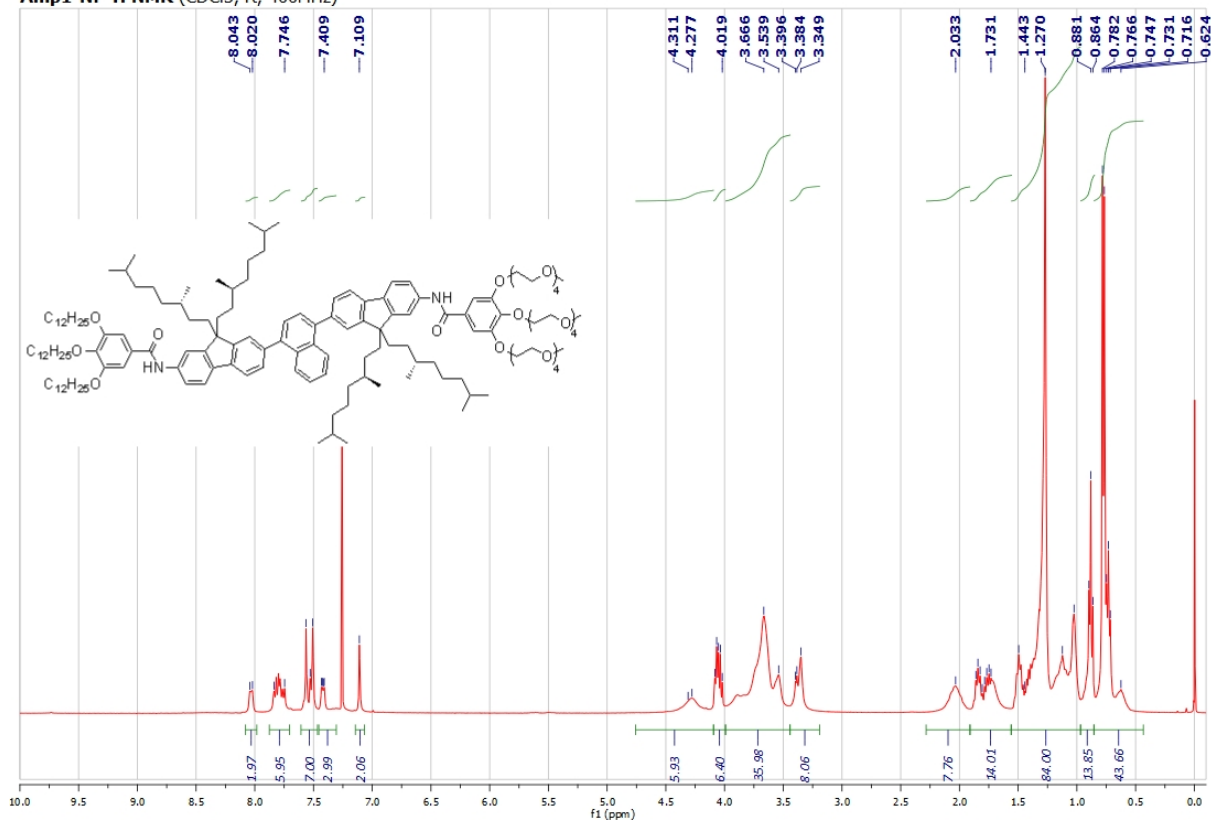
Bola2-N was formed during the synthesis of **Amp2-N**, and could be purified by column chromatography and recycling GPC, yielding a clear oil (38 mg, 0.02 mmol, 20 %). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 2H), 7.99-8.02 (m, 2H), 7.83 (dd, ³J = 8.2 Hz, ⁴J = 1.8 Hz, 2H), 7.78 (d, ³J = 7.7 Hz, 2H), 7.75 (d, ⁴J = 1.8 Hz, 2H), 7.74 (d, ³J = 8.3 Hz, 2H), 7.58 (s, 2H), 7.55 (s, 2H), 7.53 (dd, ³J = 7.8 Hz, ⁴J = 1.3 Hz, 2H), 7.43-7.46 (m, 2H), 7.28 (s, 4H), 4.23-4.28 (m, 12H), 3.87 (t, ³J = 4.6 Hz, 8H), 3.81 (t, ³J = 3.8 Hz, 4H), 3.67-3.74 (m, 12H), 3.61-3.69 (m, 48H), 3.51-3.55 (m, 12H), 3.37 (m, 6H), 3.31 (m, 20H), 3.25-3.27 (m, 20H), 2.90-2.99 (m, 8H), 2.39-2.50 (m, 8H), 2.05 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 165.25, 152.56, 150.12, 149.06, 141.78, 139.94, 139.45, 139.30, 137.97, 136.40, 132.07, 130.13,

129.43, 126.49, 126.34, 125.88, 124.89, 120.29, 119.67, 119.26, 115.25, 107.58, 72.37, 71.89, 71.85, 71.71, 70.64, 70.60, 70.57, 70.55, 70.51, 70.49, 70.45, 70.44, 70.43, 69.85, 69.74, 69.17, 67.23, 58.97, 58.93, 58.89, 51.43, 39.66; MALDI TOF MS: calc. [M+] 2350.61, found 2339.97, 2362.94 [M-Na+], 2378.94 [M-K+].

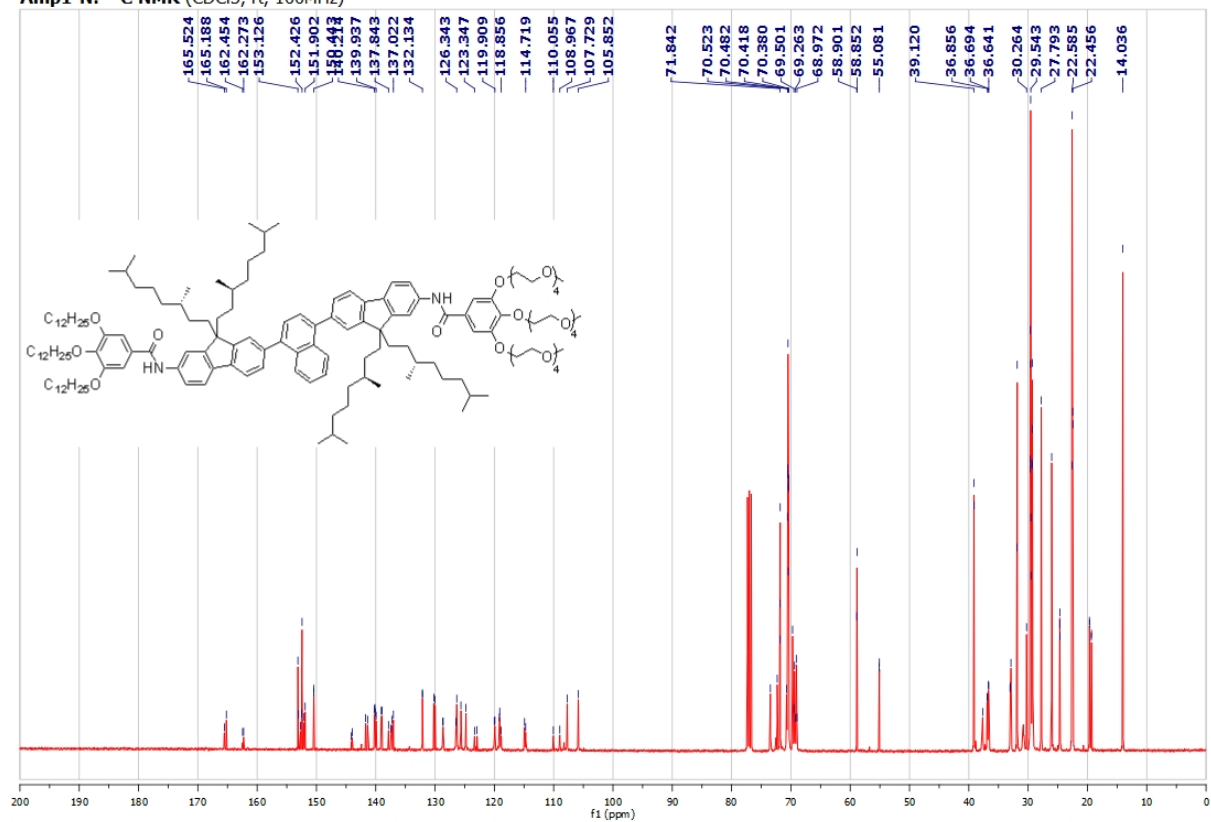
Bola2-B was formed during the synthesis of **Amp2-B**, and could be purified by column chromatography and recycling GPC, yielding a clear oil (38 mg, 0.02 mmol, 20 %). ¹H NMR (400 MHz, THF-d₈) δ 8.49 (br, 2H), 8.07 (d, ³J = 7.8 Hz, 2H), 8.03 (s, 2H), 7.90 (s, 2H), 7.81-7.85 (m, 4H), 7.74-7.78 (m, 5H), 7.29 (m, 4), 4.24-4.29 (m, 12H), 3.89 (m, 8H), 3.82 (t, ³J = 4.6 Hz, 4H), 3.62-3.75 (m, 60H), 3.51-3.56 (m, 14H), 3.38 (s, 6H), 3.31-3.34 (m, 20H), 3.24-3.27 (m, 20H), 2.89-2.99 (m, 8H), 2.44-2.58 (m, 8H); ¹³CNMR (100 MHz, CDCl₃) δ 165.25, 154.17, 152.60, 150.39, 149.28, 141.82, 140.29, 138.01, 137.96, 136.26, 136.01, 133.19, 130.14, 130.12, 128.75, 127.87, 123.90, 120.61, 119.48, 71.96, 71.79, 70.93, 70.77, 70.65, 69.96, 69.49, 67.21, 59.16, 58.98, 51.48, 39.83; MALDI TOF MS: calc. [M+] 2347.17, found 2348.06.

NMR Spectra

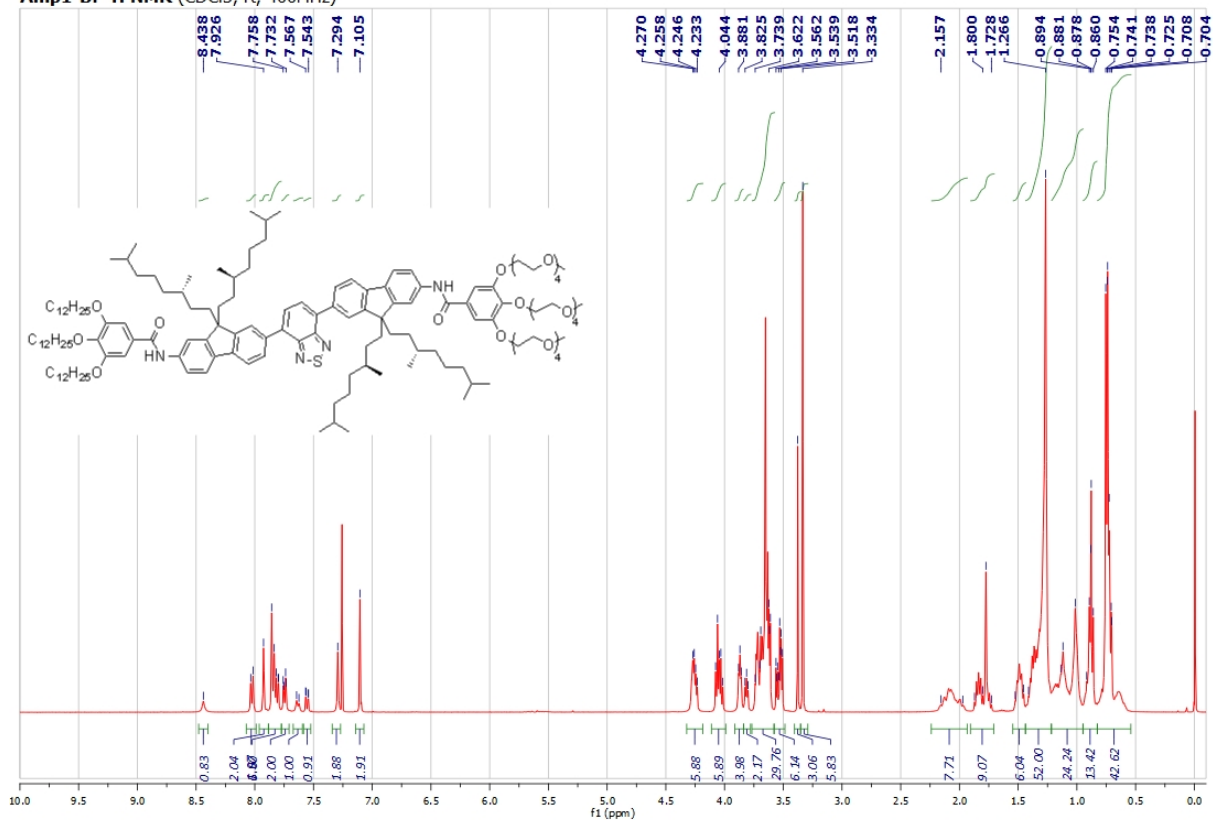
Amp1-N: ¹H NMR (CDCl₃, rt, 400MHz)



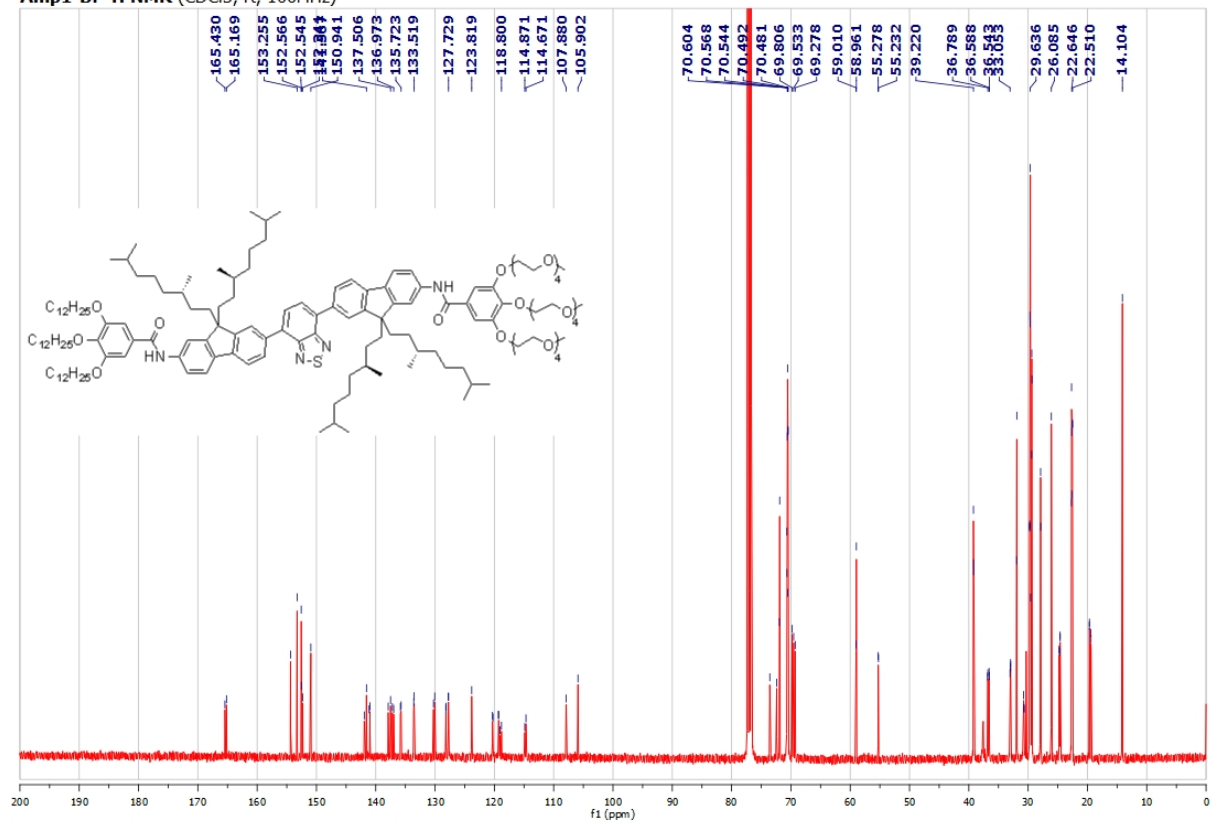
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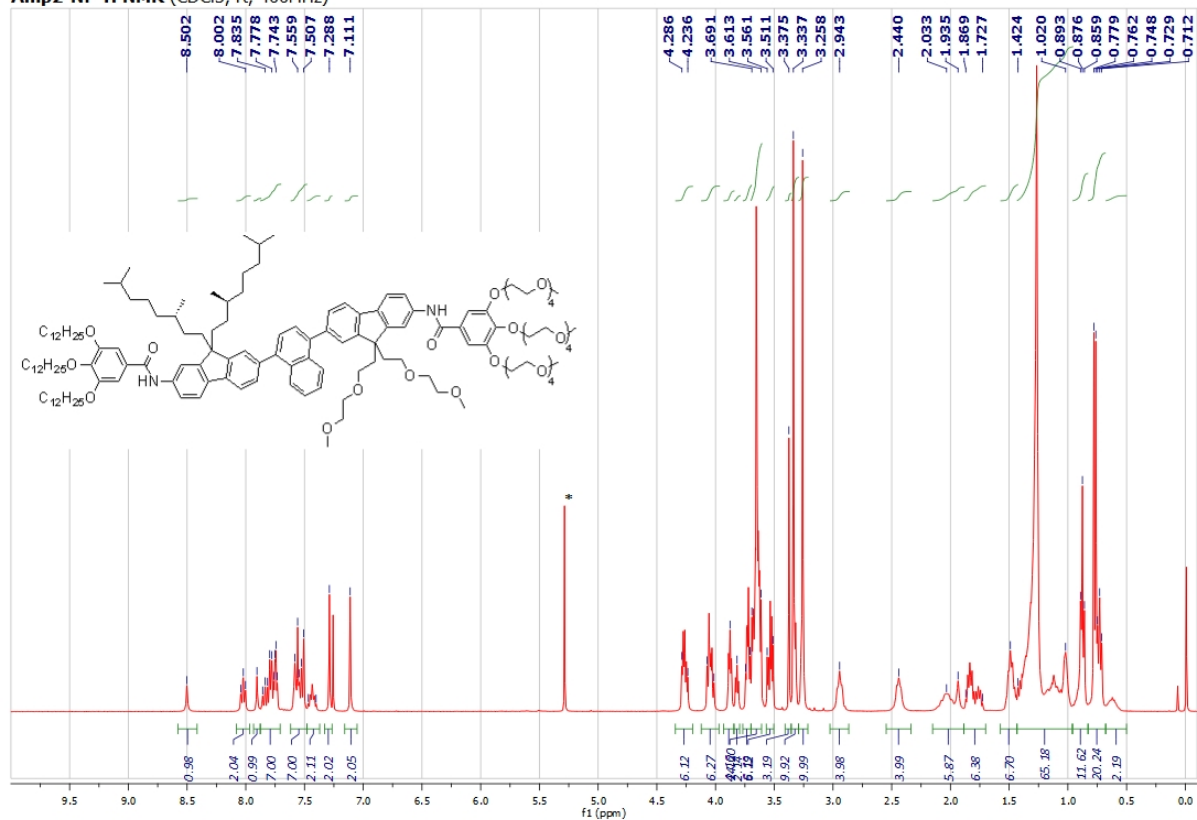
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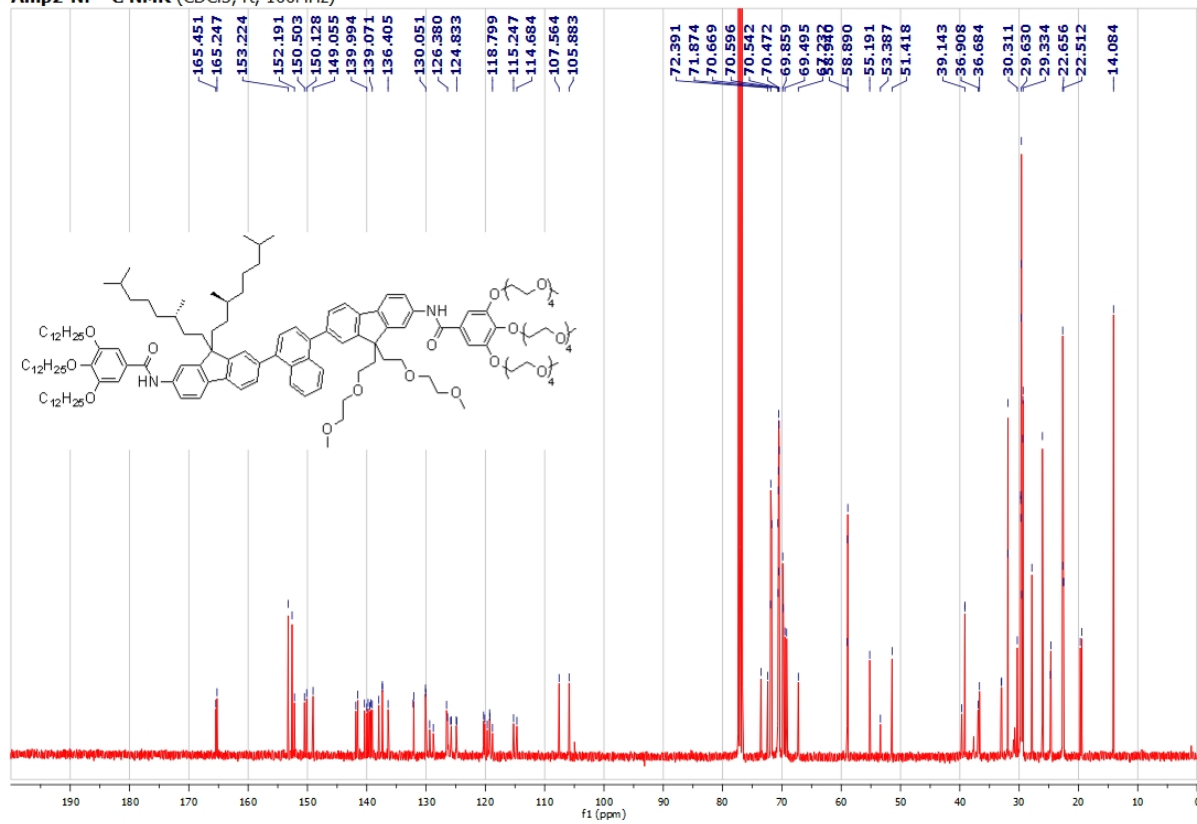
Amp1-B: ¹H NMR (CDCl₃, rt, 100MHz)



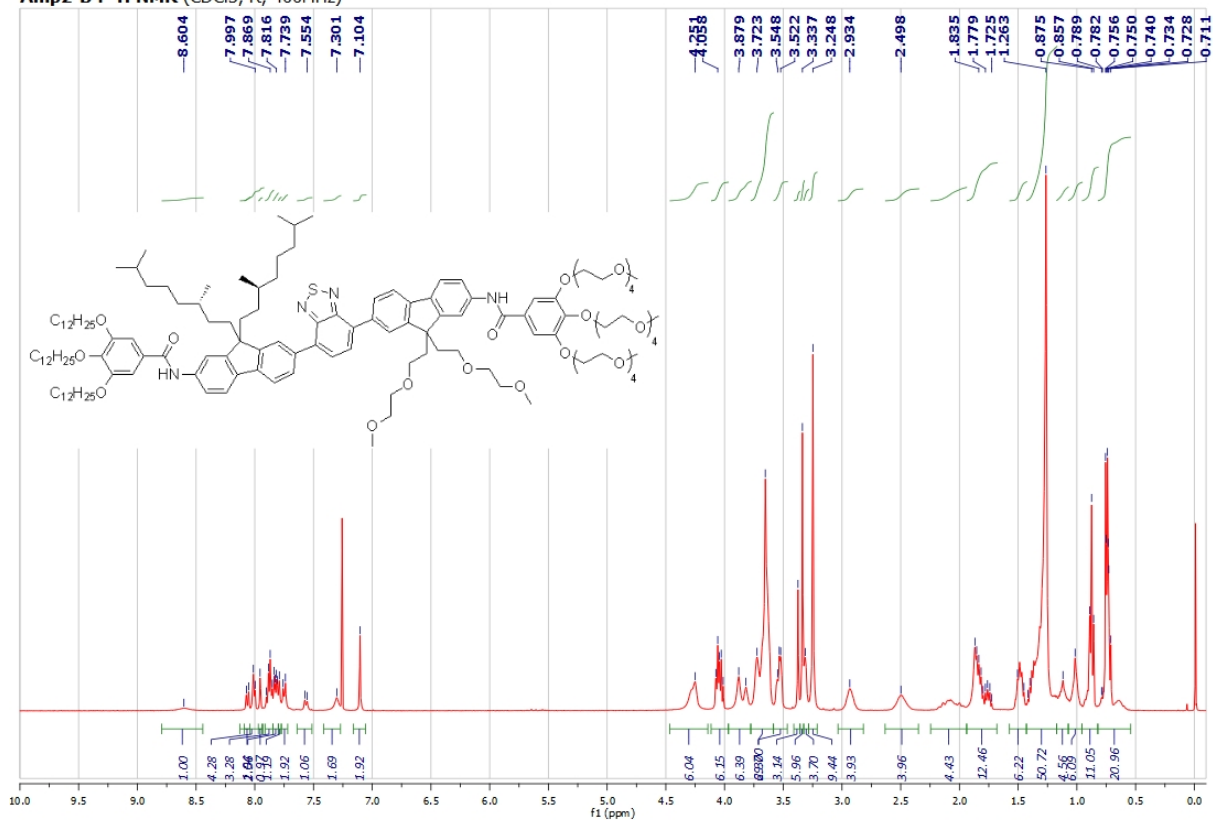
Amp2-N: ¹H NMR (CDCl₃, rt, 400MHz)



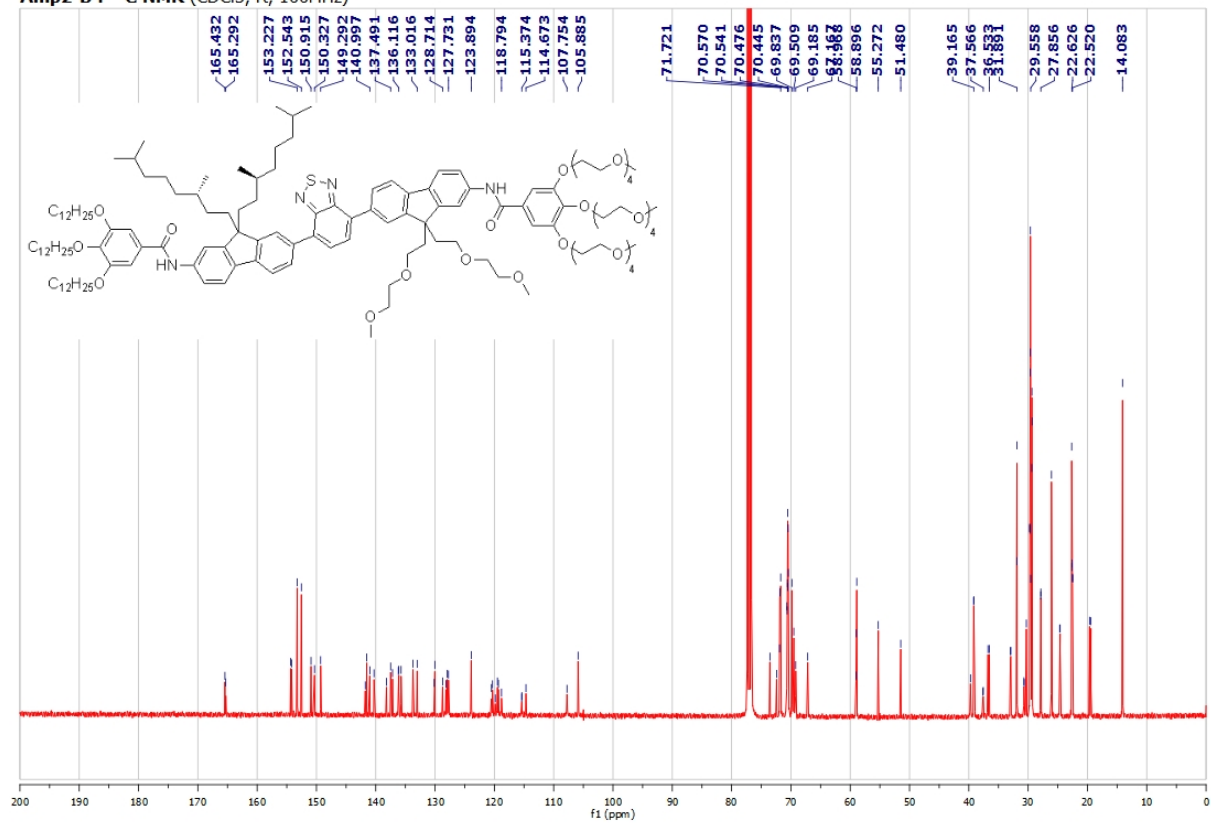
Amp2-N: ¹³C NMR (CDCl₃, rt, 100MHz)



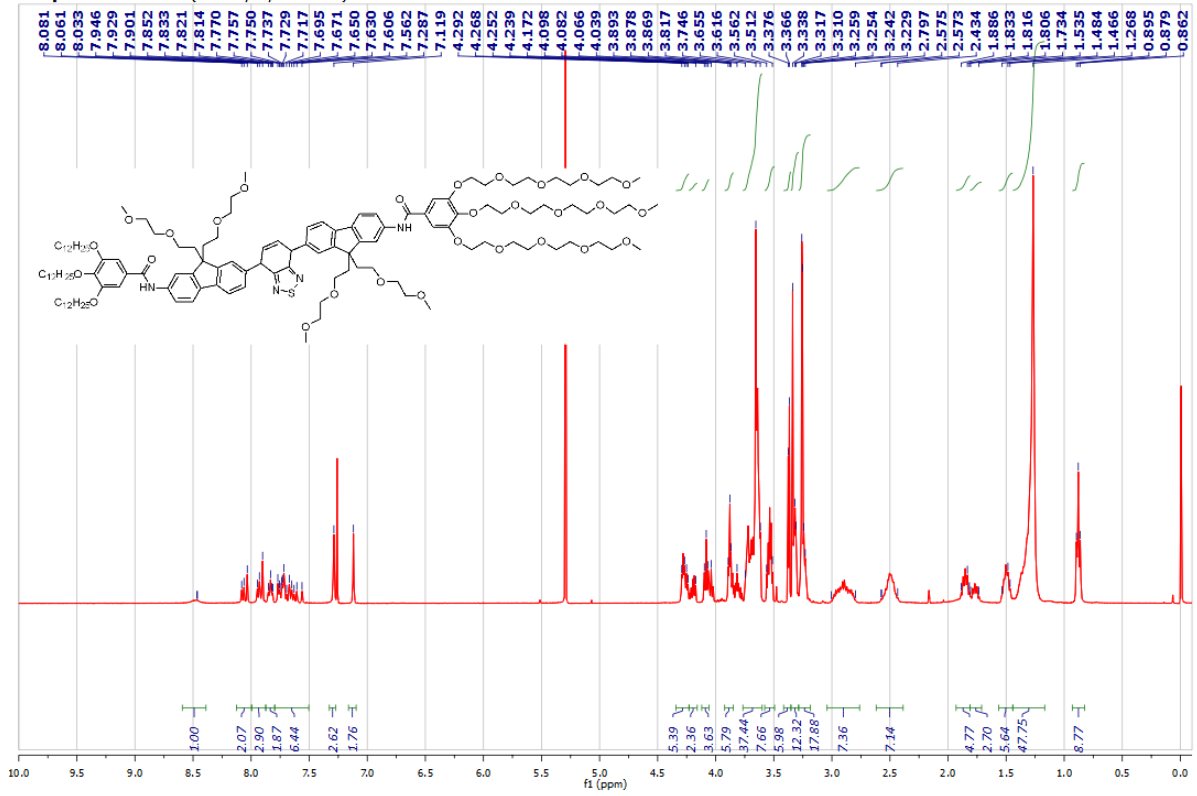
Amp2-B : ¹H NMR (CDCl₃, rt, 400MHz)



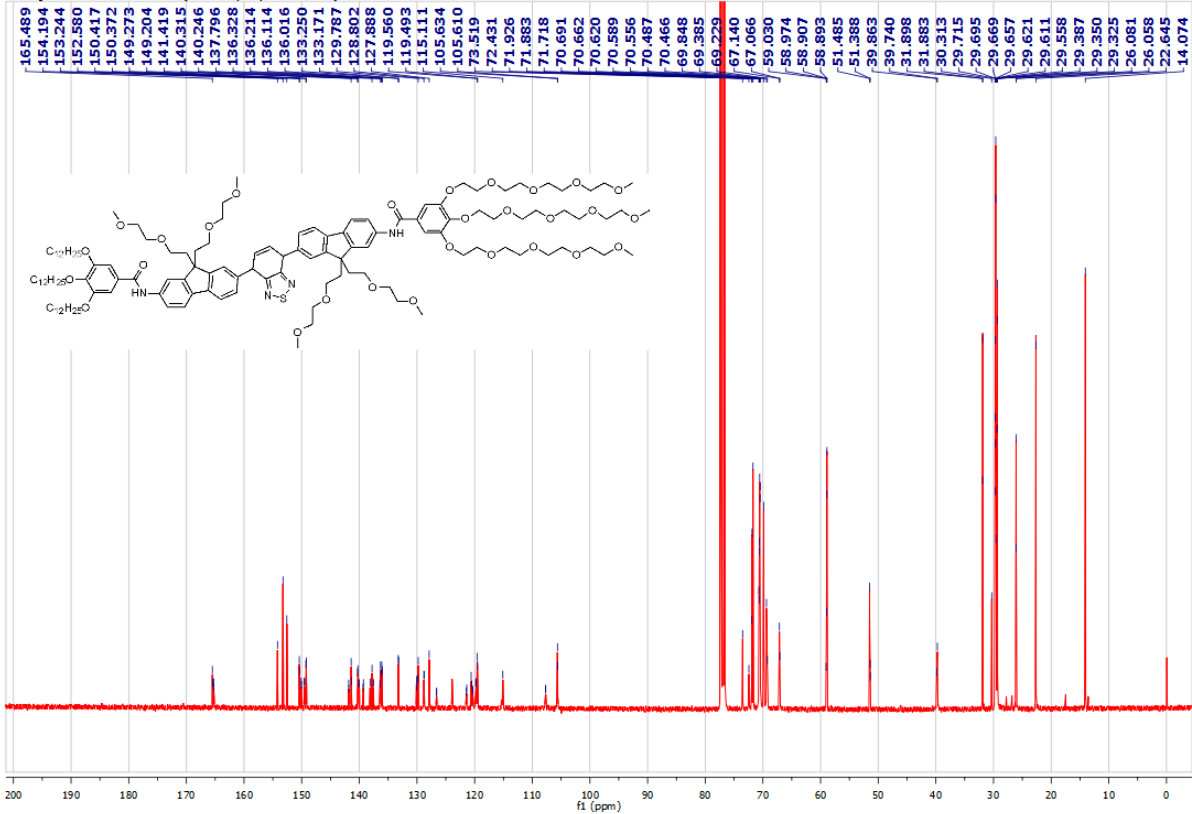
Amp2-B : ¹³C NMR (CDCl₃, rt, 100MHz)



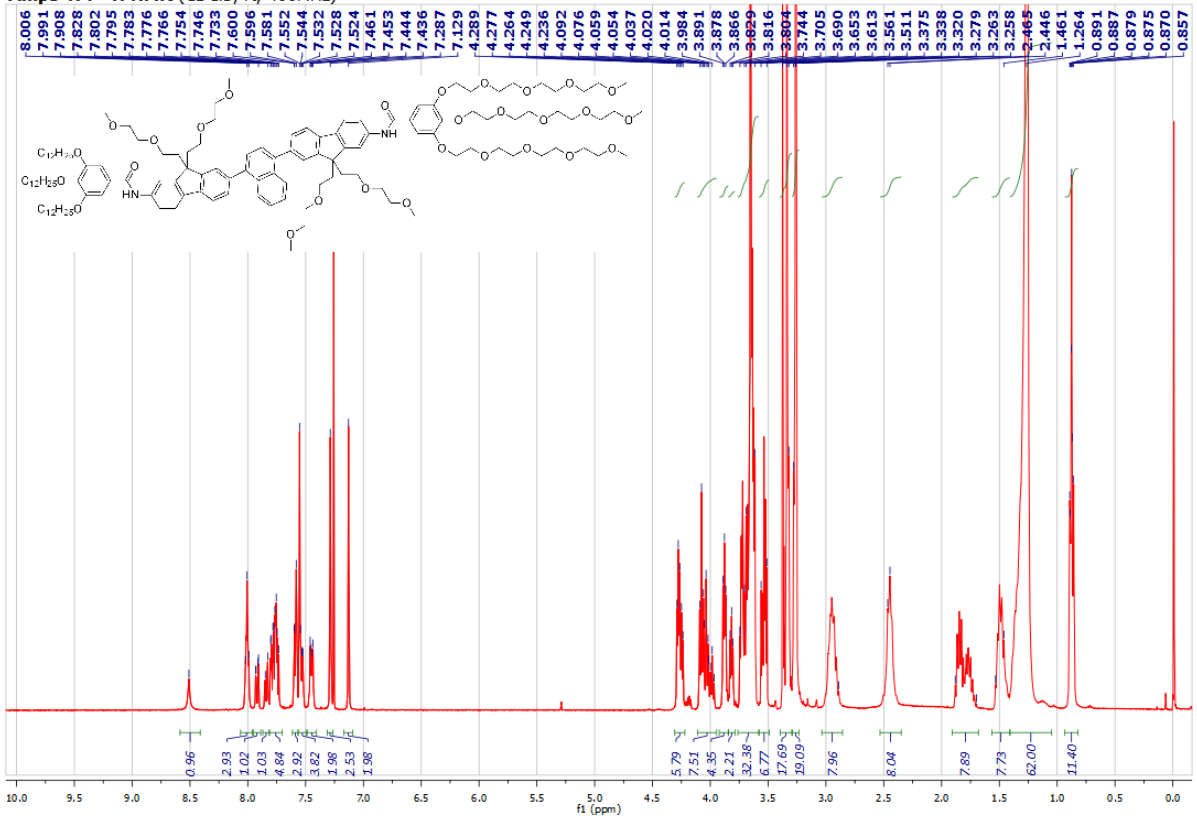
Amp3-B : ¹H NMR (CDCl₃, rt, 400MHz)



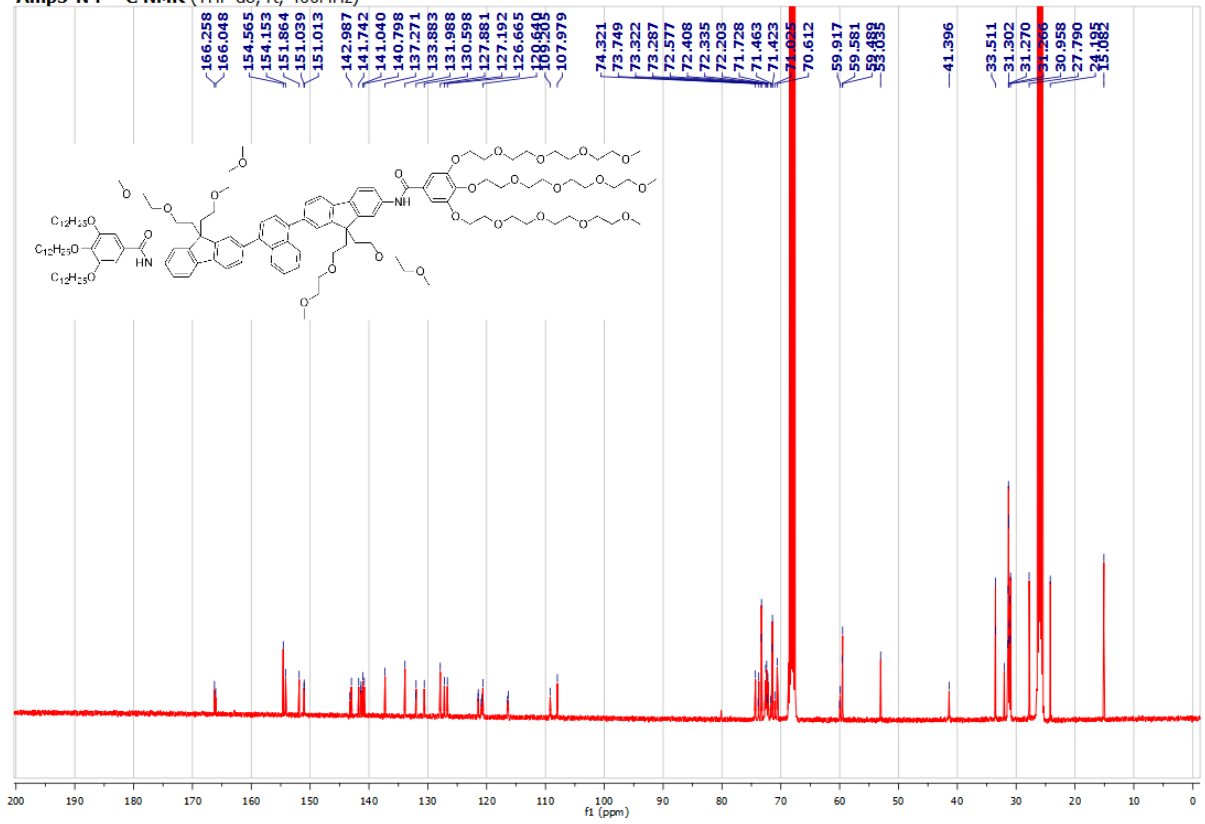
Amp3-B : ¹³C NMR (CDCl₃, rt, 400MHz)



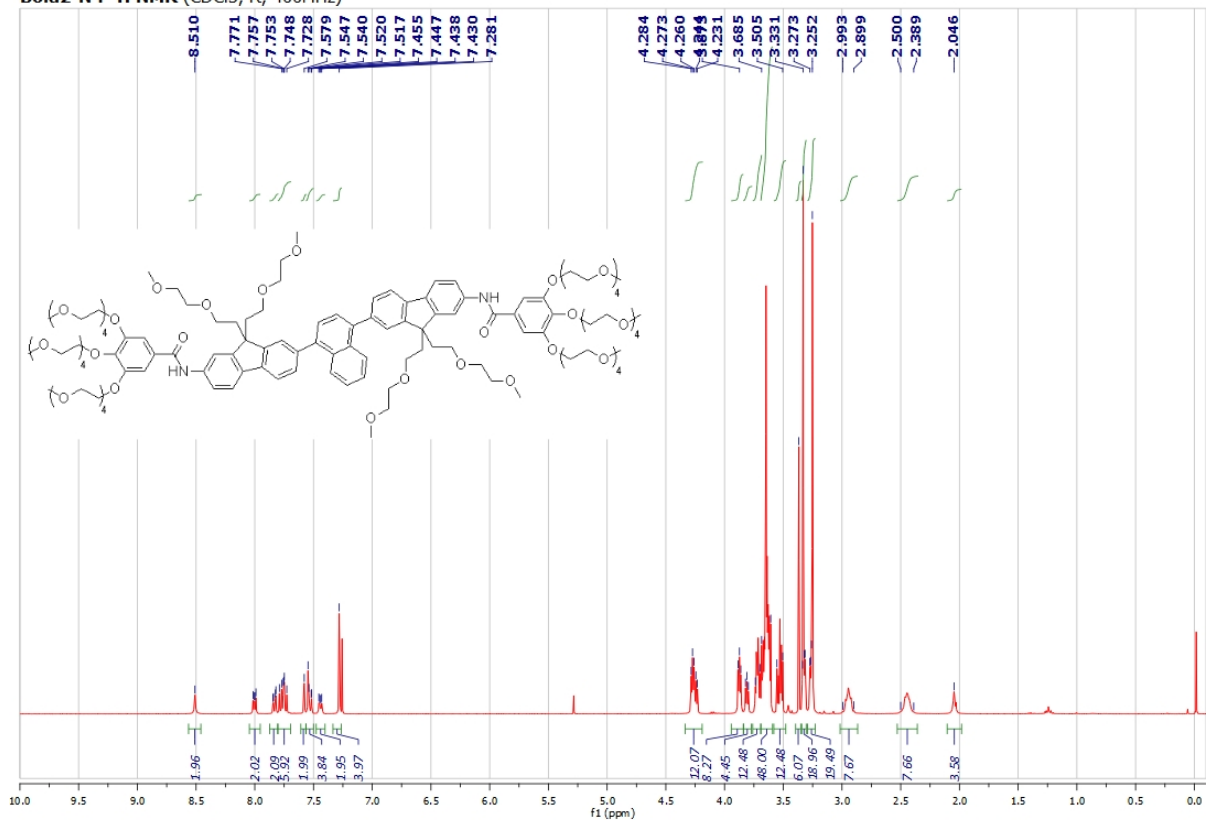
Amp3-N : ¹H NMR (CDCl₃, rt, 400MHz)



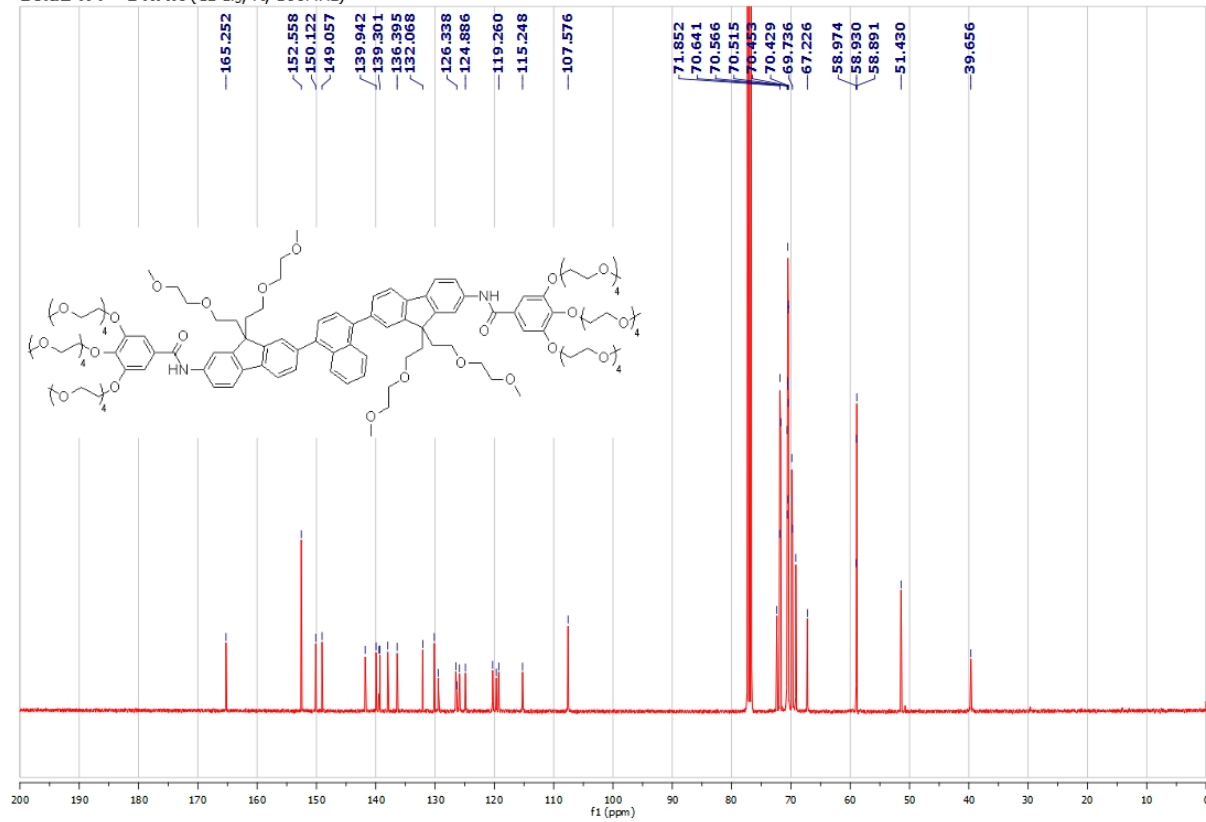
Amp3-N : ¹³C NMR (THF-d₈, rt, 400MHz)



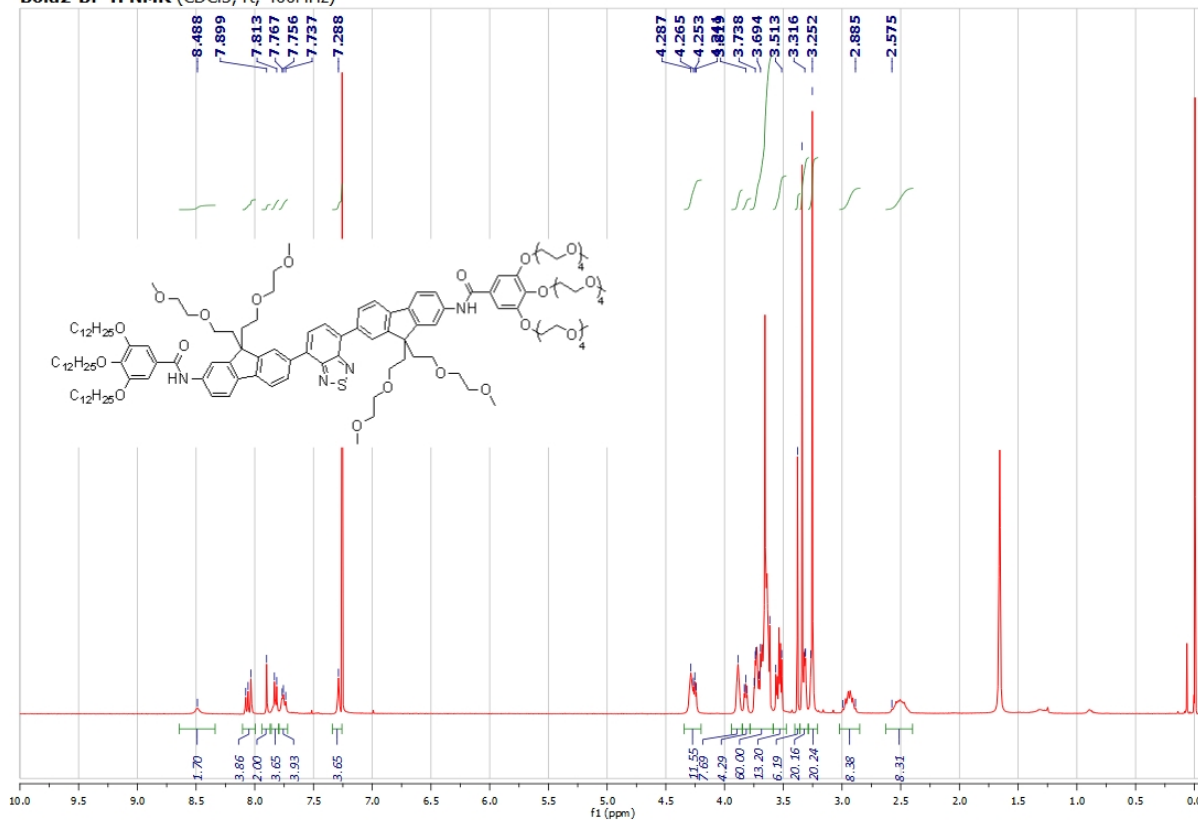
Bola2-N : ¹H NMR (CDCl₃, rt, 400MHz)



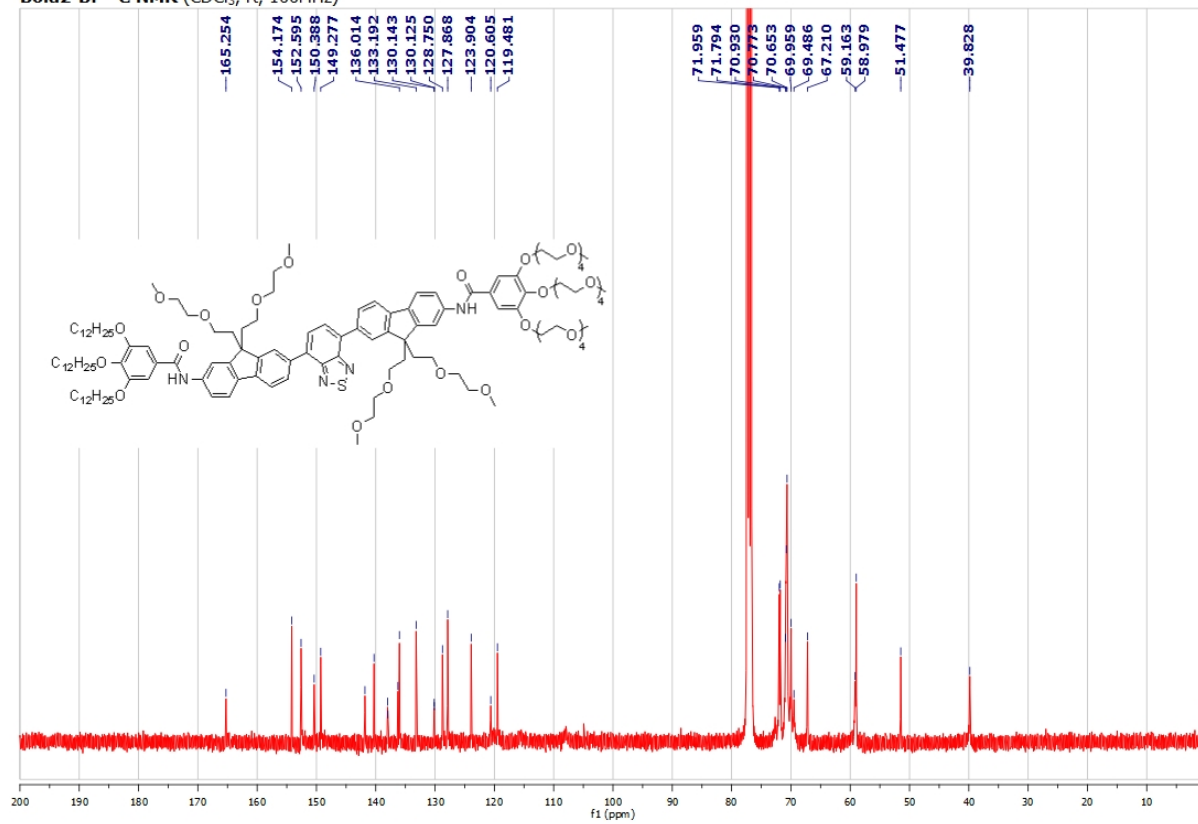
Bola2-N : ¹³C NMR (CDCl₃, rt, 100MHz)



Bola2-B: ¹H NMR (CDCl₃, rt, 400MHz)



Bola2-B: ¹³C NMR (CDCl₃, rt, 100MHz)



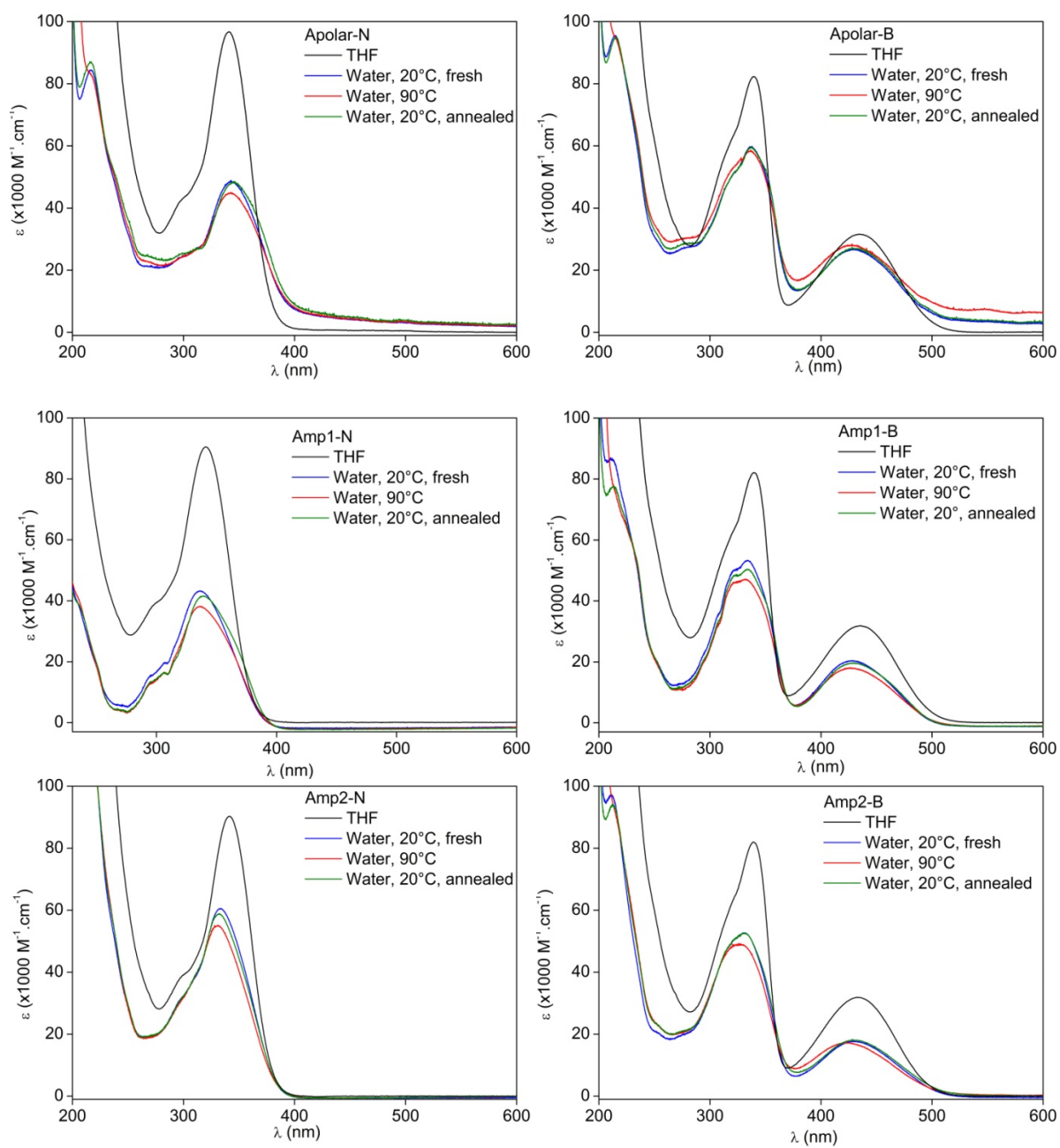
Formation and Characterization of the Self-Assembled Nanoparticles in Water

Preparation of nanoparticles: Injection of 15 μL of 1 mM THF stock solution into 5 mL of water results in a 3 μM nanoparticle solution. Annealing was performed by heating the sample to 90°C and cooling down to 20 °C.

Table S1. Optical characteristics of all compounds in THF (3 μM) and of the nanoparticles in water (before and after annealing, 3 μM). Solutions were measured in a liquid cell with a 1 cm path length for UV-vis and 1 mm path length for Fluorescence at room temperature.

	THF solution		Water solution		
	λ/nm ($\log(\epsilon)/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{PL}}/\text{nm}$ ($\Phi_{\text{PL}}(\%)$) ^a	λ/nm ($\log(\epsilon)/\text{M}^{-1}\text{cm}^{-1}$)	λ_{PL} fresh/nm ($\Phi_{\text{PL}}(\%)$)	λ_{PL} annealed/nm ($\Phi_{\text{PL}}(\%)$)
Apol-N	341(4.99)	423 (20)	344 (4.82)	422 (55)	422 (60)
Amp1-N	341 (4.96)	424 (20)	338 (4.63)	423 (40)	421 (50)
Amp2-N	342(4.96)	424 (20)	334 (4.80)	424 (20)	423 (25)
Amp3-N	342(4.98)	424 (25)	335 (4.78)	427 (35)	429 (30)
Bola1-N	341 (4.97)	425 (10)	331 (4.77)	424.5 (5)	425 (7)
Bola2-N	342 (4.95)	424 (20)	344 (4.88)	425 (7)	426 (6)
Apol-B	340 (4.91); 434 (4.50)	552 (85)	338 (4.74); 431 (4.36)	529 (40)	527 (40)
Amp1-B	340 (4.91); 436 (4.50)	553 (85)	335 (4.76); 430 (4.35)	545 (85)	528 (85)
Amp2-B	339 (4.91); 432 (4.50)	552 (85)	332 (4.74); 432 (4.27)	555 (70)	551 (70)
Amp3-B	339 (4.90); 430.5 (4.50)	553 (90)	334 (4.71); 429 (4.27)	565 (55)	568 (50)
Bola1-B	340 (4.87); 433.5 (4.46)	553 (90)	322 (4.73); 429(4.23)	550 (70)	550 (70)
Bola2-B	339 (4.89); 431 (4.48)	553 (80)	337 (4.80); 421 (4.40)	575 (15)	578 (15)

^a Excitation wavelength $\lambda_{exc} = 340$ nm; reference compound: Quinine bisulfate in 2 N H_2SO_4 for naphthalene derivatives and N,N'-bis(pentylhexyl) perylene bisimide in dichloromethane for benzothiadiazole derivatives.



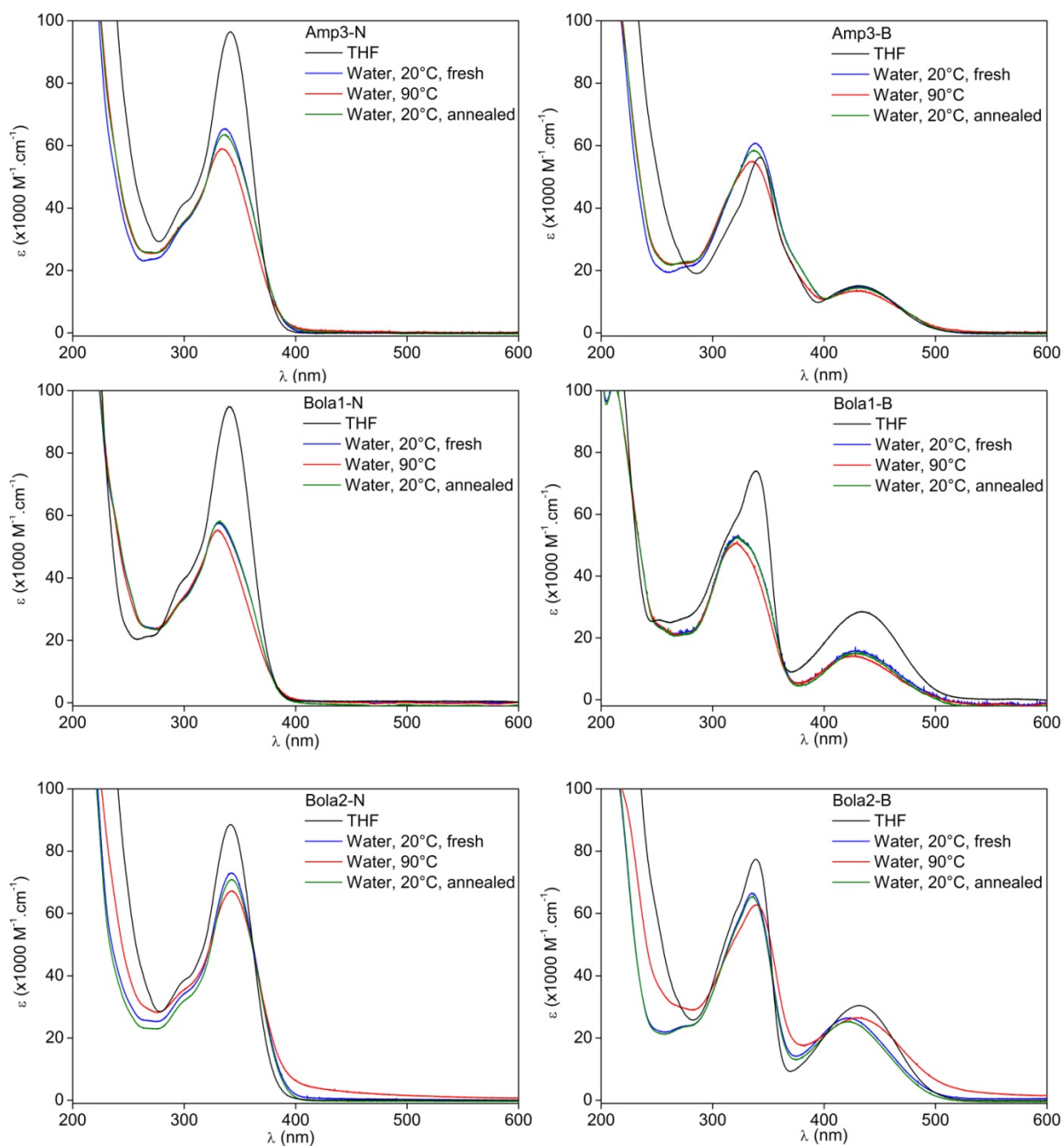


Figure S1. UV-vis spectra for **Apolar**, **Amp1**, **Amp2**, **Amp3**, **Bola1** and **Bola2** ($c = 3 \mu\text{M}$) in THF (black curve), in water at 20 °C (fresh, blue curve), in water at 90 °C (red curve) and again in water at 20 °C (annealed, green curve).

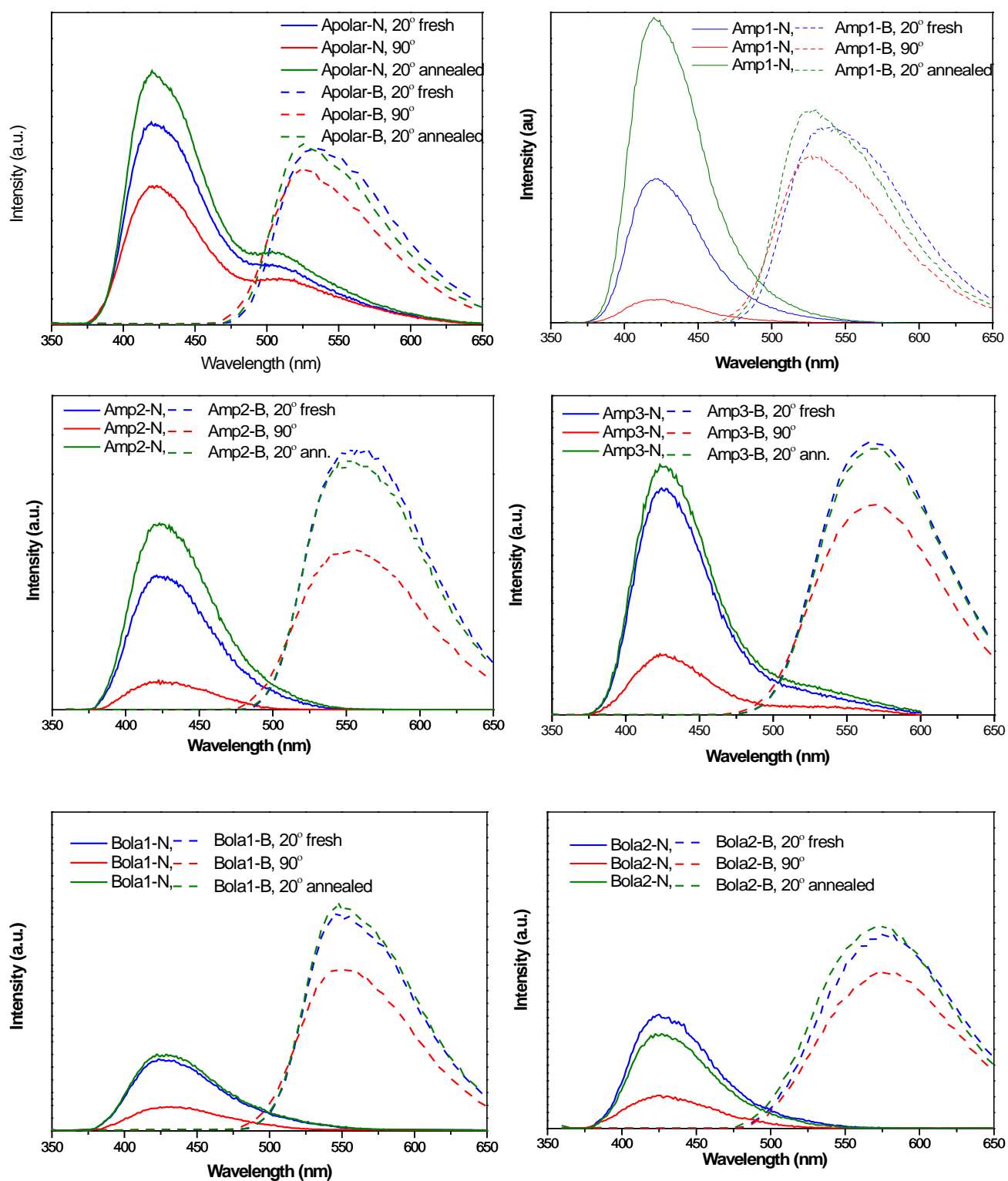


Figure S2. Emission spectra for **Apolar**, **Amp1**, **Amp2**, **Amp3**, **Bola1** and **Bola2** ($c = 3 \mu\text{M}$) in water at 20°C (fresh, blue curve), in water at 90°C (red curve) and again in water at 20°C (annealed, green curve).

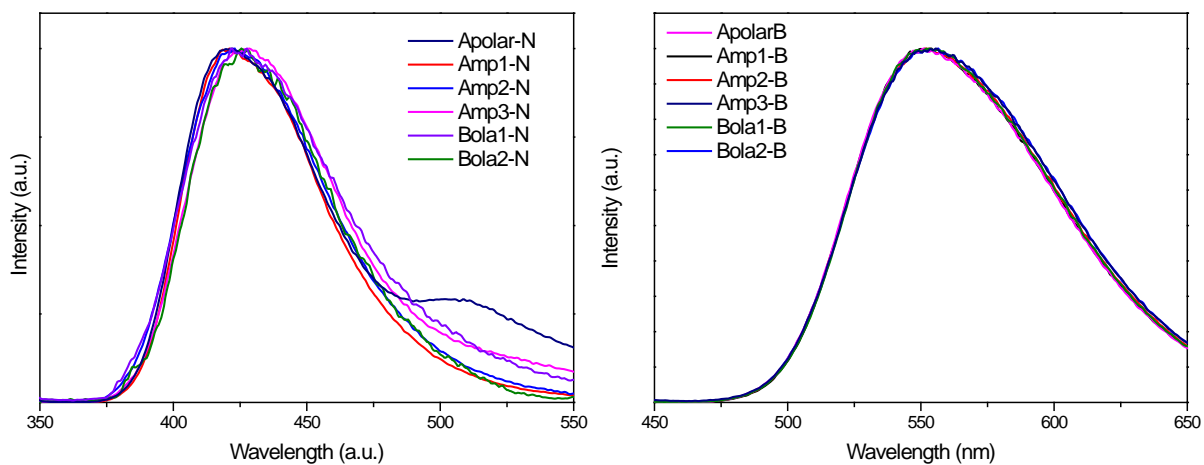
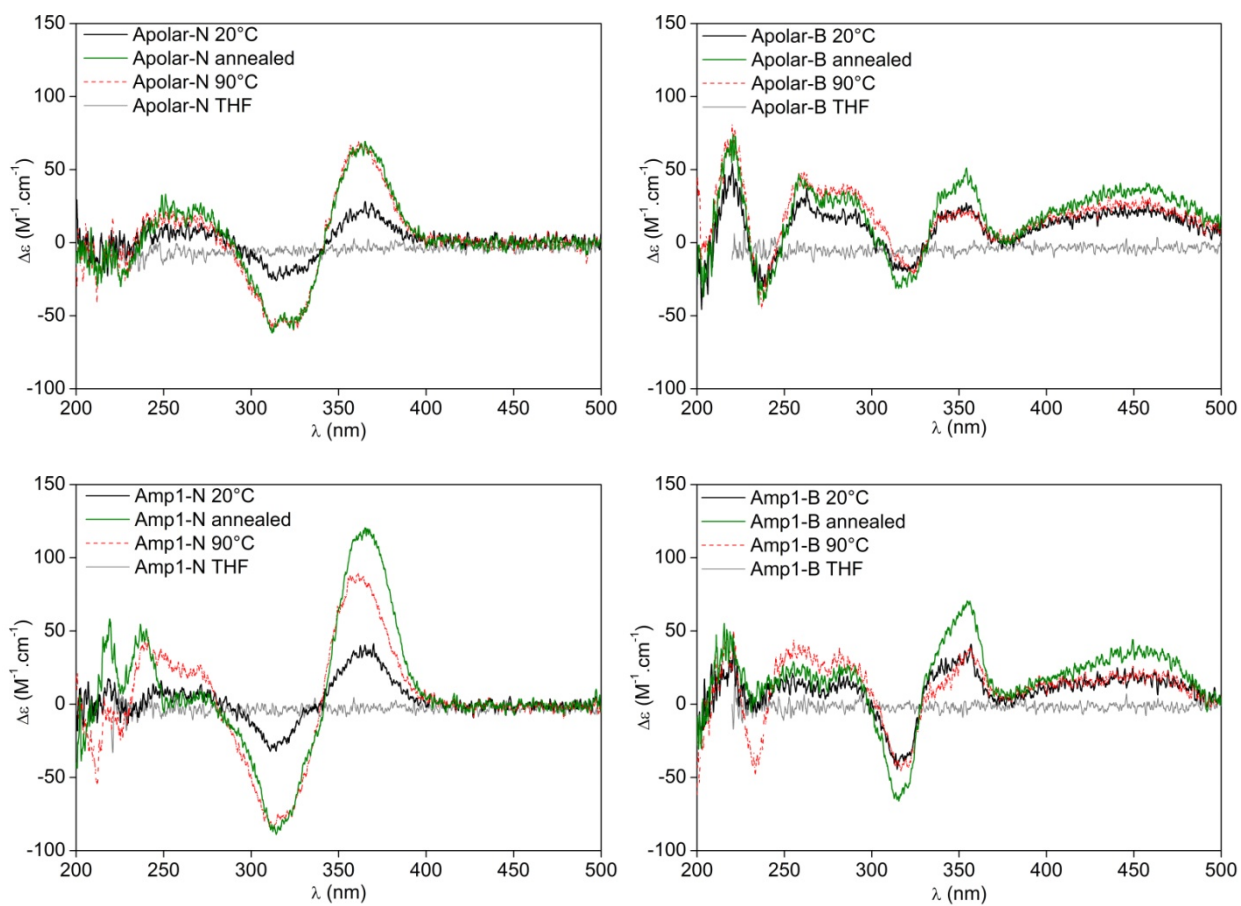


Figure S3. Emission spectra for **Apolar**, **Amp1**, **Amp2**, **Amp3**, **Bola1** and **Bola2** in THF at 20 °C. Excitation wavelength $\lambda_{exc} = 340$ nm.



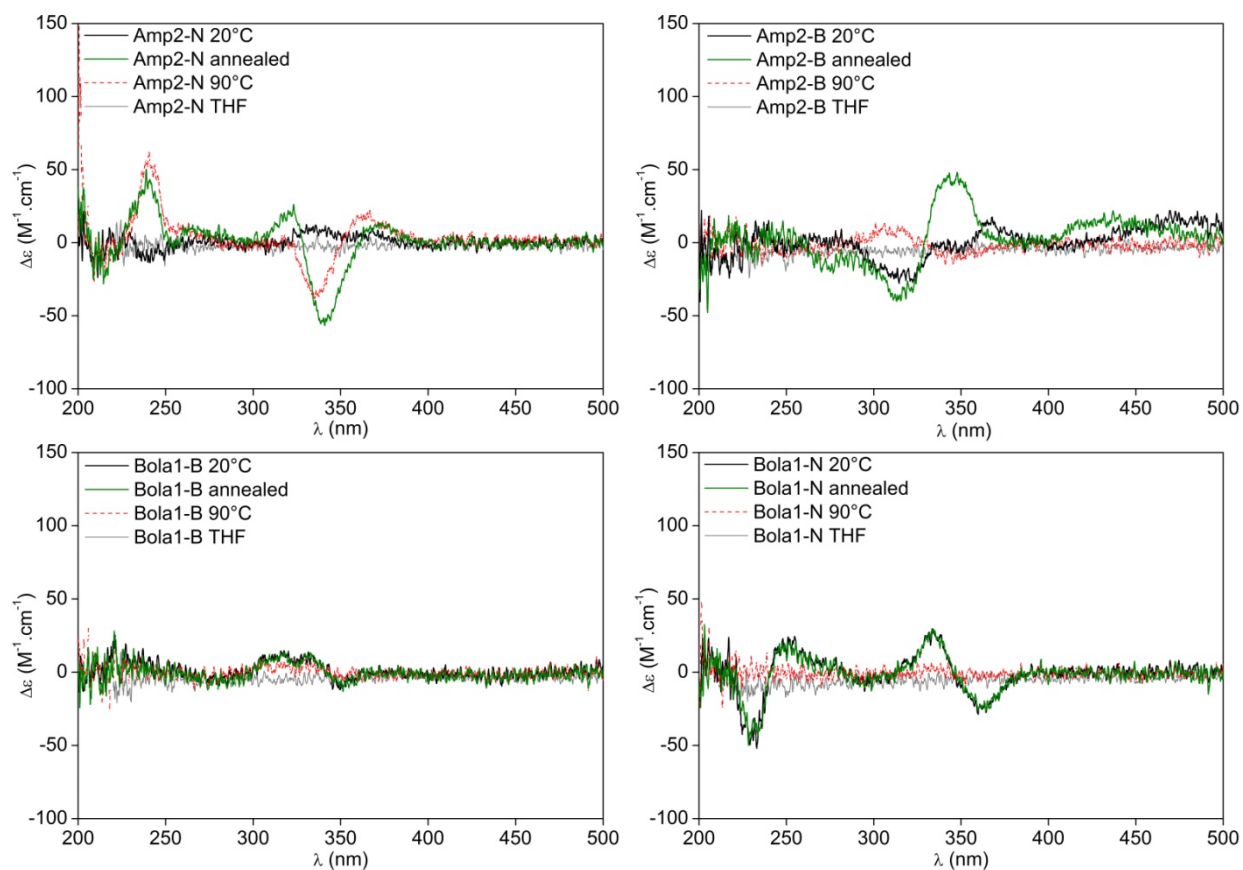
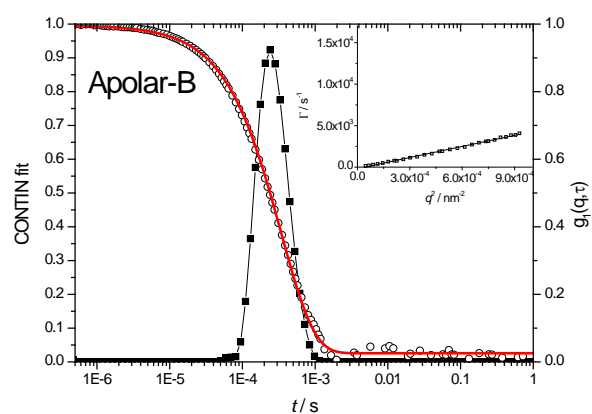
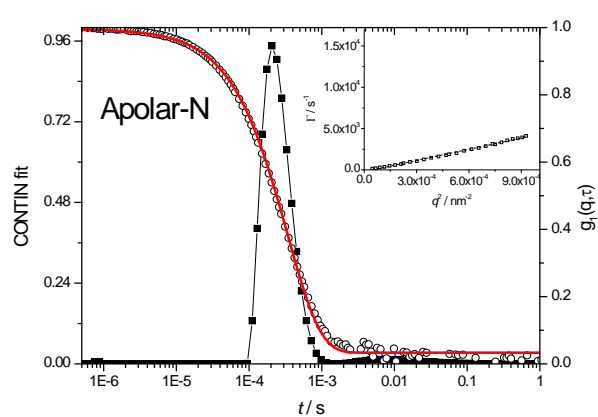
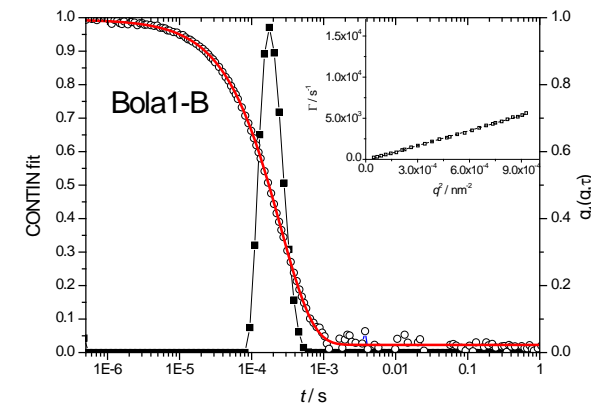
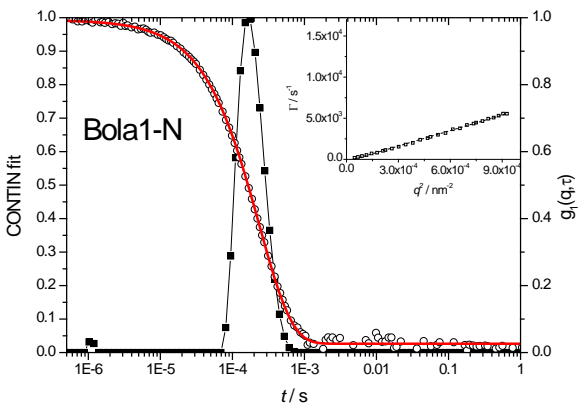
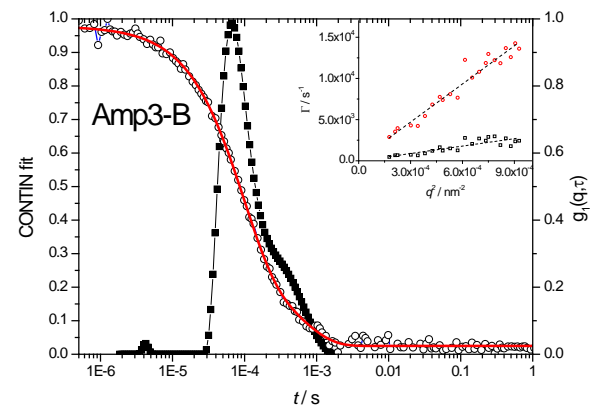
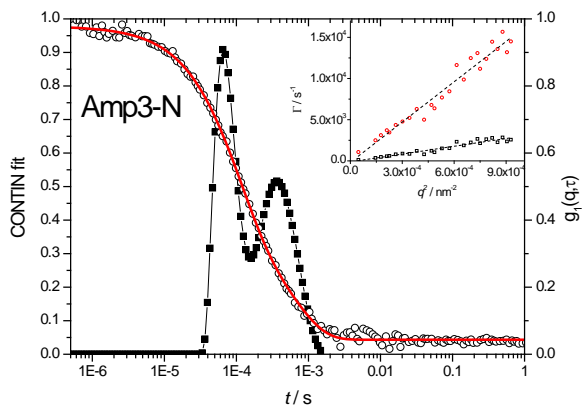
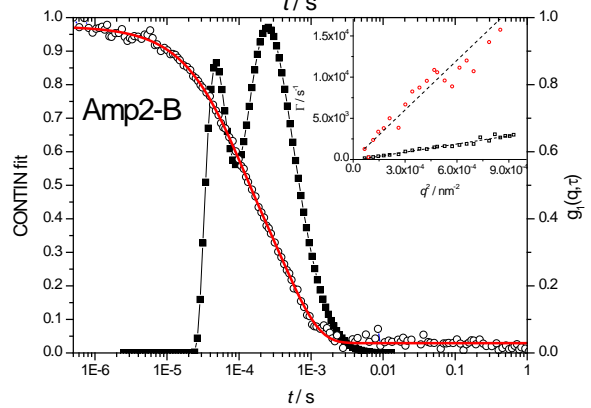
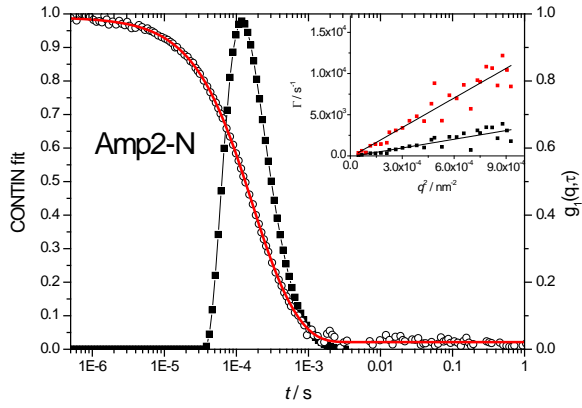
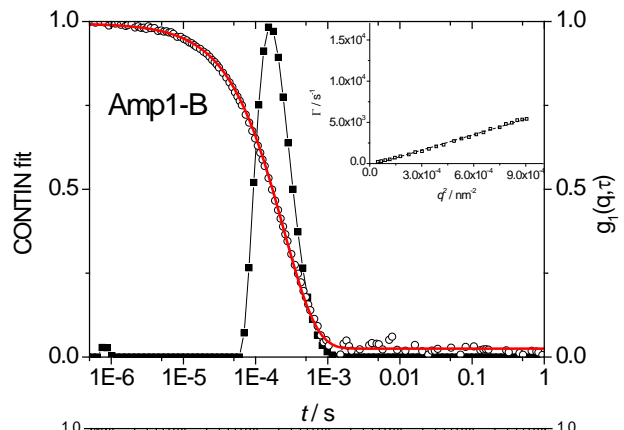
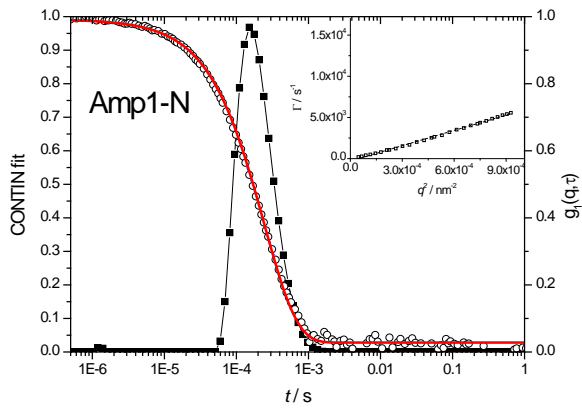


Figure S4. CD spectra for **Apolar**, **Amp1**, **Amp2** and **Bola1** ($c = 3 \mu\text{M}$) in THF (grey curve), in water at 20°C (fresh, black curve), in water at 90°C (red curve) and again in water at 20°C (annealed, green curve).

Table S2. The DLS data were fitted to a first or second order exponential decay to fit all data (mono- and bimodal samples) for best comparison. From the extracted decay rates Γ the diffusion constant was determined and hydrodynamic radii obtained by making use of the Stokes-Einstein relation. The experimental error in the hydrodynamic radius is 1%.

	Rh 1 st population, nm		Rh 2 nd population, nm	
	Fresh	Annealed	Fresh	Annealed
Apol-N	54.8	54.4	-	-
Apol-B	55.1	55.0	-	-
Bola1-N	38.8	39.1	-	-
Bola1-B	40.4	40.1	-	-
Bola2-N	81.7	80.2	-	-
Bola2-B	82.4	80.9	-	-
Amp1-N	40.8	39.6	-	-
Amp1-B	39.9	39.1	-	-
Amp2-N	79.8	69.5	24.2	20.4
Amp2-B	77.6	74.2	11.4	12.2
Amp3-N	80.0	77.7	13.8	15.0
Amp3-B	79.2	81.4	10.2	15.9





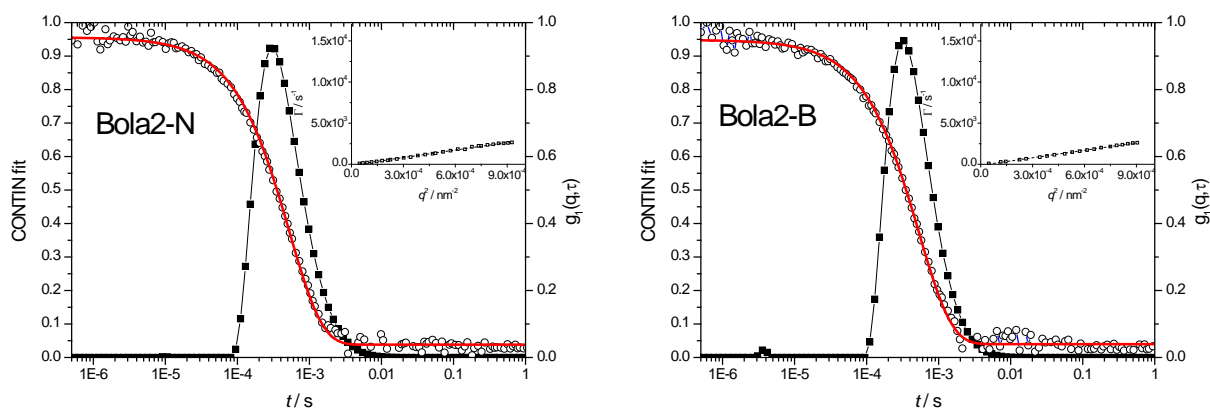


Figure S5. Correlation function and CONTIN fits of **Apolar**, **Amp1**, **Amp2**, **Amp3**, **Bola1** and **Bola2** nanoparticles at 150°, and decay rates Γ versus q^2 from first (and second) order exponential fits (inset).

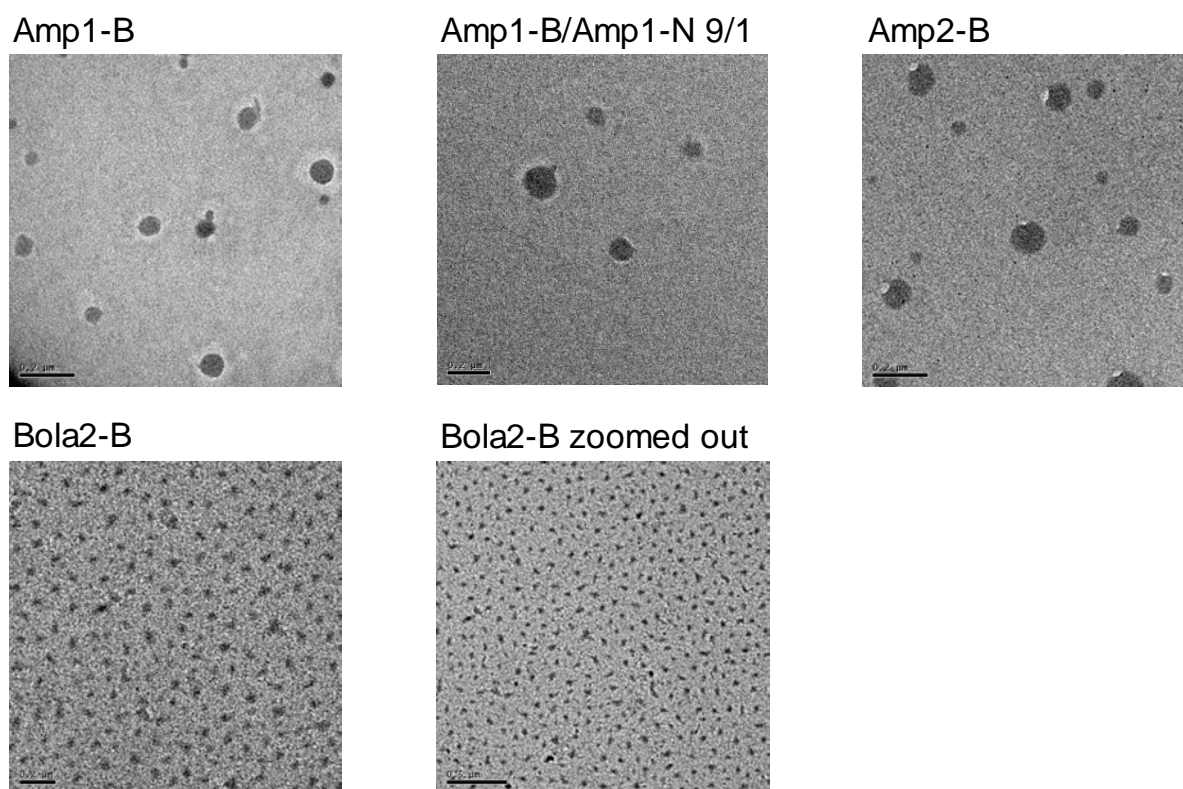


Figure S6. TEM images of **Amp1-B**, **Amp1-B/Amp1-N 9/1**, **Amp2-B** and **Bola2-B** nanoparticles. The scale bar represents 200 nm for **Amp1-B**, **Amp1-B/Amp1-N 9/1**, **Amp2-B** and **Bola2-B** and 500 nm for **Bola2-B** zoomed out.

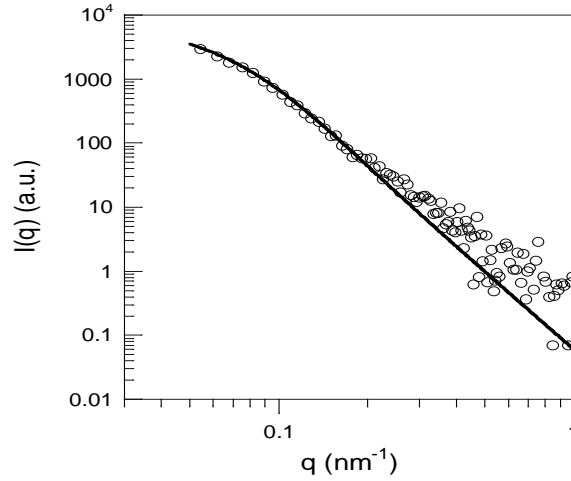


Figure S7. SAXS profile of **Apolar-B** solution (+) experimental profile: (–) calculated best fit curve, assuming the particle as polydisperse spheres of mean radius 41 nm.

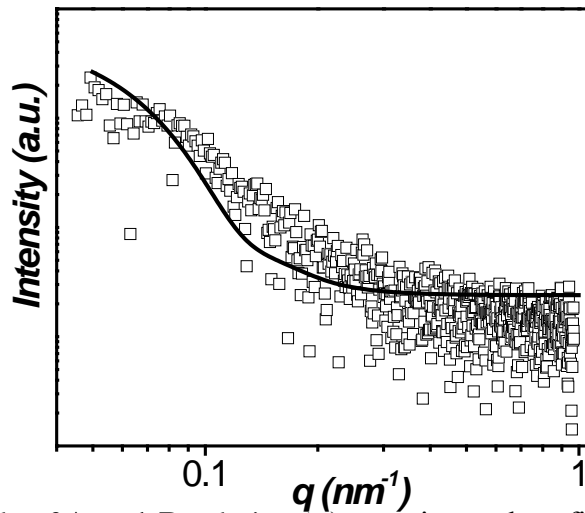


Figure S8. SAXS profile of **Amp1-B** solution (□) experimental profile: (–) calculated best fit curve, assuming the particle as polydisperse spheres of radius 40 nm.

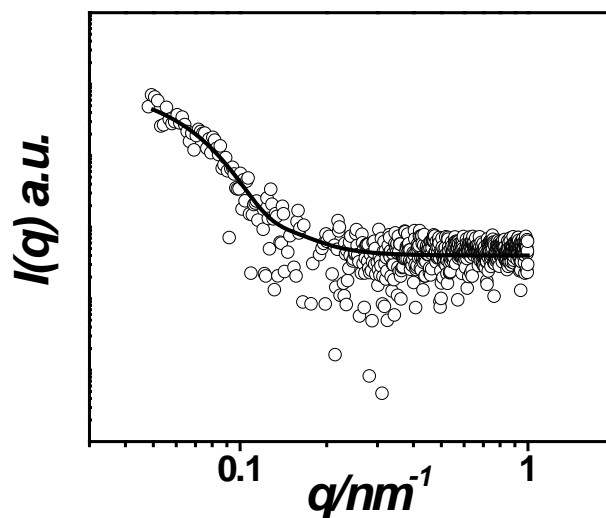


Figure S9. SAXS profile of **Bola1-B** solution (O) experimental profile: (–) calculated best fit curve, assuming the particle as polydisperse spheres of radius 43 nm.

Critical Aggregation Concentration

The critical aggregation concentration (CAC) of the particles was determined by a previous reported method^[S4] using nanoparticles containing both a naphthalene derivative, as an energy donor and benzothiadiazole, as an energy acceptor in a ratio of 95 : 5. Upon dilution, the energy transfer efficiency was measured. At a certain point an increase of the blue donor emission relative to the yellow acceptor emission was observed, revealing that the nanoparticles started to disassemble, reflecting the CAC.

Table S3. Summary of the critical aggregation concentration (CAC) for the nanoparticles.

	CAC
95 / 5	M ⁻¹
Apolar-N/Apolar-B	10 ⁻¹⁰
Amp1-N/Amp1-B	10 ⁻⁹
Amp2-N/Amp2-N	10 ⁻⁹
Amp3-N/Amp3-N	10 ⁻⁸
Bola1-N/Bola1-B	10 ⁻⁹
Bola2-N/Bola2-B	10 ⁻⁷

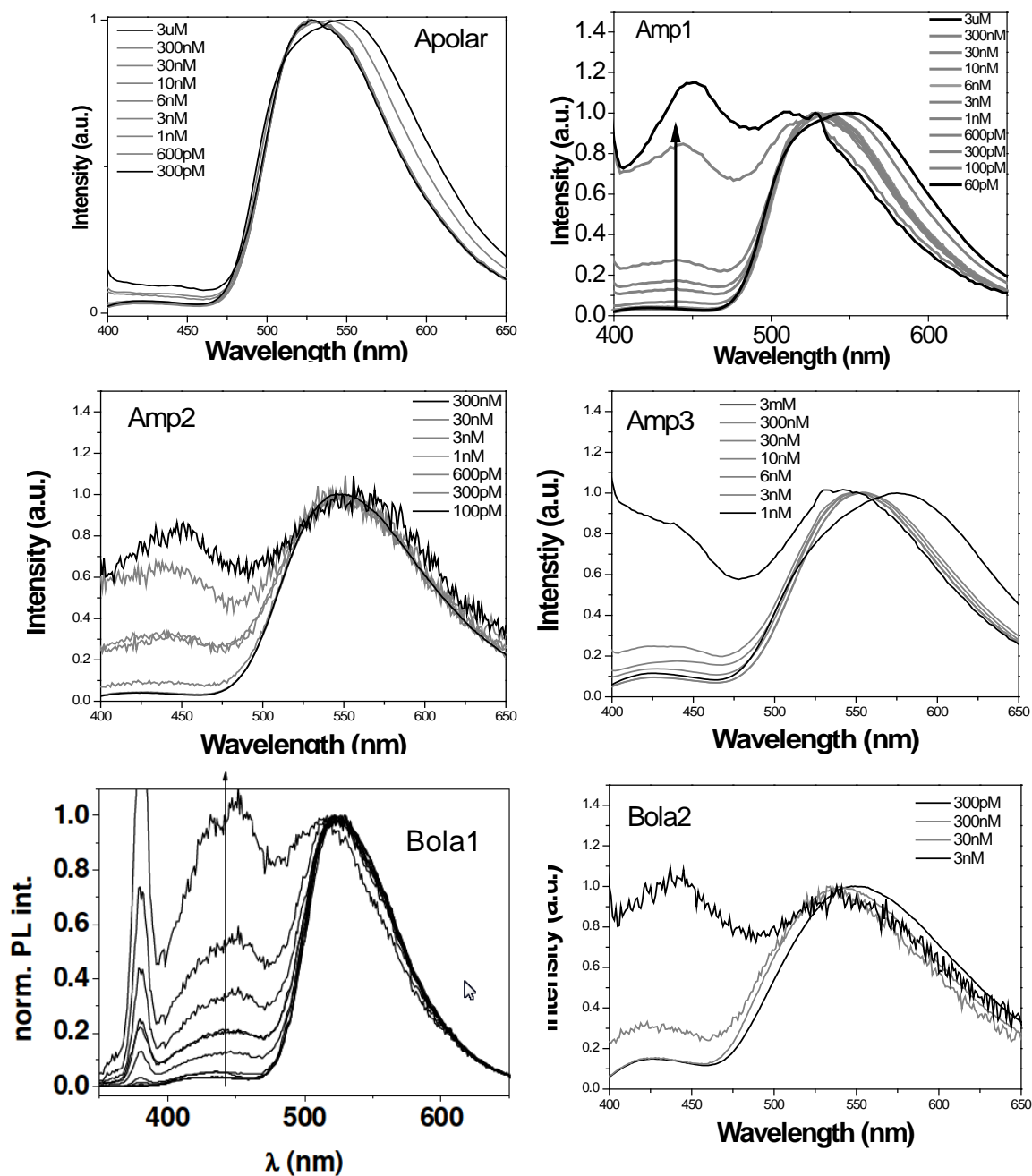


Figure S10. Concentration dependent fluorescence spectra of mixed nanoparticles from **Apolar**, **Amp1**, **Amp2**, **Amp3**, **Bola1** and **Bola2** with a composition of 95 : 5 in water, normalized acceptor emission. Excitation wavelength $\lambda_{exc} = 340$ nm.

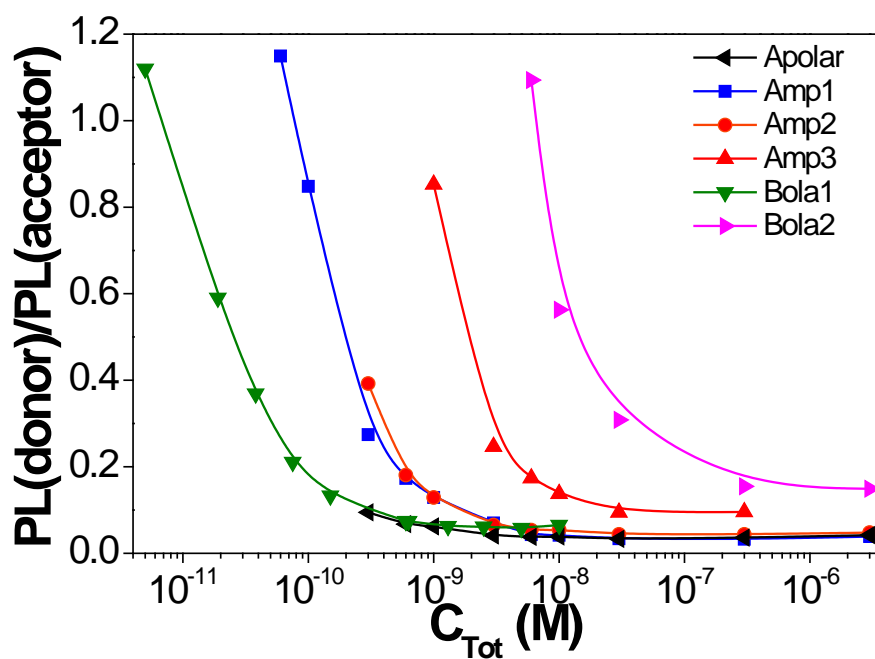


Figure S11. Concentration dependence of the ratio of donor to acceptor emission in the mixed nanoparticles (95 : 5, N : B) to determine the CAC. The lines are drawn to guide the reader.

Emission Spectra of Self-Assembled Nanoparticles of Two Chromophores with Similar Side Chain

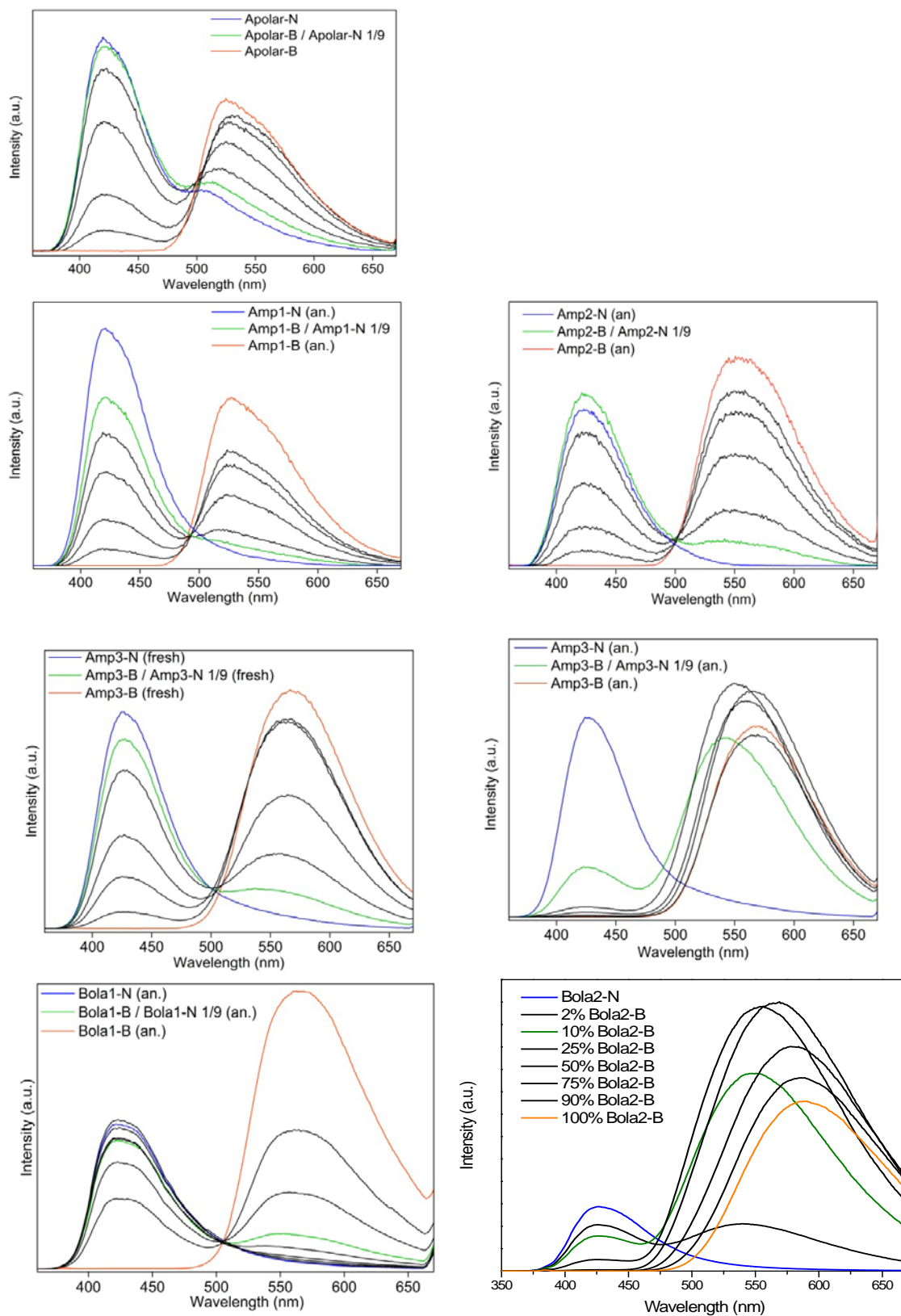


Figure S12. Emission spectra of **Apolar**, **Amp1**, **Amp2**, **Amp3**, **Bola1** and **Bola2** nanoparticles in water ($c = 3\mu\text{M}$) after annealing prepared from separate nanoparticles (method A). Excitation wavelength $\lambda_{exc} = 340\text{ nm}$.

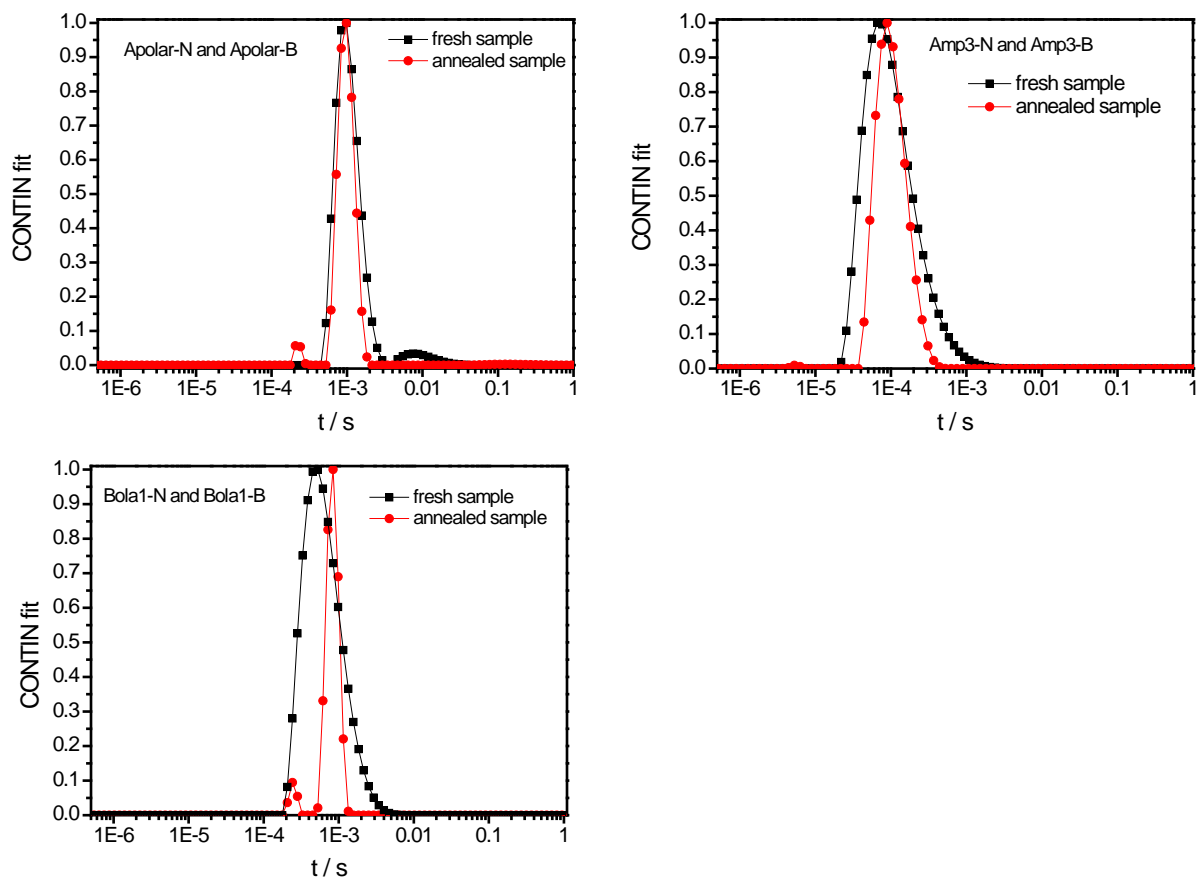
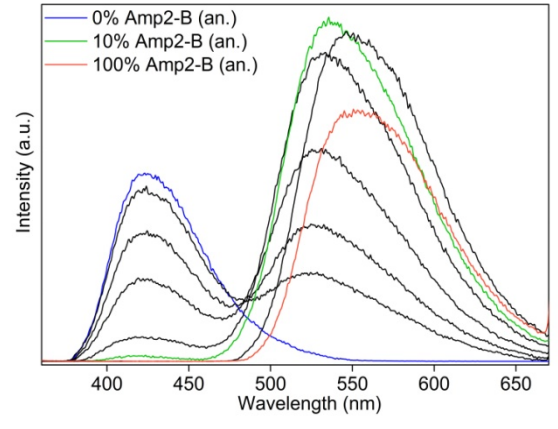
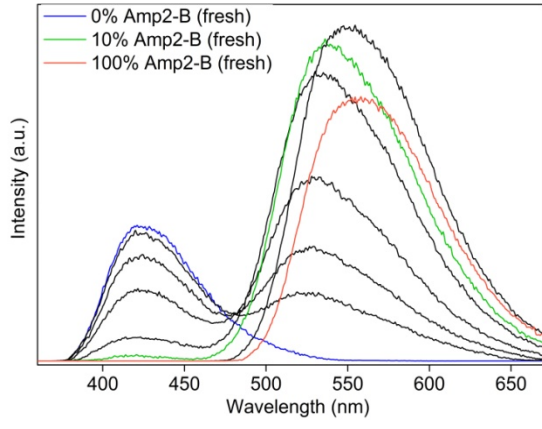
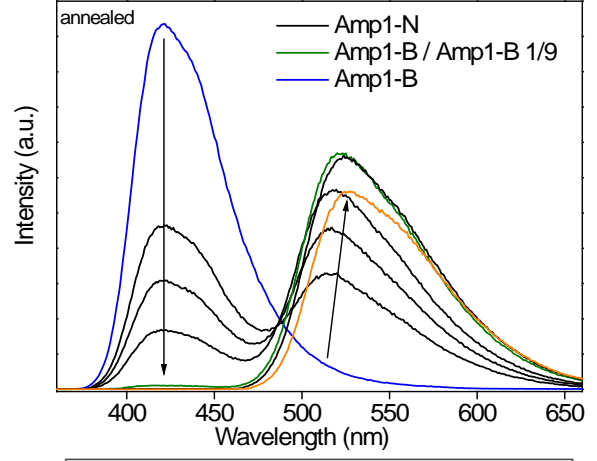
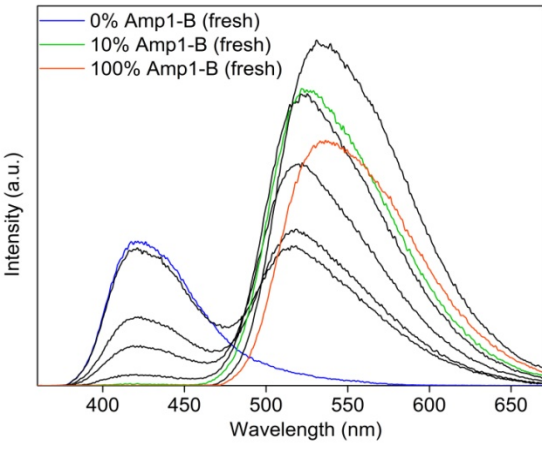
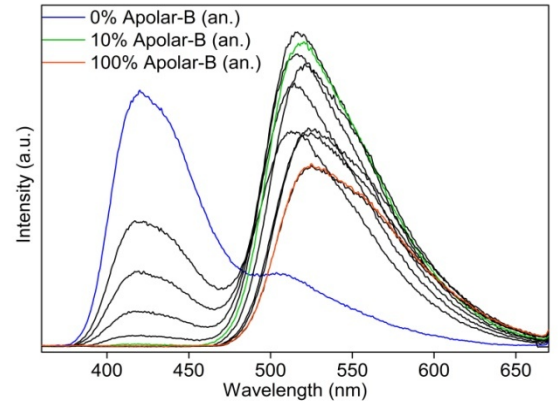
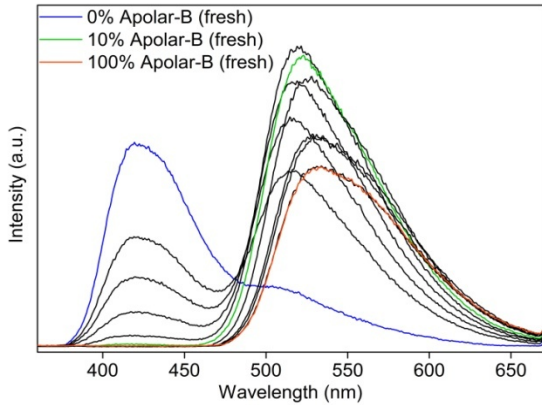


Figure S13. CONTIN fits of **Apolar-N/Apolar-B**, **Amp3-B/Amp3-N** and **Bola1-N/Bola1-B** (50/50 mixture prepared with method B) nanoparticles at 150° , showing before and after annealing a similar hydrodynamic radius.



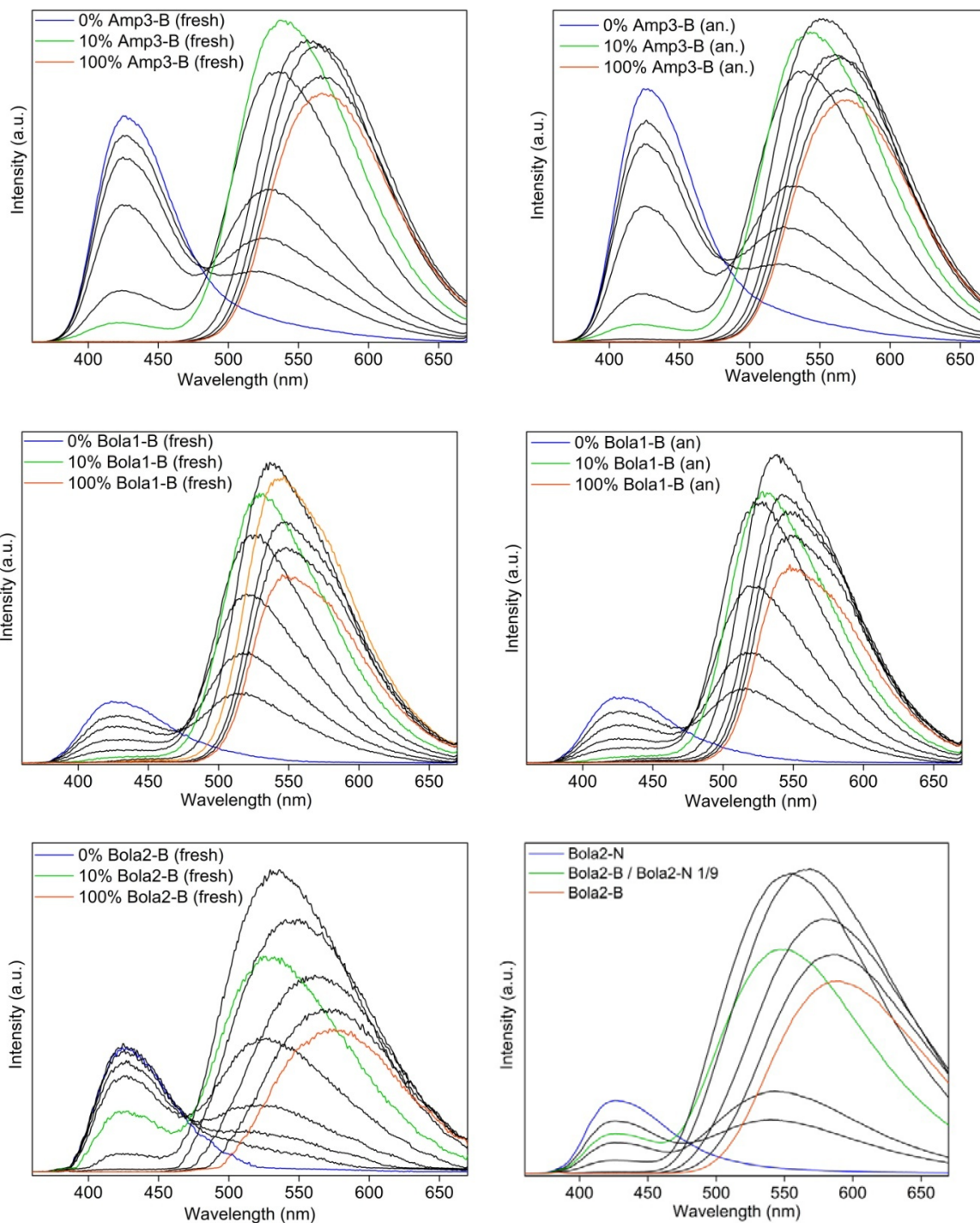


Figure S14. Emission spectra of **Apolar**, **Amp1**, **Amp2**, **Amp3**, **Bola1** and **Bola2** nanoparticles in water ($c = 3\mu\text{M}$) for fresh and annealed samples prepared from mixed nanoparticles (method B). Excitation wavelength $\lambda_{\text{exc}} = 340$ nm.

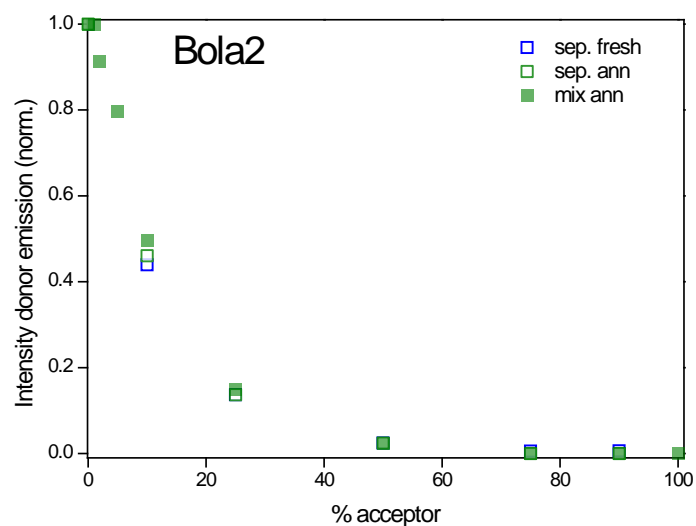


Figure S15. Dependence of naphtalene donor emission intensity (normalized) for **Bola2** nanoparticles in water ($c = 3\mu\text{M}$) for fresh and annealed samples prepared from separate nanoparticles (method A) and annealed samples prepared form mixed nanoparticles (method B). Excitation wavelength $\lambda_{\text{exc}} = 340$ nm.

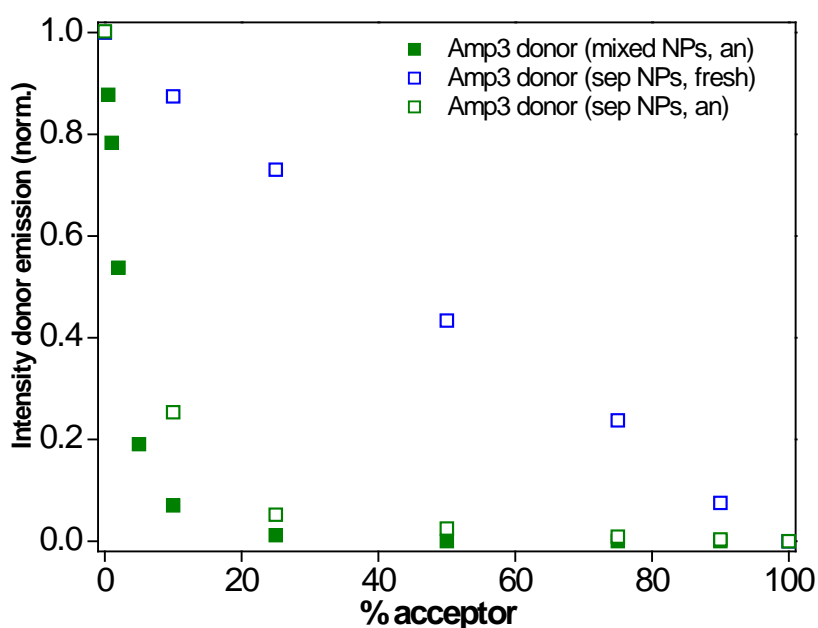


Figure S16. Dependence of naphtalene donor emission intensity (normalized) for **Amp3** nanoparticles in water ($c = 3\mu\text{M}$) for fresh and annealed samples prepared from separate nanoparticles (method A) and annealed samples prepared form mixed nanoparticles (method B). Excitation wavelength $\lambda_{\text{exc}} = 340$ nm.

Emission Spectra of Self-Assembled Nanoparticles of Two Chromophores with Different Side Chain

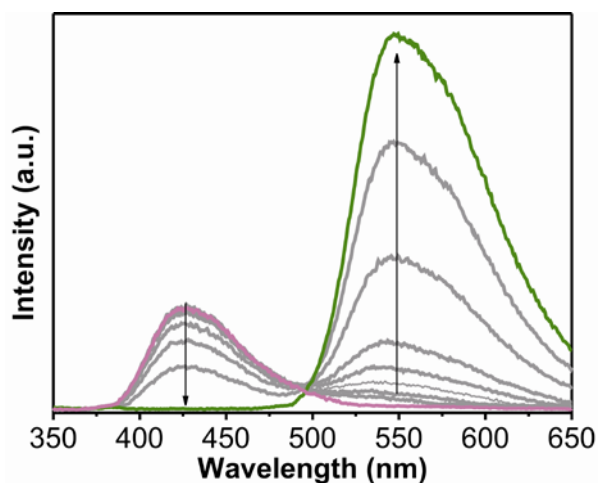


Figure S17. Emission spectra of mixtures with different ratio of **Bola1-B** (green curve) and **Bola2-N** (magenta curve), revealing narcissistic self-sorting.

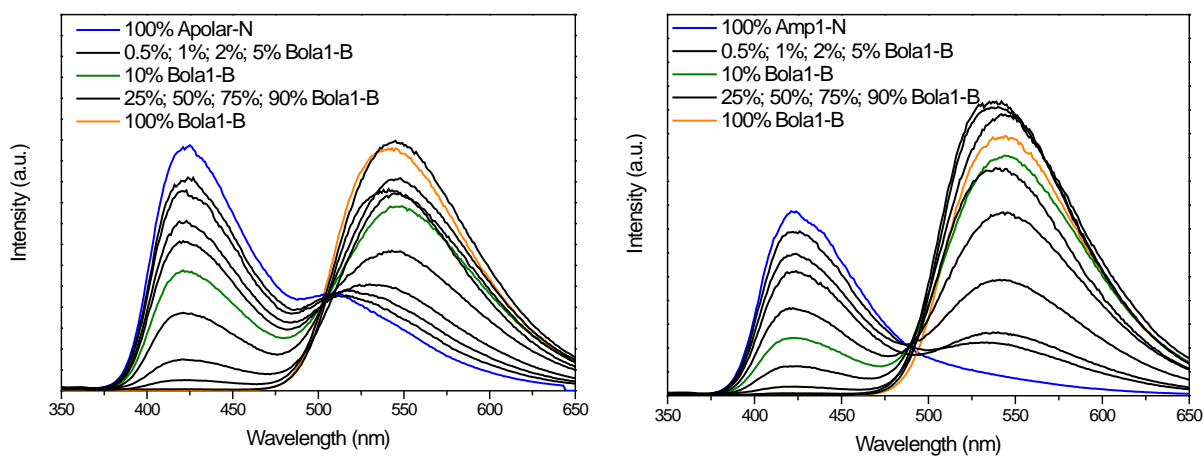


Figure S18. Emission spectra of **Apolar-N/Bola1-B** (left) and **Amp1-N/Bola1-B** (right) nanoparticles in water ($c = 3\mu\text{M}$) for annealed samples prepared from mixed nanoparticles (method B). Excitation wavelength $\lambda_{exc} = 340$ nm.

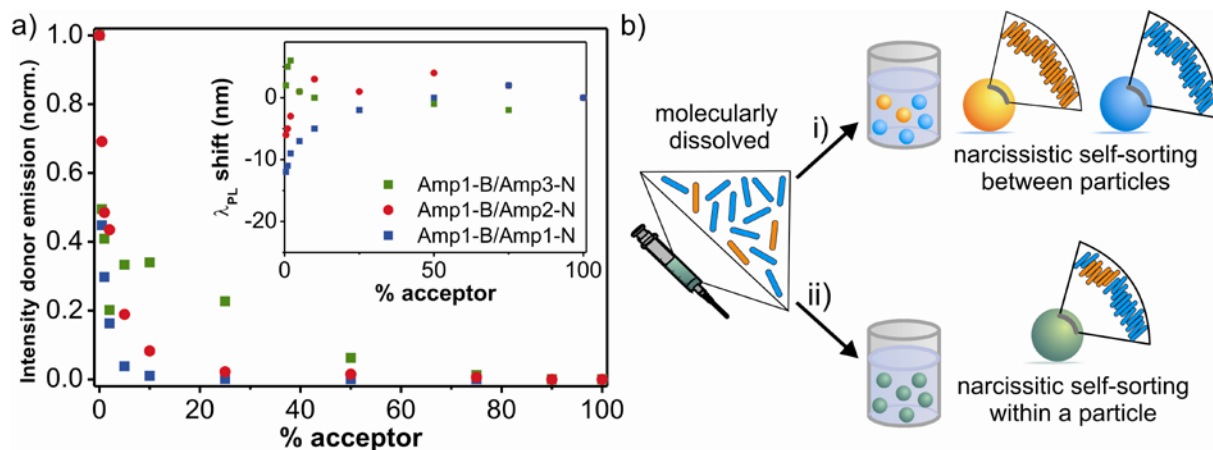


Figure S19. a) The two component nanoparticles (**Amp1-B/Amp1-N**; **Amp1-B/Amp2-N** and **Amp1-B/Amp3-N**) were self-assembled of two chromophores with distinct pendant side chains and annealed (excitation wavelength $\lambda_{exc} = 340$ nm). The intensity (normalized) of donor emission as a function of acceptor percentage decreased non-linearly revealing energy transfer. The inset displays the shift of emission maxima that showed a red shift at low acceptor concentration for the nanoparticles self-assembled from two chromophores with distinct pendant tails indicating clustering of the acceptor molecules within a particle. b) Schematic illustration of (i) the narcissistic self-sorting for **Bola1-B** in **Bola2-N** and (ii) domain formation within a particle for **Bola1-B** in **Amp1-N** and **Apolar-N** as well as **Amp1-B** in **Amp2-N** and **Amp3-N**.

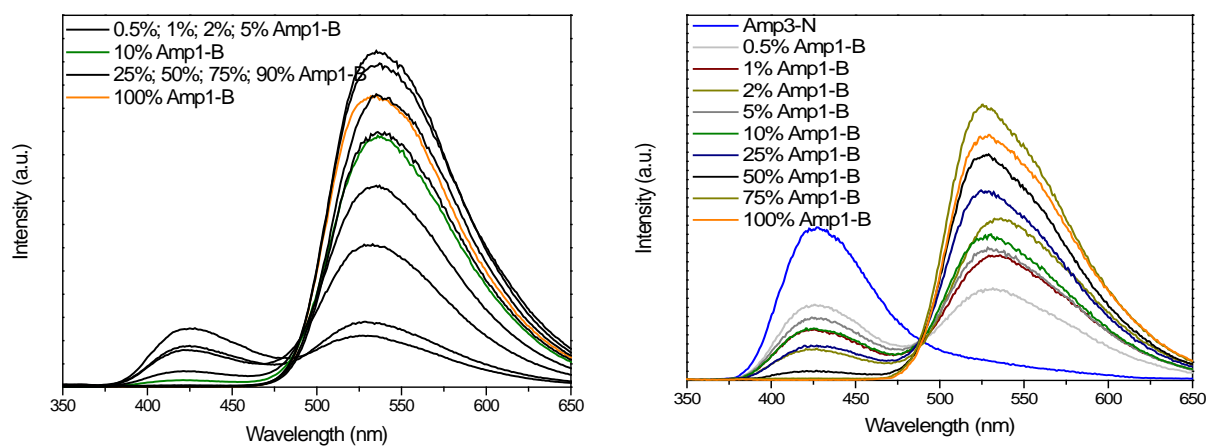


Figure S20. Emission spectra of **Amp2-N/Amp1-B** (left) and **Amp2-N/Amp1-B** (right) nanoparticles in water ($c = 3\mu\text{M}$) for annealed samples prepared from mixed nanoparticles (method B). Excitation wavelength $\lambda_{exc} = 340$ nm.

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