Supramolecular behaviour and fluorescence of rhodamine-functionalised ROMP polymers

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Instrumentations

NMR spectra were recorded on a Bruker AV2 400 MHz spectrometer; the spectra were referenced to residual ^{1}H-solvent and chemical shifts then reported in parts per million (ppm). Spectra were analysed using MestReNova or ACDLABS software.

GC-MS data was collected on an Agilent 6890 series GC with MS detector.

Single crystal XRD data were collected on a Rigaku Oxford Diffraction SuperNova single crystal diffractometer using a Cu radiation source. Sample specific details can be found in the CIF files.

GPC was conducted using PL-GPC 50 Plus system by Varian Inc. using refractive index as a detector.

DLS measurements were recorded using a Zetasizer Nano ZS instrument from Malvern Panalytical Ltd. The measurements were recorded at 25 °C using a sample refractive index value of 1.450 and an absorption value of 0.001. The dispersant used was water with a refractive index of 1.330 and a viscosity of 0.8872 cP. Automatic attenuation was used. Samples were run in a quartz cell and measurements were taken after an equilibration time of 2 minutes.

Transmission electron microscopy (TEM) was performed on a Jeol 1230 operating at an accelerating voltage of 80 kV and the images were recorded with a Gatan Multiscan 790 digital - 2 - camera. FTIR spectra were recorded on a Shimadzu IR-Affinity instrument.

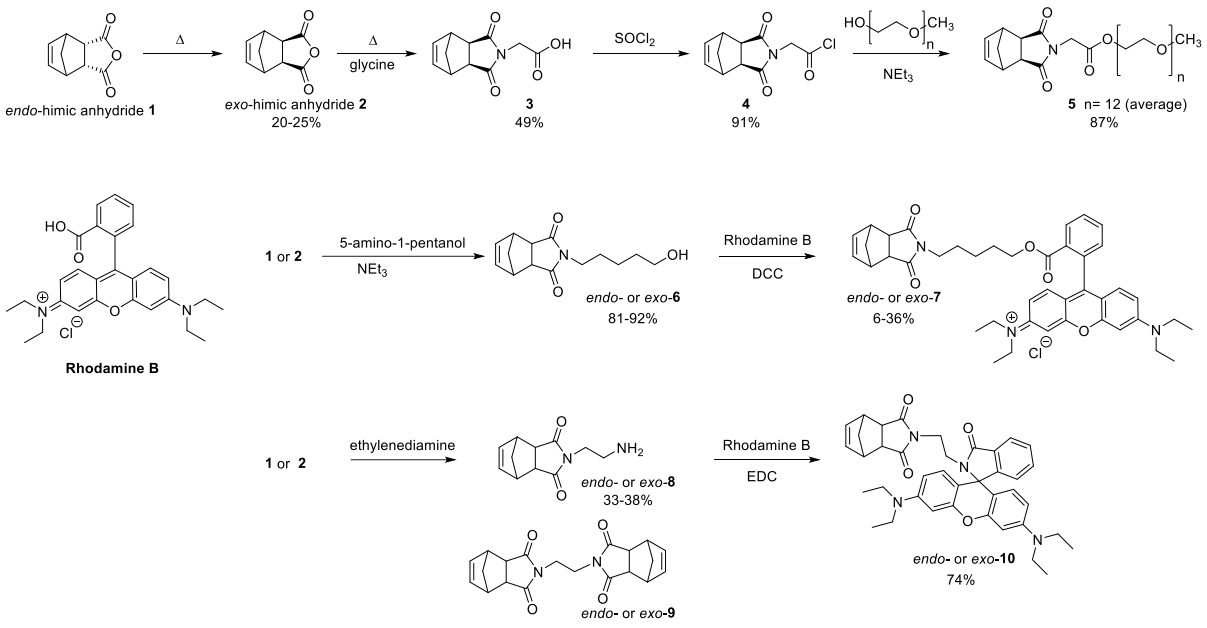
Fluorescence measurements were made using a Cary Eclipse Fluorescence Spectrophotometer by Aglient Technologies. Emission spectra were recorded within the range of 560 – 760 nm and excitation was set at 550 nm. Excitation and emission slit sizes were set at 5 nm. The scan rate was set at 600 nm / min with a data interval of 1.000 and an averaging time of 0.1 second. The excitation filter was set to auto, the emission filter set to open and the PMT detector voltage set to 600 V. The multicell holder accessory was used and the samples were measured in a quartz cell.

Materials

Carbic anhydride (*endo*); 5-amino-1-pentanol; thionyl chloride; ethyl vinyl ether; and Rhodamine B were obtained from Acros Organics. Glycine, poly(ethylene glycol) methyl ether (M_n 550) and third generation Grubbs catalyst were obtained from Sigma Aldrich. Ethylenediamine 99% was obtained from Avocado Research Chemicals. For the DNA intercalation studies, DNA1 was 5'-CTGTATGGTCAACTG-3' and DNA2 was 5'-CAGTTGACCATACAG-3' and both were purchased from Integrated DNA Technologies. The buffer solution TBE 1x was prepared by diluting a TBE 10x solution made up of Tris base (108 g), boric acid (55 g) and EDTA (7.45 g) in water (1 L). TAMg 1x buffer solution was prepared by diluting a TAMg 10x solution. TAMg 10x was prepared in a 1 L volumetric flask using Tris base (54.51 g) and $Mg(OAc)_2.4H_2O$ (26.8 g) which were taken up in water (900 mL), the pH was adjusted to 8 by the addition of acetic acid and the total volume was made up to 1 L by the addition of water.

Synthesis

The following synthetic routes were performed respectively with both *endo* and *exo* analogues of carbic anhydride. Only the *exo*-derivatives were subsequently polymerised, but we include here the preparation of the analogues and intermediates as some have not been previously reported.



Scheme S1. Monomer synthesis

Exo-himoyl glycine, **3**:

Single crystals of $C_{11}H_{11}NO_4$ (**3**) were grown by recrystallisation from a supersaturated solution of **3** in hot ethyl acetate. A suitable crystal was selected and mounted on a SuperNova diffractometer equipped with an AtlasS2 detector. The crystal was kept at 100(2) K during data collection and data were collected using Cu K_α radiation. Using Olex2,[1] the structure was solved with the olex2.solve[2] structure solution program using charge flipping and refined with the SHELXL[3] refinement package using least squares minimisation.

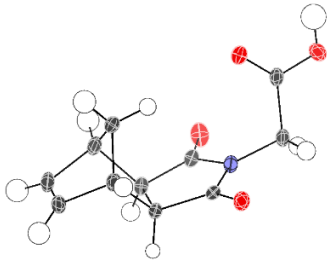
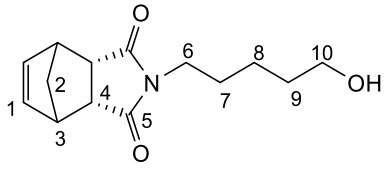


Figure S1: X-ray crystal structure of 3. Atomic displacement parameters are shown at 50% probability.

Crystal Data for $C_{11}H_{11}NO_4$ (M =221.21 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 6.29482(14) Å, b = 13.8975(3) Å, c = 11.1692(2) Å, β = 90.663(2)°, V = 977.04(4) Å^3, Z = 4, T = 100(2) K, μ(CuK_α) = 0.976 mm^{-1}, D_{calc} = 1.504 g/cm^3, 6593 reflections measured (10.16° ≤ 2ϑ ≤ 146.782°), 1934 unique (R_{int} = 0.0430, R_{sigma} = 0.0345) were used in all calculations. The final R_1 was 0.0420 (I > 2σ(I)) and wR_2 was 0.1134 (all data).

CCDC Deposition Number: 2005040

N-(hydroxypentanyl)-*cis*-5-norbornene-*endo*-2,3-dicarboximide, ***endo*-6**



To a round-bottomed flask, *endo* carbic anhydride **1** (3.92 g, 23.8 mmol), toluene (70 cm^3) and triethylamine (0.4 cm^3, 2.38 mmol) were added and stirred at room temperature until all solid had dissolved. 5-amino-1-pentanol (2.45 g, 23.8 mmol) was added to the stirring solution. A dean-stark trap was then attached, and the solution was heated under reflux for 3 hours. Once cooled, the solution was concentrated *in vacuo* to yield the crude product as a yellow oil. The crude product was dissolved in DCM (120 cm^3) and washed with HCl (2 x 20 cm^3, 0.1 M) and brine (2 x 20 cm^3). The organic phase was dried over magnesium sulfate, filtered by gravity and the solvent (DCM) was removed on a rotary evaporator affording ***endo*-6** as a yellow oil (4.82 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.32 (*m, 2H, 8*), 1.47 (*m, 2H, 7*), 1.56 (*m, 3H, 2' & 9*), 1.74 (*dt, J = 8.8, 1.6 Hz, 1H, 2*), 3.26 (*dd, J = 2.9, 1.6 Hz, 2H, 4*), 3.35 (*t, J = 7.3 Hz, 2H, 6*), 3.39 (*m, 2H, 3*), 3.63 (*t, J = 6.5 Hz, 2H, 10*), 6.11 (*t, J = 1.8 Hz, 2H, 1*); ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 22.99 (*C-8*), 27.53 (*C-7*), 32.09 (*C-9*), 38.22 (*C-6*), 44.91 (*C-3*), 45.74 (*C-4*), 52.26 (*C-2*), 62.59 (*C-10*), 134.44 (*C-1*), 177.92 (*C-5*); IR: ν_{max}/cm^{-1} 3447 (O-H alcohol stretching), 2940 (C-H alkane stretching), 2866 (C-H alkane stretching), 1763 (C=O stretching), 1736 (C=O stretching), 1682 (C=O dicarboximide stretching). LC-MS (ESI): calculated $[M+H]^+$ $[C_{14}H_{19}NO_3+H]^+$ 250.1, found 250.2.

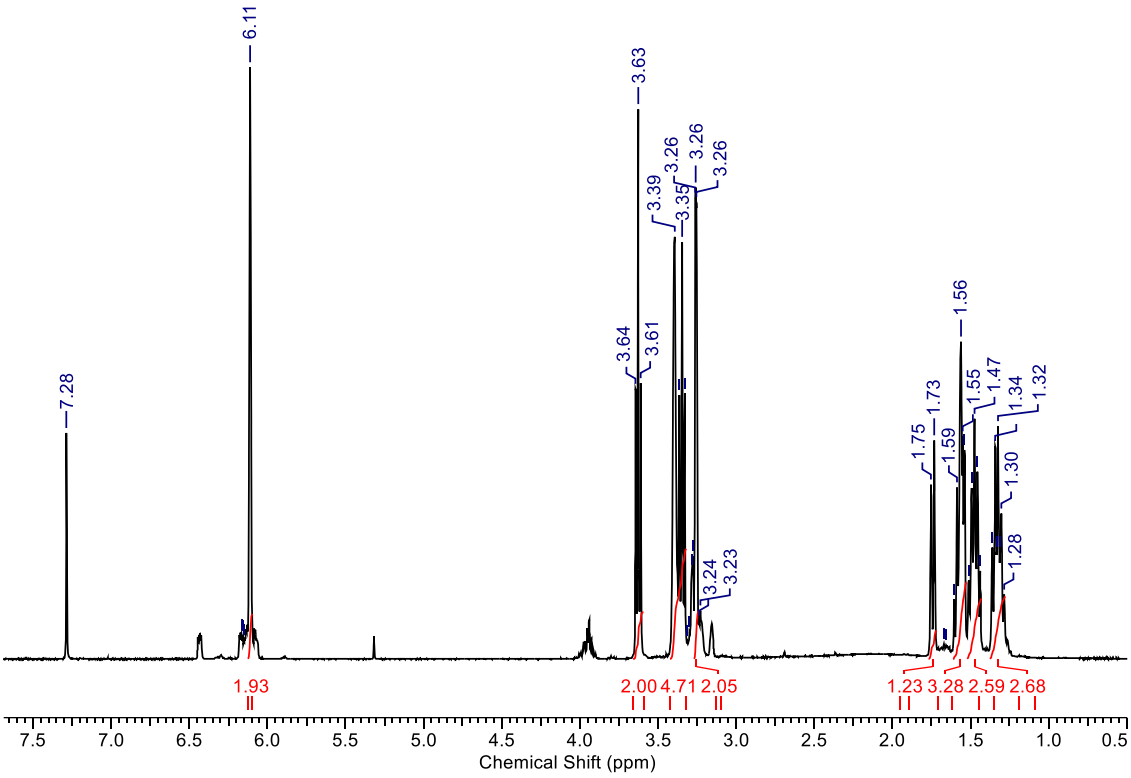


Figure S2: ^{1}H NMR of N-(hydroxypentanyl)-cis-5-norbornene-endo-2,3-dicarboximide, ***endo*-6**

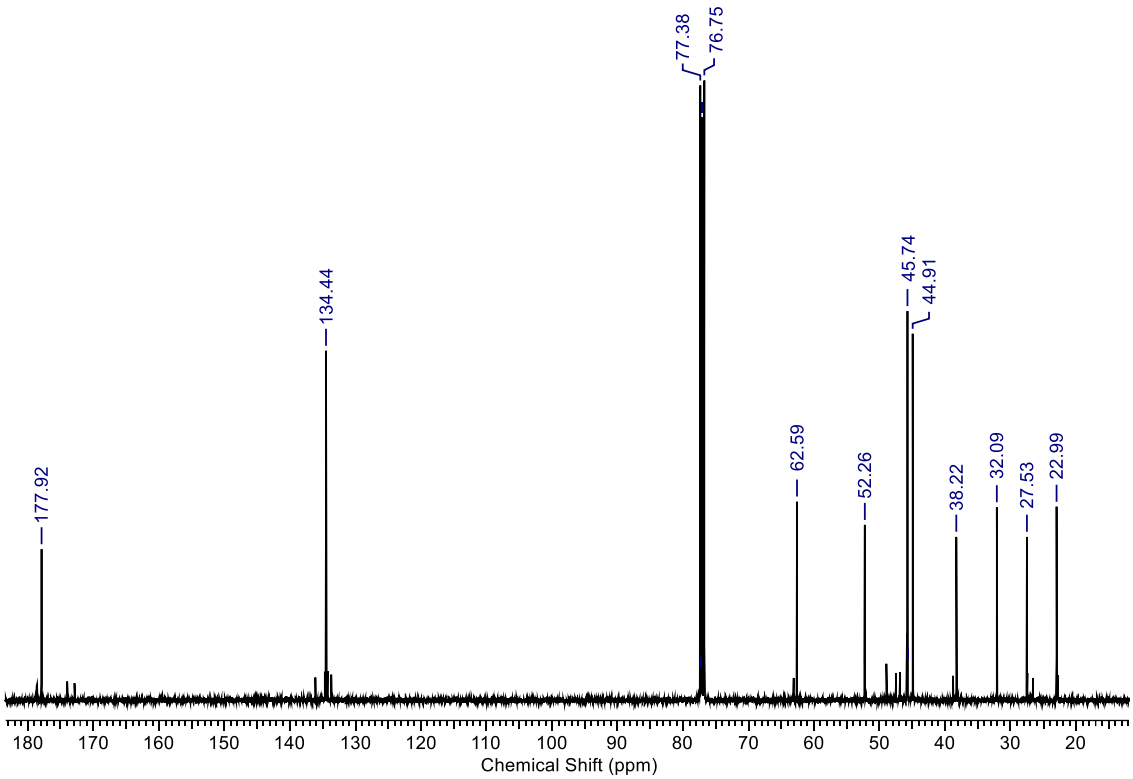
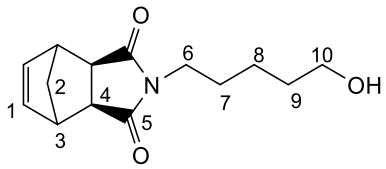


Figure S3: ^{13}C NMR of N-(hydroxypentanyl)-cis-5-norbornene-endo-2,3-dicarboximide, ***endo-6***

N-(hydroxypentanyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide, ***exo*-6**



To a round-bottomed flask, *exo* carbic anhydride **2** (3.92 g, 23.8 mmol), toluene (70 cm^3) and triethylamine (0.4 cm^3, 2.38 mmol) were addedand stirred at room temperature until all solid had dissolved. 5-amino-1-pentanol (2.45 g, 23.8 mmol) was added to the stirring solution. A dean-stark trap was then attached, and the solution was heated under reflux for 3 hours. Once cooled, the solution was concentrated *in vacuo* to yield the crude product as a yellow oil. The crude product was dissolved in DCM (120 cm^3) and washed with HCl (2 x 20 cm^3, 0.1 M) and brine (2 x 20 cm^3). The organic phase was dried over magnesium sulfate, filtered by gravity and the solvent (DCM) was removed on a rotary evaporator affording the ***exo*-6** as a yellow oil (5.47 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.25 (*d, J = 9.9 Hz, 1H, 2*), 1.40 (*m, 2H, 8*), 1.54 (*dt, J = 9.8, 1.6 Hz, 1H, 2'*), 1.62 (*m, 4H, 7 & 9*), 2.70 (*d, J = 1.3 Hz, 2H, 4*), 3.30 (*t, J = 1.70 Hz, 2H, 3*), 3.50 (*t, J = 7.43 Hz, 2H, 6*), 3.66 (*t, J = 6.5 Hz, 2H, 10*), 6.31 (*t, J = 1.8 Hz, 2H, 1*); ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 23.10 (*C-8*), 27.53 (*C-7*), 32.11 (*C-9*), 38.52 (*C-6*), 42.74 (*C-2*), 45.18 (*C-3*), 47.83 (*C-4*), 62.59 (*C-10*), 137.84 (*C-1*), 178.16 (*C-5*); IR: ν_{max}/cm^{-1} 3447 (O-H alcohol stretching), 2940 (C-H alkane stretching), 2866 (C-H alkane stretching), 1763 (C=O stretching), 1736 (C=O stretching), 1682 (C=O dicarboximide stretching); LC-MS (ESI): calculated $[M+H]^+$ $[C_{14}H_{19}NO_3+H]^+$ 250.1, found 250.2.

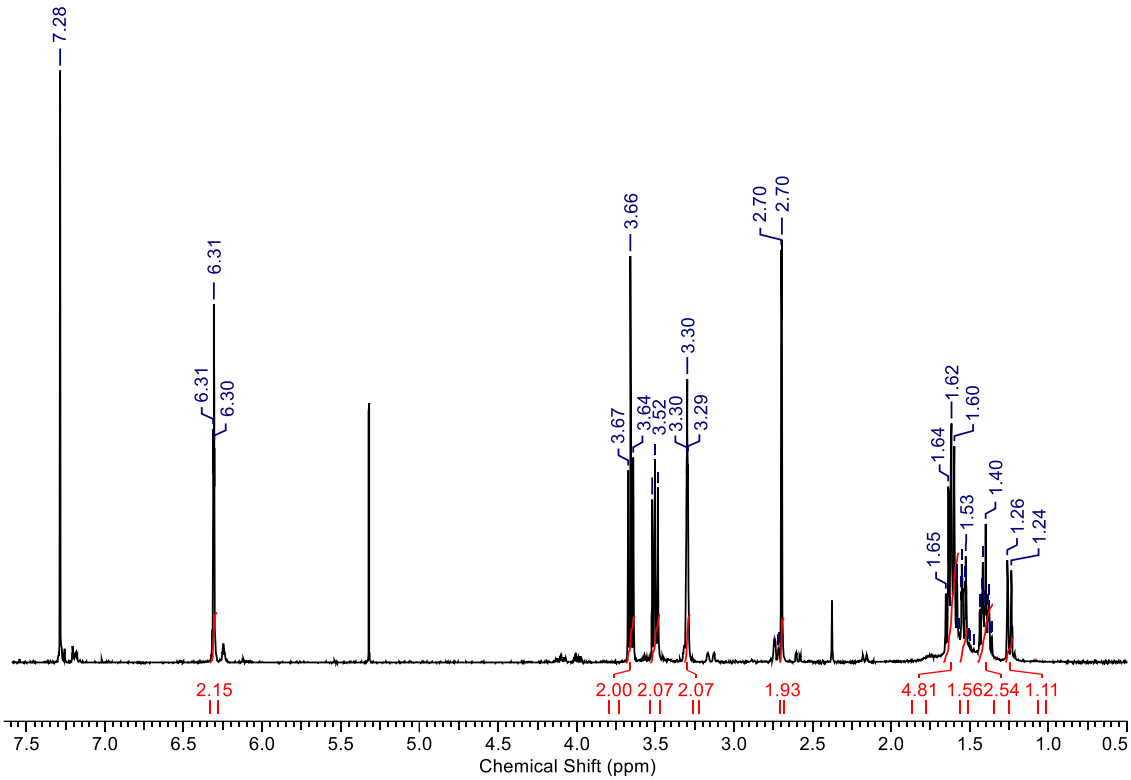


Figure S4: [1]H NMR of N-(hydroxypentanyl)-cis-5-norbornene-exo-2,3-dicarboximide, ***exo-6***

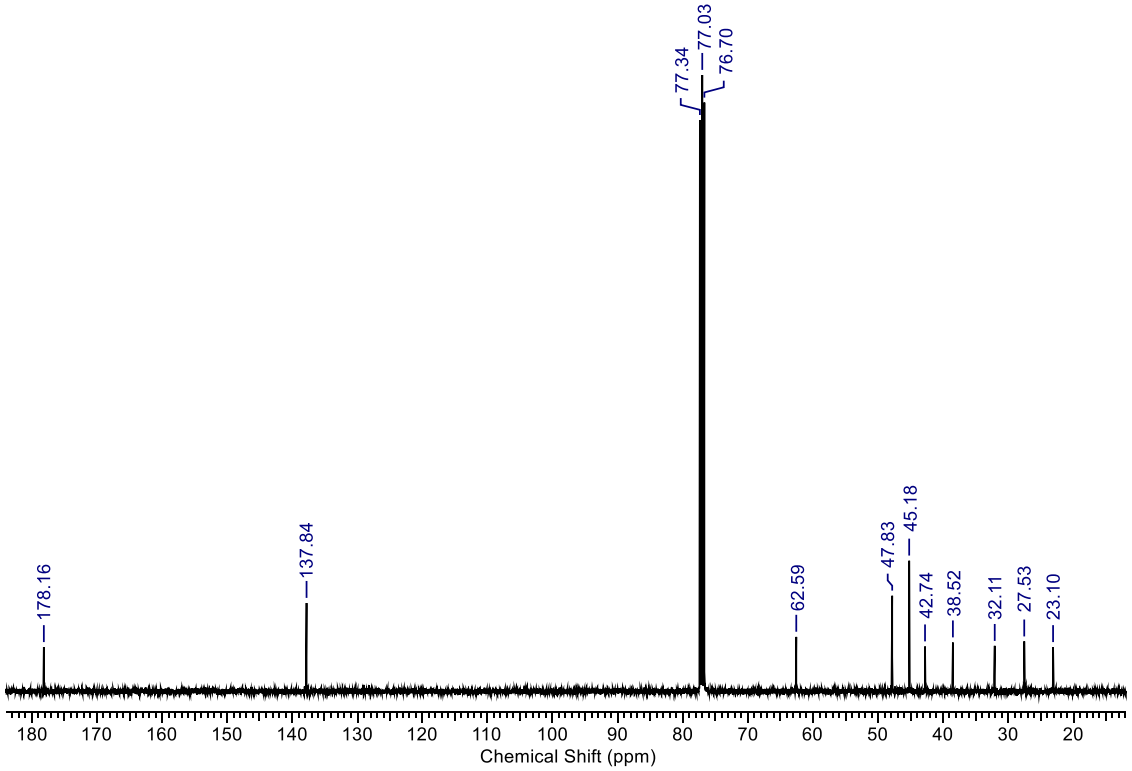
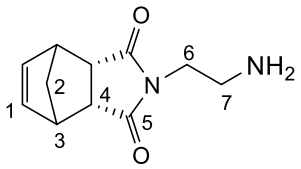


Figure S5: [13]C NMR of N-(hydroxypentanyl)-cis-5-norbornene-exo-2,3-dicarboximide, ***exo-6***

Endo-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide, ***endo*-8**



Ethylenediamine (8.15 cm^3, 121.9 mmol) was added to a stirring solution of *endo* carbic anhydride **1** (5.0 g, 30.5 mmol) in toluene (80 cm^3), and a white precipitate formed. The solution was heated to reflux for 18 hours and the precipitate re-dissolved. The solution was left to cool to room temperature and the solvent was removed *in vacuo*. The residue was taken up in toluene (150 cm^3) and washed with water (2 x 50 cm^3). The organic toluene layer was disposed of as the product stays in the aqueous layer. The aqueous layer was washed with DCM (5 x 50 cm^3) and the organic layers were combined, dried over $MgSO_4$ and filtered by gravity. The solvent was removed *in vacuo* yielding ***endo*-8** (2.06 g, 33%). m.p.: 76 – 78 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.10 (*br s, 2H, NH_2*), 1.55 (*d, J = 8.8 Hz, 1H, 2'*), 1.74 (*dt, J = 8.8, 1.7 Hz, 1H, 2*), 2.74 (*t, J = 6.4 Hz, 2H, 7*), 3.77 (*dd, J = 2.9, 1.6 Hz, 2H, 4*), 3.39 (*m, 2H, 3*), 3.40 (*t, J = 6.3 Hz, 2H, 6*), 6.12 (*t, J = 1.9 Hz, 2H, 1*). ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 40.14 (*C-7*), 47.71 (*C-6*), 44.92 (*C-3*), 45.80 (*C-4*), 52.32 (*C-2*), 134.58 (*C-1*), 177.96 (*C-5*); IR: ν_{max}/cm^{-1} 3381 (N-H amine stretching), 2997 (C-H alkane stretching), 2965 (C-H alkane stretching), 2940 (C-H alkane stretching), 2860 (C-H alkane stretching), 1759 (C=O stretching), 1684 (C=O dicarboximide stretching), 1655 (C=C alkene stretching); GC-MS: calculated $[M+H]^+$ $[C_{11}H_{14}N_2O_2+H]^+$ 207.1, found 207.0.

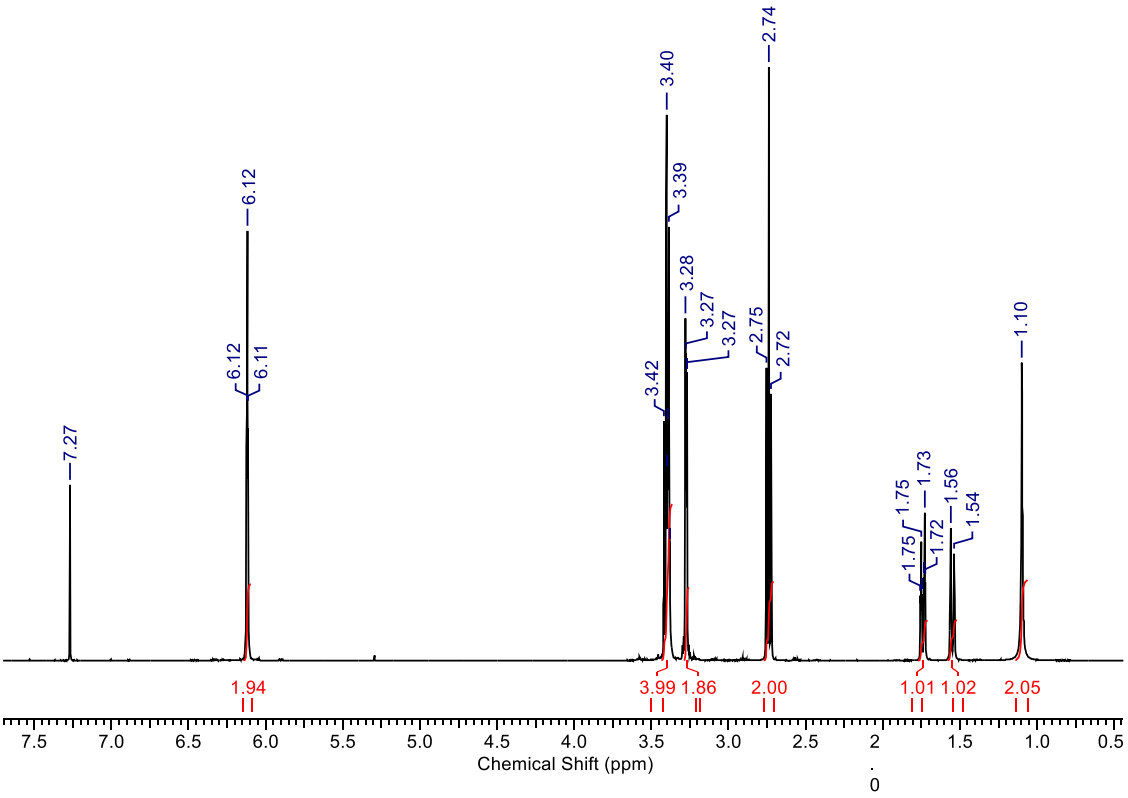


Figure S6: ^1H NMR of endo-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide, ***endo-8***

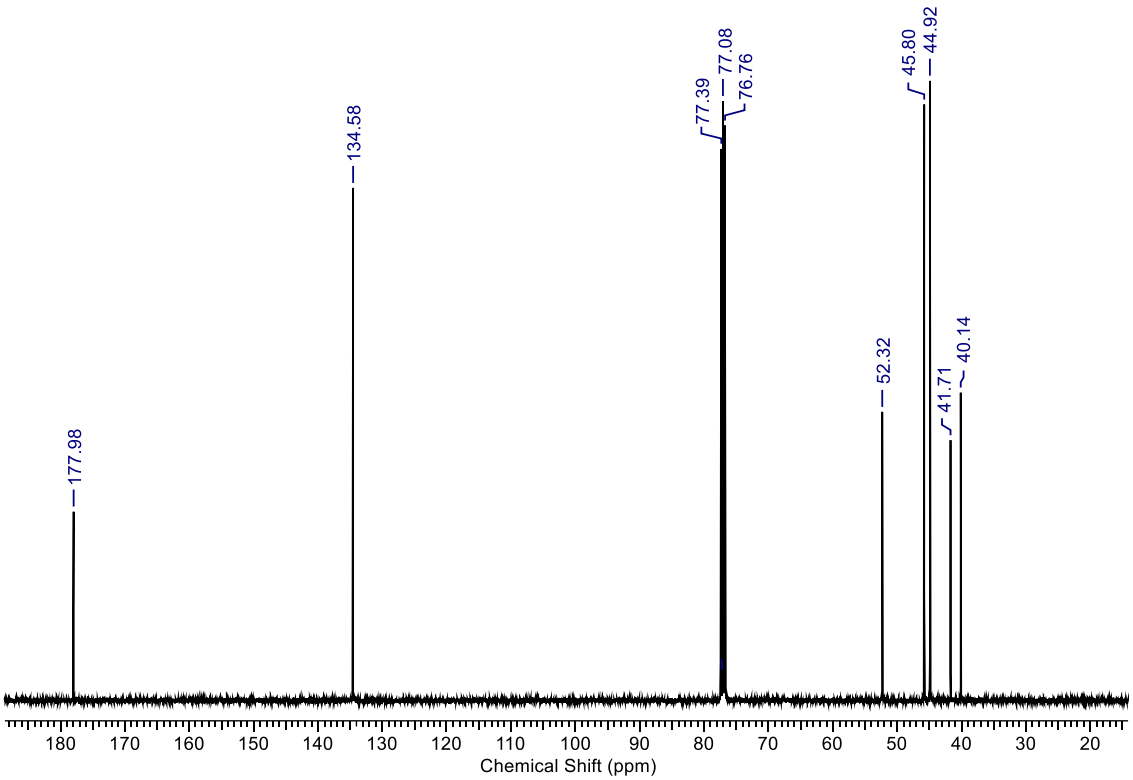
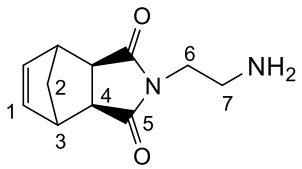


Figure S7: ^{13}C NMR of endo-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide, ***endo-8***

Exo-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide, ***exo-8***



Exo carbic anhydride **2** (5.0 g, 30.5 mmol) and toluene (80 cm^3) were added to a round-bottomed flask and stirred at room temperature until all solid had dissolved. Ethylenediamine (8.15 cm^3, 121.9 mmol) was slowly added to the stirring solution which caused a white precipitate to form. Additional toluene (50 cm^3) was added and the solution was stirred and heated under reflux overnight. The solution was left to cool, and the solvent was removed *in vacuo*, affording the crude product which was taken up in toluene (100 cm^3) and added to a separating funnel. Any additional residue was taken up in water (70 cm^3) and added to the separating funnel. The organic layer was extracted with water (2 x 50 cm^3), since the product is expected in the aqueous layer the organic toluene layer was disposed of. The aqueous layer was then extracted with DCM (3 x 50 cm^3) and brine (2 x 25 cm^3). The combined organic DCM washings were dried over $MgSO_4$, filtered by gravity and the solvent removed *in vacuo*, yielding a yellow oil which slowly crystallised as ***exo-8*** (2.37 g, 38%). m.p.: 70 – 72 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.16 (*br s, 2H, NH_2*), 1.33 (*dt, J = 9.8, 1.4 Hz, 1H, 2'*), 1.49 (*dt, J = 9.9, 1.6 Hz, 1H, 2*), 2.68 (*d, J = 1.3 Hz, 2H, 4*), 2.87 (*t, J = 6.4 Hz, 2H, 7*), 3.25 (*t, J = 1.7 Hz, 2H, 3*), 3.52 (*t, J = 6.5 Hz, 2H, 6*), 6.26 (*t, J = 1.8 Hz, 2H, 1*); ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 39.95 (*C-7*), 41.45 (*C-6*), 42.84 (*C-2*), 45.19 (*C-3*), 47.86 (*C-4*), 137.82 (*C-1*), 178.39 (*C-5*); IR: ν_{max}/cm^{-1} 3385 (N-H amine stretching), 3329 (N-H amine stretching), 2984 (C-H alkane stretching), 2951 (C-H alkane stretching), 2882 (C-H alkane stretching), 2851 (C-H alkane stretching), 1763 (C=O stretching), 1682 (C=O dicarboximide stretching); LC-MS (ESI): calculated $[M+H]^+$ $[C_{11}H_{14}N_2O_2+H]^+$ 207.1, found 207.0.

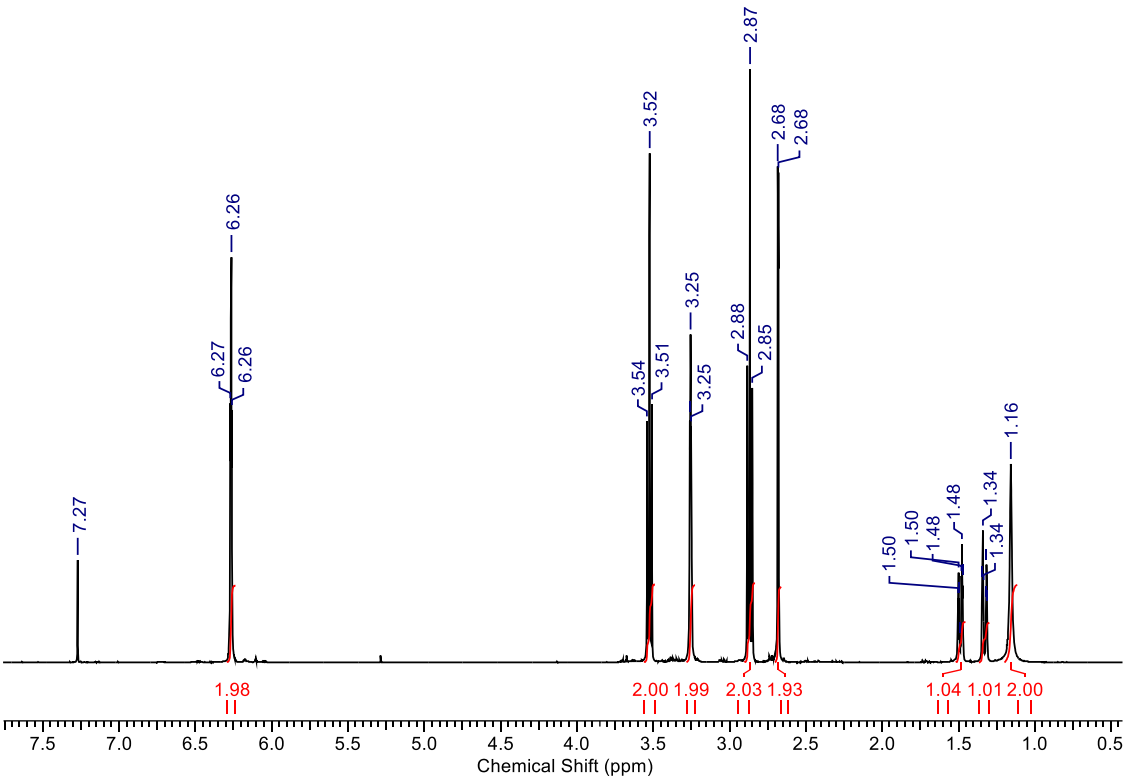


Figure S8: [1]H NMR of exo-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide, ***exo-8***

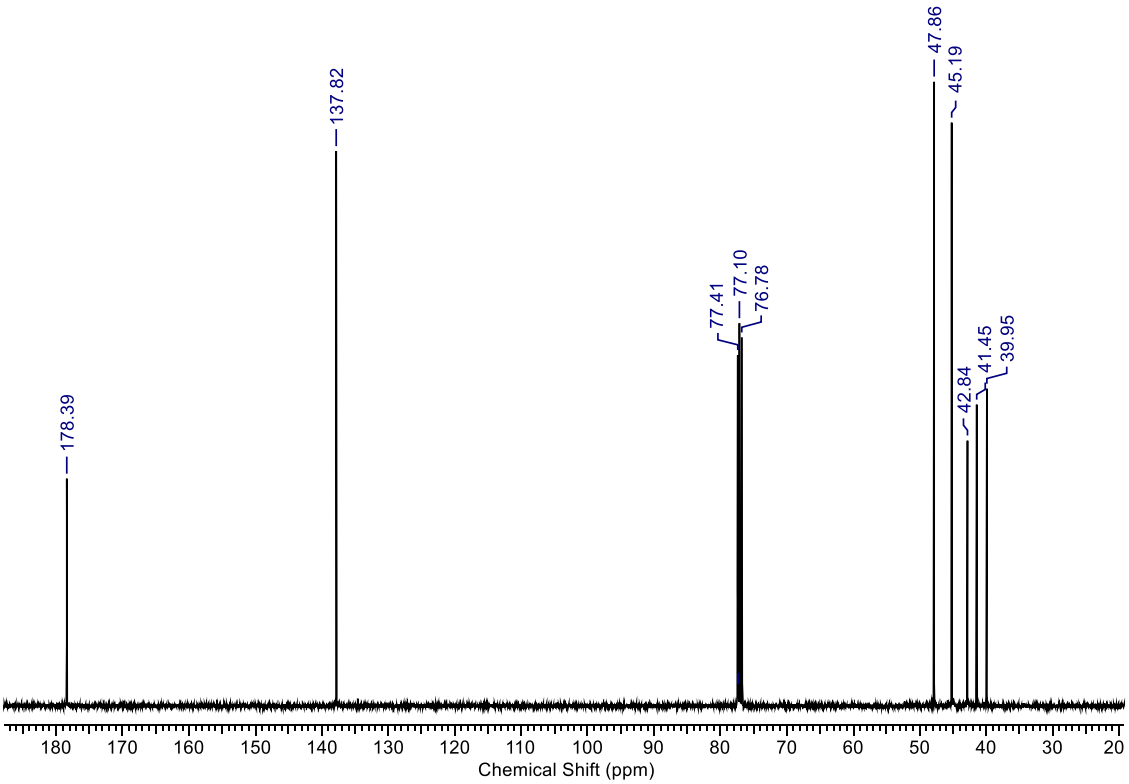
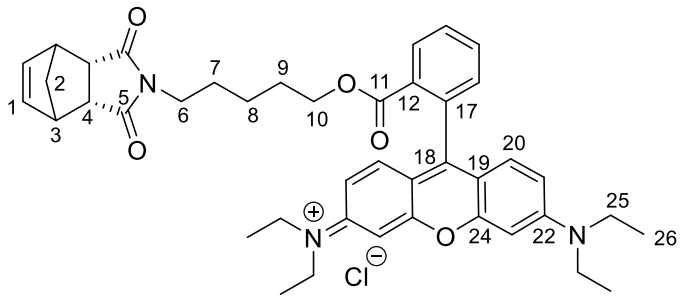


Figure S9: [13]C NMR of endo-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide, ***exo-8***

Endo-ester-RhB, ***endo*-7**



N-(hydroxypentanyl)-*cis*-5-norbornene-*endo*-2,3-dicarboximide ***endo*-6** (0.80 mg, 3.2 mmol), rhodamine-B (1.80 g, 3.8 mmol), DCC (1.13 g, 5.5 mmol) and DMAP (0.43 g, 3.53 mmol) were added to DCM (60 cm^3) and the solution was left to stir at room temperature. After 3 days the solvent was removed *in vacuo*, yielding the crude product. A sample of the crude product (300 mg), was weighed out and purified by column chromatography (R_f = 0.26, DCM:MeOH 15:1) which yielded the pure product ***endo*-7** as a shiny brown solid (136 mg, 6%). Note: This is just an isolated yield as only 300 mg of the crude was purified by column. ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.16 (*m, 2H, 8*), 1.35 (*t, J = 7.1 Hz, 12H, 26*), 1.39 (*m, 2H, 7*), 1.49 (*m, 2H, 9*), 1.57 (*d, J = 8.8 Hz, 1H, 2'*), 1.75 (*dt, J = 8.8 Hz, 1.5 Hz, 1H, 2*), 3.27 (*m, 4H, 4 & 6*), 3.39 (*d, J = 1.2 Hz, 2H, 3*), 3.67 (*m, 8H, 25*), 4.01 (*t, J = 6.5 Hz, 2H, 10*), 6.06 (*t, J = 1.8 Hz, 2H, 1*), 6.87 (*d, J = 2.4 Hz, 2H, 23*), 6.93 (*dd, J = 9.5, 2.4 Hz, 2H, 21*), 7.09 (*d, J = 9.5 Hz, 2H, 20*), 7.34 (*dd, J = 7.5, 1.0 Hz, 1H, 16*), 7.76 (*td, J = 7.7, 1.2 Hz, 1H, 14*), 7.84 (*td, J = 7.6, 1.3 Hz, 1H, 15*), 8.30 (*dd, J = 7.9, 1.0 Hz, 1H, 13*); ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 12.68 (*C-26*), 23.26 (*C-8*), 27.35 (*C-7*), 27.87 (*C-9*), 37.94 (*C-6*), 44.90 (*C-3*), 45.75 (*C-4*), 46.16 (*C-25*), 52.28 (*C-2*), 65.44 (*C-10*), 96.45 (*C-23*), 113.57 (*C-21*), 114.26 (*quaternary*), 129.99 (*quaternary*), 130.31 (*C-16*), 130.39 (*C-14*), 131.30 (*C-20*), 133.12 (*C-15 & C-13*), 134.41 (*C-1*), 155.59 (*quaternary*), 157.77 (*quaternary*), 158.88 (*quaternary*), 165.04 (*C-11*), 177.72 (*C-5*); IR: v_{max}/cm^{-1} 3356 (O-H stretching (starting material)), 3063 (C-H aromatic stretching), 2972 (C-H alkane stretching), 2932 (C-H alkane stretching), 2868 (C-H alkane stretching), 1763 (C=O stretching), 1715 (C=O ester stretching), 1690 (C=O dicarboximide stretching), 1647 (C=C alkene stretching), 1584 (C=C aromatic stretching).

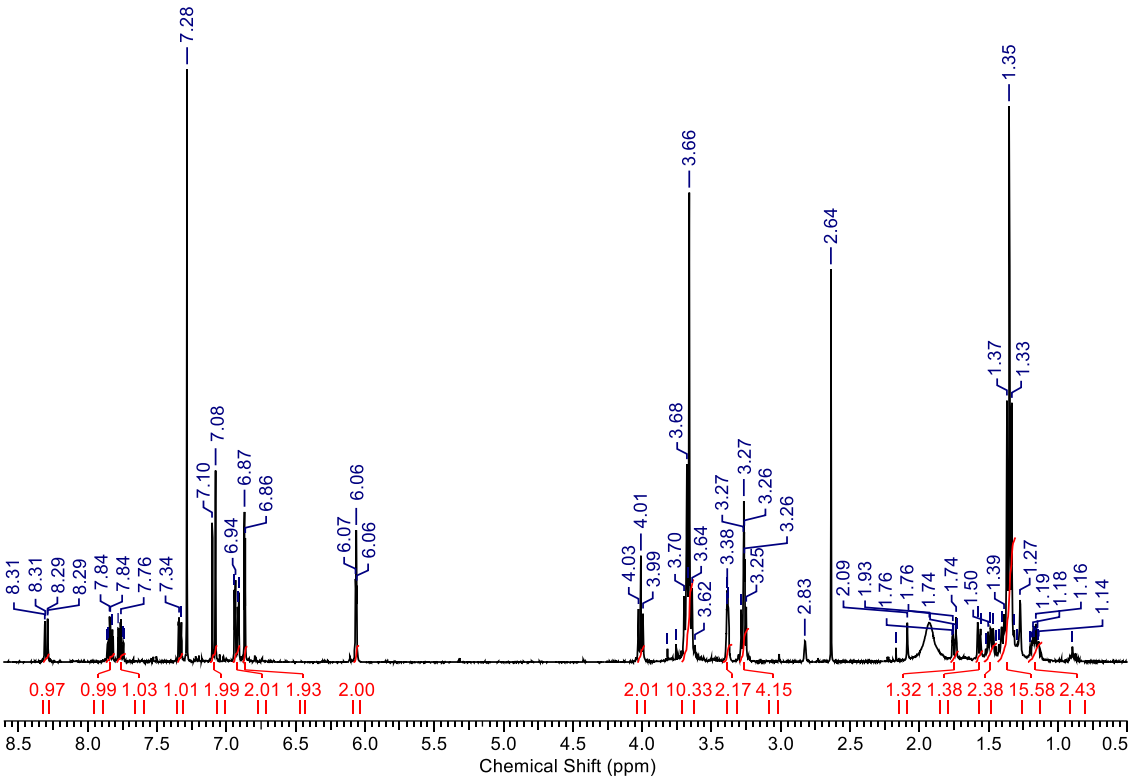


Figure S10: [1]H NMR of endo-ester-RhB, ***endo-7***

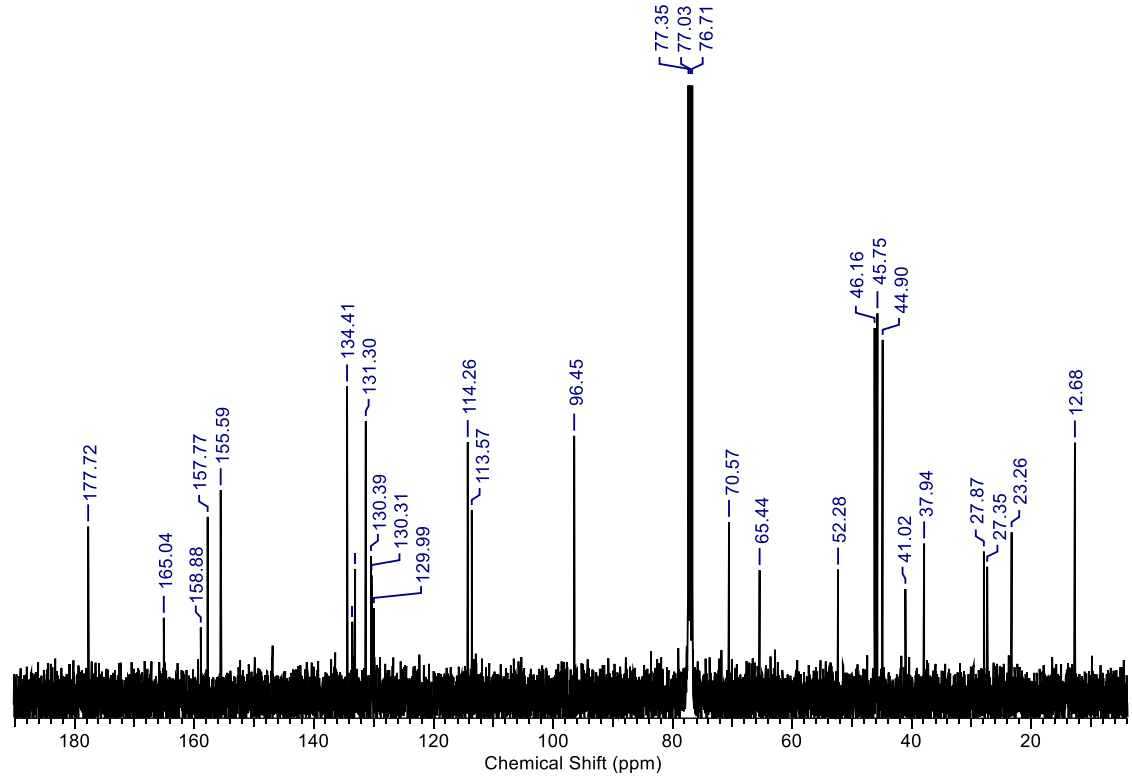
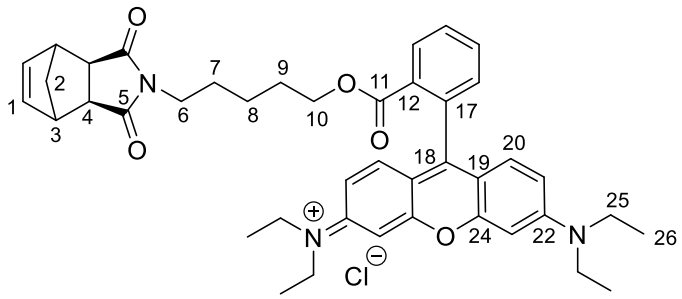


Figure S11: [13]C NMR of endo-ester-RhB, ***endo-7***

Exo-ester-RhB, ***exo*-7**



N-(hydroxypentanyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide ***exo*-6** (0.81 g, 3.2 mmol), DCC (1.13 g, 5.5 mmol), DMAP (0.43 g, 3.5 mmol), rhodamine-B (1.80 g, 3.8 mmol) and DCM (60 cm^3) were added to a round-bottomed flask and the solution was stirred at room temperature for 24 hours. Once complete, the solvent was removed *in vacuo*, yielding the crude product as a shiny brown solid. Column chromatography (R_f = 0.28, DCM:MeOH 15:1) was used twice in order to obtain pure ***exo*-7** (0.736 g, 32 %). m.p.: 120 – 130 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.19 (*m, 2H, 8*), 1.24 (*m, 1H, 2'*), 1.34 (*t, J = 7.1 Hz, 12H, 26*), 1.50 (*m, 5H, 2, 7 & 9*), 2.68 (*d, J = 0.9 Hz, 2H, 4*), 3.26 (*s, 2H, 3*), 3.40 (*t, J = 7.6 Hz, 2H, 6*), 3.66 (*m, 8H, 25*), 4.02 (*t, J = 6.5 Hz, 2H, 10*), 6.30 (*t, J = 1.7 Hz, 2H, 1*), 6.85 (*d, J = 2.4 Hz, 2H, 23*), 6.93 (*dd, J = 9.5, 2.4 Hz, 2H, 21*), 7.08 (*d, J = 9.5 Hz 2H, 20*), 7.32 (*dd, J = 7.5, 0.9 Hz, 1H, 16*), 7.75 (*m, 1H, 14*), 7.83 (*m, 1H, 15*), 8.29 (*dd, J = 7.9, 1.0 Hz, 1H, 13*); ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 12.68 (*C-26*), 23.37 (*C-8*), 27.35 (*C-7*), 27.88 (*C-9*), 38.27 (*C-6*), 42.71 (*C-2*), 45.15 (*C-3*), 46.17 (C-*25*), 47.81 (C-*4*), 65.37 (C-*10*), 96.40 (C-*23*), 113.54 (*quaternary*), 114.28 (C-*21*), 129.97 (*quaternary*), 130.30 (C-*16*), 130.39 (C-*14*), 131.30 (C-*20 &* C-*13*), 133.12 (*C-15*), 133.57 (*quaternary*), 137.80 (*C-1*), 155.58 (*quaternary*), 157.75 (*quaternary*), 158.86 (*quaternary*), 165.03 (*C-11*), 178.02 (*C-5*); IR: ν_{max}/cm^{-1} 3360 (O-H stretching (starting material)), 3057 (C-H aromatic stretching), 2972 (C-H alkane stretching), 2932 (C-H alkane stretching), 2868 (C-H alkane stretching), 1769 (C=O stretching), 1717 (C=O ester stretching), 1692 (C=O dicarboximide stretching), 1647 (C=C alkene stretching), 1582 (C=C aromatic stretching).

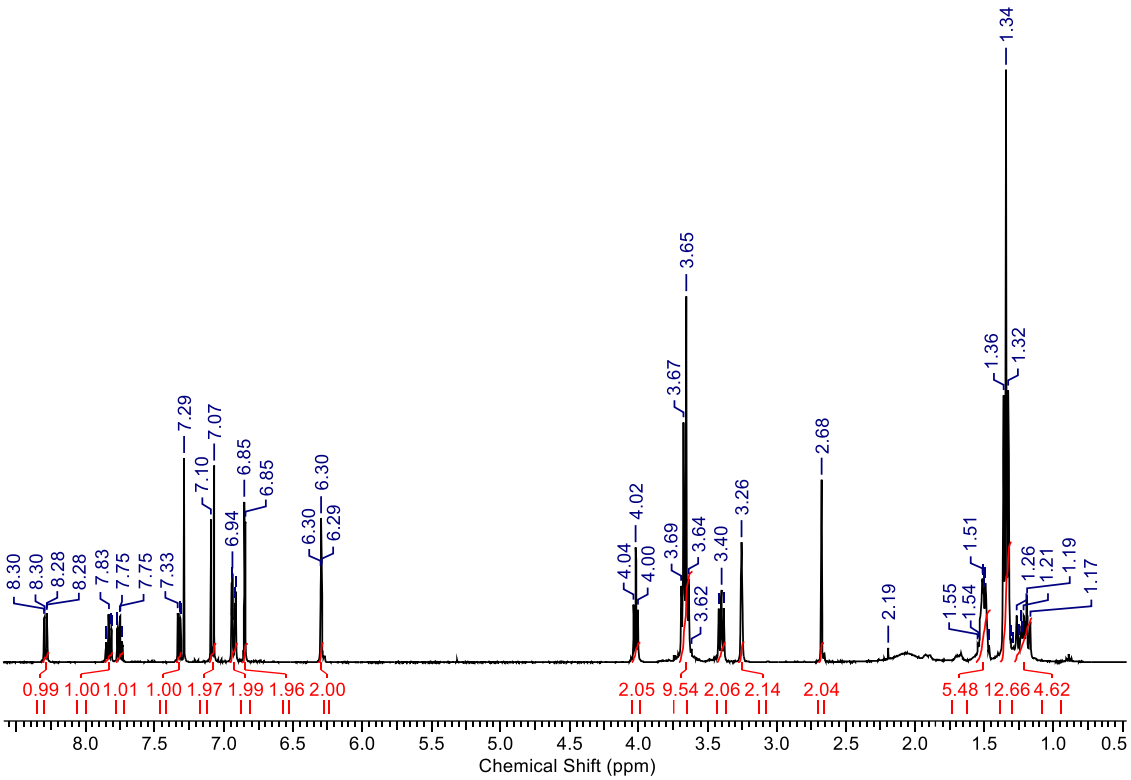


Figure S12: ^{1}H NMR of exo-ester-RhB, ***exo-7***

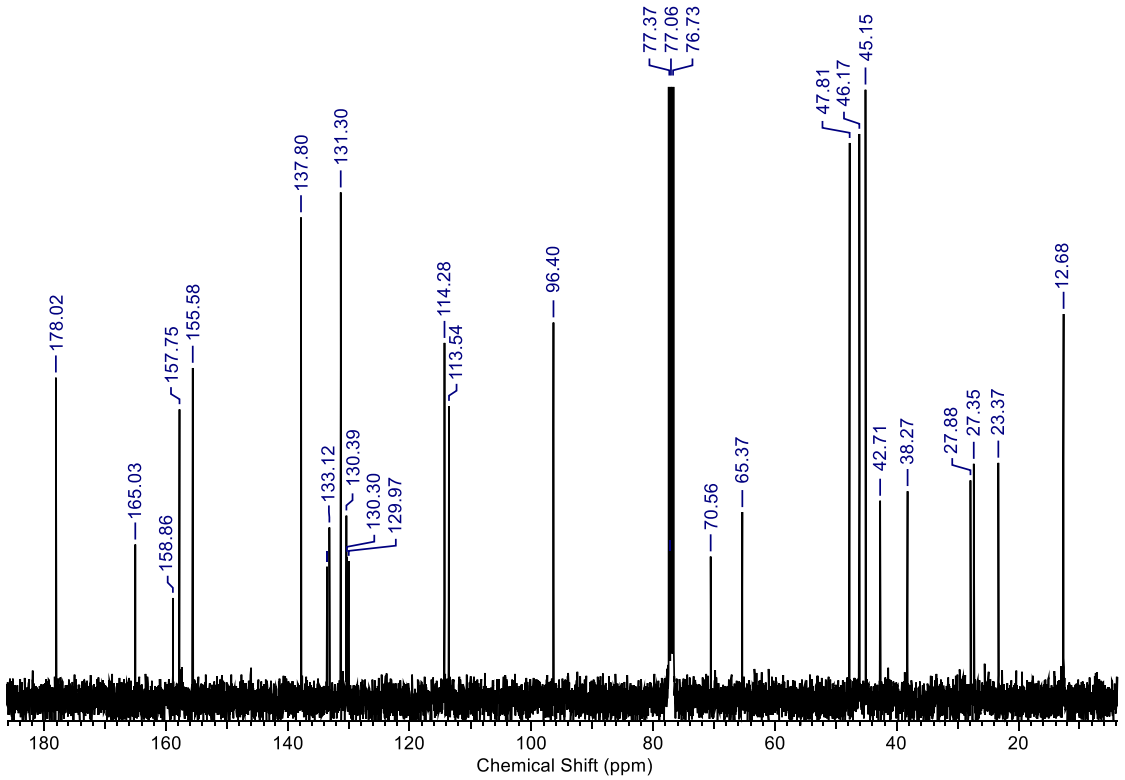
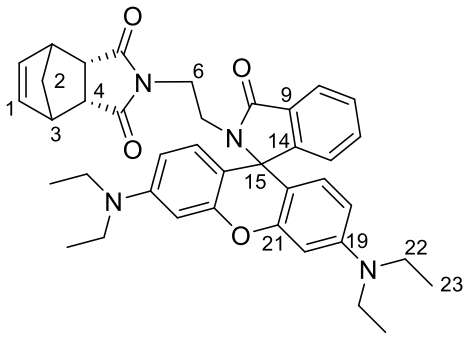


Figure S13: ^{13}C NMR of exo-ester-RhB, ***exo-7***

Endo-amide-RhB, ***endo*-10**



A flask was charged with *endo*-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide ***endo*-8** (0.33 g, 1.62 mmol), Rhodamine B (0.90 g, 1.88 mmol), EDC hydrochloride (0.53 g, 2.74 mmol), DMAP (0.22 g, 1.77 mmol) and DCM (60 cm^3). The solution was stirred at room temperature for 48 hours, after which the solvent was removed *in vacuo* leaving a purple residue. As much of the residue as possible was taken up in ethyl acetate (2 x 50 cm^3). Water (50 cm^3) was also added to the residue and as much of the residue was taken up in water as possible. The organic and aqueous phases were added to a separating funnel and the organic layer was extracted. The solvent was removed *in vacuo*, yielding ***endo*-10** as a purple solid (0.64 g, 59 %). m.p.: 174 – 176 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δppm 1.13 (*t, J = 7.1 Hz, 12H, 23*), 1.42 (*d, J = 8.6 Hz, 1H, 2'*), 1.61 (*d, J = 8.6 Hz, 1H, 2*), 2.98 (*s, 1H, NH open form*), 3.11 (*dd, J = 2.9, 1.5 Hz, 2H, 4*), 3.20 (*s, 4H, 6 & 7*), 3.23 (*m, 2H, 3*), 3.30 (*m, 8H, 22*), 5.94 (*t, J = 1.7 Hz, 2H, 1*), 6.26 (*dd, J = 8.9, 2.6 Hz, 2H, 18*), 6.37 (*d, J = 2.6 Hz, 2H, 20*), 6.45 (*d, J = 8.9 Hz, 2H, 17*), 6.99 (*m, 1H, 13*), 7.35 (*m, 1H, 11*), 7.38 (*m, 1H, 12*), 7.82 (*m, 1H, 10*) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 12.64 (*C-23*), 37.39 (*C-6*), 38.29 (*C-7*), 44.50 (*C-22*), 45.95 (*C-4*), 52.09 (*C-2*), 65.23 (*quaternary*), 97.79 (*C-20*), 105.43 (*quaternary*), 108.07 (*C-18*), 122.72 (*C-10*), 123.78 (*C-13*), 127.95 (*C-11*), 129.09 (*C-17*), 130.90 (*quaternary*), 132.40 (*C-12*), 134.34 (*C-1*), 148.73 (*quaternary*), 153.40 (*quaternary*), 153.59 (*quaternary*), 168.72 (*C-8*), 177.58 (*C-5*); IR: ν_{max}/cm^{-1} 2974 (C-H alkane stretching), 2932 (C-H alkane stretching), 2891 (C-H alkane stretching), 2874 (C-H alkane stretching), 1771 (C=O stretching), 1734 (C=O stretching), 1695 (C=O amide stretching), 1684 (C=O dicarboximide stretching), 1616 (C=C alkene stretching), 1516 (C=C aromatic stretching).

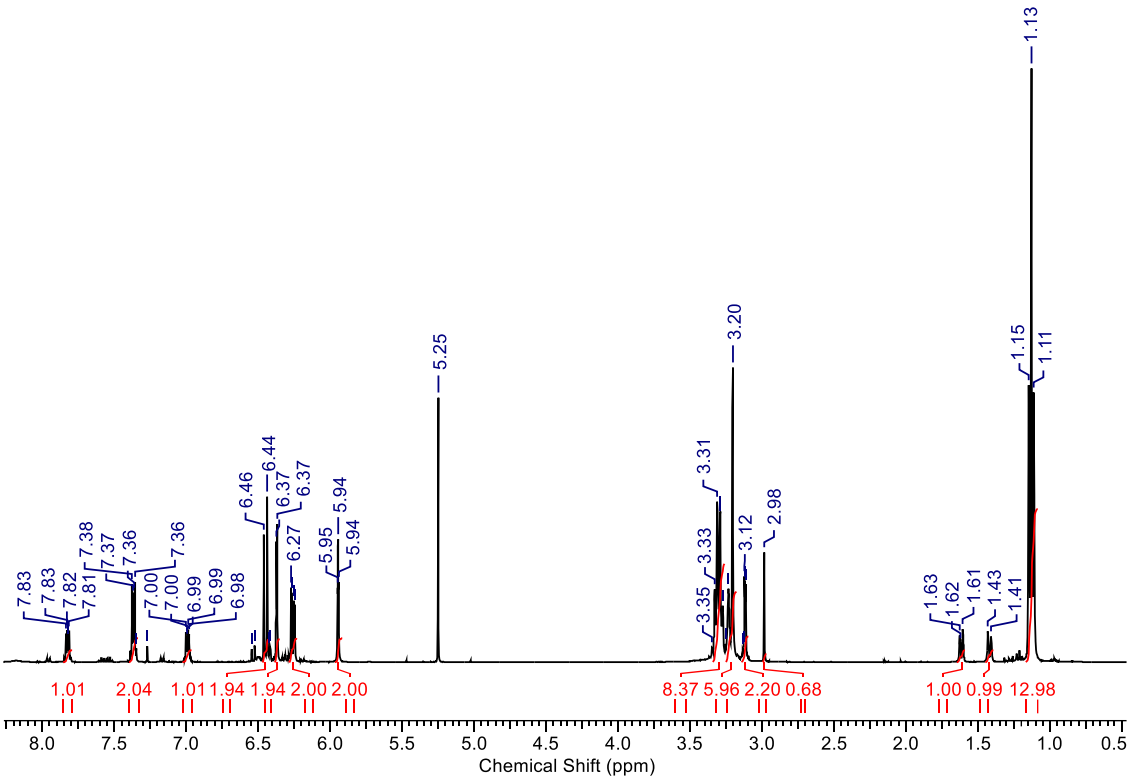


Figure S14: ^{1}H NMR of endo-amide-RhB, ***endo-10***

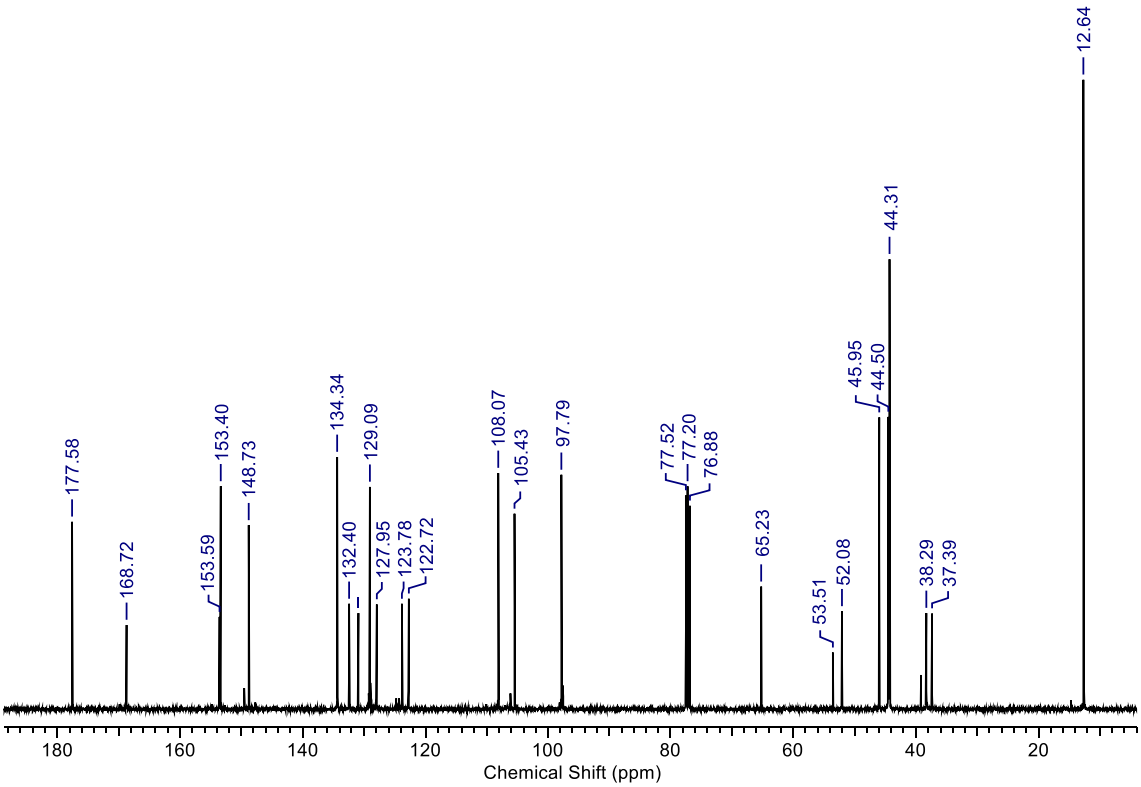


Figure S15: ^{13}C NMR of endo-amide-RhB, ***endo-10***

Crystallisation of *endo*-amide-RhB, ***endo*-10**

Single crystals of $C_{41}H_{46}N_4O_5$ (***endo*-10**).0.5(EtOAc) were grown by slow evaporation of a solution of ***endo*-10** in ethyl acetate. A suitable crystal was selected and mounted on a SuperNova diffractometer equipped with an AtlasS2 detector. The crystal was kept at 293(2) K during data collection. Using Olex2,[1] the structure was solved with the olex2.solve[2] structure solution program using charge flipping and refined with the SHELXL[3] refinement package using least squares minimisation.

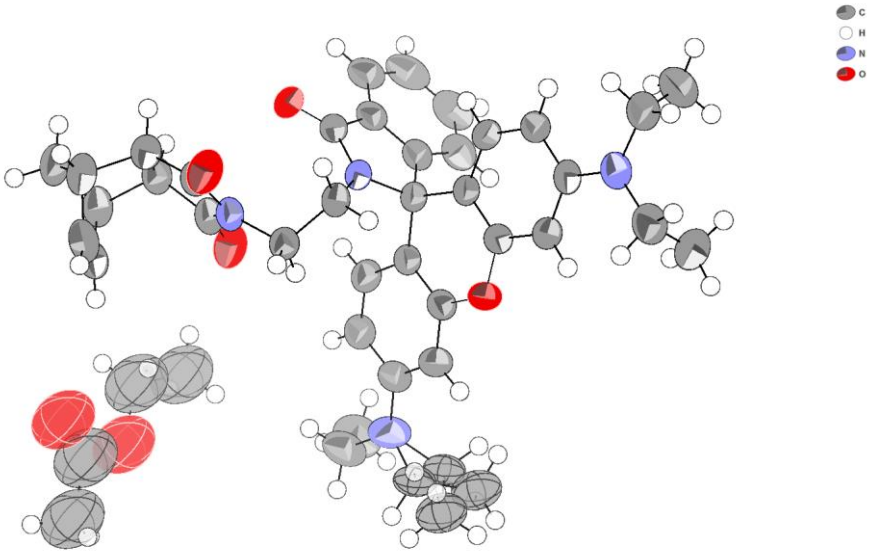
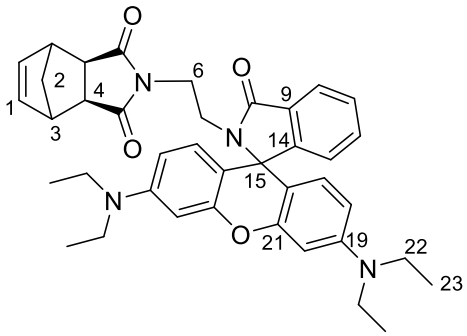


Figure S16: X-ray crystal structure of endo-10. Atomic displacement parameters are shown at 50% probability.

Crystal Data for ***endo*-10**, $C_{41}H_{46}N_4O_5$ (M =670.78 g/mol): triclinic, space group *P*-1 (no. 2), a = 10.4936(3) Å, b = 12.3484(3) Å, c = 16.1383(4) Å, α = 99.335(2)°, β = 102.497(2)°, γ = 112.561(2)°, V = 1814.32(9) Å^3, Z = 2, T = 293(2) K, μ(CuK$_\alpha$) = 0.653 mm^{-1}, D_{calc} = 1.228 g/cm^3, 31068 reflections measured (8.058° ≤ 2ϑ ≤ 146.788°), 7133 unique (R_{int} = 0.0295, R_{sigma} = 0.0203) which were used in all calculations. The final R_1 was 0.0512 (I > 2σ(I)) and wR_2 was 0.1571 (all data).

An ethyl acetate solvate was heavily disordered across a special position within the structure and as a consequence, heavy restraints were required to model this disorder. Further details can be found in the crystallographic information file. CCDC Deposition Number: 2005042

Exo-amide-RhB, ***exo*-10**



Exo-N-(2-aminoethyl)-5-norbornene-2,3-dicarboximide ***exo*-8** (0.33 g, 1.6 mmol), EDC-hydrochloride (0.53 mg, 2.7 mmol) and DMAP (0.22 g, 1.8 mmol) were added to DCM (60 cm^3) in a round-bottomed flask and stirred until all solid had dissolved. Rhodamine-B (0.90 g, 1.9 mmol) was added to the stirring

solution which was stoppered and left to stir at room temperature for 3 days. The solvent was then removed *in vacuo*, leaving the crude product as a purple solid. Ethyl acetate (2 x 60 cm^3) was added to the crude residue and was swirled vigorously to dissolve as much as possible before being transferred to a separating funnel. Water (2 x 50 cm^3) was also added to the crude residue and swirled vigorously to dissolve as much as possible before transfer to the separating funnel. The organic layer was extracted, and the aqueous layer was washed with ethyl acetate (2 x 25 cm^3). The combined organic extracts were back extracted with water (25 cm^3). The organic extracts were dried over $MgSO_4$, filtered by gravity and the solvent was removed *in vacuo* yielding the product as a pink/purple solid ***exo*-10** (0.49 g, 46%). m.p. 132 – 135 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.10 (*t, J = 6.6 Hz, 13 H, 23 & 2'*), 1.34 (*d, J = 9.5 Hz, 1H, 2*), 2.49 (*s, 2H, 4*), 2.92 (*s, 1H, NH open form*), 3.09 (*s, 2H, 3*), 3.27 (*m, 10H, 22 & 7*), 3.37 (*t, J = 5.7 Hz, 2H, 6*), 6.14 (*s, 2H, 1*), 6.22 (*dd, J = 8.9, 2.6 Hz, 2H, 18*), 6.34 (*d, J = 2.4 Hz, 2H, 20*), 6.43 (*d, J = 8.8 Hz, 2H, 17*), 6.95 (*m, 1H, 13*), 7.32 (*m, 1H, 11*), 7.34 (*m, 1H, 12*), 7.80 (*m, 1H, 10*); ^{13}C NMR (100 MHz, $CDCl_3$): δ_{ppm} 12.65 (*C-23*), 37.81 (*C-6*), 38.41 (*C-7*), 43.06 (*C-2*), 44.27 (*C-22*), 44.83 (*C-3*), 47.92 (*C-4*), 65.28 (*quaternary*), 97.74 (*C-20*), 105.38 (*quaternary*), 108.03 (*C-18*), 122.69 (*C-10*), 123.79 (*C-13*), 127.98 (*C-11*), 129.05 (*C-17*), 130.89 (*quaternary*), 132.44 (*C-12*), 137.63 (*C-1*), 148.72 (*quaternary*), 153.42 (*quaternary*), 153.58 (*quaternary*), 168.82 (*C-8*), 177.91 (*C-5*); IR: ν_{max}/cm^{-1} 2968 (C-H alkane stretching), 2918 (C-H alkane stretching), 2872 (C-H alkane stretching), 2849 (C-H alkane stretching), 1773 (C=O stretching), 1749 (C=O stretching), 1697 (C=O amide stretching), 1636 (C=C alkene stretching), 1541 (C=C aromatic stretching), 1508 (C=C aromatic stretching).

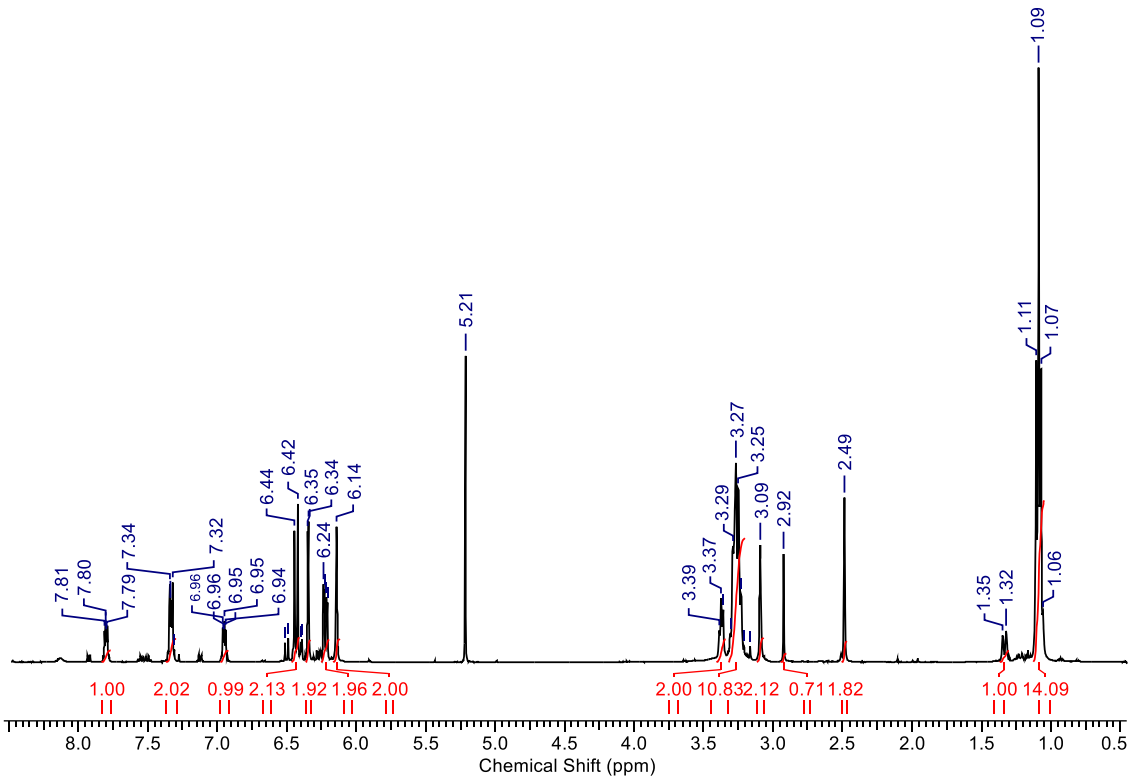


Figure S17: ^1H NMR of exo-amide-RhB, ***exo*-10**

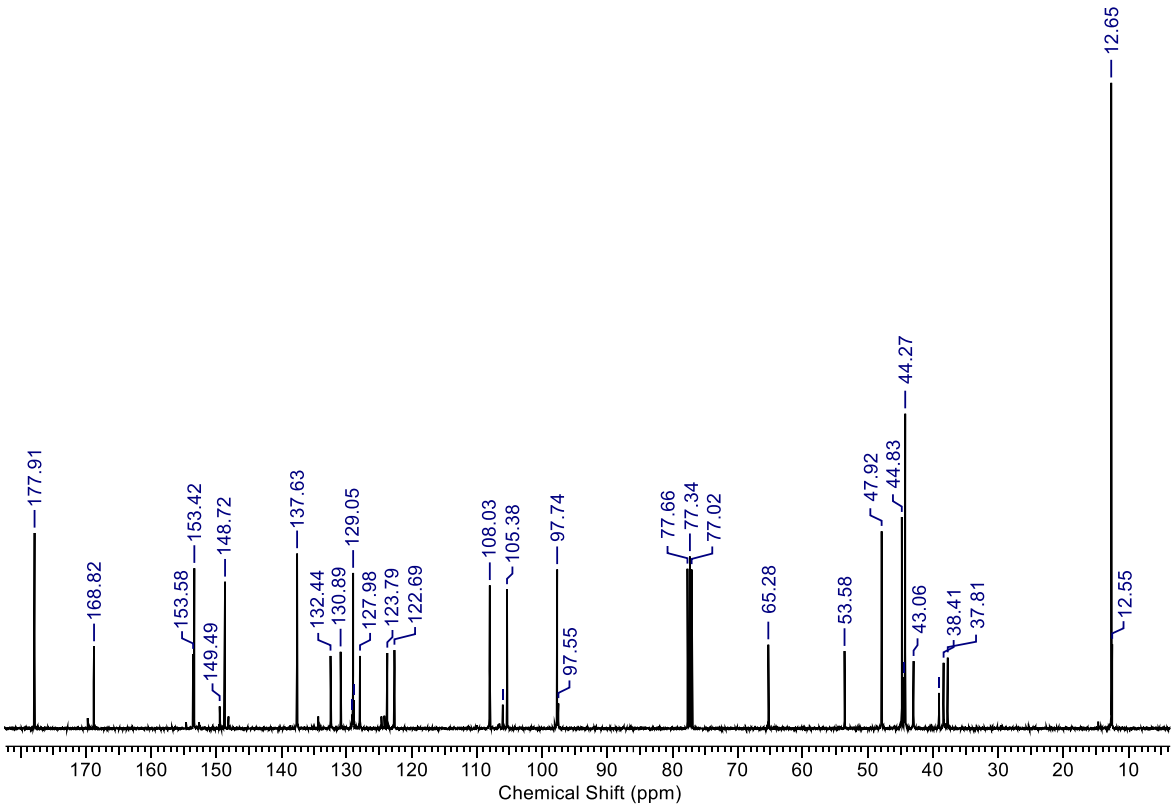


Figure S18: ^{13}C NMR of exo-amide-RhB, ***exo-10***

Crystallisation of *exo*-amide-RhB, ***exo*-10**

Single crystals of $C_{39}H_{42}N_4O_4$ ***exo*-10** were grown from a solution of ***exo*-10** in DMSO. A suitable crystal was selected and mounted on a SuperNova diffractometer equipped with an AtlasS2 detector. The crystal was kept at 293(2) K during data collection. Using Olex2,[1] the structure was solved with the olex2.solve[2] structure solution program using charge flipping and refined with the SHELXL[3] refinement package using least squares minimisation.

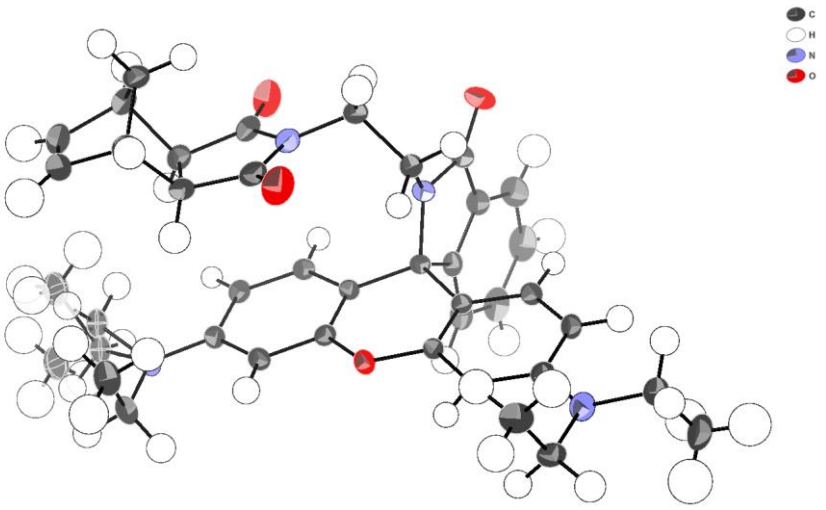
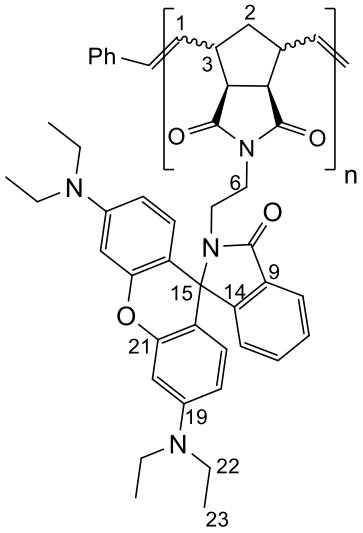


Figure S19: X-ray crystal structure of ***exo-10****. Atomic displacement parameters are shown at 50% probability.*

Crystal Data for ***exo*-10**, $C_{39}H_{42}N_4O_4$ (M =630.76 g/mol): orthorhombic, space group *Pbca* (no. 61), a = 15.72214(17) Å, b = 19.9433(2) Å, c = 20.9335(3) Å, V = 6563.71(13) Å3, Z = 8, T = 150.0(3) K, μ(CuKα) = 0.663 mm^{-1}, D_{calc} = 1.277 g/cm^3, 23316 reflections measured (8.314° ≤ 2ϑ ≤ 146.198°), 6468 unique (R_{int} = 0.0285, R_{sigma} = 0.0239) which were used in all calculations. The final R_1 was 0.0366 (I > 2σ(I)) and wR_2 was 0.0948 (all data). CCDC Deposition Number: 2005041

Homopolymerisation: Poly(nor-amide-RhB), poly *exo*-10



Grubbs 3rd generation catalyst (1.0 mg, 0.001 mmol) was taken up in dry DCM (0.5 mL) and stirred until all solid had dissolved. The solution was added to *exo*-amide RhB ***exo*-10** (15.1 mg, 0.02 mmol) and allowed to stir at room temperature under inert atmosphere for 100 min. The reaction was quenched by the addition of ethyl vinyl ether (1 drop) and the solution was left to stir for an additional 30 min. The solution was transferred to a PCR tube, where the solvent was removed by blowing with compressed air until a small amount of solvent remained. Diethyl ether (2 mL) was added to the PCR tube, causing a precipitate to form. The PCR tube was placed on a centrifuge to collect the precipitate, after which the remaining solvent was decanted off. The solid was washed again with diethyl ether (2 x 2 mL) and the product was dried under high vacuum affording **poly *exo*-10** as a purple solid (11 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.13 (H-*23*), 1.46 (H-*2*), 1.71 (H-*4*), 2.84 (*6 & 7*), 3.11 (H-*3*), 3.30 (H-*22*), 5.42 (H-*1 cis*), 5.73 (H-*2 trans*), 6.35 (H-*18*), 6.45 (H-*20*), 6.59 (H-*17*), 6.98 (H-*13*), 7.34 (H-*11 & 12*), 7.81 (H-*10*). GPC: M_n = 8 800, M_w = 11 800, Đ = 1.35.

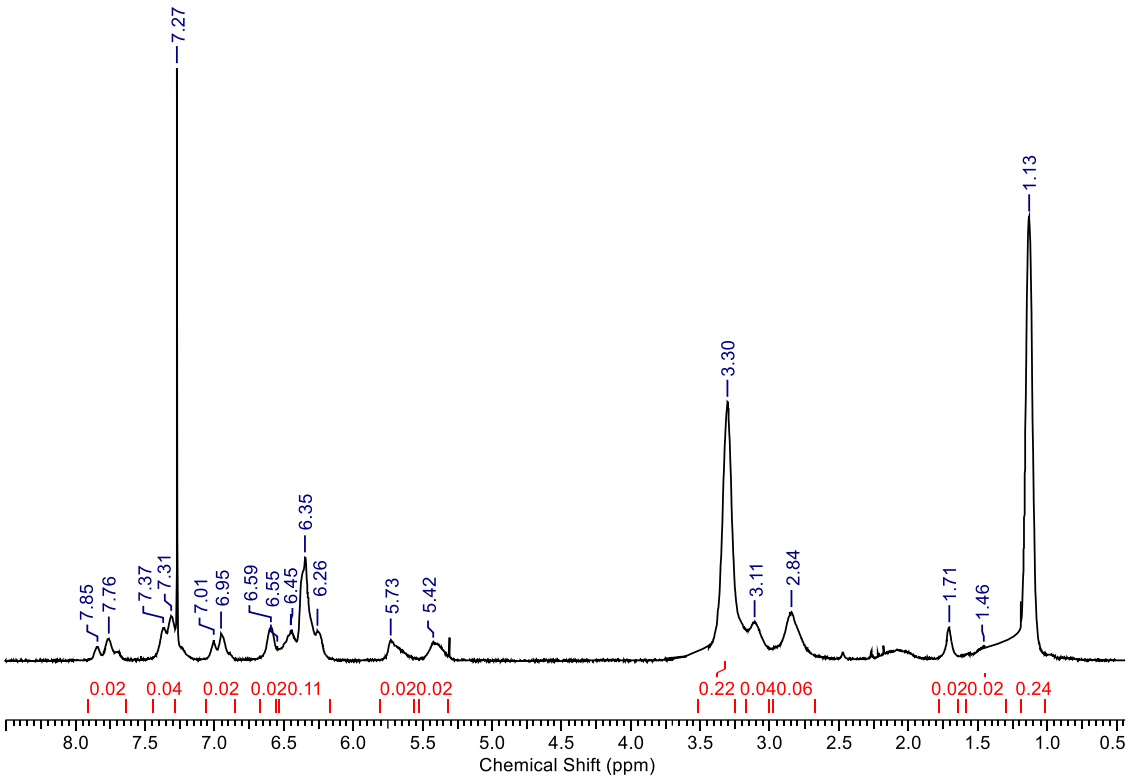
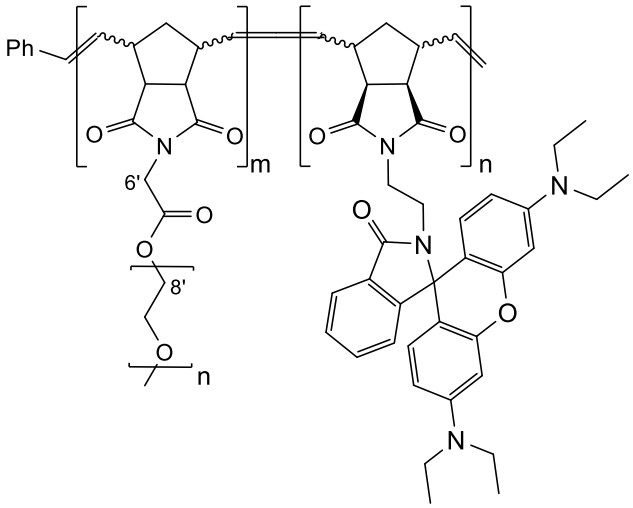


Figure S20: ^{1}H NMR of poly(nor-amide-RhB), ***poly-10***

Block copolymer: poly(nor-PEGOMe)-b-poly(nor-amide-RhB), **poly 5-*b*-*exo*-10**



Under an inert atmosphere, the 3rd generation Grubbs catalyst (3 mg, 0.0034 mmol) was dissolved in anhydrous DCM (1.5 mL) and added to *N*-(exo-himoyl)-glycine poly(ethylene glycol) ester monomer ***exo*-6** (51 mg, 0.068 mmol). During the reaction the colour changed from a green solution to a pale brown solution. After 10 minutes, a solution of *exo*-amide-RhB monomer, ***exo*-10** (45 mg, 0.068 mmol) in anhydrous DCM (0.3 mL) was added to the former reaction mixture and left to stir for 10 minutes. The reaction was then terminated by ethyl vinyl ether and stirred for further 20 minutes. The solvent was removed in *vacuo* until a minimum amount of solvent was left. The polymer was purified by

precipitation from diethyl ether affording **poly 5-*b-exo*-10** as a purple solid (77 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_{ppm} 1.13 (H-*23*), 1.43 (H-*2*), 2.21 (H-*4*), 2.83 (*6 & 7*), 3.11 (H-*3*), 3.30 (H-*22*), 3.38 (H-*10'*), 3.56 – 3.54 (H-*9'*), 3.66 (H-*PEG*), 4.27 (H-*6'* & *8'*), 5.49 (H-*1 cis*), 5.72 (H-*2 trans*), 6.25 – 6.58 (H-*18 & 20*), 6.98 (H-*13*), 7.34 (H-*11 & 12*), 7.81 (H-*10*); GPC: M_n = 17 000, M_w = 21 800, Đ = 1.29.

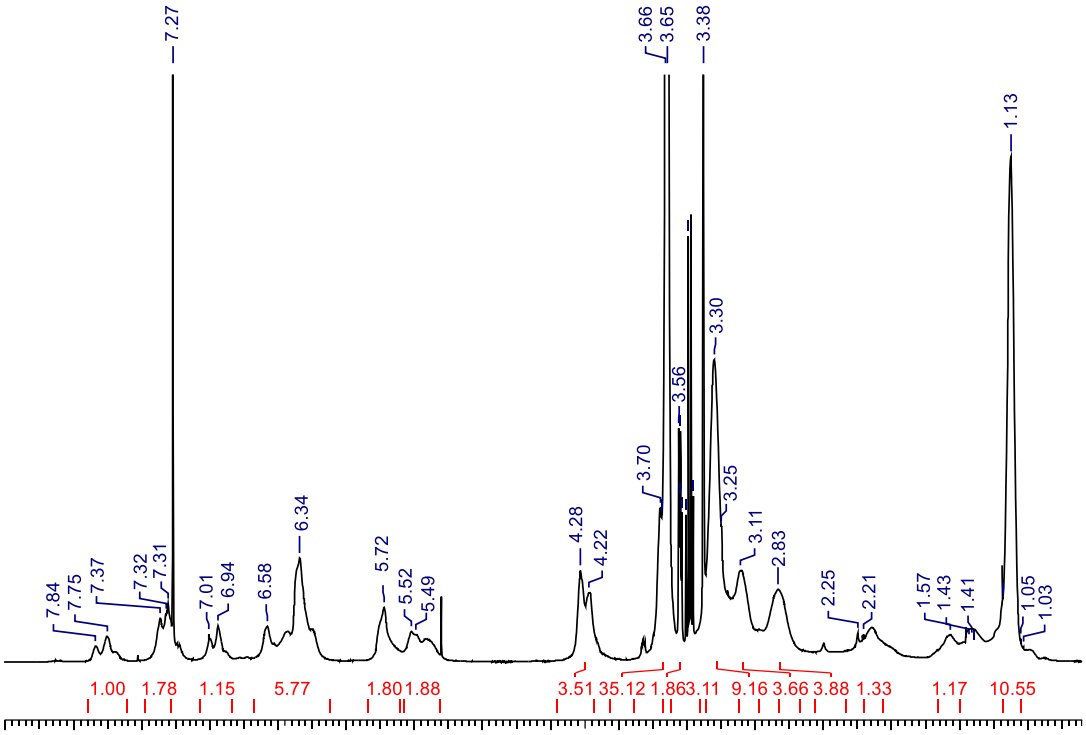


Figure S21: ^{1}H NMR of poly(nor-PEGOMe)-b-poly(nor-amide-RhB), ***poly (5-b-10)***

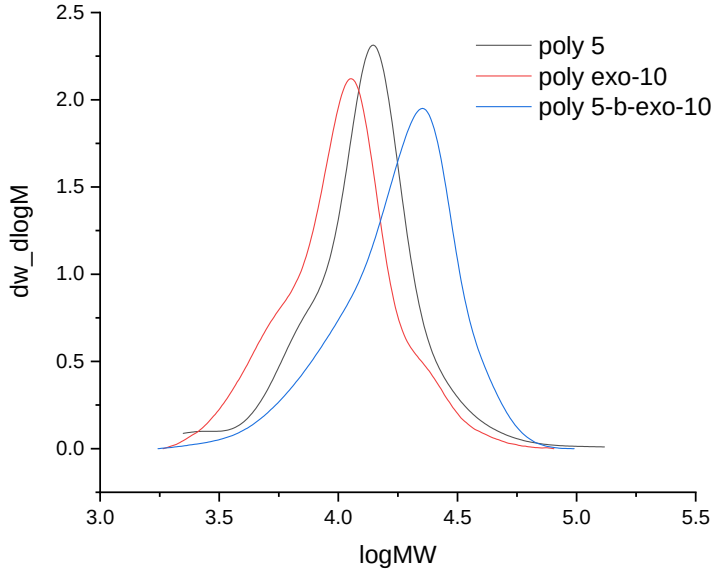


*Figure S22: GPC traces of homopolymers poly-**5** (reference 2) and poly exo-**10** and copolymer poly **5**-**b**-exo-**10**.*

Co-assembly procedure for the micelles and dyes for the FRET measurements

Co-assembly procedure for the micelles and dyes for the FRET measurements was as follows: the solution of micelles which had already been self-assembled were mixed with a solution of the dye in a PCR tube and the PCR tube was put on the vortex stirrer to mix it well and then it was put on the centrifuge before being analysed by fluorescence spectrometry. A 1:1 ratio of RhB unit : 6-FAM (or other added dye) was used, and the ratio was not varied.

Characterisation of Micelles

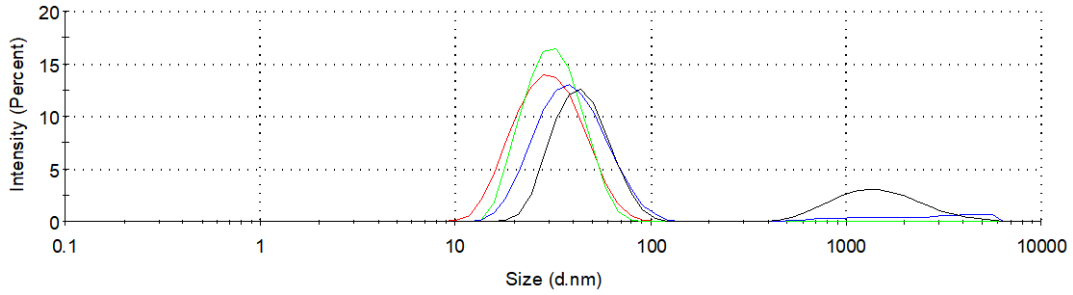


*Figure S23: DLS size distributions by intensity for poly **5-b**-exo-**10** self-assembled from acetone in water. Red = 0.1 mg/mL, green = 0.01 mg/mL, blue = 0.001 mg/mL, black =0.0001 mg/mL.*

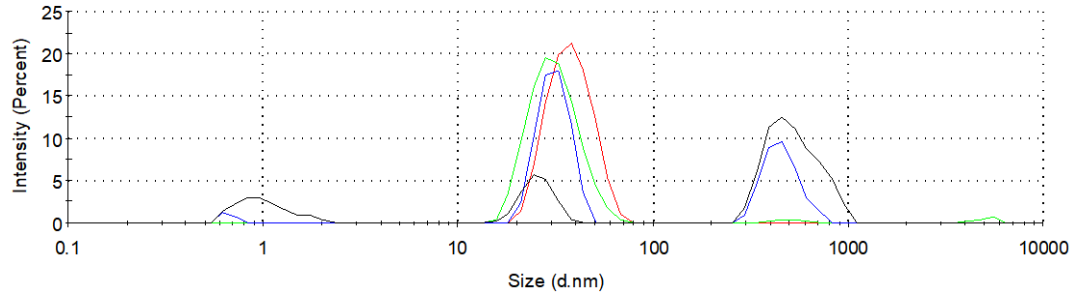


*Figure S24: DLS size distributions by intensity for poly **5-b**-exo-**10** self-assembled from acetone in TBE buffer. Red = 0.1 mg/mL, green = 0.01 mg/mL, blue = 0.001 mg/mL, black =0.0001 mg/mL.*

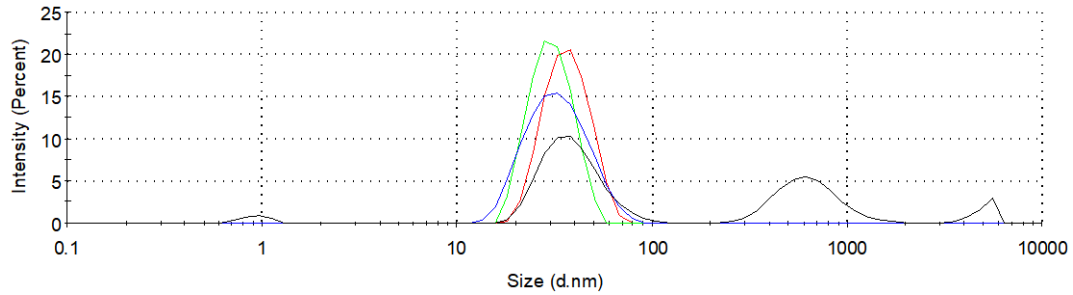


*Figure S25: DLS size distributions by intensity for poly **5-b**-exo-**10** self-assembled from acetone in TAMg buffer. Red = 0.1 mg/mL, green = 0.01 mg/mL, blue = 0.001 mg/mL, black =0.0001 mg/mL.*

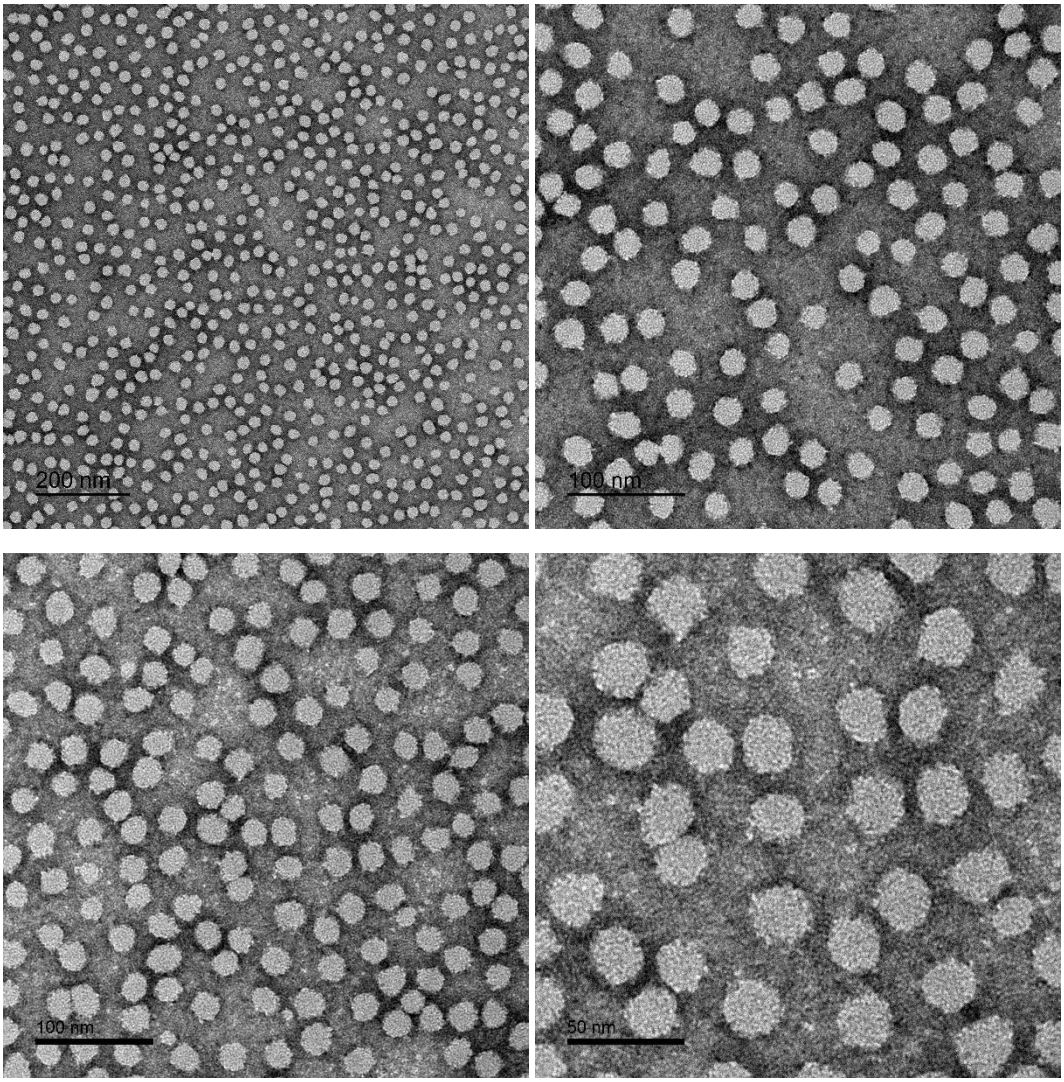


*Figure S26: TEM images of poly **5-b**-exo-**10** self-assembled from acetone in water.*

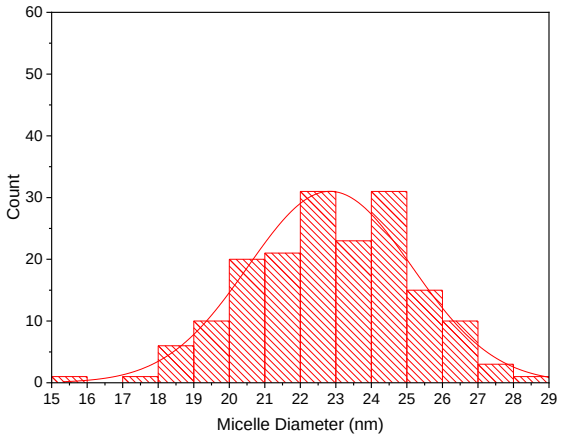


*Figure S27: Size distribution of poly **5-b**-exo-**10** micelles from acetone in water. Average nanoparticles size (22 ± 2 nm).*

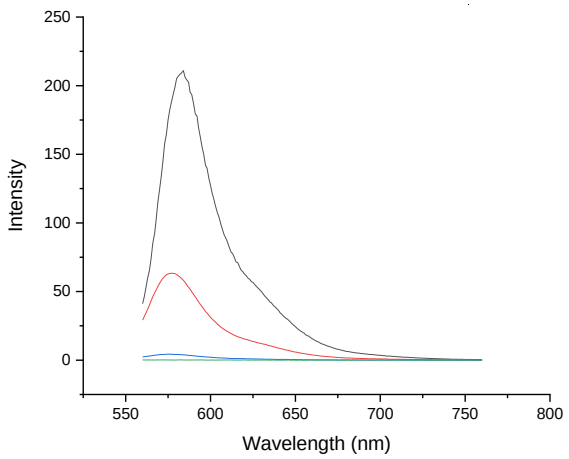


*Figure S28: Fluorescence spectra of poly **5-b**-exo-**10** self-assembled from acetone in water. Black = 0.1 mg/mL, red = 0.01 mg/mL, blue = 0.001 mg/mL, green =0.0001 mg/mL. λ_{ex} = 550 nm.*

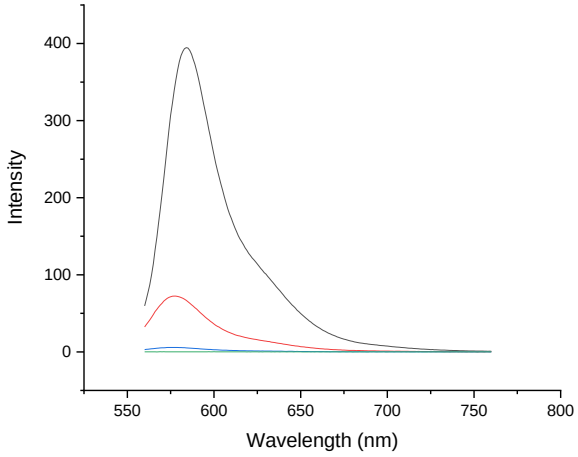


*Figure S29: Fluorescence spectra of poly **5-b**-exo-**10** self-assembled from acetone in TBE buffer. Black = 0.1 mg/mL, red = 0.01 mg/mL, blue = 0.001 mg/mL, green =0.0001 mg/mL. λ_{ex} = 550 nm.*

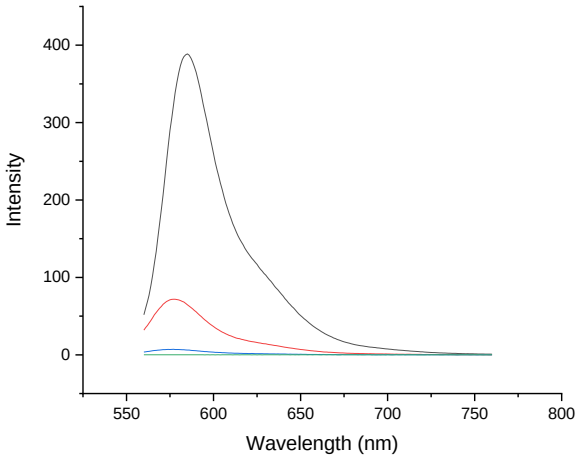


*Figure S30: Fluorescence spectra of poly **5-b**-exo-**10** self-assembled from acetone in TAMg buffer. Black = 0.1 mg/mL, red = 0.01 mg/mL, blue = 0.001 mg/mL, green =0.0001 mg/mL. λ_{ex} = 550 nm.*

Interaction with DNA

Poly **5-b-*exo*-10** (1 mmol wrt. monomer) in THF (20 µL) and either no DNA, DNA1 (1 mmol wrt. bases), DNA2 (complement to DNA1, 1 mmol wrt. bases) or a mix of both DNA1 & DNA2 in the specific buffer solution (water, TBE 1x or TAMg 1x,) (200 µL) were combined to give a final volume of 220 µL. These solutions were analysed by DLS and fluorescence spectroscopy where each measurement was repeated three times and averaged.

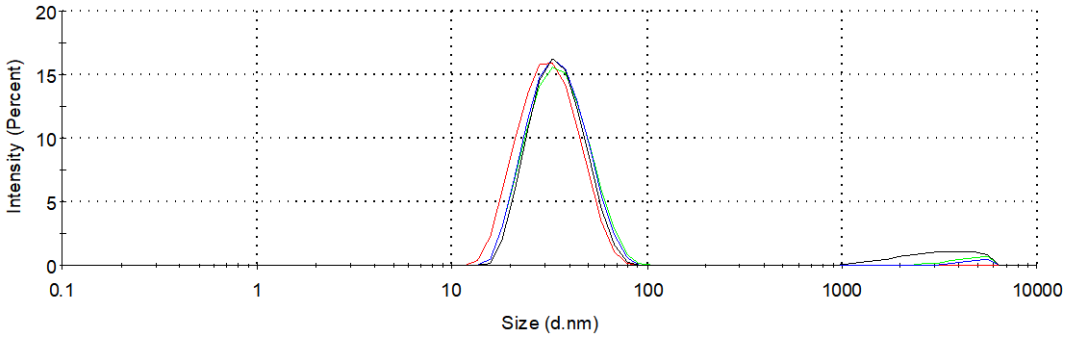


*Figure S31: DLS size distributions by intensity for poly **5-b-**exo-**10** self-assembled from acetone in water with no DNA (red), ssDNA1 (green), ssDNA2 (blue), and dsDNA (black). Recorded at 150 µM w.r.t RhB and/or nucleobases.*

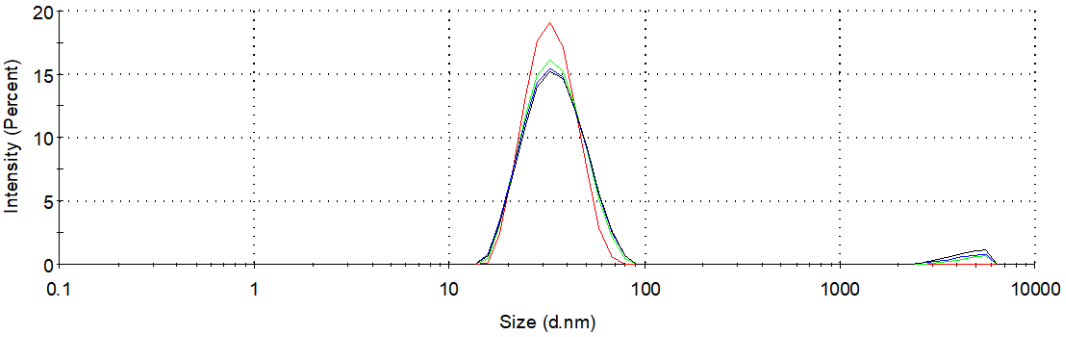


*Figure S32:. DLS size distributions by intensity for poly **5-b-**exo-**10** self-assembled from acetone in TBE buffer with no DNA (red), ssDNA1 (green), ssDNA2 (blue), and dsDNA (black). Recorded at 150 µM w.r.t RhB and/or nucleobases.*

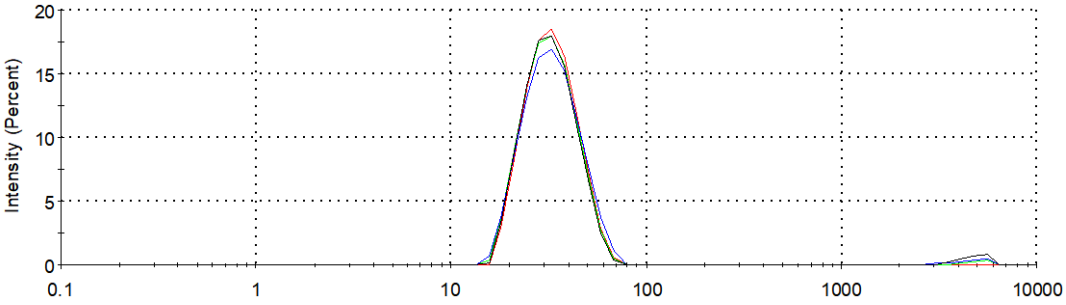


*Figure S33: DLS size distributions by intensity for poly **5-b-**exo-**10** self-assembled from acetone in TAMg buffer with no DNA (red), ssDNA1 (green), ssDNA2 (blue), and dsDNA (black). Recorded at 150 µM w.r.t RhB and/or nucleobases.*

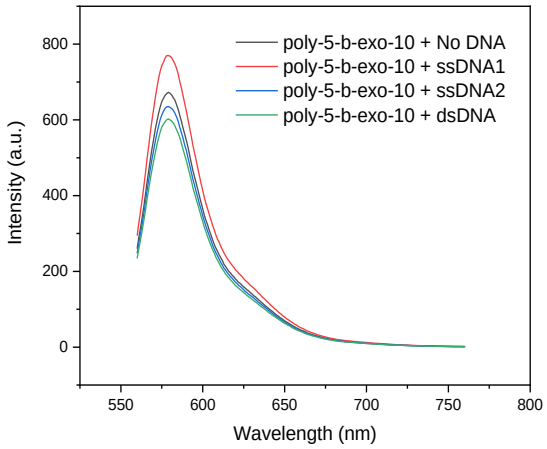


*Figure S34: Fluorescence spectra of poly **5-b**-exo-**10** micelles from acetone in acetate buffer (pH 5) with and without DNA.*

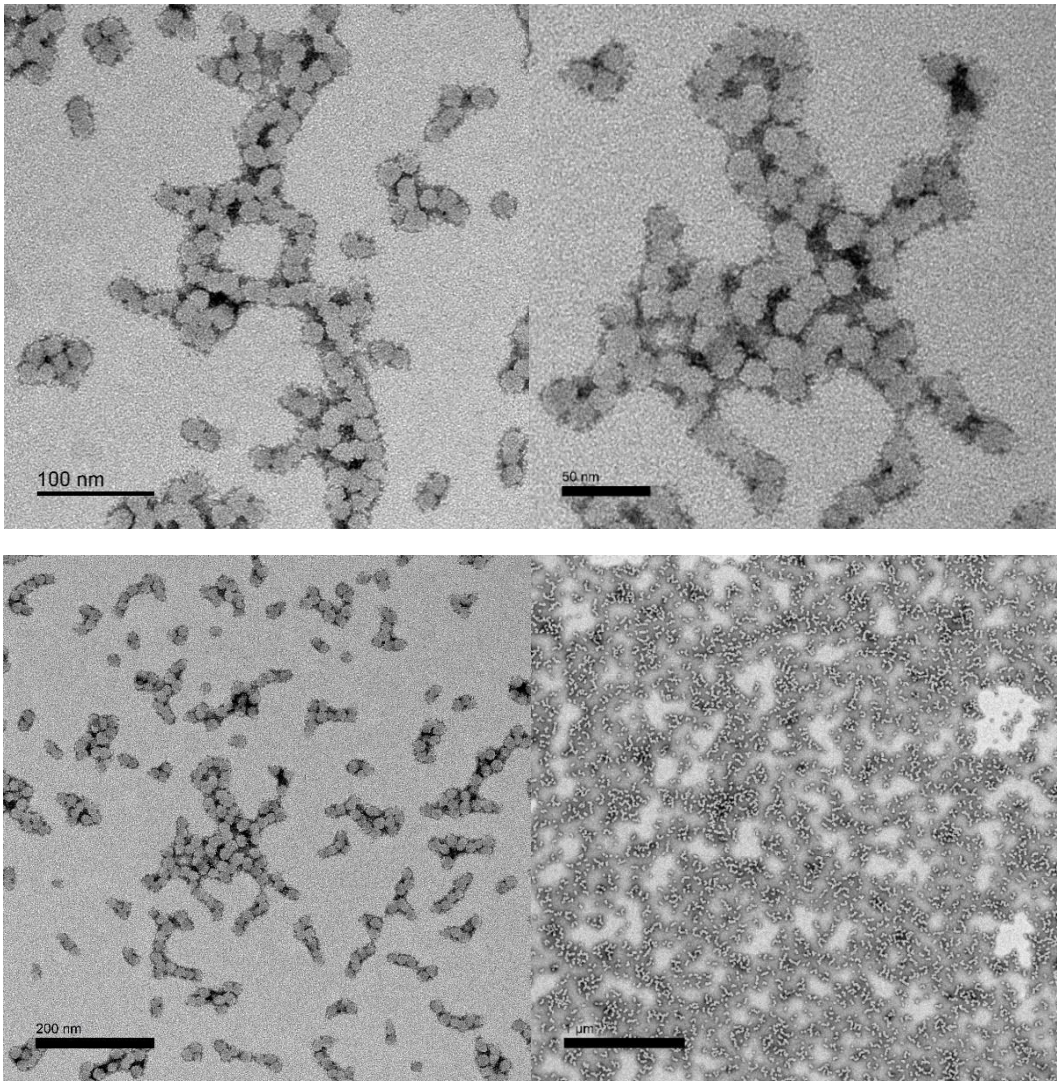


*Figure S35: TEM images of poly **5-b**-exo-**10** micelles (acetone into TAMg) in the absence of DNA after annealing from 95 C to 4 C over 1 hr. Negatively stained using uranyl acetate.*

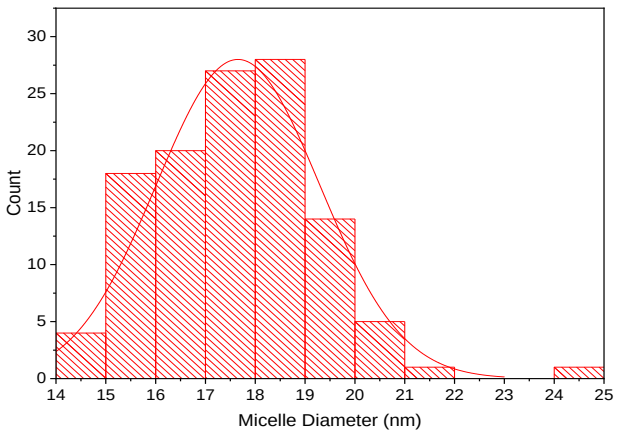


*Figure S36: Size distribution of poly-**5-b**-exo-**10** from acetone in TAMg in absence of DNA after annealing from 95 C to 4 C over 1 hr. Average nanoparticles size (18 ± 2).*

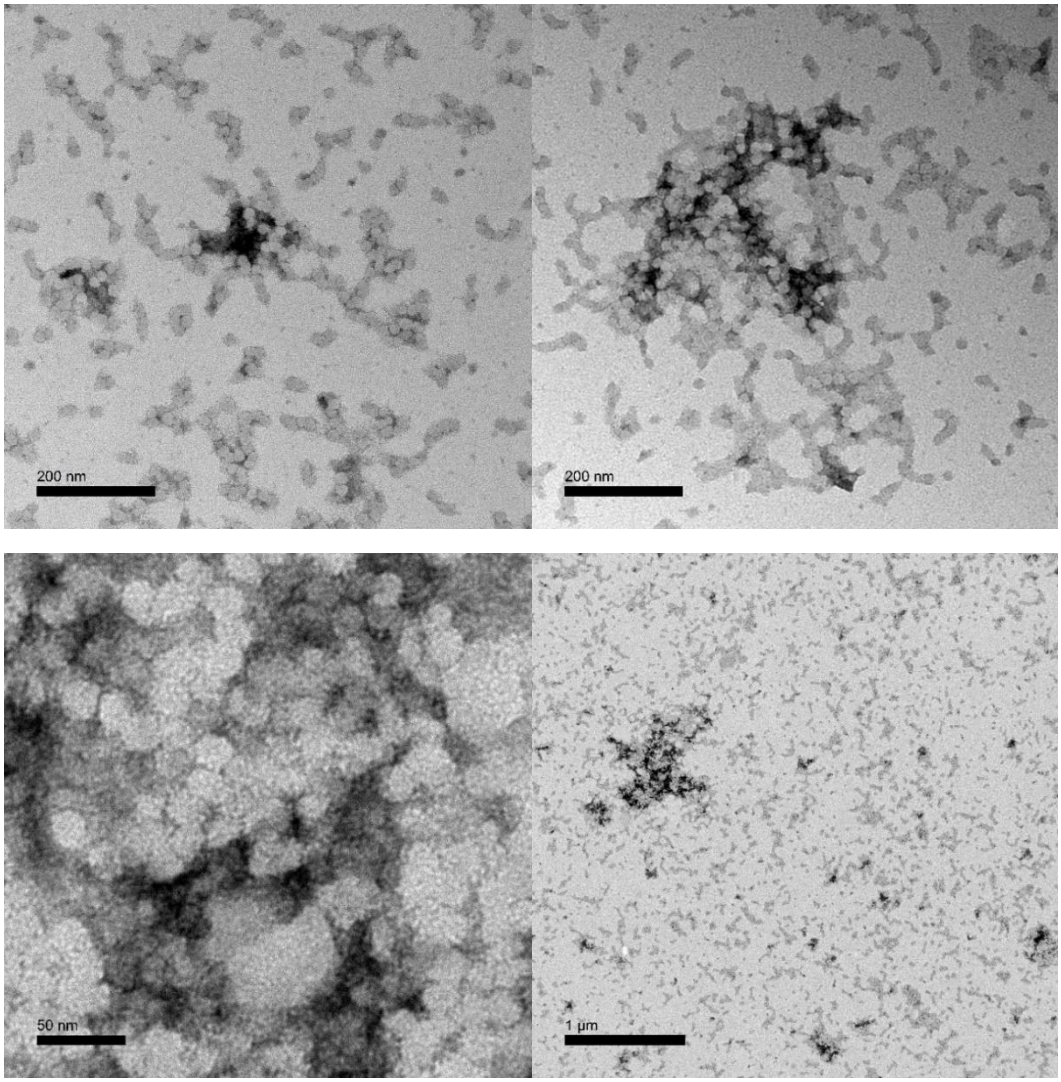


*Figure S37: TEM images of poly-**5-b**-exo-**10** micelles (acetone into TAMg) with ssDNA1 after annealing from 95 C to 4 C over 1 hr. Negatively stained using uranyl acetate.*

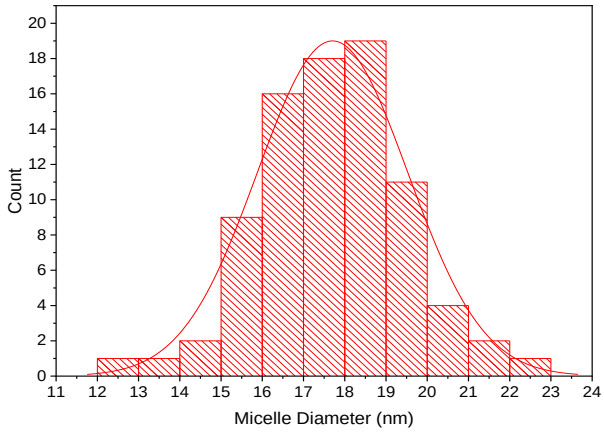


*Figure S38: Size distribution of poly-**5-b**-exo-**10** from acetone in TAMg in presence of ssDNA1 after annealing from 95 C to 4 C over 1 hr. Average nanoparticles size (18 ± 2).*

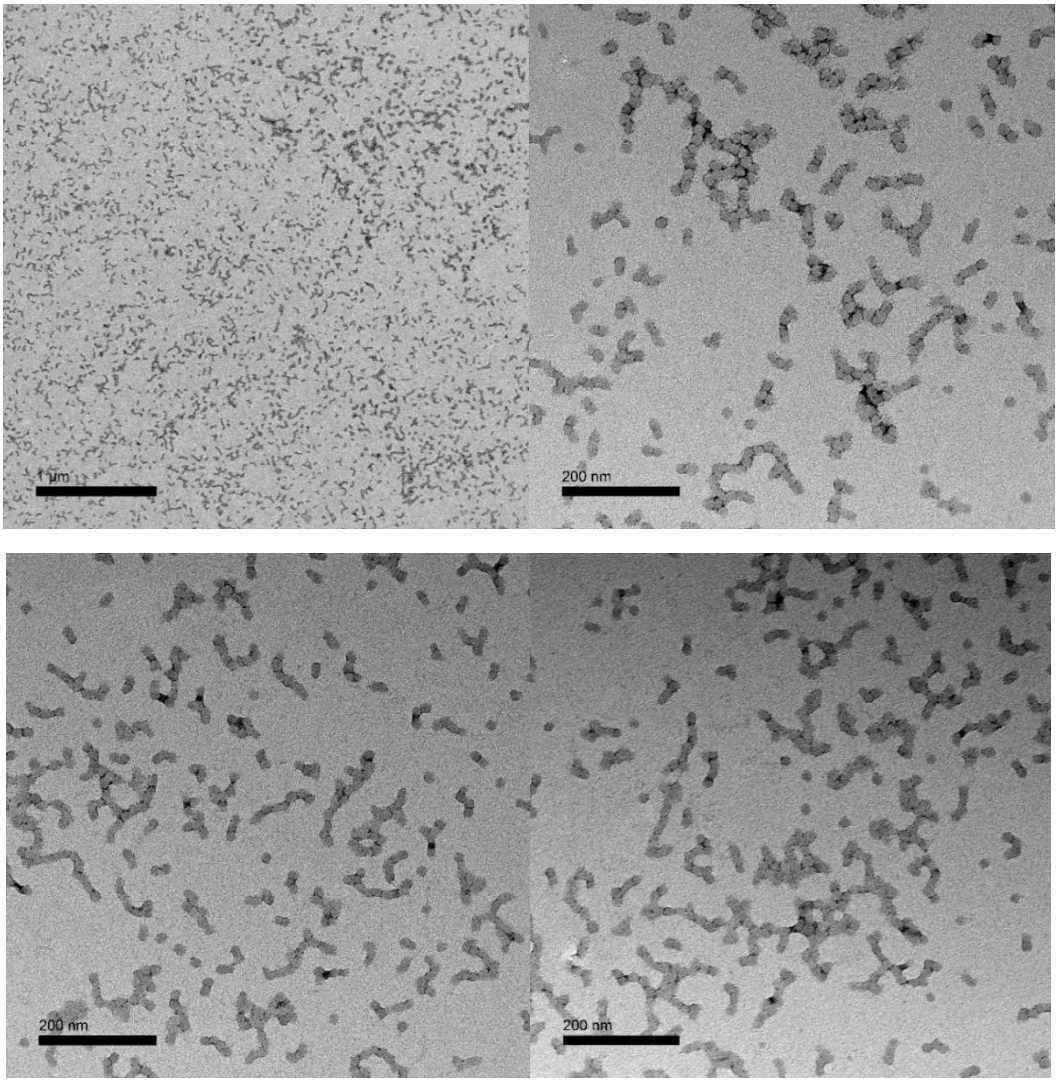


*Figure S39: TEM images of poly **5-b**-exo-**10** micelles (acetone into TAMg) with ssDNA2 after annealing from 95 C to 4 C over 1 hr. Negatively stained using uranyl acetate.*

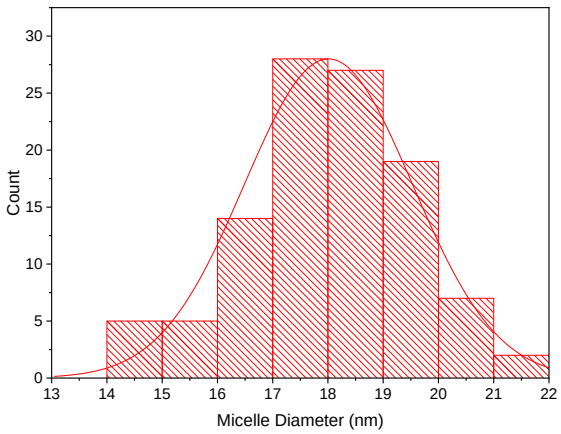


*Figure S40: Size distribution of poly-**5-b**-exo-**10** from acetone in TAMg in presence of ssDNA2 after annealing from 95 C to 4 C over 1 hr. Average nanoparticles size (18 ± 2).*

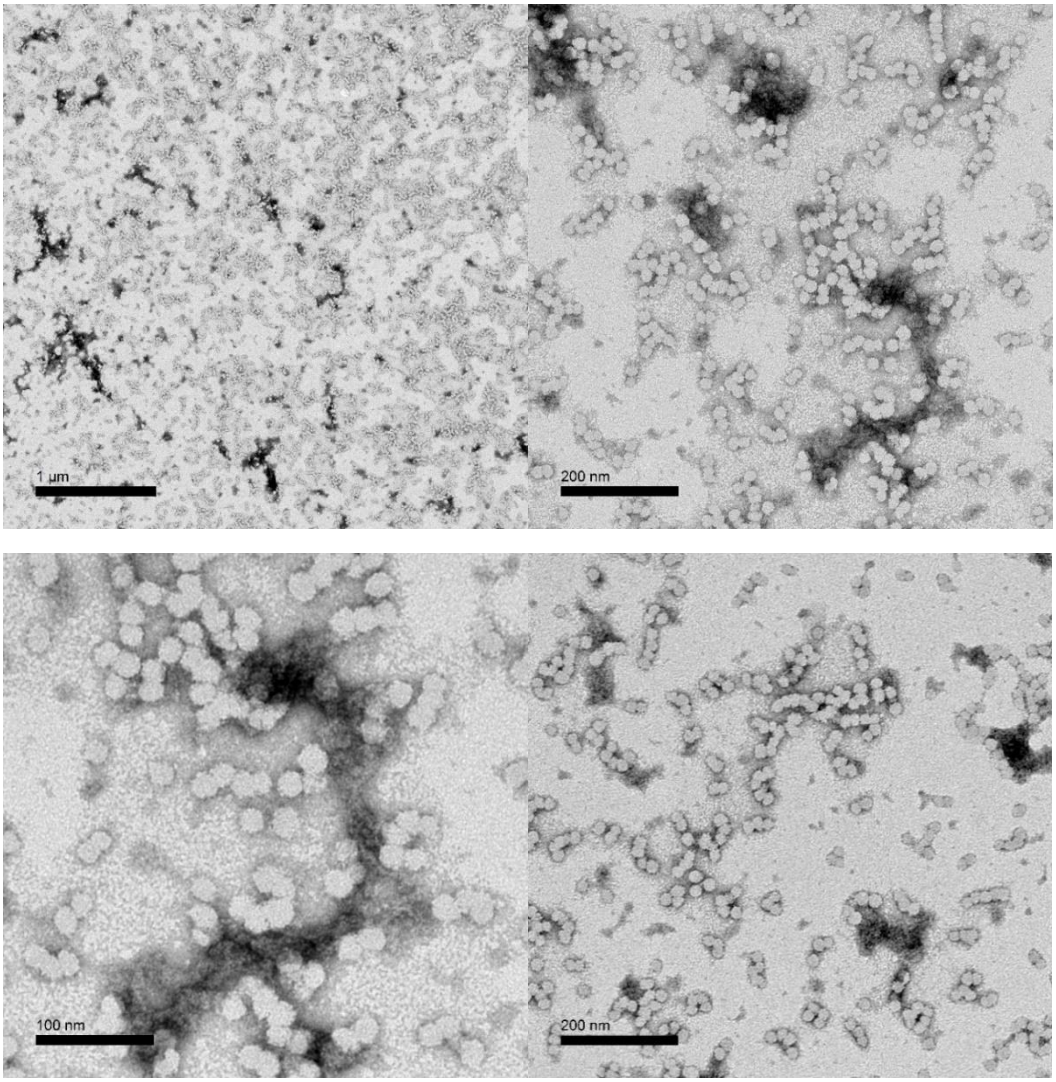


*Figure S41: TEM images of poly **5-b**-exo-**10** micelles (acetone into TAMg) with dsDNA after annealing from 95 C to 4 C over 1 hr. Negatively stained using uranyl acetate*

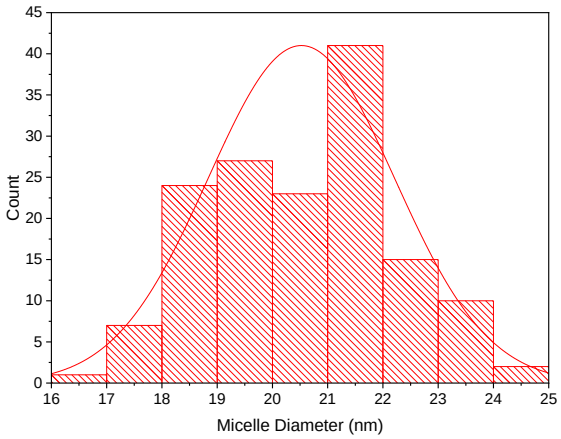


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*Figure S42: Size distribution of poly-**5-b**-exo-**10** from acetone in TAMg in presence of dsDNA after annealing from 95 C to 4 C over 1 hr. Average nanoparticles size (21 ± 2).*

Agarose Gel Electrophoresis

The agarose gel was made using 2.5% agarose in the chosen buffer solution. The samples were made at a concentration of 150 µM with respect to nucleobase and/or RhB, and each well was loaded using 25 µL sample and 5 µL glycerol. Agarose gel electrophoresis was performed using the following conditions: 80V, max mA, 1hr. The gels were stained using Gel Red stain (7.6 µL in 50 mL water). Gels were imaged using a UV transilluminator.

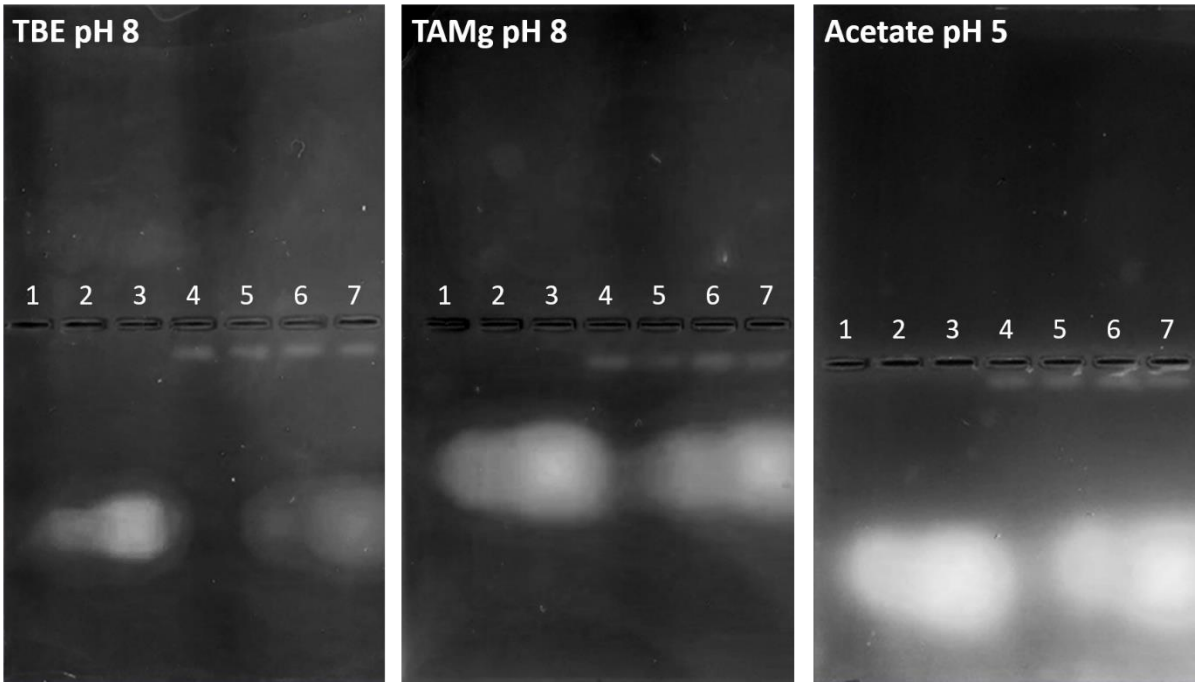

*Figure S43: Agarose gels of poly **5-b**-exo-**10** micelles with DNA in buffers as indicated. Lanes are: (1) ssDNA1; (2) ssDNA2; (3) dsDNA; (4) poly **5-b**-exo-**10** micelles; (5) micelles + ssDNA1; (6) micelles + ssDNA2; (7) micelles + dsDNA.*

References

1 O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard & H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

2 L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, *Acta Cryst.,* 2015, **A71**, 59-75.

3 G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.