Fluorescent nanoparticles from PEGylated polyfluorenes

- Supporting Information

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Experimental

¹H NMR Spectra were recorded on a Bruker Avance AV 400 MHz Ultrashield spectrometer in the solvent stated at 25 °C. ¹³C NMR Spectra were recorded on a Bruker Avance AV 100 MHz Ultrashield in the solvent stated at 25 °C. All spectra are referenced to the residual solvent peak. Gel permeation chromatography was carried out in THF at 35 °C using a Viscotek GPCmax VE2001 solvent/sample module with 2 × PL gel 10 μ m Mixed-B and PL gel 500A columns, a Viscotek VE3580 RI detector and a VE 3240 UV/VIS multichannel detector. The flow rate was 1 mL/min and the system was calibrated with low polydispersity polystyrene standards in the range of 200 to 180 ×10⁴ g/mol from Polymer Laboratories. The analysed samples contained *n*-dodecane as a flow marker. UV-Vis absorption spectra were recorded on a Varian Cary 5000UV-Vis-NIR spectrophotometer, in either tetrahydrofuran (linear polymer) or water (nanoparticles) at room temperature.



Scheme 1 Synthesis of brominated PEG

2-(2-(2-Methoxyethoxy)ethoxy)ethyl methanesulfonate 1

To a solution of 2-(2-(2-methoxyethoxy)ethoxy)ethanol (9.74 mL, 61.0 mmol) and methanesulfonyl chloride (5.70 mL, 73.2 mmol) in anhydrous dichloromethane (100 mL) was added triethylamine, dropwise. The reaction mixture was stirred at room temperature for 16 hours, followed by addition of water (250 mL). The organic phase was separated and washed with water (9 x 250 mL) and was then dried over magnesium sulphate. The solvent was removed under reduced pressure to afford the title compound as a yellow oil (8.77 g, 3.62 mmol, 59%).

 $\delta_{\rm H}$ (400 MHz; CDCl₃) 3.06 (3H, s), 3.56 (3H, s), 3.52 (2H, m), 3.60-3.66 (6H, m), 3.75 (2H, m), 4.37 (2H, m); $\delta_{\rm C}$ (100 MHz; CDCl₃) 37.6, 58.9, 68.9, 69.2, 70.4, 70.5, 71.8

1-Bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane 2

To a solution of **1** (6.12 g, 35.1 mmol) in acetone (100 mL) was added lithium bromide (4.57 g). The reaction mixture was stirred at reflux for 16 hours before cooling to room temperature and addition of water (150 mL). This solution was extracted with diethyl ether (3×150 mL) and the combined organic phases were washed with brine (150 mL). The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure to afford the title compound as a yellow oil (6.12 g, 26.9 mmol, 77%).

 $δ_{\rm H}$ (400 MHz; CDCl₃) 3.39 (3H, m), 3.48 (2H, t, *J* = 8 Hz), 3.56 (2H, m), 3.65-3.70 (6H, m), 3.84 (2H, t, *J* = 8.0 Hz); $δ_{\rm C}$ (100 MHz; CDCl₃) 30.3, 59.0, 70.5, 70.6, 71.2, 71.9



2,7-Dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluorene 3

Scheme 2 PEGylation of 2,7-dibromofluorene

A solution of **2** (3.08 g, 13.6 mmol), 2,7-dibromofluorene (2.00 g, 6.18 mmol) and potassium iodide (33.8 mg, 0.136 mmol) in dimethylsulfoxide (20 mL) was degassed under vacuum and cooled to 0 °C. Potassium hydroxide (1.14 g, 20.4 mmol) was added and the solution was allowed to heat back up to room temperature and was stirred at this temperature for 16 hours. The reaction mixture was then carefully poured into 50 mL of water. The solvents were removed by evaporation under reduced pressure and the crude residue was dissolved in dichloromethane (100 mL). This solution was washed with water (3 x 100 mL) and brine (100 mL) and the organic layer was removed under reduced pressure. The crude product was separated by silica column chromatography, eluting with ethyl acetate/light petroleum (2:3) and then ethyl acetate. The title compound was further treated to remove any monoalkyl defects using the procedure reported by Meijer *et al.*.[M. R. Craig, M. M. de Kok, J. W. Hofstraat, A. P. H. J. Shenning, E. J. Meiher *J. Mater. Chem.* **2003**, *13*, 2861-2861]. Briefly, the product was stirred at room temperature for 15 minutes with potassium *t*-butoxide (755 mg, 6.18 mmol) in tetrahydrofuran (100 mL) and then filtered through neutral alumina, which was then washed with tetrahydrofuran (150 mL). The solvent was removed under reduced pressure to afford the title compound as a colourless solid (2.64 g, 4.37 mmol, 71%).

 δ_{H} (400 MHz; CDCl₃) 2.34 (4H, m), 2.78 (4H, m), 3.21 (4H, m), 3.35 (6H, s), 3.40 (4H, m), 3.48-3.55 (8H, m), 7.46-7.54 (6H, m); δ_{C} (100 MHz; CDCl₃) 39.5, 51.8, 59.0, 66.7, 70.0, 70.5, 71.8, 121.2, 121.7, 126.7, 130.6, 138.4, 150.86.

Monomer synthesis

2,7-Dibromo-9,9-dioctyl-9H-fluorene, **4**, was synthesised from 2,7-dibromofluorene using a standard literature procedure, [R. Grisorio, P. Mastrorilli, C. F. Nobile, G. Romanazzi, G. P. Suranna, D. Acierno, E. Amendola, Macromol. Chem. Phys. 2005, 206, 448-455] and was further purified to remove monoalkyl defects using the procedure reported by Meijer et. al. [M. R. Craig, M. M. de Kok, J. W. Hofstraat, A. P. H. J. Schenning, E. W. Meijer, *J. Mater. Chem.* **2003**, *13*, 2861-2862] Subsequently, 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), **5**, was prepared from 2,7-dibromo-9,9-dioctyl-9H-fluorene, again using a standard literature procedure. [S. Y. Cho, A. C. Grimsdale, D. J. Jones, S. E. Watkins, A. B. Holmes, J. Am. Chem. Soc. 2007, 129, 11910-11911] The spectroscopic data for each compound was in agreement with that reported in the literature.



General Suzuki-Miyaura Coupling Polymerisation Procedure

Scheme 3 Synthesis of polyfluorenes

Fable 1 Amounts of fluorene monomers fo	r Suzuki-Miyaura	coupling polymerisation
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Polymer	PEG loading	Monomer 3	Monomer 4	Monomer 5	
	(mol. %)	(mass, moles)	(mass, moles)	(mass, moles)	
Polymer 1	0	Not added	118 mg, 0.215 mmol	138 mg, 0.215 mmol	
Polymer 2	25	65.3 mg, 0.108 mmol	64.7 mg, 0.107 mmol	138 mg, 0.215 mmol	
Polymer 3	50	130 mg, 0.215 mmol	Not added	138 mg, 0.215 mmol	

All co-monomers (see table 1) and Aliquat 336 (308 mg, 0.763 mmol) were dissolved in toluene (4 mL), which was degassed by bubbling argon through the solution for 10 minutes. Tetrakis(triphenylphosphine)palladium(0) (5.2 mg, 4.5 nmol) was added to the reaction mixture, followed by aqueous sodium carbonate (2M, 1.4 mL) and degassing was continued for a further 10 minutes. The reaction mixture was heated to 90 °C for 24 hours and was then cooled to room temperature. The polymer was precipitated by dropwise addition of the reaction mixture to methanol (400 mL), collected by filtration and washed with methanol (100 mL), water (3 x 100 mL) and methanol (100 mL). The product was then dissolved in dichloromethane (25 mL) and this solution was washed with aqueous sodium thiocarbamate solution (3 x 25 mL), water (25 mL) and brine (25 mL). The total volume of the polymer solution was reduced to ~4 mL by evaporation of dichloromethane under reduced pressure and the polymer was precipitated by dropwise addition to methanol (400 mL). The product was then collected by filtration and dried *in vacuo*. ¹H NMR spectra of each co-polymer were recorded using chloroform-d (CDCl₃) as the solvent.

General Nanoparticle Synthesis

Polymer (20 mg, 10 mg or 5 mg) was dissolved in tetrahydrofuran (10 g) to form a 2000 ppm, 1000 ppm or 500 ppm solution respectively. 750 μ L of polymer solution was then rapidly injected into water (3 mL) with stirring at room temperature. Residual tetrahydrofuran was removed from the resultant nanoparticle suspension by blowing nitrogen over the solution for 2 hours at room temperature.

Size and zeta-potential of nanoparticles

The size and zeta potential of the nanoparticle dispersions were measured using a Malvern Zetasizer Nano ZS, at a temperature of 20 °C.

TEM of nanoparticles

Solutions of graphene oxide were synthesised as reported previously.^[10a] Aqueous solutions of graphene oxide (0.10 mg mL⁻¹) were sonicated for 30 s prior to use. Lacey carbon grids (400 Mesh, Cu) (Agar Scientific) were cleaned using air plasma from a glow-discharge system (2 min, 20 mA). The TEM grids were placed on a filter paper and one drop (≈ 0.08 mL) of the sonicated GO solution was deposited onto each grid from a height of ≈ 1 cm, allowing the filter paper to absorb the excess solution, and the grids were left to air-dry in a dessicator cabinet for ≈ 60 min. 4 µL of the nanoparticle dispersion (~20 ppm) was pipetted onto a GO grid and left to air-dry in a dessicator cabinet for ≈ 60 min. Brightfield TEM images were captured with a transmission electron microscope (JEOL TEM-2011), operating at 200 kV. Average sizes of the nanoparticles were determined from counting the size of 150 particles for each sample.





Figure 3 ¹H NMR spectrum of polymer 2 (50% PEG)

GPC Analysis of Polyfluorenes

Table 1 Relative molecular weights of polyfluorenes, measured by GPC

Polymer	PEG loading	Mn	M _w	PDI
	(mol. %)	(Da)	(Da)	
Polymer 1	0	20, 600	44, 800	2.2
Polymer 2	25	20, 300	47, 600	2.3
Polymer 3	50	33, 500	96,500	2.5





Ultraviolet/Visible (UV/vis) Spectra of Polyfluorenes



Figure 5 UV/vis spectra of polymers 1-3

Photoluminescence (PL) Spectra of Polyfluorenes



Figure 6 PL spectra of polymers 1-3

DLS analysis of Polyfluorene Nanoparticles

Initial polymer concentration	Batch 1 D ^{DLS}	Batch 2 D ^{DLS}	Batch 3 D ^{DLS}	Average D ^{DLS}	Batch 1 PDI	Batch 2 PDI	Batch 3 PDI
(ppm)	(nm)	(nm)	(nm)	(nm)			
500	114	110	131	118±6	0.11	0.10	0.03
1000	115	120	107	114±3	0.07	0.08	0.10
2000	187	105	174	155±22	0.09	0.06	0.19

Table 1 DLS analysis of nanoparticles formed from polymer 1 (0% PEG)

Table 2 DLS analysis of nanoparticles formed from polymer 2 (25% PEG)

Initial polymer concentration	Batch 1 D ^{DLS}	Batch 2 D ^{DLS}	Batch 3 D ^{DLS}	Average D ^{DLS}	Batch 1 PDI	Batch 2 PDI	Batch 3 PDI
(ppm)	(nm)	(nm)	(nm)	(nm)			
500	124	107	86	106±10	0.12	0.08	0.14
1000	161	83	163	108±23	0.06	0.10	0.11
2000	87	88	80	85±2	0.11	0.09	0.09

Table 3 DLS analysis of nanoparticles formed from polymer 3 (50% PEG)

Initial polymer concentration	Batch 1 D ^{DLS}	Batch 2 D ^{DLS}	Batch 3 D ^{DLS}	Average D ^{DLS}	Batch 1 PDI	Batch 2 PDI	Batch 3 PDI
(ppm)	(nm)	(nm)	(nm)	(nm)			
500	144	81	46	90±25	0.08	0.11	0.11
1000	66	61	62	63±1	0.09	0.12	0.08
2000	80	101	100	94±6	0.09	0.16	0.08



Figure 7 Histograms comparing DLS size distributions of nanoparticles formed with a) polymer 1 (batch 1), b) polymer 2 (batch 2) and c) polymer 3 (batch 1) at an initial polymer concentration of 1000 ppm





Figure 8 UV/vis (left) and PL (right) spectra of nanoparticles of polymer 1 (0% PEG) formed with different initial polymer concentrations (500 – 2000 ppm)



Figure 9 UV/vis (left) and PL (right) spectra of nanoparticles of polymer 2 (25% PEG) formed with different initial polymer concentrations (500 – 2000 ppm)



Figure 10 UV/vis (left) and PL (right) spectra of nanoparticles of polymer 3 (50% PEG) formed with different initial polymer concentrations (500 – 2000 ppm)