Synthesis of Porphyrin-CdSe Quantum Dot Assemblies: Controlling Ligand Binding by Substituent Effects

Isabelle Chambrier, Chiranjib Banerjee, Sonia Remiro-Buenamañana, Yimin Chao, Andrew N. Cammidge* and Manfred Bochmann*

Supporting Information

Preparation of 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrinato zinc (2). This was prepared following a modified procedure from the literature.[S1] *5-(4-Carboxyphenyl)-10,15,20-triphenyl-porphyrin:* 4-Formylbenzoic acid (2 g, 13.3 mmol) and benzaldehyde (4.24 g, 0.04 mol) were refluxed in propionic acid (150 mL). Pyrrole (3.6 g, 0.054 mol) was added and reflux continued for 1 h. After cooling, the solution was poured into excess light petroleum (bp. 40-60 °C). A black solid residue was separated, leaving a red solution. The solvent was removed under reduced pressure. The residue was adsorbed on silica and placed on top of a chromatography column filled with silica. The column was eluted with light petroleum/THF 4:1. A first fraction was collected which contained tetrabenzoporphyrin. The eluent was changed to light petroleum/THF 2:1. A second fraction was obtained which was further purified as above. The pure fraction was collected and the solvent removed under vacuum. The product was recrystallized from THF/hexane. The solid obtained was very fine and could not be separated by filtration. It was therefore isolated by centrifugation (344 mg, 3.9 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.83-8.9 (m, 6H), 8.81 (d, 2H, *J* 4.5 Hz), 8.52 (d, 2H, *J* 8.3 Hz). 8.36 (d, 2H, *J* 7.7 Hz), 8.21-8.24 (m, 6H), 7.73-7.82 (m, 9H), -2.78 (s, 2H). UV/vis: λ_{max} (CH_2Cl_2) 418, 514, 548, 590, 647 nm. MALDI-TOF: isotopic cluster at m/z 658.27 [M^+, 100%].

*5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrinato zinc (**2**):* Metal-free 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (140 mg, 0.21 mmol) was refluxed in THF (5 mL). Excess $Zn(OAc)_2$ dihydrate (70 mg) was added and reflux continued until UV analysis showed no more starting

material was present (*ca*. 30 min). The solvent was then removed under reduced pressure. The residue was filtered through silica, eluent light petroleum (bp. 40-60 °C)/THF 2:1 and recrystallized from THF/hexane (145 mg, 96 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.97 (d, 2H, *J* 4.6 Hz), 8.96 (s, 4H), 8.91 (d, 2H, *J* 4.6 Hz), 8.52 (d, 2H, *J* 7.9 Hz), 8.37 (d, 2H, *J* 8.0 Hz), 8.21-8.24 (m, 6H), 7.73-7.81 (m, 9H). λ_{max} (CH_2Cl_2) 419, 548, 585 nm. MALDI-TOF: isotopic cluster at m/z 720.32 [M^+, 100%].

Preparation of 5-[4-(Carboxy-n-alkyloxy)phenyl]-10,15,20-tri(4-decyloxyphenyl)porphyrinato zinc (3, 4).

4-Decyloxybenzaldehyde: 4-Hydroxybenzaldehyde (5.0 g, 41 mmol) in DMF (100 mL) was stirred in the presence of bromodecane (10 g, 45 mmol) and potassium carbonate (15 g, 0.1 mol) at 90 °C under N_2 for 5 h. The mixture was cooled, poured into water and extracted with dichloromethane. The organic layer was washed with water (x4), brine, dried ($MgSO_4$), filtered and the solvent removed, leaving a yellow oil which was used without further purification. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.83 (s, 1H), 7.77 (d, 2H, *J* 8.8 Hz), 6.94 (d, 2H, *J* 8.8 Hz), 3.98 (t, 2H, *J* 6.5 Hz), 1.72-1.81 (m, 2H), 1.28-1.46 (m, 2H), 1.17-1.35 (m, 12H), 0.85 (t, 3H, *J* 7.1 Hz).

4-((5-carboxyethyl)pentyloxy)benzaldehyde: 4-Hydroxybenzaldehyde (2.0 g, 16 mmol) in DMF (50 mL) was stirred in the presence of ethyl-6-bromohexanoate (3.8 g, 17 mmol) and potassium carbonate (11 g, 80 mmol) at 90 °C under N_2 for 5 h. The mixture was cooled, poured into water and extracted with dichloromethane. The organic layer was washed with water (x4), brine, dried ($MgSO_4$), filtered and the solvent removed to give a pale yellow oil (4.2 g, 99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.85 (s, 1H), 7.79 (d, 2H, *J* 8.8 Hz), 6.95 (d, 2H, *J* 8.8 Hz), 4.1 (q, 2H, *J* 7.1 Hz), 4.01 (t, 2H, *J* 6.4 Hz), 2.32 (t, 2H, *J* 7.3 Hz), 1.81 (quintet, 2H, *J* 7.1 Hz), 1.69 (quintet, 2H, *J* 7.8 Hz), 1.49 (quintet, 2H, *J* 7.1 Hz), 1.23 (t, 3H, *J* 7.1 Hz).

4-((10-carboxymethyl)decyloxy)benzaldehyde: This was prepared as above using methyl-11-bromoundecanoate. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.83 (s, 1H), 7.77 (d, 2H, *J* 8.7 Hz), 6.95 (d, 2H, *J* 8.8 Hz), 4.1 (t, 2H, *J* 6.3 Hz), 3.67 (s, 3H), 2.32 (t, 2H, *J* 7.3 Hz), 1.81 (quintet, 2H, *J* 7.15 Hz), 1.49-1.69 (m, 14H).

5-((5-carboxyethyl)pentyloxy)phenyl)-10,15,20-tri(4-decyloxyphenyl)porphyrin: 4-Decyloxybenzaldehyde (3.0 g, 11.5 mmol) and 4-(*5-carboxyethyl)pentyloxy*)benzaldehyde (1 g, 3.8 mmol) were refluxed in propionic acid (100 mL). Pyrrole (1 g, 15 mmol) was added and reflux continued for 1 h. After cooling the solution was poured into methanol. A black solid residue separated. The residue was adsorbed on silica and placed on top of a chromatography column filled with silica. The column was eluted with light petroleum (bp. 40-60 °C)/THF 4:1. A first fraction was collected which contained 5,10,15,20-tetra(4-decyloxyphenyl)porphyrin. The eluent was changed to light petroleum/THF 2:1. A second fraction was obtained which was further purified as above. The pure fraction was collected and the solvent removed under vacuum. The product was recrystallized from THF/methanol. The

solid was separated by filtration (327 mg, 9.2 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.87 (s, 8H), 8.1 (d, 8H, *J* 8.4 Hz), 7.27 (m, 8H), 4.25 (t, 8H, *J* 6.55 Hz), 4.19 (q, 2H, *J* 7.24 Hz), 2.44 (t, 2H, *J* 7.24 Hz), 1.99 (quintet, 8H, *J* 6.84 Hz), 1.84 (quintet, 2H, *J* 7.56 Hz), 1.59-1.74 (m, 8H), 1.29-1.52 (m, 39H), 0.91 (t, 9H, *J* 6.48 Hz), -2.77 (s, 2H). λ_{max} (CH_2Cl_2) 420, 517, 555, 593, 649 nm. MALDI-TOF: isotopic cluster at m/z 1240.79 [M^+, 100%].

5-((10-carboxymethyl)decyloxy)phenyl-10,15,20-tri(4-decyloxyphenyl)porphyrin: This was prepared as above using 4-(methyl-11-undecanoateoxy)benzaldehyde. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.87 (s, 8H), 8.1 (d, 8H, *J* 8.5 Hz), 7.27 (d, 8H, *J* 8.6 Hz), 4.25 (t, 8H, *J* 6.4 Hz), 3.69 (s, 3H), 2.34 (t, 2H, *J* 7.6 Hz), 1.98 (quintet, 8H, *J* 7.5 Hz), 1.59-1.69 (m, 10H), 1.33-1.52 (m, 46H), 0.93 (t, 9H, *J* 7.1 Hz), -2.73 (s, 2H). λ_{max} (CH_2Cl_2) 420, 517, 555, 593, 649 nm. MALDI-TOF: isotopic cluster at m/z 1296.76 [M^+, 100%].

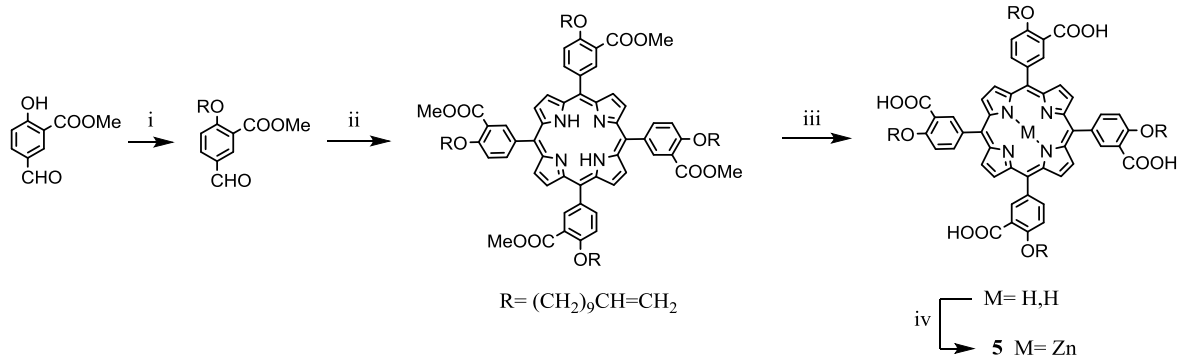
5-(4-(5-Carboxy-pentyloxy)phenyl)-10,15,20-tri(4-decyloxyphenyl)porphyrin: 5-(4-(carboxyethyl)pentyloxyphenyl)-10,15,20-tri(4-decyloxyphenyl)porphyrin (150 mg, 0.16 mmol) was refluxed in THF (5 mL). An aqueous solution of 2 *M* NaOH was added dropwise and the reaction followed by tlc (eluent light petroleum (bp. 40-60 °C)/THF 2:1). When all starting material had been converted, the reaction mixture was cooled and the solvent removed under vacuum. The residue was purified by column chromatography on silica (eluent light petroleum (bp. 40-60 °C)/THF 1:1) followed by crystallization from THF/methanol to afford a purple powder (140 mg, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.86 (s, 8H), 8.1 (d, 8H, *J* 7.8 Hz), 7.25-7.28 (m, 8H), 4.25 (t, 8H, *J* 6.6 Hz), 2.49 (t, 2H, *J* 7.1 Hz), 1.95-2.03 (m, 8H), 1.22-1.74 (m, 46H), 0.89-0.92 (m, 9H), -2.75 (s, 2H). λ_{max} (DCM) 420, 517, 555, 592, 650 nm. MALDI-TOF: isotopic cluster at m/z 1214.24 [M^+, 100%].

5-(4-(10-Carboxydecyloxy)phenyl)-10,15,20-tri(4-decyloxyphenyl)porphyrin: This was prepared as above using 5-((10-carboxymethyl)decyloxy)phenyl-10,15,20-tri(4-decyloxyphenyl)porphyrin. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85 (s, 8H), 8.09 (d, 8H, *J* 8.4 Hz), 7.25-7.26 (m, 8H), 4.23 (t, 8H, *J* 6.2 Hz), 2.36 (t, 2H, *J* 7.6 Hz), 1.94-2.02 (m, 8H), 1.57-1.67 (m, 10H), 1.2-1.47 (m, 46H), 0.9 (t, 9H, *J* 6.95 Hz), -2.75 (s, 2H). λ_{max} (CH_2Cl_2) 420, 517, 555, 593, 649 nm. MALDI-TOF: isotopic cluster at m/z 1284.34 [M^+, 100%].

*5-(4-(5-Carboxypentyloxy)phenyl)-10,15,20-tri(4-decyloxyphenyl)porphyrinato zinc (**3**):* Metal-free (140 mg, 0.15 mmol) was refluxed in THF (5 mL). Excess $Zn(OAc)_2$ dihydrate (60 mg) was added and reflux continued until UV analysis showed no more starting material was present (*ca*. 30 mins). The solvent was then removed under reduced pressure. The residue was filtered through silica, eluent light petroleum (bp. 40-60 °C)/THF 1:1 and recrystallized from THF/methanol (140 mg, 94 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.97 (s, 8H), 8.09 (d, 8H, *J* 8.5 Hz), 7.25-7.27 (m, 8H), 4.25 (t, 8H, *J* 6.3 Hz), 2.37 (t, 2H, *J* 7.3 Hz), 1.98 (quintet, 8H, *J* 7.15 Hz), 1.29-1.69 (m, 46H), 0.91 (t, 9H, *J* 6.7 Hz). λ_{max} (CH_2Cl_2) 423, 550, 590 nm. MALDI-TOF: isotopic cluster at m/z 1275.61 [M^+, 100%].

*5-(4-(10-Carboxydecyloxy)phenyl)-10,15,20-tri(4-decyloxyphenyl)porphyrinato zinc (**4**):* This was prepared as above using 5-(4-carboxy-10-decyloxyphenyl)-10,15,20-tri(4-decyloxyphenyl)porphyrin. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.96 (s, 8H), 8.09 (d, 8H, *J* 8.5 Hz), 7.24-7.27 (m, 8H), 4.24 (t, 8H, *J* 6.6 Hz), 2.36 (t, 2H, *J* 7.4 Hz), 1.97 (quintet, 8H, *J* 7.4 Hz), 1.28-1.66 (m, 46H), 0.9 (t, 9H, *J* 6.7 Hz). λ_{max} (CH_2Cl_2) 423, 551, 590 nm. MALDI-TOF: isotopic cluster at m/z 1345.09 [M^+, 100%].

Preparation of 5,10,15,20-tetrakis(3-carboxy-4-undec-10-enyloxyphenyl)porphyrinato zinc (5).



Scheme S1. Preparation of 5,10,15,20-tetra(3-carboxy-4-undecyloxyphenyl)porphyrinato zinc (**5**) [Reagents: i. K_2CO_3, DMF, $Br(CH_2)_9CH=CH_2$; ii. Propionic acid, pyrrole; iii. THF, aq. NaOH; iv. pyridine, $Zn(OAc)_2$].

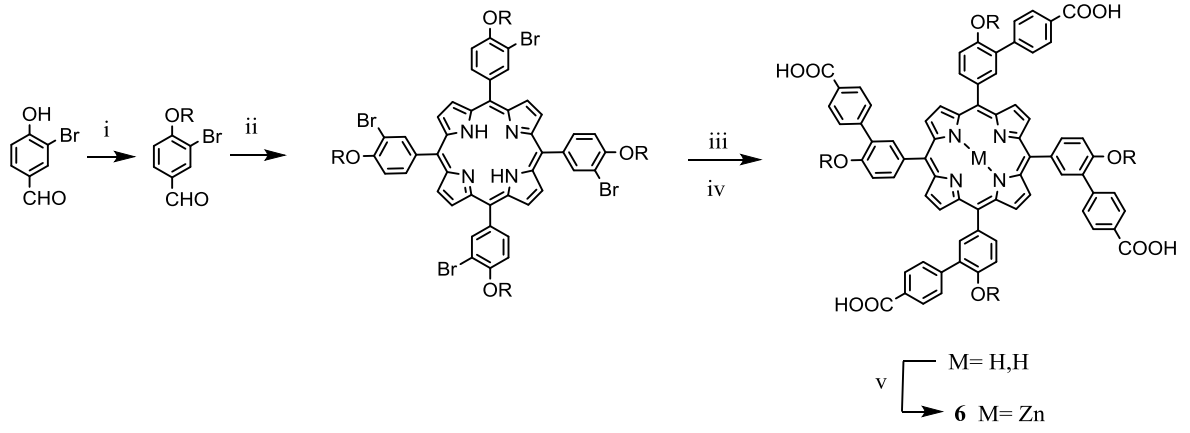
Methyl-5-formyl-2-undec-10-enyloxybenzoate: Methyl 5-formyl-2-hydroxybenzoate (1.9 g, 10.6 mmol), 11-bromoundecene (2.5 g, 10.7 mmol), K_2CO_3 (7 g, 51 mmol) in DMF (20 mL) was heated at 90 °C with stirring under N_2 for 3 h. Water was added and the mixture was cooled. The white solid was filtered, washed with water and air dried to afford the title product (3.2 g, 91%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.91 (s, 1H), 8.32 (d, 1H, *J* 2.2 Hz), 7.99 (dd, 1H, J_1 8.7 Hz, J_2 2.2 Hz), 7.07 (d, 1H, *J* 8.7 Hz), 5.77-5.85 (m, 1H), 4.9-5.01 (m, 2H), 3.91 (s, 3H), 2.01-2.06 (m, 2H), 1.83-1.89 (m, 2H), 1.47-1.53 (m, 2H), 1.27-1.41 (m, 12H).

5,10,15,20-Tetrakis(3-carboxymethyl-4-undec-10-enyloxyphenyl)porphyrin: Methyl 5-formyl-2-undecenyloxybenzoate (3.2 g, 9.6 mmol) was refluxed in propionic acid (50 mL). Pyrrole (0.64 g, 9.6 mmol) was added. The mixture darkened immediately and was refluxed 2 h. The solvent was removed under reduced pressure. The residue was filtered through silica gel, eluent light petroleum (bp 40-60 °C)/THF 4:1, then 2:1. A purple fraction was separated. The solvents were removed under reduced pressure. The residue was washed with methanol, and then recrystallized twice from THF/MeOH to afford the title compound as a purple powder (270 mg, 16 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.85 (s, 8H), 8.62 (s, 4H), 8.25 (d, 4H, *J* 8.15 Hz), 7.35 (d, 4H, *J* 8.2 Hz), 5.8-5.88 (m, 4H), 4.94-5.04 (m, 8H), 4.34 (t, 8H, *J* 6.4 Hz), 3.93 (s, 12H), 2.01-2.1 (m, 8H), 1.63-1.69 (m, 8H), 1.32-1.53 (m, 48H), -2.75 (s, 2H). λ_{max} (THF) 421, 517, 553, 594, 651 nm.

5,10,15,20-Tetrakis(3-carboxy-4-undec-10-enyloxyphenyl)porphyrin: 5,10,15,20-Tetrakis(3-carboxymethyl-4-undec-10-enyloxy)porphyrin (270 mg, 0.18 mmol) was refluxed in a mixture of THF (20 mL) and ethanol (2 mL). An aqueous solution of NaOH (2N) (1 mL) was added and reflux continued until tlc analysis (eluent light petroleum (bp 40-60 °C)-THF 2:1) indicated reaction was complete (*ca*. 30 mins-1 hr). An excess of aq. HCl (1N) was added which caused the formation of a green precipitate. This was filtered. The precipitate was dissolved in ethylacetate and filtered through silica gel. The red fraction was collected. Attempted crystallization from THF/methanol afforded a very fine powder that could not be filtered. Instead, the product was collected by centrifugation and dried under vacuum (205 mg, 79 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.96-9.02 (m, 4H), 8.79-8.82 (m, 8H), 8.29-8.34 (m, 4H), 7.41-7.47 (m, 4H), 5.8-5.88 (m, 4H), 4.94-5.04 (m, 8H), 4.54 (brs, 8H), 1.35-2.14 (m, 68H), -2.84 (s, 2H). λ_{max} (THF) 421, 517, 552, 591, 650 nm. MALDI-TOF: isotopic cluster at m/z 1463.56 [M^+, 100%].

*5,10,15,20-Tetrakis(3-carboxy-4-undec-10-enyloxyphenyl)porphyrinato zinc (**5**):* Metal-free 5,10,15,20-tetrakis(3-carboxy-4-undec-10-enyloxyphenyl)porphyrin (50 mg, 34 μmol) was refluxed in pyridine (5 mL). Excess $Zn(OAc)_2$ dihydrate (60 mg, 0.27 mmol) was added and reflux continued until UV analysis showed no more starting material was present (*ca*. 30 min). After cooling the solution was added to water (10 mL). This was transferred to a 15 mL centrifuge tube and the solid separated after centrifugation. After several washings with water the purple powder was left to dry in air (48 mg, 94 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.27 (brs, 4H), 8.96-9.0 (m, 4H), 8.79-8.84 (m, 8H), 8.29-8.35 (m, 4H), 7.37-7.41 (m, 4H), 5.8-5.88 (m, 4H), 4.94-5.04 (m, 8H), 4.52 (brs, 8H), 2.06-2.1 (m, 8H), 1.65 (brs, 8H), 1.37-1.52 (m, 48H). λ_{max} (DCM) 423, 550, 592 nm. MALDI-TOF: isotopic cluster at m/z 1525.12 [M^+, 100%].

Preparation of 5,10,15,20-tetrakis(3-(4-carboxyphenyl)-4-undec-10-enyloxyphenyl)porphyrinato zinc (6)



Scheme S2. Preparation of 5,10,15,20-tetra[3-(4-carboxyphenyl)-4-undecyloxyphenyl]porphyrinato zinc (**6**) [Reagents: i. K_2CO_3, DMF, $Br(CH_2)_9CH=CH_2$; ii. Propionic acid, pyrrole; iii. $PdCl_2$, PPh_3, toluene, Et_3N, ethylphenyl-4-carboxylate boronic acid; iv. THF, aq. NaOH; v. pyridine, $Zn(OAc)_2$].

3-Bromo-4-(10-undecenyloxy)benzaldehyde: 4-Hydroxy-3-bromobenzaldehyde (2 g, 10 mmol), 11-bromoundecene (2.5 g, 10.7 mmol), K_2CO_3 (7 g, 51 mmol) in DMF (10 mL) was heated at 90 °C with stirring under N_2 for 3 h. Water was added and the mixture was cooled. The white solid was filtered, washed with water and air dried to afford the title product (3.5 g, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.83 (s, 1H), 8.07 (d, 1H, *J* 2 Hz), 7.79 (dd, 1H, J_1 2 Hz, J_2 8.8 Hz), 6.98 (d, 1H, *J* 8.5 Hz), 5.77-5.86 (m, 1H), 4.92-5.01 (m, 2H), 4.11 (t, 2H, *J* 6.5 Hz), 2.04 (m, 2H), 1.87 (quintet, 2H, *J* 8.5 Hz), 1.51 (quintet, 2H, J 7.1 Hz), 1.26-1.42 (m, 10H).

5,10,15,20-Tetrakis(3-bromo-4-undec-10-enyloxyphenyl)porphyrin: 3-Bromo-4-(10-undecenyloxy)-benzaldehyde (3.5 g, 0.01 mol) was refluxed in propionic acid (100 mL). Pyrrole (0.7 g, 10.4 mmol) was added. The mixture darkened immediately and was refluxed 2 h. The solvent was removed under reduced pressure. The residue was washed with methanol and filtered through silica gel, eluent dichloromethane/hexane 1:1. A purple fraction was separated. The solvent was removed under reduced pressure and the residue precipitated from THF/MeOH to afford the title compound as a purple powder (850 mg, 21%). ^{1}H NMR ($CDCl_3$, 500 MHz): 8.87 (s, 8H), 8.39 (brs, 4H), 8.06 (d, 4H, *J* 7.8 Hz), 7.24-7.26 (m, 4H), 5.8-5.88 (m, 4H), 4.93-5.04 (m, 8H), 4.32 (t, 8H, *J* 6.4 Hz), 2.01-2.1 (m, 16H), 1.67 (quintet, 8H, *J* 7.7 Hz), 1.36-1.52 (m, 40H), -2.86 (s, 2H). λ_{max} (THF) 421, 517, 552, 591, 650 nm. MALDI-TOF: isotopic cluster at m/z 1604.27 [M^+, 100%].

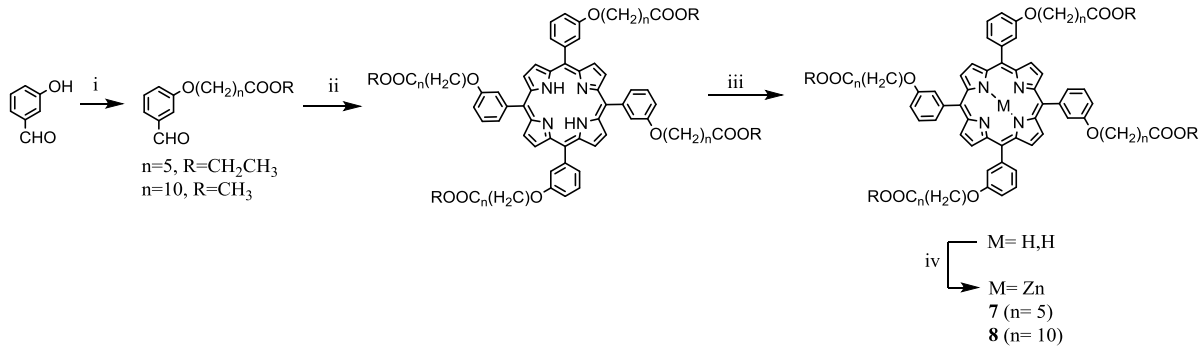
5,10,15,20-Tetrakis(3-(4-ethoxycarbonylphenyl)-4-undec-10-enyloxyphenyl)porphyrin: 5,10,15,20-Tetrakis(3-bromo-4-undecenyloxyphenyl)porphyrin (100 mg, 63 μmol), 4-(ethoxycarbonyl)phenyl-boronic acid (100 mg, 0.5 mmol, 8 eq.), $PdCl_2$ (5 mg, 28 μmol), PPh_3 (15 mg, 57 μmol) and sodium carbonate (60 mg, 0.6 mmol) were brought to reflux in a solvent mixture (30 mL) of toluene/ethanol/water 3:3:1. The reaction was followed by TLC (eluent light petroleum/THF 4:1). When reaction was complete (ca. 6 h), the solvents were removed under reduced pressure. The coloured residue was filtered through silica, eluent light petroleum/THF 4:1 and a purple fraction was isolated. The solvent was removed and the residue precipitated from THF/methanol to afford a purple powder (85 mg, 72%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.97 (s, 8H), 8.21-8.24 (m, 4H), 8.16 (d, 4H, *J* 7.9 Hz), 8.08-8.12 (m, 8H), 7.87-7.92 (m, 8H), 7.37 (d, 4H, *J* 8.5 Hz), 5.8-5.89 (m, 4H), 4.94-5.04 (m, 8H), 4.36-4.4 (m, 8H), 4.28 (t, 8H, *J* 6.4 Hz), 2.05-2.09 (m, 8H), 1.92 (quintet, 8H, *J* 7.8 Hz), 1.53-1.59 (m, 8H), 1.34-1.43 (m, 52H), -2.72 (s, 2H). λ_{max} (THF) 423, 518, 553, 592, 651 nm.

5,10,15,20-Tetrakis(3-(4-carboxyphenyl)-4-undec-10-enyloxyphenyl)porphyrin: 5,10,15,20-Tetrakis(3-(4-ethoxycarbonylphenyl)-4-undecenyloxyphenyl)porphyrin (85 mg, 45 μmol) was refluxed in a mixture of THF (10 mL) and ethanol (1 mL). An aqueous solution of NaOH (2N) (0.5 mL) was added and reflux continued until TLC analysis (eluent light petroleum (bp 40-60 °C)/THF 2:1) indicated reaction was complete (*ca*. 30 mins-1 hr). An excess of aq. HCl (1N) was added which caused the formation of a green precipitate. This was filtered. The precipitate was dissolved in

ethylacetate and filtered through silica gel. The red fraction was collected. Attempted crystallization from THF/methanol afforded a very fine powder that could not be filtered. Instead, the product was collected by centrifugation and dried under vacuum (76 mg, 95 %). ^{1}H NMR (THF-d_8, 500 MHz): δ 11.34 (brs, 4H), 8.97 (s, 8H), 8.24-8.28 (m, 4H), 8.16-8.19 (m, 4H), 8.04-8.09 (m, 8H), 7.89-7.95 (m, 8H), 7.47-7.51 (m, 4H), 5.78-5.86 (m, 4H), 4.89-5.02 (m, 8H), 4.31 (brs, 8H), 2.05-2.09 (m, 8H), 1.93 (quintet, 8H, *J* 7.1 Hz), 1.59 (quintet, 8H, *J* 7.6 Hz), 1.34-1.47 (m, 40H), -2.62 (s, 2H). λ_{max} (THF) 423, 518, 552, 591, 651 nm. MALDI-TOF: isotopic cluster at m/z 1767.74 [M^+, 100%].

*5,10,15,20-Tetrakis(3-(4-carboxyphenyl)-4-undecenyloxyphenyl)porphyrinato zinc (**6**):* Metal-free 5,10,15,20-tetrakis(3-(4-carboxyphenyl)-4-undecenyloxyphenyl)porphyrin (76 mg, 43 μmol) was refluxed in pyridine (5 mL). Excess $Zn(OAc)_2$ dihydrate (60 mg, 0.27 mmol) was added and reflux continued until UV analysis showed no more starting material was present (*ca*. 30 mins). After cooling the solution was added to water (10 mL). This was transferred to a 15 mL centrifuge tube and the solid separated after centrifugation. After several washings with water the purple powder was left to dry in air (75 mg, 96 %). ^{1}H NMR (THF-d_8, 500 MHz): δ 11.29 (brs, 4H), 8.99 (s, 8H), 8.2-8.25 (m, 4H), 8.14-8.18 (m, 4H), 8.04-8.08 (m, 8H), 7.89-7.95 (m, 8H), 7.47 (d, 4H, *J* 8.4 Hz), 5.78-5.86 (m, 4H), 4.89-5.01 (m, 8H), 4.32 (t, 8H, *J* 6.4 Hz), 2.05-2.09 (m, 8H), 1.93 (quintet, 8H, *J* 7.85 Hz), 1.6 (quintet, 8H, *J* 7.5 Hz), 1.35-1.47 (m, 40H). λ_{max} (THF) 429, 559, 600 nm. MALDI-TOF: isotopic cluster at m/z 1829.85 [M^+, 100%].

5,10,15,20-Tetrakis(3-(carboxy-n-alkyloxy)phenyl)porphyrinato zinc (7, 8)



Scheme S3. Preparation of 5,10,15,20-tetra[3-(carboxyhexyl-6-oxyphenyl)]porphyrinato zinc (**7**) and 5,10,15,20-tetra[3-(carboxyundecyl-11-oxyphenyl)]porphyrinato zinc (**8**) [Reagents: i. K_2CO_3, DMF, $Br(CH_2)_nCH=CH_2$; ii. Propionic acid, pyrrole; iii. THF, aq. NaOH; iv. pyridine, $Zn(OAc)_2$].

3-(5-Carboxyethylpentyloxy)benzaldehyde: 3-Hydroxybenzaldehyde (2.7g, 22.4 mmol) in DMF (50 mL) was stirred in the presence of ethyl-6-bromohexanoate (5 g, 22.4 mmol) and potassium carbonate (10 g, 72 mmol) at 90 °C under N_2 overnight. The mixture was cooled, poured into water and extracted with dichloromethane. The organic layer was washed with water (x4), brine, dried ($MgSO_4$), filtered and the solvent removed to give a pale yellow oil (4.5 g, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz):

δ 9.94 (s, 1H), 7.38-7.42 (m, 2H), 7.33-7.35 (m, 1H), 7.12-7.14 (m, 1H), 4.1 (q, 2H, *J* 7.2 Hz), 3.98 (t, 2H, *J* 6.4 Hz), 2.31 (t, 2H, *J* 7.4 Hz), 1.8 (quintet, 2H, *J* 7.9 Hz), 1.68 (quintet, 2H, *J* 7.8 Hz), 1.46-1.52 (m, 2H), 1.23 (t, 3H, *J* 7.2 Hz).

3-(10-Carboxymethyl-decyloxy)benzaldehyde: This was prepared as above from methyl-11-bromoundecanoate. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.96 (s, 1H), 7.4-7.44 (m, 2H), 7.36-7.37 (m, 1H), 7.14-7.18 (m, 1H), 3.99 (t, 2H, *J* 6.6 Hz), 3.65 (s, 3H), 2.29 (t, 2H, *J* 7.7 Hz), 1.78 (quintet, 2H, *J* 7.2 Hz), 1.6 (quintet, 2H, *J* 7.1 Hz), 1.45 (quintet, 2H, *J* 7.7 Hz), 1.27-1.35 (m, 10H).

5,10,15,20-Tetrakis(3-(5-carboxyethylpentyloxy)phenyl)porphyrin: 3-(5-Carboxyethylpentyloxy)-benzaldehyde (4.5 g, 17 mmol) was refluxed in propionic acid (75 mL). Pyrrole (1.15 mL, 17 mmol) was added. The mixture darkened immediately and was refluxed 2 h. The solvent was removed under reduced pressure. The residue was washed with methanol. The residue was adsorbed on silica and placed on top of a chromatography column filled with silica. The column was eluted with light petroleum (bp. 40-60 °C)/THF 2:1 and a purple fraction was isolated. The solvent was removed and the residue precipitated from THF/methanol to afford a purple powder (1.15 g, 22%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.89 (s, 8H), 7.79 (d, 4H, *J* 7.6 Hz), 7.76 (brs, 4H), 7.63 (t, 4H, *J* 7.9 Hz), 7.31 (dd, 4H, J_1 8.4 Hz, J_2 2.5 Hz), 4.15 (t, 8H, *J* 6.9 Hz), 4.1 (q, 8H, *J* 6.9 Hz), 2.34 (t, 8H, *J* 7.5 Hz), 1.89 (quintet, 8H, *J* 7.6 Hz), 1.73 (quintet, 8H, *J* 7.4 Hz), 1.54-1.59 (m, 8H), 1.22 (t, 12H, *J* 7.15 Hz), -2.82 (s, 2H). λ_{max} (THF) 422, 518, 552, 592, 651 nm. MALDI-TOF: isotopic cluster at m/z 1246.93 [M^+, 100%]].

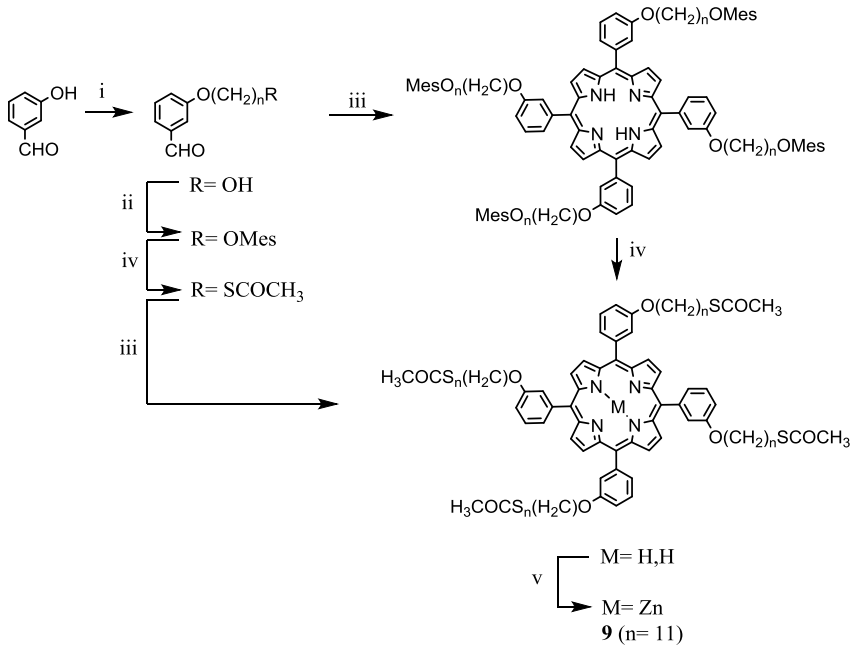
5,10,15,20-Tetrakis(3-(10-carboxymethyl-decyloxy)phenyl)porphyrin: This was prepared as above from 3-(10-carboxymethyl-decyloxy)benzaldehyde. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.89 (s, 8H), 7.77-7.8 (m, 8H), 7.63 (t, 4H, *J* 7.7 Hz), 7.32 (ddd, 4H, J_1 8.4 Hz, J_2 2.45 Hz, J_3 0.8 Hz), 4.14 (t, 8H, *J* 6.8 Hz), 3.63 (s, 12H), 2.27 (t, 8H, *J* 7.7 Hz), 1.87 (quintet, 8H, *J* 7.7 Hz), 1.56-1.64 (m, 8H), 1.47-1.54 (m, 8H), 1.26-1.4 (m, 40H), -2.8 (s, 2H). λ_{max} (THF) 423, 519, 552, 591, 651 nm. MALDI-TOF: isotopic cluster at m/z 1471.22 [M^+, 100%]].

*5,10,15,20-Tetrakis(3-(5-carboxy-pentyloxy)phenyl)porphyrinato zinc (**7**):* 5,10,15,20-Tetrakis(3-(5-carboxyethyl-pentyloxy)phenyl)porphyrin (220 mg, 0.18 mmol) was refluxed in a mixture of THF (20 mL) and ethanol (2 mL). An aqueous solution of NaOH (2N) (1 mL) was added and reflux continued until TLC analysis (eluent light petroleum/THF 2:1) indicated reaction was complete (*ca*. 3 h). An excess of aq. HCl (1N) was added which caused the formation of a green precipitate that was filtered, washed with water and dried. The product was then refluxed in pyridine (5 mL). Excess $Zn(OAc)_2$ dihydrate (80 mg) was added and reflux continued for 2 h. After cooling, water was added. The solution was transferred to a centrifuge tube and centrifuged. The solid residue was separated and washed several times with water and dried under vacuum to afford a purple powder (185 mg, 86%). ^{1}H NMR (THF-d_8, 500 MHz): δ 10.56 (brs, 4H), 8.85 (s, 8H), 7.75 (brs, 4H), 7.72 (d, 4H, *J* 7.3 Hz), 7.57 (t, 4H, *J* 7.8 Hz), 7.29 (dd, 4H, J_1 8.4 Hz, J_2 2.2 Hz), 4.15 (t, 8H, *J* 6.5 Hz), 2.23 (t, 8H, *J* 7.3

Hz), 1.86 (quintet, 8H, *J* 6.9 Hz), 1.65 (quintet, 8H, *J* 7.3 Hz), 1.52-1.58 (m, 8H). λ_{max} (THF) 424, 555, 595 nm. MALDI-TOF: isotopic cluster at m/z 1196.91 [M^+, 100%]].

*5,10,15,20-Tetrakis(3-(10-carboxydecyloxy)phenyl)porphyrinato zinc (**8**):* This was prepared as above from 5,10,15,20-tetrakis(3-(10-carboxymethyl-decyloxy)phenyl)porphyrin. ^{1}H NMR (THF-d_8, 500 MHz): δ 10.51 (brs, 4H), 8.86 (s, 8H), 7.76 (brs, 4H), 7.73 (d, 4H, *J* 7.4 Hz), 7.58 (t, 4H, *J* 7.9 Hz), 7.3 (dd, 4H, J_1 8.4 Hz, J_2 2 Hz), 4.16 (t, 8H, *J* 6.5 Hz), 2.16 (t, 8H, *J* 7.4 Hz), 1.86 (quintet, 8H, *J* 7.7 Hz), 1.5-1.58 (m, 16H), 1.29-1.42 (m, 40H). λ_{max} (acetone) 422, 554, 593 nm. MALDI-TOF: isotopic cluster at m/z 1477.3 [M^+, 100%]].

5,10,15,20-Tetrakis(3-(thioacetate-11-undecenyloxy)phenyl)porphyrinato zinc (9)



Scheme S4. Preparation of 5,10,15,20-tetra[3-(thioacetate-11-undecyloxyphenyl)]porphyrinato zinc (**9**) [Reagents: i. K_2CO_3, DMF, $Br(CH_2)_nOH$; ii. CH_3SO_2Cl, pyridine, DCM; iii. Propionic acid, pyrrole; iv. CH_3COSK, DMF, K_2CO_3; v. THF, $Zn(OAc)_2$].

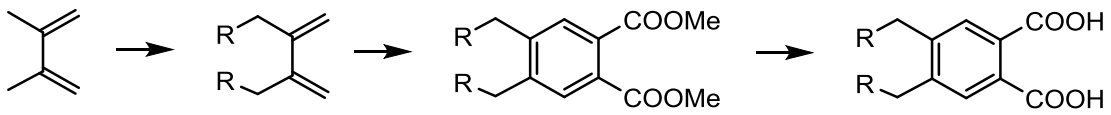
3-(11-hydroxy-undecenyloxy)benzaldehyde: 3-Hydroxybenzaldehyde (6.2g, 51 mmol) in DMF (120 mL) was stirred in the presence of 11-bromoundecanol (12.5 g, 50 mmol) and potassium carbonate (25 g, 0.2 mol) at 90 °C under N_2 overnight. The mixture was cooled, poured into water and extracted with dichloromethane. The organic layer was washed with water (x4), brine, dried ($MgSO_4$), filtered and the solvent removed to give a pale yellow oil (13.2 g, 89%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.96 (s, 1H), 7.4-7.44 (m, 2H), 7.37-7.38 (m, 1H), 7.14-7.18 (m, 1H), 4.0 (t, 2H, *J* 6.5 Hz), 3.63 (brt, 2H), 1.79 (quintet, 2H, *J* 7.4 Hz), 1.56 (quintet, 2H, *J* 7.4 Hz), 1.45 (quintet, 2H, *J* 7.8 Hz). 1.29-1.38 (m, 12H).

3-(11-Methanesulfonyloxyundecyloxy)benzaldehyde: 3-(11-Hydroxyundecyloxy)benzaldehyde (13.2 g, 45 mmol) was dissolved in dichloromethane (50 mL) and Et_3N (10 mL) under N_2. The solution was cooled with an ice bath and excess methanesulfonylchloride (5 mL) was added dropwise. The solution was allowed to warm to room temperature and was stirred a further 1 hr. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water (x2), brine, dried ($MgSO_4$), filtered and the solvent removed to give a pale yellow oil (15.6 g, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.96 (s, 1H), 7.4-7.44 (m, 2H), 7.36-7.38 (m, 1H), 7.14-7.18 (m, 1H), 4.21 (t, 2H, *J* 6.6 Hz), 4.0 (t, 2H, *J* 6.2 Hz), 2.99 (s, 3H), 1.79 (quintet, 2H, *J* 7.5 Hz), 1.74 (quintet, 2H, *J* 7.1 Hz), 1.46 (quintet, 2H, *J* 7.5 Hz), 1.29-1.4 (m, 12H).

3-(11-Thioacetatoundecyloxy)benzaldehyde: 3-(11-Methanesulfonyloxyundecyloxy)benzaldehyde (6.0 g, 16 mmol) in DMF (25 mL) was stirred at room temperature in the presence of potassium thioacetate (2 g, 17 mmol) for 3 h. Water was added and the flask placed in the fridge overnight. The solid was filtered, washed with water and dried in air (5.6 g, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.96 (s, 1H), 7.41-7.45 (m, 2H), 7.37-7.38 (m, 1H), 7.15-7.18 (m, 1H), 4.01 (t, 2H, *J* 6.6 Hz), 2.86 (t, 2H, *J* 7.4 Hz), 2.31 (s, 3H), 1.79 (quintet, 2H, *J* 7.9 Hz), 1.56 (quintet, 2H, *J* 7.4 Hz), 1.46 (quintet, 2H, *J* 7.7 Hz), 1.26-1.39 (m, 12H).

*5,10,15,20-Tetrakis(3-(11-thioacetato-undecyloxy)phenyl)porphyrinato zinc (**9**):* 3-(11-Thioacetatoundecyloxy)benzaldehyde (5.6 g, 16 mmol) was refluxed in propionic acid (75 mL). Pyrrole (1.1 mL, 16 mmol) was added. The mixture darkened immediately and was refluxed 2 h. The solvent was removed under reduced pressure. The residue was washed with methanol then filtered through silica, eluent CH_2Cl_2. The solvent was removed (MALDI-TOF: isotopic cluster at m/z 1590.98 [M^+, 100%]). The residue was then refluxed in dichloromethane in the presence of excess $Zn(OAc)_2$ dihydrate. Reflux was continued until UV analysis showed no more starting material was present (*ca*. 30 min). The solvent was then removed under vacuum. The residue was filtered through silica, eluent CH_2Cl_2, to afford the product which was precipitated from dichloromethane/methanol (530 mg, 8%). ^{1}H NMR ($CDCl_3$ + a drop of pyridine-d_5, 500 MHz): δ 8.85 (s, 8H), 7.69-7.71 (m, 8H), 7.51 (t, 4H, *J* 7.8 Hz), 7.22 (ddd, 4H, J_1 8.4 Hz, J_2 2.6 Hz, J_3 0.9 Hz), 4.06 (t, 8H, *J* 6.5 Hz), 2.75 (t, 8H, *J* 7.4 Hz), 2.21 (s, 12H), 1.79 (quintet, 8H, *J* 7.7 Hz), 1.39-1.5 (m, 16H), 1.18-1.3 (m, 48H). λ_{max} (CH_2Cl_2) 420, 548, 588 nm. MALDI-TOF: isotopic cluster at m/z 1653.4 [M^+, 100%].

Preparation of 4,5-didodecylphthalic acid

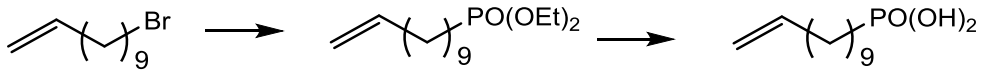


2,3-Bis(dodecyl)buta-1,3-diene: To a solution of *t*-BuOK (11 g, 0.1 mol) in dry *n*-pentane (50 mL) at room temperature under N_2 was added a solution of 2.5 M *n*-BuLi in hexanes (40 mL, 0.01 mol). The mixture was stirred for 10 min. Then a solution of buta-1,3-diene (4.1 g, 0.05 mol) in *n*-pentane (10 mL) was added dropwise. The solution was stirred for 30 min and turned deep orange. The solution was cooled to -78 °C. Dry THF (50 mL) was added, followed by 1-bromoundecane (23.5 g, 0.1 mol) in THF (20 ml). The solution was left to warm to room temperature and stirred overnight. The pale yellow solution was poured into water (200 mL) and the organics extracted with ethylacetate (3x50 mL). These were dried (MgSO4), filtered and the solvents removed under reduced pressure to leave a pale yellow oil (50 g crude) which was used further without purification. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.05 (s, 2H), 4.9 (s, 2H), 2.23 (t, 4H, *J* 7.4 Hz), 1.61 (quintet, 4H, *J* 7.2 Hz), 1.21-1.29 (m, 36H), 0.88 (t, 6H, *J* 6.9 Hz).

Dimethyl-4,5-di(dodecyl)phthalate: The pale yellow crude oil obtained above (50 g) containing 2,3-bis(dodecyl)buta-1,3-diene was refluxed in toluene (50 mL) in the presence of dimethylacetylene-dicarboxylate (7.1 g, 50 mmol) for 1 h. DDQ (12 g, 53 mmol) was added slowly in portions to the refluxing solution. Reflux was continued for 1 h. After cooling, the solid was filtered off. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica (eluent: CH_2Cl_2-light petroleum (bp. 40-60 °C)) to yield dimethyl-4,5-di(dodecyl)phthalate as a pale orange oil which solidified upon standing (5.3 g, 0.01 mol). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.49 (s, 2H), 3.88 (s, 6H), 2.65 (t, 4H, *J* 7.4 Hz), 1.56 (quintet, 4H, *J* 6.8 Hz), 1.22-1.34 (m, 36H), 0.87 (t, 6H, *J* 6.8 Hz).

4,5-Di(dodecyl)phthalic acid: Dimethyl-4,5-di(dodecyl)phthalate (5.3 g, 0.01 mol) was refluxed in ethanol (50 mL). A 20% solution of NaOH in water (5 mL) was added and reflux continued for 2 h. After cooling, this was poured into 5% aqu. HCl (100 mL). The organic fraction was extracted with ethylacetate (2x50 mL), washed with brine (50 mL), dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to yield 4,5-di(dodecyl)phthalic acid as a cream solid (94%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.22 (br s, 2H), 7.63 (s, 2H), 2.66 (t, 4H, *J* 8.1 Hz), 1.59 (quintet, 4H, *J* 7.6 Hz), 1.18-1.42 (m, 36H), 0.87 (t, 6H, *J* 7.1 Hz); mp 80-81 °C.

Preparation of 11-undecenylphosphonic acid



Diethylundec-10-enylphosphonate: 11-Bromoundecene (2 g, 8.6 mmol) and triethylphosphite (3 mL) were refluxed overnight in toluene (3 mL) under N_2. After cooling, excess water was added and the

mixture was stirred at room temperature for 3 h. The organic portion was extracted using dichloromethane, dried ($MgSO_4$), filtered and the solvent removed under vacuum to afford a pale yellow oil. Yield: 2.3 g (89%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.69-5.77 (m, 1H), 4.84-4.94 (m, 2H), 3.96-4.07 (m, 4H), 1.93-1.99 (m, 2H), 1.61-1.68 (m, 2H), 1.48-1.57 (m, 2H), 1.27-1.33 (m, 4H), 1.25 (t, 6H, *J* 7.06 Hz), 1.21 (br s, 8H). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 32.52.

Undec-10-enylphosphonic acid: To diethyl-undec-10-enylphosphonate (2.3 g, 7.8 mmol) in dry CH_2Cl_2 (20 mL) under N_2 was added Me_3SiBr (4 mL) and the solution was stirred overnight at rt. The mixture was then refluxed 4 h. After cooling, the solvent was removed under vacuum. MeOH was added to the residue and the solution was stirred 2 h at rt. The solvent was removed under reduced pressure leaving a cream solid. Yield 1.87 g (100%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.93 (br s, 2H), 5.78-5.86 (m, 1H), 4.92-5.02 (m, 2H), 2.02-2.07 (m, 2H), 1.7-1.81 (br m, 2H), 1.56-1.66 (br m, 2H), 1.34-1.42 (m, 4H), 1.25-1.33 (m, 8H). ^{31}P NMR ($CDCl_3$, 500 MHz): 37.5.

Luminescence studies and quantum yields

Solutions of CdSe were prepared in chloroform and their concentration calculated from their UV absorption. Solutions of porphyrins were subsequently prepared. Aliquots of these were added to the solution of CdSe and their fluorescence emission recorded over the range 370-700 nm (λ_{ex} 350 nm) and/or 560-700 nm (λ_{ex} 547 nm).

Fluorescence quantum yields were calculated using the comparative method described by Williams *et al*.[S2] as follows.

A series of dilutions of quinine sulphate in 0.1 N H_2SO_4 were prepared and their UV absorption and fluorescence emission measured and plotted (λ_{ex} 350 nm). A series of dilutions of CdSe in chloroform were prepared and their UV absorption and fluorescence emission measured and plotted (λ_{ex} 350 nm). The quantum yield was calculated from equation 1 using the gradient of the slopes obtained from the plots.

$$Q=Q_R\,(Grad/Grad_R)(\eta^2/\eta_R^2) \qquad (1)$$

where Q_R is the reference quantum yield of quinine sulphate in 0.1 N H_2SO_4 (54.6%), Grad and $Grad_R$ are the gradients measured from the plots for CdSe and quinine sulphate respectively, η and η_R are the refractive indexes of the solutions (1.4242 for DCM, 1.346 for 0.1 N H_2SO_4 respectively)

Determination of the number of ligands/nm^2 from integration against ferrocene internal standard

The nanoparticle diameter was calculated using eq 2 from the absorption wavelength as described by Peng.[S3] The extinction coefficient was then calculated from the diameter with eq 3.

$$D = 1.6122\text{x}10^{-9}\,\lambda^4 - 2.6575\text{x}10^{-6}\,\lambda^3 + 1.6242\text{x}10^{-3}\,\lambda^2 - 0.4277\,\lambda + 41.57 \qquad (2)$$

$$\varepsilon = 5857\ D^{2.65} \qquad (3)$$

The concentration was then calculated using Beer-Lambert law, eq 4

$$A = \varepsilon c l \qquad (4)$$

where A is the absorption at a given concentration *c* (mol/L) and path length *l* (cm).

The number of ligands/nm^2 was calculated as follows.

A UV solution in chloroform of concentration [CdSe+oleates] = 83.95 mg/L was prepared with the following absorption characteristics: λ = 497 nm, A = 0.13674, *l* = 1 cm.

The concentration of CdSe in the solution was calculated from this as [CdSe] = 2.51 x 10^{-6} M (D = 2.32 nm, ε = 54477.7)

An NMR solution in $CDCl_3$ of concentration [CdSe+oleates] = 16000 mg/L was prepared yielding [CdSe] = 4.78 x 10^{-4} M (by UV) , *i.e*. 2.87 x 10^{-7} mol. To this was added 1.304 x 10^{-6} mol of ferrocene.

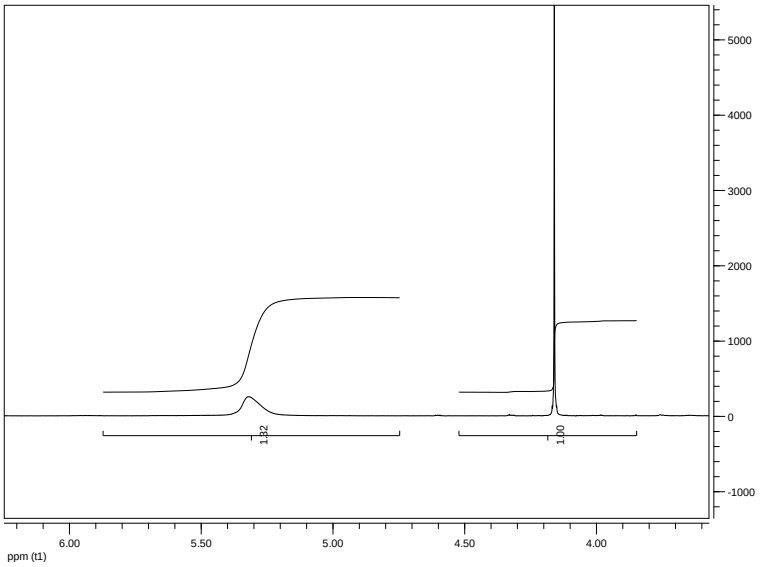


Figure S1. Integration of oleates (2H):ferrocene (10H) 1.32:1

Based on the integration of the peaks, [oleates] = 8.61 x 10^{-6} mol, *i.e*. 8.61 x 10^{-6}/2.87 x 10^{-7} = 30 oleates/NP
Surface area of NP (D=2.32 nm) = 16.9 nm^2
So there are *ca*. 1.8 oleate molecules per nm^2

	D = 2.0 nm	D = 2.32 nm	D = 2.5 nm
Volume of single NP $V = 4/3\Pi r^3$	4.18x10^{-21} cm^3	6.54x10^{-21} cm^3	8.18x10^{-21} cm^3
Weight of single NP = density CdSe[a] x V	2.44x10^{-20} g	3.80x10^{-20} g	4.76x10^{-20} g

Number of moles of CdSe per NP = weight of NP/MW[b]	1.27×10^{-21} mol	1.99×10^{-22} mol	2.49×10^{-22} mol
Number of atoms per NP = number of moles x $2N_A$	153	239	300
Cd_xSe_y[c]	$Cd_{82}Se_{71}$	$Cd_{128}Se_{111}$	$Cd_{160}Se_{140}$
Molecular weight	14824	23153	29040

[a]Bulk density of CdSe = 5.816 g/cm^3

[b]Molecular weight of CdSe = 191.37 g/mol

[c]Assuming a ratio of Cd:Se per nanoparticle of *ca*. 1.15:1

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S3 Yu, W. W.; Qu, L. H.; Guo, W. H.; Peng, X. G. *Chem. Mater*. **2003**, *15*, 2854-2860.