# Photoinduced Electron-Transfer within Porphyrin-Containing Poly(Amide) Dendrimers

Gregory J. Capitosti, Susan J. Cramer, Cheruvallil S. Rajesh and David A. Modarelli*

Department of Chemistry and The Center for Laser and Optical Spectroscopy, Knight Chemical Laboratory, The University of Akron, Akron, OH 44325-3601

## SUPPORTING INFORMATION

1) General experimental description

2) Photophysical measurements

3) Electrochemical measurements

4) Syntheses

5) References for synthetic procedures

## Experimental

All reactions were run under a nitrogen atmosphere unless indicated otherwise. THF was distilled from Na/benzophenone ketyl, while all other solvents were used as received. All starting materials were used as received from Aldrich or Acros. Flash chromatography was carried out on silica gel (230-400 mesh) or neutral alumina (60-325 mesh). All melting points were taken using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton NMR were acquired using a Varian Gemini 300 MHz solution NMR. Carbon-13 NMR (75 MHz) were acquired using the same instrument, and were proton decoupled. MALDI-TOF-MS were recorded using µ-cyano-4-hydroxycinnamic acid (CCA) as the matrix. Samples were prepared[1] by mixing 1.0 mL of a solution of the dendrimer in $CH_2Cl_2$ with 1 mL of a solution of the matrix in MeCN/EtOH/$H_2O$ 50:45:5. The polydispersity data was determined using GPC by comparison with known polystyrene standards. Relative molecular weights were determined by gel permeation chromatography (GPC) at 35 °C using $CHCl_3$ as the solvent (1.0 mL/min), a set of 50 Å, 100Å, 500Å, 104 Å and linear (50-104 Å) Styragel 5 m columns, a Waters 486 tunable UV/Vis detector set at 420 nm, and a Waters 410 differential refractometer. MALDI spectra were obtained with a Bruker Reflex 3 mass spectrometer.

## Photophysical Measurements

### Steady State Fluorescence

Steady-state fluorescence measurements were run on a ISA Jobin Yvon-SPEX Fluorolog 3-22 fluorometer having dual input and output monochromators. Fluorescence spectra were collected using argon-saturated solutions by exciting at the Soret maxima in S/R mode to correct for changes in the lamp output intensity. Quantum yield measurements were made relative to TPP and ZnTPP.

### Time-resolved fluorescence measurements

All solvents used for spectroscopic measurements were either Spectral or HPLC-grade. Time-resolved fluorescence experiments were performed using the time-correlated single-photon counting (TCSPC) technique. The experimental apparatus used in this work utilizes the pulses from a Coherent cavity dumped 702 dye laser pumped by the 532-nm output of a Coherent Antares 76-s CW mode-locked Nd:YAG laser. The fluorescence signal was detected at 55° with an emission polarizer and depolarizer, using a Hamamatsu R3809U-51 red-sensitive multichannel plate detector. Data collection and analysis is accomplished with an Edinburgh Instruments data collection system. The time-resolution of this system is estimated at ~7 - 9 ps. All experiments were run with argon-saturated solutions, and were excited with 590 nm light and the decay profiles monitored at 655 nm.

Electron-transfer rate constants were calculated using Eqn 1:

$$k_{\mathrm{ET}} = \frac{1}{\tau_{\mathrm{AQ}}} - \frac{1}{\tau_{\mathrm{Et}}} \qquad (1)$$

where $\tau_{AQ}$ represents the fluorescence lifetime of the anthraquinone-terminated dendrimers (**FbP-G$_a$-AQ$_n$**) and includes contributions from each fluorescent lifetime, such that $\tau_{AQ} = a_1(\tau_1) + a_2(\tau_2) + a_3(\tau_3)$, and a-c represent the pre-exponential factors for each component as determined by the equation: $a_i = (a_i\tau_i/\Sigma a_i\tau_i)100$. For each anthraquinone-terminated dendrimer, an analogous measurement was made for the corresponding ethyl-terminated dendrimer (**FbP-G$_a$-Et$_n$** of the same generation) to provide the values of $\tau_{Et}$.[16]

## Electrochemical Measurements

Cyclic voltammograms were recorded on a BAS-100 electrochemistry apparatus from Bioanalytical Systems, Inc. at 20 °C. A three-electrode configuration was used with a platinum working and auxiliary electrodes, and a non-aqueous Ag/$AgNO_3$ reference electrode (Ag wire in an $CH_3CN$ solution of 0.01 M $AgNO_3$ and 0.1 supporting electrolyte, tetrabutyl ammonium hexafluorophosphate, $Bu_4NPF_6$) or tetrabutyl ammonium perchlorate (Ag/AgCl, reference electrode). Measurements were also made against the standard calomel electrode as a reference ($Bu_4NPF_6$ electrolyte). All electrochemical experiments were run in spectroscopic grade $CH_2Cl_2$ that was distilled prior to use from $CaH_2$. Samples were prepared at a variety of concentrations, with an optimum concentration of $3.0 \times 10^{-4}$ M.

| Dendrimer | Solvent | Electrolyte | $E_{1/2}$ (ox)[a] | $E_{1/2}$ (red)[a] | $E_{1/2}$ (ox)[b] | $E_{1/2}$ (red)[b] | $E_S$ | $\Delta G_{ET}$ |
|---|---|---|---|---|---|---|---|---|
| TPP[d] | $CH_2Cl_2$ | $TBAPF_6$ | 0.730 | | 0.972 | | 1.91 | |
| FbP-$G_1$-$Et_{12}$ | $CH_2Cl_2$ | $TBAPF_6$ | 0.855 | | 1.07 | | 1.91 | |
| FbP-$G_1$-$AQ_{12}$ | $CH_2Cl_2$ | $TBAPF_6$ | 0.811 | $-1.18$ | 1.04[d] | $-0.966$ | 1.90 | 0.11[c] |
| TPP | $CH_2Cl_2$ | TBAP | 1.03 | | | | 1.91 | |
| FbP-$G_1$-$Et_{12}$ | $CH_2Cl_2$ | TBAP | 1.14 | | | | 1.91 | |
| FbP-$G_1$-$AQ_{12}$ | $CH_2Cl_2$ | TBAP | 1.08 | $-0.891$ | | | 1.90 | 0.071[e] |

[a] Volts, referenced vs. Ag/AgCl (TBAP electrolyte soltuion) or Ag/$AgNO_3$ ($TBAPF_6$ electrolyte solution). [b] Volts, referenced vs. SCE reference electrode. [c] Estimated using the Weller equation ($\Delta G_{ET} = E_{ox} - E_{red} - E_S$*), from the values recorded using the SCE reference electrode. The more complete form of the Weller eqn, $\Delta G_{ET} = E_{ox} - E_{red} - e_0^2/\varepsilon r_{12} - E_S$*, was not used due to uncertainties in $r_{12}$. [d] Estimated from the $E_p$ value. [e] Estimated using the Weller equation, from the values recorded using the Ag/AgCl reference electrode.

Measurements were attempted for all free base porphyrin dendrimers: **FbP-$G_a$-$Et_n$** and **FbP-$G_a$-$AQ_n$**. Reliable $E_{1/2}$(ox) values were obtained only for the first generation dendrimers **FbP-$G_1$-$Et_{12}$** and **FbP-$G_1$-$AQ_{12}$**. Newkome et al. ( See, for example, Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2023-2026 and Newkome, G.R.; Narayanan, V.V.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. *Macromolecules* **1997**, *30*, 5187-5159, Deiderich *Helv. Chim. Acta* **1997**, *80*, 1773-1801) have reported that the CV spectra of ruthenium bis-terpyridyl containing dendrimers are dominated by kinetic effects at higher generations, and thermodynamically correct values may not result from these measurements. The first generation dendrimers were observed to have slightly higher oxidation potentials than TPP. $E_{1/2}$

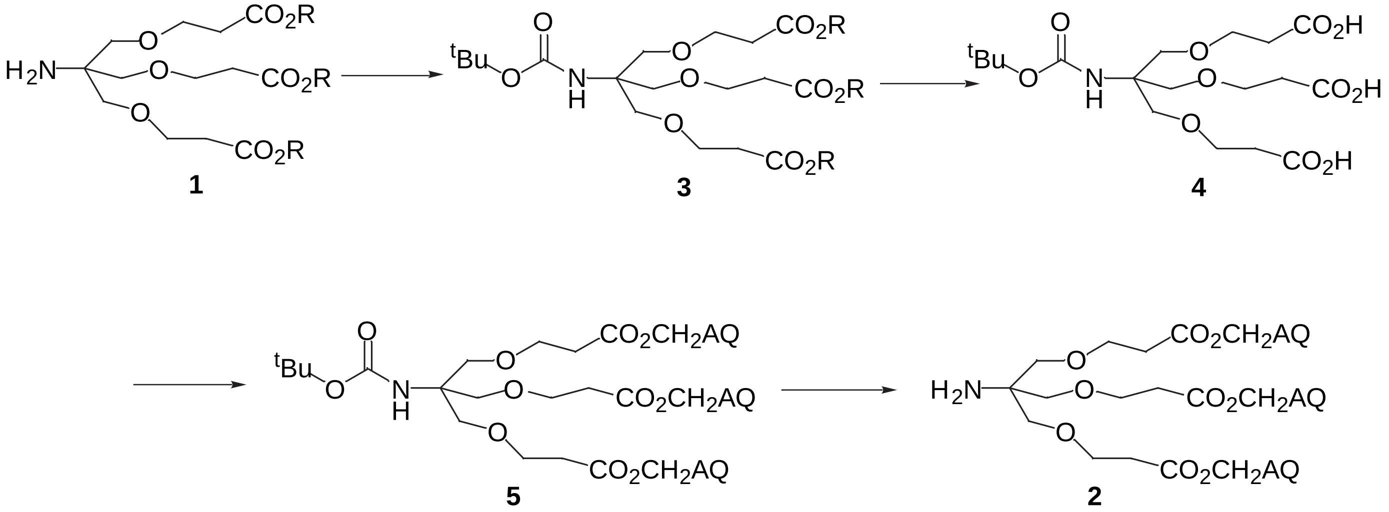
values of 1.28, 0.95 and -1.28 V for the first two oxidation waves and the first reduction wave for TPP have been obtained vs. SCE (Brown, G.M.; Hopf, F.R.; Ferguson, J.A.; Meyer, T.J.; Whitten, D.G. *J. Am. Chem. Soc.* **1973**, *95*, 5939-5942.; Chen, H.L.; Ellis, P.E.; Wijesekera, T.; Hagan, T.E.; Groh, S.E.; Lyons, J.E.; Ridge, D.P. *J. Am. Chem. Soc.* **1994**, *116*, 1086-1089), in good agreement with our results (1.31, 0.97, -1.25 V) under the same conditions. Using the silver reference electrode, we have determined very similar values to Ravikanth, M.; Chandrashekar, T.K. *J. Photochem. Photobiol. A.* **1993**, *74*, 181-187.; Ravikanth, M.; Chandrashekar, T.K. *J. Ind. Chem. Soc.* **1993**, *70*, 1023-1034.; Ravikanth, M.; Reddy, D.; Chandrashekar, T.K. *J. Chem. Soc., Dalton Trans.* **1993**, 1137-1141). The oxidation potentials of the anthraquinone-terminated dendrimers are lower than the ethyl-terminated dendrimers, consistent with the absorption results, which show shifts to lower energies for the anthraquinone-terminated dendrimers and not the ethyl-terminated dendrimers. These results are reproducible with two different electrolytes ($Bu_4NPF_6$ and $Bu_4NClO_4$) as well as the Ag/AgCl, $Ag/AgNO_3$ and SCE reference electrodes. This information will be reported in full in a future publication.

Because the microenvironment at the porphyrin core is expected to change with increasing generations, values of $\Delta G_{ET}$ cannot be accurately determined for the G2 and G3 dendrimers. We have therefore reported the values of $\Delta G_{ET}$ using the G1 oxidation potentials. We must again emphasize that because these results include only the two G1 dendrimers; the data does not reflect any generation-dependent changes in $\Delta G_{ET}$ that will surely result from any generation-dependent changes in $E_{1/2}$(ox). Values of $S_1$ were estimated in the usual manner from the wavelengths of the longest Q-band absorption and the $S_1 \rightarrow S_0$ emission.

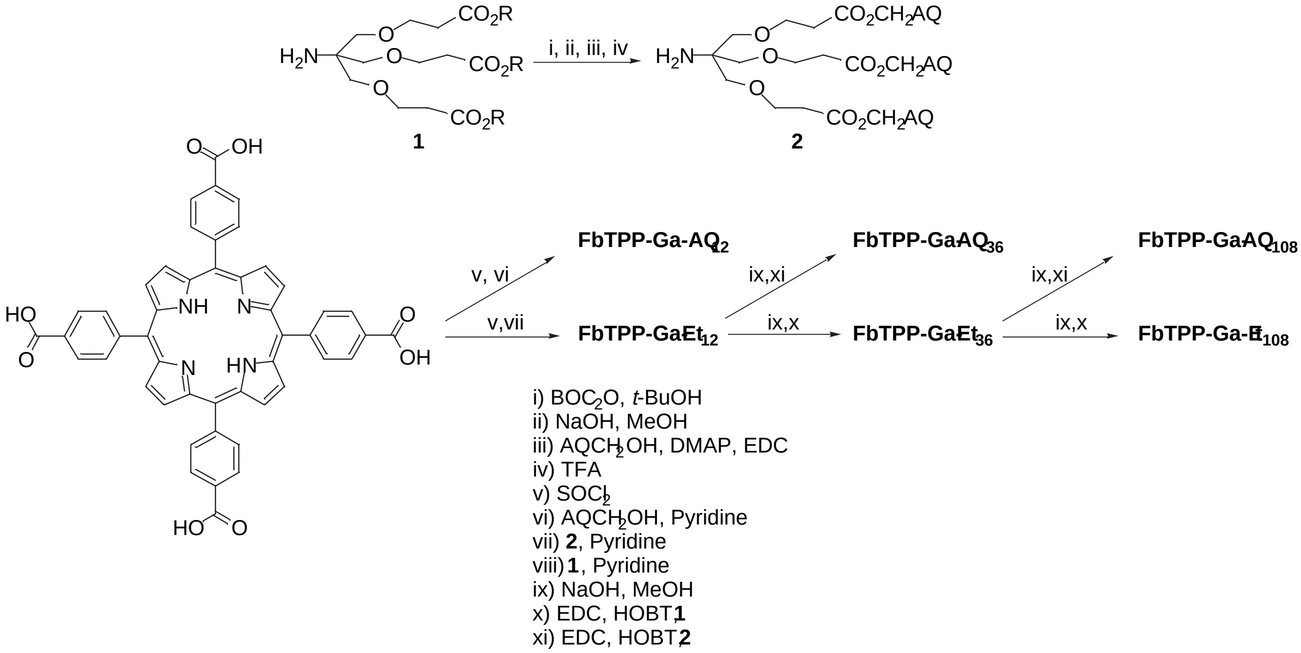
## Synthesis

The synthesis used by us refers to the compounds presented in Schemes 1 and 2.

**Scheme 1**



Scheme 2



### Tris[(alkyl ester ethoxy)methyl]t-boc protected amine, **3**

To a solution of **1** (R = Et or Me) (1.050 g, 2.77 mmol) in 8 mL *tert*-butyl alcohol was added di-*tert*-butyl dicarbonate (0.684 g, 3.13 mmol, 1.1 eq).[2] This solution was heated to 48 °C while stirring under nitrogen for 22 h. The reaction mixture was cooled and poured into 100 mL of water and extracted with $CH_2Cl_2$. The organic layer was washed with 10% HCl, saturated $NaHCO_3$ and water, dried over $Na_2SO_4$ and concentrated. The product was isolated as a pale yellow oil, (1.236 g, 2.58 mmol 92%). $^1H$ NMR ($CDCl_3$): δ 1.42 (9H, s), 2.60 (6H, t, J = 6.0 Hz), 3.63 (6H, s), 3.70-3.68 (15H, m). $^{13}C$ NMR ($CDCl_3$): δ 28.5, 35, 52, 58.5,67,69.5, 85, 155, 172.5. IR: 1727.6 $cm^{-1}$ (C=O).

Tris[(carboxylic acid ethoxy)methyl]t-boc protected amine, **4**

To a solution of (0.123g, 0.26 mmol) of **3** in 3 mL MeOH was added dropwise a 1 mL 10% solution of NaOH at 0 °C under nitrogen. The reaction was allowed to warm to room temperature and stirred 36 h.[3,4] The reaction was acidified to pH 3 using 10 % HCl. The reaction mixture was saturated with salt and extracted with THF. The THF was evaporated and the resulting solution was extracted with $CHCl_3$. The organic layer was dried over $Na_2SO_4$ and concentrated to give a pale yellow oil (0.090 g, 0.21 mmol, 80%). $^1H$ NMR ($CDCl_3$): δ 1.41 (9H, s), 2.59 (6H, t, J = 6.0 Hz), 3.76-3.65 (12H, m). $^{13}C$ NMR ($CDCl_3$): δ 28.5, 35, 58.7, 66.7, 69.9, 155, 177.4.

Tris[(methylanthraquinone ester ethoxy)methyl]t-boc protected amine, **5**

To a solution of **4** (0.090g, 0.21 mmol) in 15 mL dry $CH_2Cl_2$ was added dimethyl amino pyridine (DMAP) (0.013g, 1.1 mmol, 0.5 eq) and 2-hydroxymethylanthraquinone (0.220g, 0.93 mmol, 4.5 eq). This solution was stirred at 0 °C under nitrogen for 5 min then 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide (EDC) (0.142g, 0.75 mmol, 3.5 eq) was added.[1] The reaction was allowed to warm to room temperature and stirred for 48 h. The resulting solution was poured into 15 mL $CH_2Cl_2$ and extracted with water, 10% HCl, saturated $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and concentrated to give a pale yellow solid, and was used without further purification.

Tris[(methylanthraquinone ester ethoxy)methyl]aminomethane, **2** (isolated as the monohydrate)

To a solution of **5** (3.397 g, 3.1 mmol) in 10 mL $CH_2Cl_2$ cooled to 0 °C was added dropwise 12 mL trifluoroacetic acid (0.15 mol, 50 eq). This solution stirred at 0 °C under nitrogen for 1 h at which point the excess trifluoroacetic acid was neutralized with cold triethylamine. The reaction mixture was then extracted with water, dried over $MgSO_4$ and concentrated. Column chromatography on silica (100% ethyl acetate) gave a pale yellow solid (1.937 g, 1.9 mmol, 63 %, mp 120-123 °C). $^1H$ NMR ($CDCl_3$): δ 1.64 (4H, s), 2.67 (6H, t, J = 6.0 Hz), 3.32 (6H, s), 3.73 ( 6H, t, J = 6.0 Hz), 5.27 (6H, s), 7.81-7.75 (9H, m), 8.28-8.22 (12H, m). $^{13}C$ NMR ($CDCl_3$): δ 35.1, 65.2, 66.9, 72.9, 126.24, 127.5, 127.9, 133.2, 133.9, 134.5. Anal. Cal. for the monohydrate, $C_{58}H_{49}NO_{16}$ (1016.033): C 68.56, H 4.87, N 1.38; found C 68.78, H 4.81, N 1.37.

### FbP-G1-Et$_{12}$

4, 4’, 4’’, 4’’’-(21*H*, 23*H*-porphine-5,10,15,20-tetrayl)tetrakis-(benzoic acid) (0.6667 g, 0.8431 mmol) was placed into a 50 mL round bottom flask. To this solid was added excess thionyl chloride (25 mL). The resulting purple solution was stirred vigorously under nitrogen for 24 h, at which time the excess thionyl chloride was removed under vacuum, leaving behind the tetraacid chloride as a dark green solid. This solid was dissolved in dichloromethane and cooled to 0 °C under nitrogen. To this solution was added **1** (R = Et) (1.777 g, 4.216 mmol) and triethylamine (0.6827g, 6.745 mmol). The reaction was allowed to warm up to room temperature, where it was stirred under nitrogen for 48 h. The reaction mixture was then washed with 10% HCl, saturated $NaHCO_3$, and water. The organic layer was dried over $MgSO_4$ and filtered. Evaporation of the solvent, followed by column chromatography (75% ethyl acetate/hexanes) yielded **FbP-G1-Et$_{12}$** as a viscous purple oil (0.3824 g, 25%). $^1H$ NMR (300 MHz, $CDCl_3$) δ $^-$2.80 (s, 2H), 1.28 (t, 36H, J=7 Hz), 2.65 (t, 24H, J=6 Hz), 3.86 (t, 24H, J=6 Hz), 4.01 (s, 24H), 4.18 (q, 24H, J=7 Hz), 6.95 (s, 4H), 8.20 (d, 8H, J=8 Hz), 8.27 (d, 8H, J=8 Hz), 8.83 (s, 8H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.27, 35.09, 60.28, 60.50, 66.90, 69.33, 119.46, 125.62, 134.40, 134.76, 144.94, 167.43, 171.65; MALDI-TOF -MS: 2403.4 (calculated for $C_{124}H_{162}N_8O_{40}$: 2404.9); polydispersity: 1.03

### FbP-G1-(CO$_2$H)$_{12}$[1,3,5]

In a 25 mL round bottom flask, **FbP-G1-Et$_{12}$** (0.8198 g, 0.3409 mmol) was dissolved in methanol and cooled to 0 °C. An aqueous solution of 20% NaOH (1.55 mL, 8.181 mmol) was added via syringe, and the reaction was allowed to warm to room temperature, where it stirred for 48 h. The resulting solution was acidified with 0.4 M HCl until a precipitate began to form. The solid was extracted into ethyl acetate until no purple color remained in the aqueous layer. The organic layer was dried over $Na_2SO_4$, filtered and concentrated via vacuum to yield **FbP-G1-($CO_2H$)$_{12}$** as a purple solid (0.2379g, 82%). MP 96-99 °C; $^1$H-NMR (300 MHz, $CD_3OD$) $\delta$ $^-$2.50 (s, 2H), 2.66 (t, 24H, J=6 Hz), 3.86 (t, 24H, J=6 Hz), 4.02 (s, 24H), 6.90 (s, 4H), 8.35 (d, 8H, J=8 Hz), 8.60 (d, 8H, J=8 Hz), 8.63 (s, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 35.80, 62.25, 68.14, 69.99, 123.52, 128.60, 130.52, 138.11, 139.60, 143.05, 146.92, 169.72, 174.06; MALDI-TOF-MS: 2067.5 (calculated for $C_{100}H_{114}N_8O_{40}$: 2068.1).

### FbP-G1-AQ$_{12}$[1,6,7]

To a 25 mL round bottom flask containing **FbP-G1-($CO_2H$)$_{12}$** (0.0456 g, 0.02139 mmol) dissolved in THF was added 2-(hydroxymethyl)anthraquinone (0.1223 g, 0.5134 mmol) and HOBT (0.0694 g, 0.5134 mmol) as solids. This solution was cooled to 0 °C, at which point EDC (0.09023 g, 0.4706 mmol) was added rapidly as a solid. The reaction was allowed to warm to room temperature, where it was stirred under nitrogen for 72 h. The THF was then evaporated, and the residue dissolved in chloroform. The resulting solution was washed with 10% HCl, saturated $NaHCO_3$ and water. The organic layer was dried over $Na_2SO_4$ and filtered. Column chromatography on alumina (50% ethyl acetate-methanol) yielded **FbP-G1-AQ$_{12}$** as a purple solid (0.0726 g, 75%). MP 110-113 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ $^-$3.60 (s, 2H), 2.79 (t, 24H, J=6 Hz), 3.91 (t, 24H, J=6 Hz), 4.05 (s, 24H), 5.28 (s, 24H), 7.04 (s, 4H), 7.44 (m, 23H), 7.69 (d, 14H, J=8 Hz), 7.91 (m, 23H), 8.15 (m, 40H) 8.58 (m, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 35.00, 60.32, 65.10, 66.80, 69.48, 125.74, 126.79, 127.57, 132.63, 132.75, 132.94, 133.37, 133.73, 133.79, 134.57, 142.50, 162.75, 171.31, 182.19, 182.38; MALDI-TOF-MS: 4711.2 (calculated for $C_{280}H_{210}N_8O_{64}$: 4710.9); polydispersity: 1.01.

### FbP-G2-Me$_{36}$[4,6,7]

To a 50 mL round bottom flask containing **FbP-G1-($CO_2H$)$_{12}$** (0.4009 g, 0.1938 mmol) in THF was added amine **1** (R = Me) (1.324 g, 3.489 mmol) and HOBT (0.5763 g, 4.265 mmol). The resulting solution was cooled to 0 °C, at which time EDC (0.8177 g, 4.265 mmol) was rapidly added as a solid. The reaction was allowed to slowly warm to room temperature where it stirred under nitrogen for

48 h. The THF was then evaporated, and the residue dissolved in chloroform. The resulting solid was washed with 10% HCl, saturated $NaHCO_3$ and water. The organic layer was dried over $Na_2SO_4$ and filtered. Column chromatography on silica (methanol) yielded **FbP-G2-Me$_{36}$** as a purple oil (0.8491 g, 68%). $^1$H NMR (300 MHz, $CDCl_3$) δ $^-$2.83 (s, 2H), 2.52 (m, 72H, J=6 Hz), 2.56 (t, 24H, J=6 Hz), 3.66 (m, 252H), 3.82 (t, 24H, J=6 Hz), 4.00 (s, 24H) 6.25 (s, 16H), 8.24 (s, 16H), 8.84 (s, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 34.62, 37.22, 51.57, 59.74, 60.45, 66.69, 67.64, 69.08, 69.15, 119.45, 125.87, 134.39, 134.62, 144.91, 167.27, 170.97, 171.98; MALDI-TOF-MS: 6407.1 (calculated for $C_{292}H_{438}N_{20}O_{136}$: 6405.5); polydispersity: 1.06.

**FbP-G2-(CO$_2$H)$_{36}$**[1,3,5]

In a 50 mL round bottom flask, **FbP-G2-Me$_{36}$** (0.5281 g, 0.08244 mmol) was dissolved in methanol. The resulting solution was cooled to 0 °C, and 1.13 mL of 20% NaOH was added. The mixture was allowed to warm to room temperature, where it was stirred for 48 h. Enough NaCl was then added to saturate the solution, at which point it was acidified to a pH of approximately 3-4. The product was then extracted with THF. The organic layer was dried over $Na_2SO_4$, filtered, and concentrated to give **FbP-G2-(CO$_2$H)$_{36}$** as a purple/green solid (0.3782 g, 78%). MP 64-67 °C; $^1$H NMR (300 MHz, $CD_3OD$) δ $^-$2.50 (s,2H), 2.49 (t, 72H, J=6 Hz), 2.55 (t, 24H, J=6 Hz), 3.66 (t, 72H, J=6 Hz), 3.73 (s, 72H), 3.83 (t, 24H, J=6 Hz), 4.01 (s, 24H), 8.43 (d, 8H, J=8 Hz), 8.57 (d, 8H, J=8 Hz), 8.98 (s, 8H); $^{13}$C NMR (75 MHz, $CD_3OD$) δ 30.89, 35.66, 38.11, 61.46, 68.04, 68.20, 68.93, 70.01, 70.33, 122.21, 126.12, 128.09, 132.16, 136.80, 169.85, 173.85, 175.26; MALDI-TOF-MS: 5899.8 (calculated for $C_{256}H_{366}N_{20}O_{136}$: 5900.2).

**FbP-G2-AQ$_{36}$**[1,6,7]

To a 50 mL round bottom flask containing **FbP-G1-(CO$_2$H)$_{12}$** (0.1000 g, 0.04835 mmol) in THF was added amine **2** (0.8204 g, 0.8220 mmol) and HOBT (0.1568 g, 1.160 mmol) as solids, and the mixture was cooled to 0 °C. The EDC (0.2260 g, 1.160 mmol) was then added rapidly as a solid. The mixture was gradually warmed to room temperature, where it stirred under nitrogen for 72 h. The THF was then evaporated, and the residue was dissolved in chloroform. This was washed with 10% HCl, saturated $NaHCO_3$ and water. The organic layer was dried over $Na_2SO_4$, filtered, and evaporated. Column chromatography on alumina (50:50 methylene chloride-methanol) resulted in **FbP-G2-AQ$_{36}$** as a purple solid (0.3300 g, 49%). MP 88-90 °C; $_1$H NMR (300 MHz, $CDCl_3$) $\delta$ $^-$4.32 (s, 2H), 2.64 (bs, 96H), 3.74 (m, 144H), 3.87 (bs, 24H), 4.06 (bs, 24H), 5.11 (bs, 72H), 6.43 (s, 16H), 7.54 (m, 108H), 7.95 (m, 144H), 8.26 (bs, 16H), 8.47 (s, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 34.78, 37.20, 59.88, 64.89, 66.68, 67.81, 69.23, 125.51, 126.85, 127.34, 132.51, 132.95, 133.14, 133.83, 142.45, 167.54, 171.13, 182.03, 182.18; MALDI-TOF-MS: 13828.5 (calculated for $C_{796}H_{654}N_{20}O_{208}$: 13828.5); polydispersity: 1.04.

### **FbP-G3-Et$_{108}$**[1,6,7]

To a 50 mL round bottom flask containing **FbP-G2-(CO$_2$H)$_{36}$** (0.0986 g, 0.01671 mmol) in THF was added amine **1** (R = Et) (0.4226 g, 1.003 mmol) in THF, and HOBT (0.1626 g, 1.203 mmol) as a solid. The resulting solution was cooled to 0 °C, at which point the EDC (0.2343 g, 1.203 mmol) was added rapidly as a solid. The mixture was gradually warmed to room temperature, where it was stirred under nitrogen for 72 h. The THF was then evaporated, and the residue dissolved in chloroform. This solution was washed with 10% HCl, saturated $NaHCO_3$ and water. The organic layer was dried over $Na_2SO_4$, filtered, and concentrated. Column chromatography on silica (methanol) resulted in **FbP-G3-Et$_{108}$** as a viscous purple oil (0.2769 g, 81%). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ $^-$2.85 (s, 2H), 1.25 (m, 324H), 2.42 (m, 96H), 2.52 (m, 216H), 3.68 (bs, 624H), 4.12, (m, 216H), 6.28 (s, 52H), 8.20 (m, 16H), 8.83 (s, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.22, 34.91, 37.11, 59.80, 60.38, 66.77, 67.51, 69.08, 70.63, 170.98, 171.53; MALDI-TOF-MS: 18,884.0 (calculated for $C_{904}H_{1554}N_{56}O_{424}$: 20,424.8); polydispersity: 1.08.

### **FbP-G3-AQ$_{108}$**[1,6,7]

To a 50 mL round bottom flask containing **FbP-G2-(CO$_2$H)$_{36}$** (0.1010 g, 0.01712 mmol) in THF was added amine **2** (1.025 g, 1.027 mmol) and HOBT (0.1666 g, 1.232 mmol) as solids, and the mixture was cooled to 0 °C. The EDC (0.2400 g, 1.232 mmol) was then added rapidly as a solid. The mixture was gradually warmed to room temperature, where it stirred under nitrogen for 72 h. The THF was then evaporated, and the residue was dissolved in chloroform. This solution was washed with 10% HCl, saturated $NaHCO_3$ and water. The organic layer was dried over $Na_2SO_4$, filtered, and evaporated. Column chromatography on alumina (50:50 methylene chloride-methanol) resulted in **FbP-G3-AQ$_{108}$** as a purple solid (0.1762 g, 25%). MP 109-112 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 2.46 (bs, 96H), 2.62 (bs, 216H), 3.71 (bs, 624H), 5.09 (bs, 216H), 6.44 (bs, 52H), 7.55 (bs, 432H), 7.91 (bs, 324H), 8.20 (s, 16H), 8.42 (s, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 29.68, 34.74, 37.14, 59.91, 64.84, 66.68, 67.58, 69.17, 125.43, 126.87, 127.31, 132.46, 132.94, 133.89, 142.54, 171.12, 181.97; MALDI-TOF-MS: 29,355.5 (calculated for $C_{2344}H_{1986}N_{56}O_{640}$: 41,181.3); polydispersity: 1.33.

**References:**

(1) Dandliker, P. J.; Diederich, F.; Zingg, A. *Helvetica Chimica Acta*, **1997**, *80*, 1773-1801.

(2) Frechet, J. M. J.; Uhrich K. E. *J. Chem. Soc. Perkin Trans. 1*, **1992**, 1623-1630.

(3) Newkome, G.R.; Lin, X. *Macromolecules*, **1991**, *24*, 1443-1444.

(4) Newkome G.R.; Lin, X.; Young, J.K. *Synlett*, **1992**, 53-54.

(5) Newkome, G. R.; Lin, X.; Weis, C. D. *Tetrahedron: Asymmetry* **1991**, *10*, 957.

(6) Sheehan, J. C.; Hlavka, J. J. *J. Org. Chem.* **1956**, *21*, 439.

(7) Sheehan, J. C.; Jedis, S. L. *J. Am. Chem. Soc.* **1973**, *95*, 875.