

Supporting Information for Self-Sorting and Coassembly of Fluorinated, Hydrogenated, and Hybrid Janus Dendrimers into Dendrimersomes

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1 Materials

All reagents were obtained from commercial sources and used without purification unless otherwise stated. CH₂Cl₂ (DCM) was dried over CaH₂ and freshly distilled before use. DMF was dried from CaH₂ or ninhydrin, distilled, and kept over molecular sieves prior to use. THF was distilled over Na/benzophenone immediately before use. Solvents and reagents were deoxygenated when necessary by purging with nitrogen. Milli-Q water obtained by Milli-Q UV plus with the resistivity 18.2 MΩ·cm was used for the preparation of phosphate-buffered saline (PBS). PBS (1×) was obtained by dissolving 8 g of NaCl, 0.2 g of KCl, 1.44 g of Na₂HPO₄ and 0.24 g of KH₂PO₄ in 800 ml of Milli-Q water, adjusted to pH = 7.4 and diluted to 1,000 mL.

2 Techniques

¹H, ¹³C, and ¹⁹F NMR spectra were recorded at 500 MHz, 126 MHz, and 470 MHz respectively, on a Bruker DRX (500 MHz) NMR spectrometer by Topspin. All NMR spectra were measured at 25 °C in CDCl₃. Chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The resonance multiplicities in the ¹H NMR spectra are described as “s” (singlet), “d” (doublet), “t” (triplet), “quint” (quintet) and “m” (multiplet) and broad resonances are indicated by “br”. Residual protic solvent of CDCl₃ (¹H, δ 7.26 ppm; ¹³C, δ 77.16 ppm (central resonance of the triplet)), and tetramethylsilane (TMS) were used as the internal reference in the ¹H- and ¹³C-NMR spectra. The absorptions are given in wavenumbers (cm⁻¹). Evolution of the reaction was monitored by thin-layer chromatography (TLC) using silica gel 60 F₂₅₄ precoated plates (E. Merck) and compounds were visualized by UV light with a wavelength of 254 or 356 nm. Purifications by flash column chromatography were performed using flash silica gel from Silicycle (60 Å, 40–63 μ m) with the indicated eluent. The purity of the products was determined by a combination of TLC and high pressure liquid chromatography (HPLC) using Perkin-Elmer Series 10 high pressure liquid chromatograph equipped with an LC-100 column oven, Nelson Analytical 900 Series integrator data station and two Perkin-Elmer PL gel columns of 5×10² and 1×10⁴ Å. THF was used as solvent at the oven temperature of 40 °C. Detection was done by UV absorbance at 254 nm. MALDI-TOF mass spectrometry was performed on a PerSeptive Biosystem-Voyager-DE (Framingham, MA) mass spectrometer equipped with nitrogen laser (337 nm) and operating in linear mode. Internal calibration was performed using Angiotensin II and Bombesin as standards. The analytical sample was obtained by mixing the THF solution of the sample (5–10 mg/mL) and THF solution of the matrix (2,5-dihydroxybenzoic acid, 10 mg/mL) in a 1/5 (vol/vol) ratio. The prepared solution of the sample and the matrix (0.5 μ L) was loaded on the MALDI plate and allowed to dry at 23 °C before the plate was inserted into the vacuum chamber of the MALDI instrument. The laser steps and voltages applied were adjusted depending on both

the molecular weight and the nature of each analyzed compound.

2.1 Preparation of Dendrimersomes

2.1.1 Dendrimersome by Injection

A stock solution was prepared by dissolving the required amount of amphiphilic Janus dendrimers in ethanol. Dendrimersomes were then generated by injection of 50 μL of the stock solution into 1 mL water, followed by 5 sec vortexing.

2.1.2 Giant Dendrimersome by Film Hydration

A solution of Janus dendrimer ($10 \text{ mg}\cdot\text{mL}^{-1}$, 200 μL) in THF was deposited on the top surface of a roughened Teflon sheet (1 cm^2), placed in a flat-bottom vial and followed by evaporation of the solvent for 2 h. The Teflon sheet was dried *in vacuo* for additional 12 h. PBS (2.0 mL) was added to merge the dendrimer film on Teflon sheet, and the vial was placed at 60 $^\circ\text{C}$ oven for 12 h for hydration. The sample was then mixed using a vortex mixer for 30 s with a final concentration of $1 \text{ mg}\cdot\text{mL}^{-1}$.

2.2 Dynamic Light Scattering (DLS)

DLS was performed with a Malvern Instruments particle sizer (Zetasizer® Nano S, Malvern Instruments, UK) equipped with 4 mW He-Ne laser 633 nm and avalanche photodiode positioned at 175° to the beam and temperature controlled cuvette holder. Instrument parameters were determined automatically along with measurement times. Experiments were performed in triplicate.

2.3 Differential Scanning Calorimetry (DSC)

Thermal transitions were measured on TA Instruments 2920 modulated and Q 100 differential scanning calorimeter (DSC) integrated with a refrigerated cooling system (RCS). In all cases, the heating and the cooling rates were $10 \text{ }^\circ\text{C min}^{-1}$. The transition temperatures were measured as the maxima and minima of their endothermic and exothermic peaks. Indium was used as calibration standard.

2.4 X-ray Diffraction (XRD)

X-ray diffraction measurements were performed with Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) from a Bruker-Nonius FR-591 rotating anode X-ray source with a $0.2\times 2.0 \text{ mm}^2$ filament operated at 3.4 kW. The beam was collimated and focused by Osmic confocal optics and circular pinholes, resulting in a $0.3\times 0.3 \text{ mm}^2$ spot on a Bruker Hi-Star multiwire detector 11 cm or 54 cm from the sample. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and within the sample chamber. Samples were held in between two mica sheets, mounted in a Linkam temperature controller (temperature precision: $\pm 0.1 \text{ }^\circ\text{C}$, temperature range from $-60.0 \text{ }^\circ\text{C}$ to $25.0 \text{ }^\circ\text{C}$). XRD peak position and intensity analysis was performed using Datasqueeze Software (version 3.0).

2.5 Cryogenic Transmission Electron Microscopy (Cryo-TEM)

Cryo-TEM was performed on a JEOL 2100 microscope (Tokyo, Japan) at voltage of 200 kV. Briefly, a droplet of 2.5 μL dendrimersome solution was pipetted onto a lacey carbon film coated on a copper TEM grid (200 mesh, from Electron Microscopy Services, Hatfield, PA) loaded into a Gatan Cp3 cryoplunger (Gatan, Pleasanton, CA). The sample was blotted by hand, then quickly plunged into liquefied ethane ($\sim 90\text{ K}$) cooled by a reservoir of liquid nitrogen to ensure the vitrification of water. The vitrified samples were transferred to a Gatan CT3500TR single tilt cryo transfer holder in a cryo-transfer stage immersed in liquid nitrogen. During the imaging, the cryo-holder was kept below $-170\text{ }^\circ\text{C}$ to prevent sublimation of vitreous solvent. The digital images were recorded by Orius SC200 or low-dose SerialEM camera. Image processing and analysis were completed with ImageJ 1.50 software.

2.6 Fluorescence Microscopy

Fluorescence microscopy was performed using an Olympus IX81 microscope with a 100W mercury lamp and $100\times$ NA 1.35 objective lens. For green fluorescence, the filter set was HQ470/40 excitation, Q495lp beamsplitter, HQ525/50 emission and for red fluorescence HQ575/50X excitation, HQ640/50 M dichroic, and Q610 LP emission filters were used (Chroma Technology). 16-bit images were acquired with a SensiCam QE cooled charge-coupled device camera (Cooke Corp.) and IPLab v3.7 software (Scanalytics) with 2×2 binning. Image processing and analysis were completed with ImageJ 1.50 software.

2.7 Confocal Fluorescence Microscopy

An imaging chamber ($5\text{--}10\text{ }\mu\text{L}$) containing dendrimersomes was formed between two coverslips ($25\times 25\text{ mm}$, Fisher Scientific) sealed with vacuum grease. Dendrimersomes were imaged by confocal fluorescence microscopy (FluoView 300 scanning system configured on a IX81 inverted microscope platform) with a 60×1.1 NA water immersion lens (Olympus, Center Valley, PA). Dendrimersomes containing $R_{\text{H}}\text{-RhB}$ or TR-DHPE were excited at a wavelength of $\lambda = 543\text{ nm}$, and those containing $R_{\text{F}}\text{-NBD}$ were excited at a wavelength of $\lambda = 488\text{ nm}$. Laser intensities were adjusted so that fluorescence signal was not oversaturated. Image processing and analysis were completed with ImageJ 1.50 software.

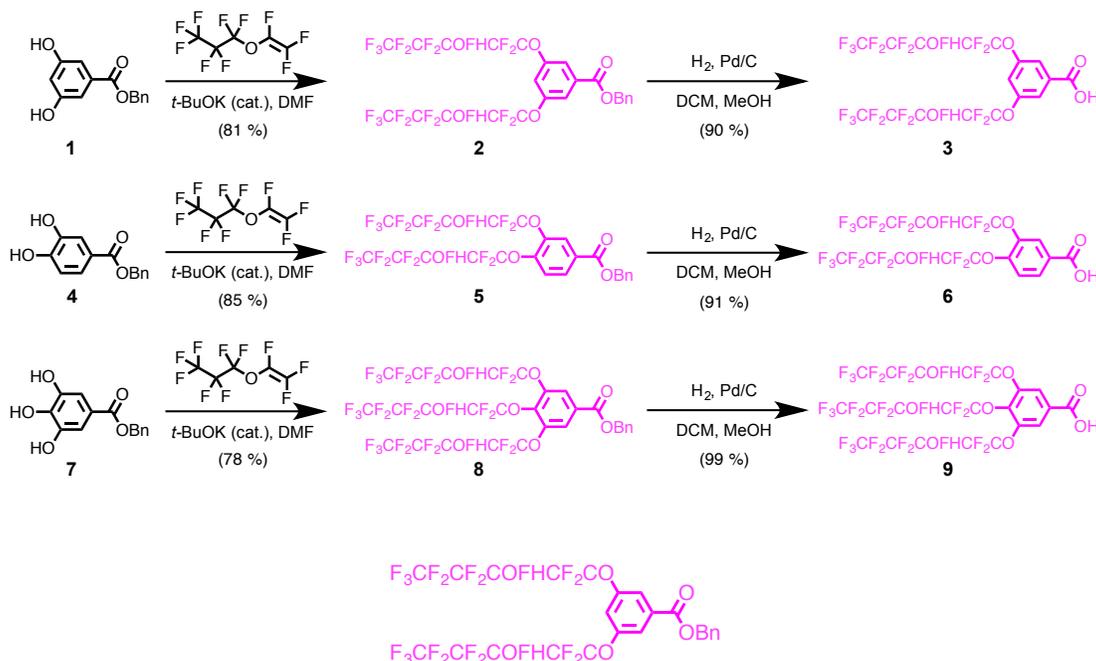
3 Synthesis

4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS),¹ benzyl 3,5-dihydroxybenzoate (**1**),^{2,3} benzyl 3,4-dihydroxybenzoate (**4**),³ benzyl 3,4,5-dihydroxybenzoate (**7**),³ 3,4,5-tris(methyl triethylene glycol)benzoic acid (**10**),⁴ (2-phenyl-1,3-dioxane-5,5-diyl)dimethanol (**11**),⁴ 3,5-bis(dodecyloxy)benzoic acid (**14**),⁴ 2-(2-(2-azidoethoxy)ethoxy)ethan-1-amine (**16**),⁵ 4-[[5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxan-5-yl]amino]-3-oxo-prop-2-yn-1-yl succinate (**18**)⁶ 2-(2-(2-azidoethoxy)ethoxy)ethan-1-ol (**20**),⁷ 2-(3,4,5-Tris(((methyl triethylene glycol)benzoyl)oxy))-2,2-bis-hydroxymethyl-3-oxo-prop-2-yn-1-yl succinate (**22**),⁶ were prepared according to literature procedures.

Hydrogenated (R_H) Janus dendrimer (**3,5**)**12G1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** was synthesized and reported previously by the Percec laboratory.⁴

3.1 Synthesis of R_F Dendrons

Scheme S1. Synthesis of R_F Dendrons.



Compound 2: Perfluoropropyl vinyl ether (PPVE, 4.8 g, 18 mmol) was added to a DMF (10 mL) solution of benzyl 3,5-dihydroxybenzoate (**1**) (2.0 g, 8.2 mmol) at 0°C under N_2 . A solution of potassium *tert*-butoxide (184 mg, 1.6 mmol) in DMF (2 mL) was added dropwise. The reaction was allowed to stir at 0 °C for 2 h and 23°C for 24 h. The reaction mixture was poured into 200 mL ice-cold water including 2 mL hydrochloride acid. Then, the mixture was extracted with DCM for 3 times. An organic extract was dried over Na_2SO_4 . The crude product was further purified by column chromatography on silica gel with a mobile phase of hexane/DCM = 6/1 (vol/vol) to yield compound **2** as a colorless oil (5.42 g, 85%). 1H NMR (500 MHz, $CDCl_3$) δ = 7.84 (d, 2H, 2×PhH, J = 2 Hz), 7.35–

7.45 (m, 5H, 5×PhH), 7.24 (t, 1H, PhH, $J = 2$ Hz), 6.03–6.14 (d, 2H, 2×CHF, $J_{\text{HF}} = 53$ Hz), 5.39 (s, 2H, COOCH₂Ph). ¹³C NMR (500 MHz, CDCl₃) $\delta = 164.1, 149.4, 135.5, 133.5, 128.9, 128.8, 128.6, 121.1, 119.8, 113.7$ – 119.2 (CF), 104.5 – 109.0 (CF), 96.6 – 99.2 (CF), 67.8.



Compound 3: Compound 2 (1.81 g, 2.3 mmol) was charged in a 250 mL round-bottom flask and dissolved in a mixed solvent with 50 mL of DCM and 50 mL of methanol. The solution was purged with H₂ for 30 min. Pd/C (0.18 g, 1/10 (wt/wt)) was then added to the solution and purged again with H₂. The reaction was allowed to stir at 23 °C for 12 h. The reaction mixture was then filtered through Celite®, and the filter cake was washed with 50 mL of DCM. The filtrate was concentrated to yield compound 3 as a colorless oily liquid (1.57 g, 99%). ¹H NMR (500 MHz, CDCl₃) $\delta = 7.89$ (d, 2H, 2×PhH, $J = 2$ Hz), 7.29 (t, 1H, PhH, $J = 2$ Hz), 6.06–6.17 (d, 2H, 2×CHF, $J_{\text{HF}} = 53$ Hz). ¹³C NMR (500 MHz, CDCl₃) $\delta = 170.1, 149.6, 132.5, 121.5, 120.7, 113.8$ – 119.8 (CF), 104.5 – 109.0 (CF), 96.6 – 99.2 (CF).



Compound 5: PPVE (4.8 g, 18 mmol) was added to a DMF (10 mL) solution of benzyl 3,4-dihydroxybenzoate (4) (2.0 g, 8.2 mmol) at 0 °C under N₂. A solution of potassium *tert*-butoxide (184 mg, 1.6 mmol) in DMF (2 mL) was added dropwise. The reaction was allowed to stir at 0 °C for 2 h and 23 °C for 24 h. The reaction mixture was poured into 200 mL ice-cold water including 2 mL hydrochloric acid. Then, the mixture was extracted with DCM for 3 times. An organic extract was dried over Na₂SO₄. The crude product was further purified by column chromatography on silica gel with a mobile phase of hexane/DCM = 6/1 (vol/vol) to yield compound 5 as a colorless oil (5.90 g, 93%). ¹H NMR (500 MHz, CDCl₃) $\delta = 8.03$ – 8.06 (m, 2H, 2×PhH), 7.35–7.46 (m, 6H, 6×PhH), 6.02–6.13 (d, 2H, 2×CHF, $J_{\text{HF}} = 53$ Hz), 5.39 (s, 2H, COOCH₂Ph). ¹³C NMR (500 MHz, CDCl₃) $\delta = 164.4, 144.9, 140.6, 135.7, 129.7, 129.2, 128.9, 128.7, 128.5, 125.4, 122.9, 113.5$ – 120.7 (CF), 104.2 – 109.1 (CF), 96.6 – 99.2 (CF), 67.6.



Compound 6: Compound 5 (5.9 g, 7.6 mmol) was charged in a 250 mL round-bottom flask and dissolved in a mixed solvent with 50 mL of DCM and 50 mL of methanol. The solution was purged with

H₂ for 30 min. Pd/C (0.59 g, 1/10 (wt/wt)) was then added to the solution and purged again with H₂. The reaction was allowed to stir at 23 °C for 12 h. The reaction mixture was then filtered through Celite®, and the filter cake was washed with 50 mL of DCM. The filtrate was concentrated to yield compound **6** as a colorless oily liquid (4.77 g, 91%). ¹H NMR (500 MHz, CDCl₃) δ = 8.01–8.11 (m, 2H, 2×PhH), 7.50 (d, 1H, PhH, *J* = 8.4 Hz), 6.04–6.14 (d, 2H, 2×CHF, *J*_(HF) = 53 Hz). ¹³C NMR (500 MHz, CDCl₃) δ = 170.2, 145.4, 140.3, 129.3, 128.3, 125.5, 122.5, 113.4–120.4 (CF), 104.2–109.0 (CF), 96.3–98.8 (CF).



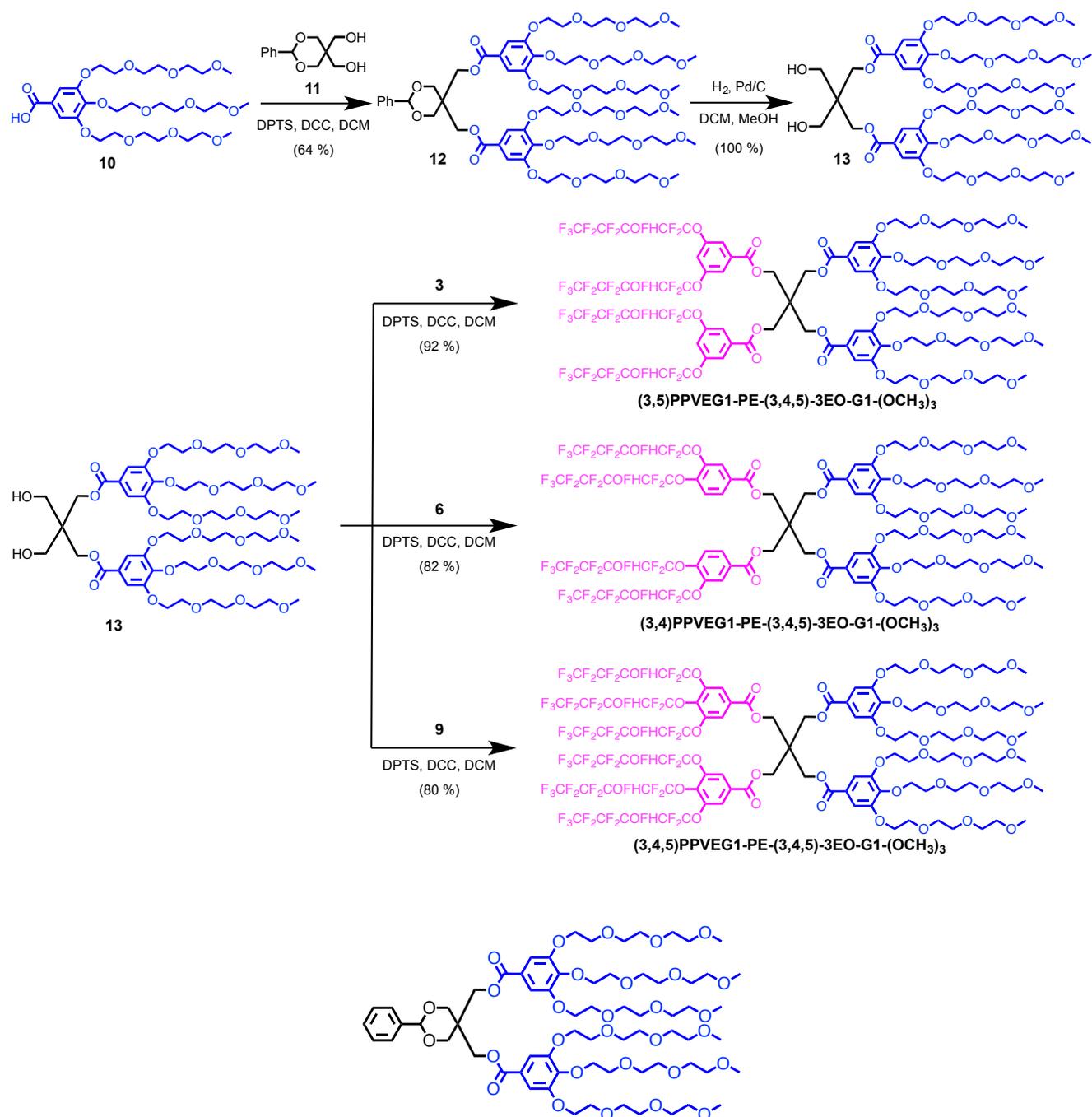
Compound 8: PPVE (4.1 g, 15.3 mmol) was added to a DMF (10 mL) solution of benzyl 3,4,5-dihydroxybenzoate (**7**) (1.21 g, 4.65 mmol) at 0°C under N₂. A solution of potassium *tert*-butoxide (157 mg, 1.4 mmol) in DMF (2 mL) was added dropwise. The reaction was allowed to stir at 0 °C for 2 h and 23°C for 24 h. The reaction mixture was poured into 200 mL ice-cold water including 2 mL hydrochloric acid. Then, the mixture was extracted with DCM for 3 times. An organic extract was dried over Na₂SO₄. The crude product was further purified by column chromatography on silica gel with a mobile phase of hexane/DCM = 6/1 (vol/vol) to yield compound **8** as a colorless oil (4.0 g, 81%). ¹H NMR (500 MHz, CDCl₃) δ = 8.03 (s, 2H, 2×PhH), 7.37–7.45 (m, 5H, 5×PhH), 6.03–6.14 (d, 3H, 3×CHF, *J*_(HF) = 53 Hz), 5.41 (s, 2H, COOCH₂Ph). ¹³C NMR (500 MHz, CDCl₃) δ = 163.5, 143.6, 137.0, 135.3, 130.5, 128.9, 128.9, 128.6, 120.7, 113.7–119.3 (CF), 104.5–109.0 (CF), 96.5–99.1 (CF), 68.1.



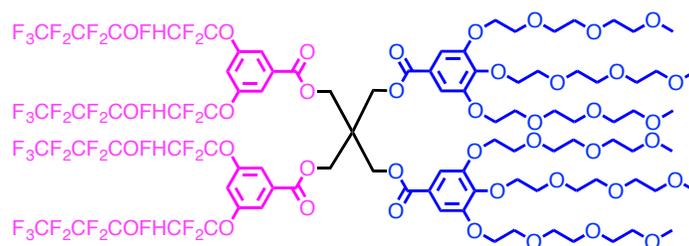
Compound 9: Compound **8** (4.0 g, 3.8 mmol) was charged in a 250 mL round-bottom flask and dissolved in a mixed solvent with 50 mL of DCM and 50 mL of methanol. The solution was purged with H₂ for 30 min. Pd/C (0.40 g, 1/10 (wt/wt)) was then added to the solution and purged again with H₂. The reaction was allowed to stir at 23 °C for 12 h. The reaction mixture was then filtered through Celite®, and the filter cake was washed with 50 mL of DCM. The filtrate was concentrated to yield compound **6** as a colorless oily liquid (3.28 g, 90%). ¹H NMR (500 MHz, CDCl₃) δ = 8.08 (s, 2H, 2×PhH), 6.05–6.12 (d, 3H, 3×CHF, *J*_(HF) = 53 Hz). ¹³C NMR (500 MHz, CDCl₃) δ = 166.1, 144.7, 137.8, 132.8, 122.9, 114.7–122.0 (CF), 105.8–110.4 (CF), 98.3–100.7 (CF).

3.2 Synthesis of R_F Janus Dendrimers

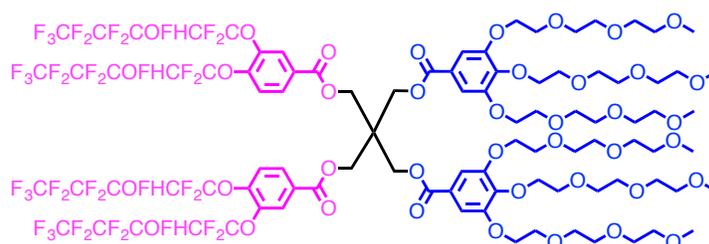
Scheme S2. Synthesis of R_F Janus dendrimers.



Compound 12: To a DCM (10 mL) solution of compound **10** (2.0 g, 3.3 mmol), compound **11** (369 mg, 1.64 mmol) and DPTS (0.98 mg, 3.3 mmol), were added dicyclohexylcarbodiimide (DCC, 1.36 g, 6.6 mmol). The mixture was allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 10/1 (vol/vol) to yield compound **13** as a colorless oily liquid (1.48 g, 64%). ¹H NMR (500 MHz, CDCl₃) δ = 7.50–7.52 (m, 2H, 2×PhH), 7.36–7.40 (m, 3H,

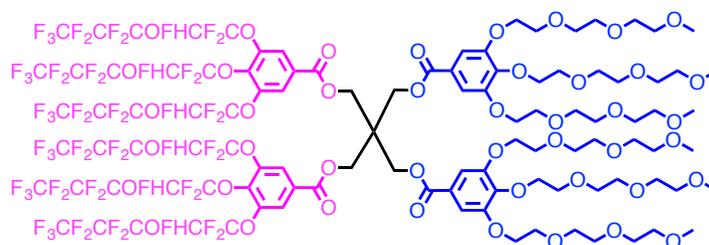


(3,5)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃: To a DCM (10 mL) solution of compound **3** (417 mg, 0.60 mmol), compound **13** (400 mg, 0.30 mmol) and DPTS (177 mg, 0.60 mmol), were added DCC (250 mg, 1.2 mmol). The mixture was allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 20/1 (vol/vol) to yield **(3,5)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** as a colorless oily liquid (730 mg, 92%). Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃) δ = 7.73 (d, 2H, 2×PhH, J = 2 Hz), 7.22 (t, 1H, PhH, J = 2 Hz), 6.06–6.18 (d, 4H, 4×CHF, $J_{(HF)}$ = 53 Hz), 4.65 (s, 4H, 2×PhCOOCH₂-), 4.58 (s, 4H, 2×PhCOOCH₂-), 4.21–4.23 (t, 4H, 2×PhOCH₂CH₂O-, J = 5 Hz), 4.16–4.18 (t, 8H, 4×PhOCH₂CH₂O-, J = 5 Hz), 3.84–3.86 (t, 8H, 4×PhOCH₂CH₂O-, J = 5 Hz), 3.78–3.80 (t, 4H, 2×PhOCH₂CH₂O-, J = 5 Hz), 3.70–3.73 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂O-), 3.61–3.65 (m, 24H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.50–3.54 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.34–3.36 (m, 18H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃). ¹³C NMR (126 MHz, CDCl₃) δ = 165.4, 163.6, 152.6, 149.4, 143.3, 132.5, 124.0, 120.8, 120.6, 120.0, 113.6–119.1 (CF), 109.3, 106.5–109.3 (CF), 96.5–99.0 (CF), 72.6, 72.0, 72.0, 70.9, 70.8, 70.6, 70.6, 69.7, 69.1, 63.8, 62.5, 59.0, 59.0, 43.6. MALDI-TOF (m/z): [M+Na]⁺ calcd for C₉₅H₁₁₂F₄₀NaO₄₀, 2675.6; found 2676.2.



(3,4)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃: To a DCM (10 mL) solution of compound **6** (500 mg, 0.73 mmol), compound **13** (436 mg, 0.33 mmol) and DPTS (215 mg, 0.73 mmol), were added DCC (340 mg, 1.65 mmol). The mixture was allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 20/1 (vol/vol) to yield **(3,4)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** as a colorless oily liquid (720 mg, 82%). Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃) δ = 7.99 (s, 2H, 2×PhH), 7.93–7.95 (dd, 2H, 2×PhH, J_1 = 2 Hz, J_2 = 2 Hz).

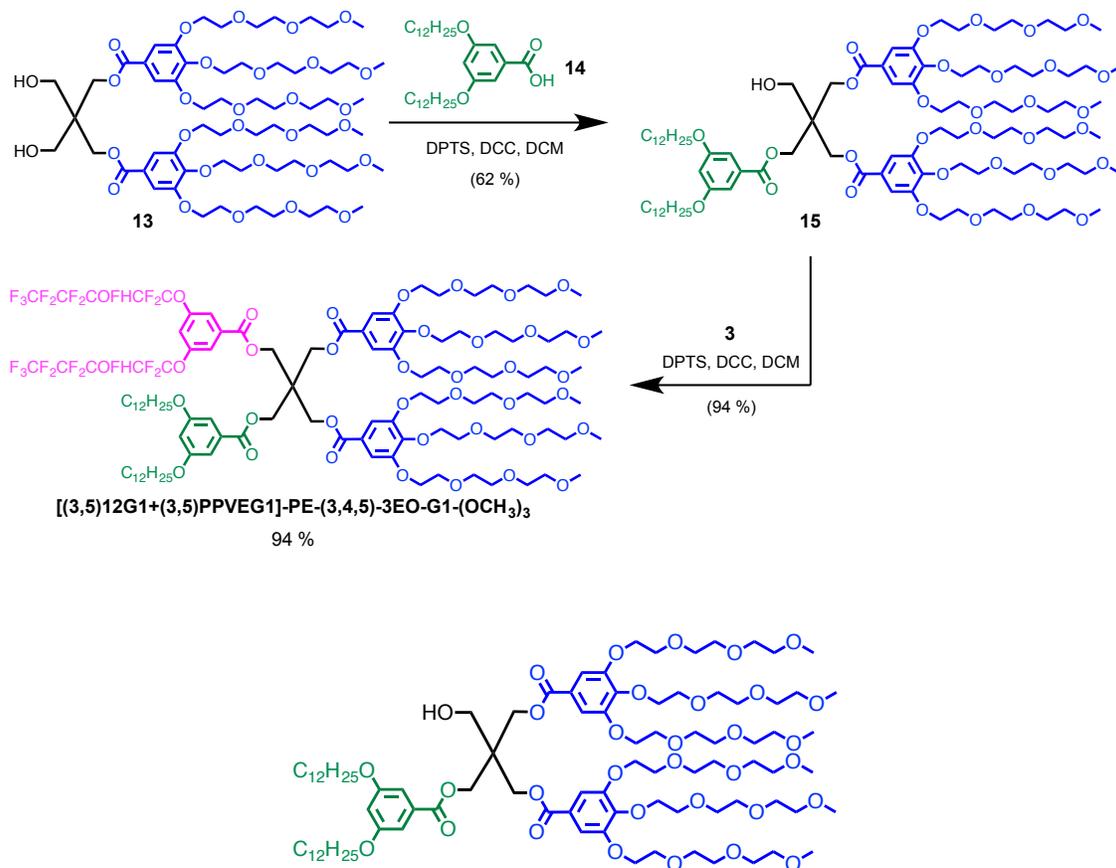
8.5 Hz), 7.41–7.42 (d, 2H, 2×PhH, $J = 8.5$ Hz), 6.04–6.15 (d, 2H, 2×CHF, $J_{(\text{HF})} = 53$ Hz), 6.02–6.13 (d, 2H, 2×CHF, $J_{(\text{HF})} = 53$ Hz), 4.66 (s, 4H, 2×PhCOOCH₂-), 4.60 (s, 4H, 2×PhCOOCH₂-), 4.22–4.24 (t, 4H, 2×PhOCH₂CH₂O-, $J = 5$ Hz), 4.18–4.20 (t, 8H, 4×PhOCH₂CH₂O-, $J = 5$ Hz), 3.86–3.88 (t, 8H, 4×PhOCH₂CH₂O-, $J = 5$ Hz), 3.79–3.81 (t, 4H, 2×PhOCH₂CH₂O-, $J = 5$ Hz), 3.71–3.74 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂O-), 3.62–3.67 (m, 24H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.52–3.54 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.35–3.37 (m, 18H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃). ¹³C NMR (126 MHz, CDCl₃) $\delta = 165.4, 163.8, 152.6, 145.1, 143.4, 140.6, 129.0, 128.7, 125.3, 125.3, 124.0, 122.9, 113.4–120.6$ (CF), 109.3, 104.7–108.6 (CF), 96.5–99.0 (CF), 72.6, 72.0, 72.0, 70.9, 70.8, 70.6, 70.6, 69.7, 69.1, 63.7, 62.6, 59.0, 43.6. MALDI-TOF (m/z): [M+Na]⁺ calcd for C₉₅H₁₁₂F₄₀NaO₄₀, 2675.6; found 2676.7.



(3,4,5)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃: To a DCM (10 mL) solution of compound **9** (542 mg, 0.56 mmol), compound **13** (337 mg, 0.25 mmol) and DPTS (215 mg, 0.56 mmol), were added DCC (263 mg, 1.28 mmol). The mixture was allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 20/1 (vol/vol) to yield **(3,4,5)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** as a colorless oily liquid (660 mg, 80%). Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃) $\delta = 7.97$ (s, 4H, 2×PhH), 7.26 (s, 4H, 2×PhH), 6.05–6.16 (d, 4H, 4×CHF, $J_{(\text{HF})} = 53$ Hz), 6.02–6.13 (d, 2H, 2×CHF, $J_{(\text{HF})} = 53$ Hz), 4.66 (s, 4H, 2×PhCOOCH₂-), 4.57 (s, 4H, 2×PhCOOCH₂-), 4.22–4.24 (t, 4H, 2×PhOCH₂CH₂O-, $J = 5$ Hz), 4.18–4.20 (t, 8H, 4×PhOCH₂CH₂O-, $J = 5$ Hz), 3.86–3.88 (t, 8H, 4×PhOCH₂CH₂O-, $J = 5$ Hz), 3.79–3.81 (t, 4H, 2×PhOCH₂CH₂O-, $J = 5$ Hz), 3.70–3.73 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂O-), 3.61–3.66 (m, 24H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.52–3.54 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.35–3.36 (m, 18H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃). ¹³C NMR (126 MHz, CDCl₃) $\delta = 165.2, 162.8, 152.6, 143.7, 143.4, 137.1, 129.4, 123.8, 121.5, 113.3–120.5$ (CF), 109.2, 113.3–118.0 (CF), 96.3–98.9 (CF), 72.6, 72.0, 72.0, 70.9, 70.7, 70.7, 70.6, 70.6, 69.7, 69.1, 63.7, 62.0, 59.0, 58.9, 43.8. MALDI-TOF (m/z): [M+Na]⁺ calcd for C₁₀₅H₁₁₂F₆₀NaO₄₄, 3239.5; found 3239.3.

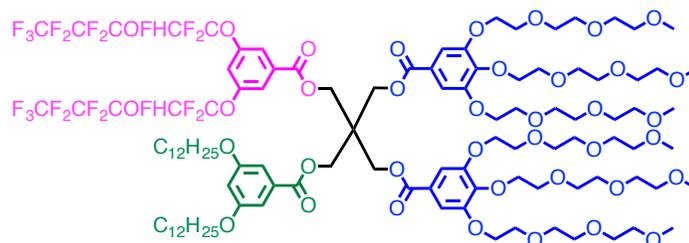
3.3 Synthesis of Hybrid R_{HF} Janus Dendrimer

Scheme S3. Synthesis of hybrid R_{HF} Janus dendrimer.



Compound 15: To a DCM (10 mL) solution of compound **13** (1.38 g, 1.05 mmol), compound **14** (514 mg, 1.05 mmol) and DPTS (310 mg, 1.05 mmol), were added DCC (310 mg, 1.6 mmol). The mixture was allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 15/1 (vol/vol) to yield compound **15** as a colorless oily liquid (1.17 g, 62%). ¹H NMR (500 MHz, CDCl₃) δ = 7.27 (s, 4H, 4×PhH), 7.10 (d, 2H, 2×PhH, *J* = 2.5 Hz), 6.62 (t, H, PhH, *J* = 2.5 Hz), 4.51–4.52 (m, 6H, 3×PhCOOCH₂-), 4.21–4.23 (t, 4H, 2×PhOCH₂CH₂O-, *J* = 5 Hz), 4.17–4.19 (t, 8H, 4×PhOCH₂CH₂O-, *J* = 5 Hz), 3.92–3.95 (t, 4H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃, *J* = 6.5 Hz), 3.84–3.86 (t, 8H, 4×PhOCH₂CH₂O-, *J* = 5 Hz), 3.78–3.80 (t, 4H, 2×PhOCH₂CH₂O-, *J* = 5 Hz), 3.70–3.74 (m, 14H, 6×PhOCH₂CH₂OCH₂CH₂O- and CH₂OH), 3.61–3.66 (m, 24H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂-), 3.51–3.54 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂-), 3.35–3.61 (m, 18H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃), 3.04–3.06 (t, 1H, CH₂OH), 1.73–1.79 (m, 4H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 1.41–1.46 (m, 4H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 1.26–1.34 (m, 32H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 0.86–0.89 (m, 6H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃). ¹³C NMR (126 MHz, CDCl₃) δ = 166.3, 166.0, 160.3, 152.5, 143.2, 131.2, 124.3, 109.4, 107.9, 106.5, 72.5, 72.0, 70.8,

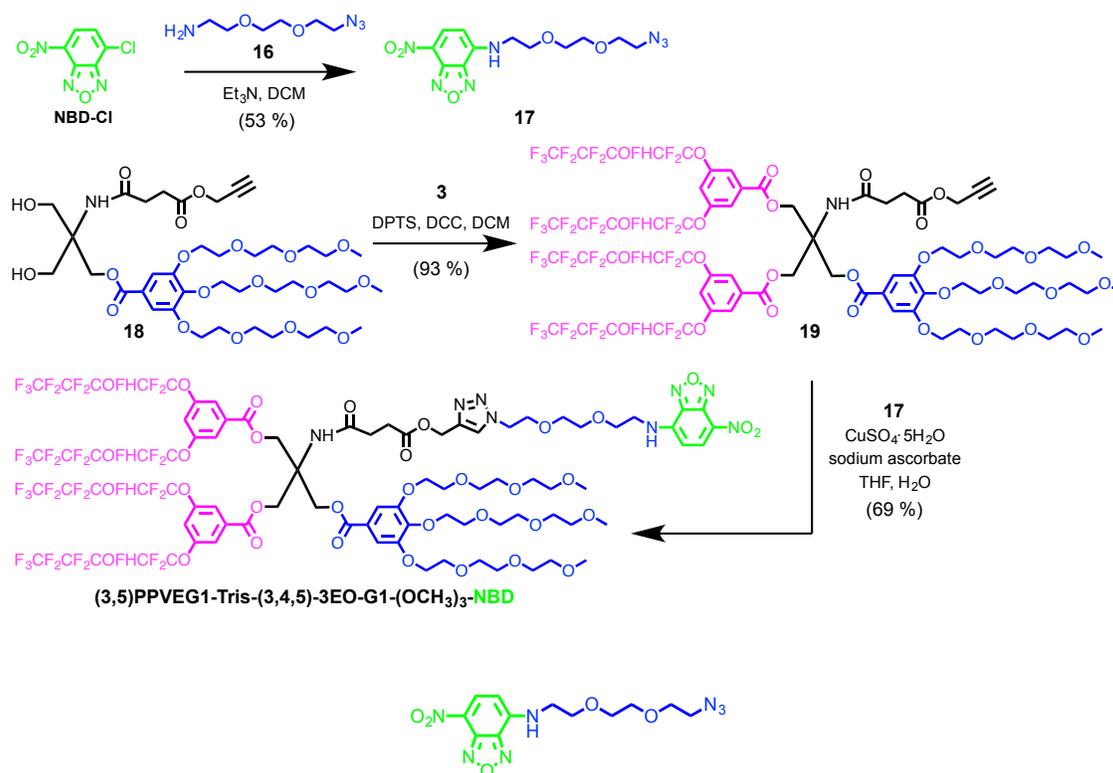
70.7, 70.6, 70.6, 69.7, 69.0, 68.4, 63.1, 63.0, 61.0, 59.1, 45.0, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.2, 26.1, 22.7, 14.1.



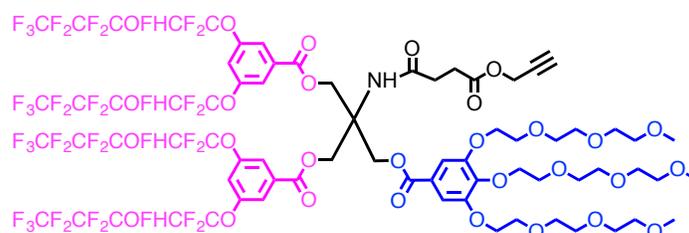
[(3,5)12G1+(3,5)PPVEG1]-PE-(3,4,5)-3EO-G1-(OCH₃)₃: To a DCM (10 mL) solution of compound **3** (270 mg, 0.393 mmol), compound **15** (670 mg, 0.374 mmol) and DPTS (116 mg, 0.393 mmol), were added DCC (160 mg, 0.79 mmol). The mixture was allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 20/1 (vol/vol) to yield **[(3,5)12G1+(3,5)PPVEG1]-PE-(3,4,5)-3EO-G1-(OCH₃)₃** as a colorless oily liquid (860 mg, 94%). Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃) δ = 7.75 (d, 2H, 2×PhH, *J* = 2 Hz), 7.24 (s, 4H, 4×PhH), 7.23 (t, 1H, PhH, *J* = 2 Hz), 7.08 (d, 2H, 2×PhH, *J* = 2 Hz), 6.62 (t, 1H, PhH, *J* = 2 Hz), 6.08–6.19 (d, 2H, 2×CHF, *J*_(HF) = 53 Hz), 4.65 (s, 2H, PhCOOCH₂-), 4.60 (s, 2H, PhCOOCH₂-), 4.58 (s, 4H, 2×PhCOOCH₂-), 4.21–4.23 (t, 4H, 2×PhOCH₂CH₂O-, *J* = 5 Hz), 4.16–4.18 (t, 8H, 4×PhOCH₂CH₂O-, *J* = 5 Hz), 3.92–3.94 (t, 4H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃, *J* = 6.5 Hz), 3.84–3.86 (t, 8H, 4×PhOCH₂CH₂O-, *J* = 5 Hz), 3.78–3.80 (t, 4H, 2×PhOCH₂CH₂O-, *J* = 5 Hz), 3.70–3.73 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂O-), 3.61–3.66 (m, 24H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.51–3.54 (m, 12H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂O-), 3.35–3.60 (m, 18H, 6×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃), 3.04–3.06 (t, 1H, CH₂OH), 1.74–1.77 (m, 4H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 1.42–1.45 (m, 4H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 1.25–1.33 (m, 32H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 0.86–0.88 (m, 6H, 2×PhOCH₂CH₂CH₂(CH₂)₈CH₃). ¹³C NMR (126 MHz, CDCl₃) δ = 165.8, 165.4, 163.6, 160.3, 152.5, 149.3, 143.2, 132.6, 130.9, 124.0, 120.8, 119.8, 113.5–119.0 (CF), 109.1, 107.8, 106.4–117.8 (CF), 96.4–100.0 (CF), 72.5, 72.0, 71.9, 70.8, 70.7, 70.6, 69.6, 69.0, 68.4, 63.9, 62.9, 62.8, 62.6, 59.0, 43.5, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. MALDI-TOF (m/z): [M+Na]⁺ calcd for C₁₀₉H₁₆₀F₂₀NaO₃₈, 2480.0; found 2480.6.

3.4 Synthesis of NBD Labeled Janus Dendrimer with R_F chains

Scheme S4. Synthesis of NBD labeled Janus dendrimer with R_F chains.

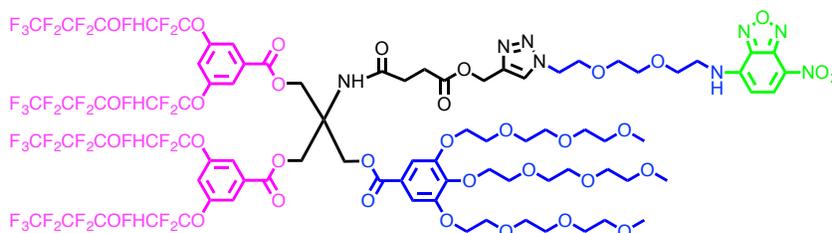


Compound 17: A DCM (1 mL) solution of Compound **16** (0.29 g, 1.67 mmol) was added dropwise to a stirred solution of NBD-chloride (NBD-Cl, 0.40 g, 2.0 mmol) and triethylamine (Et₃N, 0.28 mL, 1.2 mmol) in DCM (10 mL). The solution was allowed to stir in the dark for 12 h. The reaction mixture was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of hexane/EtOAc = 1/1 (vol/vol) to yield Compound **17** as a brown gel (0.30 g, 53%). ¹H NMR (500 MHz, CDCl₃) δ = 8.46–8.48 (d, 1H, PhH, *J* = 8.5 Hz), 6.82 (br, 1H, Ph-NH), 6.18–6.20 (d, 1H, PhH, *J* = 8.5 Hz), 3.88–3.90 (t, 2H, CH₂, *J* = 5 Hz), 3.68–3.75 (m, 8H, 4×CH₂), 3.41–3.43 (t, 2H, PhNHCH₂, *J* = 5 Hz). ¹³C NMR (126 MHz, CDCl₃) δ = 144.4, 144.2, 144.0, 136.6, 124.1, 99.0, 70.9, 70.7, 70.3, 68.4, 50.8, 43.8.



Compound 19: To a DCM (10 mL) solution of compound **3** (1.14 g, 1.66 mmol), compound **18** (0.64 g, 0.75 mmol) and DPTS (489 mg, 1.66 mmol), were added DCC (620 mg, 3 mmol). The mixture was

allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 20/1 (vol/vol) to yield Compound **19** as colorless oily liquid (1.53 g, 93%). ¹H NMR (500 MHz, CDCl₃) δ = 7.76 (d, 4H, 4×PhH, *J* = 2 Hz), 7.29 (s, 2H, 2×PhH), 7.22 (t, 2H, 2×PhH, *J* = 2 Hz), 6.61 (br, 1H, CONH), 6.06–6.17 (d, 4H, 4×CHF, *J*_(HF) = 53 Hz), 4.86–4.92 (m, 4H, 2×PhCOOCH₂), 4.76 (s, 2H, PhCOOCH₂), 4.56 (d, 2H, COOCH₂CCH, *J* = 2.5 Hz), 4.22–4.24 (t, 2H, PhOCH₂CH₂O, *J* = 5 Hz), 4.18–4.20 (t, 4H, 2×PhOCH₂CH₂O, *J* = 5 Hz), 3.84–3.86 (t, 4H, 2×PhOCH₂CH₂O, *J* = 5 Hz), 3.78–3.80 (t, 2H, PhOCH₂CH₂O, *J* = 5 Hz), 3.71–3.73 (m, 6H, 3×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃), 3.61–3.66 (m, 12H, 3×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃), 3.51–3.54 (m, 6H, 3×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃), 3.34–3.35 (m, 9H, 3×PhOCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃), 2.67–2.70 (t, 2H, CH₂, *J* = 6.5 Hz), 2.51–2.53 (t, 2H, CH₂, *J* = 6.5 Hz), 2.43–2.44 (t, 1H, COOCH₂CCH, *J* = 2.5 Hz). ¹³C NMR (126 MHz, CDCl₃) δ = 172.1, 165.9, 163.7, 152.6, 149.4, 143.5, 132.5, 123.8, 120.9, 120.6, 120.0, 119.2, 113.4–120.6 (CF), 104.7–108.6 (CF), 96.5–99.1 (CF), 75.1, 72.6, 72.1, 72.0, 70.9, 70.8, 70.8, 70.7, 70.6, 70.6, 69.8, 69.1, 64.2, 63.4, 59.1, 59.0, 59.0, 52.2, 31.4, 29.1.

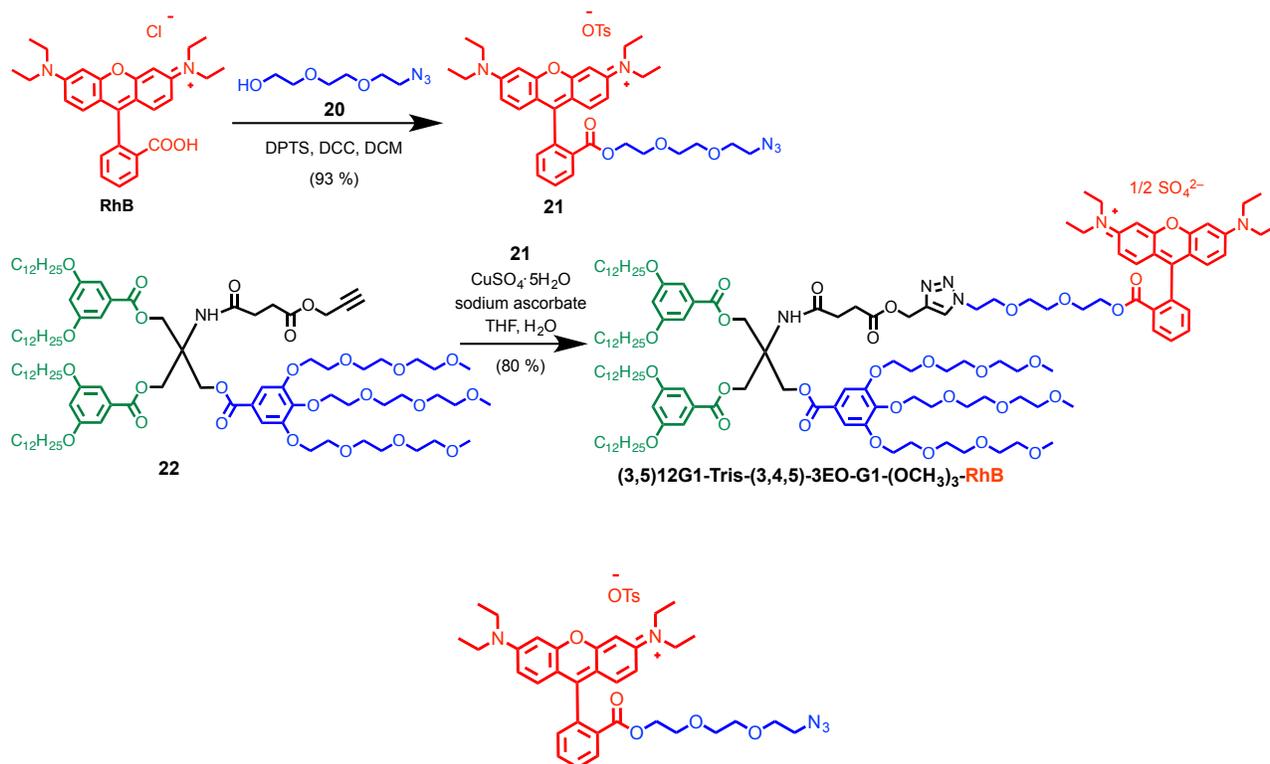


(3,5)PPVEG1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-NBD: To a mixed THF (10 mL) and water (1 mL) solution of compound **17** (46 mg, 0.137 mmol) and compound **19** (300 mg, 0.137 mmol), was added CuSO₄·5H₂O (34 mg, 0.137 mmol) in water (1 mL), and sodium ascorbate (27 mg, 0.137 mmol) in water (1 mL) successively under nitrogen atmosphere. The reaction mixture was allowed to stir at 23 °C for 24 h. The reaction mixture was concentrated to dryness. The crude product was further purified by column chromatography with a mobile phase of EtOAc/methanol = 10/1 (vol/vol) to yield compound **(3,5)PPVEG1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-NBD** as an orange gel (240 mg, 69%). Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃) δ = 8.44–8.46 (d, 1H, PhH, *J* = 8.5 Hz), 7.75 (d, 4H, 4×PhH, *J* = 2 Hz), 7.70 (s, 1H, triazole), 7.24 (s, 2H, 2×PhH), 7.21 (t, 2H, 2×PhH, *J* = 2 Hz), 6.87 (br, 1H, NH), 6.08–6.19 (m, 5H, 4×CHF and PhH), 5.13 (s, 2H, COOCH₂-(C)triazole), 4.87–4.92 (m, 4H, 2×PhCOOCH₂), 4.76 (s, 2H, PhCOOCH₂), 4.54–4.57 (t, 2H, triazole(N)-CH₂CH₂O, *J* = 5 Hz), 4.21–4.23 (t, 2H, PhOCH₂CH₂O, *J* = 5 Hz), 4.17–4.19 (t, 4H, 2×PhOCH₂CH₂O, *J* = 5 Hz), 3.91–3.93 (t, 2H, triazole(N)-

CH₂CH₂O, $J = 5$ Hz), 3.83–3.85 (t, 4H, 2×CH₂, $J = 5$ Hz), 3.76–3.79 (m, 4H, 2×CH₂), 3.68–3.72 (m, 6H, 3×CH₂), 3.61–3.65 (m, 18H, 9×CH₂), 3.51–3.54 (m, 6H, 3×CH₂), 3.34–3.36 (m, 9H, 3×CH₂), 2.62–2.65 (t, 2H, CH₂, $J = 6$ Hz), 2.56–2.58 (t, 2H, CH₂, $J = 6$ Hz). ¹³C NMR (126 MHz, CDCl₃) $\delta = 172.5, 172.5, 165.7, 163.7, 152.4, 149.4, 144.5, 144.4, 144.1, 143.0, 142.8, 136.7, 132.5, 124.7, 123.9, 123.4, 120.8, 120.0, 113.3–120.6$ (CF), 109.3, 104.7–108.6 (CF), 99.0, 96.5–99.0 (CF), 72.5, 71.9, 70.7, 70.6, 70.6, 70.5, 70.5, 69.6, 69.4, 68.9, 68.3, 64.2, 63.4, 59.0, 58.9, 58.8, 57.9, 50.2, 43.8, 31.2, 29.3. MALDI-TOF (m/z): [M+Na]⁺ calcd for C₈₅H₈₆F₄₀N₈NaO₃₄, 2545.4; found 2545.3.

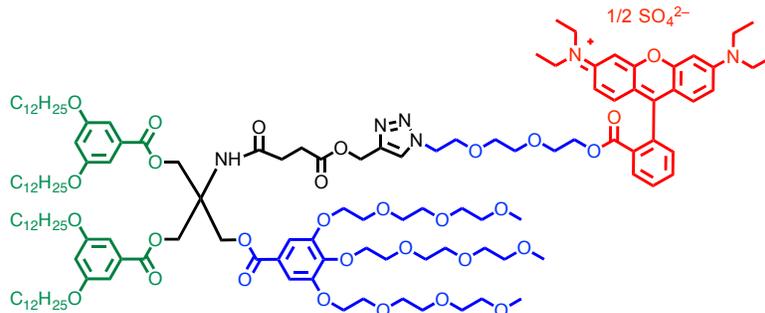
3.5 Synthesis of Rhodamine B Labeled Janus Dendrimer with R_H Chains

Scheme S5. Synthesis of rhodamine B labeled Janus dendrimer with R_H chains.



Compound 21: To a DCM (10 mL) solution of rhodamine B (RhB, 1.0 g, 2.09 mmol), compound 20 (0.40 g, 2.30 mmol) and DPTS (0.68 mg, 2.30 mmol), were added DCC (0.87 g, 4.2 mmol). The mixture was allowed to stir at 23 °C for 12 h. The precipitate was then filtered and the filtrate was concentrated to dryness. The crude product was further purified by column chromatography on silica gel with a mobile phase of DCM/methanol = 10/1 (vol/vol) to yield Compound 21 as a dark purple gel (1.50 g, 93%). ¹H NMR (500 MHz, CDCl₃) $\delta = 8.31–8.33$ (d, 1H, PhH, $J = 8$ Hz), 7.81–7.84 (d, 2H, 2×PhH(tosyl), $J = 8$ Hz), 7.78–7.81(t, 1H, PhH, $J = 7.5$ Hz), 7.71–7.74 (t, 1H, PhH, $J = 7.5$ Hz), 7.27–7.29 (d, 1H, PhH, $J = 8$ Hz), 7.04–7.05 (m, 4H, 2×PhH and 2×PhH(tosyl)), 6.84–6.86 (dd, 2H, 2×PhH, $J_1 = 2.5$ Hz, $J_2 = 9.5$ Hz), 6.81 (d, 2H, PhH, $J = 2$ Hz), 4.16–4.17 (t, 2H, COOCH₂, $J = 4.5$ Hz), 3.54–3.63 (m, 16H, COOCH₂CH₂OCH₂CH₂OCH₂CH₂N₃ and 4×NCH₂CH₃) 3.33–3.35 (t, 2H, OCH₂CH₂N₃),

2.26 (s, 3H, CH₃(tosyl)), 1.29–1.31 (t, 12H, 4×NCH₂CH₃, *J* = 7 Hz). ¹³C NMR (126 MHz, CDCl₃) δ = 164.9, 158.6, 157.7, 155.5, 138.0, 133.6, 133.1, 131.4, 131.2, 130.3, 130.1, 129.7, 128.0, 126.2, 114.1, 113.5, 96.3, 70.5, 70.4, 69.9, 68.7, 64.6, 50.6, 46.0, 21.2, 12.5.



(3,5)12G1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-RhB: To a mixed THF (10 mL) and water (1 mL) solution of compound **21** (77 mg, 0.10 mmol) and compound **22** (215 mg, 0.12 mmol), was added CuSO₄·5H₂O (25 mg, 0.1 mmol) in water (1 mL), and sodium ascorbate (40 mg, 0.2 mmol) in water (1 mL) successively under nitrogen atmosphere. The reaction mixture was allowed to stir at 23 °C for 24 h. The reaction mixture was concentrated to dryness. The crude product was further purified by column chromatography with a mobile phase of DCM/methanol = 15/1 (vol/vol) to yield compound **(3,5)12G1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-RhB** as a dark purple gel (195 mg, 80%). Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃) δ = 8.30–8.31 (d, 1H, PhH, *J* = 7.5 Hz), 7.84 (s, 1H, triazole), 7.78–7.81 (t, 1H, PhH, *J* = 7.5 Hz), 7.72–7.75 (t, 1H, PhH, *J* = 7.5 Hz), 7.29 (s, 1H, CONH), 7.27–7.28 (m, 2×PhH and PhH), 7.08–7.09 (d, 4H, 4×PhH, *J* = 2.5 Hz), 7.07 (s, 2H, 2×PhH, *J* = 9.5 Hz), 6.89–6.91 (dd, 2H, 2×PhH, *J*₁ = 2 Hz, *J*₂ = 9.5 Hz), 6.82–6.83 (d, 2H, 2×PhH, *J* = 2.5 Hz), 6.59–6.60 (t, 2H, 2×PhH, *J* = 3 Hz), 5.10 (s, 2H, COOCH₂-(C)triazole), 4.81–4.85 (m, 6H, 3×PhCOOCH₂), 4.50–4.52 (t, 2H, triazole(N)-CH₂CH₂O, *J* = 5 Hz), 4.21 (t, 2H, PhOCH₂CH₂O, *J* = 5 Hz), 4.18 (t, 4H, 2×PhOCH₂CH₂O, *J* = 5 Hz), 4.14 (t, 2H, COOCH₂, *J* = 5 Hz), 3.91 (t, 8H, 4×PhOCH₂CH₂CH₂(CH₂)₈CH₃, *J* = 6.5 Hz), 3.84–3.88 (m, 6H, 3×CH₂), 3.78–3.80 (t, 2H, CH₂, *J* = 5 Hz), 3.71–3.73 (m, 6H, 3×CH₂), 3.55–3.66 (m, 22H, 11×CH₂), 3.51–3.55 (m, 8H, 4×CH₂), 3.45–3.48 (m, 4H, 2×CH₂), 3.35–3.37 (m, 9H, 3×CH₃), 2.61 (s, 4H, 2×CH₂), 1.72–1.78 (m, 8H, 4×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 1.40–1.46 (m, 8H, 4×PhOCH₂CH₂CH₂(CH₂)₈CH₃), 1.26–1.33 (m, 76H, 4×PhOCH₂CH₂CH₂(CH₂)₈CH₃ and 4×NCH₂CH₃), 0.86–0.89 (m, 12H, 4×PhOCH₂CH₂CH₂(CH₂)₈CH₃). ¹³C NMR (126 MHz, CDCl₃) δ = 172.5, 172.3, 166.1, 165.9, 165.0, 160.3, 159.0, 157.9, 155.6, 152.4, 143.0, 142.8, 133.7, 133.2, 131.6, 131.4, 131.3, 130.6, 130.2, 129.9, 124.7, 124.3, 114.4, 113.7, 109.3, 107.9, 106.7, 96.4, 72.0, 72.0, 70.8, 70.8, 70.7, 70.7, 70.6, 70.5, 70.5, 69.7, 69.5, 69.0, 68.8, 68.5, 64.7, 63.8, 59.1, 59.1, 58.1, 50.2, 46.2, 32.0, 29.8, 29.7, 29.7, 29.5, 29.4, 29.3, 26.2, 22.8, 14.2, 12.8. MALDI-TOF (*m/z*): [M–1/2(SO₄²⁻)]⁺ calcd for C₁₃₅H₂₀₉N₆O₃₀, 2394.5; found 2394.2.

5 Supporting Figures

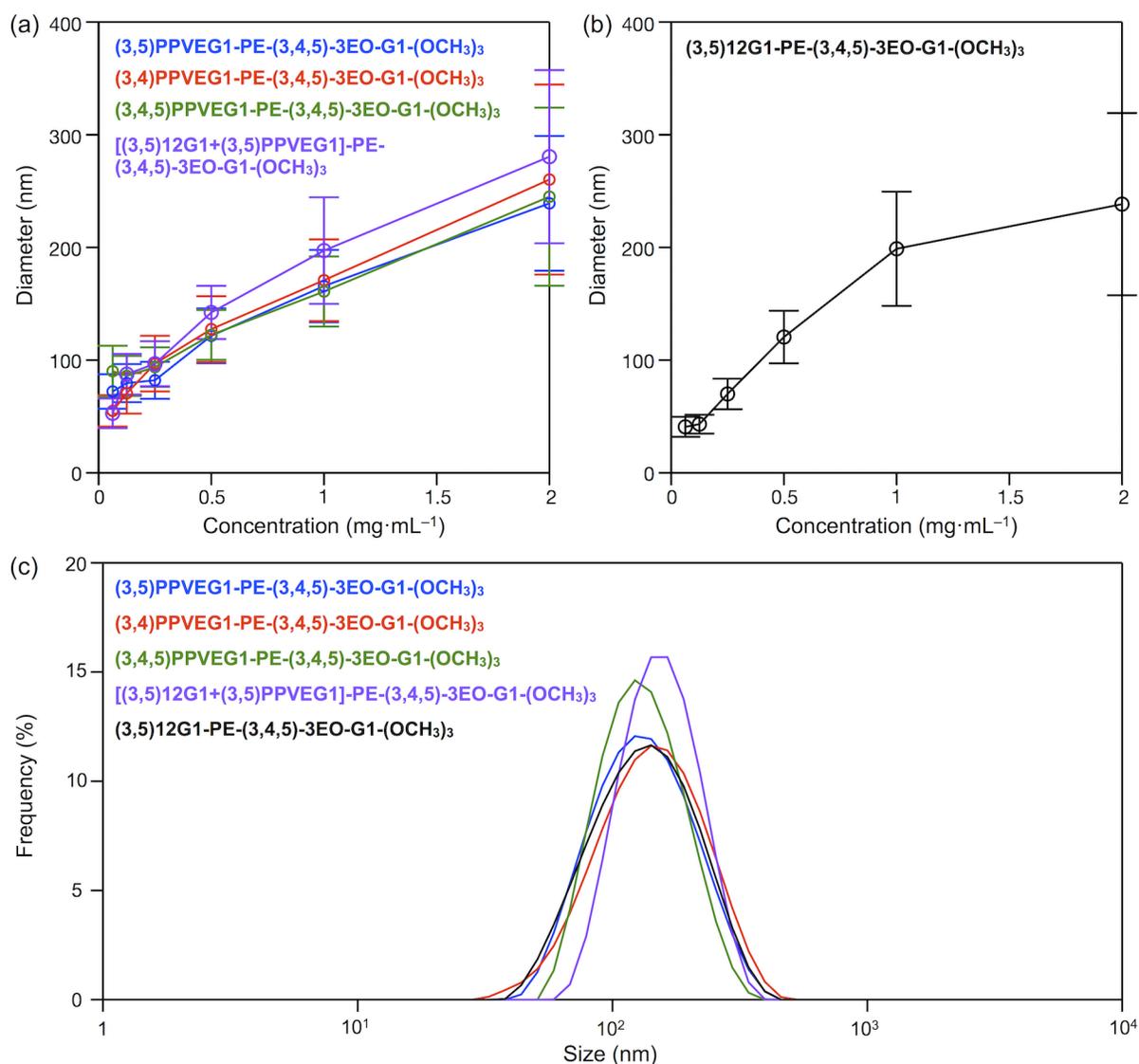


Figure S1. Concentration dependence of the diameter (D_{DLS} , in nm) of dendrimersomes assembled from (a) R_{F} , hybrid R_{HF} Janus dendrimers, and (b) R_{H} Janus dendrimer in water. Error bars indicate the width of distribution calculated from PDI. (c) Representative DLS histograms of dendrimersomes obtained by injection of their ethanol solution into water (final concentration: $0.5 \text{ mg}\cdot\text{mL}^{-1}$).

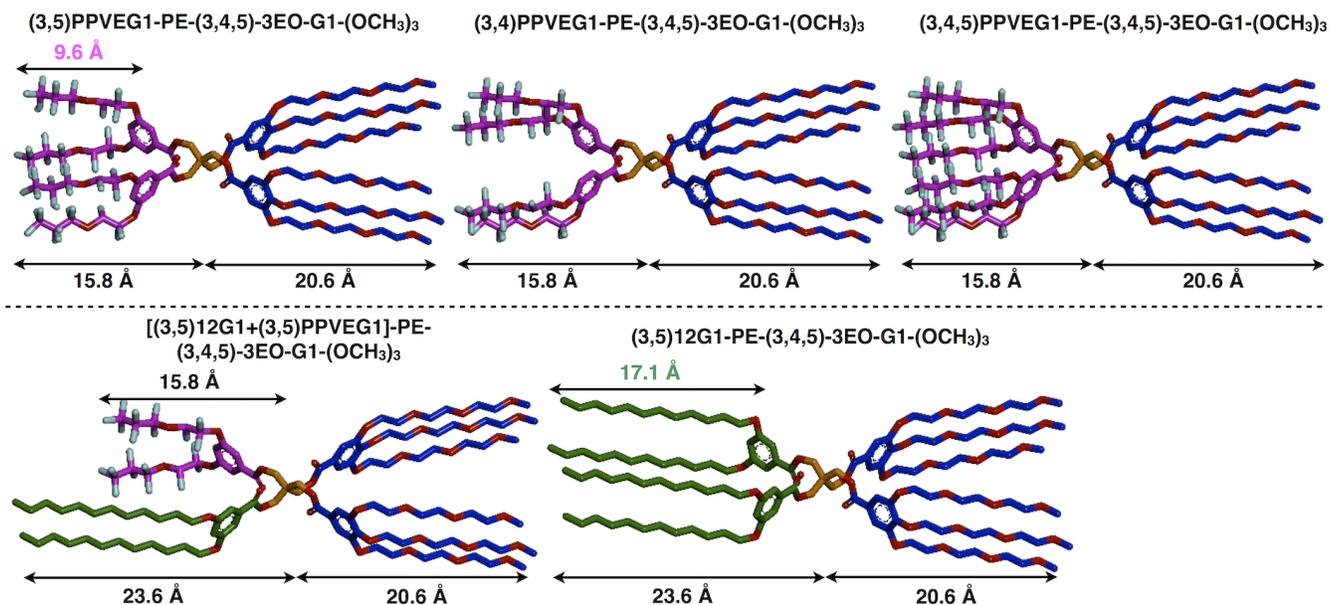


Figure S2. Molecular models of Janus dendrimers with estimated lengths from the center to their terminals, and the lengths of chains (magenta for R_F chain and green for R_H chain).

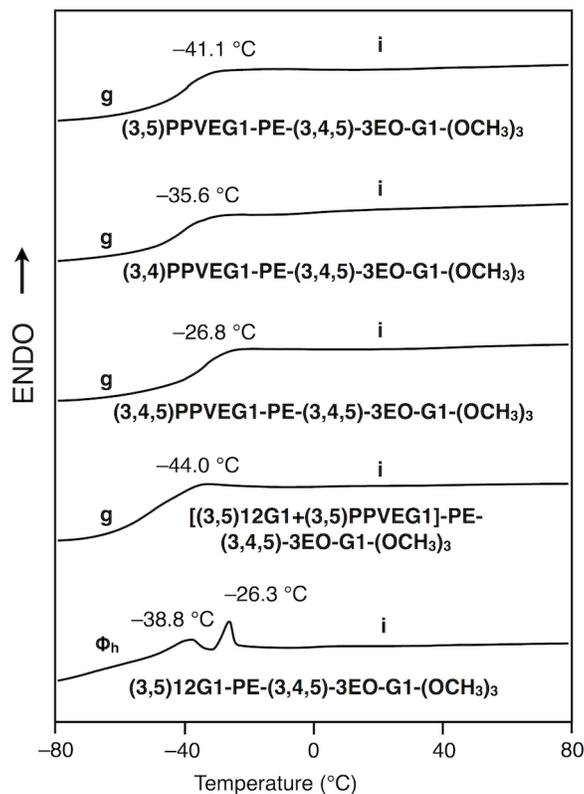


Figure S3. DSC traces of the Janus dendrimers at heating, and cooling rates of $10\text{ °C}\cdot\text{min}^{-1}$ for the first heating. Phases, transition temperatures have been indicated. Notation of the structure assembled in bulk: **g**, glassy phase; **i**, isotropic phase, and Φ_h , hexagonal columnar phase, determined by X-ray diffraction.

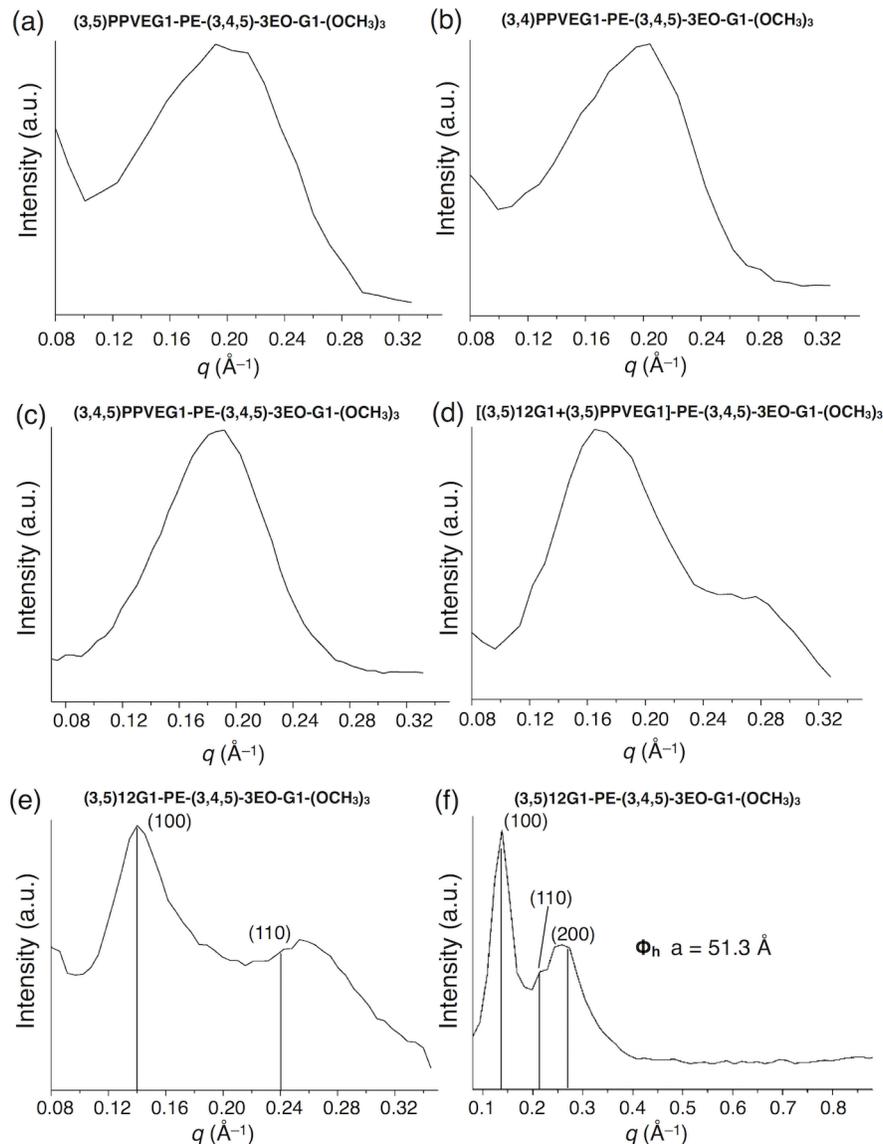


Figure S4. Small-angle (sample-detector distance 54 cm) of scattered intensity versus momentum transfer ($q = (4\pi/\lambda) \sin \theta$) for (a) $(3,5)\text{PPVEG1-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$, (b) $(3,4)\text{PPVEG1-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$, (c) $(3,4,5)\text{PPVEG1-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$ (d) $[(3,5)12\text{G1}+(3,5)\text{PPVEG1}]\text{-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$, (e) $(3,5)12\text{G1-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$. (f) Wide-angle (sample-detector distance 11 cm) of scattered intensity for $(3,5)12\text{G1-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$. The broad diffraction peaks in (a) to (d) indicate glassy phases of the corresponding compound. Experimental (100), (110), and (200) diffraction peaks in (e) and (f) indicate hexagonal phase (Φ_h). All the data were collected at $-60 \text{ }^\circ\text{C}$.

6. Movie Captions

Movie S1. Representative confocal scanning laser tomography of giant dendrimersome from R_F Janus dendrimer **(3,5)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** and 1% (wt/wt) NBD-labeled green fluorescent Janus dendrimer with R_F chains **(3,5)PPVEG1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-NBD**.

Movie S2. Reconstructed 3D projection of dendrimersome from R_F Janus dendrimer **(3,5)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** and 1% (wt/wt) NBD-labeled green fluorescent Janus dendrimer with R_F chains **(3,5)PPVEG1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-NBD**.

Movie S3. Representative confocal scanning laser tomography of giant dendrimersome from hybrid R_{HF} Janus dendrimer **[(3,5)12G1+(3,5)PPVEG1]-PE-(3,4,5)-3EO-G1-(OCH₃)₃** and 1% (wt/wt) Texas Red (TR)-labeled phospholipid **TR-DHPE**.

7 References

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8 ^1H NMR Spectra of Janus Dendrimers

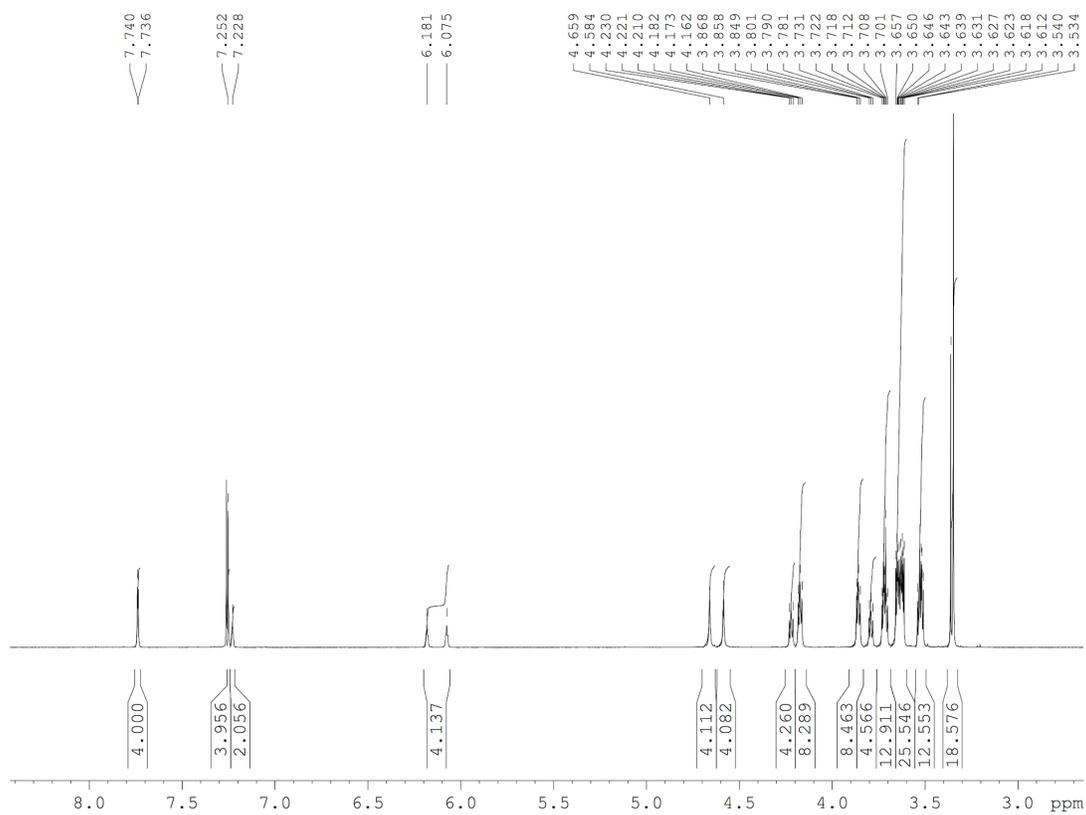


Figure S5. ^1H NMR Spectrum of **(3,5)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** (CDCl_3 , 500 MHz).

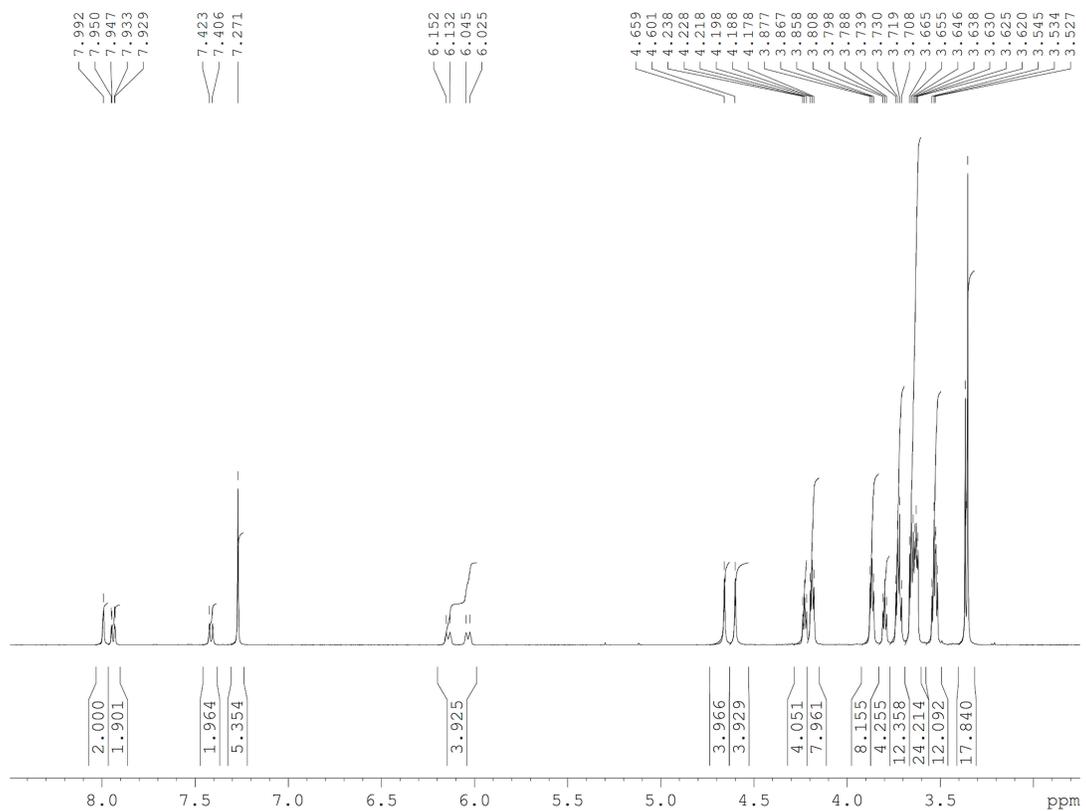


Figure S6. ^1H NMR Spectrum of **(3,4)PPVEG1-PE-(3,4,5)-3EO-G1-(OCH₃)₃** (CDCl_3 , 500 MHz).

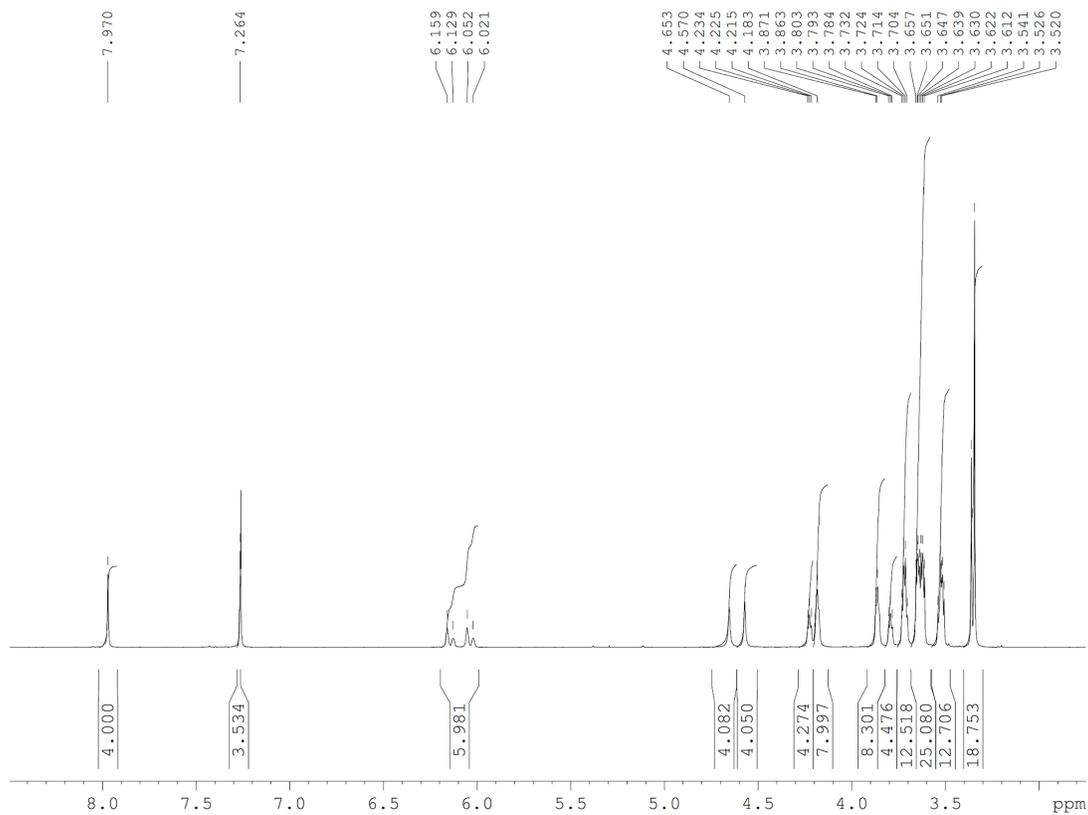


Figure S7. ^1H NMR Spectrum of $(3,4,5)\text{PPVEG1-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$ (CDCl_3 , 500 MHz).

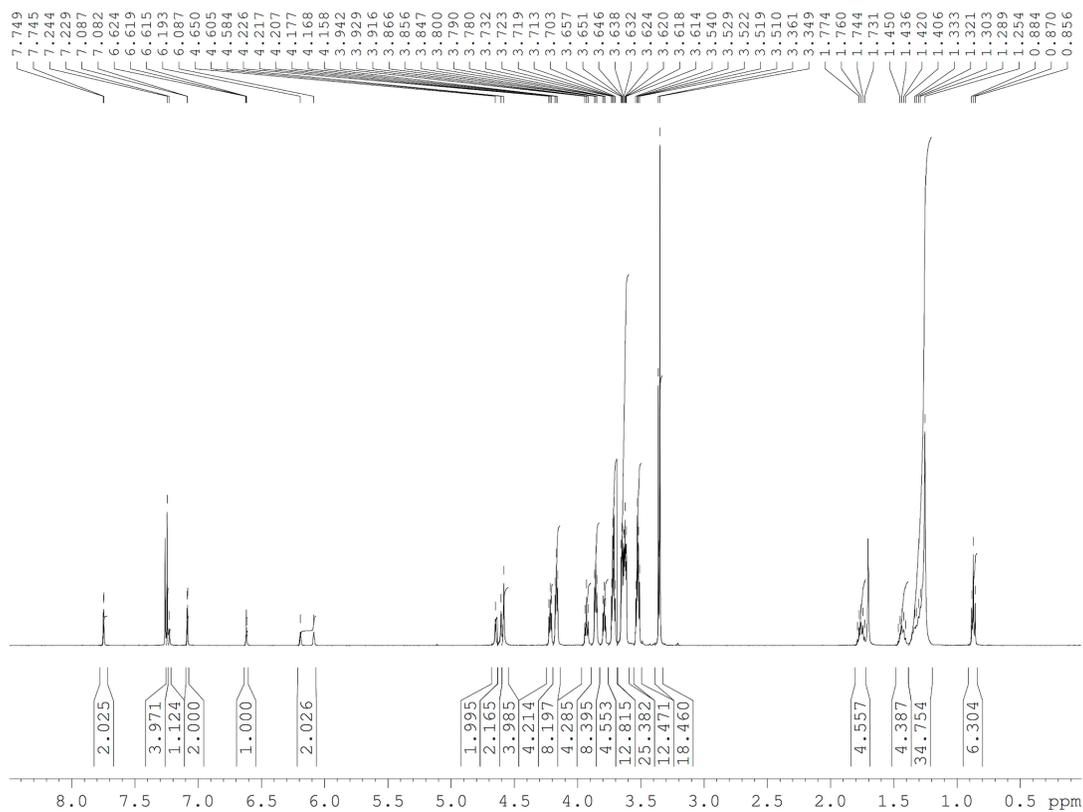


Figure S8. ^1H NMR Spectrum of $[(3,5)12\text{G1}+(3,5)\text{PPVEG1}]\text{-PE-(3,4,5)-3EO-G1-(OCH}_3)_3$ (CDCl_3 , 500 MHz).

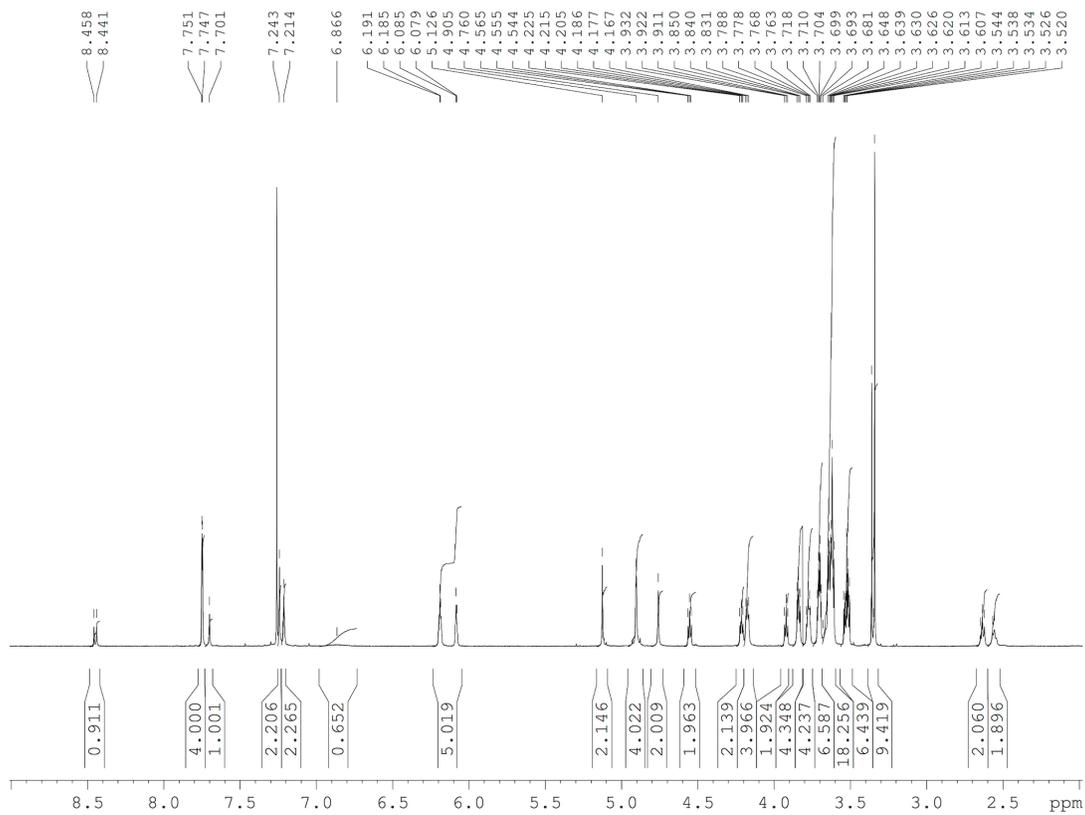


Figure S9. ^1H NMR Spectrum of **(3,5)PPVEG1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-NBD** (CDCl_3 , 500 MHz).

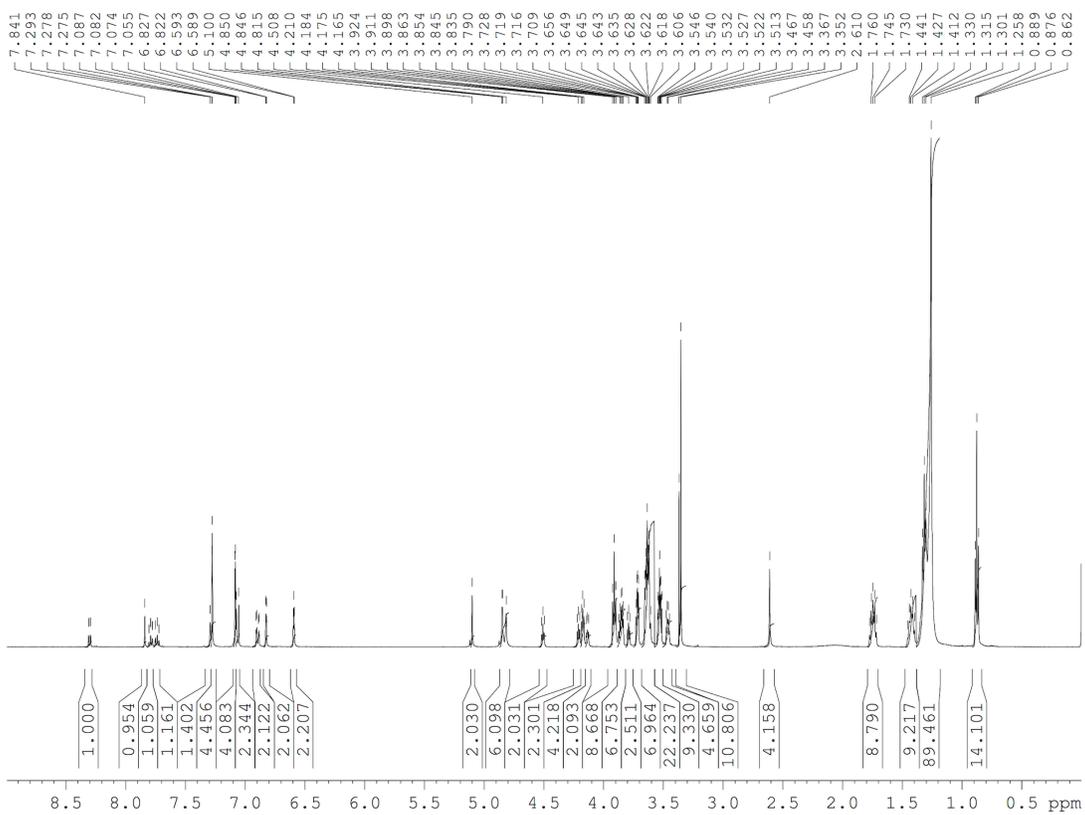


Figure S10. ^1H NMR Spectrum of **(3,5)12G1-Tris-(3,4,5)-3EO-G1-(OCH₃)₃-RhB** (CDCl_3 , 500 MHz).