First Synthesis and Characterization of Dendritic Necklaces: A New Class of Outer Sphere–Outer Sphere Connected Dendronized Organoplatinum Polymers

Hak-Fun Chow, Cham-Fai Leung, Wei Li, Kai-Wai Wong and Luan Xi

[*] Prof. Dr. H.-F. Chow, C.-F. Leung, W. Li
Department of Chemistry
The Chinese University of Hong Kong, Shatin, NT (Hong Kong SAR)
Fax: (+852)26035057
E-mail: hfchow@cuhk.edu.hk
Dr. K.-W. Wong, L. Xi
Department of Physics
The Chinese University of Hong Kong, Shatin, NT (Hong Kong SAR)

[**] We thank the Research Grants Council, HKSAR (CUHK4201/99P) for the financial support.

General Methods: All reagents were purchased from commercial suppliers (Acros or Aldrich) and used without further purification. Organic solvents were dried prior to use. All reactions were carried out under a nitrogen atmosphere. Thin layer chromatography (TLC) was performed on silica gel sheets 60 F254 (E. Merck). Column chromatography was performed on silica gel (Macherey Nagel Kieselgel 60M 230-400 mesh). All nuclear magnetic resonance (NMR) spectra were recorded either on a Brüker Advance DPX300 spectrometer (1H: 300 MHz; 13C: 75.5 MHz) or a Varian Unity INOVA400 spectrometer (31P: 161.9 MHz) and chloroform-d was used as solvent unless otherwise stated. Chemical shifts are reported as parts per million (ppm) downfield from signal of Me₄Si as internal standard for 1H and 13C NMR or from signal of PPh₃ as external standard for 31P NMR. Mass spectra were obtained by electron impact (EI) ionization on a Hewlett Packard 5989B mass spectrometer or liquid secondary ionization mass spectrometry (L-SIMS) method on a Brüker APEX 47e FTMS spectrometer or matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS) on a Brüker Biflex TOF mass spectrometer. The reported molecular mass (m/z) values were the most abundant monoisotopic mass. Elemental analyses were carried out at MEDAC Ltd. (Egham, Surrey, UK). Gel permeation chromatography (GPC) analyses were performed on Waters® Styrage columns (HR1, HR2,
HR3 and HR4 7.8 × 300 mm in serial) at 40 °C using THF as eluent (flow rate = 1.0 mL min⁻¹) on a Waters® HPLC 515 pump equipped with a Waters® 486 tunable UV absorbance detector. Molecular weights calculated from SEC measurements were based on a calibration curve derived from polystyrene (PS). Melting points were measured on an Electrothermal® 9100 digital melting point apparatus and are uncorrected.

**Synthesis**

\[
\begin{align*}
\text{I} & \quad \text{HO(CH₂)₁₀OH} \\
\text{HO(CH₂)₁₀OH} & \quad \text{DEAD, PPh₃} & \quad \text{I} \quad \text{O(CH₂)₁₀OH} \\
\text{I} \quad \text{O(CH₂)₁₀Br} & \quad \text{CBr₄, PPh₃}
\end{align*}
\]

**20**: Diethyl azodicarboxylate (6.3 mL, 32 mmol) was added dropwise to a solution of PPh₃ (8.30 g, 32 mmol) in THF (70 mL) at 0 °C. After 30 min, a mixture of 1,10-decanediol (9.20 g, 53 mmol) and 4-iodophenol (5.80 g, 26 mmol) in THF (70 mL) was added dropwise. The reaction was stirred at 25 °C for 6 h. Excess THF was then evaporated under reduced pressure and a mixture of hexane/Et₂O (1:1, 30 mL) was added. The precipitate was filtered off and washed with Et₂O (20 mL). The filtrate was then concentrated under reduced pressure to give an oil which was purified by column chromatography (eluent: hexane/EtOAc, 5:1) to give compound 20 (8.70 g, 87%) as a white solid: \( R_f: 0.23 \) (hexane/EtOAc, 5:1); m.p. 59–60 °C; \(^1\)H NMR: 1.20–1.50 (m, 13 H), 1.56 (quin, \( J = 6.6 \) Hz, 2 H), 1.76 (quin, \( J = 6.9 \) Hz, 2 H), 3.60–3.70 (m, 2 H), 3.90 (t, \( J = 6.6 \) Hz, 2 H), 6.68 (d, \( J = 6.9 \) Hz, 2 H), 7.53 (d, \( J = 6.9 \) Hz, 2 H); \(^13\)C NMR: 25.7, 25.9, 29.1, 29.3, 29.37, 29.44, 29.5, 32.8, 63.1, 68.1, 82.4, 116.9, 138.1, 159.0; MS(EI): \( m/z \) 376 (M⁺, 7); calcd (%) for C₁₆H₂₅O₂I: C, 51.07; H, 6.70; found: C, 50.89; H, 6.80.

**21**: PPh₃ (4.2 g, 16 mmol) was added to a mixture of the alcohol 20 (3.0 g, 8.0 mmol) and CBr₄ (4.0 g, 12 mmol) in THF (60 mL). The mixture was stirred at 25 °C for 1.5 h and then diluted with hexane/Et₂O (1:1, 30 mL). The precipitate formed was filtered off and washed with Et₂O (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (eluent: hexane gradient to hexane/EtOAc, 10:1) to afford compound 21 (3.0 g, 86%) as a white solid; \( R_f: 0.25 \).
hexane); m.p. 58–59 °C; \(^1\)H NMR: 1.25–1.50 (m, 12 H), 1.76 (quin, \(J = 6.9\) Hz, 2 H), 1.85 (quin, \(J = 6.9\) Hz, 2 H), 3.41 (t, \(J = 6.9\) Hz, 2 H), 3.91 (t, \(J = 6.3\) Hz, 2 H), 6.67 (d, \(J = 6.6\) Hz, 2 H), 7.53 (d, \(J = 6.6\) Hz, 2 H); \(^{13}\)C NMR: 25.9, 28.1, 28.7, 29.1, 29.28, 29.32, 29.4, 32.8, 34.0, 68.1, 82.4, 116.9, 138.1, 159.0; MS(EI): \(m/z\) 441 [M\(^{+}\) \((^{81}\text{Br}), 17\); calcd (%) for C\(_{16}\)H\(_{24}\)OBrI: C, 43.76; H, 5.51; found: C, 43.44; H, 5.59.

\[
\begin{align*}
\text{ArO}(CH_2)_2O & \quad \text{ArO}(CH_2)_3Br (1.0 \text{ equiv}) \\
\text{ArO}(CH_2)_2CO_2Me & \quad \text{K}_2\text{CO}_3 \\
\text{ArO}(CH_2)_3Br (1.0 \text{ equiv}) & \quad \text{K}_2\text{CO}_3 \\
\end{align*}
\]

23: 3-Bromo-1-(4-tert-butylphenoxy)propane \(^\text{[1]}\) (16.6 g, 60.0 mmol) was added dropwise to a mixture of methyl 3-(3,5-dihydroxyphenyl)propionate \(^\text{[2]}\) (12.0 g, 60.0 mmol), 18-crown-6 (1.0 g, 3.8 mmol) and K\(_2\)CO\(_3\) (25.0 g, 180 mmol) in acetone (250 mL) at 56 °C. The mixture was then heated at 56 °C for 6 h. The solution was filtered and the filtrate obtained was evaporated under reduced pressure and the crude product was purified by column chromatography (eluent: hexane/EtOAc, 5:1 gradient to 3:1) to afford compound 23 (19.6 g, 83%) as a white solid; \(R_f\): 0.10 (hexane/EtOAc, 5:1); m.p. 69–70 °C; \(^1\)H NMR: 1.30 (s, 9 H), 2.22 (quin, \(J = 6.0\) Hz, 2 H), 2.60 (t, \(J = 7.8\) Hz, 2 H), 2.84 (t, \(J = 7.5\) Hz, 2 H), 3.67 (s, 3 H), 4.10 (t, \(J = 6.3\) Hz, 2 H), 4.12 (t, \(J = 6.3\) Hz, 2 H), 5.10–5.25 (brs, 1 H), 6.27 (s, 2 H), 6.33 (s, 1 H), 6.85 (d, \(J = 8.7\) Hz, 2 H), 7.29 (d, \(J = 8.7\) Hz, 2 H); \(^{13}\)C NMR: 29.9, 31.6, 32.1, 34.6, 36.2, 61.1, 64.9, 65.0, 100.4, 107.7, 108.4, 114.5, 126.8, 143.8, 144.0, 157.1, 157.3, 160.8, 173.6; MS(L-SIMS): \(m/z\) 386 (M\(^{+}\), 1); calcd (%) for C\(_{23}\)H\(_{30}\)O\(_5\): C, 71.48; H, 7.82; found: C, 71.27; H, 7.84.

24: A mixture of methyl 3-(3,5-dihydroxyphenyl)propionate \(^\text{[2]}\) (7.1 g, 36 mmol), 3-bromo-1-(4-tert-butylphenoxy)propane \(^\text{[1]}\) (22.0 g, 80 mmol), 18-crown-6 (1.0 g, 3.8 mmol) and K\(_2\)CO\(_3\) (25.0 g, 18 mmol) in acetone (200 mL) was heated at 56 °C for 6 h. The mixture was then filtered and the filtrate obtained was evaporated under reduced pressure. The residue was purified by column chromatography (eluent:
hexane/EtOAc, 8:1 gradient to 5:1) to afford compound 24 (16.5 g, 75%) as a white solid; $R_f$: 0.68 (hexane/EtOAc, 5:1); m.p. 59–61 °C; $^1$H NMR: 1.32 (s, 18 H), 2.25 (quin, $J = 6.0$ Hz, 4 H), 2.62 (t, $J = 7.5$ Hz, 2 H), 2.89 (t, $J = 7.5$ Hz, 2 H), 3.69 (s, 3 H), 4.13 (t, $J = 6.0$ Hz, 4 H), 4.15 (t, $J = 6.0$ Hz, 4 H), 6.34–6.40 (m, 3 H), 6.87 (d, $J = 8.7$ Hz, 4 H), 7.32 (d, $J = 8.7$ Hz, 4 H); $^{13}$C NMR: 29.3, 31.2, 31.5, 34.0, 35.5, 51.6, 64.3, 64.4, 99.2, 107.0, 113.9, 126.2, 142.8, 143.3, 156.5, 160.1, 173.3; MS(L-SIMS): $m/z$ 577 [(M+H)$^+$, 100]; calcd (%) for C$_{36}$H$_{48}$O$_6$: C, 74.97; H, 8.39; found: C, 75.25; H, 8.49.

25: A mixture of the phenol 23 (3.8 g, 9.9 mmol), the bromide 20 (5.2 g, 12 mmol), K$_2$CO$_3$ (6.5 g, 20 mmol) and dibenzo-24-crown-8 (0.9 g, 2.0 mmol) in DMF (60 ml) was stirred at 60 °C for 1.5 h. The reaction was then quenched with water and extracted with EtOAc (50 mL × 2). The organic layers were combined, washed with saturated NaCl solution (50 mL), dried (MgSO$_4$) and concentrated under reduced pressure. The crude product obtained was purified by column chromatography (eluent: hexane/EtOAc, 9:1 gradient to 7:1) to yield compound 25 (6.2 g, 84%) as a white solid; $R_f$: 0.59 (hexane/EtOAc, 5:1); m.p. 49–50 °C; $^1$H NMR: 1.25–1.50 (m, 12 H), 1.30 (s, 9 H), 1.76-1.82 (m, 4 H), 2.23 (quin, $J = 6.0$ Hz, 2 H), 2.60 (t, $J = 7.5$ Hz, 2 H), 2.84 (t, $J = 7.5$ Hz, 2 H), 3.67 (s, 3 H), 3.85–3.93 (m, 4 H), 4.10–4.20 (m, 4 H), 6.20–6.40 (m, 3 H), 6.67 (d, $J = 6.9$ Hz, 2 H), 6.85 (d, $J = 6.9$ Hz, 2 H), 7.29 (d, $J = 6.9$ Hz, 2 H), 7.54 (d, $J = 6.9$ Hz, 2 H); $^{13}$C NMR: 25.96, 26.02, 29.1, 29.25, 29.34, 29.5, 31.2, 31.5, 34.0, 35.8, 60.4, 64.3, 64.4, 67.9, 68.1, 82.4, 99.1, 106.8, 107.0, 113.9, 116.9, 126.2, 138.1, 142.8, 143.4, 156.6, 159.0, 160.1, 160.3, 172.9; MS(L-SIMS): $m/z$ 745 [(M+H)$^+$, 100]; calcd (%) for C$_{39}$H$_{53}$O$_6$I: C, 62.90; H, 7.17; found: C, 62.92; H, 7.18.
26: A mixture of the ester 25 (6.2 g, 8.3 mmol) in toluene (50 ml) was treated with DIBAL (1.0 M in hexane) (34 mL, 33 mmol) at –60 °C to –10 °C for 1.5 h. The reaction was then quenched with EtOAc (5 mL) and water (5 mL). The resulting mixture was acidified to pH 6 by adding HCl solution (2 M) and then extracted with EtOAc (40 mL × 2). The combined organic layers were washed with brine (40 mL), dried (MgSO₄) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) afforded compound 26 (5.7 g, 96%) as a colorless oil; \( R_f \): 0.39 (hexane/EtOAc, 3:1); \(^1\)H NMR: 1.20–1.50 (m, 13 H) 1.29 (s, 9 H), 1.70–1.80 (m, 4 H), 1.80–1.91 (m, 2 H), 2.23 (quin, \( J = 6.0 \) Hz, 2 H), 2.63 (t, \( J = 7.2 \) Hz, 2 H), 3.67 (q, \( J = 6.0 \) Hz, 2 H), 3.90 (t, \( J = 6.6 \) Hz, 4 H), 4.12 (t, \( J = 6.0 \) Hz, 2 H), 4.13 (t, \( J = 6.0 \) Hz, 2 H), 6.31 (t, \( J = 2.4 \) Hz, 1 H), 6.35 (d, \( J = 2.1 \) Hz, 2 H), 6.67 (d, \( J = 6.9 \) Hz, 2 H), 6.85 (d, \( J = 6.9 \) Hz, 2 H), 7.29 (d, \( J = 6.9 \) Hz, 2 H), 7.53 (d, \( J = 6.9 \) Hz, 2 H); \(^{13}\)C NMR: 25.96, 26.03, 29.1, 29.3, 29.5, 31.5, 32.4, 33.9, 34.0, 62.3, 64.3, 64.4, 67.9, 68.1, 82.4, 98.7, 106.9, 107.2, 113.9, 116.9, 126.2, 138.1, 143.4, 144.1, 156.6, 159.0, 160.0, 160.3; MS(L-SIMS): \( m/z \) 717 [(M+H)+, 100]; calcd (%) for C₃₈H₅₃O₅I: C, 63.68; H, 7.45; found: C, 63.77; H, 7.58.

10: A mixture of the alcohol 26 (1.9 g, 2.7 mmol), CBr₄ (1.4 g, 4.0 mmol) and PPh₃ (1.4 g, 5.3 mmol) in THF (25 ml) was stirred at 25 °C for 1.5 h. The mixture was diluted with hexane/Et₂O (1:1, 6 mL) and the precipitate formed was filtered off and washed with Et₂O (10 mL). The filtrate was concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 100:1 gradient to 8:1) afforded compound 10 (2.0 g, 97%) as a colorless oil; \( R_f \): 0.70 (hexane/EtOAc, 5:1); \(^1\)H NMR: 1.25–1.50 (m, 12 H), 1.32 (s, 9 H), 1.77 (quin, \( J = 6.9 \) Hz, 4 H), 2.15 (quin, \( J = 6.9 \) Hz, 2 H), 2.24 (quin, \( J = 6.0 \) Hz, 2 H), 2.70 (t, \( J = 7.2 \) Hz, 2 H), 3.39 (t, \( J = 6.6 \) Hz, 2 H), 3.91 (t, \( J = 6.3 \) Hz, 4 H), 4.13 (t, \( J = 6.0 \) Hz, 2 H), 4.14 (t, \( J = 6.0 \) Hz, 2 H), 6.30–6.40 (m, 3 H), 6.68 (d, \( J = 8.7 \) Hz, 2 H), 6.87 (d, \( J = 8.7 \) Hz, 2 H), 7.31 (d, \( J = 8.7 \) Hz, 2 H), 7.55 (d, \( J = 8.7 \) Hz, 2 H); \(^{13}\)C NMR: 25.95, 26.02, 29.1, 29.25, 29.33, 29.4, 31.5, 33.1, 33.9, 34.0, 34.2, 64.3, 64.4, 67.9, 68.1, 82.4, 99.0, 107.0, 107.3,
113.9, 116.9, 126.3, 138.1, 142.7, 143.4, 156.5, 159.0, 160.1, 160.3; MS(L-SIMS): $m/z$ 781 [(M+H)$^+$ ($^{81}$Br), 100]; calcld (%) for C$_{38}$H$_{52}$O$_4$Br: C, 58.54; H, 6.72; found: C, 58.80; H, 6.57.

27: A mixture of the ester 24 (4.1 g, 7.1 mmol) and LiAlH$_4$ (0.4 g, 11 mmol) in THF (25 mL) was stirred from 0 $^\circ$C to 25 $^\circ$C for 1.5 h. The reaction was then quenched with EtOAc (5 mL) and water (5 mL). The mixture was acidified to pH 6 by adding HCl solution (2 M) and then extracted with EtOAc (35 mL × 2). The organic layers were combined, washed with brine (35 mL), dried (MgSO$_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1) afforded compound 27 (3.8 g, 99%) as a white solid; $R_f$: 0.32 (hexane/EtOAc, 3:1); m.p. 60–61 $^\circ$C; $^1$H NMR (OH signal not observed): 1.30 (s, 18 H), 1.86 (quin, $J = 6.9$ Hz, 2 H), 2.22 (quin, $J = 6.0$ Hz, 4 H), 2.62 (t, $J = 7.2$ Hz, 2 H), 3.66 (q, $J = 4.8$ Hz, 2 H), 4.12 (t, $J = 6.0$ Hz, 4 H), 4.13 (t, $J = 6.0$ Hz, 4 H), 6.32 (t, $J = 2.1$ Hz, 1 H), 6.36 (d, $J = 1.8$ Hz, 2 H), 6.85 (d, $J = 8.7$ Hz, 4 H), 7.30 (d, $J = 8.7$ Hz, 4 H); $^{13}$C NMR: 30.0, 32.1, 32.9, 34.5, 34.6, 62.9, 64.9, 65.1, 99.4, 107.8, 114.5, 126.8, 144.0, 144.8, 157.2, 160.7; MS(EI): $m/z$ 549 [(M+H)$^+$], 100; calcld (%) for C$_{33}$H$_{48}$O$_5$: C, 76.61; H, 8.82; found: C, 76.31; H, 8.89.
28: A mixture of the alcohol 27 (3.8 g, 6.9 mmol), CBr₄ (3.5 g, 10 mmol) and PPh₃ (3.7 g, 14 mmol) in THF (50 mL) was stirred at 25 °C for 1.5 h. The mixture was diluted with hexane/Et₂O (1:1, 20 mL) and the precipitate formed was filtered off and washed with Et₂O (20 mL). The filtrate was concentrated under reduced pressure and the residue was purified by chromatography (eluent: hexane/EtOAc, 100:1 gradient to 5:1) to give compound 28 (4.1 g, 97%) as a colorless oil; Rf: 0.84 (hexane/EtOAc, 5:1); ¹H NMR: 1.30 (s, 18 H), 2.13 (quin, J = 6.9 Hz, 2 H), 2.23 (quin, J = 6.0 Hz, 4 H), 2.69 (t, J = 7.2 Hz, 2 H), 3.38 (t, J = 6.6 Hz, 2 H), 4.12 (t, J = 6.0 Hz, 4 H), 4.13 (t, J = 6.0 Hz, 4 H), 6.32–6.37 (m, 3 H), 6.87 (d, J = 8.7 Hz, 4 H), 7.29 (d, J = 8.7 Hz, 4 H); ¹³C NMR: 30.0, 32.1, 33.8, 34.5, 34.7, 34.8, 64.9, 65.1, 99.6, 107.9, 114.5, 126.8, 143.4, 144.0, 157.2, 160.7; MS(L-SIMS): m/z 612 [M⁺(⁸¹Br), 100]; calcd (%) for C₃₅H₄₇O₄Br: C, 68.73; H, 7.75; found: C, 68.54; H, 7.74.

29: A mixture of compound 22 (2.1 g, 11 mmol), the bromide 28 (14.0 g, 23 mmol), dibenzo-24-crown-8 (1.4 g, 3.1 mmol) and Cs₂CO₃ (10.0 g, 31 mmol) in DMF (20 mL) was stirred at 60 °C for 1.5 h. The reaction mixture was then quenched with water and extracted with EtOAc (50 mL × 2). The organic layers were combined, washed with brine (50 mL), dried (MgSO₄) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 3:1) gave compound 29 (10.0 g, 74%) as a colorless oil; Rf: 0.66 (hexane/EtOAc, 3:1); ¹H NMR: 1.29 (s, 36 H), 2.05 (quin, J = 5.4 Hz, 4 H), 2.21 (quin, J = 6.0 Hz, 8 H), 2.59 (t, J = 7.5 Hz, 2 H), 2.70 (t, J = 7.2 Hz, 4 H), 2.86 (t, J = 7.5 Hz, 2 H), 3.66 (s, 3 H), 3.90 (t, J = 6.0 Hz, 4 H), 4.09 (t, J = 6.3 Hz, 8 H), 4.11 (t, J = 6.3 Hz, 8 H), 6.31 (t, J = 2.1 Hz, 3 H), 6.36 (d, J = 1.8 Hz, 6 H), 6.85 (d, J = 8.7 Hz, 8 H), 7.29 (d, J = 8.7 Hz, 8 H); ¹³C NMR: 29.3, 30.6, 31.2, 31.5, 32.4, 34.0, 35.5, 51.6, 64.3, 64.4, 66.9, 98.9, 99.2, 106.8, 107.2, 113.9, 126.2, 142.7, 143.3, 143.8, 156.5, 160.0, 160.3, 173.3; MS(L-SIMS): m/z 1258 (M⁺, 100); calcd (%) for C₈₀H₁₀₄O₁₂: C, 76.39; H, 8.35; found: C, 76.54; H, 8.41.

30: A mixture of the ester 29 (9.90 g, 7.9 mmol) and LiAlH₄ (0.50 g, 12 mmol) in THF (60 mL) was stirred from 0 °C to 25 °C for 1.5 h. The reaction was then quenched with EtOAc (5 mL) and water (5
mL). The resulting mixture was acidified to pH 6 by adding HCl solution (2 M) and extracted with EtOAc (40 mL x 2). The organic layers were combined, washed with brine (40 mL), dried (MgSO4) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1 gradient to 2:1) afforded compound 30 (8.90 g, 92%) as a colorless oil; Rf: 0.25 (hexane/EtOAc, 3:1); 1H NMR (OH signal not observed): 1.29 (s, 36 H), 1.86 (quin, J = 6.6 Hz, 2 H), 2.05 (quin, J = 5.7 Hz, 4 H), 2.21 (quin, J = 6.0 Hz, 8 H), 2.61 (t, J = 7.2 Hz, 2 H), 2.71 (t, J = 7.2 Hz, 4 H), 3.65 (q, J = 5.4 Hz, 2 H), 3.91 (t, J = 6.0 Hz, 4 H), 4.09 (t, J = 6.3 Hz, 8 H), 4.10 (t, J = 6.3 Hz, 8 H), 6.25–6.40 (m, 9 H), 6.84 (d, J = 8.7 Hz, 8 H), 7.29 (d, J = 8.7 Hz, 8 H); 13C NMR: 29.3, 30.6, 31.5, 32.3, 32.4, 33.96, 34.03, 62.2, 64.35, 64.44, 66.8, 98.9, 107.1, 107.2, 113.9, 126.2, 143.4, 143.9, 144.1, 156.6, 160.0, 160.2; MS(L-SIMS): m/z 1230 (M+, 100); calcd (%) for C79H104O11: C, 77.16; H, 8.52; found: C, 76.90; H, 8.52.

12: A mixture of the alcohol 30 (3.0 g, 2.4 mmol), CBr4 (1.2 g, 3.7 mmol) and PPh3 (1.3 g, 4.9 mmol) in THF (30 mL) was stirred at 25 °C for 1.5 h. The reaction mixture was diluted with hexane/Et2O (1:1, 5 mL) and the precipitate formed was filtered off and washed with Et2O (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by chromatography (eluent: hexane/EtOAc, 100:1 gradient to 5:1) to furnish compound 12 (2.9 g, 93%) as a colorless oil; Rf: 0.73 (hexane/EtOAc, 3:1); 1H NMR: 1.30 (s, 36 H), 2.06 (quin, J = 6.9 Hz, 4 H), 2.13 (quin, J = 6.0 Hz, 2 H), 2.22 (quin, J = 6.0 Hz, 8 H), 2.64–2.77 (m, 6 H), 3.38 (t, J = 6.3 Hz, 2 H), 3.93 (t, J = 6.0 Hz, 4 H), 4.10 (t, J = 7.8 Hz, 8 H), 4.13 (t, J = 7.8 Hz, 8 H), 6.30–6.40 (m, 9 H), 6.86 (d, J = 8.7 Hz, 8 H), 7.30 (d, J = 8.7 Hz, 8 H); 13C NMR: 29.3, 30.6, 31.5, 32.4, 33.1, 33.9, 34.0, 34.2, 64.3, 64.4, 66.9, 98.9, 99.1, 107.2, 113.9, 126.2, 142.8, 143.3, 143.8, 156.5, 160.0, 160.3; MS(FAB): m/z 1294 [M+(81Br), 100]; calcd (%) for C79H103O10Br: C, 73.41; H, 8.03; found: C, 73.46; H, 7.95.
31: A mixture of compound 22 (9.1 g, 46 mmol), benzyl bromide (12.0 mL, 97 mmol) and K₂CO₃ (19.2 g, 0.14 mol) in acetone (150 mL) was heated at 56 °C for 6 h. The solution was allowed to cool to room temperature and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (eluent: hexane/EtOAc, 4:1) to afford compound 31 (17.0 g, 97%) as a colorless oil; R_f: 0.36 (hexane/EtOAc, 5:1); ^1H NMR: 2.62 (t, J = 7.2 Hz, 2 H), 2.90 (t, J = 7.5 Hz, 2 H), 3.68 (s, 3 H), 5.02 (s, 4 H), 6.42–6.52 (m, 3 H), 7.30–7.50 (m, 10 H); ^13C NMR: 31.2, 35.4, 51.7, 70.0, 99.9, 107.5, 127.5, 128.0, 136.9, 142.9, 160.0, 173.2; MS(EI): m/z 376 (M⁺, 100); calcld (%) for C₂₄H₂₄O₄: C, 76.57; H, 6.43; found: C, 76.57; H, 6.45.

32: A mixture of the dibenzyl ether 31 (8.3 g, 22 mmol) and 10% palladium on charcoal (0.8 g) in EtOH/EtOAc (1:1, 100 mL) was stirred under hydrogen atmosphere (1 atm) at 25 °C for 2 h. The mixture was then filtered and the filtrate obtained was evaporated under reduced pressure. Chromatographic purification (eluent: hexane/EtOAc, 4:1) of the residue afforded compound 32 (3.0 g, 47%) as a colorless oil; R_f: 0.22 (hexane/EtOAc, 3:1); ^1H NMR (OH signal not observed): 2.61 (t, J = 7.8 Hz, 2 H), 2.86 (t, J = 7.5 Hz, 2 H), 3.68 (s, 3 H), 5.01 (s, 2 H), 6.29 (s, 1 H), 6.34 (s, 1 H), 6.42 (s, 1
H), 7.30–7.50 (m, 5 H); $^{13}$C NMR: 30.9, 35.3, 51.7, 70.0, 100.2, 107.4, 108.0, 127.5, 128.0, 128.6, 136.8, 143.2, 156.7, 160.2, 173.4; MS(EI): $m/z$ 286 (M$^+$, 46); calcd (%) for C$_{17}$H$_{18}$O$_4$: C, 71.31; H, 6.34; found: C, 71.44; H, 6.29.

33: A mixture of the phenol 32 (1.6 g, 5.6 mmol), the bromide 28 (4.1 g, 6.7 mmol), Cs$_2$CO$_3$ (3.7 g, 11 mmol) and dibenzo-24-crown-8 (0.5 g, 1.1 mmol) in DMF (40 mL) was stirred at 60 °C for 1.5 h. The mixture was then quenched with water and extracted with EtOAc (80 mL × 2). The combined extracts were washed with brine (80 mL), dried (MgSO$_4$) and evaporated under reduced pressure. Column chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) yielded compound 33 (4.0 g, 88%) as a colorless oil; $R_f$: 0.43 (hexane/EtOAc, 5:1); $^1$H NMR: 1.29 (s, 18 H), 2.05 (quin, $J$ = 6.6 Hz, 2 H), 2.21 (quin, $J$ = 6.0 Hz, 4 H), 2.61 (t, $J$ = 7.5 Hz, 2 H), 2.70 (t, $J$ = 7.2 Hz, 2 H), 2.88 (t, $J$ = 7.5 Hz, 2 H), 3.67 (s, 3 H), 3.91 (t, $J$ = 6.3 Hz, 2 H), 4.09 (t, $J$ = 6.3 Hz, 4 H), 4.12 (t, $J$ = 6.3 Hz, 4 H), 5.01 (s, 2 H), 6.30–6.50 (m, 6 H), 6.83 (d, $J$ = 8.7 Hz, 4 H), 7.28 (d, $J$ = 8.7 Hz, 4 H), 7.30–7.45 (m, 5 H); $^{13}$C NMR: 29.3, 30.5, 31.2, 31.5, 32.4, 34.0, 35.5, 51.6, 64.35, 64.45, 66.9, 70.0, 98.9, 99.5, 107.1, 107.2, 107.3, 113.9, 126.2, 127.5, 127.9, 128.6, 136.9, 142.8, 143.4, 143.8, 156.6, 160.0, 160.3, 173.3; MS(L-SIMS): $m/z$ 817 [(M+H)$^+$, 100]; calcd (%) for C$_{52}$H$_{64}$O$_8$: C, 76.44; H, 7.90; found: C, 76.27; H, 7.88.

34: A mixture of the benzyl ether 33 (4.5 g, 5.5 mmol) and 10% palladium on charcoal (0.4 g) in EtOH/EtOAc (1:1, 30 mL) was stirred at 25 °C for 2 h under hydrogen atmosphere (1 atm). The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: hexane/EtOAc = 4:1) to afford compound 34 (3.8 g, 96%) as a colorless oil; $R_f$: 0.25 (hexane/EtOAc, 3:1); $^1$H NMR: 1.31 (s, 18 H), 2.05 (quin, $J$ = 6.9 Hz, 2 H), 2.22 (quin, $J$ = 6.0 Hz, 4 H), 2.60 (t, $J$ = 7.8 Hz, 2 H), 2.71 (t, $J$ = 7.5 Hz, 2 H), 2.85 (t, $J$ = 7.8 Hz, 2 H), 3.68 (s, 3 H), 3.89 (t, $J$ = 6.3 Hz, 2 H), 4.10 (t, $J$ = 6.0 Hz, 4 H), 4.13 (t, $J$ = 6.0 Hz, 4 H), 5.25 (s, 1 H), 6.25 (s, 2 H), 6.33 (s, 2 H), 6.37 (s, 2 H), 6.85 (d, $J$ = 8.7 Hz, 4 H), 7.29 (d, $J$ = 8.7 Hz, 4 H); $^{13}$C NMR:
A mixture of the bromide 10 (2.9 g, 3.6 mmol), the phenol 34 (2.2 g, 3.0 mmol), Cs$_2$CO$_3$ (2.0 g 6.0 mmol) and dibenzo-24-crown-8 (0.3 g, 0.6 mmol) in DMF (30 ml) was stirred at 60 °C for 1.5 h. The reaction was then quenched with water, and extracted with EtOAc (20 mL × 2). The organic layers were combined, washed with brine (20 mL), dried (MgSO$_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1) yielded compound 35 (4.2 g, 97%) as a colorless oil; $R_f$: 0.47 (hexane/EtOAc, 5:1); $^1$H NMR: 1.25–1.50 (m, 12 H), 1.30 (s, 27 H), 1.70–1.80 (m, 4 H), 2.05 (quin, $J = 6.6$ Hz, 4 H), 2.22 (quin, $J = 6.0$ Hz, 6 H), 2.63 (t, $J = 7.5$ Hz, 2 H), 2.71 (t, $J = 7.2$ Hz, 4 H), 2.87 (t, $J = 7.5$ Hz, 2 H), 3.67 (s, 3 H), 3.80–4.00 (m, 8 H), 4.10 (t, $J = 6.1$ Hz, 6 H), 7.30 (d, $J = 8.7$ Hz, 6 H), 7.54 (d, $J = 8.4$ Hz, 2 H); $^{13}$C NMR: 25.96, 26.03, 29.1, 29.4, 29.5, 30.6, 31.5, 32.5, 34.0, 35.5, 51.6, 64.4, 64.5, 66.9, 67.9, 68.1, 82.4, 98.9, 99.3, 106.9, 107.2, 113.9, 116.9, 126.2, 138.1, 142.8, 143.4, 143.8, 156.6, 160.0, 160.3, 173.3; MS(FAB): $m/z$ 1425.5 (M$^+$, 100); calcd (%) for C$_{83}$H$_{109}$O$_{12}$I: C, 69.93; H, 7.71; found: C, 70.24; H, 7.89.

A solution of the ester 35 (2.0 g, 1.4 mmol) in toluene (20 ml) was treated with DIBAL (1.0 M in hexane) (5.6 mL, 5.6 mmol) at –60 °C. The reaction mixture was stirred for 1.5 h and allowed to warm to –10 °C. The reaction was then quenched with EtOAc (5 mL) and water (5 mL). The resulting mixture was acidified to pH 6 by adding HCl solution (2 M) and then extracted with EtOAc (10 mL × 2). The combined organic layers were washed with brine (10 mL), dried (MgSO$_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1) yielded compound 36 (1.6 g, 81%) as a colorless oil; $R_f$: 0.36 (hexane/EtOAc, 3:1) $^1$H NMR (OH signal not observed): 1.20–1.50 (m, 12 H), 1.29 (s, 27 H), 1.70–1.80 (m, 4 H), 1.87 (quin, $J = 7.5$ Hz, 2 H), 2.22 (quin, $J = 6.6$ Hz, 4 H), 2.63 (t, $J = 7.5$ Hz, 2 H), 3.67 (s, 3 H), 3.80–4.00 (m, 8 H), 4.10 (t, $J = 6.1$ Hz, 6 H), 4.12 (t, $J = 6.0$ Hz, 6 H), 4.14 (t, $J = 6.0$ Hz, 6 H), 6.20–6.40 (m, 9 H), 6.67 (d, $J = 8.7$ Hz, 2 H), 6.85 (d, $J = 8.4$ Hz, 6 H), 7.30 (d, $J = 8.7$ Hz, 6 H), 7.54 (d, $J = 8.4$ Hz, 2 H); $^{13}$C NMR: 25.96, 26.03, 29.1, 29.4, 29.5, 30.6, 31.5, 32.5, 34.0, 35.5, 51.6, 64.4, 64.5, 66.9, 67.9, 68.1, 82.4, 98.9, 99.3, 106.9, 107.2, 113.9, 116.9, 126.2, 138.1, 142.8, 143.4, 143.8, 156.6, 160.0, 160.3, 173.3; MS(FAB): $m/z$ 1425.5 (M$^+$, 100); calcd (%) for C$_{83}$H$_{109}$O$_{12}$I: C, 69.93; H, 7.71; found: C, 70.24; H, 7.89.
2.05 (quin, \( J = 6.9 \) Hz, 4 H), 2.21 (quin, \( J = 6.0 \) Hz, 6 H), 2.62 (t, \( J = 7.5 \) Hz, 2 H), 2.71 (t, \( J = 6.3 \) Hz, 4 H), 3.66 (q, \( J = 5.4 \) Hz, 2 H), 3.80–3.95 (m, 8 H), 4.09 (t, \( J = 6.6 \) Hz, 6 H), 4.12 (t, \( J = 6.6 \) Hz, 6 H), 6.25–6.40 (m, 9 H), 6.67 (d, \( J = 8.7 \) Hz, 2 H), 6.85 (d, \( J = 8.7 \) Hz, 6 H), 7.30 (d, \( J = 8.7 \) Hz, 6 H), 7.54 (d, \( J = 8.7 \) Hz, 2 H); \(^{13}\text{C} \text{ NMR:} 25.96, 26.03, 29.1, 29.3, 29.5, 30.6, 31.5, 32.35, 32.44, 33.96, 34.03, 62.2, 64.35, 64.44, 66.9, 67.9, 68.1, 82.4, 98.9, 107.0, 107.1, 107.2, 113.9, 116.9, 126.2, 138.1, 143.4, 143.8, 144.1, 156.6, 159.0, 160.0, 160.2, 160.3; MS(L-SIMS): \( m/\ce{z} \) 1397.8 [(\( \text{M}^{+} \))+, 100]; calcd (%) for \( \text{C}_{82}\text{H}_{109}\text{O}_{11}\text{I} \): C, 70.47; H, 7.86; found: C, 70.99; H, 8.00.

\[ \text{11: A mixture of the alcohol 36 (1.50 g, 1.0 mmol), CBr}_{4} (0.60 g, 1.6 mmol) and PPh}_{3} (0.6 g, 2.2 mmol) in THF (15 ml) was stirred at 25 °C for 1.5 h. The reaction mixture was diluted with hexane/Et}_{2}O (1:1, 2 mL) and the precipitate formed was filtered off and washed with Et}_{2}O (3 mL). The filtrate was concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane gradient to hexane/EtOAc, 10:1) gave compound 11 (1.40 g, 89%) as a colorless oil; \( R_{f} \): 0.61 (hexane/EtOAc, 5:1); \(^{1}\text{H} \text{ NMR:} 1.20–1.50 (m, 12 H), 1.29 (s, 27 H), 1.70–1.80 (m, 4 H), 2.05 (quin, \( J = 6.9 \) Hz, 4 H), 2.10–2.17 (m, 2 H), 2.21 (quin, \( J = 6.0 \) Hz, 6 H), 2.62–2.76 (m, 6 H), 3.37 (t, \( J = 6.6 \) Hz, 2 H), 3.83–3.93 (m, 8 H), 4.09 (t, \( J = 6.3 \) Hz, 6 H), 4.11 (t, \( J = 6.3 \) Hz, 6 H), 6.30–6.40 (m, 9 H), 6.67 (d, \( J = 8.7 \) Hz, 2 H), 6.85 (d, \( J = 8.7 \) Hz, 6 H), 7.29 (d, \( J = 8.7 \) Hz, 6 H), 7.53 (d, \( J = 8.7 \) Hz, 2 H); \(^{13}\text{C} \text{ NMR:} 25.95, 26.02, 29.1, 29.3, 29.4, 30.6, 31.5, 32.4, 33.1, 33.9, 34.0, 34.2, 64.3, 64.4, 66.9, 67.9, 68.1, 82.4, 98.9, 99.1, 106.9, 107.2, 113.9, 116.9, 126.2, 138.1, 142.8, 143.3, 143.8, 156.5, 159.0, 160.0, 160.3; MS(FAB): \( m/\ce{z} \) 1461.4 [\( \text{M}^{+}^{\text{81Br}} \), 100]; calcd (%) for \( \text{C}_{82}\text{H}_{108}\text{O}_{10}\text{BrI} \): C, 67.43, H, 7.45; found: C, 67.45; H, 7.54. \]
37: Chloromethyl methyl ether (1.7 mL, 22 mmol) was added dropwise to a mixture of compound 32 (3.1 g, 11 mmol), dibenzo-24-crown-8 (1.0 g, 2.2 mmol) and cesium carbonate (7.1 g, 22 mmol) in DMF (40 mL) at 25 °C. After 2 h, the mixture was quenched with water and extracted with dichloromethane (80 mL × 2). The combined extracts were washed with brine (80 mL), dried (MgSO₄) and evaporated to dryness under reduced pressure followed by chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) to afford compound 37 (2.1 g, 58%) as a colorless oil; Rf: 0.59 (hexane/EtOAc, 3:1); ¹H NMR: 2.62 (t, J = 7.5 Hz, 2 H), 2.90 (t, J = 7.5 Hz, 2 H), 3.47 (s, 3 H), 3.68 (s, 3 H), 5.02 (s, 2 H), 5.12 (s, 2 H), 6.50 (d, J = 2.1 Hz, 2 H), 6.56 (t, J = 2.1 Hz, 1 H), 7.30–7.50 (m, 5 H); ¹³C NMR: 31.1, 35.4, 51.6, 56.0, 70.0, 94.5, 101.2, 108.4, 108.8, 127.5, 127.9, 128.5, 136.8, 142.9, 158.4, 159.9, 173.2; MS(EI): m/z 330 (M⁺, 17); calcd (%) for C₁₉H₂₂O₅: C, 69.07; H, 6.71; found: C, 68.93; H, 6.78.

38: A solution of the ester 37 (2.0 g, 6.1 mmol) in THF (5 mL) was added dropwise to a slurry of LiAlH₄ (0.4 g, 9.1 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at 25 °C for 1.5 h and then quenched with EtOAc and water. The mixture was extracted with EtOAc (30 mL × 2). The combined extracts were washed with brine (30 mL), dried (MgSO₄) and evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 2:1) afforded compound 38 (1.8 g, 97%) as a colorless oil; Rf: 0.16 (hexane/EtOAc, 3:1); ¹H NMR: 1.31 (brs, 1 H), 1.88 (quin, J = 6.3 Hz, 2 H), 2.65 (t, J = 7.2 Hz, 2 H), 3.50 (s, 3 H), 3.66 (t, J = 5.7 Hz, 2 H), 5.03 (s, 2 H), 5.17 (s, 2 H), 6.49–6.57 (m, 3 H), 7.30–7.50 (m, 5 H); ¹³C NMR: 32.3, 33.9, 56.0, 62.2, 70.0, 94.5, 100.8, 108.6, 108.9,
127.5, 127.9, 128.5, 136.9, 144.3, 158.4, 159.8; MS(EI): m/z 302 (M⁺, 5); calcd (%) for C₁₈H₂₂O₄: C, 71.50; H, 7.33; found: C, 71.22; H, 7.09.

39: A mixture of the alcohol 38 (1.7 g, 5.6 mmol), CBr₄ (2.8 g, 8.4 mmol) and PPh₃ (3.0 g, 11 mmol) in THF (40 mL) was stirred at 25 °C for 1.5 h. The reaction mixture was diluted with hexane/Et₂O (1:1, 20 mL) and the precipitate formed was filtered off and washed with Et₂O (10 mL). The filtrate was evaporated under reduced pressure and the residue was purified by chromatography (eluent: hexane/EtOAc, 100:1 gradient to 10:1) to produce compound 39 (1.7 g, 82%) as a colorless oil; Rf: 0.73 (hexane/EtOAc, 3:1); ¹H NMR: 2.14 (quin, J = 6.6 Hz, 2 H), 2.71 (t, J = 7.2 Hz, 2 H), 3.39 (t, J = 6.6 Hz, 2 H), 3.48 (s, 3 H), 5.03 (s, 2 H), 5.15 (s, 2 H), 6.51 (d, J = 2.4 Hz, 2 H), 6.56 (t, J = 2.1 Hz, 1 H), 7.30–7.50 (m, 5 H); ¹³C NMR: 33.0, 33.9, 34.2, 56.0, 70.0, 94.5, 101.1, 108.8, 109.1, 127.6, 128.0, 128.6, 136.8, 143.0, 158.5, 159.9; MS(L-SIMS): m/z 366 [M⁺ (⁸¹Br), 100]; calcd (%) for C₁₈H₂₁O₂Br: C, 59.19; H, 5.79; found: C, 59.25; H, 5.88.

13: A mixture of the bromide 39 (1.70 g, 4.6 mmol), hydroquinone (0.23 g, 2.1 mmol), dibenzo-24-crown-8 (0.3 g, 0.62 mmol) and Cs₂CO₃ (2.0 g, 6.2 mmol) in DMF (20 mL) was heated at 110 °C for 1 h. The reaction was then quenched with water and extracted with EtOAc (40 mL × 2). The combined extracts were washed with brine (40 mL), dried (MgSO₄) and evaporated to dryness under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) afforded compound 13 (0.84 g, 59%) as a colorless oil; Rf: 0.59 (hexane/EtOAc, 3:1); ¹H NMR: 2.05 (quin, J = 6.6 Hz, 4 H), 2.74 (t, J = 7.2 Hz, 4 H), 3.46 (s, 6 H), 3.89 (t, J = 6.0 Hz, 4 H), 4.98 (s, 4 H), 5.12 (s, 4 H), 6.45–6.55 (m, 6 H), 6.82 (s, 4 H), 7.30–7.50 (m, 10 H); ¹³C NMR: 30.6, 32.4, 56.0, 67.4, 69.9, 94.4, 101.0, 108.6, 109.0, 115.4, 127.5, 127.9, 128.5, 136.9, 144.0, 153.1, 158.3, 159.8; MS(L-SIMS): m/z 678 (M⁺, 100); calcd (%) for C₄₂H₄₆O₈: C, 74.31; H, 6.83; found: C, 74.34; H, 6.95.
4: A mixture of hydroquinone (0.45 g, 4.0 mmol), the bromide 10 (6.8 g, 8.7 mmol), Cs₂CO₃ (3.9 g, 12 mmol) and dibenzo-24-crown-8 (0.5 g, 1.2 mmol) in DMF (40 mL) was heated at 110 °C for 2 h. The mixture was then quenched with water and extracted with EtOAc (50 mL × 2). The combined extracts were washed with brine (50 mL), dried (MgSO₄) and evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 7:1) afforded compound 4 (4.8 g, 78%) as a white solid; Rf: 0.41 (hexane/EtOAc, 5:1); m.p. 89–93 °C; ¹H NMR: 1.20–1.50 (m, 24 H), 1.29 (s, 18 H), 1.70–1.80 (m, 8 H), 2.05 (quin, J = 7.5 Hz, 4 H), 2.21 (quin, J = 6.0 Hz, 4 H), 2.71 (t, J = 6.9 Hz, 4 H), 3.82–3.92 (m, 12 H), 4.09 (t, J = 6.0 Hz, 4 H), 4.11 (t, J = 6.0 Hz, 4 H), 6.35 (d, J = 2.1 Hz, 4 H), 6.39 (d, J = 8.7 Hz, 4 H), 6.69 (s, 4 H), 6.81 (d, J = 6.9 Hz, 4 H), 7.29 (d, J = 6.9 Hz, 4 H); ¹³C NMR: 25.97, 26.03, 29.1, 29.4, 29.5, 29.9, 30.7, 31.5, 32.5, 34.0, 64.36, 64.43, 67.5, 67.9, 68.1, 82.4, 98.9, 107.0, 107.2, 113.9, 115.4, 116.9, 126.2, 138.1, 143.4, 143.9, 153.2, 156.6, 159.0, 160.0, 160.3; MS(L-SIMS): m/z 1506.7 (M⁺, 100); calcd (%) for C₈₂H₁₀₈O₁₀I₂: C, 65.33; H, 7.22; Found: C, 65.15; H, 7.29.

5: A mixture of hydroquinone (60 mg, 0.50 mmol), the bromide 11 (1.60 g, 1.1 mmol), Cs₂CO₃ (0.5 g, 1.5 mmol) and dibenzo-24-crown-8 (0.07 g, 0.15 mmol) in DMF (10 mL) was heated at 110 °C for 2 h. The mixture was then quenched with water and extracted with EtOAc (30 mL × 2). The combined
extracts were washed with brine (30 mL), dried (MgSO₄) and evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 5:1) afforded compound 5 (0.60 g, 42%) as a colorless oil; Rf: 0.80 (hexane/EtOAc, 3:1); ¹H NMR: 1.20–1.50 (m, 24 H), 1.29 (s, 54 H), 1.70–1.80 (m, 8 H), 2.04 (quin, J = 6.9 Hz, 12 H), 2.20 (quin, J = 6.0 Hz, 12 H), 2.70 (t, J = 7.5 Hz, 12 H), 3.80–4.00 (m, 20 H), 4.09 (t, J = 6.0 Hz, 12 H), 4.11 (t, J = 6.0 Hz, 12 H), 6.30–6.40 (m, 18 H), 6.65 (d, J = 9.0 Hz, 4 H), 6.80 (s, 4 H), 6.84 (d, J = 8.7 Hz, 12 H), 7.28 (d, J = 8.7 Hz, 12 H), 7.53 (d, J = 8.7 Hz, 4 H); ¹³C NMR: 25.97, 26.04, 29.1, 29.4, 29.5, 30.7, 30.8, 31.5, 32.5, 34.0, 64.36, 64.45, 66.9, 67.3, 67.6, 67.9, 68.1, 82.4, 98.9, 107.0, 107.1, 107.2, 113.9, 115.4, 116.9, 126.2, 138.1, 143.4, 143.9, 153.2, 156.6, 159.0, 160.0, 160.2, 160.3; MS(MALDI-TOF): m/z 2890.7 [(M+Na)⁺, 100]; calcd (%) for C₁₇₀H₂₂₀O₂₂I₂: C, 71.16; H, 7.73; found: C, 71.31; H, 7.94.

14: A solution of hydrogen chloride in ethanol (2.0 M, 10 mL) was added dropwise to a solution of compound 13 (0.80 g, 1.2 mmol) in THF (5 mL) at 0 °C. After 1 h, the mixture was quenched with water and extracted with EtOAc (10 mL × 2). The combined extracts were washed with brine (10 mL), dried (MgSO₄) and evaporated to dryness under reduced pressure. Chromatographic purification of the
crude product (eluent: hexane/EtOAc, 2:1) afforded compound 14 (0.58 g, 83%) as a white solid; \( R_f \): 0.27 (hexane/EtOAc, 2:1); m.p. 92–94 °C; \(^1\)H NMR: 2.04 (quin, \( J = 6.6 \) Hz, 4 H), 2.71 (t, \( J = 7.2 \) Hz, 4 H), 3.88 (t, \( J = 6.0 \) Hz, 4 H), 4.84 (s, 2 H), 4.97 (s, 4 H), 6.25–6.35 (m, 4 H), 6.43 (s, 2 H), 6.81 (s, 4 H), 7.30–7.50 (m, 10 H); \(^{13}\)C NMR: 31.1, 32.8, 67.9, 70.5, 100.5, 108.3, 108.9, 116.0, 128.1, 128.5, 129.2, 137.5, 144.9, 153.7, 157.2, 160.7; MS(L-SIMS): \( m/z \) 590 (M\(^+\), 100); calcd (%) for C\(_{38}\)H\(_{38}\)O\(_6\): C, 77.27; H, 6.48; found: C, 77.04; H, 6.64.

15: A mixture of the bisphenol 14 (0.80 g, 1.4 mmol), the bromide 12 (3.70 g, 3.0 mmol), dibenzo-24-crown-8 (0.20 g, 0.41 mmol) and Cs\(_2\)CO\(_3\) (1.4 g, 4.1 mmol) in DMF (25 mL) was stirred at 60 °C for 3 h. The mixture was then quenched with water and extracted with EtOAc (50 mL × 2). The combined extracts were washed with brine (50 mL), dried (MgSO\(_4\)) and evaporated to dryness under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 6:1 gradient to 4:1) afforded compound 15 (3.30 g, 81%) as a colorless oil; \( R_f \): 0.40 (hexane/EtOAc, 3:1); \(^1\)H NMR: 1.30 (s, 72 H), 2.00–2.15 (m, 16 H), 2.22 (quin, \( J = 6.0 \) Hz, 16 H), 2.67–2.78 (m, 16 H), 3.85–3.93 (m, 16 H), 4.09 (t, \( J = 7.8 \) Hz, 16 H), 4.12 (t, \( J = 7.8 \) Hz, 16 H), 4.97 (s, 4 H), 6.30–6.50 (m, 24 H), 6.82 (s, 4 H), 6.86 (d, \( J = 6.9 \) Hz, 16 H), 7.27 (d, \( J = 6.9 \) Hz, 16 H), 7.30–7.50 (m, 10 H); \(^{13}\)C NMR: 29.3, 30.7, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.5, 69.9, 98.9, 99.3, 107.2, 107.6, 113.9, 115.4, 126.2, 127.5, 127.9, 128.5, 137.0, 143.3, 143.9, 153.2, 156.6, 160.0, 160.2; MS(MALDI-TOF) \( m/z \) 3038 [(M+Na\(^+\), 100); calcd (%) for C\(_{196}\)H\(_{242}\)O\(_{26}\): C, 78.11; H, 8.09; found: C, 77.98; H, 8.16.

16: A mixture of compound 15 (2.00 g, 0.66 mmol) and 10% palladium on charcoal (0.2 g) in EtOAc/EtOH (1:1, 20 mL) was stirred under hydrogen atmosphere (1 atm) at 25 °C for 6 h. The mixture was then filtered and the filtrate was evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1) afforded compound 16 (1.70 g, 90%) as a colorless oil; \( R_f \): 0.27 (hexane/EtOAc, 3:1); \(^1\)H NMR: 1.29 (s, 72 H), 1.95–2.10 (m, 16 H), 2.22 (quin, \( J = 6.0 \) Hz, 16 H), 2.60–2.80 (m, 16 H), 3.80–4.00 (m, 16 H), 4.08 (t, \( J = 5.7 \) Hz, 16 H), 4.11 (t, \( J = 5.7 \) Hz, 16 H), 5.06
(s, 2 H), 6.20–6.40 (m, 24 H), 6.79 (s, 4 H), 6.84 (d, \( J = 7.8 \) Hz, 16 H), 7.28 (d, \( J = 7.8 \) Hz, 16 H); 13C NMR: 29.3, 30.6, 31.5, 32.2, 32.4, 34.0, 64.4, 64.5, 66.7, 66.9, 67.4, 98.9, 99.5, 107.3, 107.4, 107.9, 113.9, 115.4, 126.2, 143.4, 143.7, 143.9, 144.2, 153.1, 156.5, 156.7, 160.0, 160.2; MS(MALDI-TOF) 
\( m/z \) 2830.5 (M+, 100); calcd (%) for C182H230O26: C, 77.14; H, 8.18; found: C, 77.25; H, 8.25.

6: A mixture of the bromide 11 (1.50 g, 1.0 mmol), the bisphenol 16 (1.30 g, 0.47 mmol), Cs2CO3 (1.0 g, 2.8 mmol) and dibenzo-24-crown-8 (70 mg, 0.14 mmol) in DMF (15 ml) was stirred at 60 °C for 3 h. The reaction was then quenched with water and extracted with EtOAc (30 mL \( \times 2 \)). The organic extracts were combined, washed with brine (30 mL), dried (MgSO4) and concentrated under reduced pressure. Column chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 2:1) afforded compound 6 (2.50 g, 97%) as a colorless oil; \( R_f \): 0.64 (hexane/EtOAc, 3:1); 1H NMR: 1.20–1.50 (m, 24 H), 1.28 (s, 126 H), 1.65–1.80 (m, 8 H), 1.95–2.05 (m, 28 H), 2.20 (quin, \( J = 6.0 \) Hz, 28 H), 2.69 (t, \( J = 6.9 \) Hz, 28 H), 3.80–3.95 (m, 36 H), 4.07 (t, \( J = 6.3 \) Hz, 28 H), 4.09 (t, \( J = 6.3 \) Hz, 28 H), 6.31 (brs, 14 H), 6.35 (brs, 28 H), 6.65 (d, \( J = 8.7 \) Hz, 4 H), 6.80 (s, 4 H), 6.83 (d, \( J = 7.8 \) Hz, 28 H), 7.27 (d, \( J = 7.8 \) Hz, 28 H), 7.52 (d, \( J = 8.7 \) Hz, 4 H); 13C NMR: 25.96, 26.03, 29.1, 29.3, 29.5, 29.7, 30.7, 30.9, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.7, 67.9, 68.1, 82.4, 98.9, 107.0, 107.2, 113.9, 115.4, 116.9, 126.2, 138.1, 143.3, 143.9, 153.2, 156.6, 159.0, 160.0, 160.3; MS(MALDI-TOF): \( m/z \) 5617.6 [(M+Na)\(^+\), 100]; calcd (%) for C346H444O46I2: C, 74.30; H, 8.00; found: C, 74.37; H, 8.19.

\[
\begin{align*}
4 & \xrightarrow{\text{TMSCCH, Pd(PPh}_3)_2\text{Cl}_2} 5 \\
& \xrightarrow{\text{CuI, NEt}_3, \text{PPh}_3} 6 \\
& \xrightarrow{\text{K}_2\text{CO}_3} 7 \\
& \xrightarrow{\text{MeOH}} 8 \\
& \xrightarrow{\text{K}_2\text{CO}_3} 9 \\
& \xrightarrow{\text{MeOH}} 1
\end{align*}
\]

7: A mixture of the diiodide 4 (160 mg, 0.11 mmol), TMSC≡CH (0.2 mL, 1.1 mmol), Pd(PPh3)2Cl2 (40 mg, 53 µmol), PPh3 (10 mg, 21 µmol), CuI (10 mg, 21 µmol) and NEt3 (0.2 mL, 1.1 mmol) in toluene (4.0 mL) was placed inside a sealed tube equipped with a stirrer bar. The reaction mixture was degassed
and stirred at 60 °C for 24 h. The mixture was filtered and then washed with Et₂O (10 mL). The combined filtrates were concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane gradient to hexane/EtOAc, 10:1) afforded compound 7 (120 mg, 78%) as a yellow oil; Rf: 0.34 (hexane/EtOAc, 8:1); ¹H NMR: 0.24 (s, 18 H), 1.20–1.50 (m, 24 H), 1.30 (s, 18 H), 1.70–1.82 (m, 8 H), 2.05 (quin, J = 6.6 Hz, 4 H), 2.21 (quin, J = 5.7 Hz, 4 H), 2.71 (t, J = 7.5 Hz, 4 H), 3.80–4.00 (m, 12 H), 4.09 (t, J = 6.3 Hz, 4 H), 4.11 (t, J = 6.3 Hz, 4 H), 6.29–6.37 (m, 6 H), 6.70–6.90 (m, 12 H), 7.29 (d, J = 8.4 Hz, 4 H), 7.39 (d, J = 8.4 Hz, 4 H); ¹³C NMR: 0.1, 25.99, 26.04, 29.2, 29.3, 29.4, 29.5, 30.7, 31.5, 32.5, 34.0, 64.38, 64.43, 67.6, 67.9, 68.0, 92.3, 98.8, 105.3, 107.0, 107.3, 113.9, 114.3, 115.0, 115.4, 126.2, 133.4, 143.4, 143.9, 153.1, 156.6, 159.3, 160.0, 160.3; MS(MALDI-TOF): m/z 1470 [(M+Na)⁺, 100]; calcd (%) for C₉₂H₁₂₆O₁₀Si₂: C, 76.30; H, 8.77; found: C, 76.35; H, 8.55.

8: A mixture of the diiodide 5 (0.50 g, 0.17 mmol), TMSC≡CH (0.3 mL, 1.7 mmol), Pd(PPh₃)₂Cl₂ (70 mg, 87 µmol), PPh₃ (10 mg, 35 µmol), CuI (10 mg, 35 µmol) and NEt₃ (0.3 mL, 1.7 mmol) in toluene (15 mL) was placed inside a sealed tube equipped with a stirrer bar. The reaction mixture was degassed, and stirred at 60 °C for 24 h. The mixture was filtered and then washed with Et₂O (10 mL). The combined filtrates were concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane gradient to hexane/EtOAc, 5:1) afforded compound 8 (0.43 g, 88%) as a yellow oil; Rf: 0.50 (hexane/EtOAc, 5:1); ¹H NMR: 0.23 (s, 18 H), 1.20–1.50 (m, 24 H), 1.28 (s, 54 H), 1.70–1.80 (m, 8 H), 2.04 (quin, J = 6.9 Hz, 12 H), 2.20 (quin, J = 6.0 Hz, 12 H), 2.69 (t, J = 7.2 Hz, 12 H), 3.80–4.00 (m, 20 H), 4.08 (t, J = 6.3 Hz, 12 H), 4.10 (t, J = 6.3 Hz, 12 H), 6.29–6.38 (m, 18 H), 6.78–6.85 (m, 20 H), 7.28 (d, J = 8.4 Hz, 12 H), 7.38 (d, J = 8.4 Hz, 4 H); ¹³C NMR: 0.1, 26.0, 26.1, 29.2, 29.4, 29.5, 30.7, 30.8, 31.5, 32.5, 34.0, 64.37, 64.45, 66.9, 67.6, 67.9, 68.0, 98.9, 107.1, 107.2, 113.9, 114.3, 115.4, 126.2, 133.4, 143.4, 143.9, 153.2, 156.6, 160.0, 160.2, 160.3; MS(MALDI-TOF): m/z 2833.6 [(M+Na)⁺, 100]; calcd (%) for C₁₈₀H₂₃₈O₂₂Si₂: C, 76.94; H, 8.54; found: C, 76.87; H, 8.39.
A mixture of the diiodo compound 6 (0.90 g, 0.16 mmol), TMSC≡CH (0.3 mL, 1.6 mmol), Pd(PPh3)2Cl2 (0.10 g, 0.16 mmol), PPh3 (10 mg, 32 µmol), copper(I) iodide (10 mg, 32 µmol) and NEt3 (0.3 mL, 1.6 mmol) in toluene (10 mL) was placed inside a sealed tube equipped with a stirrer bar. The reaction mixture was degassed and stirred at 60 °C for 24 h. The mixture was filtered and then washed with Et₂O (10 mL). The combined filtrates were concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 5:1) gave compound 9 (0.63 g, 71%) as a yellow oil; \(R_f\): 0.34 (hexane/EtOAc, 5:1); \(^1\)H NMR: 0.22 (s, 18 H), 1.20–1.50 (m, 24 H), 1.28 (s, 126 H), 1.70–1.80 (m, 8 H), 2.00–2.10 (br, 28 H), 2.21 (quin, \(J = 6.0\) Hz, 28 H), 2.69 (t, \(J = 6.9\) Hz, 28 H), 3.80–4.00 (m, 36 H), 4.07 (t, \(J = 6.6\) Hz, 28 H), 4.10 (t, \(J = 6.6\) Hz, 28 H), 6.31, (t, \(J = 2.1\) Hz, 14 H), 6.36 (d, \(J = 2.1\) Hz, 28 H), 6.70–6.90 (m, 36 H), 7.28 (d, \(J = 8.4\) Hz, 28 H), 7.38 (d, \(J = 8.7\) Hz, 4 H); \(^{13}\)C NMR:\[^{[4]}\] 0.1, 26.0, 29.2, 29.3, 29.5, 30.7, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.0, 67.7, 67.9, 68.0, 98.9, 105.3, 107.1, 107.2, 113.9, 114.3, 115.4, 126.2, 133.4, 143.3, 143.9, 153.2, 156.6, 159.3, 160.0, 160.2; MS(MALDI-TOF): \(m/z\) 5558.0 [(M+Na)+, 100]; calcld (%) for C\(_{356}\)H\(_{462}\)O\(_4\)Si\(_2\): C, 77.27; H, 8.41; found: C, 77.24; H, 7.99.

General synthetic procedure for bis(ethynyl) Gn-dendrimers (n = 1–3) 1–3: Anhydrous K\(_2\)CO\(_3\) (5.0 equiv) was added to a solution of bis(trimethylsilylethynyl) surface functionalized Gn-dendrimers 7–9 (1.0 equiv) in methanol/THF (1:1) (2 mL/mmol). The mixture was stirred at 25 °C for 1.5 h and then quenched with water and extracted with ethyl acetate (25 mL x 2). The combined organic layers were washed with brine, dried (MgSO\(_4\)) and concentrated under reduced pressure. The residue was purified by silica column chromatography eluting with hexane/EtOAc = 8/1.

1: Starting from compound 7 (100 mg, 69 µmol) and after chromatographic purification, compound 1 was obtained (90 mg, 98%) as a white solid; \(R_f\): 0.50 (hexane/EtOAc, 5:1); m.p. 86–89 °C; \(^1\)H NMR: 1.20–1.50 (m, 24 H), 1.29 (s, 18 H), 1.70–1.80 (m, 8 H), 2.04 (quin, \(J = 6.6\) Hz, 4 H), 2.21 (quin, \(J = 6.3\) Hz, 4 H), 2.71 (t, \(J = 7.2\) Hz, 4 H), 2.98 (s, 2 H), 3.80–4.00 (m, 12 H), 4.09 (t, \(J = 6.3\) Hz, 4 H), 4.11 (t, \(J = 6.3\) Hz, 4 H), 6.31 (t, \(J = 2.1\) Hz, 14 H), 6.36 (d, \(J = 2.1\) Hz, 28 H), 6.70–6.90 (m, 36 H), 7.28 (d, \(J = 8.4\) Hz, 28 H), 7.38 (d, \(J = 8.7\) Hz, 4 H); \(^{13}\)C NMR:\[^{[4]}\] 0.1, 26.0, 29.2, 29.3, 29.5, 30.7, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.0, 67.7, 67.9, 68.0, 98.9, 105.3, 107.1, 107.2, 113.9, 114.3, 115.4, 126.2, 133.4, 143.3, 143.9, 153.2, 156.6, 159.3, 160.0, 160.2; MS(MALDI-TOF): \(m/z\) 5558.0 [(M+Na)+, 100]; calcld (%) for C\(_{356}\)H\(_{462}\)O\(_4\)Si\(_2\): C, 77.27; H, 8.41; found: C, 77.24; H, 7.99.
= 6.3 Hz, 4 H), 6.30 (s, 2 H), 6.35 (s, 4 H), 6.80–6.90 (m, 12 H), 7.29 (d, $J = 8.7$ Hz, 4 H), 7.41 (d, $J = 8.7$ Hz, 4 H); $^{13}$C NMR: 25.96, 26.01, 29.1, 29.26, 29.33, 29.5, 30.7, 31.5, 32.4, 34.0, 64.4, 67.5, 67.9, 68.0, 75.6, 77.2, 83.7, 98.8, 106.9, 107.2, 113.9, 114.4, 115.4, 126.2, 133.5, 143.3, 143.8, 153.1, 156.6, 159.5, 160.0, 160.3; MS(MALDI-TOF): $m/z$ 1326.1 [(M+Na)$^+$, 100]; calcd (%) for C$_{86}$H$_{110}$O$_{10}$: C, 79.22; H, 8.50; found: C, 79.05; H, 8.52.

2: Starting from compound 8 (60 mg, 21 µmol) and after chromatographic purification, compound 2 (50 mg, 88%) was obtained as a colorless oil; $R_f$: 0.41 (hexane/EtOAc, 5:1); $^1$H NMR: 1.20–1.50 (m, 24 H), 1.28 (s, 54 H), 1.70–1.80 (m, 8 H), 2.04 (quin, $J = 6.9$ Hz, 12 H), 2.20 (quin, $J = 6.0$ Hz, 12 H), 2.69 (t, $J = 7.5$ Hz, 12 H), 2.98 (s, 2 H), 3.80–4.00 (m, 20 H), 4.09 (t, $J = 6.0$ Hz, 12 H), 4.11 (t, $J = 6.0$ Hz, 12 H), 6.30–6.40 (m, 18 H), 6.80–6.90 (m, 20 H), 7.28 (d, $J = 8.7$ Hz, 12 H), 7.41 (d, $J = 8.7$, 4 H); $^{13}$C NMR: 26.0, 29.1, 29.4, 29.5, 30.7, 31.5, 32.5, 34.0, 64.36, 64.44, 66.9, 67.6, 67.9, 68.0, 75.6, 77.2, 83.9, 98.9, 107.1, 107.2, 113.9, 114.4, 126.2, 133.5, 143.3, 143.9, 153.2, 156.6, 159.5, 160.0, 160.2; MS(MALDI-TOF): $m/z$ 2689.5 [(M+Na)$^+$, 100]; calcd (%) for C$_{174}$H$_{222}$O$_{22}$: C, 78.40; H, 8.39; found: C, 78.21; H, 8.25.

3: Starting from compound 9 (0.25 g, 45 µmol) and after chromatographic purification, compound 3 (0.16 g, 66%) was obtained as a colorless oil; $R_f$: 0.27 (hexane/EtOAc, 5:1); $^1$H NMR: 1.20–1.50 (m, 24 H), 1.28 (s, 126 H), 1.70–1.80 (m, 8 H), 2.00–2.10 (m, 28 H), 2.20 (quin, $J = 6.0$ Hz, 28 H), 2.69 (t, $J = 6.6$ Hz, 28 H), 2.98 (s, 2 H), 3.80–4.00 (m, 36 H), 4.08 (t, $J = 6.6$ Hz, 28 H), 4.10 (t, $J = 6.6$ Hz, 28 H), 6.31 (brs, 14 H), 6.36 (brs, 28 H), 6.75–6.90 (m, 36 H), 7.25–7.30 (m, 28 H), 7.42 (d, $J = 8.7$ Hz, 4 H); $^{13}$C NMR: 26.0, 29.2, 29.3, 30.7, 30.9, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.7, 67.9, 68.0, 68.1, 75.7, 77.2, 82.9, 98.9, 107.1, 107.2, 113.9, 114.4, 114.6, 115.4, 126.2, 128.4, 128.6, 133.5, 134.0, 143.3, 143.9, 153.2, 156.6, 159.8, 160.0, 160.2; MS(MALDI-TOF): $m/z$ 5415.3 [(M+Na)$^+$, 100]; calcd (%) for C$_{350}$H$_{446}$O$_{46}$: C, 77.92; H, 8.38; found: C, 77.72; H, 8.33.
General synthetic procedure for Gn-dendritic necklaces (n = 1–3) 17–19. A catalytic amount of CuI (5 mg) was added to a mixture of the bis(ethynyl) surface-functionalized Gn-dendrimer 1–3 (1.0 equiv) and trans-[(Et3P)2PtCl2] (1.0 equiv) in CH2Cl2/diisopropylamine (1:1) (20 mL/mmol) at 25 °C. The mixture was stirred for 12 h and the solvent was evaporated under reduced pressure. The residue was redissolved in dichloromethane and filtered through a short pad of alumina. The filtrate collected was concentrated to about 1 mL under reduced pressure and then precipitated successively to acetone and to methanol (200 mL each). The dendritic polymer was collected by filtration.

G1-dendritic necklace 17: Starting from compound 1 (500 mg, 77 µmol) and trans-[(Et3P)2PtCl2] (190 mg, 38 µmol), the dendritic polymer 17 (600 mg, 88%) was obtained as a yellow solid; Td: 500 °C; 1H NMR: 1.10–1.20 (m, 18 H), 1.20–1.50 (m, 24 H), 1.29 (s, 18 H), 1.65–1.80 (m, 8 H), 1.98–2.20 (m, 20 H), 2.60–2.80 (m, 4 H), 3.80–4.00 (m, 12 H), 4.09 (t, J = 6.6 Hz, 4 H), 4.11 (t, J = 6.6 Hz, 4 H), 6.30 (s, 2 H), 6.35 (s, 4 H), 6.74 (d, J = 8.7 Hz, 4 H), 6.81 (s, 4 H), 6.84 (d, J = 8.7 Hz, 4 H), 7.19 (d, J = 8.7 Hz, 4 H), 7.29 (d, J = 8.7 Hz, 4 H); 13C NMR: 8.4 (PCH2C), 16.3 (pseudo quin, J = 17 Hz; PCH2), 26.0, 29.1, 29.4, 29.5, 30.7, 31.5, 32.5, 34.0, 64.4, 67.6, 67.9, 98.8, 107.0, 107.2, 108.7 (s, C≡CPt), 113.9, 114.1, 114.5, 115.4, 126.2, 131.9, 143.3, 143.9, 153.2, 156.6, 156.8, 160.0, 160.3; 31P{1H} NMR: 17.58 [1J(Pt,P) = 2375 Hz]; UV (CH2Cl2, 25 °C): λmax (logε) = 268 (4.05), 344 nm (3.93).

G2-dendritic necklace 18: Starting from compound 2 (380 mg, 0.14 mmol) and trans-[(Et3P)2PtCl2] (72 mg, 0.14 mmol), the dendritic polymer 18 (350 mg, 78%) was obtained as a yellow solid; Td: 500 °C; 1H NMR: 1.10–1.30 (m, 18 H), 1.20–1.50 (m, 24 H), 1.28 (s, 54 H), 1.65–1.80 (m, 8 H), 1.95–2.30 (m, 36 H), 2.60–2.80 (m, 12 H), 3.80–4.00 (m, 20 H), 4.08 (t, J = 6.6 Hz, 12 H), 4.10 (t, J = 6.6 Hz, 12 H), 6.30 (s, 6 H), 6.35 (s, 12 H), 6.75 (d, J = 8.7 Hz, 4 H), 6.80 (s, 4 H), 6.84 (d, J = 8.7 Hz, 12 H), 7.17 (d, J = 8.7 Hz, 4 H), 7.28 (d, J = 8.7 Hz, 12 H); 13C NMR: 8.4 (PCH2C), 16.3 (pseudo quin, J = 17 Hz; PCH2), 26.1, 29.4, 30.7, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 68.0, 98.9, 107.2, 113.9, 114.1, 115.4, 126.2,
131.9, 143.3, 143.9, 156.6, 160.0, 160.2; $^{31}$P{^1}H NMR: 17.51 [$^1J$(Pt,P) = 2381 Hz]; UV (CH$_2$Cl$_2$, 25 °C): $\lambda_{\text{max}}$ (log ε) = 272 (3.94), 343 nm (3.83).

G3-dendritic necklace 19: Starting from compound 3 (400 mg, 0.074 mmol) and trans-[(Et$_3$P)$_2$PtCl$_2$] (37 mg, 0.074 mmol), the dendritic polymer 19 (250 mg, 58%) was obtained as a yellowish green solid; T$_d$: 500 °C; $^1$H NMR: 1.10–1.30 (m, 18 H), 1.20–1.50 (m, 24 H), 1.27 (s, 126 H), 1.65–1.80 (m, 8 H), 1.95–2.30 (m, 68 H), 2.60–2.80 (m, 28 H), 3.80–4.00 (m, 36 H), 4.07 (t, $J$ = 6.6 Hz, 28 H), 4.09 (t, $J$ = 6.6 Hz, 28 H), 6.30 (s, 14 H), 6.35 (s, 28 H), 6.71 (d, $J$ = 8.7 Hz, 4 H), 6.80 (s, 4 H), 6.83 (d, $J$ = 8.7 Hz, 28 H), 7.20 (d, $J$ = 8.7 Hz, 4 H), 7.27 (d, $J$ = 8.7 Hz, 28 H); $^{13}$C NMR[5]: 8.4 (PCH$_2$C), 16.3 (pseudo quin, $J$ = 17 Hz; PCH$_2$), 26.1, 29.3, 30.7, 30.9, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.7, 67.9, 98.9, 107.1, 107.2, 113.9, 114.1, 115.4, 126.2, 131.9, 143.3, 143.9, 153.2, 156.6, 160.0, 160.2; $^{31}$P{^1}H NMR: 16.28 [$^1J$(Pt,P) = 2393 Hz]; UV (CH$_2$Cl$_2$, 25 °C): $\lambda_{\text{max}}$ (log ε) = 276 (3.93), 343 nm (3.56).

References:

[3] The intensities of the $^{13}$C signals (δ ~ 92 and 105) of the two acetylenic carbons were too weak to be observed.
[4] One of the $^{13}$C signals of the acetylenic carbons (δ ~ 92) was too weak to be observed.
[5] One of the $^{13}$C signals of the acetylenic carbons of the G1- 17 dendritic necklace and both the $^{13}$C signals of the two acetylenic carbons of the G2- 18 and G3- 19 dendritic necklaces are too weak to be observed.
H =...= G2 =...= H

Current Data Parameters
NAME  A-62
EXPNO  1
PROCNO  1

F2 - Acquisition Parameters
Date  20010115
Time  14:07
INSTRUM  dpx300
PROBHD  5 mm Dual 13
PULPROG  zg
TO  32768
SOLVENT  Acetone
NS  4
DS  0
SNH  8992.805 Hz
FORES  0.274439 Hz
AQ  1.8219508 sec
RG  405.4
DW  55.600 usec
DE  5.000 usec
TE  300.0 K
D1  1.00000000 sec

************* CHANNEL 1 *************
NUC1  1H
F1  4.500 usec
PL1  -2.000 dB
SF01  300.1312000 MHz

F2 - Processing parameters
SI  32768
SF  300.1300049 MHz
WM  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00

1D NMR plot parameters
CX  23.00 cm
F1P  10000 ppm
F1  3001.30 Hz
F2P  -0.500 ppm
F2  150.07 Hz
PPMCW  8.45052 ppm/cm
HzCM  137.01587 Hz/cm
G1-dendritic necklace 17
G2-dendritic necklace 18
G3-dendritic necklace 19

Current Data Parameters
NAME      pPtAg3
EXPNOD    1
PROCNO    1

F2 - Acquisition Parameters
Date      20020221
Time      12:46
INSTRUM   30x300
PROBHD    5 mm Dual 13
PULPROG   zg
TD        32768
SOLVENT   CDCl3
MS        0
DS        0
SWMT      8992.806 Hz
FIDRES    0.274439 Hz
AQ        1.8219508 sec
AG        724.1
DW        55.600 usec
DE        6.00 usec
TE        300.0 K
DI        1.000000000 sec

---------- CHANNEL 11 ---------
NUC1       1H
P1         4.50 usec
PL1        -2.00 dB
SFd1       300.131000 MHz

F2 - Processing parameters
SI        32768
SF        300.1296207 MHz
MDW       Em
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

1D NMR plot parameters
CX        23.00 cm
F1P       10.000 ppm
F1        300.130 Hz
F2P       -0.500 ppm
F2        -150.06 Hz
PPMCM     0.45552 ppm/cm
HZCM      137.01569 Hz/cm