Electronic Supplementary Information

Dendronized Graphenes: Remarkable Dendrimer Size Effect on Solvent Dispersity and Bulk Electrical Conductivity

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Reagents and Conditions: a) 1-bromododecane, K_2CO_3 , DMF, 80 °C; b) LiAlH₄, THF, 0 °C; c) 4-nitrophenol, diethyl azodicarboxylate (DEAD), PPh₃, THF; d) methyl 3,5-dihydroxy benzoate, DEAD, PPh₃, THF; e) *tert*-butylchlorodiphenylsilane, imidazole, DMF; f) CBr₄, PPh₃, Et₂O; g) **9**, 18-crown-6, KF, THF, reflux.

Compound 1. To a DMF solution (50 mL) of 3,5-dihydroxy benzoate (3.02 g, 17.94 mmol) was added K_2CO_3 (6.21 g, 44.92 mmol), and the mixture was stirred at 25 °C for 30 min. After the addition of 1-bromododecane (11 mL, 44.14 mmol), the reaction mixture was stirred at 70 °C overnight, poured into water (50 mL), and extracted with ether. The combined organic extract

was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, hexane), to allow isolation of **1** (9.01 g, 17.84 mmol) as white powder in 99% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.15 (d, *J* = 3 Hz, 2H), 6.63 (t, *J* = 3 Hz, 1H), 3.96 (t, *J* = 6 Hz, 4H), 3.90 (s, 3H), 1.73–1.80 (m, 4H), 1.27–1.45 (br., 36H), 0.88 (t, *J* = 6 Hz, 6H).

Compound 2. To a THF solution (60 mL) of **1** (9.01 g, 17.84 mmol) was added LiAlH₄ (1.02 g, 26.76 mmol) at 0 °C under Ar, and the mixture was stirred at 0 °C for 4 h. Afterwards, the reaction was quenched by careful addition of a saturated NH₄Cl solution (20 mL) and the resulted mixture was extracted with ethyl acetate. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 1/1), to allow isolation of **2** (6.8 g, 14.27 mmol) as white powder in 80% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.50 (d, *J* = 3 Hz, 2H), 6.38 (t, *J* = 3 Hz, 1H), 4.62 (d, *J* = 6 Hz, 2H), 3.93 (t, *J* = 6 Hz, 4H), 1.72–1.79 (m, 4H), 1.26–1.44 (m, 36H), 0.88 (t, *J* = 6 Hz, 6H).

Compound D₀PhNO₂. To a THF solution (50 mL) of **2** (4.34 g, 9.11 mmol), 4-nitrophenol (1.90 g, 13.67 mmol), PPh₃ (3.58 g, 13.67 mmol) was dropwise added diethyl azodicarboxylate (DEAD, 2.8 mL, 18.3 mmol) at 0 °C. After stirring at 25 °C for 20 h, the reaction mixture was evaporated off volatile fractions under reduced pressure, and the residue was added with H₂O (50 mL) and extracted with ether three times. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 2/1) to allow isolation of **D₀PhNO₂** (4.46 g, 7.47 mmol) as white solid in 82% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.18 (d, *J* = 9 Hz, 2H), 7.00 (d, *J* = 9 Hz, 2H), 6.52 (d, *J* = 3 Hz, 2H), 6.42 (t, *J* = 3 Hz, 1H), 5.08 (s, 2H), 3.93 (t, *J* = 6 Hz, 4H), 1.72–1.79 (m, 4H), 1.26–1.44 (m, 36H), 0.88 (t, *J* = 6 Hz, 6H). Calcd. for C₃₇H₅₉NO₅: C 74.33, H 9.95, N 2.34; Found: C 74.09, H 9.83, N 2.28.

Compound 3. To a THF solution (100 mL) of **2** (12 g, 25.17 mmol), 3,5-dihydroxy benzoate (1.92 g, 11.44 mmol), and PPh₃ (6.6 g, 25.17mmol) was dropwise added diethyl azodicarboxylate (6 mL, 37.73 mmol) at 0 °C. After stirring at 25 °C for 20 h, the reaction mixture was evaporated off volatile fractions under reduced pressure, and the residue was added with H₂O (50 mL) and extracted with CH₂Cl₂ three times. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 2/1) to allow isolation of **3** (10.96 g, 10 mmol) as white pwoder in 88% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.28 (d, *J* = 3 Hz, 2H), 6.79 (t, *J* = 3 Hz, 1H), 6.56 (d, *J* = 3 Hz, 4H), 6.41 (t, *J* = 3 Hz, 2H), 4.98 (s, 4H), 3.94 (t, *J* = 6 Hz, 8H), 1.72–1.81 (m, 8H), 1.26–1.44 (m, 72H), 0.88 (t, *J* = 6 Hz, 12H).

Compound 4. To a THF solution (30 mL) of **3** (5.48 g, 5 mmol) was added LiAlH₄ (0.28 g, 7.5 mmol) at 0 $^{\circ}$ C under Ar, and the reaction mixture was stirred for 3 h. Afterwards, the reaction

was quenched by careful addition of a saturated NH₄Cl solution (10 mL) and the resulted mixture was extracted with ethyl acetate. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 1/2), to allow isolation of **4** (3.96 g, 3.75 mmol) as white pwder in 75% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.61 (d, *J* = 3 Hz, 2H), 6.54 (m, 5H), 6.40 (t, *J* = 3 Hz, 2H), 4.95 (s, 4H), 4.63 (d, *J* = 6 Hz, 2H), 3.93 (t, 8H), 1.74–1.83 (m, 8H), 1.26–1.44 (m, 72H), 0.88 (t, *J* = 6 Hz, 12H).

Compound D₁PhNO₂. To a THF solution (30 mL) of **4** (2.83 g, 2.67 mmol), 4-nitrophenol (0.56 g, 4 mmol), PPh₃ (1.05 g, 4 mmol) was dropwise added diethyl azodicarboxylate (0.8 mL, 2.16 mmol) at 0 °C. After stirring at 25 °C for 15 h, the reaction mixture was evaporated off volatile fractions under reduced pressure, and the residue was added with H₂O (20 mL) and extracted with CH₂Cl₂ three times. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 2/1) to allow isolation of **D₁PhNO₂** (2.55 g, 7.47 mmol) as colorless sticky oil in 81% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.16 (d, *J* = 12 Hz, 2H), 7.00 (d, *J* = 12 Hz, 2H), 6.62 (d, *J* = 3 Hz, 2H), 6.58 (t, *J* = 3 Hz, 1H), 6.53 (d, *J* = 3 Hz, 4H), 6.40 (t, *J* = 3 Hz, 2H), 5.09 (s, 2H), 4.95 (s, 4H), 3.93 (t, *J* = 9 Hz, 8H), 1.71–1.78 (m, 8H), 1.26–1.44 (m, 72H), 0.88 (t, *J* = 6 Hz, 12H). Calcd. for C₇₅H₁₁₉NO₉: C 76.42, H 10.18, N 1.19; Found: C 77.05, H 10.23, N 1.11. MALDI-TOF Mass: calcd. for C₇₅H₁₁₉NO₉ 1178.7, found 1201.3 for [M + Na]⁺.

Compound 5. To a DMF solution (100 mL) of 3,5-dihydroxy benzoate (8.41 g, 50 mmol) and imidazole (8.57 g, 125.8 mmol) was added *tert*-butylchlorodiphenylsilane (35 mL, 136 mmol) over 30 min. The reaction mixture was stirred at 25 °C overnight, poured into brine (100 mL), and extracted with ether. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 2/1), to allow isolation of **5** (30.35 g, 47 mmol) as white powder in 94% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.49 (d, *J* = 9 Hz, 8H), 7.36 (t, *J* = 9 Hz, 4H), 7.23–7.27 (m, 8H), 7.04 (d, *J* = 3 Hz, 2H), 6.27 (t, *J* = 3 Hz, 1H), 3.76 (s, 3H), 0.98 (s, 18H).

Compound 6. To a THF solution (200 mL) of **5** (30.35 g, 47 mmol) was added LiAlH₄ (2.67 g, 70.5 mmol) at 0 °C under Ar, and the mixture was stirred at 0 °C for 4 h. Afterwards, the reaction was quenched by careful addition of a saturated NH₄Cl solution (50 mL) and the resulted mixture was extracted with CH₂Cl₂. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 1/1), to allow isolation of **6** (23.19 g, 37.6 mmol) as white powder in 80% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.53(d, J = 6 Hz, 8H), 7.36 (t, J = 6 Hz, 4H), 7.24–7.29 (m, 8H), 6.31 (d, J = 3 Hz, 2H), 6.1 (t, J = 3 Hz, 1H), 4.31 (d, J = 6 Hz, 2H), 0.98 (s, 18H).

Compound 7. To a THF solution (20 mL) of **6** (6.79 g, 11 mmol), 3,5-dihydroxy benzoate (0.84 g, 5 mmol), and PPh₃ (2.89 g, 11 mmol) was added dropwise diethyl azodicarboxylate (2.6 mL, 16.5 mmol) at 0 °C. After stirring at 25 °C for 17 h, the reaction mixture was evaporated off volatile fractions under reduced pressure, and the residue was added with H₂O (30 mL) and extracted with CH₂Cl₂ three times. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 2/1) to allow isolation of **7** (5.78 g, 4.25 mmol) as white powder in 85% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.52 (d, *J* = 9 Hz, 16H), 7.35 (t, *J* = 9 Hz, 8H), 7.22–7.27 (m, 16H), 7.06 (d, *J* = 3 Hz, 2H), 6.39 (d, *J* = 3 Hz, 5H), 6.14 (d, *J* = 3 Hz, 2H), 4.67 (s, 4H), 3.89 (s, 3H), 0.98 (s, 36H).

Compound 8. To a THF solution (50 mL) of **7** (4.41 g, 3.23 mmol) was added LiAlH₄ (0.19 g, 5.12 mmol) at 0 °C under Ar, and the mixture was stirred at 0 °C for 2 h. Afterwards, the reaction was quenched by careful addition of a saturated NH₄Cl solution (10 mL) and the resulted mixture was extracted with ethyl acetate. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 1/2), to allow isolation of **8** (3.09 g, 2.33 mmol) as white powder in 72% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.52 (d, *J* = 9 Hz, 16H), 7.35 (t, *J* = 9 Hz, 8H), 7.22–7.27 (m, 16H), 6.40 (d, *J* = 3 Hz, 4H), 6.38 (d, *J* = 3 Hz, 2H), 6.16 (t, *J* = 3 Hz, 1H), 6.13 (t, *J* = 3 Hz, 2H)4.65 (s, 4H), 4.53 (d, *J* = 6 Hz, 2H), 0.98 (s, 36H).

Compound 9. To a solution of **8** (1.34 g, 1 mmol), 4-nitrophenol (0.22 g, 1.5 mmol), PPh₃ (0.39 g, 1.5 mmol) in THF (10 mL) was dropwise added diethyl azodicarboxylate (0.32 mL, 2.03 mmol) at 0 °C. After stirring at 25 °C for 14 h, the reaction mixture was evaporated off volatile fractions under reduced pressure, and the residue was added with H₂O (20 mL) and extracted with CH₂Cl₂ three times. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off insoluble fractions. The filtrate was evaporated to dryness and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 1/1) to allow isolation of **9** (1.18 g, 0.81 mmol) as slightly yellow solid in 81% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.17 (d, *J* = 9 Hz, 2H), 7.52 (d, *J* = 6 Hz, 16H), 7.35 (t, *J* = 6 Hz, 8H), 7.22–7.27 (m, 16H), 6.96 (d, *J* = 9 Hz, 2H), 6.42 (d, *J* = 3 Hz, 2H), 6.39 (d, *J* = 3 Hz, 4H), 6.22 (br., 1H), 6.14 (br., 2H), 4.99 (s, 2H), 4.64 (s, 4H), 0.98 (s, 36H). Calcd. for C₉₁H₉₅NO₉Si₄: C 74.91, H 6.56, N 0.96; Found: C 74.85, H 6.70, N 1.06. MALDI-TOF Mass: calcd. for C₉₁H₉₅NO₉Si₄ 1459.0, found 1498.3 for [M + K]⁺.

Compound 10. To an Et₂O solution (30 mL) of **2** (4.76 g, 10 mmol) were portion-wise added Ph₃P (5.25 g, 20 mmol) and CBr₄ (6.63 g, 20 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at 25 °C for 2 h. Afterwards, the reaction was quenched by addition of brine (20 mL) and resulted mixture was extracted with ether. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtrated off insoluble fractions. The filtrate was evaporated to dryness under reduced pressure and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 2/1), to allow isolation of **10** (4.64 g, 8.6mmol) as white powder in 86% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.51 (d, *J* = 3 Hz, 2H), 6.38 (t,

J = 3 Hz, 1H), 4.41 (s, 2H), 3.92 (d, *J* = 6 Hz, 4H), 1.71–1.81 (m, 4H), 1.26–1.44 (m, 36H), 0.88 (t, *J* = 6 Hz, 6H).

Compound D₂PhNO₂. A mixture of **10** (2.73 g, 5.05 mmol), **9** (1.46 g, 1.0 mmol), potassium fluoride (0.58 g, 10.0 mmol) and 18-crown-6 (0.55 g, 2.1 mmol) in THF (20 mL) was refluxed and stirred vigorously under Ar for 48 h. After evaporation off volatile fractions under reduced pressure, water was added and the resulted mixture was extracted with CH₂Cl₂. The combined organic extract was dried over anhydrous MgSO₄ and filtrated off insoluble fractions. The filtrate was evaporated to dryness under reduced pressure and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 1/1), to allow isolation of **D₂PhNO₂** (1.76 g, 0.75 mmol) as slightly yellow oil in 75% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.14 (d, *J* = 9 Hz, 2H), 6.96 (d, *J* = 9 Hz, 2H), 6.65 (d, *J* = 3 Hz, 4H), 6.61 (d, *J* = 3 Hz, 2H), 6.58 (br., 1H), 6.54(br., 10H), 6.40 (t, *J* = 3 Hz, 4H), 5.08 (s, 2H), 4.97 (s, 4H), 4.94 (s, 8H),3.92 (t, *J* = 6 Hz, 16H), 1.71–1.74 (m, 16H), 1.26–1.44 (m, 144H), 0.88 (t, *J* = 9 Hz, 24H). MALDI-TOF Mass: calcd. for C₁₅₁H₂₃₉NO₁₇ 2340.5, found 2363.2 for [M + Na]⁺.

Compound 11. To an Et₂O solution (20 mL) of **4** (3.36 g, 3.18 mmol) were portion-wise added Ph₃P (1.67 g, 6.38 mmol) and CBr₄ (2.11 g, 6.36 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at 25 °C for 2 h. Then, the reaction was quenched by addition of brine (20 mL) and resulted mixture was extracted with ether. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtrated off insoluble fractions. The filtrate was evaporated to dryness under reduced pressure and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ 2/1 v/v), to allow isolation of **11** (2.84 g, 2.54 mmol) as white powder in 80% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.63 (d, J = 3 Hz, 2H), 6.54 (d, J = 3 Hz, 5H), 6.40 (t, J = 3 Hz, 2H), 4.94 (s, 4H), 4.41 (s, 2H), 3.93 (t, J = 6 Hz, 8H), 1.70–1.82 (m, 8H), 1.26–1.44 (m, 72H), 0.88 (t, J = 6 Hz, 12H).

Compound D₃PhNO₂. A mixture of **11** (1.23 g, 1.1 mmol), **9** (0.37 g, 0.25 mmol), potassium fluoride (0.10 g, 1.73 mmol), and 18-crown-6 (0.20 g, 0.75 mmol) in THF (10mL) was refluxed and stirred vigorously under Ar for 48 h. After evaporation off volatile fractions under reduced pressure, water was added and the resulted mixture was extracted with CH₂Cl₂. The combined organic extract was dried over anhydrous MgSO₄ and filtrated off insoluble fractions. The filtrate was evaporated to dryness under reduced pressure and the residue was subjected to column chromatography (SiO₂, hexane/CH₂Cl₂ v/v 4/1 to 2/1, then to 1/1), to allow isolation of **D₃PhNO₂** (1.0 g, 0.22 mmol) as slightly yellow oil in 89% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.14 (d, *J* = 9 Hz, 2H), 6.96 (d, *J* = 9 Hz, 2H), 6.65 (d, *J* = 3 Hz, 4H), 6.61 (d, *J* = 3 Hz, 2H), 6.58 (br., 1H), 6.54(br., 10H), 6.40 (t, *J* = 3 Hz, 4H), 5.08 (s, 2H), 4.97 (s, 4H), 4.94 (s, 8H),3.92 (t, *J* = 6 Hz, 16H), 1.71–1.74 (m, 16H), 1.26–1.44 (m, 144H), 0.88 (t, *J* = 9 Hz, 24H). MALDI-TOF Mass: calcd. for C₃₀₃H₄₇₉NO₃₃ 4664.0, found 4687.02 for [M + Na]⁺.

2. Determination of dendritic loading amount of D_nG

During the dendronization reaction, the precursor $D_n PhNH_2$ has three possible conversions: one part was successfully attached to graphene sheets; one part was subjected to side reactions such as oxidation; while the last part was remained unchanged. But irrespective of which conversion, the ¹H NMR peak of -CH₂O- $(2^{n+2}H)$ at the periphery of dendritic structure remained unchanged at around 3.93 ppm. Furthermore, all the unreacted part of D_nPhNH₂ and those subjected to side reactions stayed in the filtrate of the filtration and wash treatments during the Thus, we collected all the filtrate, concentrated, and added with workup procedure. 4'-bromoacetophenone (0.2 g, 1 mmol), and measured ¹H NMR spectra. 4'-bromoacetophenone was chosen as an internal standard since it exhibits an easily distinguished ¹H NMR signal at 2.60 ppm due to its methyl unit (3H). Therefore, by comparison of integrals of these two peaks, we can roughly estimate the dendritic loading amount. For example, the integral ratio of 2.60 ppm peak to 3.93 ppm peak is 0.72 for D_0G (Fig. S1). The consumption amount of dendritic precursors for 1.22 g GO can be calculated by: $2 - 3/(4 \times 0.72) = 0.96$ mmol. Thus, the dendritic loading amount of $\mathbf{D}_0 \mathbf{G}$ is 0.79 mmol per gram \mathbf{GO} . Similarly, the dendritic loading amount of D₁G, D₂G, and D₃G are determined to be 0.47, 0.37, and 0.32 mmol per gram GO, respectively.



Fig. S1 ¹H NMR spectra for determination of dendritic loading amount of (a) D_0G , (b) D_1G , (c) D_2G , and (d) D_3G .

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3. Supporting figures



Fig. S2 FT-IR spectra of **GO** and D_nG (n = 0–3).



Fig. S3 XPS spectra of **GO** and D_nG (n = 0–3).



Fig. S4 Raman spectra of **GO** and D_nG (n = 0–3).



Fig. S5 AFM image and the corresponding height profile of GO